

Unexpected Preparation of Butterfly Fe/S Cluster Complexes Containing a Quaternary Phosphorus Atom via Reactions of the Anions $(\mu\text{-RS})(\mu\text{-S}^-)\text{Fe}_2(\text{CO})_6$ and $(\mu\text{-RS})(\mu\text{-S}^-)[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ with Diphenylchlorophosphine

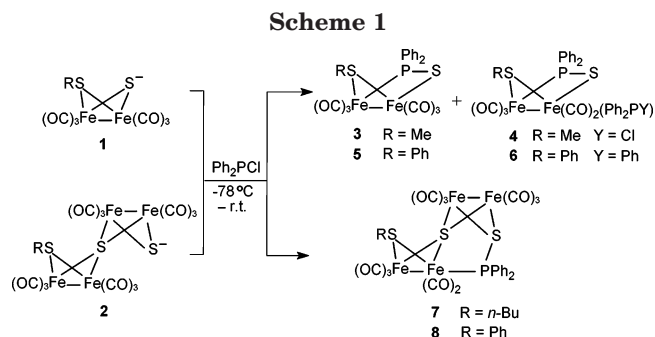
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Summary: Six new butterfly Fe/S cluster complexes, $(\mu\text{-RS})(\eta^1\text{-Ph}_2\text{PS-}\eta^1)[\text{Fe}_2(\text{CO})_6]$ (**3**, R = Me; **5**, R = Ph), $(\mu\text{-RS})(\eta^1\text{-Ph}_2\text{PS-}\eta^1)[\text{Fe}_2(\text{CO})_5(\text{Ph}_2\text{PY})]$ (**4**, R = Me, Y = Cl; **6**, R = Y = Ph), and $(\mu\text{-RS})(\eta^1\text{-Ph}_2\text{PS-}\eta^2)[\text{Fe}_2(\text{CO})_6](\mu_4\text{-S})$ (**7**, R = *n*-Bu; **8**, R = Ph), were unexpectedly prepared by a “one-pot” synthetic method involving reactions of the *in situ* generated S-centered monoanions $(\mu\text{-RS})(\mu\text{-S}^-)\text{Fe}_2(\text{CO})_6$ (**1**) and $(\mu\text{-RS})(\mu\text{-S}^-)[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ (**2**) with Ph_2PCL . While the possible mechanisms for the unexpected reactions are suggested, the structures of products **3–8** have been fully characterized.

Butterfly iron–sulfur cluster complexes have drawn increased attention, largely due to their unique structures and novel reactivities,¹ as well as the closely related biological relevance to the active site of the Fe-only hydrogenases.² Among such complexes, the butterfly S-centered anions $(\mu\text{-RS})(\mu\text{-S}^-)\text{Fe}_2(\text{CO})_6$ (**1**) and $(\mu\text{-RS})(\mu\text{-S}^-)[\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ (**2**) are of particular interest, since they have become important synthons for preparing a variety of single-, double-, and multiple-butterfly cluster complexes.^{3,4} To develop the new chemistry of these two anions and to prepare the corresponding Fe/S cluster core containing phosphines,⁵ we carried out reactions of the *in situ* generated anions **1** and **2** with diphenylchlorophosphine, a common



phosphorus-based electrophile. As a result, although the expected cluster phosphines were not obtained, a series of unexpected butterfly Fe/S cluster complexes, each containing an Fe atom bonded quaternary phosphorus atom, namely $(\mu\text{-RS})(\eta^1\text{-Ph}_2\text{PS-}\eta^1)[\text{Fe}_2(\text{CO})_6]$ (**3**, **5**), $(\mu\text{-RS})(\eta^1\text{-Ph}_2\text{PS-}\eta^1)[\text{Fe}_2(\text{CO})_5(\text{Ph}_2\text{PY})]$ (**4**, **6**), and $(\mu\text{-RS})(\eta^1\text{-Ph}_2\text{PS-}\eta^2)[\text{Fe}_2(\text{CO})_6](\mu_4\text{-S})$ [$\text{Fe}_2(\text{CO})_5$] (**7**, **8**), were isolated and fully characterized (Scheme 1).

As a typical experiment, the reaction of anion **1** (R = Me) with Ph_2PCL to produce the single-butterfly complexes **3** and **4** was performed as follows. To the green solution of the IMg derivative of anion **1** (R = Me), prepared from 0.344 g (1 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$, ca. 1 mmol of the Grignard reagent MeMgI , and 20 mL of THF at -78°C ,^{3a} was added 0.2 mL (1 mmol) of Ph_2PCL , resulting in a color change to red. The mixture was stirred at -78°C for 15 min and then 30 min at room temperature. Solvent was removed at reduced pressure, and the residue was subjected to TLC on silica gel 60H. Elution with CH_2Cl_2 /petroleum ether (1/4 v/v) gave an orange-red band and a brown-red band, from which **3** and **4** were obtained in 58% and 10% yields, respectively. Similarly, when PhMgBr was used instead of MeMgI , **5** and **6** were isolated in 63% and 20% yields, respectively.

Products **3–6** have been fully characterized by elemental analysis, spectroscopy,⁶ and X-ray diffraction

(5) The attempted preparation of such phosphines was originally due to our need for further preparation of novel fullerene complexes that contain transition-metal cluster cores. For preparation of fullerene complexes that contain mononuclear metal phosphines such as a dppf ligand, see our following papers: (a) Song, L.-C.; Liu, J.-T.; Hu, Q.-M.; Wang, G.-F.; Zanello, P.; Fontani, M. *Organometallics* **2000**, *19*, 5342. (b) Song, L.-C.; Wang, G.-F.; Liu, P.-C.; Hu, Q.-M. *Organometallics* **2003**, *22*, 4593.

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(1) For example, see: (a) Ogino, H.; Inomata, S.; Tobita, H. *Chem. Rev.* **1998**, *98*, 2093. (b) Seyferth, D.; Song, L.-C.; Henderson, R. S. *J. Am. Chem. Soc.* **1981**, *103*, 5103. (c) Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125. (d) Bose, K. S.; Sinn, E.; Averill, B. A. *Organometallics* **1984**, *3*, 1126. (e) Song, L.-C.; Fan, H.-T.; Hu, Q.-M. *J. Am. Chem. Soc.* **2002**, *124*, 4566. (f) Song, L.-C.; Gong, F.-H.; Meng, T.; Ge, J.-H.; Cui, L.-N.; Hu, Q.-M. *Organometallics* **2004**, *23*, 823.

(2) For example, see: (a) Gloaguen, F.; Lawrence, J. D.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2001**, *123*, 9476. (b) Darenbourg, M. Y.; Lyon, E. J.; Smea, J. *J. Coord. Chem. Rev.* **2000**, *206–207*, 533. (c) Ott, S.; Kritikos, M.; Åkermark, B.; Sun, L. *Angew. Chem., Int. Ed.* **2003**, *42*, 3285. (d) Song, L.-C.; Yang Z.-Y.; Bian, H.-Z.; Hu, Q.-M. *Organometallics* **2004**, *23*, 3082.

(3) For example, see: (a) Seyferth, D.; Henderson, R. S.; Song, L.-C. Womack, G. B. *J. Organomet. Chem.* **1985**, *292*, 9. (b) Song, L.-C.; Hu, Q.-M.; Fan, H.-T.; Sun, B.-W.; Tang, M.-Y.; Chen, Y.; Sun, Y.; Sun, C.-X.; Wu, Q.-J. *Organometallics* **2000**, *19*, 3909.

(4) For example, see: (a) Song, L.-C.; Lu, G.-L.; Hu, Q.-M.; Fan, H.-T.; Chen, Y.; Sun, J. *Organometallics* **1999**, *18*, 3258. (b) Song, L.-C.; Lu, G.-L.; Hu, Q.-M.; Sun, J. *Organometallics* **1999**, *18*, 5429. (c) Wang, Z.-X.; Jia, C.-S.; Zhou, Z.-Y.; Zou, X.-G. *J. Organomet. Chem.* **2000**, *601*, 108.

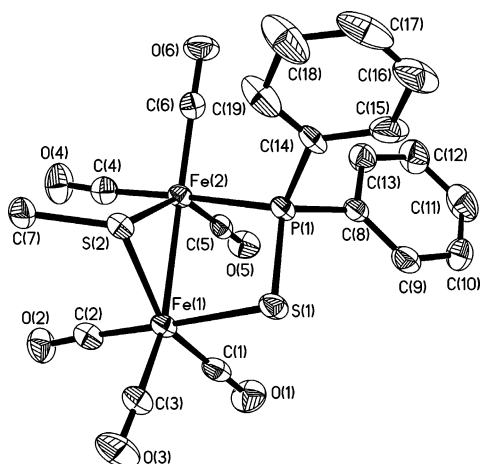


Figure 1. Molecular structure of **3**. Selected bond lengths (Å) and angles (deg): Fe(1)–S(2) = 2.237(2), Fe(1)–S(1) = 2.3541(19), Fe(2)–P(1) = 2.2600(19), Fe(2)–S(2) = 2.2540(19), P(1)–S(1) = 2.030(2), Fe(1)–Fe(2) = 2.6431(16); S(2)–Fe(1)–S(1) = 85.84(7), S(1)–Fe(1)–Fe(2) = 85.21(5), S(2)–Fe(2)–P(1) = 86.36(7), P(1)–Fe(2)–Fe(1) = 79.00(5), Fe(1)–S(2)–Fe(2) = 72.11(7), S(1)–P(1)–Fe(2) = 104.26(8), P(1)–S(1)–Fe(1) = 90.90(8).

analysis.⁷ Figures 1 and 2 show the molecular structures of **3** and **6** with their selected bond lengths and angles, respectively. As can be seen in Figures 1 and 2, both **3** and **6** consist of the butterfly cluster core Fe(1)Fe(2)–S(1)P(1)S(2), in which the P(1) atom has two phenyl substituents. However, while **3** contains Fe(1) and Fe(2) atoms each bonded to three terminal CO ligands, **6** has Fe(2) bound to three terminal CO ligands and Fe(1) attached to two terminal CO ligands and one Ph₃P ligand. In addition, the S(2) atom of **3** is bonded to an equatorial methyl group, whereas S(2) of **6** is attached to an equatorial phenyl group.⁸ Therefore, the crystal and molecular structures of **3** and **6** are in good agreement with the elemental analysis and spectroscopic data of **3–6**, respectively. For instance, the IR spectra of **3–6** displayed four or five absorption bands in the region 2074–1932 cm⁻¹ for their terminal carbonyls, whereas the ³¹P NMR spectrum of **3** or **5** showed a singlet at

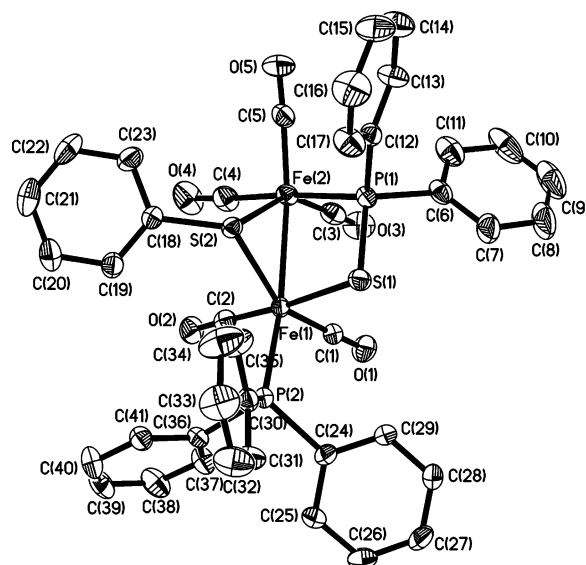


Figure 2. Molecular structure of **6**. Selected bond lengths (Å) and angles (deg): Fe(1)–S(1) = 2.3551(19), Fe(1)–Fe(2) = 2.668(2), Fe(1)–S(2) = 2.2464(18), Fe(1)–P(2) = 2.279(2), Fe(2)–P(1) = 2.256(2), Fe(2)–S(2) = 2.272(2), P(1)–S(1) = 2.033(2); S(2)–Fe(1)–P(2) = 112.38(7), S(2)–Fe(1)–S(1) = 82.53(7), P(2)–Fe(1)–S(1) = 90.61(7), S(2)–Fe(1)–Fe(2) = 54.25(5), S(1)–P(1)–Fe(2) = 104.68(8), P(1)–S(1)–Fe(1) = 90.86(8).

44–67 ppm for its P atom in the SPPH₂ group and that of **4** or **6** displayed a singlet at 58–71 ppm for its P atom in the SPPH₂ group. In addition, the ³¹P NMR spectra of **4** and **6** each exhibited another singlet at ca. 70 and ca. 150 ppm for the P atom in the PPH₃ and Ph₂PCL ligands, respectively. It is worth pointing out that **3–6** are the first examples of butterfly FeSP cluster complexes with one triangular Fe(1)Fe(2)S(2) wing and one tetragonal Fe(1)Fe(2)S(1)P(1) wing, although numerous butterfly FeSP cluster complexes are known to have two triangular wings, such as (μ-Ph₂P)(μ-RS)Fe₂(CO)₆ (R = Ph,⁹ C₆H₁₁¹⁰), [μ-Ph(Cl)P](μ-*t*-BuS)Fe₂(CO)₆,¹¹ and (μ-Me₂P)(μ-*t*-BuS)Fe₂(CO)₆.¹² It is due to such a striking difference in wing structures of these two types of butterfly FeSP cluster complexes that the geometric parameters involved in their cluster cores are so different. As exemplified by **3** and (μ-Me₂P)(μ-*t*-BuS)Fe₂(CO)₆,¹² such differences can be clearly seen from the following geometric parameters (for the latter complex the corresponding values are given in parentheses): Fe(1)–Fe(2) = 2.6437 (2.585), Fe(1)–S(2) = 2.237 (2.273), Fe(2)–S(2) = 2.254 (2.267), Fe(2)–P(1) = 2.260 (2.216, 2.229) Å; Fe(1)–S(2)–Fe(2) = 72.11 (69.4)°.

As another typical experiment, the sequential reaction of anion **2** (R = *n*-Bu) with Ph₂PCL to afford the double-butterfly complex **7** was carried out as described below. Treatment of the Li derivative of the anion [(μ-RS)-(μ-CO)Fe₂(CO)₆]⁻ (R = *n*-Bu), prepared from 0.50 g (1 mmol) of Fe₃(CO)₁₂, 0.12 mL (1 mmol) of *n*-BuSH, and 1 mmol of *n*-BuLi in 20 mL of THF, with 0.344 g (1

(6) Characterization data are as follows. **3**: mp 113–114 °C. Anal. Calcd for C₁₉H₁₅Fe₂O₆PS₂: C, 41.91; H, 2.39. Found: C, 41.99; H, 2.17. IR (KBr disk): ν_{C=O} 2064 (vs), 2021 (vs), 2003 (vs), 1998 (vs), 1966 (s) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 2.59 (s, 3H, CH₃), 7.31–7.76 (m, 10H, 2C₆H₅). ³¹P NMR (81.0 MHz, CDCl₃, H₃PO₄): δ 66.72 (s). **4**: mp 121–122 °C. Anal. Calcd for C₃₀H₂₃ClFe₂O₅P₂S₂: C, 48.88; H, 3.12. Found: C, 48.51; H, 2.96. IR (KBr disk): ν_{C=O} 2047 (vs), 1986 (vs), 1962 (vs), 1942 (s) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 2.12 (s, 3H, CH₃), 7.27–7.84 (m, 20H, 4C₆H₅). ³¹P NMR (81.0 MHz, CDCl₃, H₃PO₄): δ 70.76 (s, SPPH₂), 151.72 (s, ClPPH₂). **5**: mp 112–113 °C. Anal. Calcd for C₂₄H₁₅Fe₂O₆PS₂: C, 47.55; H, 2.49. Found: C, 47.69; H, 2.73. IR (KBr disk): ν_{C=O} 2068 (vs), 2038 (vs), 2018 (vs), 1999 (vs), 1981 (vs) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 7.25–7.83 (m, 15H, 3C₆H₅). ³¹P NMR (81.0 MHz, CDCl₃, H₃PO₄): δ 44.55 (s). **6**: mp 126–127 °C. Anal. Calcd for C₄₁H₃₀Fe₂O₅P₂S₂·CH₂Cl₂: C, 54.49; H, 3.46. Found: C, 54.59; H, 3.47. IR (KBr disk): ν_{C=O} 2040 (vs), 1982 (vs), 1951 (vs), 1932 (s) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 5.29 (s, 2H, CH₂Cl₂), 6.97–7.76 (m, 30H, 6C₆H₅). ³¹P NMR (81.0 MHz, CDCl₃, H₃PO₄): δ 58.76 (s, SPPH₂), 70.40 (s, PPH₃).

(7) Crystal data are as follows. **3**: monoclinic, space group C2/c, *a* = 20.697(9) Å, *b* = 9.741(4) Å, *c* = 22.862(10) Å, β = 109.674(6)°, *F*(000) = 2192, *V* = 4340(3) Å³, *Z* = 8, *D_c* = 1.665 g cm⁻³, μ(Mo Kα) = 1.636 mm⁻¹, *R* = 0.0694, *R_w* = 0.0660, GOF = 1.008. **6**: triclinic, space group P1̄, *a* = 10.074(9) Å, *b* = 13.125(12) Å, *c* = 15.977(14) Å, α = 15.977(14)°, β = 83.658(16)°, γ = 89.174(17)°, *F*(000) = 944, *V* = 2092(3) Å³, *Z* = 2, *D_c* = 1.469 g cm⁻³, μ(Mo Kα) = 1.041 mm⁻¹, *R* = 0.0585, *R_w* = 0.1334, GOF = 0.977.

(8) Shaver, A.; Fitzpatrick, P. J.; Steliou, K.; Butler, I. S. *J. Am. Chem. Soc.* **1979**, *101*, 1313.

(9) Job, B. E.; McLean, R. A. N.; Thompson, D. T. *J. Chem. Soc., Chem. Commun.* **1966**, 895.

(10) Winter, A.; Zsolnai, L.; Huttner, G. *J. Organomet. Chem.* **1983**, *250*, 409.

(11) Song, L.-C.; Wang, R.-J.; Li, Y.; Wang, H.-G.; Wang, J.-T. *Chin. J. Org. Chem.* **1989**, *9*, 512.

(12) Song, L.-C.; Hu, Q.-M.; Zhou, Z.-Y.; Hu, G.-Z. *Chin. J. Org. Chem.* **1991**, *11*, 533.

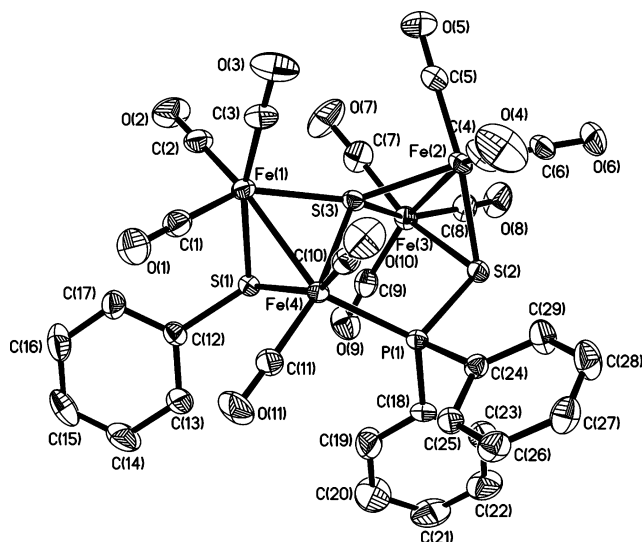


Figure 3. Molecular structure of **8**. Selected bond lengths (Å) and angles (deg): Fe(1)–S(3) = 2.2490(14), Fe(1)–Fe(4) = 2.5409(12), Fe(1)–S(1) = 2.2957(15), Fe(2)–S(3) = 2.2433(14), Fe(2)–Fe(3) = 2.5363(14), Fe(3)–S(3) = 2.2506(15), P(1)–S(2) = 2.1694(17), P(1)–Fe(4) = 2.2106(15); S(3)–Fe(1)–S(1) = 76.05(5), S(3)–Fe(1)–Fe(4) = 55.12(4), S(3)–Fe(2)–S(2) = 80.87(5), P(1)–Fe(4)–Fe(1) = 142.59(4), S(2)–P(1)–Fe(4) = 112.02(6), P(1)–S(2)–Fe(3) = 104.86(6).

mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ at room temperature for 2 h resulted in formation of a green solution of the Li derivative of the S-centered anion **2** ($R = n\text{-Bu}$).^{4a} To this green solution was added 0.2 mL (1 mmol) of Ph_2PCL at -78°C , and this new mixture was stirred for 15 min at -78°C and then for 4 h at room temperature to give a brown-red mixture. After the same workup as that in the preparation of **3** and **4** but using THF/petroleum ether (1/30 v/v) as eluent, a major brown-red band developed, from which **7** was obtained in 42% yield. Similarly, when PhSH was employed in place of $n\text{-BuSH}$, **8** was afforded in 56% yield.

Products **7** and **8** were fully characterized by elemental analysis, spectroscopy,¹³ and X-ray crystallography.¹⁴ Figure 3 presents the molecular structure of **8** with selected bond lengths and angles. It can be seen in Figure 3 that (i) **8** comprises two butterfly subcluster cores $\text{Fe}(1)\text{Fe}(4)\text{S}(1)\text{S}(3)$ and $\text{Fe}(2)\text{Fe}(3)\text{S}(2)\text{S}(3)$ joined to a spiran type of $\mu_4\text{-S}$, namely the S(3) atom, (ii) the S(1) atom is attached to the C(12) atom by an equatorial type of bond, whereas the P(1) atom is attached to the S(2) atom by an axial type of bond⁸ and attached to the Fe(4) atom by a bond trans to the Fe(1)–Fe(4) bond, and (iii) each of the three CO's attached to Fe(1), Fe(2),

and Fe(3), as well as each of the two CO's attached to Fe(4), are terminal. Therefore, this type of structure is consistent with the elemental analysis and spectroscopic data of **7** and **8**. For example, the IR spectra of **7** and **8** exhibited six absorption bands in the range 2080–1939 cm^{-1} typical of their terminal carbonyls, whereas the ³¹P NMR spectra of **7** and **8** each displayed a singlet at ca. 162 ppm for their P atoms in SPPH_2 groups. It is noteworthy that these chemical shifts of the P atoms of **7** and **8** are considerably larger than those of the corresponding P atoms in **3–6**. Apparently, this is not only due to the electron-withdrawing ability of $\text{Fe}_2(\text{CO})_5$ and $\text{SFe}_2(\text{CO})_6$ groups attached to the P atom in **7** and **8** being stronger than that of the corresponding $\text{Fe}(\text{CO})_3$ and $\text{SFe}(\text{CO})_3$ or $\text{SFe}(\text{CO})_2(\text{Ph}_2\text{PY})$ groups in **3–6** but also due to the effect of the ring size of the metallacycles, i.e., a P–S–Fe–Fe four-membered ring in **3–6** and a P–S–Fe–S–Fe five-membered ring in **7** and **8**.¹⁵

Interestingly, complexes **7** and **8** are the first $\mu_4\text{-S}$ -containing double-butterfly Fe/S cluster complexes that contain a group, here a Ph_2P group, axially bonded to the bridged $\mu\text{-S}$ atom of such clusters, while all the reported $\mu_4\text{-S}$ double-butterfly Fe/S cluster complexes, such as $[(\mu\text{-RS})\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ ($R = \text{Me}$,¹⁶ Et)¹⁷, have two R groups equatorially bonded to their $\mu\text{-S}$ atoms in order to avoid the sterically strong repulsions with their neighboring subclusters.^{4a,b} The $\mu\text{-S}$ atom axially bonded Ph_2P group in clusters **7** and **8** is obviously stabilized by coordination of the P atom of the Ph_2P group to the Fe atom of the neighboring Fe/S subcluster core.

At present, the mechanisms of the unexpected reactions described above are not clear to us. However, on the basis of the well-known nucleophilic reactivity of the S-centered monoanions **1**^{3,18} and **2**,^{4,19} we might suggest that the reactions of anions **1** and **2** with Ph_2PCL would first give the expected butterfly Fe/S cluster phosphines **M**₁ and **M**₂ by intermolecular nucleophilic substitution. Then, **3** and **5** would be produced from **M**₁ by intramolecular nucleophilic attack of the P atom at iron with displacement of mercaptide from iron, whereas **7** and **8** would be yielded from **M**₂ by intramolecular nucleophilic attack of the P atom at the iron atom of the neighboring subcluster followed by loss of one CO ligand (Scheme 2). In addition, the minor products **4** and **6** most likely would be produced through intermolecular nucleophilic CO substitution of **3** and **5** with unreacted Ph_2PCL and Ph_3P (formed in situ from Ph_2PCL and the Grignard reagent PhMgBr present in the sequential reaction systems), respectively. In fact, the intramolecular or intermolecular nucleophilic attack at iron followed by loss of an Fe-bonded ligand in such butterfly Fe/S cluster systems was previously well-documented.²⁰

(13) Characterization data are as follows. **7**: mp 162°C dec. Anal. Calcd for $\text{C}_{27}\text{H}_{19}\text{Fe}_4\text{O}_{11}\text{PS}_3$: C, 37.24; H, 2.18. Found: C, 37.09; H, 2.29. IR (KBr disk): $\nu_{\text{C=O}}$ 2079 (s), 2043 (vs), 2009 (vs), 1971 (s), 1958 (s), 1939 (s) cm^{-1} . ¹H NMR (200 MHz, CDCl_3): δ 0.95 (t, $J = 7.2$ Hz, 3H, CH_3), 1.44–1.58 (m, 2H, CH_2CH_3), 1.69–1.84 (m, 2H, SCH_2CH_2), 2.44–2.76 (m, 2H, SCH_2), 7.40–7.80 (m, 10H, $2\text{C}_6\text{H}_5$). ³¹P NMR (81.0 MHz, CDCl_3 , H_3PO_4): δ 162.36 (s). **8**: mp 167°C dec. Anal. Calcd for $\text{C}_{29}\text{H}_{15}\text{Fe}_4\text{O}_{11}\text{PS}_3$: C, 39.10; H, 1.69. Found: C, 38.85; H, 1.90. IR (KBr disk): $\nu_{\text{C=O}}$ 2080 (vs), 2043 (vs), 2015 (vs), 2003 (vs), 1988 (vs), 1942 (s) cm^{-1} . ¹H NMR (200 MHz, CDCl_3): δ 7.25–7.84 (m, 15H, $3\text{C}_6\text{H}_5$). ³¹P NMR (81.0 MHz, CDCl_3 , H_3PO_4): δ 161.28 (s).

(14) Crystal data are as follows. **8**: triclinic, space group $\text{P}\bar{1}$, $a = 9.408(4)$ Å, $b = 10.438(4)$ Å, $c = 19.084(8)$ Å, $\alpha = 91.396(7)^\circ$, $\beta = 103.410(7)^\circ$, $\gamma = 106.192(6)^\circ$, $F(000) = 888$, $V = 1742.7(12)$ Å³, $Z = 2$, $D_c = 1.696$ g cm^{-3} , $\mu(\text{Mo K}\alpha) = 1.913$ mm⁻¹, $R = 0.0482$, $R_w = 0.1153$, GOF = 0.985.

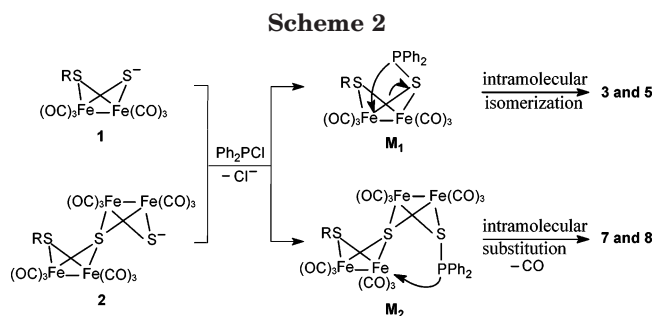
(15) Lindner, E.; Fawzi, R.; Mayer, H. A.; Eichele, K.; Hiller, W. *Organometallics* **1992**, *11*, 1033.

(16) Coleman, J. M.; Wojcicki, A.; Pollick, P. J.; Dahl, L. F. *Inorg. Chem.* **1967**, *6*, 1236.

(17) Song, L.-C.; Kadiata, M.; Wang, J.-T.; Wang, R.-J.; Wang, H.-G. *J. Organomet. Chem.* **1988**, *340*, 239.

(18) (a) Seyferth, D.; Kiwan, A. M. *J. Organomet. Chem.* **1985**, *286*, 219. (b) Song, L.-C.; Kadiata, M.; Wang, J.-T.; Wang, R.-J.; Wang, H.-G. *J. Organomet. Chem.* **1990**, *391*, 387. (c) Song, L.-C.; Yan, C.-G.; Hu, Q.-M.; Wang, R.-J.; Mak, T. C. W.; Huang, X.-Y. *Organometallics* **1996**, *15*, 1535. (d) Song, L.-C.; Hu, Q.-M.; Zhang, Q.-Y.; Feng, Q. *Chin. J. Org. Chem.* **1988**, *8*, 213.

(19) (a) Song, L.-C.; Lu, G.-L.; Hu, Q.-M.; Yang, J.; Sun, J. *J. Organomet. Chem.* **2001**, *623*, 56. (b) Wang, Z.-X.; Jia, C.-S.; Zhou, Z.-Y.; Zhou, X.-G. *J. Organomet. Chem.* **1999**, *580*, 201.



In conclusion, we have isolated and characterized the six quaternary phosphorus atom coordinating butterfly Fe/S cluster complexes **3–8**, which were produced by a “one-pot” synthetic method involving reactions of the in situ formed anions **1** and **2** with Ph_2PCl . Possible pathways for formation of these new complexes have been suggested, which involve three elementary steps: (i) the intermolecular nucleophilic attack of the negatively charged S atoms of **1** and **2** at the P atom of Ph_2PCl to give the expected intermediate cluster phosphines \mathbf{M}_1 and \mathbf{M}_2 , (ii) the intramolecular nucleophilic attack of the P atom in \mathbf{M}_1 or \mathbf{M}_2 at the Fe atom followed

by removal of a ligand from Fe to give the originally unexpected products **3/5** and **7/8**, and (iii) further CO substitution of **3** with Ph_2PCl or of **5** with Ph_3P that were present in the reaction systems to afford **4** and **6**. To further understand the mechanistic details and the scope/limits for reactions leading to complexes **3–8**, other butterfly Fe/S cluster anions, such as the dianions $(\mu\text{-S}^-)_2\text{Fe}_2(\text{CO})_6^{1b}$ and $(\mu\text{-S}^-)_2[\text{Fe}_2(\text{CO})_6]_4(\mu_4\text{-S})(\mu\text{-SZS-}\mu)$,²¹ as well as other phosphine halides and arsine halides will be the subject of future studies in this laboratory.

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Supporting Information Available: Text describing the synthesis and characterization of complexes **3–8** and CIF files giving the structural determinations of **3**, **6** and **8**, including atomic coordinates, equivalent isotropic displacement parameters, bond lengths and angles, and data collection and processing parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(20) For example, see: (a) Seyferth, D.; Womack, G. B.; Song, L.-C.; Cowie, M.; Hames, B. W. *Organometallics* **1983**, *2*, 928. (b) Song, L.-C.; Hu, Q.-M.; Wang, J.-T. *Chem. J. Chin. Univ.* **1985**, *6*, 995. (c) Hogarth, G. *J. Organomet. Chem.* **2003**, *672*, 29.

(21) Song, L.-C.; Fan, H.-T.; Hu, Q.-M.; Yang, Z.-Y.; Sun, Y.; Gong, F.-H. *Chem. Eur. J.* **2003**, *9*, 170.