

Synthesis, spectroscopic and structural characterization of the double butterfly complex $[\{(\text{CO})_6\text{Fe}_2\text{SSe}\}_2\{\mu\text{-C(H)-C(Ph)}\}]$

Pradeep Mathur^{a,*}, Aswini K. Dash^a, Md. Munkir Hossain^a, Yu-Sheng Chen^b,
Elizabeth M. Holt^c, S. Narasinga Rao^b

^a Chemistry Department, Indian Institute of Technology, Powai, Bombay-400 06, India

^b University of Central Oklahoma, 100 N. University Drive, Edmond, OK 73034-0175, USA

^c Oklahoma State University, Stillwater, OK 74078-0447, USA

Received 15 May 1996

Abstract

Stirring of $(\text{CO})_6\text{Fe}_2(\mu\text{-SSe})$ and phenylacetylene in methanol at room temperature for 16 h yielded the double butterfly complex $[\{(\text{CO})_6\text{Fe}_2\text{SSe}\}_2\{\mu\text{-C(H)-C(Ph)}\}]$. Compound $[\{(\text{CO})_6\text{Fe}_2\text{SSe}\}_2\{\mu\text{-C(H)-C(Ph)}\}]$ was characterized by IR and ^1H and ^{13}C NMR spectroscopy. Its structure was established by single crystal X-ray crystallography. It crystallized in the triclinic space group $P\bar{1}$ with $a = 8.956(10)$, $b = 9.083$, $c = 17.491(2)$ Å, $\alpha = 104.77(10)^\circ$, $\beta = 93.32(10)^\circ$, $\gamma = 94.77(10)^\circ$, $V = 1336.4(3)$ Å³, $Z = 2$, $D_{\text{calc}} = 2.175$ g cm⁻³. Full-matrix least-squares refinement of $[\{(\text{CO})_6\text{Fe}_2\text{SSe}\}_2\{\mu\text{-C(H)-C(Ph)}\}]$ converged to $R = 0.0504$ and $R_w = 0.0549$. The structure consists of two Fe_2SSe butterfly units linked to each other through a bridging PhC-CH group.

Keywords: Iron; Carbonyl; Sulphur; Selenium; Crystal structure; Phenylacetylene

1. Introduction

Transition metal-alkyne chemistry continues to attract attention because such complexes are used as models for chemisorption of alkynes on metal surfaces and for the activation and reduction of the carbon-carbon triple bond [1]. Although there is a wide variety of coordination modes of alkynes to transition metals, studies of complexes in which the alkynes are attached to main group elements are relatively few [2]. Single atom ligands or those suitably modified with alkenyl and aryl substituents, derived from main group elements of the Periodic Table, serve to stabilize the cluster nuclearity, and their utility for cluster growth reactions is now well established [3]. Compounds of the form $(\text{CO})_6\text{Fe}_2(\mu\text{-E}_2)$ ($E = \text{S, Se, Te}$) undergo facile addition of organic moieties, and these compounds are also convenient starting materials for synthesis of E-bridged mixed-metal clusters [4,5]. In $(\text{CO})_6\text{Fe}_2(\mu\text{-E}_2)$, of the three different types of bond (Fe-Fe , Fe-E and E-E), the E-E bond is usually found to be most reactive and insertion of organic and inorganic moieties into the E-E

bond is a common reactivity feature of these compounds. The nature of E influences the reactivity of these compounds. For instance, facile addition of phenylacetylene to $(\text{CO})_6\text{Fe}_2(\mu\text{-Se}_2)$ and $(\text{CO})_6\text{Fe}_2(\mu\text{-EE}')$ ($E \neq E'$, $E, E' = \text{S, Se, Te}$) readily occurs at room temperature to form $(\text{CO})_6\text{Fe}_2(\mu\text{-SeC(H)=C(Ph)Se})$ [6] and $(\text{CO})_6\text{Fe}_2(\mu\text{-EC(H)=C(Ph)E}')$ [7] respectively, whereas $(\text{CO})_6\text{Fe}_2(\mu\text{-S}_2)$ and $(\text{CO})_6\text{Fe}_2(\mu\text{-Te}_2)$ are inert towards such phenylacetylene addition under similar conditions [8]. Similarly, $(\text{CO})_6\text{Fe}_2(\mu\text{-Te}_2)$ reacts at room temperature with $\text{W}(\text{CO})_5\text{THF}$ to form the mixed-metal cluster $\text{WFe}_2(\text{CO})_{10}(\mu_3\text{-Te}_2)$, but it shows no reactivity towards $\text{Mo}(\text{CO})_5\text{THF}$ [9]. In contrast, $(\text{CO})_6\text{Fe}_2(\mu\text{-Se}_2)$ reacts with both the W and Mo carbonyl compounds to form the clusters $\text{MFe}_2(\text{CO})_{10}(\mu_3\text{-Se}_2)$ ($\text{M} = \text{W, Mo}$). In the complex $(\text{CO})_6\text{Fe}_2(\mu\text{-SeC(H)=C(Ph)Se})$, the reactive Se sites are blocked and facile additions of $(\text{CO})_6\text{Fe}_2(\mu\text{-Se}_2)$ [10] and $\text{Pt}(\text{PPh}_3)_2$ [6] occur readily; a corresponding reduction of the acetylenic $\text{C}\equiv\text{C}$ bond is observed. Addition of organometallic groups across the Fe-Fe bond of $(\text{CO})_6\text{Fe}_2(\mu\text{-SeC(H)=C(Ph)Se})$ can be carried out thermolytically as in the formation of Se -bridged mixed-metal clusters $\text{Cp}_2\text{Mo}_2\text{Fe}_2(\text{CO})_6(\mu_3\text{-Se})(\mu_3\text{-Se})_2$ [11].

* Corresponding author.

Here we report the formation and structural characterization of a mixed-chalcogenide, double butterfly compound obtained from the reaction of $(\text{CO})_6\text{Fe}_2(\mu\text{-SSe})$ with phenylacetylene.

2. Experimental section

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 pathlength as hexane solutions. ^1H and ^{13}C NMR spectra were obtained on a Varian VXR-300S spectrometer in CD_2Cl_2 solutions using appropriate references at 25 °C. Elemental analyses were carried out using a Carlo Erba automatic analyzer. The compound $(\text{CO})_6\text{Fe}_2(\mu\text{-SSe})$ was prepared as reported in the literature [5]. Phenylacetylene was purchased from Aldrich Chemical Co. and used as received.

2.1. Reaction of $(\text{CO})_6\text{Fe}_2(\mu\text{-SSe})$ with phenylacetylene

A methanol solution (15 ml) containing freshly prepared $(\text{CO})_6\text{Fe}_2(\mu\text{-SSe})$ (0.6 g, 1.53 mmol), sodium acetate (0.25 g) and phenylacetylene (0.23 ml, 0.27 mmol) was stirred at room temperature for 16 h. The solvent was evaporated in vacuo, and the residue was redissolved in 5 ml of dichloromethane. The solution was filtered through Celite to remove insoluble material. After removal of the solvent, the residue was redissolved in 5 ml of hexane and subjected to chromatographic work-up on a silica gel column. Using hexane as eluent the following compounds were obtained, in order of elution: trace amounts of previously reported orange-red $(\text{CO})_6\text{Fe}_2(\mu\text{-SeC(Ph)=C(H)Se})$ and $(\text{CO})_6\text{Fe}_2(\mu\text{-SC(Ph)=C(H)Se})$, followed by deep red $\{[(\text{CO})_6\text{Fe}_2\text{SSe}_2(\mu\text{-C(H)-C(Ph))}]_2\}$ (0.3 g, 35%). IR: $\nu(\text{CO})$, 2082(m), 2068(s), 2043(s), 2035(m), 2012(s), 2002(m), 1998(m), 1988(m) cm^{-1} . ^1H NMR: δ 4.65 (s, $J_{\text{H-Se}} = 19.8$ Hz, SC(H)Se), 4.76 (s, $J_{\text{H-Se}} = 23.1$ Hz, SeC(H)Se), 6.8–7.9 (m, Ph) ppm. ^{13}C NMR: δ 47.7 (d, $J_{\text{C-H}} = 140$ Hz, SC(H)Se), 49.9 (d, $J_{\text{C-H}} = 154$ Hz, SeC(H)Se), 60.2 (s, SeC(Ph)S), 65.7 (s, SeC(Ph)Se), 120.8–132.3 (m, Ph), 207 (CO), 208 (CO) ppm. M.p. 164 °C (decomp.). Anal. Found: C, 22.1; H, 0.62. $\text{C}_{20}\text{H}_6\text{Fe}_4\text{O}_{12}\text{S}_2\text{Se}_2$. Calc.: C, 21.7; H, 0.54%.

2.2. Crystal structure determination of $\{[(\text{CO})_6\text{Fe}_2\text{SSe}_2(\mu\text{-C(H)-C(Ph))}]_2\}$

A deep red cube-shaped single crystal of approximate dimensions $0.2 \times 0.2 \times 0.3$ mm³ was selected and

Table 1

Crystallographic data for $\{[(\text{CO})_6\text{Fe}_2\text{SSe}_2(\mu\text{-C(H)-C(Ph))}]_2\}$

Empirical formula	$\text{C}_{20}\text{H}_6\text{Fe}_4\text{O}_{12}\text{S}_{1.762}\text{Se}_{2.238}$
Formula weight	894.9
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	8.9560(10)
b (Å)	9.0830(10)
c (Å)	17.491(2)
α (°)	104.770(10)
β (°)	93.320(10)
γ (°)	94.770(10)
V (Å ³)	1366.4(3)
Z	2
D_{calc} (g cm^{-3})	2.175
Absorption coefficient (mm^{-1})	5.256
hkl ranges	$h = -1$ to 11, $k = -11$ to 11, $l = -22$ to 22
$F(000)$	860.57
Corrections	Lorentz polarization, empirical absorption correction
Convergence largest shift (Å)	0.10
Minimization factor	$\sum w(F_o - F_c)^2$
Least-square weights	$w^{-1} = \sigma^2(F) + 0.0008F^2$
Total reflections measured	7442
Total observed reflections	3109
$F > 5\sigma(F)$	
R	0.0504
R_w	0.0549

mounted on a goniometer. The data were collected on a Siemens R3 m/V diffractometer generating Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation at a temperature of 301 K, using the $2\theta-\omega$ scan technique. The scan speed was variable, 15 to 30° min^{-1} in ω , and the scan range was $1.2 + K\alpha$ separation. Crystallographic data are summarized in Table 1. A total of 6239 reflections were collected, of which 3109 data with $F_o > 5\sigma(F_o)$ were used in refinement. The structure was solved by Siemens SHELXTL PLUS PC version using direct methods, and the hydrogen atoms were located in difference Fourier maps. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares. During solution of the structure, the S and Se atoms were found to be disordered. For each of the four positions, S and Se atoms were constrained to having the same positional coordinates and the same anisotropic thermal parameters using the free variable feature of the SHELX programme employed to solve the structure. The occupancy of each was initially set to 50%, but these were allowed to vary in the least-squares refinement with the constraint that the total occupancy of each position totalled one. The results were: Se/S(1) 0.754(6)/0.246(6); Se/S(2) 0.347(6)/0.653(6); Se/S(3) 0.704(6)/0.296(6); Se/S(4) 0.432(6)/0.568(6). With these coordinates and occupancies, the structure refined to a final R -factor of 0.0504 for 367 variables. The atomic coordinates are

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for $[(\text{CO})_6\text{Fe}_2\text{SSe}]_2\{\mu\text{-C(H)-C(Ph)}\}$

Atom	x	y	z	U_{eq}^a
Fe(1)	4085(2)	3396(2)	7713(1)	32(1)
Fe(2)	3876(2)	1944(1)	8751(1)	29(1)
Fe(3)	-519(2)	-2675(2)	6716(1)	31(1)
Fe(4)	-232(2)	-1319(2)	8167(1)	30(1)
Se(1)	1731(1)	2626(1)	8115(1)	31(1)
S(1)	1731(1)	2626(1)	8115(1)	31(1)
Se(2)	4316(2)	782(2)	7467(1)	34(1)
S(2)	4316(2)	782(2)	7467(1)	34(1)
Se(3)	-829(1)	-26(1)	7213(1)	33(1)
S(3)	-829(1)	-26(1)	7213(1)	33(1)
Se(4)	1835(2)	-1865(2)	7406(1)	29(1)
S(4)	1835(2)	-1865(2)	7406(1)	29(1)
C(1)	1159(10)	984(9)	7160(5)	29(3)
C(2)	2346(10)	-144(9)	6963(5)	26(3)
C(3)	2639(10)	-701(10)	6099(5)	28(3)
C(4)	3450(13)	-1939(12)	5872(6)	50(4)
C(5)	3834(16)	-2450(16)	5089(7)	76(6)
C(6)	3351(16)	-1680(18)	4552(6)	84(7)
C(7)	2528(16)	-459(16)	4770(7)	70(6)
C(8)	2176(12)	32(12)	5525(5)	46(4)
C(11)	3573(12)	3773(12)	6781(7)	46(4)
O(11)	3278(9)	4050(10)	6191(5)	64(4)
C(12)	3971(12)	5257(12)	8359(6)	46(4)
O(12)	3905(9)	6409(9)	8794(5)	73(4)
C(13)	6073(14)	3769(12)	7705(7)	49(5)
O(13)	7321(10)	4040(10)	7709(6)	79(4)
C(21)	3516(11)	3336(11)	9622(6)	36(4)
O(21)	3233(9)	4199(9)	10184(4)	65(3)
C(22)	5862(13)	2151(12)	9015(7)	47(4)
O(22)	7121(9)	2266(10)	9155(5)	65(4)
C(23)	3499(12)	354(11)	9178(5)	39(4)
O(23)	3342(9)	-553(9)	9515(4)	59(3)
C(31)	-245(12)	-2923(11)	5674(6)	44(4)
O(31)	-215(11)	-3160(10)	5004(4)	78(4)
C(32)	-2509(14)	-3187(12)	6592(8)	61(5)
O(32)	-3759(10)	-3566(10)	6500(7)	96(5)
C(33)	-203(12)	-4577(11)	6753(5)	38(4)
O(33)	-14(9)	-5764(8)	6781(4)	55(3)
C(41)	-2162(15)	-1589(13)	8331(7)	57(5)
O(41)	-3402(10)	-1770(11)	8441(6)	90(5)
C(42)	206(12)	-2815(12)	8628(6)	42(4)
O(42)	472(10)	-3751(9)	8920(4)	65(3)
C(43)	158(11)	285(11)	9029(6)	36(4)
O(43)	266(9)	1256(8)	9592(4)	51(3)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

listed in Table 2, and selected bond distances and bond angles are listed in Table 3.

3. Results and discussion

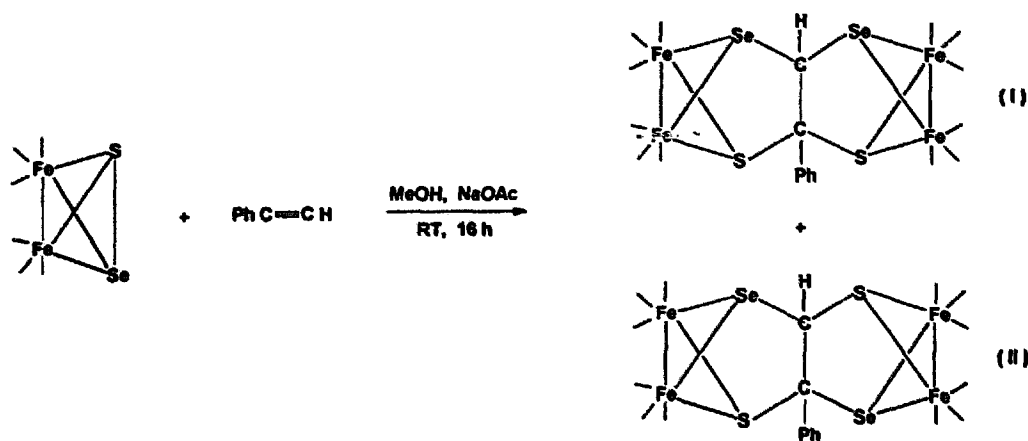
3.1. Synthesis and spectroscopic characterization of $[(\text{CO})_6\text{Fe}_2\text{SSe}]_2\{\mu\text{-C(H)-C(Ph)}\}$

The double butterfly complex $[(\text{CO})_6\text{Fe}_2\text{SSe}]_2\{\mu\text{-C(H)-C(Ph)}\}$ was obtained in a yield of 35% when

Table 3

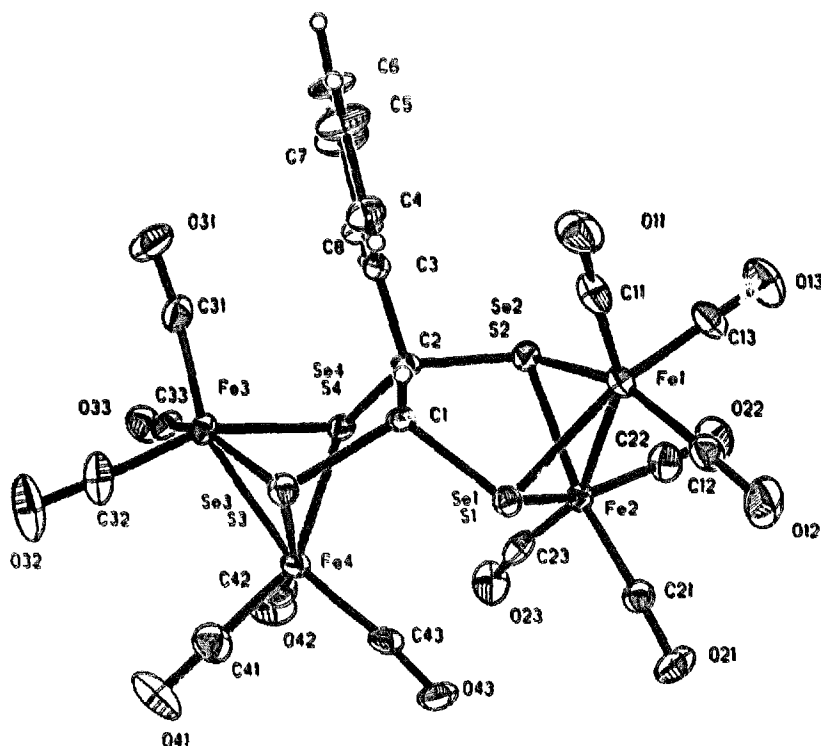
Selected bond distances and bond angles for $[(\text{CO})_6\text{Fe}_2\text{SSe}]_2\{\mu\text{-C(H)-C(Ph)}\}$

Bond distances (\AA)			
Fe(1)–Fe(2)	2.509(2)	Fe(3)–Fe(4)	2.511(2)
Fe(1)–S(1)	2.368(2)	Fe(1)–Se(1)	2.368(2)
Fe(1)–S(2)	2.331(2)	Fe(1)–Se(2)	2.331(2)
Fe(2)–Se(1)	2.370(2)	Fe(2)–S(1)	2.370(2)
Fe(2)–Se(2)	2.298(2)	Fe(2)–S(2)	2.298(2)
Fe(3)–Se(3)	2.368(2)	Fe(3)–S(3)	2.386(2)
Fe(3)–Se(4)	2.333(2)	Fe(3)–S(4)	2.333(2)
Fe(4)–S(3)	2.336(2)	Fe(4)–Se(3)	2.336(2)
Fe(4)–S(4)	2.355(2)	Fe(4)–Se(4)	2.355(2)
Se(1)–C(1)	1.944(7)	Se(2)–C(2)	1.947(8)
S(2)–C(2)	1.947(8)	Se(3)–C(1)	1.952(9)
Se(4)–C(2)	1.948(9)	C(1)–S(1)	1.944(7)
C(1)–S(3)	1.952(9)	C(1)–C(2)	1.531(13)
C(2)–S(4)	1.948(9)	C(2)–C(3)	1.513(12)
Bond angles ($^\circ$)			
Fe(2)–Fe(1)–Se(1)	58.1(1)	Fe(2)–Fe(1)–S(1)	58.1(1)
Se(1)–Fe(1)–S(1)	0.0(1)	Fe(2)–Fe(1)–Se(2)	56.5(1)
Se(1)–Fe(1)–Se(2)	81.6(1)	S(1)–Fe(1)–Se(2)	81.6(1)
Fe(2)–Fe(1)–S(2)	56.5(1)	Se(1)–Fe(1)–S(2)	81.6(1)
S(1)–Fe(1)–S(2)	81.6(1)	Se(2)–Fe(1)–S(2)	0.0(1)
Fe(1)–Fe(2)–Se(1)	58.0(1)	Fe(1)–Fe(2)–S(1)	58.0(1)
Se(1)–Fe(2)–S(1)	0.0(1)	Fe(1)–Fe(2)–Se(2)	57.8(1)
Se(1)–Fe(2)–Se(2)	82.3(1)	S(1)–Fe(2)–Se(2)	82.3(1)
Fe(1)–Fe(2)–S(2)	57.8(1)	Se(1)–Fe(2)–S(2)	82.3(1)
S(1)–Fe(2)–S(2)	82.3(1)	Se(2)–Fe(2)–S(2)	0.0(1)
Fe(4)–Fe(3)–Se(3)	56.9(1)	Fe(4)–Fe(3)–S(3)	56.9(1)
Se(3)–Fe(3)–S(3)	0.0(1)	Fe(4)–Fe(3)–Se(4)	58.0(1)
Se(3)–Fe(3)–Se(4)	81.3(1)	S(3)–Fe(3)–Se(4)	81.3(1)
Fe(4)–Fe(3)–S(4)	58.0(1)	Se(3)–Fe(3)–S(4)	81.3(1)
S(3)–Fe(3)–S(4)	81.3(1)	Se(4)–Fe(3)–S(4)	0.0(1)
Fe(3)–Fe(4)–Se(3)	58.9(1)	Fe(3)–Fe(4)–S(3)	58.9(1)
Se(3)–Fe(4)–S(3)	0.0(1)	Fe(3)–Fe(4)–Se(4)	57.2(1)
Se(3)–Fe(4)–Se(4)	81.9(1)	S(3)–Fe(4)–Se(4)	81.9(1)
Fe(3)–Fe(4)–S(4)	57.2(1)	Se(3)–Fe(4)–S(4)	81.9(1)
S(3)–Fe(4)–S(4)	81.9(1)	Se(4)–Fe(4)–S(4)	0.0(1)
Fe(1)–Se(1)–Fe(2)	64.0(1)	Fe(1)–Se(1)–C(1)	95.5(3)
Fe(2)–Se(1)–C(1)	106.8(3)	Fe(1)–S(1)–Fe(2)	64.0(1)
Fe(1)–S(1)–C(1)	95.5(3)	Fe(2)–S(1)–C(1)	106.8(3)
Fe(1)–Se(2)–Fe(2)	65.7(1)	Fe(1)–Se(2)–C(2)	103.0(3)
Fe(2)–Se(2)–C(2)	104.5(3)	Fe(1)–S(2)–Fe(2)	65.7(1)
Fe(1)–S(2)–C(2)	103.0(3)	Fe(2)–S(2)–C(2)	104.5(3)
Fe(3)–Se(3)–Fe(4)	64.3(1)	Fe(3)–Se(3)–C(1)	103.2(3)
Fe(4)–Se(3)–C(1)	99.3(3)	Fe(3)–S(3)–Fe(4)	64.3(1)
Fe(3)–S(3)–C(1)	103.2(3)	Fe(4)–S(3)–C(1)	99.3(3)
Fe(3)–Se(4)–Fe(4)	64.8(1)	Fe(3)–Se(4)–C(2)	97.6(3)
Fe(3)–Se(4)–C(2)	108.2(3)	Fe(3)–S(4)–Fe(4)	64.8(1)
Fe(3)–S(4)–C(2)	97.6(3)	Fe(4)–S(4)–C(2)	108.2(3)
Se(1)–C(1)–S(1)	0.0(1)	Se(1)–C(1)–Se(3)	110.7(4)
S(1)–C(1)–Se(3)	110.7(4)	Se(1)–C(1)–S(3)	110.7(4)
S(1)–C(1)–S(3)	110.7(4)	Se(3)–C(1)–S(3)	0.0(1)
Se(1)–C(1)–C(2)	113.2(6)	S(1)–C(1)–C(2)	113.2(6)
Se(3)–C(1)–C(2)	112.7(6)	S(3)–C(1)–C(2)	112.7(6)
Se(2)–C(2)–S(2)	0.0(1)	Se(2)–C(2)–Se(4)	106.1(4)
S(2)–C(2)–Se(4)	106.1(4)	Se(2)–C(2)–S(4)	106.1(4)
S(2)–C(2)–S(4)	106.1(4)	Se(4)–C(2)–S(4)	0.0(1)
Se(2)–C(2)–C(1)	111.1(5)	S(2)–C(2)–C(1)	111.1(5)
Se(4)–C(2)–C(3)	110.7(6)	S(4)–C(2)–C(3)	110.7(6)
C(1)–C(2)–C(3)	116.7(8)		

Scheme 1. Formation of $\{[(\text{CO})_6\text{Fe}_2\text{SSe}]_2[\mu\text{-C(H)-C(Ph)}]\}$.

a mixture of $(\text{CO})_6\text{Fe}_2(\mu\text{-SSe})$ and phenylacetylene was allowed to stir at room temperature for 16 h in methanol solvent containing sodium acetate (Scheme 1). Trace amounts of previously reported compounds $(\text{CO})_6\text{Fe}_2\{(\mu\text{-SeC(H)=C(Ph)S})\}$ and $(\text{CO})_6\text{Fe}_2\{(\mu\text{-SeC(H)=C(Ph)Se})\}$ were also isolated. It is observed that the yield of $\{[(\text{CO})_6\text{Fe}_2\text{SSe}]_2[\mu\text{-C(H)-C(Ph)}]\}$ is sensitive to the stoichiometry of the reagents used and also the duration of the reaction. When a 1:1 molar ratio of phenylacetylene and $(\text{CO})_6\text{Fe}_2(\mu\text{-SSe})$ is used, the yield of $\{[(\text{CO})_6\text{Fe}_2\text{SSe}]_2[\mu\text{-C(H)-C(Ph)}]\}$ is less than 5%, even if the reaction is allowed to stir for up to 24 h; under these conditions the major products formed are

the previously reported compounds $(\text{CO})_6\text{Fe}_2\{(\mu\text{-SeC(H)=C(Ph)S})\}$ and $(\text{CO})_6\text{Fe}_2\{(\mu\text{-SeC(H)=C(Ph)Se})\}$ [7]. An optimum yield of 35% $\{[(\text{CO})_6\text{Fe}_2\text{SSe}]_2[\mu\text{-C(H)-C(Ph)}]\}$ is obtained on using a 2:1 molar ratio of $(\text{CO})_6\text{Fe}_2(\mu\text{-SSe})$ and phenylacetylene, and a reaction time of 16 h. The IR spectrum of $\{[(\text{CO})_6\text{Fe}_2\text{SSe}]_2[\mu\text{-C(H)-C(Ph)}]\}$ displays the characteristic carbonyl stretching pattern observed in compounds containing the $\text{Fe}_2(\text{CO})_6$ unit, with a shift of corresponding bands to higher $\nu(\text{CO})$ values compared with the Se_2 compound $\{[(\text{CO})_6\text{Fe}_2\text{Se}_2]_2[\mu\text{-C(H)-C(Ph)}]\}$. The ^1H NMR spectrum of $\{[(\text{CO})_6\text{Fe}_2\text{SSe}]_2[\mu\text{-C(H)-C(Ph)}]\}$ displays two signals for the CH protons, at δ 4.65 ppm and δ

Fig. 1. Molecular structure of $\{[(\text{CO})_6\text{Fe}_2\text{SSe}]_2[\mu\text{-C(H)-C(Ph)}]\}$ with thermal ellipsoids at the 50% probability level.

4.76 ppm, with ^{77}Se satellites ($J_{\text{H-Se}} = 19.8$ and 23.1 Hz respectively). The presence of two signals indicates the presence of two isomers, and the $J_{\text{H-Se}}$ values are comparable with the $^2J_{\text{H-Se}}$ value of 24 Hz reported for $[(\text{CO})_6\text{Fe}_2\text{Se}_2\{\mu\text{-C(H)-C(H)}\}]$ [12]. On comparison with the spectrum of $[(\text{CO})_6\text{Fe}_2\text{Se}_2\{\mu\text{-C(H)-C(Ph)}\}]$ (δ 4.94 ppm, $J_{\text{H-Se}} = 24$ Hz), the downfield signal with a higher value of H–Se coupling of 23.1 Hz can be assigned to the isomer $[(\text{CO})_6\text{Fe}_2\{\mu\text{-SeSC(H)-C(Ph)SeS}\}]$ (I). The signal at δ 4.65 ppm with a smaller value of H–Se coupling can be assigned to the isomer $[(\text{CO})_6\text{Fe}_2\{\mu\text{-SSeC(H)-C(Ph)SeS}\}]$ (II). A multiplet signal in the range δ 6.8–7.9 ppm is assigned to the protons of the phenyl group. The ^{13}C NMR spectrum also confirms the presence of two isomers. The proton-coupled ^{13}C NMR spectrum shows two doublets at δ 47.7 ppm and δ 49.9 ppm with C–H couplings of 140 and 154 Hz respectively, indicating two C(H) groups which are in different environments. Two single peaks at δ 60.2 ppm and δ 65.7 ppm can be assigned to C(Ph) carbon atoms of the corresponding isomers. The spectra also display peaks for the phenyl carbon atoms at δ 120.8–132.3 ppm and two peaks in the carbonyl region, at δ 207 and 208 ppm.

3.2. Molecular structure of $[(\text{CO})_6\text{Fe}_2\text{SSe}_2\{\mu\text{-C(H)-C(Ph)}\}]$

Deep red single crystals of $[(\text{CO})_6\text{Fe}_2\text{SSe}_2\{\mu\text{-C(H)-C(Ph)}\}]$ were grown from its hexane/ CH_2Cl_2 solutions at -10°C and an X-ray analysis was carried out. Fig. 1 shows the ORTEP diagram of the molecular structure of $[(\text{CO})_6\text{Fe}_2\text{SSe}_2\{\mu\text{-C(H)-C(Ph)}\}]$. The structure can be described as two Fe_2SSe core units linked to each other through a bridging PhC-CH group. As a result of the phenylacetylene addition to the Fe_2SSe cores, the acetylenic bond is reduced to beyond an olefinic bond order, $\text{C(1)-C(2)} = 1.531(13)$ Å, which is longer than the corresponding bond lengths of $1.48(1)$ Å in $[(\text{CO})_6\text{Fe}_2\text{Se}_2\{\mu\text{-C(H)-C(Ph)}\}]$ [10], $1.47(1)$ Å in $(\text{CO})_6\text{Fe}_2\{\mu\text{-Se(CH}_2)_2\text{Se}\}$ [13], 1.494 Å in $(\text{CO})_6\text{Fe}_2\{\mu\text{-Te(CH}_2)_2\text{Te}\}$ [14] and $1.423(15)$ Å in $[(\text{CO})_6\text{Fe}_2\{\mu\text{-SeC(Ph)C(H)}\}]\text{Pt(PPh}_3)_2$ [6]. Each iron atom has three terminally bonded carbonyl groups, and the $\mu_3\text{-S}$ ligand, $\mu_3\text{-Se}$ ligand and the Fe–Fe bond define a distorted octahedral geometry around it. The average Fe–Se bond distance (2.365 Å) in $[(\text{CO})_6\text{Fe}_2\text{SSe}_2\{\mu\text{-C(H)-C(Ph)}\}]$ is longer than the average Fe–S bond distance (2.327 Å). All other bond metrics are unexceptional.

Acknowledgements

We thank the Council of Scientific and Industrial Research, Government of India, for financial support.

References

- [1] D. Braga, F. Grepioni, B.F.G. Johnson, J. Lewis and M. Monari, *J. Organomet. Chem.*, **377** (1989) C1; A.J.L. Pombeiro and R.L. Richards, *Coord. Chem. Rev.*, **104** (1990) 13.
- [2] A.J. Deeming, *Adv. Organomet. Chem.*, **26** (1986) 1; D. Braga, F. Grepioni, B.F.G. Johnson, J. Lewis and J.A. Lunniss, *J. Chem. Soc., Dalton Trans.*, (1992) 1101; H. Bonnemant, *Angew. Chem., Int. Ed. Engl.*, **24** (1985) 248; E. Sappa, A. Tiripicchio and P. Braunstein, *Chem. Rev.*, **83** (1983) 1081; M.D. Vargas and J.N. Nicholls, *Adv. Inorg. Chem. Radiochem.*, **30** (1986) 123.
- [3] H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, **14** (1975) 322; K.H. Whitmire, *J. Coord. Chem.*, **17** (1988) 95; L.C. Roof and J.W. Kolis, *Chem. Rev.*, **93** (1993) 1037; M.A. Ansari and J.A. Ibers, *Coord. Chem. Rev.*, **100** (1990) 223; R.D. Adams, in D.F. Shriver, H.D. Kaesz and R.D. Adams (eds.), *The Chemistry of Metal Cluster Complexes*, VCH, New York, 1990, Chap. 3; P. Mathur, I.J. Mavunkal and A.L. Rheingold, *J. Chem. Soc., Chem. Commun.*, (1989) 382.
- [4] P. Mathur, D. Chakrabarty and I.J. Mavunkal, *J. Cluster Sci.*, **4** (1993) 351; P. Mathur, B. Manimaran, Md.M. Hossain, R. Shanbag, J. Murthy, I.S. Saranathan, C.V.V. Satyanarayana and M.M. Bhadbhade, *J. Organomet. Chem.*, **490** (1995) 173; P. Mathur, Md.M. Hossain and A.L. Rheingold, *Organometallics*, **13** (1994) 3909; P. Mathur, Md.M. Hossain, S.B. Umbarkar, C.V.V. Satyanarayana, A.L. Rheingold, L.M. Liable-Sands and G.P.A. Yap, *Organometallics*, **15** (1996) 1898.
- [5] P. Mathur, P. Sekar, C.V.V. Satyanarayana and M.F. Mahon, *Organometallics*, **14** (1995) 2115.
- [6] P. Mathur, Md.M. Hossain, K. Das and U.C. Sinha, *J. Chem. Soc., Chem. Commun.*, (1993) 46.
- [7] P. Mathur, Md.M. Hossain, S.B. Umbarkar, C.V.V. Satyanarayana, S.S. Tavale and V.G. Puranik, *Organometallics*, **14** (1995) 959.
- [8] D. Seyferth and G.B. Womack, *Organometallics*, **5** (1986) 2360; T. Fassler, D. Buchholz, G. Huttner and L. Zsolnai, *J. Organomet. Chem.*, **369** (1989) 297.
- [9] P. Mathur, D. Chakrabarty, Md.M. Hossain, R.S. Rashid, V. Rugmini and A.L. Rheingold, *Inorg. Chem.*, **31** (1992) 1106.
- [10] P. Mathur and Md.M. Hossain, *Organometallics*, **12** (1993) 2398.
- [11] P. Mathur, Md.M. Hossain and A.L. Rheingold, *Organometallics*, **12** (1993) 5029.
- [12] P. Mathur, A.K. Dash, Md.M. Hossain and C.V.V. Satyanarayana, *J. Organomet. Chem.*, **493** (1995) 257.
- [13] P. Mathur, B. Manimaran, R. Trivedi, Md.M. Hossain and M. Arabati, *J. Organomet. Chem.*, **515** (1996) 155.
- [14] M. Shieh and M.-H. Shieh, *Organometallics*, **13** (1994) 920.