

# Novel Reaction of Complex Salts $[(\mu\text{-RE})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6][\text{HNET}_3]$ (E = S, Se) with Phosphaalkene $t\text{-Bu}(\text{Me}_3\text{SiO})\text{C}=\text{PSiMe}_3$ . Synthesis and Spectroscopic and Crystallographic Characterization of Butterfly $\text{Fe}_2\text{EP}$ Clusters $(\mu\text{-RE})[\mu\text{-}t\text{-Bu}(\text{Me}_3\text{SiO})\text{CHPH}]\text{Fe}_2(\text{CO})_6$ (E = S, Se)

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Reaction of complex salts  $[(\mu\text{-RE})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6][\text{HNET}_3]$  (**1**, E = S, Se) with phosphaalkene  $t\text{-Bu}(\text{Me}_3\text{SiO})\text{C}=\text{PSiMe}_3$  (**2**) has been found to afford a series of new butterfly-shaped  $\text{Fe}_2\text{-EP}$  clusters of type  $[(\mu\text{-RE})[\mu\text{-}t\text{-Bu}(\text{Me}_3\text{SiO})\text{CHPH}]\text{Fe}_2(\text{CO})_6]$  (**3**, RE = EtS; **4**, n-PrS; **5**, n-BuS; **6**, t-BuS; **7**, PhSe; **8**, *p*-MeC<sub>6</sub>H<sub>4</sub>Se) in quite high yields. This type of cluster may exist as three isomers, namely, e(R)e(H), e(R)a(H), and a(R)a(H), which differ in whether the R group and H atom are attached to E and P atoms with an axial or an equatorial bond. Clusters **3–8** have been characterized by elemental analysis and <sup>1</sup>H, <sup>31</sup>P, and <sup>77</sup>Se NMR spectroscopy, as well as for isomers **3e(R)a(H)**, **6e(R)a(H)**, **8e(R)e(H)**, and **8a(R)a(H)** by single-crystal X-ray diffraction analyses. In addition, a possible reaction mechanism has been preliminarily suggested.

## Introduction

In recent years the complex salts  $[(\mu\text{-RE})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6][\text{HNET}_3]$  (**1**, E = S, Se) have been intensively

studied and successfully utilized in the synthesis of Fe–E cluster complexes containing a great variety of organic and inorganic bridging groups.<sup>1–8</sup> Furthermore, the compounds containing phosphorus–carbon multiple bonds,<sup>9</sup> such as phosphaalkyne  $t\text{-BuC}\equiv\text{P}^{10}$  and phosphaalkene  $t\text{-Bu}(\text{Me}_3\text{SiO})\text{C}=\text{PSiMe}_3$ ,<sup>11</sup> have also been extensively studied and up to now have become important synthons for phosphorus-containing organic and organometallic compounds. However, to our knowledge, only one example is so far reported concerning the reaction of complex salts **1** with the compounds containing phosphorus–carbon multiple bonds, in which the E

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**Table 1.** <sup>1</sup>H{<sup>31</sup>P} and <sup>31</sup>P NMR Data for Products 3–8

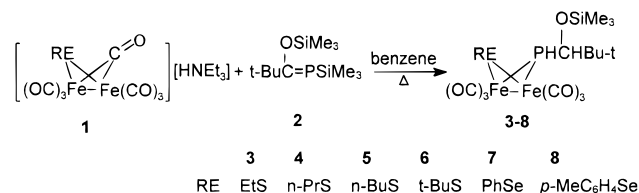
product	<sup>1</sup> H{ <sup>31</sup> P} NMR (CDCl <sub>3</sub> ) δ (ppm), J (Hz)	<sup>31</sup> P NMR (CDCl <sub>3</sub> ) δ (ppm)
<b>3e(R)e(H)</b>	0.18 (s, 9H, SiMe <sub>3</sub> ), 0.95 (s, 9H, t-Bu), 1.35 (t, J = 7.3, 3H, CH <sub>3</sub> ), 2.46 (q, J = 7.3, 2H, SCH <sub>2</sub> ), 3.83 (dd, <sup>1</sup> J <sub>PH</sub> = 11.5, J <sub>HH</sub> = 6.3, 1H, CH), 4.45 (dd, <sup>1</sup> J <sub>PH</sub> = 360.2, J <sub>HH</sub> = 6.3, 1H, PH)	92.74(s)
<b>3e(R)a(H)</b>	0.20 (s, 9H, SiMe <sub>3</sub> ), 1.06 (s, 9H, t-Bu), 1.33 (t, J = 7.4, 3H, CH <sub>3</sub> ), 2.45 (q, J = 7.4, 2H, SCH <sub>2</sub> ), 2.63 (dd, <sup>1</sup> J <sub>PH</sub> = 350.4, J <sub>HH</sub> = 10.4, 1H, PH), 4.15 (dd, <sup>2</sup> J <sub>PH</sub> = 13.6, J <sub>HH</sub> = 10.4, 1H, CH)	88.08(s)
<b>4e(R)e(H)</b>	0.18 (s, 9H, SiMe <sub>3</sub> ), 0.95 (s, 9H, t-Bu), 1.03 (t, J = 7.1, 3H, CH <sub>3</sub> ), 1.59–1.79 (m, 2H, CH <sub>2</sub> ), 2.43 (t, J = 7.2, 2H, SCH <sub>2</sub> ), 3.84 (dd, <sup>2</sup> J <sub>PH</sub> = 12.5, J <sub>HH</sub> = 6.3, 1H, CH), 4.45 (dd, <sup>1</sup> J <sub>PH</sub> = 359.7, J <sub>HH</sub> = 6.3, 1H, PH)	92.89(s)
<b>4e(R)a(H)</b>	0.20 (s, 9H, SiMe <sub>3</sub> ), 1.01 (t, J = 7.3, 3H, CH <sub>3</sub> ), 1.06 (s, 9H, t-Bu), 1.59–1.79 (m, 2H, CH <sub>2</sub> ), 2.42 (t, J = 7.3, 2H, SCH <sub>2</sub> ), 2.61 (dd, <sup>1</sup> J <sub>PH</sub> = 350.2, J <sub>HH</sub> = 10.4, 1H, PH), 4.14 (dd, <sup>2</sup> J <sub>PH</sub> = 13.6, J <sub>HH</sub> = 10.4, 1H, CH)	88.32(s)
<b>5e(R)e(H)</b>	0.18 (s, 9H, SiMe <sub>3</sub> ), 0.92 (t, J = 7.2, 3H, CH <sub>3</sub> ), 0.95 (s, 9H, t-Bu), 1.37–1.48 (m, 2H, CH <sub>2</sub> CH <sub>3</sub> ), 1.57–1.73 (m, 2H, SCH <sub>2</sub> CH <sub>2</sub> ), 2.44 (t, J = 7.5, 2H, SCH <sub>2</sub> ), 3.83 (dd, <sup>2</sup> J <sub>PH</sub> = 11.5, J <sub>HH</sub> = 6.3, 1H, CH), 4.44 (dd, <sup>1</sup> J <sub>PH</sub> = 359.7, J <sub>HH</sub> = 6.3, 1H, PH)	92.87(s)
<b>5e(R)a(H)</b>	0.20 (s, 9H, SiMe <sub>3</sub> ), 0.90 (t, J = 7.3, 3H, CH <sub>3</sub> ), 1.06 (s, 9H, t-Bu), 1.33–1.47 (m, 2H, CH <sub>2</sub> CH <sub>3</sub> ), 1.55–1.69 (m, 2H, SCH <sub>2</sub> CH <sub>2</sub> ), 2.43 (t, J = 7.3, 2H, SCH <sub>2</sub> ), 2.63 (dd, <sup>1</sup> J <sub>PH</sub> = 350.3, J <sub>HH</sub> = 10.4, 1H, PH), 4.14 (dd, <sup>2</sup> J <sub>PH</sub> = 13.5, J <sub>HH</sub> = 10.4, 1H, CH)	88.35(s)
<b>6e(R)e(H)</b>	0.18 (s, 9H, SiMe <sub>3</sub> ), 0.96 (s, 9H, t-Bu), 1.37 (s, 9H, t-BuS), 3.93 (dd, <sup>2</sup> J <sub>PH</sub> = 10.5, J <sub>HH</sub> = 6.3, 1H, CH), 4.40 (dd, <sup>1</sup> J <sub>PH</sub> = 353.5, J <sub>HH</sub> = 6.3, 1H, PH)	90.13(s)
<b>6e(R)a(H)</b>	0.20 (s, 9H, SiMe <sub>3</sub> ), 1.06 (s, 9H, t-Bu), 1.39 (s, 9H, t-BuS), 2.39 (dd, <sup>1</sup> J <sub>PH</sub> = 359.7, J <sub>HH</sub> = 10.4, 1H, PH), 4.15 (dd, <sup>2</sup> J <sub>PH</sub> = 12.5, J <sub>HH</sub> = 10.4, 1H, CH)	87.34(s)
<b>7e(R)e(H)/a(R)a(H)</b>	0.20, 0.26 (2s, 9H, SiMe <sub>3</sub> ), 1.00, 1.05 (2s, 9H, t-Bu), 3.11, 4.73 (2dd, <sup>1</sup> J <sub>PH</sub> = 359.24, J <sub>HH</sub> = 10.0; <sup>1</sup> J <sub>PH</sub> = 365.96, J <sub>HH</sub> = 6.64, 1H, PH), 4.03–4.19 (m, 1H, CH), 7.33–7.52 (m, 5H, Ph) <sup>a</sup>	95.61(s) 101.91(s)
<b>8e(R)e(H)</b>	0.22 (s, 9H, SiMe <sub>3</sub> ), 0.99 (s, 9H, t-Bu), 2.29 (s, 3H, CH <sub>3</sub> ), 3.71–3.90 (m, 1H, CH), 4.66 (dd, <sup>1</sup> J <sub>PH</sub> = 359.7, J <sub>HH</sub> = 7.3, 1H, PH), 7.16 (q, AA'BB', J = 8.1, 4H, C <sub>6</sub> H <sub>4</sub> )	95.89(s)
<b>8a(R)a(H)</b>	0.18 (s, 9H, SiMe <sub>3</sub> ), 0.96 (s, 9H, t-Bu), 2.28 (s, 3H, CH <sub>3</sub> ), 3.09 (dd, <sup>1</sup> J <sub>PH</sub> = 364.94, J <sub>HH</sub> = 9.4, 1H, PH), 3.98–4.16 (m, 1H, CH), 7.04 (q, AA'BB', J = 7.6, 4H, C <sub>6</sub> H <sub>4</sub> )	102.19(s)

<sup>a</sup> Measured in acetone-*d*<sub>6</sub>.

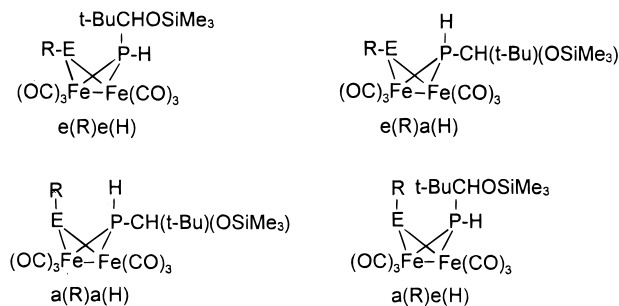
atom of complex salts **1** is sulfur and the phosphorus compound is a phosphaaalkene.<sup>6</sup> To further explore the reactivity of the complex salts **1** (E = S, Se) toward phosphaaalkenes and to prepare organometallic complexes containing both Fe–E and P–C structural units, we initiated a study on the reaction of **1** (E = S, Se) with another type of phosphaaalkene, *t*-Bu(Me<sub>3</sub>SiO)C=PSiMe<sub>3</sub> (**2**). In this article we report the interesting results concerning this study.

## Results and Discussion

**Synthesis via Reaction of 1 with 2 and Characterization of (μ-RE)[μ-*t*-Bu(Me<sub>3</sub>SiO)CHPH]Fe<sub>2</sub>(CO)<sub>6</sub> (3–8).** As described in the Experimental Section a benzene solution of complex salt **1** (RE = EtS) was prepared from Fe<sub>3</sub>(CO)<sub>12</sub>, EtSH, and NEt<sub>3</sub> in benzene at 35–40 °C. The IR spectrum of **1** (RE = EtS) in this benzene solution showed a strong μ-CO peak at 1635 cm<sup>−1</sup>, which is somewhat different from that at 1743 cm<sup>−1</sup> displayed by its THF solution.<sup>1,5</sup> To the prepared benzene solution was added 0.5 equiv of phosphaaalkene **2**, and then the mixture was stirred at 45–50 °C for 8 h. After TLC separation, a butterfly-shaped Fe<sub>2</sub>EP (E = S) cluster (μ-RE)[μ-*t*-Bu(Me<sub>3</sub>SiO)CHPH]Fe<sub>2</sub>(CO)<sub>6</sub> (**3**, RE = EtS) was obtained in 90% yield. Similarly, the other five Fe<sub>2</sub>EP (E = S, Se) clusters (μ-RE)[μ-*t*-Bu(Me<sub>3</sub>SiO)CHPH]Fe<sub>2</sub>(CO)<sub>6</sub> (**4–8**, RE = *n*-PrS; *n*-BuS; *t*-BuS; PhSe; *p*-MeC<sub>6</sub>H<sub>4</sub>Se) were produced in 32–84% yields (Scheme 1).

**Scheme 1**

In principle, clusters **3–8** each might exist as four isomers *e*(R)*e*(H), *e*(R)*a*(H), *a*(R)*a*(H), and *a*(R)*e*(H) (Scheme 2), which differ in whether the R group and H

**Scheme 2**

atom are attached to the E atom and P atom in an equatorial bond or an axial bond.<sup>12</sup>

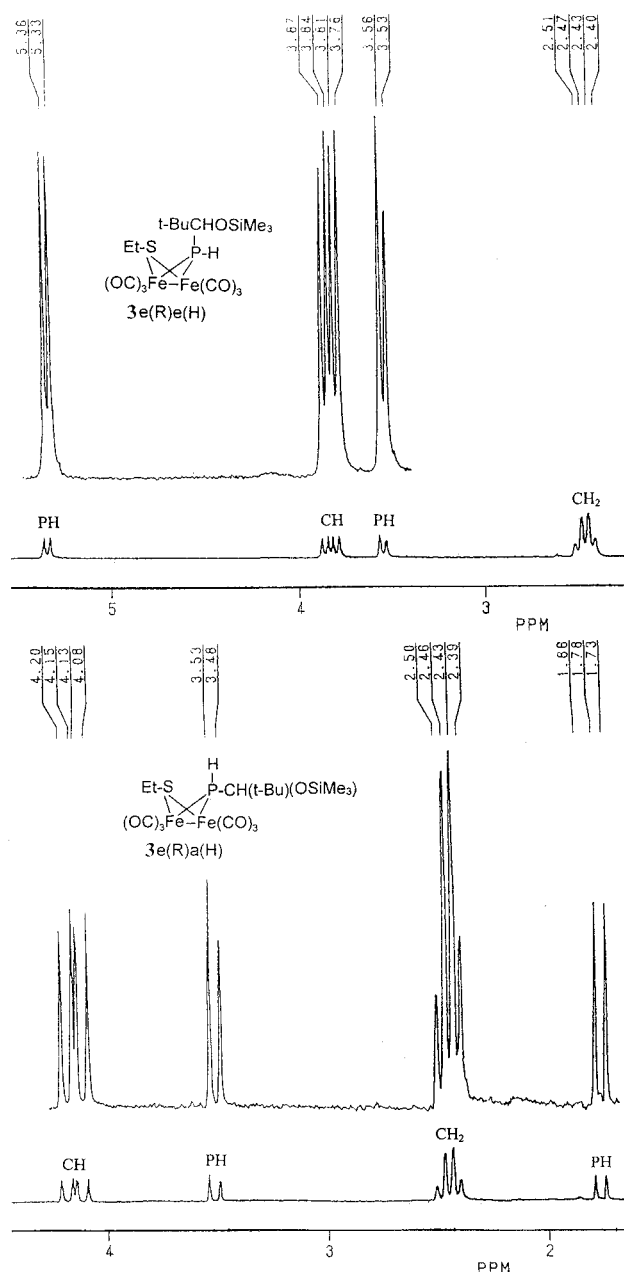
(12) The isomer designation *a* = axial and *e* = equatorial is used: Shaver, A.; Fitzpatrick, P. J.; Steliou, K.; Butler, I. S. *J. Am. Chem. Soc.* **1979**, *101*, 1313.

In fact, we obtained clusters **3–6** as two single isomers e(R)e(H) and e(R)a(H), cluster **7** as a mixture of two isomers e(R)e(H) and a(R)a(H), and cluster **8** as two single isomers e(R)e(H) and a(R)a(H), respectively. The isomers of type a(R)e(H) could not be obtained, possibly due to great steric repulsion between the two large axially bonded groups R and t-BuCH(OSiMe<sub>3</sub>). All the obtained isomers for **3–6** and **8** and the isomer mixture for **7** have been characterized by combustion analysis and spectroscopy, as well as, for some, by X-ray diffraction techniques. The <sup>1</sup>H and <sup>31</sup>P NMR spectral data of these compounds are presented in Table 1. According to the <sup>1</sup>H NMR data of SCH<sub>2</sub> in clusters **3–5** and t-BuS in cluster **6**, it seems to be reasonable that the R groups of **3–5** and **6** are bonded to the S atom through an equatorial type of bond.<sup>8m–k</sup> Fortunately, for **3** and **6** this assignment has been confirmed by X-ray diffraction analyses of isomers **3e(R)e(H)** and **6e(R)a(H)** (see below). As for **7** and **8**, since the <sup>1</sup>H NMR data of R (phenyl and tolyl) groups are complicated, we cannot establish whether such groups are attached to the Se atom by an axial or equatorial bond. However, for **8** the X-ray diffraction analysis has indicated that in its one isomer, i.e., **8e(R)e(H)**, the tolyl group is bonded to the Se atom by an equatorial bond and in another isomer, i.e., **8a(R)a(H)**, by an axial bond (also see below). In addition, since the <sup>31</sup>P NMR spectral data of the two isomers of **7** (95.61 and 101.91 ppm) are almost the same as those of the two isomers of **8** (95.89 and 102.19 ppm), we might conclude that **7** consists of the same type of isomers, i.e., **7e(R)e(H)** and **7a(R)a(H)**.

In addition, we can see from the <sup>1</sup>H NMR data that the chemical shifts of the H atom axially bonded to the P atom are at much higher field than those of the H atom equatorially bonded to the P atom; the  $\delta_{e-PH}$  for e(R)e(H) isomers are generally in the range 4.40–4.73 ppm, and the  $\delta_{a-PH}$  for e(R)a(H) and a(R)a(H) isomers are in the range 2.39–3.09 ppm. These points mentioned above can be more clearly seen from corresponding <sup>1</sup>H{<sup>31</sup>P} NMR spectra of **3e(R)e(H)** and **3e(R)a(H)** (Figure 1). In Figure 1, the two dd-type quartets at 4.45 and 2.63 ppm can be assigned to the equatorially bonded H atom and axially bonded H atom in the PH group of **3e(R)e(H)** and **3e(R)a(H)**, respectively.

These dd-type of quartets are apparently generated by joint coupling of the <sup>31</sup>P nucleus and the H atom in the neighboring CH group. In addition, the H atom of the neighboring CH group can also be coupled with the <sup>31</sup>P nucleus and the H atom of the PH group to give another two dd-type quartets at 3.83 and 4.15 ppm assigned to the H atom in the CH group of **3e(R)e(H)** and **3e(R)a(H)**, respectively. It is worth noting that the coupling constants for these two isomers between <sup>31</sup>P and its directly linked H atom, namely, <sup>1</sup>J <sup>1</sup>H{<sup>31</sup>P} are 350.2 and 360.2 Hz, which are similar to those reported for (μ-PhPH)(μ-η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>PhP)Fe<sub>2</sub>(CO)<sub>6</sub><sup>13</sup> and (μ-PhP-PPh-μ)[(μ-PhPH)Fe<sub>2</sub>(CO)<sub>6</sub>]<sub>2</sub>.<sup>14</sup>

The <sup>31</sup>P NMR spectral data of **3–8** indicate that the <sup>31</sup>P chemical shifts for isomers e(R)e(H), e(R)a(H), and a(R)a(H) are in the range 90–96, 84–88, and 101–103



**Figure 1.** Partial <sup>1</sup>H{<sup>31</sup>P} NMR spectra of **3e(R)e(H)** and **3e(R)a(H)**.

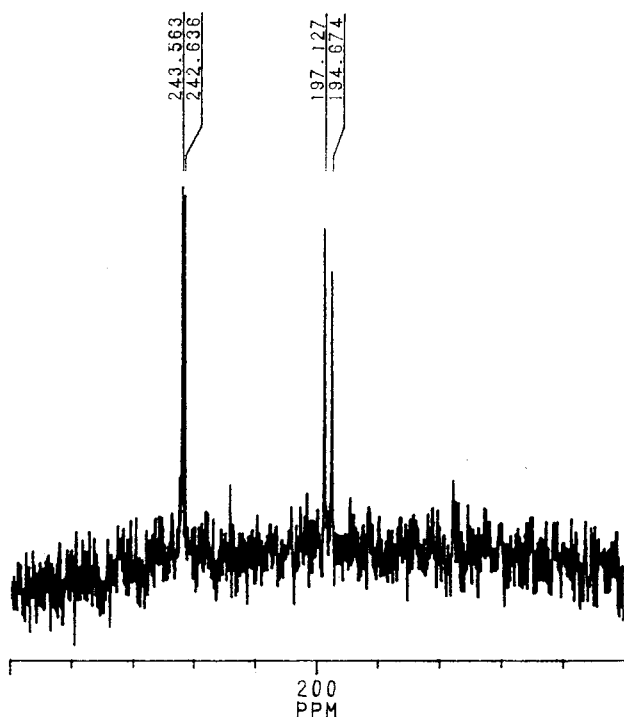
ppm, respectively, following the trend of a(R)a(H) > e(R)e(H) > e(R)a(H). Such <sup>31</sup>P NMR values are close to those of reported compounds, such as (μ-PhPH)(μ-η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>PhP)Fe<sub>2</sub>(CO)<sub>6</sub> (97.0 ppm)<sup>13</sup> and (μ-PhP-PPh-μ)[(μ-PhPH)Fe<sub>2</sub>(CO)<sub>6</sub>]<sub>2</sub> (81.2 ppm).<sup>14</sup>

We determined the <sup>77</sup>Se NMR spectra of **8e(R)e(H)**, **8a(R)a(H)**, and a mixture of **7e(R)e(H)** and **7a(R)a(H)**. The spectrum of **8e(R)e(H)** shows a doublet at 237.7 ppm (<sup>2</sup>J<sub>PSe</sub> = 33.7 Hz), and that of **8a(R)a(H)** displays a doublet at 191.7 ppm (<sup>2</sup>J<sub>PSe</sub> = 97.2 Hz). Similarly, the <sup>77</sup>Se NMR spectrum of the isomer mixture of **7e(R)e(H)** and **7a(R)a(H)** (Figure 2) shows two doublets characteristic of their two bridged Se atoms. The doublet at 243.1 ppm (<sup>2</sup>J<sub>PSe</sub> = 35.4 Hz) is assigned to the Se atom attached to the equatorial phenyl group in isomer **7e(R)e(H)**, whereas that at 195.9 ppm (<sup>2</sup>J<sub>PSe</sub> = 93.8 Hz) is attributed to the Se atom attached to an axial phenyl group in isomer **7a(R)a(H)**. It is apparent that such <sup>77</sup>Se

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**Figure 2.** <sup>77</sup>Se NMR spectrum of a mixture of **7e(R)e(H)** and **7a(R)a(H)**.

**Table 2. Selected Bond Lengths (Å) and Angles (deg) for **3e(R)a(H)** and **6e(R)a(H)****

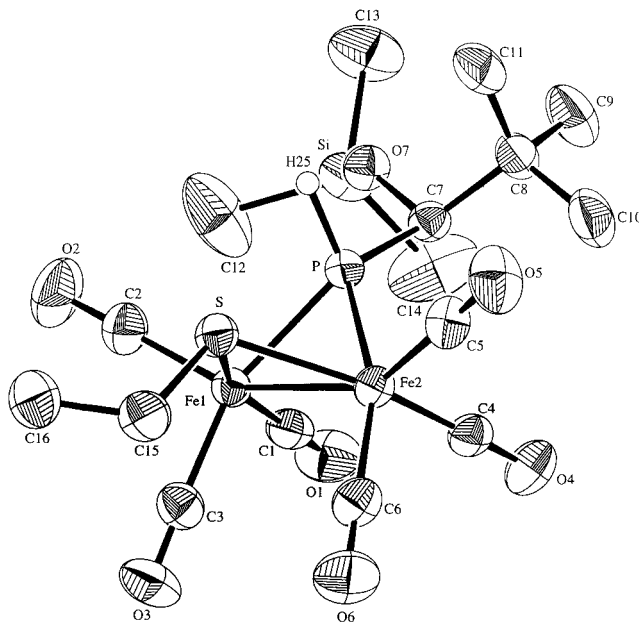
	<b>3e(R)a(H)</b>	<b>6e(R)a(H)</b>
Fe(1)–Fe(2)	2.5617(6)	2.5611(9)
Fe(1)–S	2.271(1)	2.260(1)
Fe(1)–P	2.2244(8)	2.231(1)
S–C(15)	1.832(3)	1.875(3)
P–C(7)	1.870(3)	1.873(3)
Fe(2)–Fe(1)–S	55.61(3)	55.69(3)
Fe(2)–Fe(1)–P	54.84(2)	54.79(3)
S–Fe(1)–P	75.27(3)	74.27(4)
Fe(1)–S–Fe(2)	68.70(2)	68.89(3)
Fe(1)–P–Fe(2)	70.31(3)	70.17(3)
Fe(1)–S–C(15)	114.6(1)	122.0(1)
Fe(1)–P–C(7)	126.84(9)	130.1(1)

NMR spectral data are comparable with those of similar Fe<sub>2</sub>Se<sub>2</sub> butterfly complexes.<sup>15,16</sup>

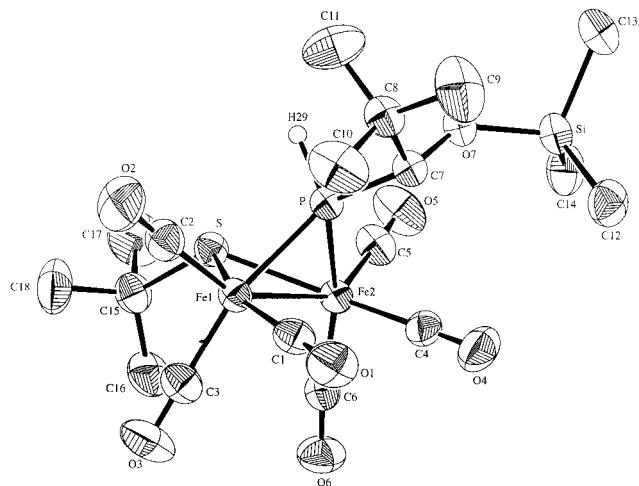
**Crystal Molecular Structures of **3e(R)a(H)**, **6e(R)a(H)**, **8e(R)e(H)**, and **8a(R)a(H)**.** To unambiguously confirm the structures of the products isolated from the above type of reactions, single-crystal X-ray diffraction analyses for **3e(R)a(H)**, **6e(R)a(H)**, **8e(R)e(H)**, and **8a(R)a(H)** were undertaken. Tables 2 and 3 list the selected bond lengths and angles. Figures 3–6 show their molecular structures. As seen in Figures 3–6, each molecule contains one S or Se atom and one P atom bridged to the two Fe atoms of two Fe(CO)<sub>3</sub> structural units to construct a butterfly-shaped Fe<sub>2</sub>EP (E = S, Se) skeleton. In addition, while each molecule has one R (Et, *t*-Bu, *p*-MeC<sub>6</sub>H<sub>4</sub>) group bonded to the E (E = S, Se) atom of the butterfly skeleton through an equatorial or axial bond, it has one H atom and one *t*-Bu(Me<sub>3</sub>SiO)-CH group attached to the P atom of the butterfly skeleton through corresponding equatorial and axial bonds.

**Table 3. Selected Bond Lengths (Å) and Angles (deg) for **8e(R)e(H)** and **8a(R)a(H)****

	<b>8e(R)e(H)</b>	<b>8a(R)a(H)</b>
Fe(1)–Fe(2)	2.5761(8)	2.587(1)
Fe(1)–Se	2.3983(5)	2.3807(9)
Fe(1)–P	2.2316(9)	2.213(1)
Se–C(7)	1.935(3)	1.944(4)
P–C(14)	1.890(3)	1.871(4)
Fe(2)–Fe(1)–Se	57.36(2)	57.35(3)
Fe(2)–Fe(1)–P	54.47(3)	53.96(4)
Se–Fe(1)–P	77.89(3)	81.65(4)
Fe(1)–Se–Fe(2)	65.06(2)	65.66(3)
Fe(1)–P–Fe(2)	70.69(3)	71.72(4)
Fe(1)–Se–C(7)	113.43(9)	112.9(1)
Fe(1)–P–C(14)	123.15(9)	127.4(1)



**Figure 3.** ORTEP drawing of **3e(R)a(H)** with atom-labeling scheme.

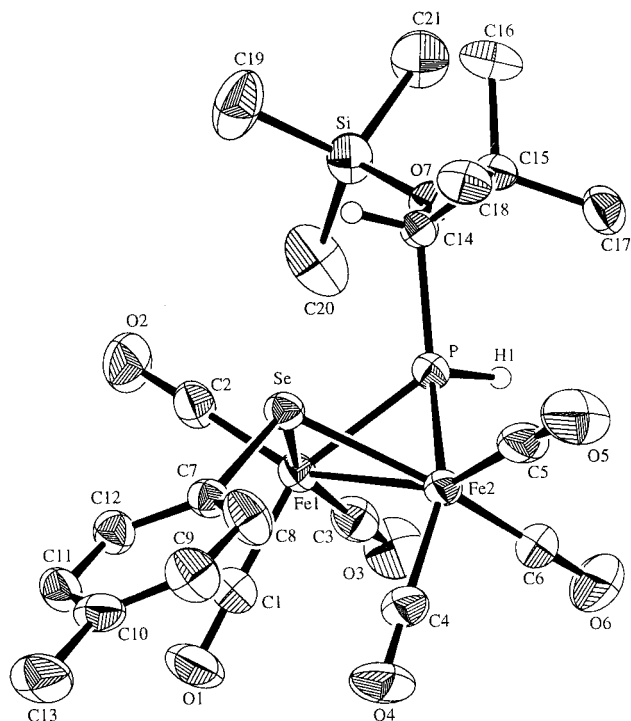


**Figure 4.** ORTEP drawing of **6e(R)a(H)** with atom-labeling scheme.

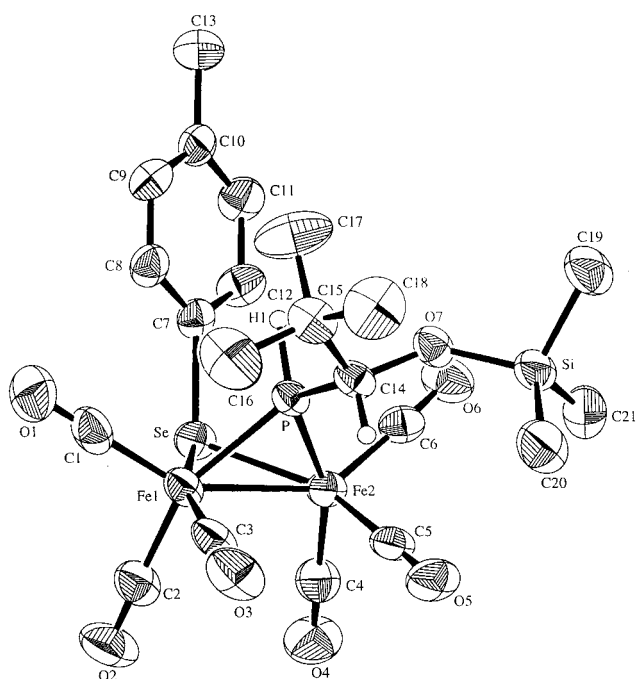
The X-ray diffraction analyses indicated that the dihedral angles between two wings of the isomers increase in the order **6e(R)a(H)** (94.59°) < **3e(R)a(H)** (96.04°) < **8e(R)e(H)** (98.69°) < **8a(R)a(H)** (104.65°). The Fe(1)–Fe(2) bond lengths of the Fe<sub>2</sub>SP clusters of **3e(R)a(H)** (2.5617(1) Å) and **6e(R)a(H)** (2.5611(9) Å) are very close to those of the Fe<sub>2</sub>SeP clusters of **8e(R)e(H)**

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**Figure 5.** ORTEP drawing of **8e(R)e(H)** with atom-labeling scheme.



**Figure 6.** ORTEP drawing of **8a(R)a(H)** with atom-labeling scheme.

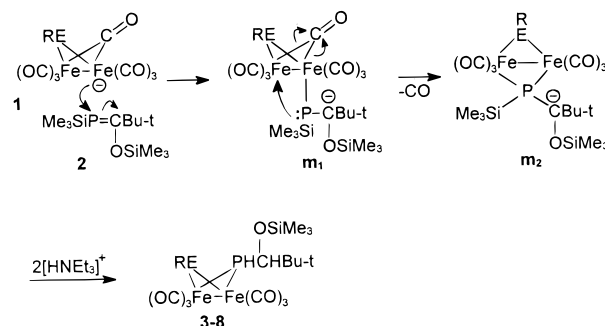
(2.5761(8) Å) and **8a(R)a(H)** (2.587(1) Å), and those of other  $\text{Fe}_2\text{SP}$  clusters such as  $(\mu\text{-C}_6\text{H}_{11}\text{S})(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6$  (2.568(2) Å),<sup>17</sup>  $(\mu\text{-PhS})(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6$  (2.610(2) Å),<sup>18</sup> and  $(\mu\text{-t-BuS})(\mu\text{-PhClP})\text{Fe}_2(\text{CO})_6$  (2.6017(9) Å).<sup>19</sup> In **3e(R)a(H)**, **6e(R)a(H)**, **8e(R)e(H)**, and **8a(R)a(H)**, the Fe–P bond lengths of 2.203–2.231 Å and the Fe–P–

Fe bond angles of 70.17–71.72° are about the same as those of the reported  $\text{Fe}_2\text{SP}$  clusters mentioned above (2.194–2.233 Å, 70.6–72.6°). In addition, the P–C bond lengths in these four isomers (1.87–1.89 Å) are reasonable for a P–C single bond (1.79–1.99 Å)<sup>20</sup> and very close to that (average 1.879 Å) in a similar compound,  $(\mu\text{-o-C}_6\text{H}_4)(\text{CH}_2\text{PPh})_2\text{Fe}_2(\text{CO})_6$ .<sup>21</sup>

**Mechanistic Considerations.** According to the structures of products **3–8**, the reaction between **1** and **2** would involve, at least, both addition of **1** toward the P=C double bond of **2** and replacement of  $\text{SiMe}_3$  of **2** by a proton. In fact, there were several reports about the addition reaction toward a P=C double bond, such as in the reaction of  $(\text{Me}_3\text{Si})_2\text{NP}=\text{CHSiMe}_3$  with  $[(\mu\text{-EtS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6][\text{HNET}_3]^6$  and the others.<sup>22</sup> It was also reported that  $\text{Me}_3\text{Si}$  linked to the P atom of the P=C double bond could be substituted by some electrophilic groups, such as in the reactions of  $t\text{-Bu}(\text{Me}_3\text{SiO})\text{C}=\text{PSiMe}_3$  with  $t\text{-BuCOCl}$  to give  $t\text{-BuC}(\text{O})\text{P}=\text{C}(t\text{-Bu})(\text{OSiMe}_3)$  and  $\text{Me}_3\text{SiP}=\text{C}(\text{NET}_2)_2$  with  $\text{Ph}_3\text{YCl}$  to give  $\text{Ph}_3\text{YP}=\text{C}(\text{NET}_2)_2$  (Y = Si, Ge, Sn).<sup>23</sup>

On the basis of the above observations, we might propose a mechanism to account for the formation of cluster complexes **3–8**, as shown in Scheme 3.

**Scheme 3**



First, the iron-centered anion of **1** attacks the phosphorus atom of **2** to give a carbanion intermediate **m<sub>1</sub>**. Then, **m<sub>1</sub>** converts into another carbanion intermediate **m<sub>2</sub>** through coordination of the P atom to another Fe atom and concomitant loss of the  $\mu\text{-CO}$  ligand. Finally, **3–8** would be produced via protonation of the two atoms of the P–C bond and cleavage of the P–Si bond of intermediate **m<sub>2</sub>** with counterion  $[\text{HNET}_3]^+$ .

In terms of this reaction pathway, the two H atoms in the PHCH unit of the products should originate from the counterion  $[\text{HNET}_3]^+$  of the starting complex salts **1**, which has been fortunately verified by the following experiments. (i) When the  $\text{Li}^+$  salt of anion  $[(\mu\text{-EtS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ ,<sup>2</sup> instead of its  $[\text{HNET}_3]^+$  salt, was reacted with **2** in 2:1 molar ratio in benzene at room temperature for 36 h and then at 35 °C for 24 h, the IR

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spectrum of the reaction mixture showed that the intensity of the two peaks at 1671 and 1730 cm<sup>-1</sup> characteristic of the  $\mu$ -CO ligand of the Li<sup>+</sup> salt<sup>2</sup> was only slightly decreased and very little product **3** was obtained. (ii) If [( $\mu$ -EtS)( $\mu$ -CO)Fe<sub>2</sub>(CO)<sub>6</sub>]<sup>-</sup>Li<sup>+</sup> was reacted with **2** in 2:1 molar ratio in the presence of excess [HNEt<sub>3</sub>]<sup>+</sup>Cl<sup>-</sup> under similar conditions, the IR spectrum of the reaction mixture indicated that those two IR peaks characteristic of the  $\mu$ -CO disappeared completely and isomers **3e(R)e(H)** and **3e(R)a(H)** were separated in a total yield of 40%. (iii) Reaction of [( $\mu$ -RE)( $\mu$ -CO)-Fe<sub>2</sub>(CO)<sub>6</sub>][HNEt<sub>3</sub>] (**1**) with **2** in 1:1 molar ratio gave corresponding products in half of the yields obtained from the standard reaction procedure (see Experimental Section), which used a 2:1 molar ratio stoichiometry. So, the 2:1 stoichiometry in the standard reaction procedure for preparation of **3–8** is due to the need of two [HNEt<sub>3</sub>]<sup>+</sup> groups to provide two protons for each P=C double bond.

## Experimental Section

**General Comments.** All reactions were carried out under an atmosphere of highly prepurified nitrogen using standard Schlenk techniques. Benzene was distilled under nitrogen from sodium/benzophenone ketyl, while triethylamine from potassium hydroxide. Mercaptans were of commercial origin and used without further purification. Fe<sub>3</sub>(CO)<sub>12</sub>,<sup>24</sup> PhSeH,<sup>25</sup> *p*-MeC<sub>6</sub>H<sub>4</sub>SeH,<sup>25</sup> and *t*-Bu(Me<sub>3</sub>SiO)C=PSiMe<sub>3</sub><sup>26</sup> were prepared according to literature procedures.

Products were separated by thin-layer chromatography (TLC glass plates of 20 × 25 × 0.25 cm coated with silica gel G). The eluents, light petroleum ether, acetone, and methylene chloride, were of reagent grade and were used as purchased. The yields were calculated on the basis of phosphalkene **2**.

Melting points were determined on a Yanaco MP-500 melting point apparatus. Elemental analyses were performed on a Yanaco CORDER MT-3 analyzer. <sup>1</sup>H NMR, <sup>31</sup>P NMR (with 85% H<sub>3</sub>PO<sub>4</sub> as external standard), and <sup>77</sup>Se NMR (relative to Me<sub>2</sub>Se) spectra were recorded on a Bruker AC-P 200 NMR spectrometer. IR spectra were obtained on a Nicolet FT-IR 170X spectrophotometer with KBr disk or liquid film.

**Synthesis of ( $\mu$ -EtS)[ $\mu$ -*t*-Bu(Me<sub>3</sub>SiO)CHPH]Fe<sub>2</sub>(CO)<sub>6</sub> **3e(R)e(H)** and **3e(R)a(H)**.** A 100 mL three-necked flask equipped with a stir-bar, a N<sub>2</sub> inlet tube, and a serum cap was charged with 1.00 g (2.0 mmol) of Fe<sub>3</sub>(CO)<sub>12</sub>, 20 mL of benzene, 0.16 mL (2.1 mmol) of EtSH, and 0.32 mL (2.3 mmol) of Et<sub>3</sub>N. The mixture was stirred at 35–40 °C for 0.5 h, during which time the green solution turned red-brown. To the solution was added 0.262 g (1.0 mmol) of phosphalkene **2**, and the reaction mixture was stirred at 45–50 °C for 8 h. The resulting solution was evaporated in vacuo, and the residue was separated by TLC using light petroleum ether as eluent. The first band gave a small amount of ( $\mu$ -EtS)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>.<sup>27</sup> From the second and third yellow bands 0.152 g (29%) of **3e(R)e(H)** and 0.324 g (61%) of **3e(R)a(H)** were respectively obtained, both as orange solids. **3e(R)e(H)**: mp 45–47 °C. Anal. Calcd for C<sub>16</sub>H<sub>25</sub>Fe<sub>2</sub>O<sub>7</sub>PSSi: C, 36.11; H, 4.70. Found: C, 36.10; H, 4.56. IR (KBr):  $\nu_{\text{C=O}}$  2062(vs), 2021(vs), 1980(vs) cm<sup>-1</sup>. **3e(R)a(H)**: mp 83–84 °C. Anal. Calcd for C<sub>16</sub>H<sub>25</sub>Fe<sub>2</sub>O<sub>7</sub>PSSi: C, 36.11; H, 4.70. Found: C, 36.04; H, 4.70. IR (KBr):  $\nu_{\text{C=O}}$  2061(vs), 2022(vs), 1985(vs) cm<sup>-1</sup>.

**Synthesis of ( $\mu$ -*n*-PrS)[ $\mu$ -*t*-Bu(Me<sub>3</sub>SiO)CHPH]Fe<sub>2</sub>(CO)<sub>6</sub> **4e(R)e(H)** and **4e(R)a(H)**.** The same procedure as for **3e(R)e(H)** and **3e(R)a(H)** was followed, but 0.19 mL (2.1 mmol) of *n*-PrSH was used instead of EtSH. A total of 0.189 g (35%) of **4e(R)e(H)** was obtained as a red oil, and 0.268 g (49%) of **4e(R)a(H)** as an orange solid. **4e(R)e(H)**: Anal. Calcd for C<sub>17</sub>H<sub>27</sub>Fe<sub>2</sub>O<sub>7</sub>PSSi: C, 37.38; H, 4.98. Found: C, 37.25; H, 4.97. IR (film):  $\nu_{\text{C=O}}$  2062(vs), 2021(vs), 1982(vs) cm<sup>-1</sup>. **4e(R)a(H)**: mp 57–59 °C. Anal. Calcd for C<sub>17</sub>H<sub>27</sub>Fe<sub>2</sub>O<sub>7</sub>PSSi: C, 37.38; H, 4.98. Found: C, 37.64; H, 4.89. IR (KBr):  $\nu_{\text{C=O}}$  2062(s), 2021(vs), 1985(vs), 1966(vs) cm<sup>-1</sup>.

**Synthesis of ( $\mu$ -*n*-BuS)[ $\mu$ -*t*-Bu(Me<sub>3</sub>SiO)CHPH]Fe<sub>2</sub>(CO)<sub>6</sub> **5e(R)e(H)** and **5e(R)a(H)**.** The same procedure as for **3e(R)e(H)** and **3e(R)a(H)** was followed, but 0.23 mL (2.1 mmol) of *n*-BuSH was used instead of EtSH. A total of 0.214 g (38%) of **5e(R)e(H)** was obtained as a red oil, and 0.253 g (45%) of **5e(R)a(H)** as an orange solid. **5e(R)e(H)**: Anal. Calcd for C<sub>18</sub>H<sub>29</sub>Fe<sub>2</sub>O<sub>7</sub>PSSi: C, 38.59; H, 5.21. Found: C, 38.42; H, 4.98. IR (film):  $\nu_{\text{C=O}}$  2062(vs), 2020(vs), 1980(vs) cm<sup>-1</sup>. **5e(R)a(H)**: mp 52–54 °C. Anal. Calcd for C<sub>18</sub>H<sub>29</sub>Fe<sub>2</sub>O<sub>7</sub>PSSi: C, 38.59; H, 5.21. Found: C, 38.68; H, 5.12. IR (KBr):  $\nu_{\text{C=O}}$  2061(vs), 2020(vs), 1976(vs) cm<sup>-1</sup>.

**Synthesis of ( $\mu$ -*t*-BuS)[ $\mu$ -*t*-Bu(Me<sub>3</sub>SiO)CHPH]Fe<sub>2</sub>(CO)<sub>6</sub> **6e(R)e(H)** and **6e(R)a(H)**.** The same procedure as for **3e(R)e(H)** and **3e(R)a(H)** was followed, but 0.24 mL (2.1 mmol) of *t*-BuSH was used instead of EtSH. A total of 0.192 g (34%) of **6e(R)e(H)** was obtained as a red oil, and 0.203 g (36%) of **6e(R)a(H)** as an orange solid. **6e(R)e(H)**: Anal. Calcd for C<sub>18</sub>H<sub>29</sub>Fe<sub>2</sub>O<sub>7</sub>PSSi: C, 38.59; H, 5.21. Found: C, 38.54; H, 5.25. IR (film):  $\nu_{\text{C=O}}$  2057(vs), 2019(vs), 1979(vs) cm<sup>-1</sup>. **6e(R)a(H)**: mp 85–87 °C. Anal. Calcd for C<sub>18</sub>H<sub>29</sub>Fe<sub>2</sub>O<sub>7</sub>PSSi: C, 38.59; H, 5.21. Found: C, 38.46; H, 4.92. IR (KBr):  $\nu_{\text{C=O}}$  2058(s), 2023(vs), 1982(vs), 1966(vs) cm<sup>-1</sup>.

**Synthesis of ( $\mu$ -PhSe)[ $\mu$ -*t*-Bu(Me<sub>3</sub>SiO)CHPH]Fe<sub>2</sub>(CO)<sub>6</sub> (**7**).** The same procedure as for **3e(R)e(H)** and **3e(R)a(H)** was followed, but 0.33 mL (2.1 mmol) of PhSeH was used instead of EtSH and the eluent was a mixture of acetone and light petroleum ether (v/v = 1:10). From the first, yellow major band 0.199 g (32%) of the mixture of **7e(R)e(H)** and **7e(R)a(H)** was obtained as an orange solid. Anal. Calcd for C<sub>20</sub>H<sub>25</sub>Fe<sub>2</sub>O<sub>7</sub>PSeSi: C, 38.30; H, 4.01. Found: C, 38.51; H, 3.88. IR (KBr):  $\nu_{\text{C=O}}$  2057(s), 2021(vs), 2002(s), 1977(vs), 1959(s) cm<sup>-1</sup>. <sup>77</sup>Se NMR (CDCl<sub>3</sub>):  $\delta$  195.9 (d,  $J_{\text{P-Fe-Se}}$  = 93.8 Hz), 243.1 (d,  $J_{\text{P-Fe-Se}}$  = 35.4 Hz) ppm. The second, orange major band gave 0.200 g (34%) of ( $\mu$ -PhSe)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>.<sup>28</sup>

**Synthesis of ( $\mu$ -*p*-MeC<sub>6</sub>H<sub>4</sub>Se)[ $\mu$ -*t*-Bu(Me<sub>3</sub>SiO)CHPH]Fe<sub>2</sub>(CO)<sub>6</sub> **8e(R)e(H)** and **8e(R)a(H)**.** The same procedure as for **3e(R)e(H)** and **3e(R)a(H)** was followed, but 0.360 g (2.2 mmol) of *p*-MeC<sub>6</sub>H<sub>4</sub>SeH was used instead of EtSH and the eluent was a mixture of acetone and light petroleum ether (v/v = 1:10). From the second, orange major band 0.237 g (38%) of ( $\mu$ -*p*-MeC<sub>6</sub>H<sub>4</sub>Se)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub><sup>8i</sup> was obtained. The first, yellow major band, after further TLC separation, afforded 0.107 g (17%) of **8a(R)a(H)** from the front band and 0.233 g (36%) of **8e(R)e(H)** from the other, both as orange solids. **8a(R)a(H)**: mp 95–97 °C. Anal. Calcd for C<sub>21</sub>H<sub>27</sub>Fe<sub>2</sub>O<sub>7</sub>PSeSi: C, 39.34; H, 4.24. Found: C, 39.32; H, 4.27. IR (KBr):  $\nu_{\text{C=O}}$  2059(s), 2019(vs), 1999(s), 1981(s), 1970(vs), 1954(s) cm<sup>-1</sup>. <sup>77</sup>Se NMR (CDCl<sub>3</sub>):  $\delta$  191.7 (d,  $J_{\text{P-Fe-Se}}$  = 97.2 Hz) ppm. **8e(R)e(H)**: mp 98–100 °C. Anal. Calcd for C<sub>21</sub>H<sub>27</sub>Fe<sub>2</sub>O<sub>7</sub>PSeSi: C, 39.34; H, 4.24. Found: C, 39.34; H, 4.31. IR (KBr):  $\nu_{\text{C=O}}$  2061(vs), 2020(vs), 1991(vs), 1974(vs) cm<sup>-1</sup>. <sup>77</sup>Se NMR (CDCl<sub>3</sub>):  $\delta$  237.7 (d,  $J_{\text{P-Fe-Se}}$  = 33.7 Hz) ppm.

**X-ray Crystallography of **3e(R)a(H)**, **6e(R)a(H)**, **8e(R)e(H)**, and **8a(R)a(H)**.** Single crystals of **3e(R)a(H)**, **6e(R)a(H)**, **8e(R)e(H)**, and **8a(R)a(H)** suitable for X-ray diffraction analyses were grown by slow evaporation of their pentane solutions at about 5 °C under nitrogen. A single crystal of **3e(R)a(H)** with

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**Table 4.** Crystal Data and Structural Refinements Details for **3e(R)a(H)**, **6e(R)a(H)**, **8e(R)e(H)**, and **8a(R)a(H)**

	<b>3e(R)a(H)</b>	<b>6e(R)a(H)</b>	<b>8e(R)e(H)</b>	<b>8a(R)a(H)</b>
formula	C <sub>16</sub> H <sub>25</sub> Fe <sub>2</sub> O <sub>7</sub> PSSi	C <sub>18</sub> H <sub>29</sub> Fe <sub>2</sub> O <sub>7</sub> PSSi	C <sub>21</sub> H <sub>27</sub> Fe <sub>2</sub> O <sub>7</sub> PSeSi	C <sub>21</sub> H <sub>27</sub> Fe <sub>2</sub> O <sub>7</sub> PSeSi
fw	52.18	560.24	641.15	641.15
cryst syst	triclinic	triclinic	triclinic	triclinic
cryst size, mm	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.40	0.20 × 0.20 × 0.30
space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> , Å	11.727(4)	12.035(4)	9.740(3)	11.528(2)
<i>b</i> , Å	13.448(3)	12.204(3)	16.116(7)	12.066(3)
<i>c</i> , Å	9.322(2)	10.763(4)	9.457(3)	10.538(3)
$\alpha$ , deg	94.28(2)	116.09(2)	90.38(3)	90.54(2)
$\beta$ , deg	112.36(2)	111.11(3)	108.29(2)	93.76(2)
$\gamma$ , deg	111.90(2)	79.84(3)	97.28(4)	103.78(2)
<i>V</i> , Å <sup>3</sup>	1220.6(7)	1324.1(8)	1396.5(9)	1420.0(6)
<i>Z</i>	2	2	2	2
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.448	1.405	1.525	1.499
<i>F</i> (000)	548	580	648	648
$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	14.17	13.10	24.76	24.35
temp, K	293	293	293	293
wavelength, Å	0.71069	0.71069	0.71069	0.71069
scan type	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$
2 $\theta$ <sub>max</sub> , deg	50.9	49.9	50	50
no. of reflcns	3554	3770	4043	4373
no. of indep reflcns	3314	3529	3728	4103
<i>R</i> <sub>int</sub>	0.036	0.046	0.025	0.024
no. of observns, <i>n</i>	2917	2901	3280	2882
no. of variables, <i>p</i>	254	359	299	299
<i>R</i>	0.026	0.027	0.027	0.030
<i>R</i> <sub>w</sub>	0.036	0.032	0.034	0.034
goodness of fit	1.59	1.20	1.60	1.16
largest diff peak e Å <sup>-3</sup>	0.32	0.17	0.53	0.34

dimensions 0.20 × 0.20 × 0.30 mm was glued to a glass fiber and mounted on a Rigaku AFC7R diffractometer with graphite-monochromated Mo K $\alpha$  ( $\lambda$  = 0.71069 Å) radiation and a 12 kW rotating anode generator. Data were collected at 20 °C using the  $\omega$ -2 $\theta$  scan techniques to a maximum 2 $\theta$  value of 50.9° and were corrected for *Lp* factors of the 3554 reflections, of which 3314 were unique (*R*<sub>int</sub> = 0.036).

The structure was first solved by direct methods (SHELX 86) and then refined via full-matrix least-squares and Fourier techniques (DIRDIF 92). The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included but not refined. The final cycle of the full-matrix least-squares refinement was based on 2917 observed reflections (*I* > 3.00 $\sigma$ (*I*)) and 254 variable parameters and converged with unweighted and weighted agreement factors of 0.026 (*R*) and 0.036 (*R*<sub>w</sub>). The maximum peak on the final difference Fourier map was 0.32 e/Å<sup>3</sup>. All calculations were performed using the TEXSAN crystallographic software package of the Molecular Structure Corporation.

The procedures for **6e(R)a(H)**, **8e(R)e(H)**, and **8a(R)a(H)** are similar. Crystal and refinement data for **3e(R)a(H)**, **6e(R)a(H)**, **8e(R)e(H)**, and **8a(R)a(H)** are listed in Table 4.

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**Supporting Information Available:** Tables of atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and data collection and processing parameters for **3e(R)a(H)**, **6e(R)a(H)**, **8e(R)e(H)**, and **8a(R)a(H)**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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