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Journal of Organometallic Chemistry 590 (1999) 46–51

Journal of Organometallic Chemistry

Acetylenic bond reduction anchored on $(CO)_6Fe_2(\mu\text{-}Se_2)$: synthesis and characterization of $[(CO)_6Fe_2\{\mu\text{-}SeC(H){=}C(R)Se\}]$ and $[\{(CO)_6Fe_2Se_2\}_2\{\mu\text{-}C(H){-}C(R)\}]$ (R = 3-Th, 2-Th; Th = C_4H_3S)

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Received 8 April 1999; received in revised form 14 July 1999

Abstract

Thiopheneacetylene (RC≡CH; R = 3-Th, 2-Th; Th = C_4H_3S) adds across the Se–Se bond of $(CO)_6Fe_2(\mu\text{-}Se_2)$ at room temperature in methanol solvent containing sodium acetate to yield the adduct $(CO)_6Fe_2\{\mu\text{-}SeC(H){=}C(R)Se\}$ (R = 3-Th (**1**); 2-Th (**3**)) and the double butterfly complex $[\{(CO)_6Fe_2Se_2\}_2\{\mu\text{-}C(H){-}C(R)\}]$ (R = 3-Th (**2**); 2-Th (**4**)). Compounds **1**–**4** were characterized by spectroscopic techniques (IR and ^1H-, ^{13}C- and ^{77}Se-NMR) and their composition confirmed by elemental analysis. Structures of **2** and **4** were further confirmed by single-crystal X-ray diffraction study. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Iron; Selenium; Thiopheneacetylene; Carbonyl; X-ray

1. Introduction

Transition metal complexes of thiophene continue to attract considerable interest from the perspective of understanding the hydrodesulfurization process in fossil fuels [1,2] and to investigate the contrast between thiophene and the much investigated acetylene bonding in transition metal complexes [3,4]. Studies on the activation of thiophene by transition metals have focused mainly on the reactions involving the cleavage of C–S bond [5], metal insertion into C–S bond [6,7], activation of thiophene ring protons [8] and the isomerization of the bonding mode from η^2(S) to η^2(C) of thiophene [9]. In previous investigations [10], we have looked at the addition of acetylene [11,12], phenylacetylene [13,14] and some diacetylenes [15] to the chalcogen atoms of $Fe_2(CO)_6(\mu\text{-}EE')$ (E, E′ = S, Se, Te) compounds. As an extension of our earlier work and to investigate any contrast in the way thiopheneacetylene may add, we have studied the reactions of 3-thiopheneacetylene and 2-thiopheneacetylene with $Fe_2(CO)_6(\mu\text{-}Se_2)$ and report our findings in this paper.

2. Experimental

2.1. General procedures

Reactions and manipulations were carried out under an inert atmosphere of nitrogen or argon using standard Schlenk techniques. Solvents were purified and deoxygenated immediately prior to use. Infrared spectra were recorded on a Nicolet Impact 400 Fourier transform spectrometer in an NaCl cell of 0.1 mm path length as hexane solutions. ^1H-, ^{13}C- and ^{77}Se-NMR spectra were obtained on a Varian VXR-300S spectrometer in $CDCl_3$ solutions using appropriate references at 25°C. The ^{77}Se-NMR signals were referenced to Me_2Se ($\delta = 0$) and the spectra were obtained at an

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PII: S0022-328X(99)00420-9

operating frequency of 57.23 MHz; 90° pulses were used with 2 s delay and 1 s acquisition time. Elemental analyses were carried out using a Carlo Erba automatic analyzer. $(CO)_6Fe_2(\mu\text{-}Se_2)$ [16], 2-thiopheneacetylene and 3-thiopheneacetylene [17] were prepared as reported in the literature.

2.1.1. Preparation of $(CO)_6Fe_2\{\mu\text{-}SeC(H){=}C(R)Se\}$ *(**1**, R = 3-Th; **3**, R = 2-Th; Th =* C_4H_3S*) and* $[\{(CO)_6Fe_2Se_2\}_2\{\mu\text{-}C(H){-}C(R)\}]$ *(**2**, R = 3-Th; **4**, R = 2-Th; Th =* C_4H_3S*)*

A methanol solution (15 ml) containing freshly prepared $(CO)_6Fe_2(\mu\text{-}Se_2)$ (0.62 g, 1.42 mmol), sodium acetate (0.25 g) and 3-thiopheneacetylene (0.4 ml) was stirred at room temperature for 20 h. The reaction was monitored by TLC and terminated when all the $(CO)_6Fe_2(\mu\text{-}Se_2)$ had been consumed. The solution was filtered through Celite to remove insoluble materials. After removal of solvent in vacuo, the residue was redissolved in hexane (5 ml) and subjected to chromatographic workup on a silica gel column. Elution with hexane yielded dark orange–red $(CO)_6Fe_2\{\mu\text{-}SeC(H){=}C(3\text{-}Th)Se\}$ (**1**) (0.37 g, 48%) followed by deep yellow $[\{(CO)_6Fe_2Se_2\}_2\{\mu\text{-}C(H){-}C(3\text{-}Th)\}]$ (**2**) (0.5 g, 36%).

1: IR(CO): ν 2073 (s), 2039 (vs), 2030 (m), 2001 (vs), 1987 (m) cm^{-1}; ^1H-NMR: δ 6.93 (dd, $J_{H-H} = 1.5$ and 5.1 Hz, 1H), 7.24 (s, $^2J_{H-Se} = 54$ Hz, $^3J_{H-Se} = 8$ Hz, CH), 7.28 (dd, $J_{H-H} = 3$ and 5.1 Hz, 1H), 7.38 (dd, $J_{H-H} = 1.5$ and 3 Hz, 1H) ppm; $^{13}C(^1H)$-NMR: δ 124.8 (d, $J_{C-H} = 183$ Hz, CH), 125.8–127.2 (m, Thiophene CH), 137.1 (s, Thiophene C), 150.2 (s, CCH), 209 (s, CO) ppm; ^{77}Se-NMR: δ 369.2 (d, $^2J_{Se-H} = 54$ Hz), 437 (dd, $^3J_{Se-H} = 8$ Hz, $^4J_{Se-H} = 2.3$ Hz) ppm. M.p. 106–108°C. Anal. Calc. (Found) for $C_{12}H_4Fe_2O_6SSe_2$: C, 26.37 (26.6); H, 0.73 (0.83).

2: IR(CO): ν 2079 (m), 2065 (vs), 2040 (vs), 2032 (m), 2009 (s), 2000 (m), 1996 (w), 1986 (w), 1982 (w) cm^{-1}; ^1H-NMR: δ 4.62 (s, $^2J_{H-Se} = 22.2$ H, CH), 6.79 (bs, 1H), 7.38 (bs, 1H), 7.45 (bs, 1H) ppm; $^{13}C(^1H)$-NMR: 52.8 (d, $J_{C-H} = 158$ Hz, CH), 63.6 (s, CCH), 116.8–130 (m, Thiophene CH), 138. 4 (s, Thiophene C), 208, 209 (s, CO) ppm. M.p. 178°C(decomp). Anal. Calc. (Found) for $C_{18}H_4Fe_4O_{12}SSe_4$: C, 21.95 (22.18); H, 0.51 (0).

Conditions used for isolation of $(CO)_6Fe_2\{\mu\text{-}SeC(H){=}C(2\text{-}Th)Se\}$(**3**, 0.31 g, 40%) and $[\{(CO)_6Fe_2Se_2\}_2\{\mu\text{-}C(H){-}C(2\text{-}Th)\}]$ (**4**, 0.49 g, 35%) were identical to those described for obtaining **1** and **2**.

3: IR(CO): ν 2073 (vs), 2039 (vs), 2031 (w), 2001 (vs), 1987 (m) cm^{-1}; ^1H-NMR: δ 6.98 (dd, $J_{H-H} = 3.6$ and 5.1 Hz, 1H), 7.11 (dd, $J_{H-H} = 0.9$ and 3.6 Hz, 1H), 7.19 (s, $^2J_{H-Se} = 54$ Hz, $^3J_{H-Se} = 7$ Hz, CH), 7.33 (dd, J_{H-} $H = 0.9$ and 5.1 Hz, 1H) ppm; $^{13}C(^1H)$-NMR: δ 125.1 (d, $J = 183$ Hz, CH), 127.9–128 (m, Thiophene CH), 138.9 (s, Thiophene C), 148 (s, CCH), 209 (s, CO) ppm; ^{77}Se-NMR: δ 374.8 (d, $^2J_{Se-H} = 54$ Hz), 456.7 (d, $^3J_{Se-H} = 6.8$ Hz) ppm. M.p. 102–104°C. Anal. Calc. (Found) for $C_{12}H_4Fe_2O_6SSe_2$: C, 26.37 (26.58); H, 0.73 (0.82).

4: IR(CO): ν 2079 (s), 2065 (vs), 2040 (vs), 2033 (m), 2009 (vs), 2001 (s), 1997 (m), 1983 (w), 1987 (w) cm^{-1}; ^1H-NMR: δ 4.59 (s, $^2J_{H-Se} = 22.8$ Hz, CH), 6.96 (bs, 2H), 7.32 (bs, 1H); $^{13}C(^1H)$-NMR: δ 52.8 (d, $J_{C-H} = 158$ Hz, CH), 63.6 (s, CCH), 116–130(m, Thiophene CH), 138. 4 (s, Thiophene C), 208, 209 (s, CO) ppm. M.p. 166°C. Anal. Calc. (Found) for $C_{18}H_4Fe_4O_{12}SSe_4$: C, 21.95 (22.2); H, 0.51 (0.62).

2.1.2. Crystal structure determination of $[\{(CO)_6Fe_2Se_2\}_2\{\mu\text{-}C(H)\text{-}C(R)\}]$ *(**2**, R = 3-Th; **4**, R = 2-Th; Th =* C_4H_3S*)*

A suitable crystal was selected for X-ray diffraction study for each compound. The data were collected on an Enraf–Nonius CAD-4 diffractometer employing Mo–K_α ($\lambda = 0.71073$ Å) radiation at room temperature using $2\theta-\omega$ scan. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 25 reflections (20° < 2θ < 25°) [18]. Crystallographic data for **2** and **4** are summarized in Table 1. Empirical absorption correction was based on azi-

Table 1
Crystallographic data for **2** and **4**.

	2	**4**
Formula	$C_{18}O_{12}H_4Fe_4SSe_4$	$C_{18}O_{12}H_4Fe_4SSe_4$
Formula weight	983.5	983.5
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	8.9509(9)	8.987(6)
b (Å)	9.1070(3)	9.148(5)
c (Å)	17.380(2)	17.139(16)
α (°)	74.32(2)	104.16(5)
β (°)	85.568(9)	92.95(6)
γ (°)	86.56(3)	94.11(5)
V (Å^3)	1358.8(5)	1359.3(17)
$D_{calc.}$ (Mg m^{-3})	2.404	2.403
Z	2	2
θ_{max} (°)	55.4	50.0
Color	Blue	Violet
Crystal size (mm)	0.47 × 0.38 × 0.34	0.41 × 0.34 × 0.21
Temperature (K)	295(3)	295(3)
Index ranges	$-12<h<12$, $0<k<12$, $-22<l<24$	$-10<h<10$, $0<k<10$, $-20<l<19$
Radiation	Mo–K_α ($\lambda = 0.71073$ Å)	Mo–Kα ($\lambda = 0.71073$ Å)
μ (mm^{-1})	7.53	7.53
Reflections collected	5876	5102
Independent reflections	3983	3293
T_{max}/T_{min}	2.99	1.97
$R(wF)$%	7.5	5.9
$R(F)$%	5.8	4.6

Table 2
Selected bond distances (Å) and angles (°) for **2**

Bond lengths			
Se(1)–C(13)	1.989(8)	Se(1)–Fe(2)	2.3462(17)
Se(1)–Fe(1)	2.3843(16)	Se(2)–C(14)	2.003(8)
Se(2)–Fe(1)	2.3699(14)	Se(2)–Fe(2)	2.3844(15)
Se(3)–C(13)	1.978(8)	Se(3)–Fe(4)	2.3676(16)
Se(3)–Fe(3)	2.3770(15)	Se(4)–C(14)	2.029(8)
Se(4)–Fe(3)	2.3499(15)	Se(4)–Fe(4)	2.3654(16)
Fe(1)–Fe(2)	2.5235(17)	Fe(3)–Fe(4)	2.5201(19)
C(13)–C(14)	1.478(11)	C(14–C(15)	1.516(11)
C(15)–C(18)	1.366(14)	C(15)–C(16)	1.418(14)
C(16)–C(17)	1.558(14)	S–C(17)	1.599(12)
S–C(18)	1.680(12)		
Bond angles			
C(13)–Se(1)–Fe(2)	99.9(2)	C(13)–Se(1)–Fe(1)	103.9(2)
Fe(2)–Se(1)–Fe(1)	64.47(5)	C(14)–Se(2)–Fe(1)	97.8(2)
C(14)–Se(2)–Fe(2)	107.7(2)	Fe(1)–Se(2)–Fe(2)	64.11(5)
C(13)–Se(3)–Fe(4)	97.3(2)	C(13)–Se(3)–Fe(3)	107.9(2)
Fe(4)–Se(3)–Fe(3)	64.17(5)	C(14)–Se(4)–Fe(3)	103.7(2)
C(14)–Se(4)–Fe(4)	102.7(2)	Fe(3)–Se(4)–Fe(4)	64.61(5)
Se(2)–Fe(1)–Fe(2)	58.22(4)	Se(1)–Fe(1)–Fe(2)	57.03(5)
Se(1)–Fe(2)–Se(2)	81.24(5)	Se(1)–Fe(2)–Fe(1)	58.50(5)
Se(2)–Fe(2)–Fe(1)	57.66(4)	Se(4)–Fe(3)–Se(3)	81.27(5)
Se(3)–Fe(3)–Fe(4)	57.74(5)	Se(4)–Fe(3)–Fe(4)	57.99(5)
Se(4)–Fe(4)–Se(3)	81.15(5)	Se(2)–C(14)–Se(4)	106.4(3)
Se(4)–Fe(4)–Fe(3)	57.40(5)	Se(3)–Fe(4)–Fe(3)	58.10(5)
C(14)–C(13)–Se(3)	113.8(5)	C(14)–C(13)–Se(1)	113.3(6)
Se(3)–C(13)–Se(1)	110.1(4)	C(13)–C(14)–C(15)	116.4(7)
C(13)–C(14)–Se(2)	108.7(5)	C(15)–C(14)–Se(2)	110.4(6)
C(13)–C(14)–Se(4)	110.9(5)	C(15)–C(14)–Se(4)	103.6(6)

Table 3
Selected bond distances (Å) and angles (°) for **4**

Bond lengths			
Se(1)–C(14)	2.019(10)	Se(1)–Fe(2)	2.349(3)
Se(1)–Fe(1)	2.373(2)	Se(2)–C(13)	1.987(10)
Se(2)–Fe(1)	2.360(2)	Se(2)–Fe(2)	2.372(2)
Se(3)–C(13)	1.982(11)	Se(3)–Fe(3)	2.353(2)
Se(3)–Fe(4)	2.387(2)	Se(4)–C(14)	2.008(10)
Se(4)–Fe(4)	2.360(2)	Se(4)–Fe(3)	2.384(2)
Fe(1)–Fe(2)	2.527(3)	Fe(3)–Fe(4)	2.519(3)
C(13)–C(14)	1.494(14)	C(14)–C(15)	1.502(15)
C(15)–C(16)	1.470(19)	C(16)–C(17)	1.44(2)
C(17)–C(18)	1.31(2)	S–C(15)	1.674(12)
S–C(18)	1.646(18)		
Bond angles			
C(14)–Se(1)–Fe(2)	103.7(3)	C(14)–Se(1)–Fe(1)	103.2(3)
Fe(2)–Se(1)–Fe(1)	64.70(6)	C(13)–Se(2)–Fe(1)	96.9(3)
C(13)–Se(2)–Fe(2)	108.3(3)	Fe(1)–Se(2)–Fe(2)	64.55(8)
C(13)–Se(3)–Fe(3)	100.7(3)	C(13)–Se(3)–Fe(4)	104.4(3)
Fe(3)–Se(3)–Fe(4)	64.22(7)	C(14)–Se(4)–Fe(4)	97.7(3)
C(14)–Se(4)–Fe(3)	107.8(3)	Fe(4)–Se(4)–Fe(3)	64.15(8)
Se(2)–Fe(1)–Se(1)	80.92(6)	Se(2)–Fe(1)–Fe(2)	57.96(6)
Se(1)–Fe(1)–Fe(2)	57.18(7)	Se(1)–Fe(2)–Se(2)	81.16(8)
Se(1)–Fe(2)–Fe(1)	58.11(8)	Se(2)–Fe(2)–Fe(1)	57.48(6)
Se(3)–Fe(3)–Se(4)	81.01(7)	Se(3)–Fe(3)–Fe(4)	58.55(8)
Se(4)–Fe(3)–Fe(4)	57.45(6)	Se(4)–Fe(4)–Se(3)	80.82(6)
Se(4)–Fe(4)–Fe(3)	58.40(6)	Se(3)–Fe(4)–Fe(3)	57.23(6)
C(14)–C(13)–Se(3)	112.5(7)	C(14)–C(13)–Se(2)	113.0(7)
Se(3)–C(13)–Se(2)	109.3(5)	C(13)–C(14)–C(15)	115.7(9)
C(13)–C(14)–Se(4)	109.2(7)	C(15)–C(14)–Se(4)	109.8(7)
C(13)–C(14)–Se(1)	110.4(7)	C(15)–C(14)–Se(1)	104.4(7)
Se(4)–C(14)–Se(1)	107.0(5)		

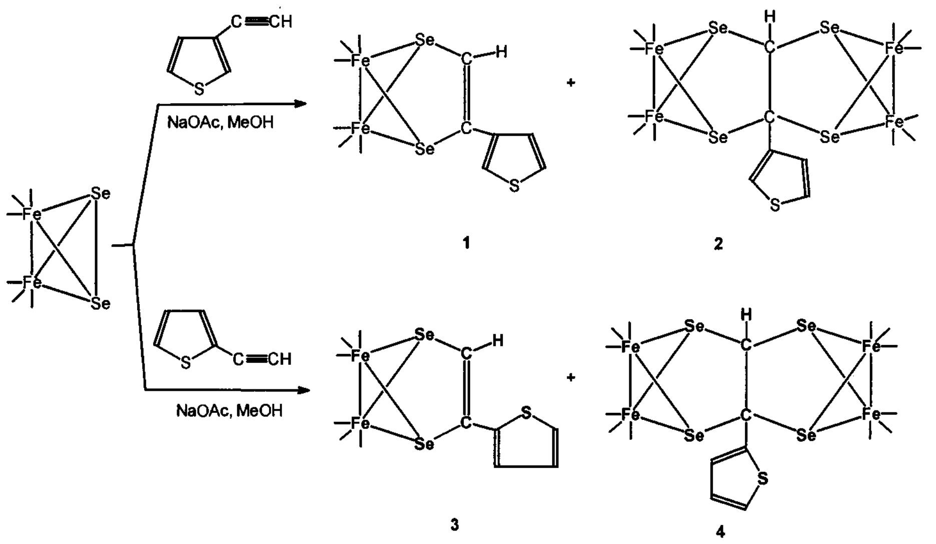
muthal rotation from three reflections [19]. Three strong standard reflections checked every hour varied within 3%. Significant reflections with $I > 2.5\sigma(I)$ were used for the structure determinations, applying the program NRCVX in UNIX compiler [20]. The initial phase was determined by direct methods. The function minimized in full-matrix least-squares fit was $\Sigma w(|F_o| - |F_c|)^2$, where w is from counting statistics. The distances the atoms deviate from the least-squares plane of the five-membered ring containing S atom are all within 0.02 Å for both the compounds, **2** and **4**. All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were treated as idealized isotropic contributions, riding on their parents. Tables 2 and 3 list the selected bond lengths and bond angles for **2** and **4**, respectively.

3. Results and discussion

3.1. Synthesis and spectroscopic characterization of **1**–**4**

Room-temperature stirring of 3-thiopheneacetylene with freshly prepared $(CO)_6Fe_2(\mu\text{-}Se_2)$ in methanol solvent containing sodium acetate for 20 h, afforded the adducts, $(CO)_6Fe_2\{\mu\text{-}SeC(H){=}C(3\text{-}Th)Se\}$ (**1**, 48%) and $[\{(CO)_6Fe_2Se_2\}_2\{\mu\text{-}C(H){-}C(3\text{-}Th)\}]$ (**2**, 36%) (Scheme 1). Similarly, adducts of 2-thiopheneacetylene, $(CO)_6Fe_2\{\mu\text{-}SeC(H){=}C(2\text{-}Th)Se\}$ (**3**) and $[\{(CO)_6Fe_2Se_2\}_2\{\mu\text{-}C(H){-}C(2\text{-}Th)\}]$ (**4**) were obtained in 40 and 35% yield, respectively, from the reaction of 2-thiopheneacetylene and$(CO)_6Fe_2(\mu\text{-}Se_2)$ (Scheme 1). The exact role of the sodium acetate in these reactions is not known at present, but when the above reactions were performed in its absence much lower yields of the products was obtained. Compounds **1**–**4** were characterized by IR and ^{1}H-, ^{13}C- and ^{77}Se-NMR spectroscopy. The molecular structures of **2** and **4** were established by X-ray diffraction methods.

Compounds **1** and **3** show identical carbonyl stretching patterns in the terminal CO absorption region between 2073 and 1987 cm^{-1}, similar to the corresponding acetylenic derivatives $(CO)_6Fe_2\{\mu\text{-}SeC(H){=}C(R)Se\}$ [12,14] reported earlier. The ^{1}H-NMR spectra of **1** and **3** display 4-sets of signals each; three signals for the thiophene ring protons (δ 6.93–7.38 ppm) and a signal for acetylenic CH proton (δ 7.24 and 7.19 ppm, respectively). Each signal for the thiophene ring protons is split into a doublet of doublet ($J = 0.9$ to 5.1 Hz) and the acetylenic signal shows both short-range (54 Hz) and long-range H-Se coupling (8 Hz for **1** and 7 Hz for **3**). Both coupling constants are within the



Scheme 1. Formation of [(CO)$_6$Fe$_2${μ-SeC(H) = C(R)Se}] (**1**, **3**) and [{(CO)$_6$Fe$_2$Se$_2$}$_2${μ-C(H)-C(R)}] (**2**, **4**) (R = 3-Th, 2-Th; Th = C_4H_3S).

range of H–Se coupling observed previously in compounds containing the SeC(H)=C(R) (~ 50–60 Hz) and SeC(R)=C(H) (~ 7–10 Hz) units [12,14]. ^{13}C-NMR spectra confirm the presence of both thiophene and C_2H group. The ^{13}C(^{1}H)-NMR spectra of **1** and **3** show signals at δ 124.8 ppm and δ 125.1 ppm, respectively with a C–H coupling of 183 Hz, for the acetylenic CH group, and multiple signals for thiophene ring CH groups at δ 125–128 ppm. A single peak at δ 209 ppm for the carbonyl ligands is observed for both compounds, indicating the equivalence of the carbonyl groups on the NMR time scale at room temperature. The ^{77}Se-NMR spectra of **1** and **3** display two signals each, in the range of chemical shifts observed in (CO)$_6$Fe$_2${μ-SeC(H)=C(Ph)E} (E = S, Se, Te) [12]. The signal at δ 369.2 ppm and δ 374.8 ppm observed for **1** and **3**, respectively is split into a doublet with a Se–H coupling of 54 Hz, comparable to the two-bond distance Se–H coupling observed in (CO)$_6$Fe$_2${μ-SeC-(H)=C(Ph)Se} and therefore this signal can be assigned to SeC(H). Unlike **3**, the downfield signal at δ 437 ppm for **1** is split into a doublet of doublets as shown in Fig. 1. The multiple nature of the signal is due to the coupling with acetylenic CH proton ($^3J_{\mathrm{Se-H}} = 8$ Hz) and with α-CH proton of thiophene ring, i.e. $^4J_{\mathrm{Se-H}}$ of 2.3 Hz, and therefore this signal can be assigned to Se(Th).

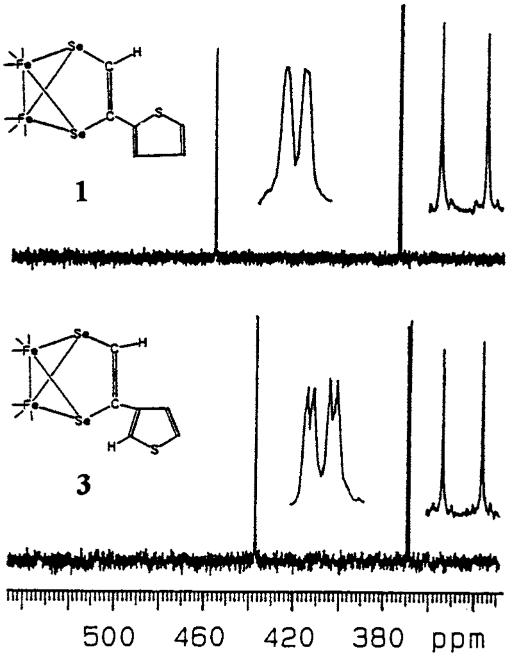


Fig. 1. ^{77}Se-NMR of **1** and **3**.

The solution IR spectra of **2** and **4** in hexane show an identical carbonyl stretching pattern for terminally bonded CO-groups, typically observed for compounds containing Fe$_2$(CO)$_6$ groups. The ^{1}H-NMR spectra of **2** and **4** each display a single peak at δ 4.62 ppm and δ 4.59 ppm, respectively with a pair of ^{77}Se satellites. The H–Se coupling constant in the range 22–23 Hz, observed in **2** and **4**, is consistent with a decrease in the s-character in the acetylenic carbon atoms. The spectra also display three broad signals for thiophene ring protons in **2**, and in **4**, two broad signals with an intensity ratio of 2:1 are observed. ^{13}C-NMR spectra confirm the presence of both thiophene and acetylenic groups. The ^{13}C(^{1}H)-NMR spectra of **2** and **4**, both display a signal centred at δ 52.8 ppm with a C–H coupling of 158 Hz, multiple signals for thiophene ring CH group and two single peaks in the CO region for each compound. For both compounds, two single peaks at δ 63.6 ppm and δ 138.4 ppm are observed for the quaternary carbon atom of acetylenic group and

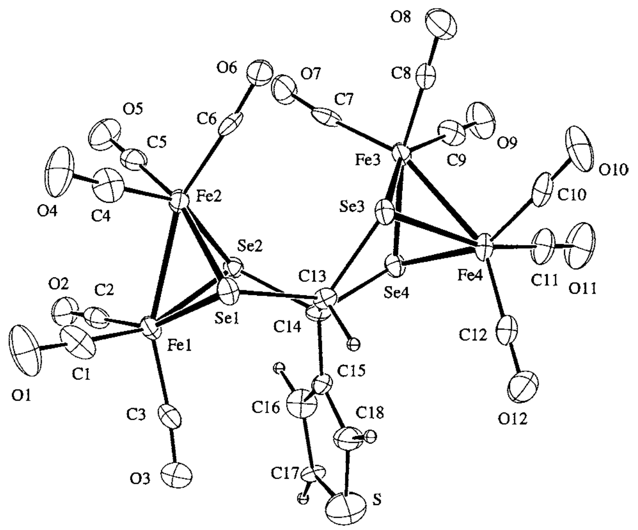


Fig. 2. Molecular structure of $[\{(CO)_6Fe_2Se_2\}_2\{\mu\text{-}C(H)\text{–}C(3\text{-}Th)\}]$ (**2**) with atom numbering scheme.

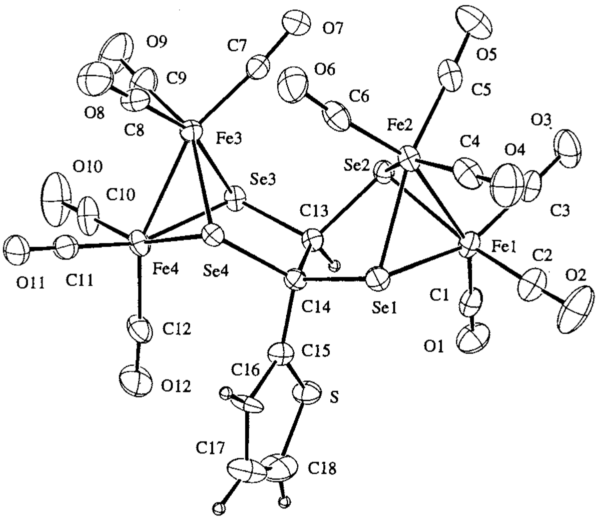


Fig. 3. Molecular structure of $[\{(CO)_6Fe_2Se_2\}_2\{\mu\text{-}C(H)\text{–}C(2\text{-}Th)\}]$ (**4**) with atom numbering scheme.

thiophene group, respectively. Poor solubility prevented the ^{77}Se-NMR spectra for **2** and **4** from being obtained.

3.2. Molecular structure of $[\{(CO)_6Fe_2Se_2\}_2\{\mu\text{-}C(H)\text{–}C(R)\}]$ (2, R = 3-Th; 4, R = 2-Th)

Single and air-stable crystals of **2** and **4** were grown from hexane–CH_2Cl_2 solvent at −10°C and X-ray diffraction study was undertaken. Figs. 2 and 3 show the molecular structures of **2** and **4**, respectively with atom labelling scheme. Both compounds have identical structure that can be envisaged as two Fe_2Se_2 butterfly units, which are linked to each other through a bridging ThC–CH group. Each iron atom has three terminally bonded carbonyl groups. The carbonyl groups, bridging μ_3-Se ligands and the Fe–Fe bond define a distorted octahedral geometry around Fe centre. Overall, the structures of **2** and **4** are similar to that of $[\{(CO)_6Fe_2Se_2\}_2\{\mu\text{-}C(H)\text{–}C(Ph)\}]$ [21]. The acetylenic bond distance in **2** is 1.478(11) Å whereas the C(13)–C(14) bond distance in **4** is 1.494(14) Å, indicating the reduction of acetylenic bond to beyond an olefinic bond order. It is similar to the corresponding bond distance in related compounds: $[\{(CO)_6Fe_2Se_2\}_2\{\mu\text{-}C(H)\text{–}C(Ph)\}]$ (1.48(1) Å) [21], $(CO)_6Fe_2\{\mu\text{-}Se(CH_2)_2Se\}$ (1.47(1) Å) [22], $(CO)_6Fe_2\{\mu\text{-}Te(CH_2)_2Te\}$ (1.494 Å) [23], but longer than the 1.423(15) Å observed in $[(CO)_6Fe_2\{\mu\text{-}SeC(H)C(Ph)Se\}Pt(PPh_3)_2]$ [13]. The bond distances of Fe–Se, Fe–Fe and Se–C for compound **2** lie in the ranges 2.3462 to 2.3844 Å, 2.5201 to 2.5235 Å and 1.978 to 2.029 Å, respectively whereas for compound **4**, they span from 2.349 to 2.387 Å, 2.519 to 2.526 Å and 1.982 to 2.019 Å, respectively. The average Fe–Se bond distances in **2** (2.368 Å) and **4** (2.367 Å) are similar to those observed in $[\{(CO)_6Fe_2Se_2\}_2\{\mu\text{-}C(H)\text{-}C(Ph)\}]$ (2.367 Å) and in $(CO)_6Fe_2\{\mu\text{-}Se(CH_2)_2Se\}$ (2.36 Å).

4. Supplementary material

The complete crystallographic data for **2** and **4** have been deposited and are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, on request, quoting the deposition numbers CCDC 112579 (for **2**) and CCDC 112580 (for **4**).

Acknowledgements

We thank the Council of Scientific and Industrial Research, Government of India, for financial support. We also thank the National Science Council:1, ROC, for support under grant NSC87-2112-M007-009. A.K.D is grateful to Professor Moris S. Eisen for his encouragement.

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