ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 599 (2000) 256–260

Journal of Organometallic Chemistry

# Reactions of $(\mu\text{-}\eta^2\text{-RCH=CH})(\mu\text{-Cl})\mathrm{Fe_2(CO)_6}$ with $[(\mu\text{-E})(\mu\text{-R}^1\text{E}^1)\mathrm{Fe_2(CO)_6}]^-$ (E, $\text{E}^1 = \text{S}$ or Se). Synthesis and characterization of $(\mu\text{-}\eta^2\text{-RCH=CH})(\mu\text{-R}^1\text{S})[\mathrm{Fe_2(CO)_6}]_2(\mu_4\text{-E})$ and $[(\mu\text{-}\eta^2\text{-PhCH=CH})\mathrm{Fe_2(CO)_6}]_2(\mu_4\text{-Se})$

Zhong-Xia Wang [a,*], Hui Zhao [a], Zhong-Yuan Zhou [b], Xiang-Ge Zhou [b]

[a] *Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, PR China*
[b] *Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, PR China*

Received 1 October 1999; received in revised form 10 November 1999; accepted 6 December 1999

## Abstract

A new synthetic route to $\mu_4$-S clusters $(\mu\text{-}\eta^2\text{-RCH=CH})(\mu\text{-R}^1\text{S})[\mathrm{Fe_2(CO)_6}]_2(\mu_4\text{-S})$ has been discovered, which involves the reaction of $(\mu\text{-}\eta^2\text{-RCH=CH})(\mu\text{-Cl})\mathrm{Fe_2(CO)_6}$ (**1**) with $[(\mu\text{-S})(\mu\text{-R}^1\text{S})\mathrm{Fe_2(CO)_6}]^-$. A similar reaction between **1** and $[(\mu\text{-Se})(\mu\text{-R}^1\text{S})\mathrm{Fe_2(CO)_6}]^-$ gives $\mu_4$-Se complexes $(\mu\text{-}\eta^2\text{-RCH=CH})(\mu\text{-R}^1\text{S})[\mathrm{Fe_2(CO)_6}]_2(\mu_4\text{-Se})$, while the reaction of **1** (R = Ph) with $[(\mu\text{-Se})(\mu\text{-PhSe})\mathrm{Fe_2(CO)_6}]^-$ yields $[(\mu\text{-}\eta^2\text{-PhCH=CH})\mathrm{Fe_2(CO)_6}]_2(\mu_4\text{-Se})$. The crystal structure of complex $(\mu\text{-}\eta^2\text{-PhCH=CH})(\mu\text{-EtS})[\mathrm{Fe_2(CO)_6}]_2(\mu_4\text{-S})$ was determined by single-crystal X-ray diffraction. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Iron; Alkenyl ligand; Bridging-sulfur ligand; Bridging-selenium ligand; Complexes

## 1. Introduction

In previous papers [1,2] we reported the synthesis of the anionic complexes $[(\mu\text{-}\eta^2\text{-C(R}^1\text{)=CHR}^2)(\mu\text{-S})\{\mathrm{Fe_2(CO)_6}\}_2(\mu_4\text{-S})]^-$ and their reactions with electrophiles such as alkyl halides and acid chlorides, producing complexes of the type $[\mu\text{-}\eta^2\text{-C(R}^1\text{)=CHR}^2](\mu\text{-RS})[\mathrm{Fe_2(CO)_6}]_2(\mu_4\text{-S})$ (R = alkyl or acyl). To develop a new synthetic route for this type of complex and to synthesize their analogues with the $\mu_4$-Se ligand, we recently studied the reaction of $(\mu\text{-}\eta^2\text{-RCH=CH})(\mu\text{-Cl})\mathrm{Fe_2(CO)_6}$ with $[(\mu\text{-E})(\mu\text{-R}^1\text{E}^1)\mathrm{Fe_2(CO)_6}]^-$ (E, $\text{E}^1$ = S, Se). We report the results herein.

## 2. Results and discussion

It has been reported [3] that the reaction of $[\mu\text{-}\eta^2\text{-C(R}^1\text{)=CHR}^2](\mu\text{-Cl})\mathrm{Fe_2(CO)_6}$ with $\text{RS}^-$ proceeds readily to yield $[\mu\text{-}\eta^2\text{-C(R}^1\text{)=CHR}^2](\mu\text{-RS})\mathrm{Fe_2(CO)_6}$. $[\mu\text{-}\eta^2\text{-C(R}^1\text{)=CHR}^2](\mu\text{-Cl})\mathrm{Fe_2(CO)_6}$ is also anticipated to react with $[(\mu\text{-S})(\mu\text{-R}^1\text{S})\mathrm{Fe_2(CO)_6}]^-$ because the latter is a well-known sulfur-centered nucleophile. When $(\mu\text{-}\eta^2\text{-PhCH=CH})(\mu\text{-Cl})\mathrm{Fe_2(CO)_6}$ was added to a solution of $[(\mu\text{-S})(\mu\text{-EtS})\mathrm{Fe_2(CO)_6}]^-$ derived from $(\mu\text{-S}_2)\mathrm{Fe_2(CO)_6}$ and EtMgBr at −78°C, a reaction did occur accompanied by a slow color change from green to red. After stirring overnight at room temperature, $(\mu\text{-}\eta^2\text{-PhCH=CH})(\mu\text{-EtS})[\mathrm{Fe_2(CO)_6}]_2(\mu_4\text{-S})$ was isolated in high yield. The same method gave complexes **3b**–**3d** in good yields. When $[(\mu\text{-Se})(\mu\text{-R}^1\text{S})\mathrm{Fe_2(CO)_6}]^-$ prepared from $[(\mu\text{-CO})(\mu\text{-R}^1\text{S})\mathrm{Fe_2(CO)_6}]^-$ and Se powder at −78°C was treated with $(\mu\text{-}\eta^2\text{-RCH=CH})(\mu\text{-Cl})\mathrm{Fe_2(CO)_6}$, the $\mu_4$-Se complexes $(\mu\text{-}\eta^2\text{-RCH=CH})(\mu\text{-R}^1\text{S})[\mathrm{Fe_2(CO)_6}]_2(\mu_4\text{-Se})$ (**4a**–**4c**) were obtained (Eq. (1)). However, when $(\mu\text{-}\eta^2\text{-PhCH=CH})(\mu\text{-Cl})\mathrm{Fe_2(CO)_6}$ was treated with $[(\mu\text{-Se})(\mu\text{-PhSe})\mathrm{Fe_2(CO)_6}]^-$ prepared from $[(\mu\text{-CO})(\mu\text{-PhSe})\mathrm{Fe_2(CO)_6}]^-$ and excess Se powder, the expected complex $(\mu\text{-}\eta^2\text{-PhCH=CH})(\mu\text{-PhSe})[\mathrm{Fe_2(CO)_6}]_2(\mu_4\text{-Se})$ was not produced. Instead, complex **5** was obtained (Eq. (2)). The possible effect of excess Se

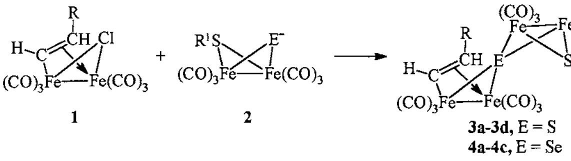
---

[*] Corresponding author. Present address: Department of Chemistry, The Chinese University of Hong Kong, Shakin, NT, Hong Kong, PR China. Fax: +852-2603-5057.

*E-mail address:* wangzx_99@yahoo.com (Z.-X. Wang)

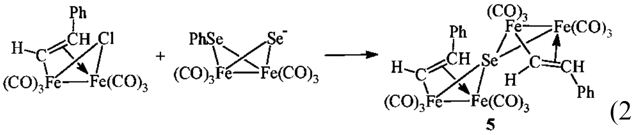
0022-328X/00/$ - see front matter © 2000 Elsevier Science S.A. All rights reserved.
PII: S0022-328X(00)00007-3

powder was ruled out by an alternative experiment in which one equivalent of Se powder was used and the resultant product was still complex **5**.



| | 3a | 3b | 3c | 3d | 4a | 4b | 4c |
|---|---|---|---|---|---|---|---|
| R | Ph | Ph | Ph | 2-furyl | Ph | Ph | 2-furyl |
| R¹ | Et | Ph | Bu$^t$ | Ph | Ph | Bu$^t$ | Bu$^t$ |

(1)



(2)

Although several $\mu_4$-Se iron complexes are known [4–6], complexes of the type ($\mu$-$\eta^2$-RCH=CH)($\mu$-R$^1$S)[$Fe_2(CO)_6$]$_2$($\mu_4$-Se) and [($\mu$-$\eta^2$-PhCH=CH)$Fe_2(CO)_6$]$_2$($\mu_4$-Se) have not been reported.

Complex **3a** was also prepared previously [1] by reaction of [($\mu$-$\eta^2$-PhCH=CH)($\mu$-S){$Fe_2(CO)_6$}$_2$($\mu_4$-S)]$^-$ with EtBr and the analytical data ($^1$H-NMR, IR spectra and melting point) are consistent for the product prepared by the two different methods. Complexes **3b**–**3d** and **4a**–**4c** were characterized by elemental analyses, $^1$H-NMR and IR spectra. These data are consistent with the respective structure and the IR spectra are very similar to those of complexes [$\mu$-$\eta^2$-C(R$^1$)=CHR$^2$]($\mu$-RS)[$Fe_2(CO)_6$]$_2$($\mu_4$-S) produced from [{$\mu$-$\eta^2$-C(R$^1$)=CHR$^2$}($\mu$-S){$Fe_2(CO)_6$}$_2$($\mu_4$-S)]$^-$ and RX [1,2]. Complex **5** was characterized by elemental analysis, $^1$H-NMR and IR spectroscopy and mass spectra. Its $^1$H-NMR spectrum showed only one set of PhCH=CH group signals, i.e. $\delta$ 7.28 ppm for phenyl groups and $\delta$ 4.82 and 9.05 ppm for *trans* vinyl protons, which indicated that both PhCH=CH groups are chemically equivalent. The IR spectrum showed terminal carbonyl absorption bands. The mass spectra gave corresponding fragment ions such as [$M^+ - Ph$], [$M^+ - 7CO$], [$M^+ - 6CO - 2Ph$] and $SeFe_4(C_2H_3)^+$.

In order to further characterize the complexes prepared by this new method, the structure of complex **3a** was determined by single-crystal X-ray diffraction. The structure is presented in Fig. 1. Selected bond distances and angles are listed in Table 1. The molecule consists of two doubly bridged $Fe_2(CO)_6$ units joined to a unique sulfur atom ligand, which is situated at the center of a distorted tetrahedron with four iron atoms at its apices. One of the units is also bridged by a $\mu$-$\eta^2$-phenylethenyl group and the other by an ethanethiolato group. The molecular geometry is very similar to those of the previously reported complexes, namely ($\mu$-$\eta^2$-PhCH=CH)($\mu$-$CH_2$=$CHCH_2S$)-[$Fe_2(CO)_6$]$_2$($\mu_4$-S) and ($\mu$-$\eta^2$-2-furyl-CH=CH)[$\mu$-PhCH=CHC(O)S][$Fe_2(CO)_6$]$_2$($\mu_4$-S) [2]. Most of the bond lengths and angles are also comparable to those of complexes ($\mu$-$\eta^2$-PhCH=CH)($\mu$-$CH_2$=$CHCH_2S$)-[$Fe_2(CO)_6$]$_2$($\mu_4$-S) and ($\mu$-$\eta^2$-2-furyl-CH=CH)[$\mu$-PhCH=

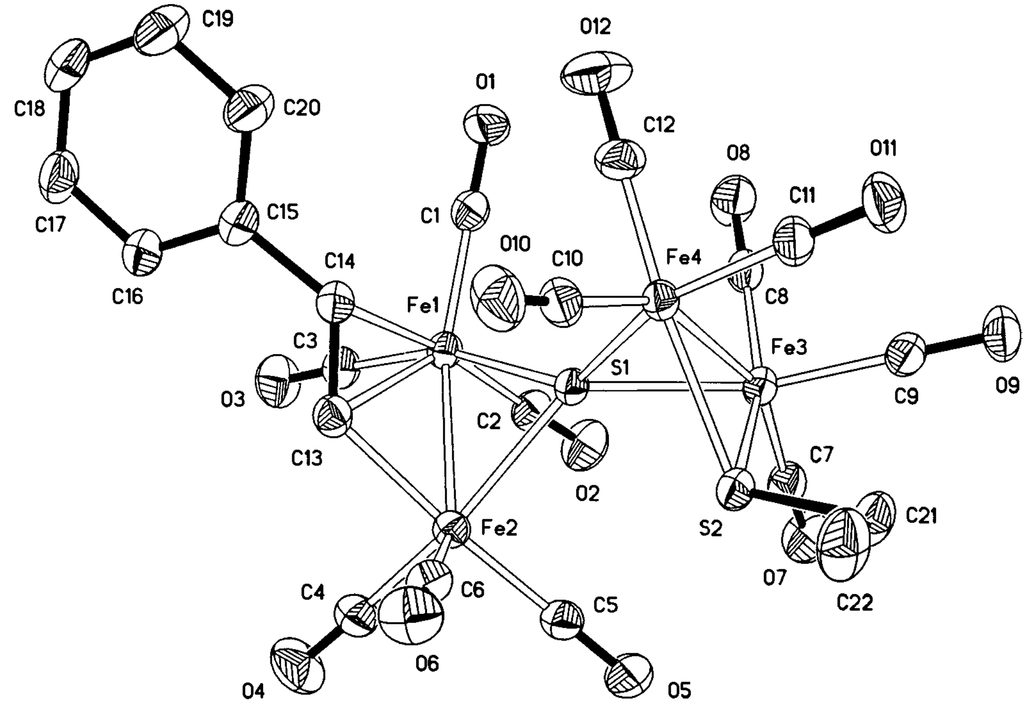


Fig. 1. ORTEP representation of the structure of complex **3a**.

Table 1
Selected bond distances (Å) and angles (°) for complex **3a**

| | | | |
|---|---|---|---|
| *Bond lengths* | | | |
| Fe(1)–C(13) | 2.097(2) | Fe(3)–S(2) | 2.2653(9) |
| Fe(1)–C(14) | 2.243(2) | Fe(3)–Fe(4) | 2.5093(6) |
| Fe(1)–S(1) | 2.2532(7) | Fe(4)–S(1) | 2.2615(6) |
| Fe(1)–Fe(2) | 2.5554(7) | Fe(4)–S(2) | 2.2785(7) |
| Fe(2)–C(13) | 1.959(2) | S(2)–C(21) | 1.823(2) |
| Fe(2)–S(1) | 2.2406(7) | C(13)–C(14) | 1.390(3) |
| Fe(3)–S(1) | 2.2517(9) | C(14)–C(15) | 1.491(3) |
| *Bond angles* | | | |
| C(13)–Fe(1)–C(14) | 37.16(9) | S(1)–Fe(4)–Fe(3) | 56.03(2) |
| C(13)–Fe(1)–S(1) | 83.05(7) | S(2)–Fe(4)–Fe(3) | 56.23(2) |
| C(14)–Fe(1)–S(1) | 83.14(6) | Fe(2)–S(1)–Fe(3) | 129.69(3) |
| C(13)–Fe(1)–Fe(2) | 48.58(7) | Fe(2)–S(1)–Fe(1) | 69.31(3) |
| C(14)–Fe(1)–Fe(2) | 78.52(6) | Fe(3)–S(1)–Fe(1) | 130.93(3) |
| S(1)–Fe(1)–Fe(2) | 55.11(2) | Fe(2)–S(1)–Fe(4) | 131.79(3) |
| C(13)–Fe(2)–S(1) | 86.56(8) | Fe(3)–S(1)–Fe(4) | 67.56(2) |
| C(13)–Fe(2)–Fe(1) | 53.40(7) | Fe(1)–S(1)–Fe(4) | 139.63(2) |
| S(1)–Fe(2)–Fe(1) | 55.58(2) | Fe(3)–S(2)–Fe(4) | 67.04(2) |
| S(1)–Fe(3)–S(2) | 75.98(3) | C(14)–C(13)–Fe(2) | 130.1(2) |
| S(1)–Fe(3)–Fe(4) | 56.41(2) | C(14)–C(13)–Fe(1) | 77.11(14) |
| S(2)–Fe(3)–Fe(4) | 56.73(2) | Fe(2)–C(13)–Fe(1) | 78.02(9) |
| S(1)–Fe(4)–S(2) | 75.53(3) | C(13)–C(14)–C(15) | 124.4(2) |
| | | C(13)–C(14)–Fe(1) | 65.72(13) |

CHC(O)S][$Fe_2(CO)_6]_2(\mu_4$-S). However, the dihedral angle between the Fe(1)Fe(2)S(1) plane and Fe(3)Fe(4)S(1) plane (93.3°) in **3a** is greater than those (84.46 and 88.9°, respectively) in the corresponding complexes mentioned above.

## 3. Experimental

All reactions were carried out under nitrogen using standard Schlenk techniques. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl. PhSeH [7], $Na_2Fe_2(CO)_8$ [8], $Na^+$[(μ-$\eta^2$-RCH=CH)(μ-CO)$Fe_2(CO)_6]^-$ [9], (μ-$\eta^2$-PhCH=CH)(μ-Cl)$Fe_2(CO)_6$ [3,10], (μ-$S_2$)$Fe_2(CO)_6$ [11], [(μ-S)(μ-RS)$Fe_2(CO)_6]^-$ [12], [(μ-CO)(μ-RS)$Fe_2(CO)_6]^-$ [13], [(μ-Se)(μ-RS)$Fe_2(CO)_6]^-$ [6] and [(μ-Se)(μ-PhSe)$Fe_2(CO)_6]^-$ [4] were prepared by published procedures. The progress of all reactions was monitored by thin-layer chromatography. Infrared spectra (KBr disc) were obtained by using a Bruker VECTOR22 spectrometer. $^1$H-NMR spectra were recorded on either a Varian EM360L or a FX-90Q spectrometer. Elemental analyses were performed with a Perkin–Elmer 240C analyzer. Melting points were uncorrected.

### 3.1. Preparation (μ-$\eta^2$-2-furyl-CH=CH)(μ-Cl)$Fe_2(CO)_6$

A mixture of furylacryloyl chloride (0.32 g, 2.04 mmol) and $Na_2Fe_2(CO)_8$ (0.80 g, 2.09 mmol) in THF (20 ml) was stirred for 15 h at room temperature (r.t.). To the solution was added $PCl_5$ (0.26 g, 1.25 mmol) and stirring was continued for 4 h. The solvent was removed at reduced pressure and the residue extracted with petroleum ether. After removal of the solvent, the mixture was purified by filtration chromatography. Elution with petroleum ether gave a purple band from which dark purple crystalline (μ-$\eta^2$-2-furyl-CH=CH)(μ-Cl)$Fe_2(CO)_6$ (0.13 g, 26%) was obtained, m.p. 40–41°C. Anal. Found: C, 35.17; H, 1.31. $C_{12}H_5ClFe_2O_7$ requires C, 35.30; H, 1.23%. IR ($\nu_{max}$, $cm^{-1}$): 2086s, 2051vs, 2013s (CO). $^1$H-NMR ($CCl_4$): $\delta$ (ppm) 4.84 (d, 1H, $J = 11.0$ Hz, CH), 6.25 (s, 2H, furyl), 7.22 (s, 1 H, furyl), 8.59 (d, 1H, $J = 11.2$ Hz, CH).

### 3.2. Preparation of (μ-$\eta^2$-RCH=CH)(μ-$R^1$S)[$Fe_2(CO)_6]_2(\mu_4$-S) (R = Ph, $R^1$ = Et, **3a**; R = $R^1$ = Ph, **3b**; R = Ph, $R^1$ = $^t$Bu, **3c**; R = 2-furyl, $R^1$ = Ph, **3d**)

To a red solution of (μ-$S_2$)$Fe_2(CO)_6$ (0.15 g, 0.44 mmol) in THF (20 ml) at −78°C an equimolar quantity of EtMgBr was added dropwise and gave a green solution. After 30 min of stirring at −78°C, (μ-$\eta^2$-PhCH=CH)(μ-Cl)$Fe_2(CO)_6$ (0.17 g, 0.41 mmol) was added. The mixture was warmed to r.t. and stirred overnight. The solvent was removed at reduced pressure and the residue extracted with petroleum ether. After removal of the solvent, the mixture was purified by filtration chromatography. Elution with petroleum ether gave a red band from which red crystalline complex **3a** (0.29 g, 94%) was isolated, m.p. 146–147°C (lit. [1], 146–148°C). IR ($\nu_{max}$, $cm^{-1}$): 2083s, 2055s, 2033vs, 1998s, 1990s (CO) (lit. [1] ($\nu_{max}$, $cm^{-1}$): 2083m, 2053s, 2031vs, 2015s, 2005s, 1987s, 1976s). $^1$H-NMR ($CCl_4$): $\delta$ (ppm) 1.43 (t, 3H, $J = 6.8$ Hz, $CH_3$), 2.39 (q, 2H, $J = 6.8$ Hz, $CH_2$), 4.65 (d, 1H, $J = 13.0$ Hz, CH), 7.14 (s, 5H, Ph), 8.62 (d, 1H, $J = 12.8$ Hz, CH) (lit. [1], in $CDCl_3$: $\delta$ (ppm) 1.33 (t, 3H, $J = 7.0$ Hz, $CH_3$), 2.42 (q, 2H, $J = 7.0$ Hz, $CH_2$), 4.76 (d, 1H, $J = 13.1$ Hz, CH), 7.30 (s, 5H, Ph), 8.70 (d, 1H, $J = 13.0$ Hz, CH)).

Complexes **3b**–**3c** were synthesized similarly, but the corresponding Grignard reagent was used instead of EtMgBr in respective reactions. Complex **3b**, red crystals in 61% yield, m.p. 191°C (dec.). Anal. Found: C, 39.20; H, 1.50. $C_{26}H_{12}Fe_4O_{12}S_2$ requires C, 38.85; H, 1.50%. IR: ($\nu_{max}$, $cm^{-1}$): 2086m, 2060s, 2043vs, 2001s, 1985s (CO). $^1$H-NMR ($CDCl_3$): $\delta$ (ppm) 4.83 (d, 1H, $J = 11.8$ Hz, CH), 7.12–7.48 (m, 10 H, Ph), 8.73 (d, 1H, $J = 12.2$ Hz, CH). Complex **3c**, deep-red crystals in 91% yield, m.p. 167°C (dec.). Anal. Found: C, 36.42; H, 2.02. $C_{24}H_{16}Fe_4O_{12}S_2$ requires C, 36.77; H, 2.06%. IR:

($\nu_{max}$, cm$^{-1}$): 2082m, 2055s, 2035vs, 2013s, 1986s,br (CO). $^1$H-NMR ($CCl_4$): $\delta$ (ppm) 1.47 (s, 9 H, $CH_3$), 4.72 (d, 1H, $J = 11.5$ Hz, CH), 7.22 (s, 5 H, Ph), 8.66 (d, 1H, $J = 11.8$ Hz, CH).

Complex **3d** was prepared by a similar procedure to that for **3a**, but PhMgCl was used instead of EtMgBr and (μ-η$^2$-2-furyl-CH=CH)(μ-Cl)$Fe_2(CO)_6$ instead of (μ-η$^2$-PhCH=CH)(μ-Cl)$Fe_2(CO)_6$. **3d**, deep-red crystals in 53% yield, m.p. 168–170°C. Anal. Found: C, 36.25; H, 1.30. $C_{24}H_{10}Fe_4O_{13}S_2$ requires C, 36.31; H, 1.27%. IR: ($\nu_{max}$, cm$^{-1}$): 2085s, 2061s, 2042vs, 2002s,br., 1989s,br (CO). $^1$H-NMR ($CDCl_3$): $\delta$ (ppm) 4.76 (d, 1H, $J = 11.6$ Hz, CH), 6.23 (s, 2H, furyl), 7.23 (s, 6 H, Ph + furyl), 8.64 (d, 1H, $J = 11.8$ Hz, CH).

### *3.3. Preparation of (μ-η$^2$-RCH=CH)(μ-R$^1$S)[$Fe_2(CO)_6$]$_2$(μ$_4$-Se) (R = R$^1$ = Ph, **4a**; R = Ph, R$^1$ = $^t$Bu, **4b**; R = 2-furyl, R$^1$ = $^t$Bu, **4c**)*

A solution of triethylammonium salt of [(μ-CO)(μ-PhS)$Fe_2(CO)_6$]$^-$ was generated by the reacting $Fe_3(CO)_{12}$ (0.23 g, 0.46 mmol), PhSH (0.05 ml, 0.48 mmol) and $Et_3N$ (0.06 ml, 0.43mmol) in THF (30 ml) at r.t. To the solution cooled at −78°C was added selenium powder (0.06 g, 0.75 mmol). After 40 min of stirring at −78°C, (μ-η$^2$-PhCH=CH)(μ-Cl)$Fe_2(CO)_6$ (0.17 g, 0.41 mmol) was added. The mixture was warmed to r.t. and stirred for 12 h. The solvent was removed at reduced pressure and the residue extracted with petroleum ether. After removal of the solvent, the material remaining was purified by filtration chromatography. Elution with petroleum ether gave a deep-red band from which complex **4a** (0.10 g, 33%) was obtained, m.p. 142°C (dec.). Anal. Found: C, 36.34; H, 1.32. $C_{26}H_{12}Fe_4O_{12}SSe$ requires C, 36.71; H, 1.42%. IR ($\nu_{max}$, cm$^{-1}$): 2086m, 2061s, 2045vs, 2038vs, 2001s, 1985s (CO). $^1$H-NMR ($CDCl_3$): $\delta$ (ppm) 4.83 (d, 1H, $J = 12.4$ Hz, CH), 7.15-7.55 (m, 10 H, Ph), 8.74 (d, 1H, $J = 12.4$ Hz, CH).

Complex **4b** was prepared similarly, but $^t$BuSH was used instead of PhSH. Elution with a 1:20 (v/v) mixture of $CH_2Cl_2$–petroleum ether yielded, after recrystallization from petroleum ether, red crystals of **4b** in 45% yield, m.p. 157–159°C. Anal. Found: C, 34.49; H, 1.95. $C_{29}H_{16}Fe_4O_{12}SSe$ requires C, 34.70; H, 1.94%. IR ($\nu_{max}$, cm$^{-1}$): 2081m, 2031vs, 2003s, 1995s, 1979s (CO). $^1$H-NMR ($CDCl_3$): $\delta$ (ppm) 1.47 (s, 9H, $CH_3$), 4.58 (d, 1H, $J = 12.4$ Hz, CH), 7.18 (s, 5 H, Ph), 8.88 (d, 1H, $J = 12.4$ Hz, CH).

Complex **4c** was prepared by a similar procedure to that for **4a**, but $^t$BuSH was used instead of PhSH and (μ-η$^2$-2-furyl-CH=CH)(μ-Cl)$Fe_2(CO)_6$ instead of (μ-η$^2$-PhCH=CH)(μ-Cl)$Fe_2(CO)_6$. Elution with a 1:20 (v/v) mixture of $CH_2Cl_2$–petroleum ether yielded, after recrystallization from petroleum ether, red crystals of **4c** in 60% yield, m.p. 126°C (dec.). Anal. Found: C, 32.50; H, 1.63. $C_{27}H_{14}Fe_4O_{13}SSe$ requires C, 32.19; H, 1.72%. IR ($\nu_{max}$, cm$^{-1}$): 2082m, 2033s, 2002s, 1993s, 1981s (CO). $^1$H-NMR ($CDCl_3$): $\delta$ (ppm) 1.48 (s, 9H, $^t$Bu), 4.69 (d, 1H, $J = 12.3$ Hz, CH), 6.24 (s, 2H, furyl), 7.24 (s, 1 H, furyl), 8.69 (d, 1H, $J = 12.5$ Hz, CH).

### *3.4. Preparation of [(μ-η$^2$-PhCH=CH)$Fe_2(CO)_6$]$_2$(μ$_4$-Se) (**5**)*

A green solution of $Fe_3(CO)_{12}$ (0.09 g, 0.18 mmol) in THF (30 ml) was added PhSeH (0.02 ml, 0.19 mmol) and $Et_3N$ (0.03 ml, 0.21 mmol) at r.t. After 10 min of stirring, the resultant red–brown solution was cooled to −78°C. To the solution was added selenium powder (0.03 g, 0.38 mmol) which was then stirred for 40 min at −78°C. Subsequently (μ-η$^2$-PhCH=CH)(μ-Cl)$Fe_2(CO)_6$ (0.07 g, 0.17 mmol) was added. The mixture was warmed to r.t. and stirred for 12 h. The solvent was removed at reduced pressure and the residue extracted with petroleum ether. After removal of the solvent, the material remaining was purified by filtration chromatography. Elution with a 1:10 (v/v) mixture of $CH_2Cl_2$–petroleum ether gave, after recrystallization from petroleum ether, a red powder of complex **5** (0.03 g, 42%), m.p. 141°C (dec.). Anal. Found: C, 40.05; H, 1.58. $C_{28}H_{16}Fe_4O_{12}Se$ requires C, 39.81; H, 1.69%. IR ($\nu_{max}$, cm$^{-1}$): 2081m, 2053s, 2035vs, 2005s, 1979s,br. (CO). $^1$H-NMR ($CDCl_3$): $\delta$ (ppm) 4.82 (d, 2H, $J = 12.3$ Hz, 2CH), 7.28 (s, 10 H, 2Ph), 9.05 (d, 1H, $J = 12.5$ Hz, 2CH). MS (EI), *m/z* (relative intensity): 768 [M$^+$ − Ph − 1, 1.15], 721 [M$^+$ − 4CO − CH, 1.20], 649 [M$^+$ − 7CO, 1.05], 588 [M$^+$ − PhCH − 6CO, 0.90], 522 [M$^+$ − 2Ph − 6CO − 2, 3.27], 420 [M$^+$ − PhCH − 12CO, 2.17], 331 [$SeFe_4CH{=}CH_2^+$, 2.64], 217 [$Fe_2SeC_2H^+$, 28.54], 193 [$Fe_2SeH^+$, 28.54], 165 [$Fe(CO)SeH^+$, 11.75], 103 [$PhC_2H_2^+$, 12.99], 91 [$C_8H_7^+$, 50.83], 77 [$Ph^+$, 15.00], 57 [$FeH^+$, 100].

In a similar reaction, [(μ-Se)(μ-PhSe) $Fe_2(CO)_6$]$^-$ was prepared from [(μ-CO)(μ-PhSe) $Fe_2(CO)_6$]$^-$ and one equivalent of Se powder at −78°C. The resultant reaction mixture was treated in situ with (μ-η$^2$-PhCH=CH)(μ-Cl)$Fe_2(CO)_6$ to give complex **5** in 23% yield.

### *3.5. Crystal data and structure determination of complex **3a***

Details are given in Table 2. Suitable crystals of complex **3a** were grown from petroleum ether solution at r.t. Data were collected on a Siemens P4 four-circle diffractometer with graphite-monochromated Mo–K$_\alpha$ radiation. A semi-empirical absorption correction was applied to the data. The structure was solved by direct method (SHELXS-86 [14]) and refined by full-matrix least-squares on $F^2$ (SHELXL-93 [15]). All non-H atoms were anisotropic.

Table 2
Crystallographic data for complex **3a**

| | **3a** |
|---|---|
| Empirical formula | $C_{22}H_{12}O_{12}S_2Fe_4$ |
| Formula weight | 755.84 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| $a$ (Å) | 19.929(4) |
| $b$ (Å) | 9.062(2) |
| $c$ (Å) | 15.925(3) |
| $\beta$ (°) | 99.09(3) |
| $V$ (Å$^3$) | 2839.9(10) |
| $Z$ | 4 |
| Crystal size (mm) | 0.40 × 0.38 × 0.32 |
| Radiation $\lambda$ (Å) | 0.71073 |
| $\mu$ (Mo–K$_\alpha$) (mm$^{-1}$) | 2.208 |
| Temperature (K) | 294(2) |
| Total reflections | 4804 |
| Independent reflections | 4663 |
| Reflections with $I>2\sigma(I)$ | 0.0481 |
| $R_1$ [a] | 0.1478 |
| $wR_2$ | 4804 |

[a] $R_1=\Sigma\|F_o|-|F_c\|/\Sigma|F_o|$, $wR_2=[\Sigma w(F_o^2-F_c^2)/\Sigma wF_o^4]^{1/2}$.

## 4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 135221. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

## Acknowledgements

We are grateful to the Chinese Ministry of Education and the Chinese Academy of Sciences for financial support.

## References

[1] Z.-X. Wang, H. Zhao, Polyhedron 18 (1999) 1131.

[2] Z.-X. Wang, H. Zhao, Z-Y. Zhou, X.-G. Zhou, J. Organomet. Chem. 595 (2000) 158.

[3] J. Ros, J.M. Viñas, R. Mathieu, X. Solans, M. Font-Bardia, J. Chem. Soc. Dalton Trans. (1988) 281.

[4] L.-C. Song, C.-G. Yan, Q.-M. Hu, R.-J. Wang, T.C.W. Mak, X.-Y. Huang, Organometallics 15 (1996) 1535.

[5] P. Mathur, R. Trivedi, C.V.V. Satyanarayana, Organometallics 15 (1996) 1062.

[6] L.-C. Song, C.-G. Yan, Q.-M. Hu, X.-Y. Huang, J. Organomet. Chem. 505 (1995) 119.

[7] D.G. Foster, Organic Synthesis, vol. 3, Wiley, New York, 1955, p. 771.

[8] C.E. Sumner Jr., J.A. Collier, R. Pettit, Organometallics 1 (1982) 1350.

[9] R. Yanez, J. Ros, R. Mathieu, J. Organomet. Chem. 414 (1991) 209.

[10] J. Ros, J.M. Vinas, R. Mathieu, X. Solans, M. Font-Bardia, J. Organomet. Chem. 307 (1988) C7.

[11] L.E. Bogan Jr., D.A. Lesch, T.B. Rauchfuss, J. Organomet. Chem. 250 (1983) 429.

[12] D. Seyferth, R.S. Henderson, J. Am. Chem. Soc. 101 (1979) 508.

[13] D. Seyferth, G.B. Womack, C.M. Archer, J.C. Dewan, Organometallics 8 (1989) 430.

[14] G.M. Sheldrick, SHELXS-86, A Package for the Solution of Crystal Structures, University of Göttingen, Germany, 1986.

[15] G.M. Sheldrick, SHELXS-93, A Package for the Solution of Crystal Refinement, University of Göttingen, Germany, 1993.