Communications

Reactions of the Three-μ-CO-Containing Trianions $\{[Fe_2(\mu\text{-}CO)(CO)_6]_3[(\mu\text{-}SCH_2CH_2)_3N]\}^{3-}$ and $\{[Fe_2(\mu\text{-}CO)(CO)_6]_3[1,3,5\text{-}(\mu\text{-}SCH_2)_3C_6H_3]\}^{3-}$ To Give Starlike Complexes Terminated with Butterfly Fe/S Cluster Cores

Li-Cheng Song,* Jia Cheng, Qing-Mei Hu, Feng-Hua Gong, Hong-Zhu Bian, and Liang-Xing Wang

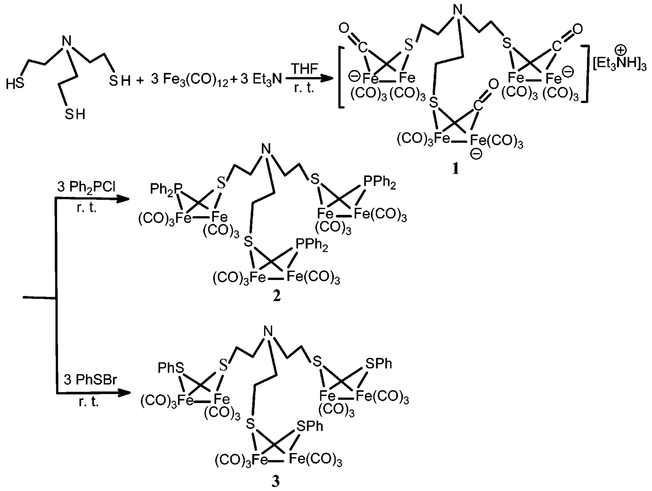
Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China

Received December 8, 2004

Summary: Five starlike complexes with terminal butterfly Fe/S cluster cores, $[Fe_2(\mu\text{-}Ph_2P)(CO)_6]_3[(\mu\text{-}SCH_2CH_2)_3N]$ *(**2**),* $[Fe_2(\mu\text{-}PhS)(CO)_6]_3[(\mu\text{-}SCH_2CH_2)_3N]$ *(**3**),* $[Fe_2(\mu\text{-}PhC{=}NPh)(CO)_6)]_3[1,3,5\text{-}(\mu\text{-}SCH_2)_3C_6H_3]$ *(**5**), and* $[Fe_2(\mu\text{-}RSC{=}S)(CO)_6]_3[1,3,5\text{-}(\mu\text{-}SCH_2)_3\ C_6H_3]$ *(**7**, R = Me; **8**, R = PhCH₂), were prepared by a "one pot" reaction of the trithiol* $N(CH_2CH_2SH)_3$ *or* $1,3,5\text{-}(HSCH_2)_3\text{-}C_6H_3$ *with* $Fe_3(CO)_{12}$ *and* Et_3N*, followed by treatment of the intermediate three-μ-CO-containing trianions* $\{[Fe_2(\mu\text{-}CO)(CO)_6]_3[(\mu\text{-}SCH_2CH_2)_3N]\}^{3-}$ *(**1**) and* $\{[Fe_2(\mu\text{-}CO)(CO)_6]_3[1,3,5\text{-}(\mu\text{-}SCH_2)_3C_6H_3]\}^{3-}$ *(**4**) with* Ph_2PCl*,* $PhSBr$*,* $PhC(Cl){=}NPh$*,* CS_2/MeI*, and* $CS_2/PhCH_2Br$*, respectively. These products have been fully characterized by elemental analysis, spectroscopy, and X-ray crystallography.*

Transition-metal complexes containing butterfly Fe/S cluster cores have recently attracted increasing attention, in view of the novelty and diversity of structures and reactivities of such complexes[1] and, particularly, the application in bionics as models for the active site of the iron-only hydrogenases.[2−5] Previously, we reported the type of double-butterfly Fe/S cluster dianion $\{[Fe_2(\mu\text{-}CO)(CO)_6]_2(\mu\text{-}SZS\text{-}\mu)\}^{2-}$, a dianion that has two μ-CO ligands capable of reaction with electrophiles to give a series of linear and macrocyclic butterfly Fe/S cluster complexes.[6] Now, as a new development, we report two novel triple-butterfly Fe/S cluster trianions, a type of trianion that has three μ-CO ligands, their formation and reactions leading to five starlike complexes terminated with butterfly Fe/S cluster cores (Schemes 1 and 2).[7,8]

Scheme 1



As shown in Scheme 1, reaction of the nitrogen-containing trithiol $N(CH_2CH_2SH)_3$[9] with $Fe_3(CO)_{12}$ and Et_3N in a 1:3:3 molar ratio at room temperature resulted in formation of the $[Et_3NH]^+$ salt of the three-μ-CO-containing trianion $\{[Fe_2(\mu\text{-}CO)(CO)_6]_3[(\mu\text{-}SCH_2CH_2)_3\text{-}N]\}^{3-}$ (**1**). Further treatment of **1** in situ with excess Ph_2PCl, through triple nucleophilic attack of the three negatively charged Fe atoms in **1** at the P atoms in three Ph_2PCl groups followed by displacement of the three μ-CO ligands in **1**, gave rise to the starlike product $[Fe_2(\mu\text{-}Ph_2P)(CO)_6]_3[(\mu\text{-}SCH_2CH_2)_3N]$ (**2**) in 32% yield. When trianion **1** was treated with PhSBr, another starlike complex **3** was produced in 33% yield via similar nucleophilic attack of the three negatively charged Fe atoms at three molecules of PhSBr followed by displacement of the three μ-CO ligands.[7]

---

* To whom correspondence should be addressed. Fax: 0086-22-23504853. E-mail: lcsong@nankai.edu.cn.

(1) For reviews, see for example: (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) Li, H.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2002**, *124*, 726. (b) Gloaguen, F.; Lawrence, J. D.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2001**, *123*, 9476. (c) Gloaguen, F.; Lawrence, J. D.; Schmidt, M.; Wilson, S. R.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2001**, *123*, 12518.

(3) (a) Lyon, E. J.; Georgakaki, I. P.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2001**, *123*, 3268. (b) Darensbourg, M. Y.; Lyon, E. J.; Zhao, X.; Georgakaki, I. P. *PNAS* **2003**, *100*, 3683.

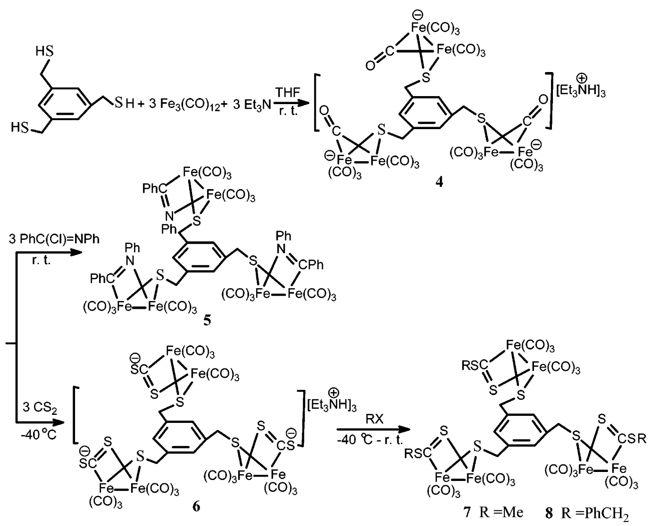
(4) Ott, S.; Kritikos, M.; Åkermark, B.; Sun, L. *Angew. Chem., Int. Ed.* **2003**, *42*, 3285.

(5) Song, L.-C.; Yang, Z.-Y.; Bian, H.-Z.; Hu, Q.-M. *Organometallics* **2004**, *23*, 3082.

(6) (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.

10.1021/om0490280 CCC: $30.25

Scheme 2



Similarly, Scheme 2 indicates that reaction of the benzene-ring-containing trithiol 1,3,5-$(HSCH_2)_3C_6H_3$[10] with $Fe_3(CO)_{12}$ and Et_3N in a 1:3:3 molar ratio afforded the $[Et_3NH]^+$ salt of another three-μ-CO-containing trianion, $\{[Fe_2(\mu\text{-}CO)(CO)_6]_3[1,3,5\text{-}(\mu\text{-}SCH_2)_3C_6H_3]\}^{3-}$ (**4**). Further treatment of **4** with excess PhC(Cl)=NPh in situ gave the corresponding starlike product $[Fe_2(\mu\text{-}PhC{=}NPh)(CO)_6]_3[1,3,5\text{-}(\mu\text{-}SCH_2)_3C_6H_3]$ (**5**) in 42% yield. However, when trianion **4** was treated with excess CS_2, the S-centered trianion $\{[Fe_2(\mu\text{-}CS_2)(CO)_6]_3\ [1,3,5\text{-}(\mu\text{-}SCH_2)_3C_6H_3]\}^{3-}$ (**6**) was formed via triple nucleophilic attack of the negatively charged Fe atoms in **4** at the C atoms in three CS_2 groups, followed by loss of the three μ-CO ligands. Further treatment of **6** with excess MeI or $PhCH_2Br$ yielded the final starlike products $[Fe_2(\mu\text{-}RSC{=}S)(CO)_6]_3[1,3,5\text{-}(\mu\text{-}SCH_2)_3C_6H_3]\}$ (**7**, R = Me; **8**, R = $PhCH_2$) in 45% and 35% yields, respectively.[8]

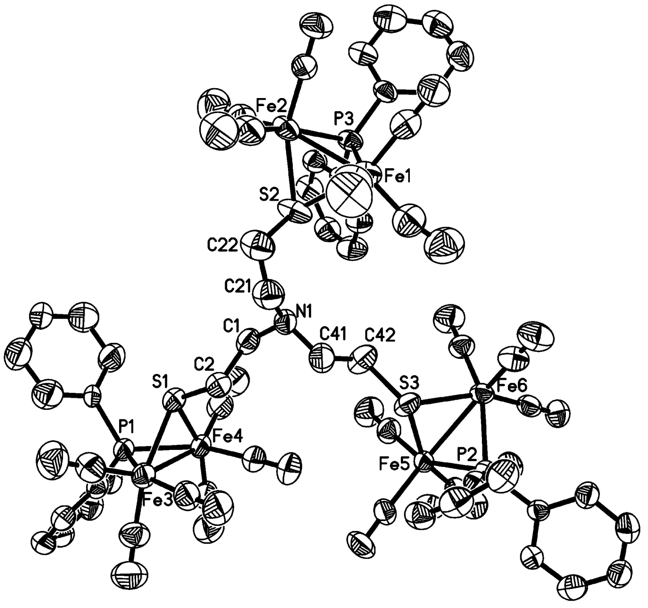


Figure 1. Structure of **2** with ellipsoids drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) = 2.5550(19), Fe(1)−S(2) = 2.268(3), Fe(2)−S(2) = 2.262(2), Fe(1)−P(3) = 2.216(2), Fe(2)−P(3) = 2.225(2), N(1)−C(1) = 1.435(8), N(1)−C(21) = 1.425(10); S(2)−Fe(1)−Fe(2) = 55.54(7), S(2)−Fe(2)−Fe(1) = 55.78(8), P(3)−Fe(2)−Fe(1) = 54.73(7), P(3)−Fe(2)−S(2) = 76.32(8), P(3)−Fe(1)−Fe(2) = 55.03(6), C(1)−N−C(21) = 116.4(7).

It is worthy of note that the $[Et_3NH]^+$ salts of the intermediate μ-CO-containing trianions **1** and **4** could not be isolated, since they are very air-sensitive and extremely labile during separation and purification. However, the presence of these two trianions might be recognized by their in situ IR spectra, which showed an absorption band at 1742 and 1716 cm^{-1} typical of the diiron-bridged μ-CO ligands.[3,11] In addition, the well-studied chemistry of the one-μ-CO-containing monoanions[12] and two-μ-CO-containing dianions[3] and, particularly, the fully characterized products **2**, **3**, **5**, **7**, and **8** by spectroscopy[7,8] and X-ray crystallography[13] strongly support the formation of trianions **1** and **4**.

The crystal molecular structures of **2** and **7** are presented in Figures 1 and 2, respectively. As can be seen in Figure 1, complex **2** contains three identical Fe_2SP butterfly cluster cores, in which each of the P atoms is attached to two phenyl groups and each of the

---

(7) **2**: a mixture of $Fe_3(CO)_{12}$ (0.75 g, 1.5 mmol), THF (20 mL), $N(CH_2CH_2SH)_3$ (0.065 mL, 0.5 mmol), and Et_3N (0.21 mL, 1.5 mmol) was stirred at room temperature for 1 h to give a brown-red solution containing the $[Et_3NH]^+$ salt of trianion **1**. To the solution was added Ph_2PCl (0.36 mL, 2.0 mmol), and the mixture was stirred at room temperature for 24 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using acetone/petroleum ether as eluent. From the main red band **2** was obtained as a red solid. Yield: 0.255 g (32%). Mp: 78−80 °C. IR (KBr disk): $\nu_{C\equiv O}$ 2059 (s), 2020 (vs), 1982 (vs) cm^{-1}. ^1H 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. **3**: to a solution of trianion **1** was added PhSBr (0.375 g, 2.0 mmol). The same workup as described above gave **3** as a red solid. Yield: 0.222 g (33%). Mp 54−56 °C. IR (KBr disk): $\nu_{C\equiv O}$ 2073 (s), 2036 (vs), 1995 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): 2.28−2.82 (m, 12H, $3SCH_2$, $3NCH_2$), 7.10−7.48 (m, 15H, $3C_6H_5$) ppm.

(8) **5**: a mixture of $Fe_3(CO)_{12}$ (0.75 g, 1.5 mmol), THF (20 mL), 1,3,5-$(HSCH_2)_3C_6H_3$ (0.114 mL, 0.5 mmol), and Et_3N (0.21 mL, 1.5 mmol) was stirred at room temperature for 1 h to give a brown-red solution containing the $[Et_3NH]^+$ salt of trianion **4**. To the solution was added PhC(Cl)=NPh (0.641 g, 3 mmol), and the mixture was stirred at room temperature for 24 h. Solvent was removed under reduced pressure. The residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (1/2 v/v) as eluent. From the main red band **5** was obtained as a red solid. Yield: 0.338 g (42%). Mp: 142−143 °C. IR (KBr disk): $\nu_{C\equiv O}$ 2066 (s), 2027 (vs), 1987 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): 3.64 (s, 6H, $3SCH_2$), 6.48−7.51 (m, 33H, C_6H_3, $6C_6H_5$) ppm. **7**: the solution containing the $[Et_3NH]^+$ salt of trianion **4** prepared above was cooled to −40 °C. To this solution was added CS_2 (0.18 mL, 3.0 mmol). After the mixture was stirred at this temperature for 1 h, MeI (0.19 mL, 3 mmol) was then added. The new mixture was stirred at room temperature for 24 h. Using the same workup as described above, **7** was obtained as a red solid. Yield: 0.297 g (45%). Mp: 56−58 °C. IR (KBr disk): $\nu_{C\equiv O}$ 2066 (s), 2028 (vs), 1993 (vs); $\nu_{C{=}S}$ 1017 (s) cm^{-1}. ^1H NMR ($CDCl_3$): 2.53 (s, 9H, $3CH_3$), 3.77 (s, 6H, $3SCH_2$), 7.20−7.40 (m, 3H, C_6H_3) ppm. **8**: similarly, when $PhCH_2Br$ (0.36 mL, 3.0 mmol) was used instead of MeI, **8** was obtained as a red solid. Yield: 0.271 g (35%). Mp: 60−62 °C. IR (KBr disk): $\nu_{C\equiv O}$ 2066 (s), 2028 (vs), 1993 (vs); $\nu_{C{=}S}$ 1016 (s) cm^{-1}. ^1H NMR ($CDCl_3$): 3.78 (s, 6H, $3SCH_2$), 4.26 (s, 6H, $3SCH_2Ph$), 7.12−7.45 (m, 18 H, C_6H_3, $3C_6H_5$) ppm.

(9) Harley-Mason, J. *J. Chem. Soc.* **1947**, 320.

(10) Houk, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1987**, *109*, 6825.

(11) Seyferth, D.; Womack, G. B.; Dewan, J. C. *Organometallics* **1985**, *4*, 398.

(12) (a) Seyferth, D.; Womack, G. B.; Archer, C. M.; Dewan, J. C. *Organometallics* **1989**, *8*, 430. (b) Seyferth, D.; Hoke, J. B.; Womack, G. B. *Organometallics* **1990**, *9*, 2662. (c) Song, L.-C.; Lu, G.-L.; Hu, Q.-M.; Sun, J. *Organometallics* **1999**, *18*, 2700. (d) Song, L.-C.; Lu, G.-L.; Hu, Q.-M.; Fan, H.-T.; Chen, Y.; Sun, J. *Organometallics* **1999**, *18*, 3258.

(13) X-ray crystal data are as follows. **2**: $C_{60}H_{42}Fe_6NO_{18}P_3S_3$, orthorhombic, $Pna2_1$, $a = 18.1190(7)$ Å, $b = 14.9011(6)$ Å, $c = 25.4867(10)$ Å, $\alpha = \beta = \gamma = 90$ °, $F(000) = 3208$, $V = 6881.2(5)$ Å^3, $D_c = 1.534$ g cm^{-3}, μ(Mo Kα) = 1.458 mm^{-1}, $R = 0.0468$, $R_w = 0.0840$, GOF = 1.000. **7**:$C_{33}H_{18}Fe_6O_{18}S_9\cdot 0.25CH_2Cl_2$, triclinic, $P\bar{1}$, $a = 13.612(5)$ Å, $b = 14.753(6)$ Å, $c = 15.879(6)$ Å, $\alpha = 64.381(7)$ °, $\beta = 70.868(7)$°, $\gamma = 81.534(8)$°, $F(000) = 1341$, $V = 2716.4(18)$ Å^3, $D_c = 1.647$ g cm^{-3}, μ(Mo Kα) = 1.991 mm^{-1}, $R = 0.0811$, $R_w = 0.2065$, GOF = 1.015.

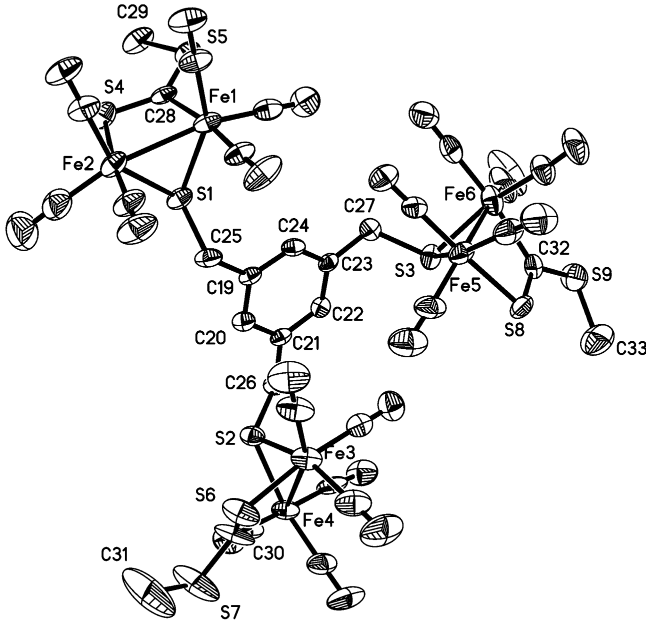


Figure 2. Structure of **7** with ellipsoids drawn at 30% probability. Selected bond lengths (Å) and angles (deg): Fe(1)−Fe(2) = 2.618(2), Fe(1)−S(1) = 2.265(3), Fe(2)−S(4) = 2.276(3), Fe(1)−C(28) = 1.988(10), Fe(2)−S(1) = 2.253(3), S(1)−C(25) = 1.826(9); S(1)−Fe(1)−Fe(2) = 54.36(8), S(1)−Fe(2)−S(4) = 82.41(12), Fe(2)−S(1)−Fe(1) = 70.83(9), S(1)−Fe(2)−Fe(1) = 54.80(8), C(28)−Fe(1)−S(1) = 81.4(4), S(4)−Fe(2)−Fe(1) = 77.89(10).

Fe atoms is attached to three terminal CO ligands. Therefore, this is consistent with their ^{31}P NMR and IR spectra, which displayed respectively one singlet at 142.45 ppm and several absorption bands at ca. 2000 cm^{-1}. Also, it can be seen that the three butterfly Fe_2SP cluster cores in **2** are connected through their S atoms to three β-C atoms of the triethyleneamine structural unit by three equatorial bonds. In fact, this is necessary to avoid the strong axial−axial repulsions between the axially bonded bulky phenyl groups at P atoms and the central part of this complex.[14]

Figure 2 shows that **7** has another three identical butterfly Fe_2S_2C cluster cores, in which the C atom is bound to the methylthio group and each of the Fe atoms is bonded to three terminal carbonyls, consistent with its ^{1}H NMR and IR spectra displaying one singlet at 2.53 ppm and several absorption bands at ca. 2000 cm^{-1}. It is noteworthy that the C═S double bonds in the butterfly Fe_2S_2C cluster cores of **7**, for example, the double bond C(28)═S(4), is extended to 1.654(12) Å due to its coordination in comparison with the C═S double bond in free CS_2 (1.554 Å),[15] but it is still shorter than its single bonds C(28)−S(5) (1.695(10) Å), S(5)−C(29), (1.818(11) Å) and S(1)−C(25) (1.826(9) Å). The double bond C(28)═S(4) is bridged to Fe(1) via a σ bond (Fe(1)−C(28) = 1.988(10) Å) and to Fe(2) via the donation of an unshared electron pair from S(4) (Fe(2)−S(4) = 2.276(3) Å). In fact, such a coordination mode of the C═S double bonds in **7** has been found in other μ-CS_2 complexes.[6,16] In addition, as can be seen in Figure 2, the three identical cluster cores in **7** are joined together by connecting their S atoms with three benzylic C atoms of the planar trimethylene benzene ring structural moiety also via three equatorial bonds.[14]

In summary, we have synthesized and structurally characterized five starlike complexes, namely **2**, **3**, **5**, **7**, and **8**, each containing three terminal butterfly Fe_2S_2 or Fe_2S_2C cluster cores radiating from a pyramidal N atom or a planar benzene ring. The “one pot” reactions for synthesizing such starlike complexes involve two new intermediates of the three-μ-CO-containing trianions **1** and **4** that were generated from $Fe_3(CO)_{12}$, Et_3N, and the trithiol $N(CH_2CH_2SH)_3$ or 1,3,5-$(HSCH_2)_3C_6H_3$. In view of the easy availability of trianions **1** and **4**, as well as their high nucleophilicity, they could become an important class of building blocks in transition-metal chemistry. Investigations to make new trianions by using other trithiols and to synthesize new starlike complexes terminated with other Fe/S cluster cores are underway in this laboratory.

Acknowledgment. We are grateful to the National Natural Science Foundation of China and the State Key Laboratory of Organometallic Chemistry for financial support of this work.

Supporting Information Available: X-ray crystallographic files for **2** and **7** in CIF format and text giving details of the synthesis and characterization of **2**, **3**, **5**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0490280

---

(14) (a) Shaver, A.; Fitzpatrick, P. J.; Steliou, K.; Butler, I. S. *J. Am. Chem. Soc.* **1979**, *101*, 1313. (b) Seyferth, D.; Henderson, R. S.; Song, L.-C. *Organometallics* **1982**, *1*, 125.

(15) Butler, I. S.; Fenster, A. E. *J. Organomet. Chem.* **1974**, *66*, 161.

(16) Patin, H.; Mignani, G.; Mahé, C.; Le Marouille, J.-Y.; Southern, T. G.; Benoit, A. *J. Organomet. Chem.* **1980**, *197*, 315.