3764 *Organometallics* **2005,** *24,* 3764−3771

Synthesis and Characterization of Starlike Complexes Containing Three Terminal Butterfly Fe/S Cluster Cores Generated via Reactions of the Three-μ-CO-Containing Trianions $\{[(\mu\text{-CO})Fe_2(CO)_6]_3[(\mu\text{-SCH}_2CH_2)_3N]\}^{3-}$ and $\{[(\mu\text{-CO})Fe_2(CO)_6]_3[1,3,5\text{-}(\mu\text{-SCH}_2)_3C_6H_3]\}^{3-}$ with Electrophiles

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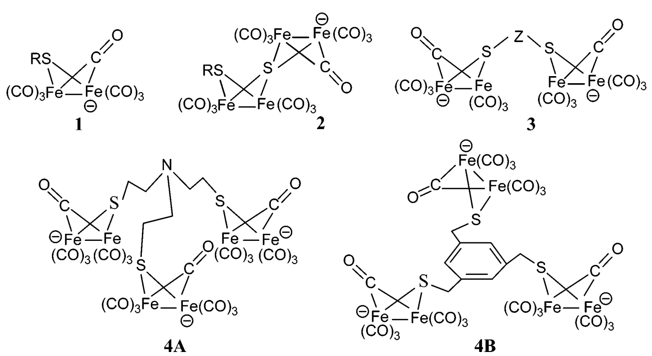
The novel three-μ-CO-containing trianions $\{[(\mu\text{-CO})Fe_2(CO)_6]_3[(\mu\text{-SCH}_2\ CH_2)_3N]\}^{3-}$ (**4A**) and $\{[(\mu\text{-CO})Fe_2(CO)_6]_3[1,3,5\text{-}(\mu\text{-SCH}_2)_3C_6H_3]\}^{3-}$ (**4B**) were prepared by reaction of trithiol $N(CH_2CH_2SH)_3$ or $1,3,5\text{-}(HSCH_2)_3C_6H_3$ with $Fe_3(CO)_{12}$ and Et_3N in 1:3:3 molar ratio in THF at room temperature. Further in situ treatment of **4A** with electrophiles Ph_2PCl, PhSBr, PhC(Cl)=NPh, and CH_2=$CHCH_2Br$ afforded starlike complexes $[(\mu\text{-Y})Fe_2(CO)_6]_3[(\mu\text{-SCH}_2CH_2)_3N]$ (**5**−**8**: Y = Ph_2P, PhS, PhC=NPh, CH_2=$CHCH_2$), whereas its reaction with CS_2 followed by treatment with organic halides RX produced complexes $[(\mu\text{-Y})Fe_2(CO)_6]_3[(\mu\text{-SCH}_2CH_2)_3N]$ (**9**−**11**: Y = MeSC=S, $PhCH_2SC$=S, CH_2=$CHCH_2SC$=S). Similarly, **4B** reacted in situ with Ph_2PCl, PhSBr, PhC(Cl)=NPh, CH_2=$CHCH_2Br$, and PhNCS to give starlike complexes $[(\mu\text{-Y})Fe_2(CO)_6]_3[1,3,5\text{-}(\mu\text{-SCH}_2)_3C_6H_3]$ (**12**−**16**: Y = Ph_2P, PhS, PhC=NPh, CH_2=$CHCH_2$, PhNHC=S), whereas its reaction with CS_2 followed by treatment with RX yielded complexes $[(\mu\text{-Y})Fe_2(CO)_6]_3[1,3,5\text{-}(\mu\text{-SCH}_2)_3C_6H_3]$ (**17**−**19**: Y = MeSC=S, $PhCH_2SC$=S, CH_2=$CHCH_2SC$=S). All the starlike complexes **5**−**19** contain three terminal butterfly Fe/S cluster cores, which have been fully characterized by elemental analysis and spectroscopy, and particularly by X-ray diffraction techniques for **5**, **12**, **15**, and **17**.

Introduction

Scheme 1



Iron−sulfur cluster complexes have attracted a great deal of attention because of their unique structures and novel chemical reactivities,[1] and particularly their practical applications such as the use as biomimetic models for the active sites of nitrogenase[2] and the Fe-only hydrogenase.[3] Among such cluster complexes the μ-CO-containing butterfly Fe/S cluster anions $(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6$ (**1**), $(\mu\text{-CO})(\mu\text{-RS})[Fe_2(CO)_6]_2(\mu_4\text{-S})$ (**2**), and $[(\mu\text{-CO})Fe_2(CO)_6]_2(\mu\text{-SZS-}\mu)$ (**3**) (Scheme 1) are of interest in terms of their ready availability and high nucleophilicity toward diverse electrophiles.[4−6] While the one-μ-CO-containing single-butterfly monoanion **1** was first prepared by Seyferth's group in 1985 through reaction of $Fe_3(CO)_{12}$ with mercaptan RSH in

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[1] (a) Ogino, H.; Inomata, S.; Tobita, H. *Chem. Rev.* **1998**, *98*, 2093. (b) Song, L.-C. In *Trends in Organometallic Chemistry*; Atwood, J. L., Corriu, R., Cowley, A. H., Lappert, M. F., Nakamura, A., Pereyre, M., Eds.; Research Trends: Trivandrum, India, 1999; Vol. 3, p 1. (c) Song, L.-C. *Acc. Chem. Res.* **2005**, *38*, 21.

[2] (a) Coucouvanis, D. *Acc. Chem. Res.* **1991**, *24*, 1. (b) Karlin, K. D. *Science* **1993**, *261*, 701. (c) Rao, P. V.; Holm, R. H. *Chem. Rev.* **2004**, *104*, 527.

[3] (a) Gloaguen, F.; Lawrence, J. D.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2001**, *123*, 9476. (b) Gloaguen, F.; Lawrence, J. D.; Schmidt, M.; Wilson, S. R.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2001**, *123*, 12518. (c) Lyon, E. J.; Georgakaki, I. P.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2001**, *123*, 3268. (d) Darensbourg, M. Y.; Lyon, E. J.; Zhao, X.; Georgakaki, I. P. *PNAS* **2003**, *100*, 3683. (e) Song, L.-C.; Yang, Z.-Y.; Bian, H.-Z.; Hu, Q.-M. *Organometallics* **2004**, *23*, 3082.

[4] For single-butterfly, one-μ-CO-containing monoanion **1**, see for example: (a) Seyferth, D.; Womack, G. B.; Dewan, J. C. *Organometallics* **1985**, *4*, 398. (b) Seyferth, D.; Hoke, J. B.; Dewan, J. C. *Organometallics* **1987**, *6*, 895. (c) Seyferth, D.; Ruschke, D. P.; Davis, W. M.; Cowie, M.; Hunter, A. D. *Organometallics* **1994**, *13*, 3834. (d) Delgado, E.; Hernández, E.; Rossell, O.; Seco, M.; Puebla, E. G.; Ruiz, C. *J. Organomet. Chem.* **1993**, *455*, 177. (e) Song, L.-C.; Hu, Q.-M. *J. Organomet. Chem.* **1991**, *414*, 219. (f) Song, L.-C.; Yan, C.-G.; Hu, Q.-M.; Wang, R.-J.; Mak, T. C. W.; Huang, X.-Y. *Organometallics* **1996**, *15*, 1535. (g) Song, L.-C.; Fan, H.-T.; Hu, Q.-M.; Qin, X.-D.; Zhu, W.-F.; Chen, Y.; Sun, J. *Organometallics* **1998**, *17*, 3454. (h) Song, L.-C.; Lu, G.-L.; Hu, Q.-M.; Fan, H.-T.; Chen, Y.; Sun, J. *Organometallics* **1999**, *18*, 3258. (i) Song, L.-C.; Lu, G.-L.; Hu, Q.-M.; Sun, J. *Organometallics* **1999**, *18*, 2700. (j) Wang, Z.-X.; Jia, C.-S.; Zhou, Z.-Y. Zhou, X.-G. *J. Organomet. Chem.* **1999**, *580*, 201.

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the presence of Et_3N,[4a] we made the double-butterfly one-μ-CO-containing monoanion **2** in 2000 via reaction of the Grignard reagent RMgX with μ-$S_2Fe_2(CO)_6$ followed by treatment of the intermediate S-centered anion $(\mu\text{-}S^-)(\mu\text{-RS})Fe_2(CO)_6$ with $Fe_3(CO)_{12}$.[5a] In 2002 we further prepared the two-μ-CO-containing double-butterfly dianion **3** by reaction of $Fe_3(CO)_{12}$ with dithiol HSZSH and Et_3N.[6a] So far, these complex anions **1**−**3** have been demonstrated to be versatile reagents for synthesizing a wide variety of Fe/S cluster complexes.[4−6] To further develop the chemistry of Fe/S cluster complexes, we recently initiated an investigation on formation and reactivities of two novel triple-butterfly three-μ-CO-containing trianions $\{[(\mu\text{-CO})Fe_2(CO)_6]_3[(\mu\text{-}SCH_2CH_2)_3N]\}^{3-}$ (**4A**) and $\{[(\mu\text{-CO})Fe_2(CO)_6]_3[1,3,5\text{-}(\mu\text{-}SCH_2)_3C_6H_3]\}^{3-}$ (**4B**) (Scheme 1), aimed at obtaining the starlike complexes terminated with three Fe/S cluster cores. In a previous communication,[7] we preliminarily reported the formation of trianions **4A** and **4B**, as well as their in situ reactions with some electrophiles leading to five starlike cluster complexes. Now, in this paper we will report the formation of trianions **4A** and **4B** in detail and the systematic study concerning their reactivities toward various electrophiles to produce 15 starlike complexes. In addition, the structural characterization of all the products, including the single-crystal structures of four representative products, will also be described.

Results and Discussion

Formation and Reactivities of the $[Et_3NH]$ Salt of Trianion $\{[(\mu\text{-CO})Fe_2(CO)_6]_3[(\mu\text{-}SCH_2CH_2)_3N]\}^{3-}$ (4A). Synthesis and Characterization of Starlike Complexes $[(\mu\text{-Y})Fe_2(CO)_6]_3[(\mu\text{-}SCH_2CH_2)_3N]$ (5−11: Y = Ph_2P, PhS, PhC=NPh, CH_2=$CHCH_2$, MeSC=S, $PhCH_2SC$=S, CH_2=$CHCH_2SC$=S). Treatment of the nitrogen-containing trithiol $N(CH_2CH_2SH)_3$ with $Fe_3(CO)_{12}$ and Et_3N in 1:3:3 molar ratio in THF at room temperature resulted in formation of the $[Et_3NH]$ salt of trianion **4A** (Scheme 2). The IR spectrum of the $[Et_3NH]$ salt of trianion **4A** in THF displayed a medium absorption band at 1742 cm^{-1} for its μ-CO ligands, which is similar to those displayed by the $[Et_3NH]$ salts of the one-μ-CO-containing monoanion **1** (R = Et)[4a] and the two-μ-CO-containing dianion **3** (Z = $CH_2(CH_2OCH_2)_3CH_2$).[6a,b] Further in situ treatment of the $[Et_3NH]$ salt of trianion **4A** with the electrophiles containing a leaving group such as Ph_2PCl, PhSBr, PhC(Cl)=NPh, and CH_2=$CHCH_2Br$ through nucleophilic attack of the three negatively charged Fe atoms in **4A** at the S, P, or C atom bearing the leaving group followed by displacement of the three μ-CO ligands in each of the corresponding intermediates afforded products **5**−**8** (Scheme 2).

However, when the $[Et_3NH]$ salt of trianion **4A** was treated in situ with an electrophile CS_2 without a leaving group, the $[Et_3NH]$ salt of an S-centered trianion was formed via nucleophilic attack of the three negatively charged Fe atoms in **4A** at the three C atoms in three molecules of CS_2 followed by loss of the three μ-CO ligands in **4A**. This type of S-centered trianion could be alkylated in situ with an alkyl halide MeI, $PhCH_2Br$, or CH_2=$CHCH_2Br$ to give products **9**−**11** (Scheme 3).

Products **5**−**11** are air-stable solids, which were characterized by elemental analysis and spectroscopy. For instance, the IR spectra of **5**−**11** showed three absorption bands in the region 2085−1972 cm^{-1} for their terminal carbonyls, whereas those of **7** and **9**−**11** displayed one additional absorption band at 1557 cm^{-1} for the bridged C=N double bonds[8,9] or at ca. 1015 cm^{-1} for the bridged C=S double bonds,[10,11] respectively. In addition, the ^{31}P NMR spectrum of **5** showed one singlet at 142.45 ppm for its three identical P atoms, which is very similar to the spectra displayed by single- and double-butterfly Fe_2SP cluster complexes.[6b,12] The ^1H NMR spectra of the methylene groups attached to the three bridged S atoms in **5**−**11** showed one signal (a triplet or a multiplet) at the chemical shift greater than 2.2 ppm, which indicates that the methylene groups are most likely attached to the bridged S atoms by an equatorial type of bond. This is because the chemical shifts of the axial and equatorial Me groups in the a/e isomer of $(\mu\text{-MeS})_2Fe_2(CO)_6$ are 1.62 and 2.13 ppm, respectively.[13]

Formation and Reactivities of the $[Et_3NH]$ Salt of Trianion $\{[(\mu\text{-CO})Fe_2(CO)_6]_3[1,3,5\text{-}(\mu\text{-}SCH_2)_3C_6H_3]\}^{3-}$ (4B). Synthesis and Characterization of Starlike Complexes $[(\mu\text{-Y})Fe_2(CO)_6]_3[1,3,5\text{-}(\mu\text{-}SCH_2)_3C_6H_3]$ (12−19: Y = Ph_2P, PhS, PhC=NPh, CH_2=$CHCH_2$, PhNHC=S, MeSC=S, $PhCH_2SC$=S, CH_2=$CHCH_2SC$=S). The benzene ring-containing trithiol $1,3,5\text{-}(HSCH_2)_3C_6H_3$ could also react with $Fe_3(CO)_{12}$ and Et_3N in 1:3:3 molar ratio in THF at room temperature to give the $[Et_3NH]$ salt of trianion **4B** (Scheme 4). The IR spectrum of **4B** in THF, similar to the IR spectra of anions **1** (R = Et),[4a] **3** (Z = $CH_2(CH_2OCH_2)_3CH_2$),[6a,b] and **4A**, showed one medium absorption band at 1738 cm^{-1} typical of its μ-CO ligands. Further treatment of the $[Et_3NH]$ salt of trianion **4B** with electrophiles such as Ph_2PCl, PhSBr, PhC(Cl)=NPh, CH_2=$CHCH_2Br$, and PhNCS or with electrophile CS_2 followed by treatment with organic halides RX, via pathways similar to those leading to **5**−**11**, gave rise to products **12**−**19** (Schemes 4 and 5).

The starlike complexes **12**−**19** are air-stable solids, which have been characterized by elemental analysis and spectroscopy. For example, the IR spectra of

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(5) For double-butterfly, one-μ-CO-containing monoanion **2**, see for example: (a) 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. (b) Song, L.-C.; Hu, Q.-M.; Sun, B.-W.; Tang, M.-Y.; Lu G.-L. *Inorg. Chim. Acta* **2003**, *346*, 12. (c) Song, L.-C.; Hu, Q.-M.; Sun, B.-W.; Tang, M.-Y.; Yang, J.; Hua, Y.-J. *Organometallics* **2002**, *21*, 1627.

(6) For double-butterfly, two-μ-CO-containing dianion **3**, see for example: (a) Song, L.-C.; Fan, H.-T.; Hu, Q.-M. *J. Am. Chem. Soc.* **2002**, *124*, 4566. (b) Song, L.-C.; Fan, H.-T.; Hu, Q.-M.; Yang, Z.-Y.; Sun, Y.; Gong F.-H. *Chem. Eur. J.* **2003**, *9*, 170. (c) Song, L.-C.; Gong, F.-H.; Meng T.; Ge, J.-H.; Cui, L.-N.; Hu, Q.-M. *Organometallics* **2004**, *23*, 823.

(7) Song, L.-C.; Cheng, J.; Hu, Q.-M.; Gong, F.-H.; Bian, H.-Z.; Wang, L.-X. *Organometallics* **2005**, *24*, 472.

(8) Seyferth, D.; Hoke, J. B. *Organometallics* **1988**, *7*, 524.

(9) Song, L.-C.; Lu, G.-L.; Hu, Q.-M.; Qin, X.-D.; Sun, C.-X.; Yang J.; Sun, J. *J. Organomet. Chem.* **1998**, *571*, 55.

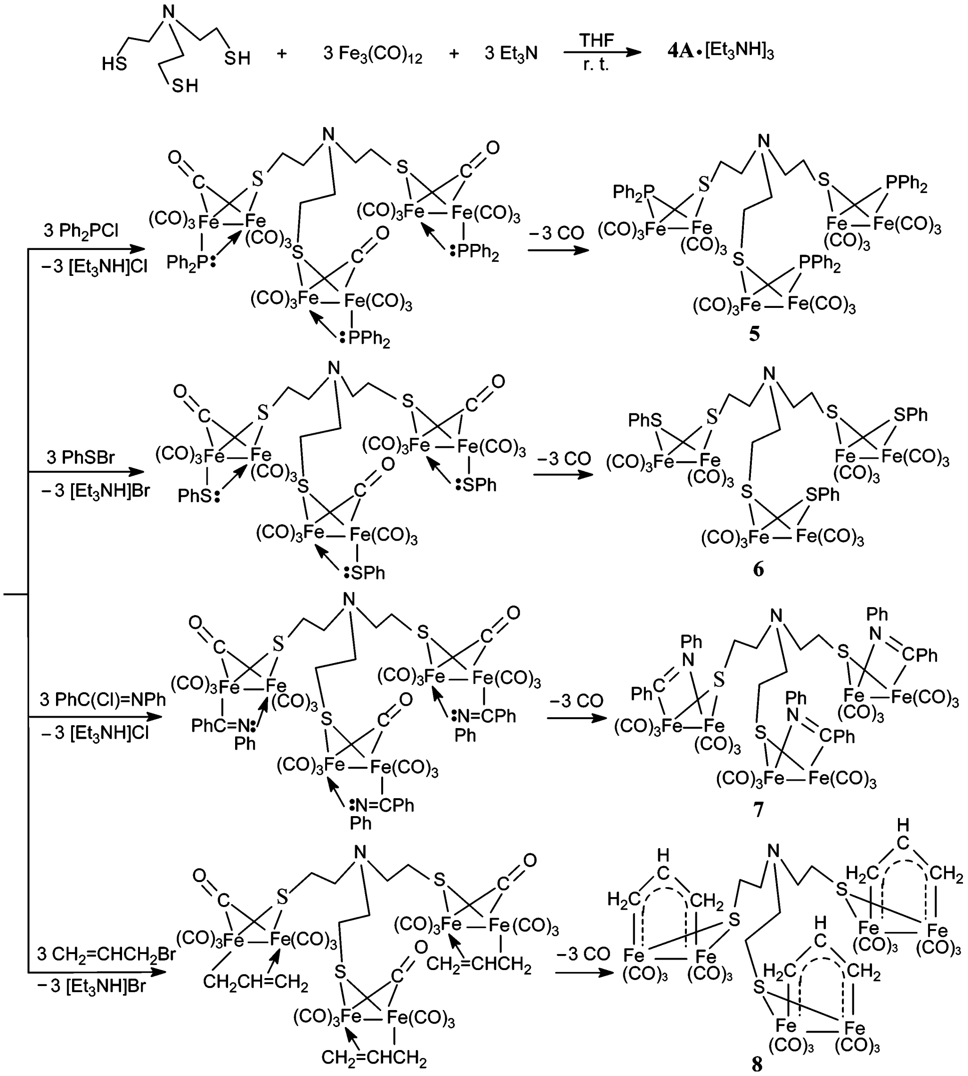
(10) Seyferth, D.; Womack, G. B.; Archer, C. M.; Fackler, J. P., Jr.; Marler, D. O. *Organometallics* **1989**, *8*, 443.

(11) Song, L.-C.; Yan, C.-G.; Hu, Q.-M.; Wang R.-J.; Mak, T. C. W. *Organometallics* **1995**, *14*, 5513.

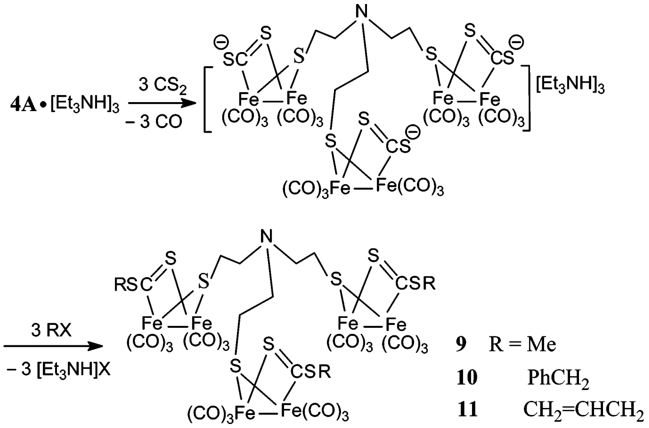
(12) Song, L.-C.; Li, Y.; Hu, Q.-M.; Liu, R.-G.; Wang, J.-T. *Acta Chim. Sin.* **1990**, *48*, 1180.

(13) Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125.

Scheme 2



Scheme 3



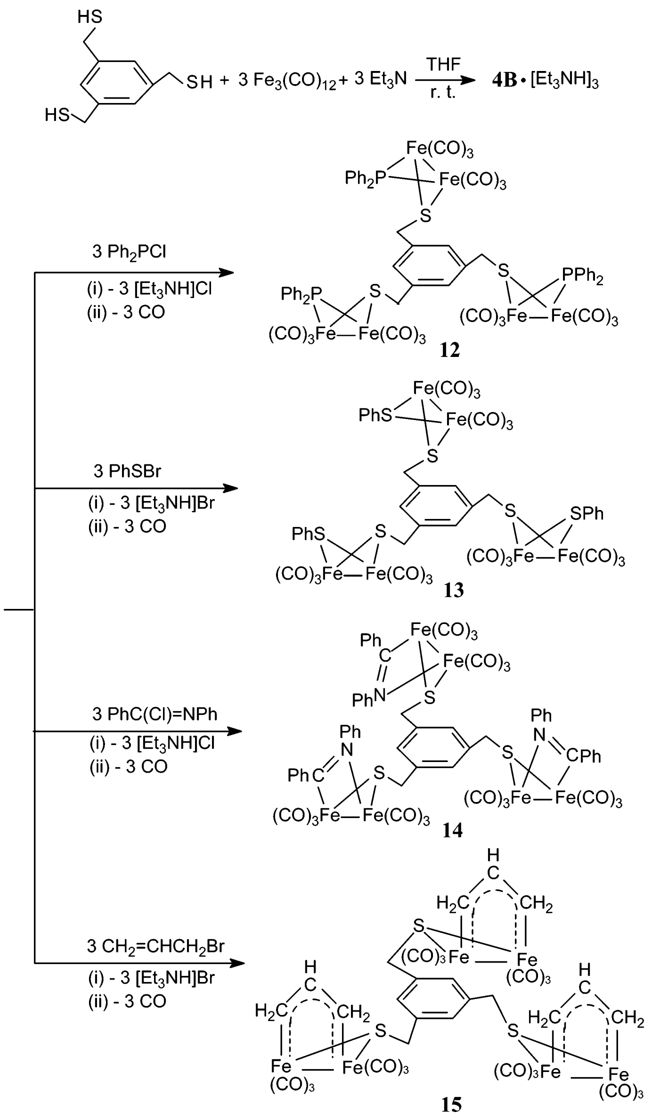
9 R = Me
10 $PhCH_2$
11 $CH_2=CHCH_2$

12−**19** displayed three absorption bands in the range 2073−1955 cm^{-1} for their terminal carbonyls. In addition, while the IR spectrum of **14** showed one additional absorption band at 1557 cm^{-1} for its bridged C=N double bonds,[8,9] **16**−**19** displayed one additional band in the range 1026−1016 cm^{-1} for their bridged C=S double bonds.[10,11] The ^{31}P NMR spectrum of **12** exhibited one singlet at 141.31 ppm for its three identical P atoms, which is almost the same as that displayed by the triple-butterfly Fe_2PS cluster **5** and very close to those displayed by the single- and double-butterfly Fe_2PS cluster complexes.[6b,12] It is worth pointing out that the three methylene groups in **12**−**19** are probably bound to the bridged S atoms by equatorial bonds. This is because in their ^1H NMR spectra the methylene groups showed only one signal (a singlet or a multiplet) at the chemical shift (>3.5 ppm) which is very close to that (3.67 ppm) of the equatorial CH_2 group in the a/e isomer of (μ-$PhCH_2S)_2Fe_2(CO)_6$.[13] Fortunately, the spectroscopically characterized structural features for **5**−**19** mentioned above have been unambiguously confirmed by X-ray crystallographic studies of complexes **5**, **12**, **15**, and **17** (vide infra).

Crystallographic Studies on 5, 12, 15, and 17. To confirm the starlike structures of **5**−**19**, X-ray crystallographic studies on **5**, **12**, **15**, and **17** were undertaken. Their ORTEP drawings are shown in Figures 1−4, whereas Tables 1−4 list their selected bond lengths and angles, respectively.

As can be seen in Figures 1 and 2, both **5** and **12** contain three identical Fe_2SP butterfly cluster cores in which each of the P atoms is attached to two phenyl groups and each of the Fe atoms is attached to three terminal CO ligands. In addition, the three butterfly Fe_2SP cluster cores in **5** are connected through their S atoms to three β-C atoms of the central triethyl-

Scheme 4



eneamine structural unit by three equatorial bonds (for example, the nonbonded angle C(2)−S(1)···P(1) = 161.1°), while those in **12** are bound through their S atoms to three α-C atoms of the central trimethylenebenzene moiety by three equatorial bonds (for example, the nonbonded angle C(19)−S(1)···P(1) = 161.3°). Such conformational arrangements are necessary to avoid the strong axial−axial repulsions between the axially bonded bulky phenyl groups at P atoms and the central part of the starlike complex.[13,14] To our knowledge, **5** and **12** are the first examples of the crystallographically characterized triple-butterfly Fe_2PS cluster complexes, although the crystallographically characterized single-butterfly Fe_2PS clusters (μ-PhS)(μ-Ph_2P)$Fe_2(CO)_6$,[15] (μ-*t*-BuS)(μ-Ph_2P)$Fe_2(CO)_6$,[16] and (μ-*t*-BuS)(μ-PhClP) $Fe_2(CO)_6$[17] were known.

Figures 3 and 4 show that **15** and **17** have three identical butterfly Fe_2SC_3 and Fe_2S_2C cluster cores, respectively. In **15** the C−C bond lengths of the allyl ligands (for example, C(19)−C(20) = 1.374 (11) Å and C(20)−C(21) = 1.394 (9) Å) lie between the values reported for the C−C single and C=C double bonds, indicating that the ligands are best regarded as delocalized π-allyl ligands.[18] In **17** the bridged C=S double bonds (for example, the double bond C(28)=S(4) = 1.654(12) Å) is slightly shorter than its neighboring single bond C(28)−S(5) (1.695(10) Å), but markedly shorter than the remote single bonds S(5)−C(29) (1.818(11) Å) and S(1)−C(25) (1.826(9) Å). In addition, the three identical cluster cores in **15** and **17** are joined together by connecting their S atoms with three benzylic C atoms of the planar trimethylene benzene ring moiety also via three equatorial bonds (for example, for **15** the nonbonded angle C(28)−S(1)···C(20) = 161.8° and for **17** the nonbonded angle C(25)−S(1)···S(4) = 168.1°).[13,14] In fact, the basic geometry of the cluster cores in **15** is very similar to that of the single-butterfly cluster complex (μ-EtS)(μ-CH_2=$CHCH_2$)$Fe_2(CO)_6$.[18] It is worthy of note that although some double-butterfly Fe_2S_2C clusters were recently crystallographically characterized,[6a,b] **17** is the first crystallographically characterized triple-butterfly Fe_2S_2C cluster compound.

In summary, we have synthesized and fully characterized the first examples of the starlike complexes with three terminal butterfly Fe_2SP, Fe_2S_2, Fe_2CNS, Fe_2C_3, or Fe_2S_2C cluster cores and a pyramidal N atom or a planar benzene ring at the central part of the complexes. The easy availablity of trianions **4A** and **4B** from reaction of trithiol $N(CH_2CH_2SH)_3$ or 1,3,5-$(HSCH_2)_3C_6H_3$ with $Fe_3(CO)_{12}$ and Et_3N, as well as their high nucleophilicity toward electrophiles, would make them very useful synthons in the development of transition metal chemistry.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen by using standard Schlenk and vacuum-line techniques. Tetrahydrofuran (THF) was distilled from Na/benzophenone ketyl under nitrogen. $Fe_3(CO)_{12}$,[19] Ph_2PCl,[20] $N(CH_2CH_2SH)_3$,[21] 1,3,5-$(HSCH_2)_3C_6H_3$,[22] PhSBr,[23] and PhC(Cl)=NPh[24] were prepared according to literature procedures. Et_3N, CS_2, MeI, $PhCH_2Br$, CH_2=$CHCH_2$Br, and PhNCS were of commercial origin and used without further purification. Preparative TLC was carried out on glass plates (25 × 15 × 0.25 cm) coated with silica gel G (10−40 μm). IR spectra were recorded on a Bio-Rad FTS 135 infrared spectrophotometer. $^1H(^{31}P)$ NMR spectra were taken on a Bruker AC-P200 or Bruker Avance 300 NMR spectrometer. Elemental analyses were performed with an Elementar Vario EL analyzer. Melting points were determined on a Yanaco MP-500 apparatus and were uncorrected.

Standard in Situ Preparations of the [Et₃NH] Salts of Trianions $\{[(\mu\text{-CO})Fe_2(CO)_6]_3[(\mu\text{-}SCH_2CH_2)_3N]\}^{3-}$ (4A) and $\{[(\mu\text{-CO})Fe_2(CO)_6]_3[1,3,5\text{-}(\mu\text{-}SCH_2)_3C_6H_3]\}^{3-}$ (4B). A 100 mL three-necked flask fitted with a magnetic stir-bar, a rubber

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[14] Song, L.-C.; Lu, G.-L.; Hu, Q.-M.; Sun, J. *Organometallics* **1999**, *18*, 5429.

[15] Le Borgne, G.; Mathieu, R. *J. Organomet. Chem.* **1981**, *208*, 201.

[16] Song, L.-C.; Hu, Q.-M.; Zhou, Z.-Y.; Hu, G.-Z. *Chin. J. Org. Chem.* **1991**, *11*, 533.

[17] Song, L.-C.; Wang, R.-J.; Li, Y.; Wang, H.-G.; Wang, J.-T. *Chin. J. Org. Chem.* **1989**, *9*, 512.

[18] Seyferth, D.; Womack, G. B.; Dewan, J. C. *Organometallics* **1985**, *4*, 398.

[19] King, R. B. *Organometallic Syntheses; Transition-Metal Compounds*; Academic Press: New York, 1965; Vol. 1, p 95.

[20] Horner, L.; Beck, P.; Toscano, V. G. *Chem. Ber.* **1961**, *94*, 2122.

[21] Harley-Mason, J. *J. Chem. Soc.* **1947**, 320.

[22] Whitesides, G. M.; Houk, J. *J. Am. Chem. Soc.* **1987**, *109*, 6825.

[23] Harpp, D. N.; Mathiaparanam, P. *J. Org. Chem.* **1972**, *37*, 1367.

[24] Vaughan, W. R.; Carlson, R. D. *J. Am. Chem. Soc.* **1962**, *84*, 769.

Scheme 5

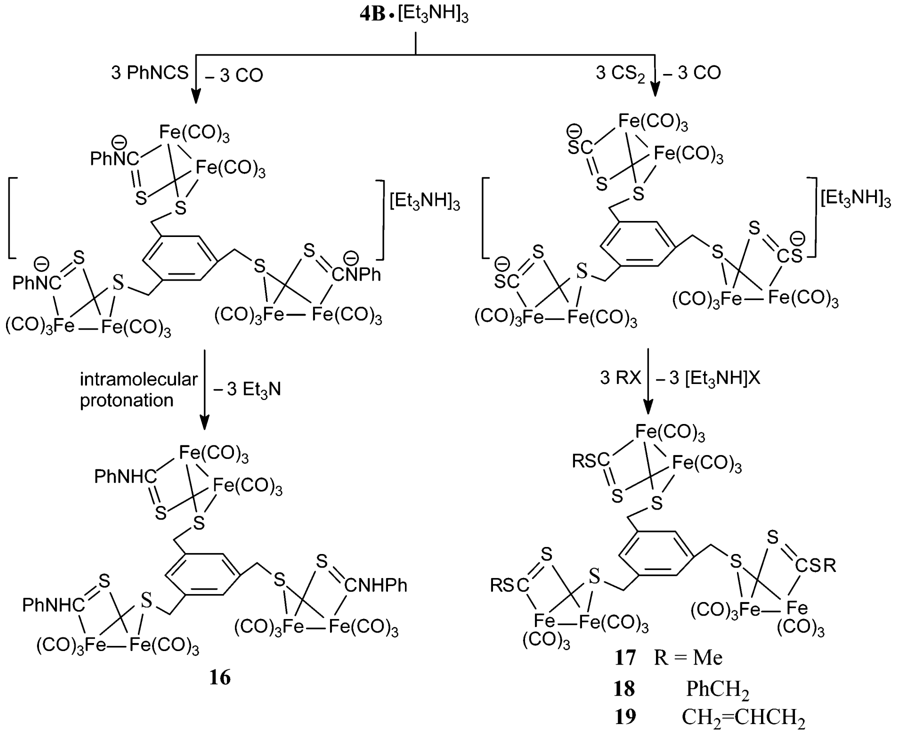

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 5

Fe(1)–S(2)	2.268(3)	Fe(1)–P(3)	2.216(2)
Fe(2)–S(2)	2.262(2)	Fe(2)–P(3)	2.225(2)
Fe(3)–P(1)	2.227(2)	Fe(3)–S(1)	2.266(2)
Fe(4)–P(1)	2.222(2)	Fe(4)–S(1)	2.283(2)
N(1)–C(1)	1.435(8)	Fe(1)–Fe(2)	2.5550(19)
S(2)–Fe(1)–Fe(2)	55.54(7)	P(1)–Fe(3)–S(1)	76.53(8)
P(3)–Fe(2)–S(2)	76.32(8)	P(1)–Fe(3)–Fe(4)	54.91(6)
P(3)–Fe(2)–Fe(1)	54.73(7)	P(1)–Fe(4)–S(1)	76.29(8)
S(1)–Fe(3)–Fe(4)	56.21(6)	C(21)–N(1)–C(1)	116.4(7)
P(3)–Fe(1)–S(2)	76.35(8)	N(1)–C(1)–C(2)	117.2(6)
S(2)–Fe(2)–Fe(1)	55.78(8)	C(1)–N(1)–C(41)	113.4(7)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 12

Fe(1)–S(1)	2.264(4)	Fe(1)–Fe(2)	2.566(3)
Fe(2)–S(1)	2.259(3)	P(1)–C(13)	1.817(11)
P(1)–C(7)	1.820(14)	Fe(2)–P(1)	2.226(4)
Fe(1)–P(1)	2.226(3)	S(1)–C(19)	1.826(12)
S(1)–Fe(1)–Fe(2)	55.34(9)	P(1)–Fe(1)–S(1)	76.47(13)
P(1)–Fe(2)–S(1)	76.59(13)	P(1)–Fe(1)–Fe(2)	54.81(10)
P(1)–Fe(2)–Fe(1)	54.82(10)	S(1)–Fe(2)–Fe(1)	55.55(11)
C(7)–P(1)–Fe(1)	122.0(5)	C(13)–P(1)–Fe(1)	122.1(4)
C(7)–P(1)–Fe(2)	120.8(5)	Fe(2)–P(1)–Fe(1)	70.37(11)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 15

Fe(1)–Fe(2)	2.6778(13)	Fe(1)–C(19)	2.121(8)
Fe(3)–Fe(4)	2.7330(12)	Fe(4)–S(2)	2.2327(17)
Fe(5)–Fe(6)	2.6790(14)	Fe(5)–S(3)	2.2391(16)
Fe(2)–S(1)	2.2402(19)	Fe(6)–S(3)	2.2370(18)
Fe(2)–C(21)	2.0936(6)	C(19)–C(20)	1.374(11)
Fe(3)–S(2)	2.243(2)	Fe(1)–C(1)	1.784(8)
S(1)–Fe(1)–C(19)	86.4(3)	C(24)–Fe(4)–S(2)	86.02(12)
S(1)–Fe(1)–Fe(2)	53.25(5)	S(2)–Fe(4)–Fe(3)	52.53(5)
C(21)–Fe(2)–S(1)	84.6(2)	Fe(2)–S(1)–Fe(1)	73.29(6)
S(1)–Fe(2)–Fe(1)	53.45(5)	Fe(4)–S(2)–Fe(3)	75.27(6)
C(22)–Fe(3)–S(2)	85.13(14)	C(19)–C(20)–Fe(1)	59.3(4)
S(2)–Fe(3)–Fe(4)	52.20(5)	C(23)–C(22)–Fe(3)	88.94(13)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 17

Fe(1)–Fe(2)	2.618(2)	Fe(3)–S(2)	2.242(3)
Fe(3)–Fe(4)	2.620(2)	Fe(3)–S(6)	2.280(5)
Fe(5)–Fe(6)	2.607(3)	S(5)–C(28)	1.695(10)
Fe(2)–S(1)	2.253(3)	S(4)–C(28)	1.654(12)
Fe(2)–S(4)	2.276(3)	S(6)–C(30)	1.655(16)
S(1)–Fe(1)–Fe(2)	54.36(8)	S(1)–Fe(2)–Fe(1)	54.80(8)
S(1)–Fe(2)–S(4)	82.41(12)	S(4)–Fe(2)–Fe(1)	77.89(10)
S(2)–Fe(3)–Fe(4)	54.55(8)	S(2)–Fe(3)–S(6)	84.58(17)
S(6)–Fe(3)–Fe(4)	76.84(13)	Fe(2)–S(1)–Fe(1)	70.83(9)
S(2)–Fe(4)–Fe(3)	54.16(8)	C(28)–S(4)–Fe(2)	91.5(3)
Fe(3)–S(2)–C(26)	112.9(3)	S(4)–C(28)–S(5)	123.7(6)

septum, and a nitrogen inlet tube was charged with $Fe_3(CO)_{12}$ (0.75 g, 1.5 mmol), THF (20 mL), Et_3N (0.21 mL, 1.5 mmol), and $N(CH_2CH_2SH)_3$ (0.065 mL, 0.5 mmol) or 1,3,5-$(HSCH_2)_3$-C_6H_3 (0.114 g, 0.5 mmol). The mixture was stirred at room temperature for 0.5–1 h to give a brown-red solution of ca. 0.5 mmol of the intermediate salt **4A**·$[Et_3NH]_3$ or **4B**·$[Et_3NH]_3$, which was utilized immediately in the following preparations.

Preparation of [(μ-Ph₂P)Fe₂(CO)₆]₃[(μ-SCH₂CH₂)₃N] (5). To the above prepared solution of **4A**·$[Et_3NH]_3$ was added Ph_2PCl (0.36 mL, 2.0 mmol). The mixture was stirred at room temperature for 24 h. Solvent was removed under reduced pressure. The residue was subjected to TLC using acetone/petroleum ether (v/v = 1:4) as eluent to give **5** (0.255 g, 32%) as a red solid, mp 78–80 °C. Anal. Calcd for $C_{60}H_{42}Fe_6NO_{18}P_3S_3$: C, 45.35; H, 2.66; N, 0.88. Found: C, 45.33; H, 2.67; N, 1.00. IR (KBr disk): $\nu_{C\equiv O}$ 2059 (s), 2020 (vs), 1982 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.46 (t, *J* = 7.0 Hz, 6H, $3SCH_2$), 2.65 (t, *J* = 7.0 Hz, 6H, $3NCH_2$), 7.19–7.61 (m, 30H, $6C_6H_5$). ^{31}P NMR (121.48 MHz, $CDCl_3$, 85% H_3PO_4): 142.45 (s) ppm.

Preparation of [(μ-PhS)Fe₂(CO)₆]₃[(μ-SCH₂CH₂)₃N] (6). The same procedure was followed as for **5**, but PhSBr (0.567 g, 3.0 mmol) was used instead of Ph_2PCl and the residue was subjected to TLC using CH_2Cl_2/petroleum ether (v/v = 1:2) as eluent. **6** (0.222 g, 33%) was obtained as a red solid, mp 54–56 °C. Anal. Calcd for $C_{42}H_{27}Fe_6NO_{18}S_6$: C, 37.06; H, 2.00; N, 1.03. Found: C, 36.96; H, 2.04; N, 1.02. IR (KBr disk): $\nu_{C\equiv O}$ 2073 (s), 2036 (vs), 1995 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.28–2.82 (m, 12H, $3SCH_2$, $3NCH_2$), 7.10–7.48 (m, 15H, $3C_6H_5$) ppm.

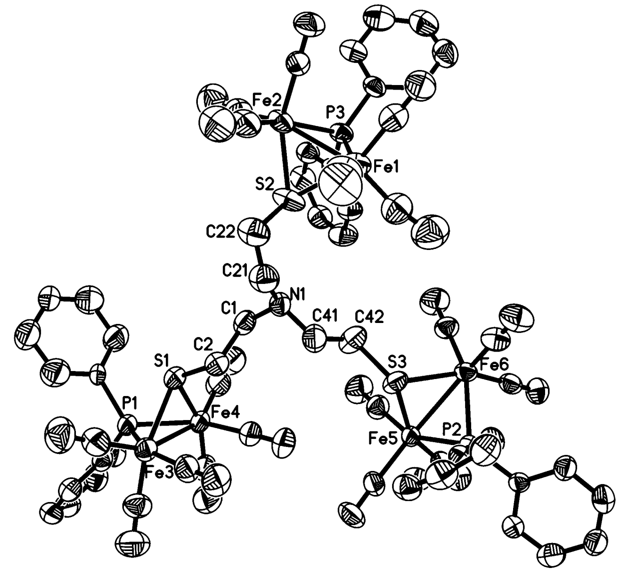

Figure 1. ORTEP drawing of **5** with atom-labeling scheme.

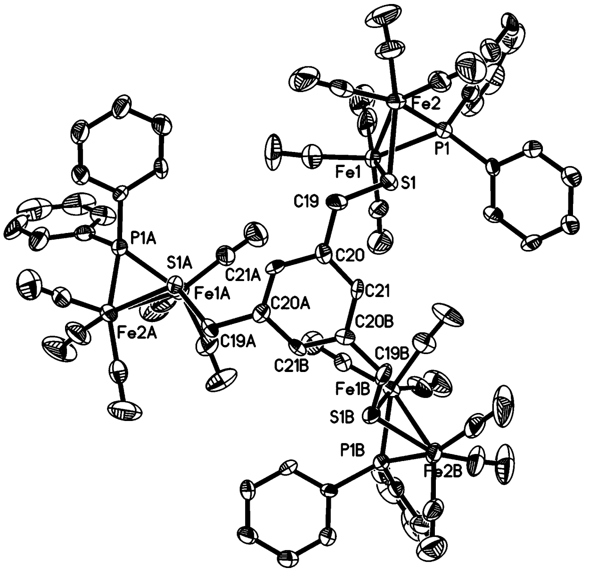

Figure 2. ORTEP drawing of **12** with atom-labeling scheme.

Preparation of $[(\mu\text{-PhC}{=}\text{NPh})\text{Fe}_2(\text{CO})_6]_3[(\mu\text{-SCH}_2\text{CH}_2)_3\text{N}]$ (7). The same procedure was followed as for **6**, but PhC(Cl)=NPh (0.54 g, 2.5 mmol) was employed in place of PhSBr. **7** (0.160 g, 20%) was obtained as a red solid, mp 64−66 °C. Anal. Calcd for $C_{63}H_{42}Fe_6N_4O_{18}S_3$: C, 48.07; H, 2.69; N, 3.56. Found: C, 48.23; H, 2.47; N, 3.64. IR (KBr disk): $\nu_{C\equiv O}$ 2085 (s), 2030 (s), 1972 (vs); $\nu_{C=N}$ 1557 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.76−2.79 (m, 6H, $3SCH_2$), 3.04−3.09 (m, 6H, $3NCH_2$), 6.51−7.24 (m, 30H, $6C_6H_5$) ppm.

Preparation of $[(\mu\text{-CH}_2{=}\text{CHCH}_2)\text{Fe}_2(\text{CO})_6]_3[(\mu\text{-SCH}_2\text{CH}_2)_3\text{N}]$ (8). The same procedure was followed as for **6**, but $CH_2{=}CHCH_2Br$ (0.27 mL, 3.0 mmol) was utilized. **8** (0.145 g, 25%) was obtained as a red solid, mp 48−51 °C. Anal. Calcd for $C_{33}H_{27}Fe_6NO_{18}S_3$: C, 34.26; H, 2.35; N, 1.21. Found: C, 34.28; H, 2.22; N, 1.20. IR (KBr disk): $\nu_{C\equiv O}$ 2062 (s), 2024 (vs), 1980 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): 0.47 (d, J = 12.4 Hz, 6H, 6 anti-FeC*H*H), 1.96 (d, J = 6.4 Hz, 6H, 6 syn-FeCH*H*), 2.47−2.51(m, 6H, $3SCH_2$), 2.62−2.67 (m, 6H, $3NCH_2$), 4.69−4.89 (m, 3H, 3CH) ppm.

Preparation of $[(\mu\text{-MeSC}{=}\text{S})\text{Fe}_2(\text{CO})_6]_3[(\mu\text{-SCH}_2\text{CH}_2)_3\text{N}]$ (9). To the above prepared solution of **4A**·$[Et_3NH]_3$ was added CS_2 (0.18 mL, 3.0 mmol). The mixture was stirred for 0.5 h and then MeI (0.18 mL, 3.0 mmol) was added. The mixture was stirred at room temperature for 12 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using acetone/petroleum ether (v/v = 1:4) as eluent to give **9** (0.204 g, 31%) as a red solid, mp 41−42 °C. Anal. Calcd for $C_{30}H_{21}Fe_6NO_{18}S_9$: C, 27.54; H, 1.61; N, 1.07. Found: C, 27.60; H, 1.71; N, 1.08. IR (KBr disk): $\nu_{C\equiv O}$ 2067 (s), 2027 (vs), 1993 (vs); $\nu_{C=S}$ 1018 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.53 (s, 9H, $3CH_3$), 2.65−2.72 (m, 6H, $3SCH_2$), 2.85−3.05 (m, 6H, $3NCH_2$) ppm.

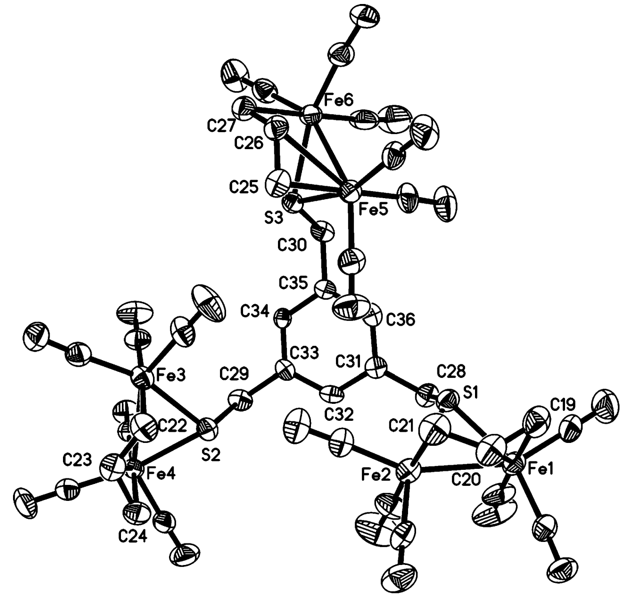

Figure 3. ORTEP drawing of **15** with atom-labeling scheme.

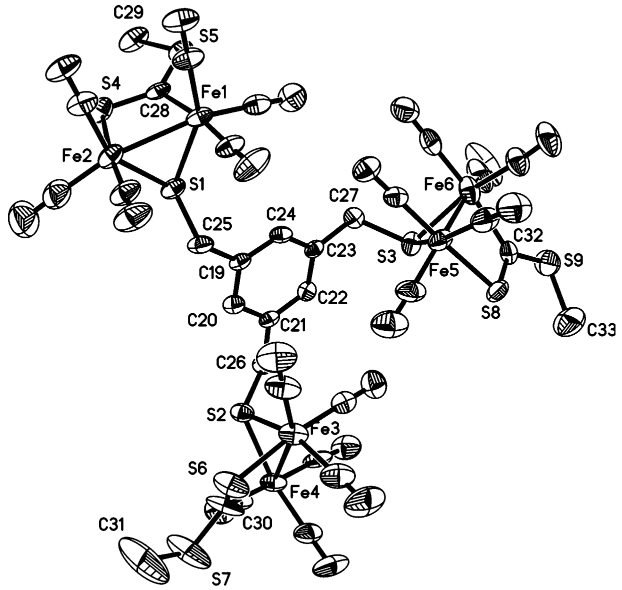

Figure 4. ORTEP drawing of **17** with atom-labeling scheme.

Preparation of $[(\mu\text{-PhCH}_2\text{SC}{=}\text{S})\text{Fe}_2(\text{CO})_6]_3[(\mu\text{-SCH}_2\text{CH}_2)_3\text{N}]$ (10). The same procedure was followed as for **9**, but $PhCH_2Br$ (0.36 mL, 3.0 mmol) and an eluent of acetone/petroleum ether (v/v = 1:2) were used. **10** (0.304 g, 40%) was obtained as a red solid, mp 59−61 °C. Anal. Calcd for $C_{48}H_{33}Fe_6NO_{18}S_9$: C, 37.55; H, 2.17; N, 0.91. Found: C,37.64; H, 2.11; N, 1.00. IR (KBr disk): $\nu_{C\equiv O}$ 2067 (s), 2028 (vs), 1993 (vs); $\nu_{C=S}$ 1016 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.71 (t, J = 8.0 Hz, 6H, $3SCH_2$), 2.95 (t, J = 8.0 Hz, 6H, $3NCH_2$), 4.28 (s, 6H, $3CH_2$), 7.18−7.30 (m, 15H, $3C_6H_5$) ppm.

Table 5. Crystal Data and Structural Refinements Details for 5, 12, 15, and 17

	5	12	15	17
mol formula	$C_{60}H_{42}Fe_6NO_{18}P_3S_3$	$C_{63}H_{39}Fe_6O_{18}P_3S_3 \cdot$ 1.5 CH_2Cl_2	$C_{72}H_{48}Fe_{12}O_{36}S_6$	$C_{33}H_{18}Fe_6O_{18}S_9 \cdot$ 0.25 CH_2Cl_2
mol wt	1589.14	1735.52	2351.66	1347.35
temp/K	298(2)	293(2)	293(2)	293(2)
cryst syst	orthorhombic	rhombohedral	triclinic	triclinic
space group	*Pna*2(1)	$R\bar{3}c$	$P\bar{1}$	$P\bar{1}$
a/Å	18.1190 (7)	28.598(5)	14.9871(19)	13.612(5)
b/Å	14.9011(6)	28.598(5)	16.828(2)	14.753(6)
c/Å	25.4867(10)	32.224(10)	20.682(4)	15.879(6)
α/deg	90	90	99.362(3)	64.381(7)
β/deg	90	90	104.027(3)	70.868(7)
γ/deg	90	120	110.708(2)	81.534(8)
V/Å^3	6881.2(5)	22823(9)	4552.8(12)	2716.4(18)
Z	4	12	2	2
D_c/g cm^{-3}	1.534	1.515	1.647	
abs coeff/mm^{-1}	1.458	1.428	2.069	1.991
F(000)	3208	10 476	1341	
limiting indices	$-23 \le h \le 22$ $-19 \le k \le 18$ $-18 \le l \le 32$	$-34 \le h \le 22$ $-23 \le k \le 34$ $-23 \le l \le 38$	$-17 \le h \le 17$ $-18 \le k \le 20$ $-22 \le l \le 24$	$-16 \le h \le 15$ $-11 \le k \le 7$ $-18 \le l \le 18$
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
no. of rflns	41 099	31 536	24 902	13 970
no. of indep rflns	11 033	4482	15 881	9525
$2\theta_{max}$/deg	54.00	50.00	50.06	50.00
R	0.0468	0.0800	0.0524	0.0811
R_w	0.0840	0.1795	0.1060	0.2065
gooodness of fit	1.000	0.953	1.017	1.015
largest diff peak and hole/e Å^{-3}	0.496/−0.369	0.958/−0.470	0.436/−0.432	1.145/−0.689

Preparation of [(μ-CH_2=$CHCH_2SC$=S)$Fe_2(CO)_6$]$_3$[(μ-SCH_2CH_2)$_3$N] (11). The same procedure was followed as for **9**, but CH_2=$CHCH_2Br$ (0.27 mL, 3.0 mmol) and an eluent of CH_2Cl_2/petroleum ether (v/v = 1:2) were utilized. **11** (0.185 g, 27%) was obtained as a red solid, mp 43−45 °C. Anal. Calcd for $C_{36}H_{27}Fe_6NO_{18}S_9$: C, 31.21; H, 1.96; N, 1.01. Found: C, 31.18; H, 2.00; N, 1.10. IR (KBr disk): $\nu_{C\equiv O}$ 2067 (s), 2028 (vs), 1994 (vs); $\nu_{C=S}$ 1017 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.69 (br s, 6H, $3SCH_2$), 2.92−2.96 (m, 6H, $3NCH_2$), 3.72 (d, *J* = 6.5 Hz, 6H, $3CSCH_2$), 5.18−5.27 (m, 6H, $3CH_2$=), 5.67−5.76 (m, 3H, 3CH) ppm.

Preparation of [(μ-Ph_2P)$Fe_2(CO)_6$]$_3$[1,3,5-(μ-SCH_2)$_3C_6H_3$] (12). The above prepared solution of **4B**$\cdot$[Et_3NH]$_3$ was cooled to −40 °C. To this cooled solution was added Ph_2PCl (0.26 mL, 1.5 mmol). The mixture was warmed to room temperature and then was stirred for 24 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 to give **12** (0.353 g, 44%) as a red solid, mp 106−108 °C. Anal. Calcd for $C_{63}H_{39}Fe_6O_{18}P_3S_3$: C, 47.05; H, 2.44. Found: C, 47.26; H, 2.48. IR (KBr disk): $\nu_{C\equiv O}$ 2059 (s), 2020 (vs), 1983 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): 3.84 (s, 6H, $3CH_2$), 6.52−7.51 (m, 33H, C_6H_3, $6C_6H_5$). ^{31}P NMR (121.48 MHz, $CDCl_3$, 85% H_3PO_4): 141.31 (s) ppm.

Preparation of [(μ-PhS)$Fe_2(CO)_6$]$_3$[1,3,5-(μ-SCH_2)$_3C_6H_3$] (13). To the above prepared solution of **4B**$\cdot$[Et_3NH]$_3$ was added PhSBr (0.567 g, 3.0 mmol). The mixture was stirred at room temperature for 24 h. After the same workup as for **12**, product **13** (0.330 g, 48%) was obtained as a red solid, mp 87−89 °C. Anal. Calcd for $C_{45}H_{24}Fe_6O_{18}S_9$: C, 39.16; H, 1.75. Found: C, 38.99; H, 1.95. IR (KBr disk): $\nu_{C\equiv O}$ 2073 (s), 2036 (vs), 1997 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): 3.51−3.62 (m, 6H, $3CH_2$), 6.92−7.42 (m, 18H, C_6H_3, $3C_6H_5$) ppm.

Preparation of [(μ-PhC=NPh)$Fe_2(CO)_6$]$_3$[1,3,5-(μ-SCH_2)$_3$-C_6H_3] (14). The same procedure was followed as for **13**, except that PhC(Cl)=NPh (0.641 g, 3.0 mmol) was used in place of PhSBr. **14** (0.338 g, 42%) was obtained as a red solid, mp 142−143 °C. Anal. Calcd for $C_{66}H_{39}Fe_6O_{18}N_3S_3$: C, 49.75; H, 2.47, N, 2.64. Found: C, 49.68; H, 2.46; N, 2.50. IR (KBr disk): $\nu_{C\equiv O}$ 2066 (s), 2027 (vs), 1987 (vs), $\nu_{C=N}$ 1557 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): 3.64 (s, 6H, $3CH_2$), 6.48−7.51 (m, 33H, C_6H_3, $6C_6H_5$) ppm.

Preparation of [(μ-CH_2=$CHCH_2$)$Fe_2(CO)_6$]$_3$[1,3,5-(μ-SCH_2)$_3C_6H_3$] (15). The same procedure was followed as for **13**, except that CH_2=$CHCH_2Br$ (0.27 mL, 3.0 mmol) was used. **15** (0.224 g, 38%) was obtained as a red solid, mp 64−65 °C. Anal. Calcd for $C_{36}H_{24}Fe_6O_{18}S_3$: C, 36.80; H, 2.06. Found: C, 36.68; H, 2.03. IR (KBr disk): $\nu_{C\equiv O}$ 2043 (vs), 1989 (vs), 1955 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): 0.47(d, *J* = 12.8 Hz, 6H, 6 anti-FeC*H*H), 1.96 (d, *J* = 6.4 Hz, 6H, 6 syn-FeCH*H*), 3.58 (s, 6H, $3CH_2$), 4.72−4.84 (m, 3H, 3CH), 7.08 (s, 3H, C_6H_3) ppm.

Preparation of [(μ-PhNHC=S)$Fe_2(CO)_6$]$_3$[1,3,5-(μ-SCH_2)$_3$-C_6H_3] (16). The same procedure was followed as for **13**, but PhNCS (0.36 mL, 3.0 mmol) was employed. **16** (0.330 g, 45%) was obtained as a red solid, mp 110−112 °C. Anal. Calcd for $C_{48}H_{27}Fe_6O_{18}N_3S_6$: C, 39.46; H, 1.86; N, 2.29. Found: C, 39.48; H, 1.88; N, 2.27. IR (KBr disk): $\nu_{C\equiv O}$ 2066 (s), 2026 (vs), 1988 (vs); $\nu_{C=S}$ 1026 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): 3.74−3.94 (m, 6H, $3CH_2$), 7.26−7.46 (m, 18H, C_6H_3, $3C_6H_5$), 8.67 (s, 3H, 3NH) ppm.

Preparation of [(μ-MeSC=S)$Fe_2(CO)_6$]$_3$[1,3,5-(μ-SCH_2)$_3$-C_6H_3] (17). The above prepared solution of **4B**$\cdot$[Et_3NH]$_3$ was cooled to −40 °C. To this cooled solution was added CS_2 (0.18 mL, 3.0 mmol). The mixture was stirred at this temperature for 1 h, and then MeI (0.19 mL, 3.0 mmol) was added. The mixture was warmed to room temperature and then was stirred for 24 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 to give **17** (0.297 g, 45%) as a red solid, mp 56−58 °C. Anal. Calcd for $C_{33}H_{18}Fe_6O_{18}S_9$: C, 29.89; H, 1.37. Found: C, 30.07; H, 1.40. IR (KBr disk): $\nu_{C\equiv O}$ 2066 (s), 2028 (vs), 1993 (vs); $\nu_{C=S}$ 1017 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): 2.53 (s, 9H, $3CH_3$), 3.77(s, 6H, $3CH_2$), 7.20−7.40 (m, 3H, C_6H_3) ppm.

Preparation of [(μ-$PhCH_2SC$=S)$Fe_2(CO)_6$]$_3$[1,3,5-(μ-SCH_2)$_3C_6H_3$] (18). The same procedure was followed as for **17**, but $PhCH_2Br$ (0.36 mL, 3.0 mmol) was used instead of MeI to give **18** (0.271 g, 35%) as a red solid, mp 60−62 °C. Anal. Calcd for $C_{51}H_{30}Fe_6O_{18}S_9$: C, 39.41; H, 1.95. Found: C, 39.68; H, 1.70. IR (KBr disk): $\nu_{C\equiv O}$ 2066 (s), 2028 (vs), 1993 (vs); $\nu_{C=S}$ 1016 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): 3.78 (s, 6H, $3SCH_2$), 4.26 (s, 6H, $3CH_2Ph$), 7.12−7.45 (m, 18H, C_6H_3, $3C_6H_5$) ppm.

Preparation of [(μ-CH$_2$=CHCH$_2$SC=S)Fe$_2$(CO)$_6$]$_3$[1,3,5-(μ-SCH$_2$)$_3$C$_6$H$_3$] (19). The same procedure was followed as for **17**, except that CH$_2$=CHCH$_2$Br (0.27 mL, 3.0 mmol) was used instead of MeI. **19** (0.350 g, 50%) was obtained as a red solid, mp 65−67 °C. Anal. Calcd for $C_{39}H_{24}Fe_6O_{18}S_9$: C, 33.36; H, 1.72. Found: C, 33.72; H, 1.75. IR (KBr disk): $\nu_{C\equiv O}$ 2067 (s), 2029 (vs), 1994 (vs); $\nu_{C=S}$ 1016 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): 3.70−3.76 (m, 12H, 6SCH$_2$), 5.16−5.26 (m, 6H, 3CH$_2$=), 5.60−5.80 (m, 3H, 3CH=), 7.34 (s, 3H, C$_6$H$_3$) ppm.

X-ray Structure Determinations of 5, 12, 15, and 17. While single crystals of **12**, **15**, and **17** suitable for X-ray diffraction analysis were grown by slow evaporation of their CH$_2$Cl$_2$/hexane solutions at 4 °C, the X-ray quality crystals of **5** were produced by slow evaporation of its Et$_3$N/MeOH solution at 4 °C. Each crystal was mounted on a Bruker SMART 1000 automated diffractometer with a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and expanded by Fourier techniques. The final refinements were accomplished by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms. The calculations were performed using the SHELXTL-97 program. Details of the crystal data, data collections, and structure refinements are summarized in Table 5.

Acknowledgment. We are grateful to the National Natural Science Foundation of China, the State Key Laboratory of Organometallic Chemistry, and the Specialized Research Fund for the Doctoral Program of Higher Education of China for financial support of this work.

Supporting Information Available: Full tables of crystal data, atomic coordinates and thermal parameters, and bond lengths and angles for **5**, **12**, **15**, and **17** as CIF files. This material is available free of charge via the Internet at http://pubs. acs.org.

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