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Article

Reactions of Monoanions $[(\mu\text{-RE})(\mu\text{-E})Fe_2(CO)_6]^-$ and Dianions $[(\mu\text{-E})_2Fe_2(CO)_6]^{2-}$ (E = Se, S) with N-Substituted Benzimidoyl Chlorides, Leading to Novel Butterfly Fe/E Cluster Complexes[†]

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We have first studied the reactions of monoanions $[(\mu\text{-RE})(\mu\text{-E})Fe_2(CO)_6]^-$ (**A**, E = Se; **B**, E = S) with electrophile PhC(Cl)=NPh or dianions $[(\mu\text{-E})_2Fe_2(CO)_6]^{2-}$ (**C**, E = Se; **D**, E = S) with electrophiles PhC(Cl)=NR′ (R′ = Ph, *p*-MeC_6H_4). While monoanion **A** was found to react with PhC(Cl)=NPh to give expected complexes $(\mu\text{-RSe})[\mu\text{-SeC(Ph)=NPh}]Fe_2(CO)_6$ (**1**, R = Me; **2**, R = Et; **3**, R = *m*-MeC_6H_4), monoanion **B** was found to react with PhC(Cl)=NPh to afford unexpected complexes $(\mu\text{-RS})[\eta^1\text{-SC(Ph)=NPh-}\eta^1]Fe_2(CO)_6$ (**4**, R = Me; **5**, R = Et). Furthermore, while dianion **C** reacted with PhC(Cl)=NR′ (R′ = Ph, *p*-MeC_6H_4) to give expected complexes $[\mu\text{-SeC(Ph)=NR}']_2Fe_2(CO)_6$ (**6**, R′ = Ph; **7**, R′ = *p*-MeC_6H_4), dianion **D** was found to react with PhC(Cl)=NR′ (R′ = Ph, *p*-MeC_6H_4) to afford unexpected complexes $[\mu\text{-SC(Ph)=NR}'][\eta^1\text{-C(Ph)=NR}'\text{-}\eta^1]Fe_2(CO)_6$ (**8**, R′ = Ph; **9**, R′ = *p*-MeC_6H_4). All the new complexes **1**−**9** were characterized by elemental analysis and spectroscopy, and complexes **1** and **4**−**8** were further structurally confirmed by X-ray crystallography.

Introduction

We are interested in studying butterfly Fe/E (E = Se, S) cluster complexes because of their unique structures and novel properties,[1] as well as their recent widespread uses as biomimetic models for the active site of [FeFe]-hydrogenases.[2] Among such cluster complexes the butterfly monoanions $[(\mu\text{-RE})(\mu\text{-E})Fe_2(CO)_6]^-$ (**A**, E = Se; **B**, E = S) and dianions $[(\mu\text{-E})_2Fe_2(CO)_6]^{2-}$ (**C**, E = Se; **D**, E = S) are of great interest, since they are easily prepared and possess high nucleophilic reactivity toward various substrates. It is well known that the $[MgX]^+$ salts of monoanions **A** and **B**[3,4] and the dilithium salts of dianions **C** and **D**[5−7] can be prepared in nearly quantitative yields by reductive cleavage of the E−E bond of cluster $(\mu\text{-E}_2)Fe_2(CO)_6$ with Grignard reagents and Super-Hydride (Et_3BHLi), respectively, in THF at −78 °C (Scheme 1). In addition, these anions have been also demonstrated to be versatile reagents for synthesis of a wide variety of novel butterfly Fe/E cluster complexes.[8−24] Recently, we published two papers that described the unexpected production of the

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[†] Part of the Dietmar Seyferth Festschrift.

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(1) For reviews, see for example: (a) Markó, L.; Markó−Monostory, B. In *The Organic Chemistry of Iron*; von Gustorf, E. A. K., Grevels, F.-W., Fischer, I., Eds.; Academic Press: New York, 1981. (b) Ogino, H.; Inomata, S.; Tobita, H. *Chem. Rev.* **1998**, *98*, 2093. (c) Song, L.-C. *Acc. Chem. Res.* **2005**, *38*, 21. (d) Song, L.-C. *Trends Organomet. Chem.* **1999**, *3*, 1. (e) Song, L.-C. *Sci. China Ser. B: Chem.* **2009**, *52*, 1.

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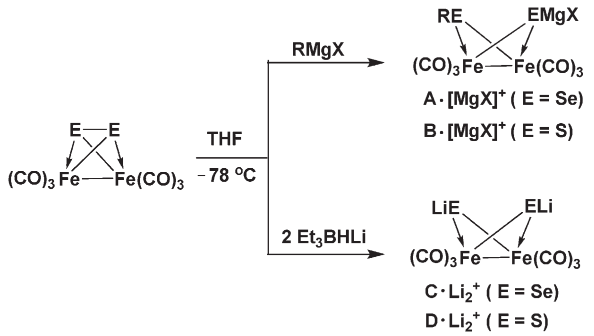
Scheme 1



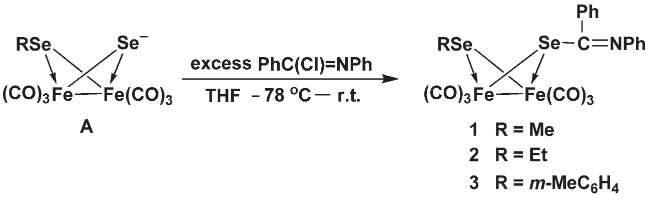
butterfly Fe/S/P cluster complexes from reactions of the butterflyFe/S cluster anions **B** and **D** with a P-based electrophile, Ph_2PCl.[25,26] Closely related to such studies, we further carried out a study on reactions of anions **A**−**D** with another type of electrophile, namely, the N-substituted benzimidoyl chlorides PhC(Cl)=NR′, in order to find new reaction modes and to prepare the corresponding butterfly cluster complexes. Interestingly, through this study we found that the Se-centered anions **A** and **C** reacted with PhC(Cl)=NR′ to give the expected butterfly Fe/Se cluster complexes, whereas reactions of the S-centered anions **B** and **D** afforded the unexpected novel butterfly Fe/S cluster complexes. Herein we report the interesting results obtained from this study.

Results and Discussion

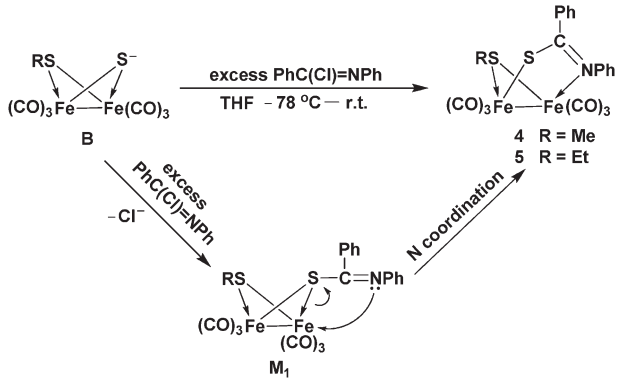
Reactions of Monoanions $[(\mu\text{-RE})(\mu\text{-E})Fe_2(CO)_6]^-$ (A, E = Se; B, E = S) with PhC(Cl)=NPh. Synthesis and Characterization of $(\mu\text{-RSe})[\mu\text{-SeC(Ph)=NPh}]Fe_2(CO)_6$ (1, R = Me; 2, R = Et; 3, R = m-MeC$_6$H$_4$) and $(\mu\text{-RS})[\eta^1\text{-SC(Ph)=NPh-}\eta^1]\text{-}Fe_2(CO)_6$ (4, R = Me; 5, R = Et). We found that monoanion $[(\mu\text{-RSe})(\mu\text{-Se})Fe_2(CO)_6]^-$ (**A**, R = Me, Et, m-MeC$_6$H$_4$) (generated from $(\mu\text{-Se}_2)Fe_2(CO)_6$ and Grignard reagents RMgX shown in Scheme 1)[4] reacted in situ with excess electrophile PhC(Cl)=NPh in THF from −78 °C to room temperature (via nucleophilic attack of the Se-centered monoanion **A** at the leaving group (Cl^-)-attached carbon atom of PhC(Cl)=NPh) to give the expected butterfly Fe/Se cluster complexes **1**−**3** in 50−77% yields (Scheme 2). However, in contrast to this, we found that monoanion $[(\mu\text{-RS})(\mu\text{-S})Fe_2(CO)_6]^-$ (**B**, R = Me, Et) (formed from $(\mu\text{-S}_2)Fe_2(CO)_6$ and Grignard reagents RMgX shown in Scheme 1)[3] reacted in situ with PhC(Cl)=NPh under similar conditions to afford unexpected butterfly Fe/S cluster complexes **4** and **5** in 51% and 77% yields, respectively (Scheme 3).

At the present stage, we are not clear about the mechanism for formation of the unexpected complexes **4** and **5**. However, according to the familiar nucleophilic mode of monoanion **B**[3,27,28] and the studied results regarding reaction of monoanion **B** with Ph_2PCl,[26] we might suggest a possible pathway to account for the formation of complexes **4** and **5**.

Scheme 2



Scheme 3



That is, as shown in Scheme 3, the initially intermolecular nucleophilic attack of the S-centered monoanion **B** at the leaving group(Cl^-)-attached C atom of electrophile PhC(Cl)=NPh would first afford intermediate **M$_1$**. Then, the intramolecular nucleophilic attack of the N atom in **M$_1$** at its Fe atom with displacement of mercaptide from Fe would give the unexpected complexes **4** and **5**. As a matter of fact, the intramolecular or intermolecular nucleophilic attack at iron followed by loss of the Fe-bound ligand in similar butterfly Fe/S cluster complexes has been well documented.[29−32]

Complexes **1**−**5** are air-stable red solids, which were fully characterized by elemental analysis and spectroscopy. For example, the IR spectra of **1**−**5** showed three strong absorption bands in the range 2071−1987 cm^{-1} for their terminal carbonyls and one medium absorption band at about 1620 or 1610 cm^{-1} for their uncoordinated and coordinated C=N functionalities. The ^{1}H NMR spectra of **1** and **4** each displayed one singlet at 1.98 and 2.50 ppm for the methyl group attached to their bridged Se and S atoms, respectively. In addition, the ^{77}Se NMR spectra of **1**−**3** exhibited two signals in the range 40−237 ppm for their two different bridged Se atoms.[33−36]

The molecular structures of **1**, **4**, and **5** were confirmed by X-ray crystallography. While their ORTEP drawings are shown in Figures 1−3, their selected bond lengths and angles

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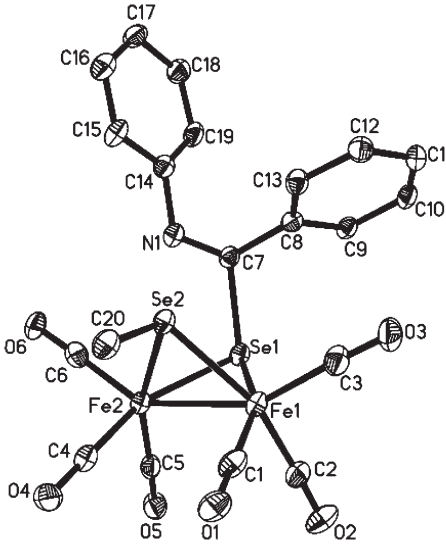

Figure 1. ORTEP view of **1** with 30% probability level ellipsoids.

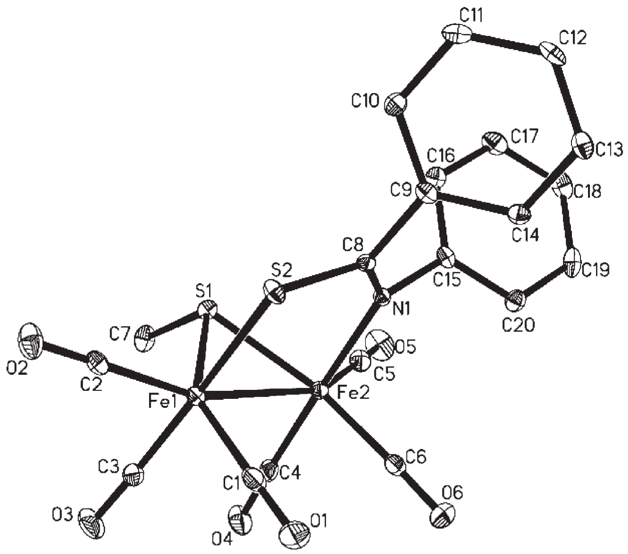

Figure 2. ORTEP view of **4** with 30% probability level ellipsoids.

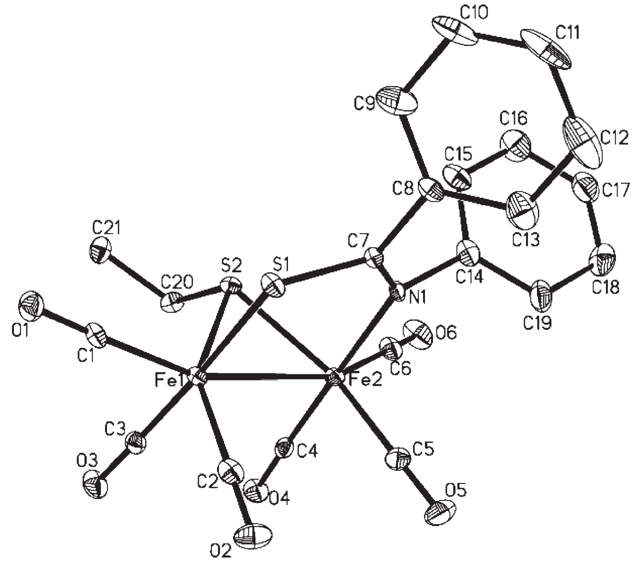

Figure 3. ORTEP view of **5** with 30% probability level ellipsoids.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1, 4, and 5

		1	
Se(2)−Fe(1)	2.3755(14)	Se(2)−Fe(2)	2.3816(11)
Se(1)−Fe(1)	2.3817(13)	Se(1)−Fe(2)	2.3665(11)
Fe(1)−Fe(2)	2.5505(13)	N(1)−C(7)	1.253(8)
Se(1)−C(7)	1.979(5)	Se(2)−C(20)	1.963(7)
Fe(2)−Se(1)−Fe(1)	64.98(3)	Se(1)−Fe(2)−Se(2)	81.664(4)
Fe(1)−Se(2)−Fe(2)	64.84(3)	C(7)−N(1)−C(14)	120.3(5)
Se(2)−Fe(1)−Se(1)	81.47(3)	N(1)−C(7)−C(8)	130.4(5)
Se(2)−Fe(1)−Fe(2)	57.69(3)	N(1)−C(7)−Se(1)	116.5(4)
		4	
Fe(1)−Fe(2)	2.6503(7)	N(1)−C(8)	1.302(3)
Fe(1)−S(1)	2.2461(9)	C(8)−C(9)	1.491(3)
Fe(1)−S(2)	2.3073(8)	S(2)−C(8)	1.712(2)
Fe(2)−S(1)	2.2427(8)	N(1)−C(15)	1.449(3)
S(1)−Fe(2)−Fe(1)	53.87(2)	N(1)−Fe(2)−Fe(1)	91.48(6)
S(1)−Fe(1)−S(2)	89.604(4)	C(8)−N(1)−Fe(2)	126.22(16)
S(1)−Fe(1)−Fe(2)	53.75(2)	N(1)−Fe(2)−Fe(1)	91.48(6)
Fe(2)−S(1)−Fe(1)	72.37(3)	C(15)−N(1)−Fe(2)	117.29(15)
		5	
Fe(1)−Fe(2)	2.6488(12)	N(1)−C(7)	1.299(5)
Fe(1)−S(1)	2.3102(13)	C(8)−C(7)	1.491(5)
Fe(1)−S(2)	2.2441(13)	S(1)−C(7)	1.712(4)
Fe(2)−S(2)	2.2455(12)	N(1)−C(14)	1.456(4)
S(2)−Fe(1)−S(1)	89.44(4)	C(7)−N(1)−Fe(2)	126.7(2)
S(1)−Fe(1)−Fe(2)	88.43(4)	C(14)−N(1)−Fe(2)	114.7(2)
S(2)−Fe(2)−Fe(1)	53.82(4)	N(1)−Fe(2)−S(2)	86.15(9)
Fe(1)−S(2)−Fe(2)	72.31(4)	N(1)−Fe(2)−Fe(1)	91.44(9)

are listed in Table 1. Figure 1 shows that complex **1** contains a butterfly Fe1Fe2Se1Se2 cluster core that is attached to a methyl group via a C20−Se2 equatorial bond and an *N*-phenyl benzimidoyl group via a C7−Se1 axial bond, as well as six terminal carbonyls via Fe1 and Fe2 atoms. The bond length of C7−N1 is 1.253 Å, which is close to normal (1.28 Å) for the C=N double bond.[37] Figures 2 and 3 display that complexes **4** and **5** are composed of a butterfly cluster core (Fe1Fe2S1S2C8N1 for **4** and Fe1Fe2S1S2C7N1 for **5**) connected to a methyl group of **4** and ethyl group of **5** through the equatorial C7−S1 and C20−S2 bonds, respectively. The striking structural feature of **4** and **5** is that they all have a five-membered ring (Fe1Fe2N1C8S2 for **4** and Fe1Fe2N1C7S1 for **5**) to serve as one wing of their butterfly cluster cores. The bond lengths of C8−N1 (1.302 Å) and C7−N1 (1.299 Å) in the five-membered rings of **4** and **5** are longer than that of C7−N1 (1.253 Å) attached to the bridged Se1 atom in complex **1**. This implies that the double bonds of C8−N1 and C7−N1 in **4** and **5** are involved in coordination with their iron atoms, but not for the double bond of C7−N1 in complex **1**. So, the crystallographic analyses of **4** and **5** have not only confirmed their molecular structures but also provided evidence for the suggested ring isomerization from a three-membered ring to a five-membered ring. In addition, the Fe1−Fe2 bond lengths in **1** (2.5505 Å), **4** (2.6503 Å), and

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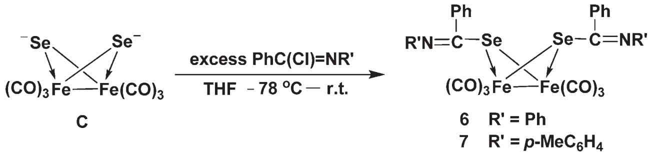
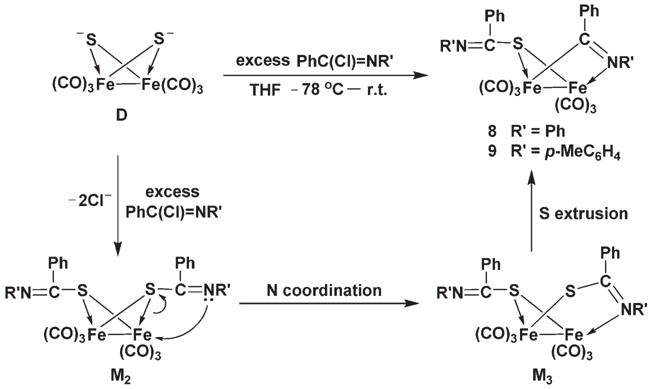
(37) Special Publication: *Chem. Soc.* (1965) No. 18: Sandorfy, C. In *The Chemistry of the Carbon Nitrogen Double Bond*; Patai, S., Ed.; Wiley: New York, 1970; Chapter 1.

Scheme 4



Scheme 5



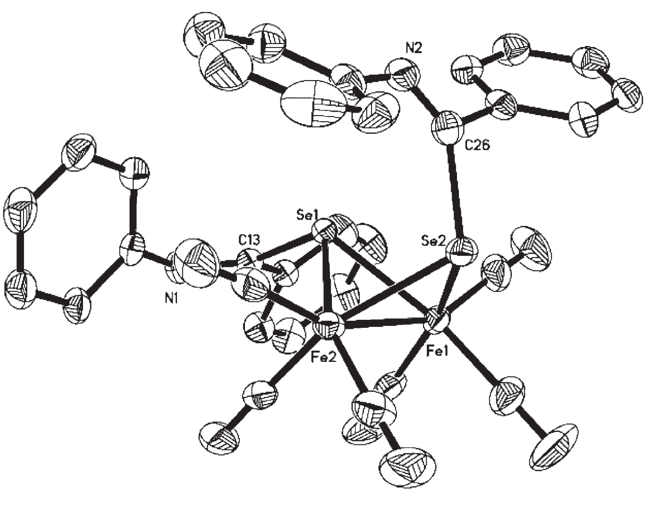


Figure 4. ORTEP view of **6** with 30% probability level ellipsoids.

5 (2.6488 Å) are very close to the corresponding metal–metal bond lengths in similar Fe/E cluster complexes.[38–42]

Reactions of Dianions $[(\mu\text{-E})_2\text{Fe}_2(\text{CO})_6]^{2-}$ (C, E = Se; D, E = S) with PhC(Cl)=NR′. Synthesis and Characterization of $[\mu\text{-SeC(Ph)=NR}']_2\text{Fe}_2(\text{CO})_6$ (6, R′ = Ph; 7, R′ = p-MeC$_6$H$_4$) and $[\mu\text{-SC(Ph)=NR}'][\eta^1\text{-C(Ph)=NR}'\text{-}\eta^1]\text{Fe}_2(\text{CO})_6$ (8, R′ = Ph; 9, R′ = p-MeC$_6$H$_4$). Similarly, treatment of dianion $[(\mu\text{-Se})_2\text{Fe}_2(\text{CO})_6]^{2-}$ (**C**) (generated from $(\mu\text{-Se}_2)\text{Fe}_2(\text{CO})_6$ and Et$_3$BHLi shown in Scheme 1)[7] in situ with excess PhC(Cl)=NR′ (R′ = Ph, p-MeC$_6$H$_4$) in THF from −78 °C to room temperature gave the expected butterfly Fe/Se complexes **6** and **7** in 26% and 55% yields, respectively (Scheme 4); however in contrast to this, reactions of dianion $[(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6]^{2-}$ (**D**) (derived from $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ and Et$_3$BHLi shown in Scheme 1)[5] with PhC(Cl)=NR′ (R′ = Ph, p-MeC$_6$H$_4$) under similar conditions resulted in formation of the unexpected butterfly Fe/S cluster complexes **8** and **9** in 32% and 40% yields, respectively (Scheme 5).

A possible pathway for production of the unexpected complexes **8** and **9** is shown in Scheme 5. First, the nucleophilic attack of the S-centered dianion **D** at the leaving group(Cl$^-$)-attached carbon atom in PhC(Cl)=NR′ would give intermediate **M$_2$**. Then, the intramolecular nucleophilic attack of the N atom in **M$_2$** at its Fe atom with displacement of mercaptide from Fe would afford intermediate **M$_3$**. Finally, products **8** and **9** could be produced by loss of one S atom from **M$_3$** followed by attachment of the C atom to the Fe atom. Although this pathway is mainly speculative, it seems reasonable. This is because (i) the nucleophilic attack of the S-centered dianion **D** at various organic halides is known to give symmetrically disubstituted complexes;[6] (ii) the intramolecular isomerization from **M$_2$** to **M$_3$** is similar to that involved in reaction of dianion **D** with Ph$_2$PCl;[26] (iii) although the extrusion of one S atom followed by C coordination in **M$_3$** is unprecedented, the extrusion of one Se atom or one CO followed by the corresponding coordination was previously observed in similar butterfly Fe/E cluster complexes;[43,44] and (iv) from the studied reactions byproducts PhC(S)NHPh (**8′**) and PhC(S)NHC$_6$H$_4$Me-p (**9′**) were isolated along with products **8** and **9**, respectively (see Experimental Section). Presumably, the two byproducts were generated from the extruded S and excess PhC(Cl)=NR′ or some species derived from PhC(Cl)=NR′. Finally, it should be further noted that the S extrusion from **M$_3$** is due to **M$_3$** (with two identical R′N=C(Ph)S structural units) being much less stable thermodynamically than complex **4** or **5**, which have only one R′N=C(Ph)S unit.

Similar to **1**–**5**, complexes **6**–**9** are also air-stable red solids, which were characterized by elemental analysis and spectroscopy. The IR spectra of **6** and **7** displayed three absorption bands in the range 2066–1992 cm^{-1} for their terminal carbonyls and one band at 1622 cm^{-1} for their two identical uncoordinated C=N double bands, whereas **8** and **9** exhibited three absorption bands in the region 2083–1979 cm^{-1} for their terminal carbonyls and two absorption bands at about 1630 and 1595 cm^{-1} for their uncoordinated and coordinated C=N double bonds, respectively. In addition, the ^{1}H NMR spectra of **6**–**9** displayed the corresponding signals for their phenyl and tolyl groups, and the ^{77}Se NMR spectra of **6** and **7** each showed one singlet at about 227 ppm for their two identical bridged Se atoms.[33–36]

The molecular structures of **6**–**8** were unequivocally confirmed by X-ray diffraction analysis. While Figures 4–6 show their ORTEP views, Table 2 presents their selected bond lengths and angles. As can be seen in Figures 4 and 5, complexes **6** and **7** are similar to complex **1**, in having a butterfly Fe1Fe2Se1Se2 cluster core. While complex **6** contains two N-phenyl benzimidoyl groups connected to its Se1 and Se2 via an equatorial Se1–C13 and an axial Se2–C26 bond, complex **7** includes two N-tolyl benzimidoyl groups attached to its Se1 and Se2 by equatorial Se1–C28 and Se2–C14 bonds. The bond lengths of C13–N1 (1.246 Å)

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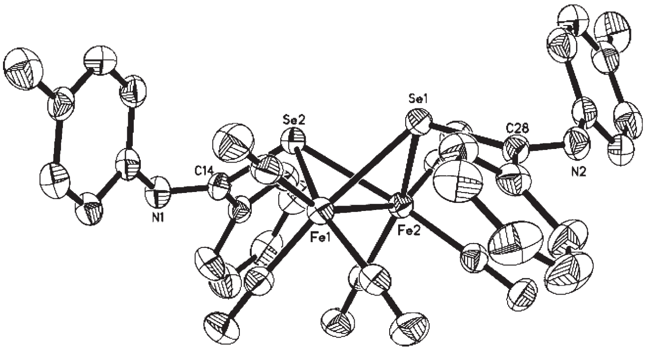

Figure 5. ORTEP view of **7** with 30% probability level ellipsoids.

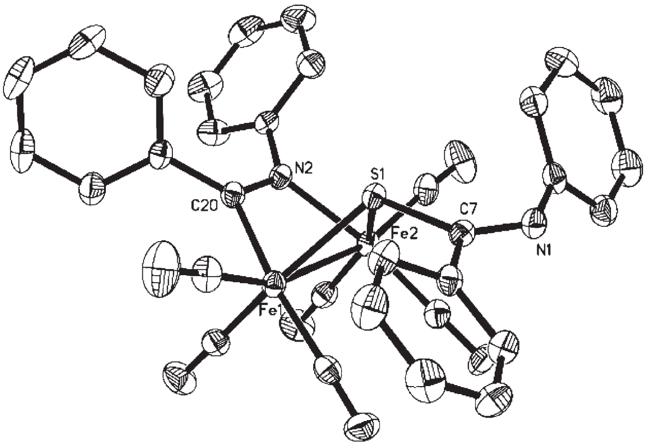

Figure 6. ORTEP view of **8** with 30% probability level ellipsoids.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 6−8

		6	
Se(1)−C(13)	1.993(6)	Se(1)−Fe(2)	2.3800(12)
Fe(1)−Se(1)	2.3919(12)	Se(2)−Fe(2)	2.4057(13)
Fe(1)−Se(2)	2.4007(13)	N(2)−C(26)	1.200(8)
Fe(1)−Fe(2)	2.5199(16)	N(1)−C(13)	1.246(7)
Fe(2)−Se(1)−Fe(1)	63.75(4)	C(13)−Se(1)−Fe(1)	111.39(18)
C(26)−Se(2)−Fe(2)	111.25(19)	C(26)−Se(2)−Fe(1)	104.9(2)
N(1)−C(13)−C(12)	120.3(6)	Fe(1)−Se(2)−Fe(2)	63.23(4)
N(2)−C(26)−Se(2)	128.1(2)	N(1)−C(13)−Se(1)	124.4(5)
		7	
Se(1)−Fe(1)	2.4080(9)	Se(1)−Fe(2)	2.4001(8)
Se(2)−Fe(2)	2.3937(9)	Se(2)−Fe(1)	2.4087(8)
Fe(1)−Fe(2)	2.5260(10)	N(2)−C(28)	1.246(6)
N1)-C(11)	1.246(6)	N(1)−C(14)	1.247(6)
Fe(2)−Se(1)−Fe(1)	63.38(3)	C(28)−Se(1)−Fe(1)	113.63(16)
C(14)−Se(2)−Fe(1)	110.32 (14)	C(14)−Se(2)−Fe(2)	112.90(3)
N(1)−C(14)−C(15)	120.6(5)	Fe(2)−Se(2)−Fe(1)	63.47(3)
N(2)−C(28)−Se(1)	122.5(4)	N(1)−C(14)−Se(2)	122.4(4)
		8	
Fe(1)−S(1)	2.2829(18)	N(1)−C(7)	1.267(5)
Fe(1)−Fe(2)	2.574(2)	N(1)−C(14)	1.417(5)
Fe(2)−N(2)	1.991(4)	C(20)−N(2)	1.292(4)
Fe(2)−S(1)	2.2780(18)	N(2)−C(27)	1.457(5)
S(1)−Fe(1)−Fe(2)	55.55(4)	Fe(2)−S(1)−Fe(1)	68.72(6)
N(2)−Fe(2)−S(1)	80.76(12)	N(1)−C(7)−S(1)	125.4(3)
C(7)−S(1)−Fe(1)	115.07(14)	N(2)−C(20)−Fe(1)	109.5(3)
S(1)−Fe(2)−Fe(1)	55.73(5)	C(20)−N(2)−Fe(2)	108.1(3)

and C26−N2 (1.200 Å) for **6** and those of C14−N1 (1.247 Å) and C28−N2 (1.246 Å) for **7** are close to the bond length of C7−N1(1.253 Å) for **1**, since these C=N double bonds are all uncoordinated in these complexes. The X-ray crystallographic study revealed that complex **8** is different from **1** and **4**−**7**, which comprises a butterfly Fe1Fe2S1C20N2 cluster core bound to the *N*-phenyl benzimidoyl group via an S1−C7 equatorial bond. Interestingly, complex **8** has a three-membered ring and a four-membered ring as its two wings of the butterfly cluster core, whereas complexes **1**, **6**, and **7** have two three-membered rings as their two wings of the butterfly cluster cores, and complexes **4** and **5** have one three-membered ring and one five-membered ring as their two wings of the butterfly cluster cores. The bond length of C20−N2 (1.292 Å) involved in the four-membered ring of **8** is very close to those of C8−N1(1.302 Å) and C7−N1(1.299 Å) in **4** and **5** since they are all coordinated with their iron atoms. The bond length of the uncoordinated C7−N1 bond (1.267 Å) in **8** is close to those of uncoordinated double bonds C7−N1 in **1**, C26−N2/C13−N1 in **6**, and C28−N2/C14−N1 in **7**. The bond lengths of Fe1−Fe2 in **6** (2.5199 Å), **7** (2.5260 Å), and **8** (2.574 Å) are very close to those of **1**, **4**, and **5** and the other similar butterfly Fe/E cluster complexes.[38−42]

Conclusions

We have synthesized the expected and unexpected new butterfly Fe/E cluster complexes **1**−**9** through reactions of anions **A**−**D** with the corresponding N-substituted benzimidoyl chlorides. According to the familiar nucleophilic substitution modes of anions **A**−**D** and the structural characterization of products **1**−**9**, as well as the isolation of byproducts **8′** and **9′** formed from reactions of dianion **D** with PhC(Cl)=NR′, we may conclude that (i) complexes **1**−**3** are generated directly by nucleophilic substitution of monoanion **A** with PhC(Cl)=NPh; (ii) complexes **4** and **5** are produced via nucleophilic substitution of monoanion **B** with PhC(Cl)=NPh followed by skeletal isomerization of the initially formed butterfly intermediate $\mathbf{M_1}$; (iii) complexes **6** and **7** are yielded through direct nucleophilic substitution of dianion **C** with PhC(Cl)=NR′; and (iv) complexes **8** and **9** are formed via the initially nucleophilic substitution of dianion **D** with PhC(Cl)=NR′ to give intermediate $\mathbf{M_2}$, the skeletal isomerization of $\mathbf{M_2}$ to give intermediate $\mathbf{M_3}$, and finally the one S extrusion from $\mathbf{M_3}$. It follows that the formation of the unexpected products **4**, **5**, **8**, and **9** involves two new reaction modes associated with monoanion **B** and dianion **D**, namely, the skeletal isomerization of intermediate $\mathbf{M_1}$ or $\mathbf{M_2}$ and the S extrusion from intermediate $\mathbf{M_3}$. Further studies on the detailed pathways for formation of such unexpected products as well as a search for new reaction modes associated with anions **A**−**D** will be carried out in this laboratory.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen by using standard Schlenk and vacuum-line techniques. THF was distilled from Na/benzophenone ketyl under nitrogen. $(\mu\text{-}S_2)Fe_2(CO)_6$,[6] $(\mu\text{-}Se_2)Fe_2(CO)_6$,[7] PhC(Cl)=NPh,[45] PhC(Cl)=NC$_6$H$_4$Me-*p*,[46] and RMgX[47] (R = Me, Et,

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m-MeC_6H_4) were prepared according to literature procedures. Et_3BHLi (1 M in THF) was of commercial origin and used without further purification. Preparative TLC was carried out on glass plates (26 × 20 × 0.25 cm) coated with silica gel G (10−40 μm). IR spectra were recorded on a Bruker Vector 22 or a Bio-Rad FTS 135 infrared spectrophotometer. ^1H NMR and ^{77}Se NMR spectra were obtained on a Bruker AC-P200, a Bruker Avance 300 NMR, or a Bruker AV 600 NMR spectrometer. Elemental analyses were performed on an Elementar Vario EL analyzer. Melting points were determined on a Yanaco MP-500 apparatus and are uncorrected.

Preparation of (μ-MeSe)[μ-SeC(Ph)=NPh]$Fe_2(CO)_6$ (1). A 100 mL three-necked flask equipped with a magnetic stir-bar, a rubber septum, and a nitrogen inlet tube was charged with (μ-Se_2)$Fe_2(CO)_6$ (0.437 g, 1.0 mmol) and THF (20 mL). The resulting red solution was stirred and cooled to −78 °C. To this solution was added an Et_2O solution of MeMgI (1.0 mmol) by syringe until the mixture turned emerald green. The mixture was stirred for an additional 30 min at −78 °C, and then PhC(Cl)=NPh (0.600, 2.78 mmol) was added. After the mixture was warmed to room temperature, it was stirred for 12 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 1:2) as eluent. From the main red band, **1** was obtained as a red solid (0.364 g, 57%), mp 33−35 °C (dec). Anal. Calcd for $C_{20}H_{13}Fe_2NO_6Se_2$: C, 37.95; H, 2.07; N, 2.21. Found: C, 37.92; H, 2.07; N, 2.36. IR (KBr disk): $\nu_{C\equiv O}$ 2065 (s), 2032 (vs),1990 (vs); $\nu_{C=N}$ 1622 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, TMS): 1.98 (s, 3H, CH_3), 6.99−7.76 (m, 10H, $2C_6H_5$) ppm. ^{77}Se NMR (76 MMz, $CDCl_3$, Me_2Se): 40.33, 236.37 ppm.

Preparation of (μ-EtSe)[μ-SeC(Ph)=NPh]$Fe_2(CO)_6$ (2). The same procedure was followed as that for **1**, but EtMgBr was used instead of MeMgI, and **2** was obtained as a red solid (0.500 g, 77%), mp 32−34 °C. Anal. Calcd for $C_{21}H_{15}Fe_2NO_6Se_2$: C, 38.99; H, 2.34; N, 2.16. Found: C, 39.00; H, 2.35; N, 2.25. IR (KBr disk): $\nu_{C\equiv O}$ 2064 (s), 2032 (vs), 1990 (vs); $\nu_{C=N}$ 1623 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, TMS): 1.30 (t, J = 7.2 Hz, 3H, CH_3), 2.48 (q, J = 7.2 Hz, 2H, CH_2), 6.95−7.72 (m, 10H, $2C_6H_5$) ppm. ^{77}Se NMR (38 MMz, $CDCl_3$, Me_2Se): 147.20, 234.70 ppm.

Preparation of (μ-m-MeC_6H_4Se)[μ-SeC(Ph)=NPh]$Fe_2(CO)_6$ (3). The same procedure was followed as that for **1**, but m-MeC_6H_4MgBr was used instead of MeMgI, and **3** was obtained as a red solid (0.354 g, 50%), mp 50−52 °C. Anal. Calcd for $C_{26}H_{17}Fe_2NO_6Se_2$: C, 44.04; H, 2.42; N, 1.98. Found: C, 43.97; H, 2.45; N, 2.02. IR (KBr disk): $\nu_{C\equiv O}$ 2067 (s), 2032 (vs), 1994 (vs); $\nu_{C=N}$ 1623 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, TMS): 2.25 (s, 3H, CH_3), 7.04−7.80 (m, 14H, $2C_6H_5$, C_6H_4) ppm. ^{77}Se NMR (38 MHz, $CDCl_3$, Me_2Se): 219.98, 228.63 ppm.

Preparation of (μ-MeS)[η^1-SC(Ph)=NPh-η^1]$Fe_2(CO)_6$ (4). The same equipped flask described above was charged with (μ-S_2)$Fe_2(CO)_6$ (0.344 g, 1.0 mmol) and THF (20 mL). The resulting red solution was stirred and cooled to −78 °C. To this solution was added an Et_2O solution of MeMgI (1.0 mmol) to cause an immediate color change from red to emerald green. The green mixture was stirred for an additional 30 min, and then PhC(Cl)=NPh (0.431 g, 2.0 mmol) was added. After the mixture was warmed to room temperature, it was stirred for 4 h. Solvent was removed under reduced pressure to give a residue, which was subjected to TLC separation. The main red band was eluted with acetone/petroleum ether (v/v = 1:4). After removel of solvent **4** was obtained as a red solid (0.277 g, 51%), mp 78 °C (dec). Anal. Calcd for $C_{20}H_{13}Fe_2NO_6S_2$: C, 44.56; H, 2.43; N, 2.60. Found: C, 44.45; H, 2.44; N, 2.59. IR (KBr disk): $\nu_{C\equiv O}$ 2071 (vs), 2033 (vs), 1987 (vs); $\nu_{C=N}$ 1613 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, TMS): 2.50 (s, 3H, CH_3), 6.47−7.89 (m, 10H, $2C_6H_5$) ppm.

Preparation of (μ-EtS)[η^1-SC(Ph)=NPh-η^1]$Fe_2(CO)_6$ (5). The same procedure was followed as that for **4**, except that EtMgBr was used in place of MeMgI and CH_2Cl_2/petroleum ether (v/v = 1:3) was used as eluent. **5** was obtained as a red solid (0.425 g, 77%), mp 38−40 °C. Anal. Calcd for $C_{21}H_{15}Fe_2NO_6S_2$: C, 45.60; H, 2.72; N, 2.54. Found: C, 45.45; H, 2.70; N, 2.57. IR (KBr disk): $\nu_{C\equiv O}$ 2070 (vs), 2032 (vs), 1994 (vs); $\nu_{C=N}$ 1613 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, TMS): 1.62 (t, J = 7.2 Hz, 3H, CH_3), 2.73 (q, J = 7.2 Hz, 2H, CH_2), 6.56−7.45 (m, 10H, $2C_6H_5$) ppm.

Preparation of [μ-SeC(Ph)=NPh]$_2Fe_2(CO)_6$ (6). A red solution of (μ-Se_2)$Fe_2(CO)_6$ (0.437 g, 1.0 mmol) in THF (20 mL) was stirred and cooled to −78 °C. To this solution was added a THF solution of Et_3BHLi (2 mL, 2 mmol) by syringe, resulting in an immediate color change from red to emerald green. The green mixture was stirred at −78 °C for 30 min, and then PhC(Cl)=NPh (1.080, 5.0 mmol) was added, causing a color change back to red. The new mixture was allowed to warm to room temperature and stirred at this temperature for 6 h. After solvent was removed under reduced pressure, the residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (1:2.5 v/v) as eluent. From the main red band, **6** was obtained as a red solid (0.210 g, 26%), mp 115−116 °C. Anal. Calcd for $C_{32}H_{20}Fe_2N_2O_6Se_2$: C, 48.16; H, 2.53; N, 3.51. Found: C, 48.39; H, 2.50; N, 3.59. IR (KBr disk): $\nu_{C\equiv O}$ 2065 (s), 2035 (vs), 1992 (vs); $\nu_{C=N}$ 1622 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): 6.96−7.73 (m, 20H, $4C_6H_5$) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$, Me_2Se): 226.10 ppm.

Preparation of [μ-SeC(Ph)=NC_6H_4Me-p]$_2Fe_2(CO)_6$ (7). The same procedure was employed as that for **6**, but PhC(Cl)=NC_6H_4Me-p (1.150 g, 5.0 mmol) was utilized in place of PhC(Cl)=NPh. From the main red band, **7** was obtained as a red solid (0.453 g, 55%), mp 128−130 °C. Anal. Calcd for $C_{34}H_{24}Fe_2N_2O_6Se_2$: C, 49.43; H, 2.93; N, 3.39 Found: C, 49.57; H, 3.09; N, 3.35. IR (KBr disk): $\nu_{C\equiv O}$ 2066 (s), 2034 (vs), 1992 (vs); $\nu_{C=N}$ 1622 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): 2.38 (s, 6H, $2CH_3$), 6.87−7.71 (m, 18H, $2C_6H_4$, $2C_6H_5$) ppm. ^{77}Se NMR (114 MHz, $CDCl_3$, Me_2Se): 228.00 ppm.

Preparation of [μ-SC(Ph)=NPh][η^1-C(Ph)=NPh-η^1]$Fe_2(CO)_6$ (8). A red solution of (μ-S_2)$Fe_2(CO)_6$ (0.344 g, 1.0 mmol) in THF (20 mL) was stirred and cooled to −78 °C, and then a THF solution of Et_3BHLi (2 mL, 2 mmol) was added. The resulting green mixture was stirred at −78 °C for 30 min, and then PhC(Cl)=NPh (1.080 g, 5.0 mmol) was added. The new mixture was allowed to warm to room temperature and stirred for 4 h. After removal of solvent, the residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (1:4 v/v) as eluent. From the main red band, **8** was obtained as a red solid (0.217 g, 32%), mp 56−57 °C . Anal. Calcd for $C_{32}H_{20}Fe_2N_2O_6S$: C, 57.17; H, 3.00; N, 4.17. Found: C, 57.15; H, 3.04; N, 4.25. IR (KBr disk): $\nu_{C\equiv O}$ 2070 (s), 2035 (s), 1997 (vs); $\nu_{C=N}$ 1620 (m), 1590 (m) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, TMS): 6.04−7.96 (m, 20H, $4C_6H_5$) ppm. From the main yellow band, the known compound PhC(S)NHPh (**8′**) was obtained as a yellow solid (0.108 g), mp 98−99 °C (lit. 97 °C).[48] Anal. Calcd for $C_{13}H_{11}NS$: C, 73.20; H, 5.20; N, 6.57. Found: C, 73.05; H, 5.17; N, 6.58. IR (KBr disk): ν_{N-H} 3328 (m); $\nu_{C=S}$ 1209 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, TMS): 7.24−7.82 (m, 10H, $2C_6H_5$), 8.98 (s, 1H, NH) ppm.

Preparation of [μ-SC(Ph)=NC_6H_4Me-p][η^1-C(Ph)=NC_6H_4Me-p-η^1]$Fe_2(CO)_6$ (9). The same procedure was employed as that for **8**, but PhC(Cl)=NC_6H_4Me-p (1.147 g, 5.0 mmol) was utilized in place of PhC(Cl)=NPh and acetone/petroleum ether (1:7 v/v) was used as eluent. From the main red band, **9** was obtained as a red solid (0.279 g, 40%), mp 58−60 °C. Anal. Calcd for $C_{34}H_{24}Fe_2N_2O_6S$: C, 58.31; H, 3.45; N, 4.00. Found: C, 58.15; H, 3.68; N, 3.70. IR (KBr disk): $\nu_{C\equiv O}$ 2083 (m), 2036 (vs), 1979 (vs); $\nu_{C=N}$ 1640 (m), 1599 (s) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, TMS): 2.20, 2.34 (2s, 6H, $2CH_3$), 6.42−8.06 (m, 18H, $2C_6H_5$, $2C_6H_4$) ppm. From the main yellow band, the known compound PhC(S)NHC_6H_4Me-p (**9′**) was obtained as a yellow solid (0.178 g), mp 129−130 °C (lit. 131 °C).[48]

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Table 3. Crystal Data and Structure Refinements for 1, 4, and 5

	1	4	5
mol formula	$C_{20}H_{13}Fe_2NO_6Se_2$	$C_{20}H_{13}Fe_2NO_6S_2$	$C_{21}H_{15}Fe_2NO_6S_2$
mol wt	632.93	539.13	553.16
cryst syst	orthorhombic	monoclinic	triclinic
space group	*Pna*2(1)	*P*2(1)/*n*	$P\bar{1}$
a/Å	7.826 (3)	14.073(3)	11.816(2)
b/Å	18.980(7)	10.611(2)	16.939(3)
c/Å	14.842(5)	15.801(3)	24.318(5)
α/deg	90	90	70.94(3)
β/deg	90	112.86(3)	88.46(3)
γ/deg	90	90	87.73(3)
V/Å^3	2204.6(14)	2174.3(8)	4596.5(16)
Z	4	4	8
D_c/g·cm^{-3}	1.907	1.647	1.599
abs coeff/mm^{-1}	14.661	1.563	1.481
F(000)	1232	1088	2240
index ranges	$-9 \le h \le 9$ $-23 \le k \le 23$ $-18 \le l \le 18$	$-16 \le h \le 16$ $-12 \le k \le 11$ $-18 \le l \le 18$	$-12 \le h \le 14$ $-18 \le k \le 20$ $-28 \le l \le 28$
no. of reflns	21 299	14 606	35 176
no. of indep reflns	4298	3841	16 150
$2\theta_{max}$/deg	145.2	50.04	50.04
R	0.0427	0.0345	0.0522
R_w	0.1043	0.0824	0.1276
goodness of fit	1.084	0.821	1.018
largest diff peak and hole/e Å^{-3}	0.878/−0.959	0.743/−0.531	1.173/−0.926

Table 4. Crystal Data and Structure Refinements for 6−8

	6	7	8
mol formula	$C_{32}H_{20}Fe_2O_6N_2Se_2\cdot CH_3OH$	$C_{34}H_{24}Fe_2O_6N_2Se_2$	$C_{32}H_{20}Fe_2N_2O_6S$
mol wt	830.16	826.17	672.26
cryst syst	monoclinic	triclinic	triclinic
space group	*P*2(1)/*c*	$P\bar{1}$	$P\bar{1}$
a/Å	11.909(4)	13.5607(19)	8.835(8)
b/Å	18.229(6)	14.769(2)	11.022(10)
c/Å	16.324(5)	17.946(3)	16.683(15)
α/deg	90	77.737(2)	102.605(14)
β/deg	108.439(5)	74.268(2)	101.422(17)
γ/deg	90	77.965(2)	102.630(15)
V/Å^3	3361.8(18)	3336.9(8)	1495(2)
Z	4	4	2
D_c/g·cm^{-3}	1.640	1.645	1.494
abs coeff/mm^{-1}	3.077	3.098	1.088
F(000)	1648	1640	684
index ranges	$-14 \le h \le 13$ $-20 \le k \le 21$ $-19 \le l \le 14$	$-16 \le h \le 12$ $-17 \le k \le 17$ $-21 \le l \le 21$	$-4 \le h \le 11$ $-13 \le k \le 13$ $-20 \le l \le 20$
no. of reflns	16 790	18 180	8646
no. of indep reflns	5923	11 649	6090
$2\theta_{max}$/deg	50.02	50.06	53.06
R	0.0457	0.0409	0.0479
R_w	0.1007	0.0747	0.0908
goodness of fit	1.107	0.967	0.992
largest diff peak and hole/e Å^{-3}	1.003/−0.411	0.467/−0.324	0.389/−0.343

X-ray Structure Determinations of 1 and 4−8. Single crystals of **1** and **4**−**8** suitable for X-ray diffraction analyses were grown by slow evaporation of the diethyl ether/hexane solutions of **1**, **4**, and **5**, the CH_2Cl_2/petroleum ether solutions of **6** and **7**, and the CH_2Cl_2 solution of **8** at 4 °C, respectively. A single crystal of **1**, **4**, or **5** was mounted on a Rigaku MM-007 (rotating anode) diffractometer equipped with Saturn 70CCD. Data were collected at 113(2) K, using a confocal monochromator with Mo Kα radiation ($\lambda = 0.71070$ Å) in the $\omega-\phi$ scanning mode. Data collection, reduction, and absorption correction were performed by the CRYSTALCLEAR program.[49] A single crystal of **6**, **7**, or **8** was mounted on a Bruker SMART 1000 automated diffractometer. Data were collected at room temperature using a graphite monochromator with Mo Kα radiation ($\lambda = 0.71073$ Å) in the $\omega-\phi$ scanning mode. Absorption correction was performed by the SADABS program.[50] All the structures were solved by direct methods using the SHELXS-97 program[51] and refined by full-matrix least-squares techniques (SHELXL-97)[52] on F^2. Hydrogen atoms were located using the geometric method. Details of crystal data, data collections, and structure refinements are summarized in Tables 3 and 4, respectively.

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Supporting Information Available: Full tables of crystal data, atomic coordinates and thermal parameters, and bond lengths and angles for **1** and **4**−**8** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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