# ORGANOMETALLICS

# Synthesis and Characterization of Single, Double, and Triple Butterfly [2Fe2E] (E = Se, S) Cluster Complexes Related to the Active Site of [FeFe]-Hydrogenases

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Supporting Information

**ABSTRACT:** As the active site mimics of [FeFe]-hydrogenases, 14 new butterfly [2Fe2E] (E = Se, S) cluster complexes have been prepared by various synthetic routes. The N-substituted single-butterfly [2Fe2Se] complexes [( $\mu$ -SeCH<sub>2</sub>)<sub>2</sub>NC(O)R]Fe<sub>2</sub>- $(CO)_6$  (1, R = Me; 2, R = Ph; 3, R = PhCH<sub>2</sub>O) were prepared by reactions of the in situ formed  $(\mu$ -LiSe)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> with  $RC(O)N(CH_2Cl)_2$ , whereas the corresponding [2Fe2S] complexes  $[(\mu - SCH_2)_2NC_6H_4R - p]Fe_2(CO)_6(4, R = CO_2Et; 5, R =$ CH<sub>2</sub>OH) were produced by reaction of the in situ generated  $(\mu$ -HS)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> with aqueous CH<sub>2</sub>O followed by treatment with *p*-RC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>. The parent single-butterfly [2Fe2Se] complex  $[(\mu-\text{SeCH}_2)_2\text{NH}]\text{Fe}_2(\text{CO})_6$  (6) could be prepared by



reaction of the N-substituted complex 3 with deprotecting reagent BBr<sub>3</sub>, BF<sub>3</sub>·OEt<sub>2</sub>/EtSH, or BF<sub>3</sub>·OEt<sub>2</sub>/Me<sub>2</sub>S, whereas the N-substituted single-butterfly [2Fe2Se] complexes [ $(\mu$ -SeCH<sub>2</sub>)<sub>2</sub>NC(O)R]Fe<sub>2</sub>(CO)<sub>6</sub> (7, R = Et; 8, R = PhCH<sub>2</sub>) were produced by reactions of 6 with acylating agents RC(O)Cl in the presence of  $Et_3N$ . While the known parent single-butterfly [2Fe2S] complex  $[(\mu$ -SCH<sub>2</sub>)<sub>2</sub>NH]Fe<sub>2</sub>(CO)<sub>6</sub> reacted with 2,6-[ClC(O)]<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N to afford double-butterfly [2Fe2S] complex [Fe<sub>2</sub>(CO)<sub>6</sub>( $\mu$ - $SCH_2_2NC(O)_2(2,6-C_5H_3N)$  (9), the new N-hydroxyethyl-substituted single-butterfly [2Fe2Se] complex [( $\mu$ -SeCH<sub>2</sub>)<sub>2</sub>N- $(CH_2)_2OH$ ]Fe<sub>2</sub>(CO)<sub>6</sub> (10) could be obtained by the in situ reaction of  $(\mu$ -HSe)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> with  $(HOCH_2)_2N(CH_2)_2OH$ . Interestingly, complex 10 could react with  $[ClC(O)]_2CH_2$  or 1,3,5- $[ClC(O)]_3C_6H_3$  in the presence of Et<sub>3</sub>N to give the corresponding double-butterfly [2Fe2Se] complex  $[Fe_2(CO)_6(\mu$ -SeCH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>O<sub>2</sub>C]<sub>2</sub>CH<sub>2</sub> (11) and triple-butterfly complex  $[Fe_2(CO)_6(\mu$ -SeCH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>O<sub>2</sub>C]<sub>3</sub>(1,3,5-C<sub>6</sub>H<sub>3</sub>) (12), whereas the known single-butterfly [2Fe2S] complex  $[(\mu$ -SCH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>N-CH<sub>2</sub>)<sub>2</sub>N-CH<sub>2</sub>N-CH<sub>2</sub>  $(CH_2)_2OH]Fe_2(CO)_6$  could react with 2,6- $[ClC(O)]_2C_5H_3N$  and 1,3,5- $[ClC(O)]_3C_6H_3$  in the presence of Et<sub>3</sub>N to afford the corresponding double-butterfly [2Fe2S] complex  $[Fe_2(CO)_6(\mu$ -SCH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>O<sub>2</sub>C]\_2(2,6-C<sub>5</sub>H<sub>3</sub>N) (13) and triple-butterfly complex  $[Fe_2(CO)_6(\mu$ -SCH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>O<sub>2</sub>C]<sub>3</sub>(1,3,5-C<sub>6</sub>H<sub>3</sub>) (14), respectively. All the new complexes 1–14 have been characterized by elemental analysis and spectroscopy, as well as by X-ray crystallography for 1-4, 7-9, and 14. In addition, the electrochemical study indicated that complexes 1 and 2 can catalyze the proton reduction of HOAc to give hydrogen.

# INTRODUCTION

The butterfly [2Fe2E] (E = Se, S) cluster complexes have received ever more attention in recent years, largely due to their unique structure and novel properties,<sup>1-9</sup> and particularly the biologically close relevance to [FeFe]-hydrogenases.<sup>10</sup> [FeFe]hydrogenases are a class of natural enzymes that can catalyze reversible proton reduction to give molecular  $H_2$  in a variety of microorganisms.<sup>11,12</sup> During 1998 and 1999, the successful determination of the high-quality crystal structures of the [FeFe]-hydrogenases CpI and DdH established<sup>13,14</sup> that they both contain a structurally uncommon active site, which consists of a butterfly [2Fe2S] cluster with one of its iron atoms connected to a cubane-like [4Fe4S] cluster via the sulfur atom of a cysteinyl ligand. The [4Fe4S] cluster is actually responsible for the electron transfer, whereas the [2Fe2S] cluster is responsible for the formation and activation of hydrogen. In addition, the two

iron atoms of the [2Fe2S] cluster are bridged by a dithiolate ligand, as well as being connected with CO and CN<sup>-</sup> ligands. Recently, the bridging dithiolate was suggested as an azadithiolate SCH<sub>2</sub>NHCH<sub>2</sub>S or its N-substituted species.<sup>15–17</sup> On the basis of structural studies regarding the active site of [FeFe]hydrogenases, a great variety of butterfly [2Fe2E] (E = Se, S) cluster complexes as biomimetic models for the active site of [FeFe]-hydrogenases have been synthesized.<sup>18–21</sup> Herein, as part of our project concerning the butterfly Fe/E (E = Se, S) cluster chemistry and the [FeFe]-hydrogenase biomimetic chemistry, we report the synthesis, structure, and some properties of a new series of Fe/E (E = Se, S) cluster complexes containing one,

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Figure 1. Molecular structure of 1 with 30% probability level ellipsoids. Selected bond lengths (Å) and angles (deg): Fe(1)-Fe(2) = 2.5523(17), Fe(1)-Se(1) = 2.3753(14), Fe(1)-Se(2) = 2.3659(16), Fe(2)-Se(1) = 2.3825(16), Fe(2)-Se(2) = 2.3743(16), Se(1)-C(7) = 1.974(10), N(1)-C(9) = 1.380(10), N(1)-C(7) = 1.432(9); Fe(1)-Se(1)-Fe(2) = 64.88(5), Fe(1)-Se(2)-Fe(2) = 65.15(5), Se(1)-Fe(1)-Se(2) = 87.03(5), Se(1)-Fe(1)-Fe(2) = 57.70(5), Se(2)-Fe(1)-Fe(2) = 57.58(4).

two, or three butterfly [2Fe2E] cluster cores, which are closely related to the active site of [FeFe]-hydrogenases.

### RESULTS AND DISCUSSION

Synthesis and Characterization of  $[(\mu-SeCH_2)_2NC(O)R]Fe_2$ (CO)<sub>6</sub> (1, R = Me; 2, R = Ph; 3, R = PhCH<sub>2</sub>O) and  $[(\mu-SCH_2)_2NC_6H_4R-p]Fe_2(CO)_6$  (4, R = CO<sub>2</sub>Et; 5, R = CH<sub>2</sub>OH). We found that the N-substituted single-butterfly [2Fe2Se] cluster



Figure 2. Molecular structure of 2 with 30% probability level ellipsoids. Selected bond lengths (Å) and angles (deg): Fe(1)-Fe(2) = 2.5401(10), Fe(1)-Se(1) = 2.3842(9), Fe(1)-Se(2) = 2.3814(9), Fe(2)-Se(1) = 2.3909(9), Fe(2)-Se(2) = 2.3739(9), Se(1)-C(7) = 1.998(5), N(1)-C(9) = 1.378(6), N(1)-C(7) = 1.430(6); Fe(1)-Se(1)-Fe(2) = 64.27(3), Fe(1)-Se(2)-Fe(2) = 64.57(3), Se(1)-Fe(1)-Fe(2) = 86.20(3), Se(1)-Fe(1)-Fe(2) = 57.99(3), Se(2)-Fe(1)-Fe(2) = 57.57(3).



Figure 3. Molecular structure of 3 with 30% probability level ellipsoids. Selected bond lengths (Å) and angles (deg): Fe(1)-Fe(2) = 2.5417(11), Fe(1)-Se(1) = 2.3750(10), Fe(1)-Se(2) = 2.3850(12), Fe(2)-Se(1) = 2.3872(9), Fe(2)-Se(2) = 2.3787(8), Se(2)-C(8) = 1.987(4), N(1)-C(9) = 1.374(5), N(1)-C(8) = 1.425(5); Fe(1)-Se(1)-Fe(2) = 64.51(3), Fe(1)-Se(2)-Fe(2) = 64.49(4), Se(1)-Fe(1)-Se(2) = 87.03(4), Se(1)-Fe(1)-Fe(2) = 57.98(3), Se(2)-Fe(1)-Fe(2) = 57.63(3).

complexes 1-3 could be prepared by treatment of  $(\mu$ -LiSe)<sub>2</sub>Fe<sub>2</sub>-(CO)<sub>6</sub> (generated in situ from  $(\mu$ -Se<sub>2</sub>)Fe<sub>2</sub>(CO)<sub>6</sub> and Et<sub>3</sub>BHLi)<sup>3</sup> with the corresponding *N*,*N*-bis(chloromethyl)amide in THF from -78 °C to room temperature in 22-36% yields (Scheme 1). In addition, the N-substituted single-butterfly [2Fe2S] complexes 4 and 5 were found to be prepared by reaction of  $(\mu$ -HS)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> (formed in situ from  $(\mu$ -LiS)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>



Figure 4. Molecular structure of 4 with 30% probability level ellipsoids. Selected bond lengths (Å) and angles (deg): Fe(1)-Fe(2) = 2.5103(10), Fe(1)-S(1) = 2.2706(8), Fe(1)-S(2) = 2.2574(9), Fe(2)-S(1) = 2.2619(9), Fe(2)-S(2) = 2.2608(9), N(1)-C(9) = 1.402(3), O(7)-C(15) = 1.209(3), N(1)-C(8) = 1.422(3); Fe(1)-S(1)-Fe(2) = 67.26(4), Fe(1)-S(2)-Fe(2) = 67.50(3), S(1)-Fe(1)-S(2) = 85.37(3), S(1)-Fe(1)-Fe(2) = 56.20(3), S(2)-Fe(1)-Fe(2) = 56.31(3), S(1)-Fe(2)-S(2) = 85.49(4).



and  $CF_3CO_2H)^{22}$  with 37% aqueous formaldehyde in THF from -78 °C to room temperature and subsequent treatment of the resulting intermediate ( $\mu$ -HOCH<sub>2</sub>S)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub><sup>23</sup> with substituted aniline *p*-RC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> in 64% and 69% yields, respectively (Scheme 2).

Complexes 1-5 are air-stable red solids, which were characterized by elemental analysis and spectroscopy, and for 1-4 by X-ray crystallography. For example, the IR spectra of 1-5 showed several absorption bands in the range 2072-1977 cm<sup>-1</sup> for their terminal carbonyls, whereas 1-4 exhibited one additional band in the range 1716-1650 cm<sup>-1</sup> for their organic carbonyls and 5 displayed one broad band at 3451 cm<sup>-1</sup> for its hydroxy group. In addition, the <sup>1</sup>H NMR spectra of 1-3 showed one multiplet at 4.0-4.8 ppm for their two SeCH<sub>2</sub> groups, whereas 4 and 5 exhibited one singlet at 4.36 and 4.31 ppm for their two SCH<sub>2</sub> groups, respectively.

The molecular structures of 1-4 were unequivocally confirmed by X-ray diffraction analysis. Their ORTEP plots with selected bond lengths and angles are presented in Figures 1-4. As shown in Figures 1-3, complexes 1-3 each contain an N-acylated azadiselenolate (ADS) ligand bridged between their two Fe(CO)<sub>3</sub> units to form the two fused six-membered rings Fe1Se1C7N1C8Se2 and Fe2Se1C7N1C8Se2 with a chair conformation and a boat conformation, respectively. Similar to 1-3, Scheme 4



complex 4 includes an *N*-*p*-ethoxycarbonylbenzene-substituted azadithiolate (ADT) ligand bridged between its two  $Fe(CO)_3$  units to form the boat six-membered ring Fe1S1C8N1C7S2 and chair six-membered ring Fe2S1C8N1C7S2, respectively. In addition, as can be seen intuitively, the N-substituted ADS and ADT ligands in 1–4 are all attached to the common N1 atoms of the two fused six-membered rings with an axial type of bond N1–C9. The Fe1–Fe2 bond lengths of 1 (2.5523 Å), 2 (2.5401 Å), 3 (2.5417 Å), and 4 (2.5103 Å) are very close to those of the other diiron ADT- and ADS-type model complexes.<sup>24</sup>

Synthesis and Characterization of  $[(\mu-\text{SeCH}_2)_2\text{NH}]\text{Fe}_2(\text{CO})_6$ (6),  $[(\mu-\text{SeCH}_2)_2\text{NC}(\text{O})\text{R}]\text{Fe}_2(\text{CO})_6$  (7,  $\text{R} = \text{Et}; 8, \text{R} = \text{PhCH}_2$ ), and  $[\text{Fe}_2(\text{CO})_6(\mu-\text{SCH}_2)_2\text{NC}(\text{O})]_2(2,6-\text{C}_5\text{H}_3\text{N})$  (9). We initially tried to prepare the parent single-butterfly [2Fe2Se] complex 6 by using a synthetic method similar to that for preparation of its sulfur analogue  $[(\mu-\text{SCH}_2)_2\text{NH}]\text{Fe}_2(\text{CO})_6$ ,<sup>25</sup> namely, the method using the "click" reaction of the three components: paraformaldehyde, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, and ( $\mu$ -HSe)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>. However, unfortunately, this "click" reaction failed to give parent complex 6. Latter, we imagined that the N-substituted complex 3 might be regarded as a derivative of parent complex 6 with the N-carbobenzoxy protecting group. So, we decided to use the N-deprotecting method to prepare parent complex 6. As a result, complex





Figure 5. Molecular structure of 7 with 30% probability level ellipsoids. Selected bond lengths (Å) and angles (deg): Fe(1) - Fe(2) = 2.5342(7), Fe(1) - Se(1) = 2.3807(6), Fe(1) - Se(2) = 2.3780(6), Fe(2) - Se(1) = 2.3786(9), Fe(2) - Se(2) = 2.3862(7), Se(2) - C(8) = 2.000(3), N(1) - C(9) = 1.386(4), N(1) - C(7) = 1.427(4); Fe(1) - Se(1) - Fe(2) = 64.35(3), Fe(1) - Se(2) - Fe(2) = 64.27(2), Se(1) - Fe(1) - Se(2) = 86.87(3), Se(1) - Fe(1) - Fe(2) = 57.79(3), Se(2) - Fe(1) - Fe(2) = 58.02(2), Se(1) - Fe(2) - Se(2) = 86.729(18).

**6** was successfully prepared when the three boron-based deprotecting reagents  $BF_3 \cdot OEt_2/Me_2S_1^{26} BBr_3_1^{27}$  and  $BF_3 \cdot OEt_2/EtSH^{28}$  were used (Scheme 3). All the deprotecting reactions of **3** with the three boron-based reagents were carried out in  $CH_2Cl_2$  under mild conditions and in moderate yields (31-57%). However, the best one uses the  $BF_3 \cdot OEt_2/Me_2S$  reagent, since the reaction time is shorter (4 h) and the yield is higher  $(57\%)_1^{28}$ .

Furthermore, we found that parent complex **6** could be used as a starting material to prepare a variety of N-substituted derivatives. Actually, one of our purposes is to find a synthetic method to prepare complex **6**. Thus, treatment of a  $CH_2Cl_2$  solution of **6** with monoacylating agent EtC(O)Cl or  $PhCH_2C(O)Cl$  in the presence of  $Et_3N$  resulted in formation of the corresponding N-substituted complexes **7** and **8** in 89% and 73% yields, respectively (Scheme 4). Interestingly, this method for preparation of such N-substituted cluster complexes is both convenient and produces high yields. For example, complex **1** could be prepared by this method in 85% yield, but it was prepared only in 22% yield by the method involving reaction of



Figure 6. Molecular structure of 8 with 30% probability level ellipsoids. Selected bond lengths (Å) and angles (deg): Fe(1)-Fe(2) = 2.5500(13), Fe(1)-Se(1) = 2.3698(12), Fe(1)-Se(2) = 2.3782(12), Fe(2)-Se(1) = 2.3758(12), Fe(2)-Se(2) = 2.3646(12), Se(1)-C(7) = 1.978(6), N(1)-C(9) = 1.375(8), N(1)-C(7) = 1.424(8); Fe(1)-Se(1)-Fe(2) = 65.01(4), Fe(1)-Se(2)-Fe(2) = 65.05(4), Se(1)-Fe(1)-Fe(2) = 86.92(4), Se(1)-Fe(1)-Fe(2) = 57.61(4), Se(2)-Fe(1)-Fe(2) = 57.22(4).

 $(\mu$ -LiSe)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> with *N*,*N*-bis(chloromethyl)acetamide as described above. Similar to parent complex **6**, the known S analogue, namely, parent complex  $[(\mu$ -SCH<sub>2</sub>)<sub>2</sub>NH]Fe<sub>2</sub>(CO)<sub>6</sub>,<sup>25</sup> could react with 2,6-pyridinedicarboxylic acid dichloride and Et<sub>3</sub>N in CH<sub>2</sub>Cl<sub>2</sub> to afford the double-butterfly [2Fe2S] cluster complex **9** in 57% yield (Scheme 5).

While complexes 6-8 are air-sensitive red solids, complex 9 is an air-stable red solid. They were all characterized by elemental analysis and spectroscopy, as well as for 7-9 by X-ray diffraction analysis. Similar to 1-5, the IR spectra of 6-9 also showed several absorption bands in the range 2080-1984 cm<sup>-1</sup> for their terminal carbonyls, whereas 6 displayed another band at 3379 cm<sup>-1</sup> for its NH group, and 7-9 exhibited another band in the region 1683-1654 cm<sup>-1</sup> for their amide carbonyls. While the <sup>1</sup>H NMR spectrum of parent complex 6 displayed two singlets at 3.74 and 3.93 ppm for its two SeCH<sub>2</sub> groups, derivatives 7 and 8 exhibited one multiplet at 3.9-4.5 ppm for their two SeCH<sub>2</sub> groups, and double-butterfly [2Fe2S] complex 9 displayed two singlets at 4.31 and 4.50 ppm for its four  $SCH_2$  groups.

In order to confirm the structures of complexes 7-9, X-ray crystal diffraction analyses of 7-9 were undertaken. Their ORTEP drawings with selected bond lengths and angles are depicted in Figures 5-7. As shown in Figures 5 and 6, the molecular structures of 7 and 8 are very similar to those of 1-3. For example, they all have an N-substituted ADS ligand bridged between their two Fe(CO)<sub>3</sub> groups. Their N-substituents are all connected to the bridgehead N1 atom by the N1–C9 axial bond of the corresponding two fused six-membered rings. The Fe1–Fe2 bond lengths of 7 (2.5342 Å) and 8 (2.5500 Å) are very close to those of 1-4 and the other diiron ADT- and ADS-type model complexes.<sup>24</sup>

Interstingly, in contrast to the ADS ligand-containing singlebutterfly complexes 7 and 8, complex 9, as shown in Figure 7, contains two diiron ADT moieties, which are combined together by the 2,6-dicarbonylpyridine unit to form a double-butterfly [2Fe2S] cluster complex. The 2,6-dicarbonylpyridine group is linked to the two diiron ADT moieties through axial-type bonds C15–N1 and C21–N3. In addition, the dihedral angle between the two triangles N1C13C14 and O13C15C16, or N3C22C23 and O14C20C21, is only about  $3.5^\circ$ , which implies that the  $\pi$ system of its amide carbonyls is well conjugated with the p obital of its bridgehead N1 atoms. In fact, this is the first crystallographycally characterized *N*-diacyl-bridged ADT-type model



Figure 7. Molecular structure of 9 with 30% probability level ellipsoids. Selected bond lengths (Å) and angles (deg): Fe(1)-Fe(2) = 2.5144(10), Fe(3)-Fe(4) = 2.5126(12), Fe(1)-S(1) = 2.2559(13), Fe(1)-S(2) = 2.2489(14), Fe(2)-S(1) = 2.2496(15), Fe(2)-S(2) = 2.2480(14), O(13)-C(15) = 1.225(5), N(1)-C(15) = 1.379(5); Fe(1)-S(1)-Fe(2) = 67.85(4), Fe(1)-S(2)-Fe(2) = 67.99(5), S(1)-Fe(1)-Fe(2) = 85.13(5), S(1)-Fe(1)-Fe(2) = 55.96(4), S(2)-Fe(1)-Fe(2) = 55.99(4).

Scheme 6

complex, although its phenylene-diacyl analogue  $[Fe_2(CO)_6(\mu - SCH_2)_2NC(O)]_2(1,4-C_6H_4)$  was previously prepared.<sup>24a</sup>

Synthesis and Characterization of  $[(\mu-\text{SeCH}_2)_2\text{N}(\text{CH}_2)_2\text{OH}]$ Fe<sub>2</sub>(CO)<sub>6</sub> (10), [Fe<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -SeCH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>O<sub>2</sub>C]<sub>2</sub>CH<sub>2</sub> (11), Fe<sub>2</sub>-(CO)<sub>6</sub>( $\mu$ -SeCH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>O<sub>2</sub>C]<sub>3</sub>(1,3,5-C<sub>6</sub>H<sub>3</sub>) (12), [Fe<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -SCH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>O<sub>2</sub>C]<sub>2</sub>(2,6-C<sub>5</sub>H<sub>3</sub>N) (13), and [Fe<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -SCH<sub>2</sub>)<sub>2</sub>N-(CH<sub>2</sub>)<sub>2</sub>O<sub>2</sub>C]<sub>3</sub>(1,3,5-C<sub>6</sub>H<sub>3</sub>) (14). It was found that the N-substituted single-butterfly [2Fe2Se] cluster complex 10 could be prepared by treatment of ( $\mu$ -HSe)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> (generated in situ from ( $\mu$ -LiSe)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> and CF<sub>3</sub>CO<sub>2</sub>H) with N,N-bis(hydroxymethyl)ethanolamine (generated in situ from ethanolamine and paraformaldehyde) in THF from -78 °C to room temperature in 39% yield (Scheme 6).

It was further found that the single-butterfly [2Fe2Se] complex 10 and the known sulfur analogue  $[(\mu$ -SCH<sub>2</sub>)<sub>2</sub>N- $(CH_2)_2OH]Fe_2(CO)_6^{29}$  could be easily converted to the corresponding double- and triple-butterfly [2Fe2E] (E = Se, S) cluster complexes under the action of di- and triacylating reagents. For example, treatment of 10 with propanedioyl dichloride or 1,3,5benzenetricarbonyl trichloride in CH2Cl2 in the presence of Et<sub>3</sub>N afforded the corresponding bridged double-butterfly [2Fe2Se] complex 11 and triple-butterfly complex 12 in 56% and 16% yields, respectively (Scheme 7). Furthermore, the corresponding double-butterfly [2Fe2S] complex 13 and triple-butterfly complex 14 could be produced in 61% and 53% yields by reaction of the sulfur analogue  $[(\mu$ -SCH<sub>2</sub>)<sub>2</sub>N- $(CH_2)_2OH$  Fe<sub>2</sub> $(CO)_6$  with 2,6-pyridinedicarboxylic acid dichloride or 1,3,5-benzenetricarbonyl trichloride under similar conditions (Scheme 8).

Complexes 10-12 are air-sensitive red solids, whereas complexes 13 and 14 are air-stable red solids. All the elemental analysis, IR, and <sup>1</sup>H NMR spectroscopic data are consistent with their structures shown in Schemes 7 and 8. For example, the IR spectra of 10–14 displayed several absorption bands in the range 2075-1983 cm<sup>-1</sup> for their terminal carbonyls, whereas 10 exhibited one additional band at 3455 cm<sup>-1</sup> for its hydroxyl group, and 11-14 showed one additional band in the region 1753-1727 cm<sup>-1</sup> for their ester carbonyls. The <sup>1</sup>H NMR spectrum of 10 exhibited three singlets at 1.43, 2.95, and 3.52 ppm for its HOCH<sub>2</sub>CH<sub>2</sub>N group and two multiplets at 3.9-4.1 ppm for its two SeCH<sub>2</sub> groups. The <sup>1</sup>H NMR spectrum of 11 showed two multiplets at 3.8-4.3 ppm for its four SeCH<sub>2</sub> groups, whereas 12 displayed one multiplet at 3.9-4.3 ppm for its six SeCH<sub>2</sub> groups. In addition, 13 and 14 each showed one singlet at 3.72 and 3.66 ppm for their four and six SCH<sub>2</sub> groups, respectively.

Fortunately, the molecular structure of triple-butterfly complex 14 has been unambiguously confirmed by X-ray crystallographic study. The ORTEP view for this complex with selected bond lengths and angles is presented in Figure 8. As can be seen in Figure 8, complex 14 indeed consists of three ADTbridged butterfly [2Fe2S] cluster cores, which are combined together by a 1,3,5-trisubstituted benzene moiety to give a





Scheme 8



star-like compound. In addition, it is worth pointing out that (i) the three ADT-bridged butterfly cluster cores are all connected to the central benzene ring moiety via the axial bonds N1–C9, N2–C20, and N3–C31, (ii) each of the six iron atoms is attached to three terminal carbonyls and adopts a square-pyramidal geometry, (iii) the bond lengths of Fe1–Fe2 (2.5006 Å), Fe3–Fe4 (2.5068 Å), and Fe5–Fe6 (2.5097 Å) are slightly shorter than those of the oxidized form (2.62 or 2.60 Å)<sup>13,14</sup> and reduced form (2.55 Å)<sup>16</sup> of [FeFe]-hydrogenases. To the best of our knowledge, it is the first crystallographically characterized ADT type of [FeFe]-hydrogenase model complex with three butterfly [2Fe2S] cluster cores.

**Electrochemistry of 1 and 2.** The electrochemical behavior of the representative complexes 1 and 2 was studied in MeCN under CO by cyclic voltammetric techniques.<sup>30</sup> Table 1 lists their electrochemical data, and Figures 9 and 10 display their cyclic voltammograms, respectively. It is shown that both 1 and 2 exhibit one quasi-reversible reduction, one irreversible reduction, and one irreversible oxidation. The first and second reduction peaks of 1 (-1.50 and -1.97 V) and 2 (-1.48 and -1.95 V) could be assigned to the one-electron reduction processes from Fe<sup>I</sup>Fe<sup>I</sup> to Fe<sup>I</sup>Fe<sup>0</sup> and Fe<sup>I</sup>Fe<sup>0</sup> to Fe<sup>0</sup>Fe<sup>0</sup>, which were supported by the calculated values of 1.05 and 0.95 Faraday/equiv obtained by the bulk electrolysis of a MeCN solution of 1 at -1.70 V and 2 at -1.68 V, respectively.

Similarly, the oxidation peaks of 1 (+0.72 V) and 2 (+0.73 V) could be attributed to the two-electron oxidation processes from Fe<sup>I</sup>Fe<sup>I</sup> to Fe<sup>II</sup>Fe<sup>II</sup>. It follows that the cyclic voltammetric behavior of 1 and 2 is very similar to that of the propanedi-selenolate-bridged diiron complex  $[\mu$ -Se(CH<sub>2</sub>)<sub>3</sub>Se- $\mu$ ]Fe<sub>2</sub>-(CO)<sub>6</sub> (its three corresponding peaks at -1.61, -2.15, and +0.73 V).<sup>24c</sup> However, it is worth noting that the first reduction peaks of 1 and 2 are positively shifted by 110 and 130 mV relative to that of  $[\mu$ -Se(CH<sub>2</sub>)<sub>3</sub>Se- $\mu$ ]Fe<sub>2</sub>(CO)<sub>6</sub>, respectively. This is obviously due to 1 or 2 having a stronger electron-withdrawing group MeC(O)N or PhC(O)N in their diselenolate ligands.

The cyclic voltammograms of 1 and 2 in the presence of acetic acid HOAc ( $pK_a = 22.3$  in MeCN) are presented in Figures 11 and 12, respectively. For comparison, the cyclic voltammograms of 1 and 2 without HOAc are also included. As shown in Figures 11 and 12, when the first 2 mM HOAc was added, the first reduction peak of 1 at -1.51 V or 2 at -1.49 V slightly increased, but it did not grow with sequential addition of the acid. However, upon addition of 2-10 mM HOAc, the second reduction peak of 1 at -1.98 V or 2 at -1.97 V considerably increased and continued to grow with sequential addition of the acid. The rapid increments in current height of the reduction peak show an electrocatalytic process.<sup>24c,31-34</sup>



Figure 8. Molecular structure of 14 with 30% probability level ellipsoids. Selected bond lengths (Å) and angles (deg): Fe(1)-Fe(2) = 2.5006(10), Fe(3)-Fe(4) = 2.5068(10), Fe(5)-Fe(6) = 2.5097(11), Fe(1)-S(1) = 2.2702(13), Fe(1)-S(2) = 2.2649(15), Fe(2)-S(1) = 2.2597(13), O(8)-C(11) = 1.207(5), N(1)-C(9) = 1.456(5); Fe(1)-S(1)-Fe(2) = 67.01(4), Fe(1)-S(2)-Fe(2) = 66.67(4), S(1)-Fe(1)-Fe(2) = 84.79(5), S(1)-Fe(1)-Fe(2) = 56.29(4), S(2)-Fe(1)-Fe(2) = 57.05(4).

Table 1. Electrochemical Data of 1 and 2	Table 1.	Electrochemical	Data of	f 1	and	<b>2</b> <sup><i>a</i></sup>
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compound	$E_{\rm pc}({ m V})~{ m Fe}^{ m I}{ m Fe}^{ m I}/$ ${ m Fe}^{ m I}{ m Fe}^{ m 0}$	$E_{\rm pc}({ m V})~{ m Fe}^{ m I}{ m Fe}^{ m 0}/$ ${ m Fe}^{ m 0}{ m Fe}^{ m 0}$	E <sub>pa</sub> (V) Fe <sup>I</sup> Fe <sup>I</sup> ∕ Fe <sup>II</sup> Fe <sup>II</sup>			
1	-1.50	-1.97	+0.72			
2	-1.48	-1.95	+0.73			
<sup><i>a</i></sup> All potentials are versus Fc/Fc <sup>+</sup> in 0.1 M <i>n</i> -Bu <sub>4</sub> NPF <sub>6</sub> /MeCN.						

## CONCLUSIONS

We have successfully prepared a series of new butterfly [2Fe2E] (E = Se, S) cluster complexes (1–14) by different synthetic methods. While the N-substituted single-butterfly complexes 1-5 and 10 were prepared by the tandem reactions starting from  $(\mu - E_2)Fe_2(CO)_6$ , the double- and triple-butterfly complexes 11-14 could be prepared by functional transformation reactions of the N-hydroxyethyl group of new complex 10 and its S analogue  $[(\mu$ -SCH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>OH]Fe<sub>2</sub>(CO)<sub>6</sub>. Particularly noteworthy is that butterfly complex 6 could not be prepared by the known method for preparation of its analogue  $[(\mu$ -SCH<sub>2</sub>)<sub>2</sub>NH]Fe<sub>2</sub>(CO)<sub>6</sub>, but it could be prepared by a new method involving removal of the N-substituent of complex 3 by using one of the three boron-based deprotecting reagents. In addition, the N-substituted single-butterfly [2Fe2Se] complexes 7 and 8 could be obtained by monoacylation reactions of complex 6, whereas double-butterfly [2Fe2S] complex 9 was prepared by diacylation reaction of  $[(\mu$ -SCH<sub>2</sub>)<sub>2</sub>NH]Fe<sub>2</sub>(CO)<sub>6</sub> in high yield. It should be noted that all the new complexes 1-14contain at least one azadithiolate- or azadiselenolate-bridged butterfly [2Fe2E] cluster moiety. So, these complexes are structurally very similar to the diiron catalytic center in the active site of [FeFe]-hydrogenases. Complexes 1-14 have been fully



Figure 9. Cyclic voltammogram of 1 (1 mM) in 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>/ MeCN under CO at a scan rate of 100 mV s<sup>-1</sup>.



Figure 10. Cyclic voltammogram of 2 (1 mM) in 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>/ MeCN under CO at a scan rate of 100 mV s<sup>-1</sup>.

characterized by elemental analysis and spectroscopy, as well as for 1 and 2 by cyclic voltammetry and for 1-4, 7-9, and 14 by X-ray crystallography.

#### EXPERIMENTAL SECTION

General Comments. All reactions were performed using standard Schlenk and vacuum-line techniques under N2. All manipulations involving selenium compounds should be carried out in a well-ventilated hood since the Se-containing compounds are usually highly toxic. THF was distilled from sodium/benzophenone ketyl under N2, whereas dichloromethane was distilled from CaH<sub>2</sub>. While  $(\mu$ -S<sub>2</sub>)Fe<sub>2</sub>(CO)<sub>6</sub>,  $(\mu$ -Se<sub>2</sub>)Fe<sub>2</sub>(CO)<sub>6</sub>, RC(O)N(CH<sub>2</sub>Cl)<sub>2</sub> (R = Me, Ph, PhCH<sub>2</sub>O), [( $\mu$ - $SCH_2$ /2NH]Fe<sub>2</sub>(CO)<sub>6</sub>,<sup>25</sup> propanedioyl dichloride,<sup>36</sup> and 1,3-pyridine-dicarbonyl dichloride<sup>37</sup> were prepared according to published methods, other chemicals were purchased from commercial suppliers and used as received. Preparative TLC was carried out on glass plates (25 imes 15 imes0.25 cm) coated with silica gel G (10-40  $\mu$ m), whereas column chromatography was performed packed with ZCX-II silica gel (200-300 mesh). IR spectra were recorded on a Bio-Rad FTS 135 or a Bio-Rad FTS 60000 infrared spectrophotometer. <sup>1</sup>H NMR spectra were taken on a Bruker Avance 300 NMR or a Varian Mercury Plus 400 NMR spectrometer, respectively. Elemental analyses were performed with an Elementar Vario EL analyzer. Melting points were determined



Figure 11. Cyclic voltammogram of 1 (1 mM) with HOAc (0-10 mM) in 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>/MeCN under CO at a scan rate of 100 mV s<sup>-1</sup>.



Figure 12. Cyclic voltammogram of 2 (1 mM) with HOAc (0-10 mM) in 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>/MeCN under CO at a scan rate of 100 mV s<sup>-1</sup>.

on an X-4 apparatus from Beijing Tech Instrument Co. Ltd. and were uncorrected.

Preparation of  $[(\mu-SeCH_2)_2NC(O)R]Fe_2(CO)_6$  (1, R = Me; 2, **R** = **Ph**; **3**, **R** = **PhCH**<sub>2</sub>**O**). A purple-red solution of  $(\mu$ -Se)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> (0.438 g, 1.00 mmol) in THF (25 mL) was cooled to -78 °C, and then Et<sub>3</sub>BHLi (2.0 mL, 2.00 mmol) was added. The mixture was stirred at -78 °C for 20 min to give a brown-red solution containing  $(\mu$ -LiSe)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>. After MeC(O)N(CH<sub>2</sub>Cl)<sub>2</sub> (0.156 g, 1.00 mmol) was added, the new mixture was warmed to room temperature and stirred at this temperature for 12 h. Volatiles were removed in vacuo, and the residue was subjected to TLC separation using CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (3:1 v/v) as eluent. From the main red band, 1 was obtained as a red solid (0.114 g, 22%), mp 121 °C (dec). Anal. Calcd for C<sub>10</sub>H<sub>7</sub>Fe<sub>2-</sub> NO7Se2: C, 22.97; H, 1.35; N, 2.68. Found: C, 23.14; H, 1.44; N, 2.65. IR (KBr disk):  $\nu_{C=0}$  2070 (s), 2028 (vs), 1989 (vs);  $\nu_{C=0}$  1667 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS): 2.12 (s, 3H, CH<sub>3</sub>), 4.07-4.43 (m, 4H, 2SeCH<sub>2</sub>) ppm. 2 was prepared using the same procedure as that for 1, except that  $PhC(O)N(CH_2Cl)_2$  (0.218 g, 1.00 mmol) was utilized in place of  $MeC(O)N(CH_2Cl)_2$ . From the main red band, 2 was obtained as a red solid (0.212 g, 36%), mp 135 °C (dec). Anal. Calcd for C15H9Fe2NO7Se2: C, 30.80; H, 1.55; N, 2.39. Found: C, 30.73; H, 1.75; N, 2.49. IR (KBr disk):  $\nu_{C\equiv O}$  2068 (s), 2026 (vs), 1988

(vs);  $\nu_{C=0}$  1650 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS): 4.25–4.72 (m, 4H, 2SeCH<sub>2</sub>), 7.40–7.54 (m, 5H, C<sub>6</sub>H<sub>5</sub>) ppm. 3 was prepared using the same procedure as that for 1, except that PhCH<sub>2</sub>O<sub>2</sub>CN(CH<sub>2</sub>Cl)<sub>2</sub> (0.248 g, 1.00 mmol) was employed. From the main red band, 3 was obtained as a red solid (0.211 g, 34%), mp 141 °C (dec). Anal. Calcd for C<sub>16</sub>H<sub>11</sub>Fe<sub>2</sub>NO<sub>8</sub>Se<sub>2</sub>: C, 31.25; H, 1.80; N, 2.28. Found: C, 31.28; H, 1.95; N, 2.27. IR (KBr disk):  $\nu_{C=O}$  2069 (s), 2028 (vs), 1990 (vs);  $\nu_{C=O}$  1716 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): 4.02–4.50 (m, 4H, 2SeCH<sub>2</sub>), 5.18 (s, 2H, OCH<sub>2</sub>), 7.37 (s, 5H, C<sub>6</sub>H<sub>5</sub>) ppm.

Preparation of  $[(\mu$ -SCH<sub>2</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>R-p]Fe<sub>2</sub>(CO)<sub>6</sub> (4, R = CH<sub>2</sub>OH; **5**,  $R = CO_2Et$ ). A red solution of  $(\mu - S_2)Fe_2(CO)_6$  (0.344 g, 1.00 mmol) in THF (20 mL) was cooled to  $-78\,^\circ\text{C}$ , and then Et<sub>3</sub>BHLi (2.0 mL, 2.00 mmol) was added. The mixture was stirred at -78 °C for 15 min, and then CF<sub>3</sub>CO<sub>2</sub>H (0.20 mL, 2.00 mmol) was added to give a brown-red solution containing  $(\mu$ -HS)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>. After aqueous CH<sub>2</sub>O (0.16 mL, 2.00 mmol) was added, the mixture was warmed to room temperature and stirred at this temperature for 1 h, and then p-H2NC6H4CO2Et (0.165 g, 1.00 mmol) was added. The new mixture was stirred for 5 h. Volatiles were removed in vacuo, and the residue was subjected to TLC separation using  $CH_2Cl_2$ /petroleum ether (1:2 v/v) as eluent. From the main red band, 4 was obtained as a red solid (0.341 g, 64%), mp 118-119 °C. Anal. Calcd for C17H13Fe2NO8S2: C, 38.16; H, 2.45; N, 2.62. Found: C, 38.27; H, 2.49; N, 2.79. IR (KBr disk):  $\nu_{C\equiv O}$  2072 (s), 2033 (vs), 2001 (vs), 1994 (s);  $\nu_{\rm C=O}$  1699 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): 1.40 (t, 3H, J = 7.0 Hz, CH<sub>3</sub>), 4.36 (s, 6H, OCH<sub>2</sub>, 2SCH<sub>2</sub>), 6.74, 6.77, 8.00, 8.02 (AB q, 4H, C<sub>6</sub>H<sub>4</sub>) ppm. 5 was prepared by the same procedure as that for 4, but p-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OH (0.123 g, 1.00 mmol) was used instead of p-H2NC6H4CO2Et . From the main red band, 5 was obtained as a red solid (0.340 g, 69%), mp 133-134 °C. Anal. Calcd for C<sub>15</sub>H<sub>11</sub>Fe<sub>2</sub>NO<sub>7</sub>S<sub>2</sub>: C, 36.54; H, 2.25; N, 2.84. Found: C, 36.75; H, 2.25; N, 3.00. IR (KBr disk):  $\nu_{C\equiv O}$  2071 (s), 2034 (vs), 2010 (vs), 1991 (vs), 1977 (vs);  $\nu_{\rm OH}$  3451 (br s) cm  $^{-1}$ . <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS): 1.56 (br s, 1H, OH), 2.28 (s, 2H, OCH<sub>2</sub>), 4.31 (s, 4H, 2SCH<sub>2</sub>), 6.65, 6.69, 7.11, 7.12 (AB q, 4H, C<sub>6</sub>H<sub>4</sub>) ppm.

**Preparation of**  $[(\mu$ -SeCH<sub>2</sub>)<sub>2</sub>NH]Fe<sub>2</sub>(CO)<sub>6</sub> (6). Method (i): To a stirred solution of 3 (0.307 g, 0.50 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) were added BF<sub>3</sub>·OEt<sub>2</sub> (0.61 mL, 4.85 mmol) and Me<sub>2</sub>S (0.99 mL, 13.55 mmol). After the mixture was stirred at room temperature for 1.5 h, additional Me<sub>2</sub>S (0.81 mL, 11.10 mmol) was added. The new mixture was stirred for another 2.5 h and then washed with water (5 mL × 2). The organic layer was separated and then evaporated to dryness at reduced pressure. The residue was subjected to column chromatography under anaerobic conditions using 1:2 v/v CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether as eluent. From the main red band, 6 was obtained as a dark red solid (0.138 g, 57%), mp 68 °C (dec). Anal. Calcd for C<sub>8</sub>H<sub>5</sub>Fe<sub>2</sub>NO<sub>6</sub>Se<sub>2</sub>: C, 19.99; H, 1.05; N, 2.91. Found: C, 20.07; H, 1.24; N, 2.69. IR (KBr disk):  $\nu_{C=0}$  2060 (s), 2021 (vs), 1984 (vs);  $\nu_{NH}$  3379 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): 1.82 (s, 1H, NH), 3.74, 3.93 (2s, 4H, 2SeCH<sub>2</sub>) ppm.

Method (ii): While stirring, a solution of 3 (0.307 g, 0.50 mmol) in  $CH_2Cl_2$  (15 mL) was cooled to about -10 °C, and then  $BBr_3$  (0.63 mL, 2.50 mmol) was added. After the mixture was stirred at this temperature for 1 h, it was warmed to room temperature and stirred at this temperature for 2 h. The same workup as that used in method (i) afforded 0.105 g (44%) of 6.

Method (iii): To a stirred solution of 3 (0.307 g, 0.50 mmol) in  $CH_2Cl_2$  (15 mL) was sequentially added  $BF_3 \cdot OEt_2$  (0.63 mL, 5.00 mmol) and EtSH (1.10 mL, 14.50 mmol). After the mixture was stirred at room temperature for 11 h, volatiles were removed at reduced pressure. The residue was subjected to column chromatography under anaerobic conditions to develop a major red band, from which 0.073 g (31%) of **6** was obtained.

Preparation of  $[(\mu-SeCH_2)_2NC(O)R]Fe_2(CO)_6$  (1, R = Me; 7,  $\mathbf{R} = \mathbf{Et}$ ; 8,  $\mathbf{R} = \mathbf{PhCH}_2$ ). A stirred solution of 6 (0.240 g, 0.50 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was cooled to 0 °C, and then Et<sub>3</sub>N (0.07 mL, 0.50 mmol) and MeC(O)Cl (0.04 mL, 0.50 mmol) were added. After the mixture was stirred at 0 °C for 0.5 h, it was allowed to warm to room temperature and then stirred at this temperature for 5 h. Solvent was removed in vacuo, and the residue was subjected to TLC separation using  $CH_2Cl_2$ /petroleum ether (2.5:1 v/v) as eluent. From the main red band, 1 was obtained as a red solid (0.221 g, 85%), which was identified by comparison of its IR and <sup>1</sup>H NMR spectra to those of the sample prepared by the method involving reaction of  $(\mu$ -LiSe)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub> with N,N-bis(chloromethyl)acetamide described above. Similarly, 7 and 8 were prepared by this acylation method, except that MeC(O)Cl used for preparing 1 was replaced by EtC(O)Cl (0.04 mL, 0.50 mmol) and PhCH<sub>2</sub>C(O)Cl (0.07 mL, 0.50 mmol), respectively. From the main red band, 7 was obtained as a red solid (0.240 g, 89%), mp 110 °C (dec). Anal. Calcd for C<sub>11</sub>H<sub>9</sub>Fe<sub>2</sub>NO<sub>7</sub>Se<sub>2</sub>: C, 24.61; H, 1.69; N, 2.61. Found: C, 24.68; H, 1.79; N, 2.42. IR (KBr disk): *v*<sub>C≡O</sub> 2066 (s), 2035 (vs), 2026 (vs), 2001 (vs), 1985 (vs);  $\nu_{C=0}$  1683 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ , TMS): 1.16 (t, 3H, J = 6.0 Hz,  $CH_2CH_3$ ), 2.29 (q, 2H, J = 6.1Hz, CH<sub>2</sub>CH<sub>3</sub>), 3.95-4.45 (m, 4H, 2SeCH<sub>2</sub>) ppm. 8 was obtained as a red solid (0.219 g, 73%), mp 119 °C (dec). Anal. Calcd for C<sub>16</sub>H<sub>11</sub>Fe<sub>2-</sub> NO7Se2: C, 32.09; H, 1.85; N, 2.34. Found: C, 32.19; H, 1.95; N, 2.39. IR (KBr disk):  $\nu_{C=0}$  2068 (s), 2026 (vs), 1988 (vs);  $\nu_{C=0}$  1666 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): 3.73 (s, 2H, PhCH<sub>2</sub>), 3.92–4.45 (m, 4H, 2SeCH<sub>2</sub>), 7.16–7.30 (m, 5H, C<sub>6</sub>H<sub>5</sub>) ppm.

**Preparation of**  $[Fe_2(CO)_6(\mu$ -SCH<sub>2</sub>)\_2NC(O)]\_2(2,6-C\_5H\_3N) (9). To a stirred solution of  $[(\mu$ -SCH<sub>2</sub>)\_2NH]Fe<sub>2</sub>(CO)<sub>6</sub> (0.192 g, 0.50 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) were added Et<sub>3</sub>N (0.09 mL, 0.68 mmol) and 2,6-[ClC(O)]<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N (0.051 g, 0.25 mmol). The mixture was stirred at room temperature for 12 h. Solvent was removed in vacuo, and the residue was subjected to TLC separation using CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (2:1 v/v) as eluent. From the main red band, 9 was obtained as a red solid (0.129 g, 57%), mp 132–133 °C. Anal. Calcd for C<sub>23</sub>H<sub>11</sub>Fe<sub>4</sub>. N<sub>3</sub>O<sub>14</sub>S<sub>4</sub>: C, 30.52; H, 1.23; N, 4.64. Found: C, 30.76; H, 1.45; N, 4.60. IR (KBr disk):  $\nu_{C\equiv O}$  2080 (s), 2037 (vs), 1999 (vs);  $\nu_{C=O}$  1654 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): 4.31, 4.50 (2s, 8H, 4SCH<sub>2</sub>), 8.04 (s, 3H, C<sub>5</sub>H<sub>3</sub>N) ppm.

Preparation of [(µ-SeCH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>OH]Fe<sub>2</sub>(CO)<sub>6</sub> (10). A solution of (µ-Se<sub>2</sub>)Fe<sub>2</sub>(CO)<sub>6</sub> (0.438 g, 1.00 mmol) in THF (20 mL) was cooled to -78 °C, and then Et<sub>3</sub>BHLi (2.00 mL, 2.00 mmol) was added. After the mixture was stirred at this temperature for 20 min, trifluoroacetic acid (0.17 mL, 2.20 mmol) was added, and then the new mixture was stirred for an additional 20 min. To the resultant mixture, containing  $(\mu$ -HSe)<sub>2</sub>Fe<sub>2</sub>- $(CO)_6$ , was added a THF solution of  $HO(CH_2)_2N(CH_2OH)_2$  (prepared by stirring a mixture of 2-aminoethanol (0.06 mL, 1.00 mmol) and paraformaldehyde (0.120 g, 4.00 mmol) in THF (14 mL) at room temperature for 10 h). After the mixture was warmed to room temperature and stirred for 8 h, solvent was removed in vacuo. The residue was subjected to column chromatography using CH2Cl2/petroleum ether/MeOH (5:1:0.17 v/v/v) as eluent under anaerobic conditions. From the main band, 10 was obtained as a dark red solid (0.202 g, 39%), mp 79-81 °C. Anal. Calcd for C10H9Fe2NO7Se2: C, 22.89; H, 1.73; N, 2.67. Found: C, 23.16; H, 1.74; N, 2.74. IR (KBr disk):  $\nu_{C=0}$  2064 (s), 2021 (vs), 1983 (vs);  $\nu_{\rm OH}$  3455 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS): 1.43 (br s, 1H, OH), 2.95 (s, 2H, NCH<sub>2</sub>CH<sub>2</sub>OH), 3.52 (s, 2H, NCH<sub>2</sub>CH<sub>2</sub>OH), 3.94-3.97, 4.29-4.31 (2 m, 4H, 2SeCH<sub>2</sub>) ppm.

Preparation of  $[Fe_2(CO)_6(\mu$ -SeCH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>O<sub>2</sub>C]<sub>2</sub>CH<sub>2</sub> (11) and  $[Fe_2(CO)_6(\mu$ -SeCH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>O<sub>2</sub>C]<sub>3</sub>(1,3,5-C<sub>6</sub>H<sub>3</sub>) (12). To a red solution of 10 (0.262 g, 0.50 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) cooled to 0 °C were added Et<sub>3</sub>N (0.07 mL, 0.50 mmol) and  $[ClC(O)]_2$ CH<sub>2</sub> (0.024 mL, 0.25 mmol). After the mixture was stirred at 0 °C for 0.5 h, it was warmed to room temperature and stirred at this temperature for 12 h. Solvent was removed in vacuo, and then the residue was subjected to TLC separation using CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (2:1 v/v) as eluent. From the main red band, 11 was obtained as a red solid (0.157 g, 56%), mp 36-38 °C. Anal. Calcd for C<sub>23</sub>H<sub>18</sub>Fe<sub>4</sub>N<sub>2</sub>O<sub>16</sub>Se<sub>4</sub>: C, 24.72; H, 1.62; N, 2.51. Found: C, 24.81; H, 1.52; N, 2.33. IR (KBr disk):  $v_{C=0}$  2064 (s), 2020 (vs), 1983 (vs);  $\nu_{\rm C=O}$  1736 (m) cm  $^{-1}$ .  $^1{\rm H}$  NMR (400 MHz, CDCl<sub>3</sub>, TMS): 3.03 (s, 4H, 2NCH<sub>2</sub>CH<sub>2</sub>O), 3.30 (s, 2H, O<sub>2</sub>CCH<sub>2</sub>CO<sub>2</sub>), 4.01 (s, 4H, 2NCH<sub>2</sub>CH<sub>2</sub>O), 3.86–3.96, 4.17–4.24 (2 m, 8H, 4SeCH<sub>2</sub>) ppm. 12 was prepared by the same procedure as that for 11, but 1,3,5-[ClC(O)] $_3C_6H_3$  (0.044 g, 0.17 mmol) was used instead of  $[ClC(O)]_2CH_2$ . From the main red band, 12 was obtained as a red solid (0.047 g, 16%), mp 136 °C (dec). Anal. Calcd for C<sub>39</sub>H<sub>27</sub>Fe<sub>6-</sub> N3O24Se6: C, 27.07; H, 1.57; N, 2.43. Found: C, 27.28; H, 1.78; N, 2.41. IR (KBr disk):  $\nu_{C\equiv O}$  2064 (s), 2020 (vs), 1983 (vs);  $\nu_{C=O}$ 1730 (m) cm  $^{-1}.$   $^1H$  NMR (400 MHz, CDCl\_3, TMS): 3.19 (s, 6H, 3NCH<sub>2</sub>CH<sub>2</sub>O), 3.99-4.27 (m, 18H, 3NCH<sub>2</sub>CH<sub>2</sub>O, 6SeCH<sub>2</sub>), 8.70 (s, 3H,  $C_6H_3$ ) ppm.

Preparation of  $[Fe_2(CO)_6(\mu$ -SCH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>O<sub>2</sub>C]<sub>2</sub>(2,6-C<sub>5</sub>H<sub>3</sub>N) (13) and  $[Fe_2(CO)_6(\mu-SCH_2)_2N(CH_2)_2O_2C]_3(1,3,5-C_6H_3)$  (14). To a red solution of  $[(\mu$ -SCH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>OH]Fe<sub>2</sub>(CO)<sub>6</sub> (0.217 g, 0.50 mmol) in  $CH_2Cl_2$  (15 mL) were added  $Et_3N$  (0.33 mL, 2.32 mmol) and 2,6-[ClC(O)] $_2C_5H_3N$  (0.065 g, 0.32 mmol). The mixture was stirred at room temperature for 14 h. Solvent was removed in vacuo, and the residue was subjected to TLC separation using CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (2:1 v/v) as eluent. From the main red band, 13 was obtained as a red solid (0.152 g, 61%), mp 66-88 °C. Anal. Calcd for C<sub>27</sub>H<sub>19</sub>Fe<sub>4-</sub> N<sub>3</sub>O<sub>16</sub>S<sub>4</sub>: C, 32.66; H, 1.93; N, 4.23. Found: C, 32.83; H, 2.18; N, 4.18. IR (KBr disk):  $\nu_{C=0}$  2075 (s), 2031 (vs), 1995 (vs);  $\nu_{C=0}$  1727 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): 3.19 (s, 4H, 2NCH<sub>2</sub>CH<sub>2</sub>O), 3.72 (s, 8H, 4SCH<sub>2</sub>), 4.30 (s, 4H, 2NCH<sub>2</sub>CH<sub>2</sub>O), 8.02, 8.25 (2s, 3H,  $C_5H_3N$ ) ppm. 14 was prepared by the same procedure as that for 13, but 1,3,5-[ClC(O)]<sub>3</sub>C<sub>6</sub>H<sub>3</sub> (0.044 g, 0.17 mmol) was used instead of 2,6-[ClC(O)]<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N. From the main red band, 14 was obtained as a red solid (0.129 g, 53%), mp 122-124 °C. Anal. Calcd for C<sub>39</sub>H<sub>27</sub>Fe<sub>6</sub>N<sub>3</sub>O<sub>24</sub>S<sub>6</sub>: C, 32.32; H, 1.88; N, 2.90. Found: C, 32.14; H, 2.10; N, 3.17. IR (KBr disk):  $\nu_{C=0}$  2074 (vs), 2031 (vs), 1995 (vs);  $\nu_{C=0}$  1728 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): 3.15 (s, 6H, 3NCH<sub>2</sub>CH<sub>2</sub>O), 3.66 (s, 12H, 6SCH<sub>2</sub>), 4.27 (s, 6H, 3NCH<sub>2</sub>CH<sub>2</sub>O), 8.73 (s, 3H, C<sub>6</sub>H<sub>3</sub>) ppm.

X-ray Structure Determinations of 1–4, 7–9, and 14. Single crystals of 1–4, 7–9, and 14 suitable for X-ray diffraction analysis were grown by slow evaporation of the CHCl<sub>3</sub>/petroleum ether solutions at about –4 °C. Each crystal was mounted on a Rigaku MM-007 (rotating anode) diffractometer equipped with Saturn 70CCD. Data were collected at room temperature, using a confocal monochromator with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) in the  $\omega$ – $\phi$  scanning mode. Data collection, reduction, and absorption correction were performed by the CRYSTALCLEAR program.<sup>38</sup> The structures were solved by direct methods using the SHELXS-97 program<sup>39</sup> and refined by full-matrix least-squares techniques (SHELXL-97)<sup>40</sup> on  $F^2$ . Hydrogen atoms were located by using the geometric method. Details of crystal data, data collections, and structure refinements are summarized in Tables 2 and 3, respectively (see Supporting Information).

**Electrochemistry.** Acetonitrile (Fisher Chemicals, HPLC grade) was used for performance of electrochemistry. A solution of 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> in MeCN was used as electrolyte in all cyclic voltammetric experiments. The electrolyte solution was degassed by bubbling with CO for about 10 min before measurement. Electrochemical measurements were made using a BAS Epsilon potentiostat. All voltammograms were obtained in a three-electrode cell with a 3 mm diameter glassy carbon working electrode, a platinum counter electrode, and an Ag/Ag<sup>+</sup> (0.01 M AgNO<sub>3</sub>/0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> in MeCN) reference electrode under CO. The working electrode was polished with 0.05  $\mu$ m alumina paste and sonicated in water for about 10 min. Bulk electrolysis was run on a vitreous carbon rod (A = 2.9 cm<sup>2</sup>) in a two-compartment, gastight,

H-type electrolysis cell containing ca. 25 mL of MeCN. Gas chromatography was performed with a Shimadzu gas chromatograph GC-2014 under isothermal conditions with nitrogen as a carrier gas and a thermal conductivity detector.

# ASSOCIATED CONTENT

Supporting Information. Full tables of crystal data, atomic coordinates, thermal parameters, and bond lengths and angles for 1-4, 7-9, and 14 as CIF files, as well as Tables 2 and 3. This material is available free of charge via the Internet at http://pubs. acs.org.

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