

Synthesis of $[(\mu\text{-RS})\text{Fe}_2(\text{CO})_6](\mu_4\text{-S})[(\mu\text{-R}'\text{S})\text{Fe}_2(\text{CO})_6]$ and $[(\mu\text{-t-BuS})\text{Fe}_2(\text{CO})_6](\mu_4\text{-Se})[(\mu\text{-PhSe})\text{Fe}_2(\text{CO})_6]$ via Reactions of $(\mu\text{-RS})(\mu\text{-p-MeC}_6\text{H}_4\text{SO}_2\text{S})\text{Fe}_2(\text{CO})_6$ with Nucleophiles. Crystal Structure of $[(\mu\text{-t-BuS})\text{Fe}_2(\text{CO})_6](\mu_4\text{-S})[(\mu\text{-PhC}\equiv\text{CS})\text{Fe}_2(\text{CO})_6]$

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Summary: A new synthetic route to $\mu_4\text{-E}$ ($E = \text{S}, \text{Se}$) twin clusters has been discovered, which involves reactions of $(\mu\text{-RS})(\mu\text{-p-MeC}_6\text{H}_4\text{SO}_2\text{S})\text{Fe}_2(\text{CO})_6$ with nucleophiles $(\mu\text{-R}'\text{S})(\mu\text{-XMgS})\text{Fe}_2(\text{CO})_6$ and $(\mu\text{-PhSe})(\mu\text{-BrMgSe})\text{Fe}_2(\text{CO})_6$ to give the twin clusters $[(\mu\text{-RS})\text{Fe}_2(\text{CO})_6](\mu_4\text{-S})[(\mu\text{-R}'\text{S})\text{Fe}_2(\text{CO})_6]$ (**5a**, $R = R' = \text{Et}$; **5b**, $R = \text{Et}$, $R' = \text{PhC}_2$; **5c**, $R = \text{t-Bu}$, $R' = \text{Me}$; **5d**, $R = \text{t-Bu}$, $R' = \text{Ph}$) and $[(\mu\text{-t-BuS})\text{Fe}_2(\text{CO})_6](\mu_4\text{-Se})[(\mu\text{-PhSe})\text{Fe}_2(\text{CO})_6]$ (**6**) characterized by combustion analysis, spectroscopy, and (for **5b**) X-ray diffraction techniques.

Introduction

In a previous paper,¹ we reported that the $[\text{Et}_3\text{NH}]^+$ salts of sulfur-centered anions $[(\mu\text{-RS})(\mu\text{-S}^-)\text{Fe}_2(\text{CO})_6]$ (**1**) reacted with *p*-toluenesulfonyl chloride to give the expected $(\mu\text{-RS})(\mu\text{-p-MeC}_6\text{H}_4\text{SO}_2\text{S})\text{Fe}_2(\text{CO})_6$ (**2**) and unexpected symmetrical $\mu_4\text{-S}$ twin clusters $[(\mu\text{-RS})\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ (**3**). In that paper, we also suggested that the unexpected compounds **3** were possibly produced through nucleophilic attack of the negatively charged sulfur atom of **1** at one of the iron atoms of **2**, followed by coordination of the sulfur atom to another iron atom of **2** and concomitant loss of the ligand $\text{SSO}_2\text{C}_6\text{H}_4\text{Me-p}$, as shown in Scheme 1.

To justify the suggested mechanism for formation of **3** and to develop a new synthetic method for corresponding $\mu_4\text{-E}$ ($E = \text{S}, \text{Se}$) twin clusters, we recently studied the reaction of **2** with nucleophiles $[(\mu\text{-R}'\text{S})(\mu\text{-S}^-)\text{Fe}_2(\text{CO})_6][\text{MgX}]^+$ and $[(\mu\text{-PhSe})(\mu\text{-Se}^-)\text{Fe}_2(\text{CO})_6][\text{Mg-Br}]^+$. Herein we report our results.

Results and Discussion

At the beginning of this study, we thought that if the suggested mechanism for formation of **3** in the reaction shown in Scheme 1 was correct, the reaction of **2** with $[\text{MgX}]^+$ salts of the sulfur-centered anions $[(\mu\text{-R}'\text{S})(\mu\text{-S}^-)\text{Fe}_2(\text{CO})_6][\text{MgX}]^+$ (**4**) would give symmetrical ($R = R'$) and asymmetrical ($R \neq R'$) $\mu_4\text{-S}$ twin clusters $[(\mu\text{-RS})\text{Fe}_2(\text{CO})_6](\mu_4\text{-S})[(\mu\text{-R}'\text{S})\text{Fe}_2(\text{CO})_6]$ (**5**). Now, this mech-

anism seems to be correct since our experiments showed that an equimolar amount of **2** reacted with **4** (prepared from $\mu\text{-S}_2\text{Fe}_2(\text{CO})_6$ and Grignard reagents $\text{R}'\text{MgX}$)^{2,3} in THF from -78°C to room temperature to afford clusters **5**, as shown in Scheme 2.

It is worth pointing out that the reaction of **2** with **4** shown in Scheme 2 provides another new synthetic method for production of symmetrical and asymmetrical $\mu_4\text{-S}$ twin clusters.^{1,3,4} In view of the nucleophilic similarity of the bridged sulfur-centered anions such as in salts **4** with their selenium analogues, it might be expected that reaction of **2** with bridged selenium-centered anions would produce corresponding $\mu_4\text{-Se}$ twin clusters.^{1,5} This has been proved to be true by our experiment, that is, the reaction of **2** ($R = \text{t-Bu}$) with the $[\text{MgBr}]^+$ salt of the bridged selenium-centered anion $[(\mu\text{-PhSe})(\mu\text{-Se}^-)\text{Fe}_2(\text{CO})_6]$ (prepared from $\mu\text{-Se}_2\text{Fe}_2(\text{CO})_6$ and PhMgBr)¹ in THF, from -78°C to room temperature to afford the $\mu_4\text{-Se}$ twin cluster $[(\mu\text{-t-BuS})\text{Fe}_2(\text{CO})_6](\mu_4\text{-Se})[(\mu\text{-PhSe})\text{Fe}_2(\text{CO})_6]$ (**6**), as shown in Scheme 3.

Interestingly, although some methods are known for preparation of $\mu_4\text{-Se}$ twin clusters,^{1,5} there has been no method reported so far for making a type of $\mu_4\text{-Se}$ clusters that contain two different bridging ligands, such as $\mu\text{-t-BuS}$ and $\mu\text{-PhSe}$ in cluster **6**.

All products shown in Schemes 2 and 3, except **5a**,³ are new and have been characterized by elemental analysis and spectroscopic methods. For example, for twin clusters **5b–d** and **6**, the IR spectra show three to four absorption bands in the range $2082\text{--}1983\text{ cm}^{-1}$ for their terminal carbonyls attached to iron atoms, in addition to the IR spectrum of **5b**, showing a weak absorption band at 2172 cm^{-1} for its $\text{C}\equiv\text{C}$ triple bond. It is well-known that twin clusters **5b–d** and **6** could exist, on the basis of the steric repulsion grounds, as only one isomer in which the two substituents are bonded to the bridged S and Se atoms with an equatorial

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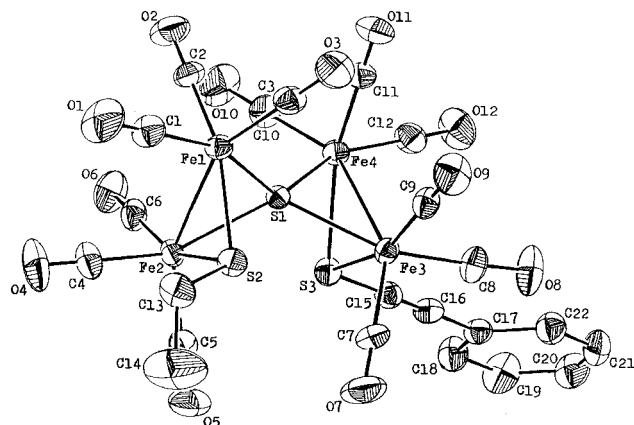
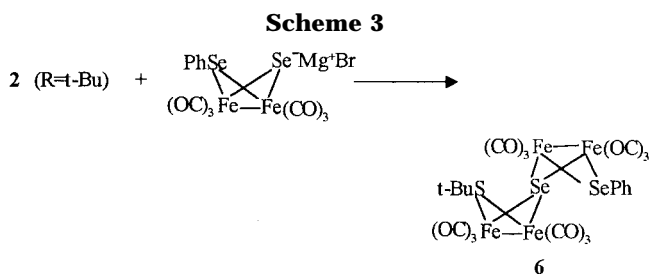
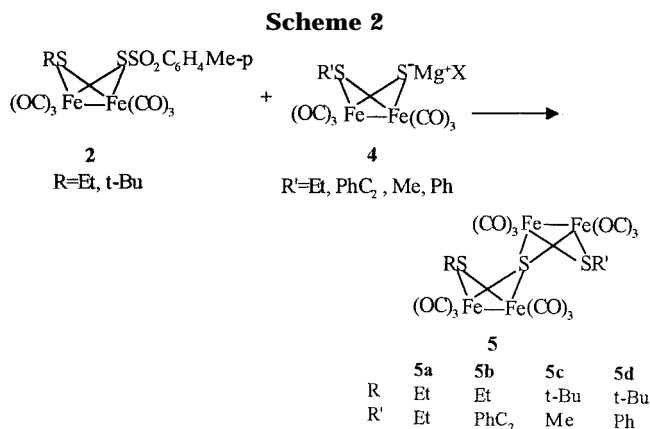
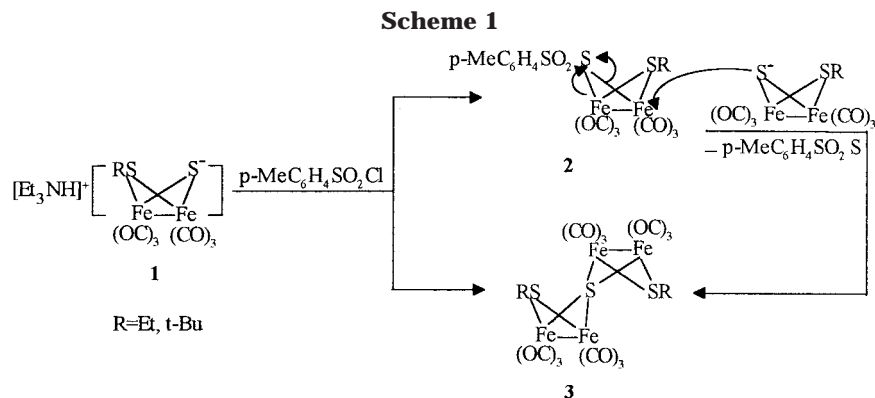
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**Figure 1.****Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 5b**

| | | | |
|------------------|-----------|------------------|-----------|
| Fe(1)–S(1) | 2.231(2) | Fe(1)–S(2) | 2.252(2) |
| Fe(1)–Fe(2) | 2.534(2) | Fe(2)–S(1) | 2.240(2) |
| Fe(3)–S(1) | 2.241(2) | Fe(3)–S(3) | 2.282(1) |
| Fe(3)–Fe(4) | 2.538(2) | Fe(4)–S(1) | 2.226(2) |
| Fe(4)–S(3) | 2.277(2) | C(15)–C(16) | 1.83(6) |
| S(3)–C(15) | 1.690(5) | C(16)–C(17) | 1.440(6) |
| S(2)–C(13) | 1.828(5) | C(17)–C(18) | 1.372(7) |
| O(1)–C(1) | 1.137(6) | O(3)–C(3) | 1.34(6) |
| C(1)–Fe(1)–C(2) | 91.2(3) | C(1)–Fe(1)–S(1) | 157.7(2) |
| S(1)–Fe(1)–S(2) | 76.52(6) | S(1)–Fe(1)–Fe(2) | 55.65(5) |
| S(2)–Fe(1)–Fe(2) | 56.15(5) | S(1)–Fe(2)–S(2) | 76.06(6) |
| S(1)–Fe(2)–Fe(1) | 55.32(5) | S(1)–Fe(3)–S(3) | 76.63(6) |
| S(2)–Fe(2)–Fe(1) | 55.63(5) | S(3)–Fe(3)–Fe(4) | 56.07(5) |
| S(1)–Fe(3)–Fe(4) | 55.10(5) | S(1)–Fe(4)–Fe(3) | 55.65(5) |
| S(1)–Fe(4)–S(3) | 77.03(7) | Fe(4)–S(1)–Fe(1) | 132.61(7) |
| S(3)–Fe(4)–Fe(3) | 56.27(5) | Fe(1)–S(1)–Fe(2) | 69.03(6) |
| Fe(4)–S(1)–Fe(2) | 136.83(6) | | |

type of bond.^{1,3,5,6} This has been verified by their ¹H NMR spectra; that is, the Et group of **5b** displays one triplet at 1.39 ppm and one quartet at 2.49 ppm and the t-Bu group of **5c,d** and **6** shows one singlet between 1.44 and 1.52 ppm.

To further confirm the structures of this type of compound, a single-crystal X-ray diffraction analysis for the representative species **5b** was carried out. The molecular structure of **5b** is depicted in Figure 1, whereas the selected bond lengths and angles of **5b** are listed in Table 1. As can be seen from Figure 1, the twin cluster **5b** is indeed composed of (*μ*-EtS)Fe₂(CO)₆ and (*μ*-PhC≡C)Fe₂(CO)₆ moieties joined to a spiran type of *μ*₄-S atom, which is very similar to other *μ*₄-S twin clusters such as [(*μ*-EtS)Fe₂(CO)₆]₂(*μ*₄-S),³ [(*μ*-n-BuS)Fe₂(CO)₆]₂(*μ*₄-S),⁷ and [(*μ*-MeS)-Fe₂(CO)₆]₂(*μ*₄-S).⁸ In **5b** the two Fe–Fe bond lengths (2.534(2), 2.538(2) Å) are very close to those of [(*μ*-EtS)-Fe₂(CO)₆]₂(*μ*₄-S) (2.542(2), 2.538(2) Å)³ and [(*μ*-n-BuS)-

Fe₂(CO)₆]₂(*μ*₄-S)[(*μ*-PhS)Fe₂(CO)₆] (2.528(2), 2.517(9) Å).⁷ The bond lengths between *μ*₄-S and the four iron atoms (2.226(2)–2.241(2) Å) in **5b** are also very close to those of [(*μ*-EtS)Fe₂(CO)₆]₂(*μ*₄-S) (2.240(2)–2.254(2) Å)³ and [(*n*-BuS)Fe₂(CO)₆]₂(*μ*₄-S)[(*μ*-PhS)Fe₂(CO)₆] (2.240(1)–2.246(1) Å).⁷ In fact, the other geometric features and parameters of these three *μ*₄-S twin clusters are all very close. However, for **5b**, it is worth pointing out that the bond angles of S(3)–C(15)–C(16) and C(15)–C(16)–C(17) are 177.9(5) and 178.3(5) Å and the bond length of C(15)–C(16) is 1.183(6) Å, both of which are consistent with the C(15)–C(16) bond being a C≡C triple bond. In addition, as seen intuitively from Figure 1, that the two substituents Et and PhC≡C are attached to bridged S(2) and S(3) atoms by an e-type of bond, that is, **5b** belongs to an e(Et)e(PhC≡C) isomer, which is in

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good agreement with the assignment according to the ^1H NMR data mentioned above.

Experimental Section

All reactions were carried out under a highly purified nitrogen atmosphere using standard Schlenk and vacuum-line techniques. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium–benzophenone ketyl, whereas triethylamine was distilled from KOH prior to use. Products were separated and purified using TLC glass plates ($20 \times 17 \times 0.3$ cm) covered with silica gel G (10–40 μm). Further purification of the products was by recrystallization from the mixed solvent CH_2Cl_2 /petroleum ether. (μ -RS)(μ -*p*- $\text{MeC}_6\text{H}_4\text{SO}_2\text{S}$) $\text{Fe}_2(\text{CO})_6$ (R = Et, *t*-Bu),¹ μ - $\text{S}_2\text{Fe}_2(\text{CO})_6$,⁹ μ - $\text{Se}_2\text{Fe}_2(\text{CO})_6$,¹⁰ RMgX (R = Et, Me, Ph),¹¹ and $\text{PhC}\equiv\text{CMgBr}$ ¹² were prepared according to literature methods. Elemental selenium was of commercial origin. IR spectra were recorded on a Nicolet FT-IR 5DX infrared spectrophotometer and ^1H NMR spectra on a JEOL FX 90 Q NMR spectrometer. C/H analyses and MS determinations were performed by using a 240C analyzer and HP 5988A spectrometer, respectively. Melting points were determined on a Yanaco MP-500 micro melting point apparatus.

Preparation of $[(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ (5a**).** A 100 mL three-necked flask fitted with a magnetic stirbar, a rubber septum, and a nitrogen inlet tube was charged with 0.211 g (0.60 mmol) of μ - $\text{S}_2\text{Fe}_2(\text{CO})_6$ and 30 mL of THF to form a red solution. The solution was stirred and cooled to -78°C using a dry ice/acetone bath, and then a given amount of $\text{EtMgBr}/\text{Et}_2\text{O}$ was slowly added until the solution turned green. To the green solution of (μ -EtS)(μ -BrMgS) $\text{Fe}_2(\text{CO})_6$ was added 0.264 g (0.50 mmol) of (μ -EtS)(μ -*p*- $\text{MeC}_6\text{H}_4\text{SO}_2\text{S}$) $\text{Fe}_2(\text{CO})_6$. The dry ice/acetone bath was removed, and the reaction mixture was stirred for 1 h at room temperature. Solvent was removed at reduced pressure, and the residue was subjected to TLC separation using petroleum ether as eluent. A main red band was developed with several tiny bands, and a large black band was left on the original spot, which was immovable even with CH_2Cl_2 as eluent. From the main red band was obtained 0.121 g (34%) of **5a** as a red solid, which has been identified by comparison of its IR and ^1H NMR spectra with those of an authentic sample.³

Preparation of $[(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6](\mu_4\text{-S})[(\mu\text{-PhC}\equiv\text{CS})\text{Fe}_2(\text{CO})_6]$ (5b**).** The same procedure was followed as that for **5a**, but a given amount of $\text{PhC}\equiv\text{CMgBr}$ was used instead of EtMgBr . From the main red band was obtained 0.072 g (18%) of **5b** as a red solid, mp 112°C (dec). Anal. Calcd for $\text{C}_{22}\text{H}_{10}\text{Fe}_4\text{O}_{12}\text{S}_3$: C, 33.62; H, 1.28. Found: C, 33.51; H, 1.40. IR (KBr disk): $\nu_{\text{C}=\text{O}}$ 2082 (m), 2073 (s), 2041 (vs), 1991 (vs); $\nu_{\text{C}=\text{C}}$ 2172 (w) cm^{-1} . ^1H NMR(CDCl_3): 1.39 (t, $J = 7.2$ Hz, 3 H, CH_3), 2.49 (q, $J = 7.2$ Hz, 2 H, CH_2), 7.24–7.40 (m, 5 H, C_6H_5) ppm. MS (EI; m/z (relative intensity)): 786 ($\text{M}^+ - 0.9$), 730 ($\text{M}^+ - 2\text{CO}$, 1.6), 702 ($\text{M}^+ - 3\text{CO}$, 3.0), 674 ($\text{M}^+ - 4\text{CO}$, 2.1), 646 ($\text{M}^+ - 5\text{CO}$, 2.7), 618 ($\text{M}^+ - 6\text{CO}$, 5.3), 590 ($\text{M}^+ - 7\text{CO}$, 8.2), 562 ($\text{M}^+ - 8\text{CO}$, 11.2), 534 ($\text{M}^+ - 9\text{CO}$, 18.3), 506 ($\text{M}^+ - 10\text{CO}$, 14.4), 478 ($\text{M}^+ - 11\text{CO}$, 20.0), 450 ($\text{M}^+ - 12\text{CO}$, 32.4), 320 (Fe_4S_3^+ , 100).

Preparation of $[(\mu\text{-t-BuS})\text{Fe}_2(\text{CO})_6](\mu_4\text{-S})[(\mu\text{-MeS})\text{Fe}_2(\text{CO})_6]$ (5c**).** The same procedure was followed as that for **5a**, but a given amount of MeMgI and 0.278 g (0.5 mmol) of (μ -*t*-BuS)(μ -*p*- $\text{MeC}_6\text{H}_4\text{SO}_2\text{S}$) $\text{Fe}_2(\text{CO})_6$ were used instead of EtMgBr and (μ -EtS)(μ -*p*- $\text{MeC}_6\text{H}_4\text{SO}_2\text{S}$) $\text{Fe}_2(\text{CO})_6$, respectively. From the main red band was obtained 0.079 g (22%) of **5c** as a red solid, mp 148°C dec. Anal. Calcd for $\text{C}_{17}\text{H}_{12}\text{Fe}_4\text{O}_{12}\text{S}_3$: C, 28.05; H,

Table 2. Crystal Data and Collection and Refinement Details for **5b**

| | |
|---|---|
| mol formula | 5b $\text{C}_{22}\text{H}_{10}\text{Fe}_4\text{O}_{12}\text{S}_3$ |
| mol wt | 785.88 |
| cryst syst | triclinic |
| space group | $P\bar{1}$ (No. 2) |
| <i>a</i> /Å | 8.895(6) |
| <i>b</i> /Å | 10.081(6) |
| <i>c</i> /Å | 17.1513(5) |
| α /deg | 95.35(4) |
| β /deg | 104.36(4) |
| γ /deg | 87.42(6) |
| <i>V</i> /Å ³ | 1483 |
| <i>Z</i> | 2 |
| density (calcd)/g cm^{-3} | 1.76 |
| <i>F</i> (000) | 780 |
| μ (Mo K α)/ cm^{-1} | 21.77 |
| diffractometer | Enraf-Nonius CAD4 |
| temp/ $^\circ\text{C}$ | 23 |
| radiation | Mo K α , $\lambda = 0.71069$ Å |
| scan type | $\omega/2\theta$ |
| $2\theta_{\text{max}}$ /deg | 50 |
| <i>R</i> | 0.039 |
| <i>R</i> _w | 0.051 |
| goodness-of-fit indicator | 1.44 |
| max shift in final cycle | 0.05 |
| largest peak in final diff map/eÅ ⁻³ | 0.41 |

1.66. Found: C, 28.24; H, 1.69. IR (KBr disk): $\nu_{\text{C}=\text{O}}$ 2082 (m), 2058 (s), 2041 (vs), 1991 (vs) cm^{-1} . ^1H NMR(CDCl_3): 1.45 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 2.15 (s, 3 H, SCH_3) ppm. MS (EI; m/z (relative intensity)): 728 ($\text{M}^+ - 0.9$), 672 ($\text{M}^+ - 2\text{CO}$, 1.9), 644 ($\text{M}^+ - 3\text{CO}$, 1.6), 616 ($\text{M}^+ - 4\text{CO}$, 3.1), 588 ($\text{M}^+ - 5\text{CO}$, 3.5), 560 ($\text{M}^+ - 6\text{CO}$, 2.8), 532 ($\text{M}^+ - 7\text{CO}$, 8.8), 504 ($\text{M}^+ - 8\text{CO}$, 13.1), 476 ($\text{M}^+ - 9\text{CO}$, 23.4), 488 ($\text{M}^+ - 10\text{CO}$, 2.3), 420 ($\text{M}^+ - 11\text{CO}$, 15.6), 392 ($\text{M}^+ - 12\text{CO}$, 2.5), 320 (Fe_4S_3^+ , 100).

Preparation of $[(\mu\text{-t-BuS})\text{Fe}_2(\text{CO})_6](\mu_4\text{-S})(\mu\text{-PhS})\text{Fe}_2(\text{CO})_6]$ (5d**).** The same procedure was followed as that for **5a**, but a given amount of PhMgBr and 0.278 g (0.50 mmol) of (μ -*t*-BuS)(μ -*p*- $\text{MeC}_6\text{H}_4\text{SO}_2\text{S}$) $\text{Fe}_2(\text{CO})_6$ were used instead of EtMgBr and (μ -EtS)(μ -*p*- $\text{MeC}_6\text{H}_4\text{SO}_2\text{S}$) $\text{Fe}_2(\text{CO})_6$, respectively. From the main red band was obtained 0.150 g (38%) of **5d** as a red solid, mp 162°C dec. Anal. Calcd for $\text{C}_{22}\text{H}_{14}\text{Fe}_4\text{O}_{12}\text{S}_3$: C, 33.45; H, 1.79. Found: C, 33.16; H, 1.73. IR (KBr disk): $\nu_{\text{C}=\text{O}}$ 2082 (m), 2041 (vs), 1991 (s) cm^{-1} . ^1H NMR (CDCl_3): 1.52 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 7.32 (br, 5 H, C_6H_5) ppm. MS (EI; m/z (relative intensity)): 790 ($\text{M}^+ - 0.4$), 734 ($\text{M}^+ - 2\text{CO}$, 1.3), 706 ($\text{M}^+ - 3\text{CO}$, 0.8), 678 ($\text{M}^+ - 4\text{CO}$, 1.8), 650 ($\text{M}^+ - 5\text{CO}$, 1.8), 622 ($\text{M}^+ - 6\text{CO}$, 3.3), 594 ($\text{M}^+ - 7\text{CO}$, 5.7), 566 ($\text{M}^+ - 8\text{CO}$, 5.9), 538 ($\text{M}^+ - 9\text{CO}$, 20.6), 510 ($\text{M}^+ - 10\text{CO}$, 3.9), 482 ($\text{M}^+ - 11\text{CO}$, 5.1), 454 ($\text{M}^+ - 12\text{CO}$, 16.3), 397 ($\text{C}_6\text{H}_5\text{Fe}_4\text{S}_3^+$, 17.9).

Preparation of $[(\mu\text{-t-BuS})\text{Fe}_2(\text{CO})_6](\mu_4\text{-Se})[(\mu\text{-PhSe})\text{Fe}_2(\text{CO})_6]$ (6**).** The same procedure was followed as that for **5a**, but 0.437 g (1.0 mmol) of μ - $\text{Se}_2\text{Fe}_2(\text{CO})_6$, a given amount of $\text{PhMgBr}/\text{Et}_2\text{O}$, and 0.820 g (1.49 mmol) of (μ -*t*-BuS)(μ -*p*- $\text{MeC}_6\text{H}_4\text{SO}_2\text{S}$) $\text{Fe}_2(\text{CO})_6$ were used instead of μ - $\text{S}_2\text{Fe}_2(\text{CO})_6$, EtMgBr , and (μ -EtS)(μ -*p*- $\text{MeC}_6\text{H}_4\text{SO}_2\text{S}$) $\text{Fe}_2(\text{CO})_6$, respectively. From the main red band was obtained 0.543 g (61%) of **6** as a red solid, mp 112 – 114°C dec. Anal. Calcd for $\text{C}_{22}\text{H}_{14}\text{Fe}_4\text{O}_{12}\text{Se}_2$: C, 29.90; H, 1.60. Found: C, 30.02; H, 1.68. IR (KBr disk): $\nu_{\text{C}=\text{O}}$ 2082 (s), 2032 (vs), 1983 (vs) cm^{-1} . ^1H NMR (CDCl_3): 1.51 [s, 9 H, $\text{C}(\text{CH}_3)_3$], 7.56 (br, 5 H, C_6H_5) ppm. MS (EI; m/z (relative intensity)): 634 ($\text{M}^+ - 9\text{CO}$, 9.9), 606 ($\text{M}^+ - 10\text{CO}$, 2.6), 578 ($\text{M}^+ - 11\text{CO}$, 6.4), 550 ($\text{M}^+ - 12\text{CO}$, 6.3), 416 ($\text{Fe}_4\text{Se}_2\text{S}^+$, 78.5).

Crystal Structure Determination of **5b.** Single crystals of **5b** suitable for X-ray diffraction analysis were obtained by slow evaporation of its hexane solution. A single crystal measuring $0.90 \times 0.50 \times 0.42$ mm was mounted on a glass fiber and placed in an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. Crystal data for **5b** are listed in Table 2.

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The structure of **5b** was solved by a direct method (MULTAN 82). The final refinements were accomplished by a full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms. All calculations were performed on a MICRO-VAX II computer by using the TEXSAN program system.

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Supporting Information Available: Tables of data collection and processing parameters, positional and thermal parameters, bond lengths, and bond angles for **5b** (4 pages). Ordering information is given on any current masthead page.

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Additions and Corrections

1997, Volume 16

**Wolfgang Ahlers, Bodo Temme, Gerhard Erker,*
Roland Fröhlich, and Frank Zippel:** Formation,
Structure, and Dynamic Behavior of a Novel Dinuclear
Cationic μ -2,4-Hexadiyne Bis(zirconocene) Complex.

Page 1443. Reference 19 is incorrect. The correct literature citation is as follows.

(19) Strauss, D. A.; Zhang, C.; Tilley, T. D. *J. Organomet. Chem.* **1989**, 369, C13.

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