

Synthesis, spectroscopic and structural characterisation of $\{(\text{CO})_3\text{Fe}(\mu\text{-CH}_2)\text{Se}\}_2$ and $(\text{CO})_6\text{Fe}_2\{\mu\text{-Se}(\text{CH}_2)_n\text{Se}\}$ ($n = 1, 2$)

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Abstract

From the room temperature reaction of $(\text{CO})_9\text{Fe}_3(\mu_3\text{-Se})_2$ or $(\text{CO})_6\text{Fe}_2(\mu\text{-Se}_2)$ with diazomethane, four products were isolated; $\{(\text{CO})_3\text{Fe}(\mu\text{-CH}_2)\text{Se}\}_2$ (**1**), $(\text{CO})_6\text{Fe}_2(\mu\text{-SeCH}_3)_2$ (**2**), $(\text{CO})_6\text{Fe}_2(\mu\text{-SeCH}_2\text{Se})$ (**3**) and $(\text{CO})_6\text{Fe}_2(\mu\text{-SeCH}_2\text{CH}_2\text{Se})$ (**4**). All four compounds were characterised by IR, ^1H , ^{13}C , and ^{77}Se NMR spectroscopy. Structures of **1**, **3** and **4** were established by single crystal X-ray structure analyses.

Keywords: Iron; Selenium; Methylene; Carbonyl; X-ray diffraction; Crystal structure

1. Introduction

Use of certain main group elements as bridging and stabilizing ligands in designed cluster growth reactions has been extensively demonstrated in recent years [1]. Early work on metal–chalcogenide complexes suggested that while sulfur and selenium showed similar behavior, the reactivity of tellurium was often unique [2]. Recently it has been evidenced that selenium displays some unique reactivity features, in its compounds of iron, towards small organic molecules [3]. The compounds $(\text{CO})_6\text{Fe}_2(\mu\text{-E}_2)$, [E = S, Se, Te] are useful starting materials for addition of organic and inorganic species [4]. There is much interest in the synthesis and characterisation of metal complexes containing methylene and other alkylidene groups, because these species are known to be intermediates in many catalytic reactions [5]. Recently, addition of CH_2 groups into S–S and Te–Te bonds of $(\text{CO})_6\text{Fe}_2(\mu\text{-E}_2)$ (E = S or Te) has been reported [6]. Typically, the reactions of compounds $(\text{CO})_6\text{Fe}_2(\mu\text{-E}_2)$ involve addition across the E–E bond. Here we report on the formation of an unusual product arising from the addition of CH_2 groups across the Fe–Se bonds, as well as three other products from the reactions of diazomethane with $(\text{CO})_9\text{Fe}_3(\mu_3\text{-Se})_2$ or $(\text{CO})_6\text{Fe}_2(\mu\text{-Se}_2)$.

2. Experimental

2.1. General procedures

All reactions and other manipulations were performed using standard Schlenk techniques under an atmosphere of pre-purified argon. Solvents were rigorously dried prior to use. Infrared spectra were recorded on a Nicolet 5DXB or Impact 400 FT spectrometer as hexane solutions in 0.1 mm pathlength NaCl cells. NMR spectra were all obtained on a Varian VXR-300S spectrometer in CDCl_3 . ^{77}Se NMR measurements were made at an operating frequency of 57.23 MHz using 90° pulses with 1.0 s delay and 1.0 s acquisition time. The spectra were referenced to Me_2Se ($\delta = 0$). Elemental analyses were carried out using a Carlo Erba automatic analyser. $(\text{CO})_9\text{Fe}_3(\mu_3\text{-Se})_2$ and $(\text{CO})_6\text{Fe}_2(\mu\text{-Se}_2)$ were prepared as previously reported [7]. Diazomethane was prepared by dissolving 2.14 g of N-methyl-N-nitroso-p-toluenesulfonamide in 30 ml of diethyl ether. The solution was cooled to 0°C and to this a solution of 0.4 g of KOH in 10 ml of 96% ethanol was added. After 5 min the ethereal solution was distilled and found to contain 0.32–0.35 g of diazomethane [8].

2.2. Reaction of $(\text{CO})_9\text{Fe}_3(\mu_3\text{-Se})_2$ with diazomethane

To a solution of $(\text{CO})_9\text{Fe}_3(\mu_3\text{-Se})_2$ (0.5 g, 0.86 mmol) in dry diethyl ether was added dropwise an

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ethereal solution of diazomethane by distilling a basic solution of N-methyl-N-nitroso-p-toluenesulfonamide in diethyl ether. Addition of diazomethane was continued until TLC and IR indicated total consumption of starting material $(\text{CO})_9\text{Fe}_3(\mu_3\text{-Se})_2$. The reaction mixture was stirred at room temperature for a further 30 min. The solution was filtered through Celite and the solvent was evaporated. The mixture was redissolved in hexane and subjected to chromatographic work-up on silica gel TLC plates using hexane as eluent. This yielded the

following four orange colored bands, in order of elution: $\{(\text{CO})_3\text{Fe}(\mu\text{-CH}_2)\text{Se}\}_2$ (**1**) (62 mg, 12%), $(\text{CO})_6\text{Fe}_2(\mu\text{-SeCH}_3)_2$ (**2**) (56 mg, 11%), $(\text{CO})_6\text{Fe}_2(\mu\text{-SeCH}_2\text{Se})$ (**3**) (42 mg, 8%), and $(\text{CO})_6\text{Fe}_2(\mu\text{-SeCH}_2\text{CH}_2\text{Se})$ (**4**) (32 mg, 6%). **1**: IR ($\nu(\text{CO}) \text{ cm}^{-1}$) 2071(w), 2056(s), 2051(m), 2001(s). $^1\text{H NMR}$: δ 4.59 (d, $J = 2.56$ Hz), δ 5.03 (d, $J = 2.56$ Hz) (CH_2). $^{13}\text{C}(^1\text{H}) \text{NMR}$: δ 52.8 (dd, $J = 160.8$ Hz), (CH_2), δ 203.9, 208.6, 209.2 (CO); $^{77}\text{Se NMR}$: $\delta -362$ (m). Anal. Found: C, 20.4; H, 0.82. $\text{C}_8\text{H}_4\text{Fe}_2\text{O}_6\text{Se}_2$ Calc.:

Table 1
Crystallographic data for **1**, **3** and **4**

Compound	1	3	4
Formula	$\text{C}_8\text{H}_4\text{Fe}_2\text{Se}_2\text{O}_6$	$\text{C}_7\text{H}_2\text{Fe}_2\text{Se}_2\text{O}_6$	$\text{C}_8\text{H}_4\text{Fe}_2\text{Se}_2\text{O}_6$
Crystal dimensions (mm^3)	$0.12 \times 0.15 \times 0.30$	$0.10 \times 0.15 \times 0.20$	$0.33 \times 0.30 \times 0.35$
FW	465.73	451.70	465.73
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/m$
a (\AA)	6.577(2)	8.8812(4)	6.8216(4)
b (\AA)	10.930(3)	12.306(1)	13.545(2)
c (\AA)	17.977(7)	11.810(1)	7.948(1)
β (deg)	96.43(3)	101.251(3)	113.716(8)
V (\AA^3)	1284.1(7)	1266.0(1)	672.4(1)
Z	4	4	2
D_{calc} (g cm^{-3})	2.41	2.37	2.30
μ (cm^{-1})	78.86	79.95	75.32
$F(000)$	880	848	440
Corrections	Lorentz and polarization, linear decay ($< 0.9\%$ on F), empirical absorption ($< 19.3\%$ on F)	Lorentz and polarization, linear decay ($< 6.0\%$ on F), empirical absorption ($< 12.8\%$ on F)	Lorentz and polarization, linear decay ($< 7.8\%$ on F), empirical absorption ($< 36.3\%$ on F)
$2\theta_{\text{max}}$ (deg)	60.88	60.88	51.50
T (K)	296(1)	296(1)	296(1)
hkl ranges	$h = -9$ to 9 $k = -15$ to 0 $l = -25$ to 0	$h = -12$ to 12 , $k = 0$ to 17 $l = 0$ to 16	$h = -8$ to 8 $k = 0$ to 16 $l = 0$ to 9
E.s.d. of observation of unit weight	2.495	1.144	1.198
Convergence, largest shift (\AA)	0.00002	0.00001	0.00000
Minimization factor	$\sum w(F_o - F_c)^2$	$\sum w(F_o - F_c)$	$\sum w(F_o - F_c)^2$
Least-squares weights	$1/\sigma(F_o)^2$	$1/\sigma(F_o)^2$	unit weights
Least-squares cut-off	$3\sigma(I)$	$3\sigma(I)$	$3\sigma(I)$
Instrument instability factor	0.040	0.040	n.a.
High peak in final difference map (e \AA^{-3})	1.292	0.412	0.576
Low peak in final difference map (e \AA^{-3})	-1.223	-0.357	-0.915
R (%)	5.62	3.25	3.00
R_w (%)	7.31	3.68	3.39
No. of reflections measured	4194	4173	1286
No. of reflections observed	2192	2111	1236
No. of parameters	175	160	94
Scale factor	1.693	2.460	1.130

Table 2
Atomic coordinates and isotropic displacement coefficients for **1**

Atom	x	y	z	B (Å ²)
Se1	0.98439(8)	0.09500(6)	0.77434(3)	2.30(1)
Se2	0.50989(8)	0.05351(6)	0.73129(3)	2.26(1)
Fe1	0.7005(1)	0.09140(8)	0.85073(4)	2.16(2)
Fe2	0.7933(1)	0.05803(8)	0.65485(4)	2.12(2)
O11	0.8801(7)	-0.1352(5)	0.9174(3)	5.9(1)
O12	0.8998(7)	0.2827(5)	0.9471(2)	5.0(1)
O13	0.3514(6)	0.0755(5)	0.9377(2)	4.5(1)
O21	1.1491(6)	0.0698(5)	0.5715(2)	4.4(1)
O22	0.6212(8)	0.2865(5)	0.5894(3)	5.4(1)
O23	0.5830(7)	-0.1252(5)	0.5556(2)	4.9(1)
C1	0.5463(9)	0.2084(6)	0.7791(3)	2.8(1)
C2	0.9518(9)	-0.0608(6)	0.7274(3)	2.4(1)
C11	0.8122(9)	-0.0473(7)	0.8918(3)	3.5(2)
C12	0.8247(9)	0.2071(6)	0.9105(3)	3.1(1)
C13	0.488(1)	0.0813(6)	0.9023(3)	3.1(1)
C21	1.0131(9)	0.0667(6)	0.6038(3)	2.6(1)
C22	0.6860(8)	0.1996(6)	0.6141(3)	2.9(1)
C23	0.6641(9)	-0.0505(7)	0.5927(3)	3.4(2)
H11	0.463(8)	0.237(5)	0.794(2)	4.0 *
H12	0.605(9)	0.279(5)	0.744(3)	4.0 *
H21	0.883(8)	-0.123(5)	0.767(3)	4.0 *
H22	0.953(7)	-0.106(5)	0.688(2)	4.0 *

* Refined isotropically.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as: $(4/3) \cdot [a^2 \cdot B(1, 1) + b^2 \cdot B(2, 2) + c^2 \cdot B(3, 3) + ab(\cos \gamma) \cdot B(1, 2) + ac(\cos \beta) \cdot B(1, 3) + bc(\cos \alpha) \cdot B(2, 3)]$.

C, 20.6; H, 0.86%. M.p. 95–97°C (dec.). **2**: IR ($\nu(\text{CO})$ cm⁻¹) 2064(m), 2031(vs), 1991(s), 1986(s). ¹H NMR: δ 2.09 (s, ²J_{H-Se} = 9.8 Hz) (CH₃). ¹³C(¹H) NMR: δ 7.9 (q, J = 143.3 Hz) (CH₃), δ 209 (CO); ⁷⁷Se NMR: δ 45.5 (q, ²J_{Se-H} = 9.8 Hz). Anal. Found: C, 20.54; H, 1.29. C₈H₆Fe₂O₆Se₂ Calc.: C, 20.62; H, 1.34%. M.p. 134–136°C. **3**: IR ($\nu(\text{CO})$ cm⁻¹) 2071(m), 2032(vs), 1999(vs), 1992(s), 1980(w). ¹H NMR: δ 4.02 (s, ²J_{H-Se} = 10.8 Hz) (CH₂). ¹³C(¹H) NMR: δ 27.6 (t, J_{C-H} = 160.5 Hz) (CH₂), 209.4 (CO). ⁷⁷Se NMR: δ 67.6 (t, ²J_{Se-H} = 10.3 Hz). Anal. Found: C, 18.72; H, 0.48. C₈H₄Fe₂O₆Se₂ Calc.: C, 18.6; H, 0.44%. M.p. 79–81°C. **4**: IR ($\nu(\text{CO})$ cm⁻¹) 2070(s), 2031(vs), 1998(s), 1990(s). ¹H NMR: δ 2.65 (s, CH₂-CH₂). ¹³C(¹H) NMR: δ 27.6 (t, J_{C-H} = 143.4 Hz) (CH₂-CH₂), 210 (CO). ⁷⁷Se NMR: δ 528 (m). Anal. Found: C, 20.6; H, 0.84. C₈H₄Fe₂O₆Se₂ Calc.: C, 20.7; H, 0.81%. M.p. 94–96°C.

2.3. Reaction of (CO)₆Fe₂(μ -Se₂) with diazomethane

Reaction of (CO)₆Fe₂(μ -Se₂) (0.5 g, 1.14 mmol) with diazomethane was carried out by following the above method. Chromatographic work-up on silica gel TLC plates using hexane as eluent yielded four compounds: **1** (46 mg, 9%), **2** (42 mg, 8%), **3** (31 mg, 6%), and **4** (22 mg, 4%).

Table 3
Selected bond distances (Å) and bond angles (deg) for **1**

Se(1)–Fe(1)	2.439(1)	Fe(2)–C(2)	2.042(6)
Se(1)–Fe(2)	2.3984(9)	Fe(1)–C(11)	1.806(7)
Se(1)–C(2)	1.902(6)	Fe(1)–C(12)	1.796(6)
Se(2)–Fe(1)	2.3981(9)	Fe(1)–C(13)	1.764(6)
Se(2)–Fe(2)	2.437(1)	Fe(2)–C(21)	1.800(6)
Se(2)–C(1)	1.901(6)	Fe(2)–C(22)	1.820(6)
Fe(1)–C(1)	2.007(6)	Fe(2)–C(23)	1.779(6)
Fe(1)–Se(1)–Fe(2)	98.30(3)	Se(1)–Fe(2)–C(2)	49.9(2)
Fe(1)–Se(1)–C(2)	100.4(2)	Se(1)–C(2)–Fe(2)	74.8(2)
Fe(2)–Se(1)–C(2)	55.3(2)	Se(2)–C(1)–Fe(1)	75.6(2)
Fe(1)–Se(2)–Fe(2)	98.34(3)	Se(2)–Fe(2)–C(2)	89.7(2)
Fe(1)–Se(2)–C(1)	54.2(2)	Se(2)–Fe(2)–C(21)	176.0(2)
Fe(2)–Se(2)–C(1)	99.9(2)	Se(2)–Fe(2)–C(22)	87.6(2)
Se(1)–Fe(1)–Se(2)	81.67(3)	Se(2)–Fe(2)–C(23)	89.9(2)
Se(1)–Fe(1)–C(1)	89.6(2)	C(1)–Fe(1)–C(11)	161.8(3)
Se(1)–Fe(1)–C(11)	86.7(2)	C(1)–Fe(1)–C(12)	95.6(3)
Se(1)–Fe(1)–C(12)	90.0(2)	C(1)–Fe(1)–C(13)	90.2(3)
Se(1)–Fe(1)–C(13)	176.4(2)	C(2)–Fe(2)–C(21)	88.8(2)
Se(2)–Fe(1)–C(1)	50.2(2)	C(2)–Fe(2)–C(22)	160.9(2)
Se(2)–Fe(1)–C(11)	111.6(2)	C(2)–Fe(2)–C(23)	98.7(3)
Se(2)–Fe(1)–C(12)	144.5(2)	C(11)–Fe(1)–C(12)	102.1(3)
Se(2)–Fe(1)–C(13)	95.4(2)	C(11)–Fe(1)–C(13)	92.5(3)
Se(1)–Fe(2)–Se(2)	81.69(3)	C(12)–Fe(1)–C(13)	93.6(3)
Se(1)–Fe(2)–C(21)	94.5(2)	C(21)–Fe(2)–C(22)	92.7(3)
Se(1)–Fe(2)–C(22)	111.0(2)	C(21)–Fe(2)–C(23)	94.0(3)
Se(1)–Fe(2)–C(23)	147.2(2)	C(22)–Fe(2)–C(23)	100.2(3)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 4
Atomic coordinates and isotropic displacement coefficients for **3**

Atom	x	y	z	B (Å ²)
Se1	0.29769(5)	0.28900(4)	0.29925(4)	3.382(9)
Se2	0.43476(5)	0.20639(4)	0.52342(4)	3.102(9)
Fe1	0.17827(7)	0.26833(6)	0.46127(6)	3.24(1)
Fe2	0.28348(7)	0.10824(5)	0.36752(5)	3.01(1)
O11	-0.1343(4)	0.2682(4)	0.3239(4)	6.3(1)
O12	0.1948(5)	0.4965(4)	0.5354(5)	8.6(1)
O13	0.0774(5)	0.1591(5)	0.6528(3)	8.6(1)
O21	0.0214(5)	0.0562(3)	0.1857(4)	7.2(1)
O22	0.2137(5)	-0.0681(3)	0.5150(4)	6.9(1)
O23	0.5236(4)	0.0101(4)	0.2637(4)	7.0(1)
C1	0.4945(6)	0.3034(4)	0.4085(5)	4.3(1)
C11	-0.0114(5)	0.2691(4)	0.3771(5)	4.1(1)
C12	0.1881(6)	0.4079(5)	0.5091(5)	5.3(1)
C13	0.1164(5)	0.2036(6)	0.5787(4)	5.3(1)
C21	0.1228(6)	0.0755(4)	0.2574(5)	4.6(1)
C22	0.2431(5)	0.0007(4)	0.4577(4)	4.3(1)
C23	0.4303(6)	0.0471(4)	0.3044(5)	4.5(1)
H1	0.590(5)	0.265(3)	0.379(4)	4.2 *
H2	0.531(4)	0.386(3)	0.440(4)	4.2 *

* Refined isotropically.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as: $(4/3) * [a^2 * B(1, 1) + b^2 * B(2, 2) + c^2 * B(3, 3) + ab(\cos \gamma) * B(1, 2) + ac(\cos \beta) * B(1, 3) + bc(\cos \alpha) * B(2, 3)]$.

2.4. Crystal structure determination of **1**, **3** and **4**

The crystallographic data of **1**, **3** and **4** are given in Table 1. The data were fully automatically collected on

Table 6
Atomic coordinates and isotropic displacement coefficients for **4**

Atom	x	y	z	B (Å ²)
Se1	-0.4582(1)	-0.250	-0.5034(1)	3.29(2)
Se2	0.0363(1)	-0.250	-0.3732(1)	2.94(1)
Fe1	-0.1901(1)	-0.34397(5)	-0.27571(9)	2.79(1)
O11	0.1710(8)	-0.3858(4)	0.0719(6)	6.1(1)
O12	-0.2151(8)	-0.5289(3)	-0.4730(7)	6.7(1)
O13	-0.4854(7)	-0.3932(4)	-0.1043(6)	6.3(1)
C1	-0.356(2)	-0.250	-0.703(1)	5.6(3)
C2	-0.122(1)	-0.250	-0.641(1)	4.6(2)
C11	0.0316(9)	-0.3695(4)	-0.0666(7)	3.8(1)
C12	-0.2042(9)	-0.4574(4)	-0.3964(7)	3.9(1)
C13	-0.3721(9)	-0.3730(4)	-0.1732(7)	3.8(1)
H1	-0.442(8)	-0.293(4)	-0.793(6)	5.6 *
H2	-0.080(8)	-0.197(4)	-0.696(6)	4.6 *

* Refined isotropically.

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as: $(4/3) * [a^2 * B(1, 1) + b^2 * B(2, 2) + c^2 * B(3, 3) + ab(\cos \gamma) * B(1, 2) + ac(\cos \beta) * B(1, 3) + bc(\cos \alpha) * B(2, 3)]$.

a Nonius CAD4MACH diffractometer employing Mo K α radiation at 296(1) K. The entire measurement, from peak search, centering, recentering, indexing, cell-transformation, Laue symmetry check, selection of data collection parameters, selection of *hkl*-borders, selection of standard reflections, data collection, selection and measurement of empirical absorption correction and determination of final unit-cell, was conducted by CAD4EXPRESS [9]. Data processing as well as refinement

Table 5
Selected bond distances (Å) and bond angles (deg) for **3**

Se(1)–Fe(1)	2.3755(9)	Fe(1)–C(11)	1.782(4)
Se(1)–Fe(2)	2.3778(8)	Fe(1)–C(12)	1.805(6)
Se(1)–C(1)	1.967(5)	Fe(1)–C(13)	1.777(6)
Se(2)–Fe(1)	2.3783(7)	Fe(2)–C(21)	1.779(5)
Se(2)–Fe(2)	2.3851(7)	Fe(2)–C(22)	1.779(5)
Se(2)–C(1)	1.957(6)	Fe(2)–C(23)	1.789(6)
Fe(1)–Fe(2)	2.527(1)		
Fe(1)–Se(1)–Fe(2)	64.22(3)	Se(1)–Fe(2)–Fe(1)	57.84(3)
Fe(1)–Se(1)–C(1)	87.7(2)	Se(1)–Fe(2)–C(21)	93.0(2)
Fe(2)–Se(1)–C(1)	87.8(2)	Se(1)–Fe(2)–C(22)	158.3(2)
Fe(1)–Se(2)–Fe(2)	64.07(3)	Se(1)–Fe(2)–C(23)	99.3(2)
Fe(1)–Se(2)–C(1)	87.9(1)	Se(2)–Fe(2)–Fe(1)	57.83(2)
Fe(2)–Se(2)–C(1)	87.8(1)	Se(2)–Fe(2)–C(21)	158.4(2)
Se(1)–Fe(1)–Se(2)	74.43(3)	Se(2)–Fe(2)–C(22)	93.6(2)
Se(1)–Fe(1)–Fe(2)	57.94(3)	Se(2)–Fe(2)–C(23)	100.8(2)
Se(1)–Fe(1)–C(11)	94.1(2)	Fe(1)–Fe(2)–C(21)	100.6(2)
Se(1)–Fe(1)–C(12)	98.5(2)	Fe(1)–Fe(2)–C(22)	100.5(2)
Se(1)–Fe(1)–C(13)	158.7(2)	Fe(1)–Fe(2)–C(23)	150.7(2)
Se(2)–Fe(1)–Fe(2)	58.10(2)	Se(1)–C(1)–Se(2)	94.2(2)
Se(2)–Fe(1)–C(11)	156.7(2)	C(11)–Fe(1)–C(12)	98.7(2)
Se(2)–Fe(1)–C(12)	102.9(2)	C(11)–Fe(1)–C(13)	92.0(2)
Se(2)–Fe(1)–C(13)	92.2(2)	C(12)–Fe(1)–C(13)	100.7(3)
Fe(2)–Fe(1)–C(11)	98.6(2)	C(21)–Fe(2)–C(22)	92.5(2)
Fe(2)–Fe(1)–C(12)	151.6(2)	C(21)–Fe(2)–C(23)	98.4(2)
Fe(2)–Fe(1)–C(13)	100.9(2)	C(22)–Fe(2)–C(23)	100.7(2)
Se(1)–Fe(2)–Se(2)	74.27(2)		

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 7
Selected bond distances (Å) and bond angles (deg) for **4**

Se(1)–Fe(1)	2.3615(8)	Fe(1)–C(13)	1.781(7)
Se(1)–C(1)	1.98(1)	Fe(1)–C(12)	1.792(6)
Se(2)–Fe(1)	2.360(1)	Fe(1)–C(11)	1.774(4)
Se(2)–C(2)	1.959(7)	C(1)–C(2)	1.47(1)
Fe(1)–Se(1)–C(1)	101.6(2)	Se(2)–Fe(1)–C(12)	100.8(2)
Fe(1)–Se(2)–C(2)	102.0(3)	Se(2)–Fe(1)–C(13)	159.7(2)
Se(1)–Fe(1)–Se(2)	82.26(3)	Se(1)–C(1)–C(2)	114.5(5)
Se(1)–Fe(1)–C(11)	158.2(2)	Se(2)–C(2)–C(1)	114.8(7)
Se(1)–Fe(1)–C(12)	101.2(2)	C(11)–Fe(1)–C(12)	100.1(2)
Se(1)–Fe(1)–C(13)	90.1(2)	C(11)–Fe(1)–C(13)	91.0(3)
Se(2)–Fe(1)–C(11)	89.3(2)	C(12)–Fe(1)–C(13)	99.1(3)

Numbers in parentheses are estimated standard deviations in the least significant digits.

and presentation were carried out using MolEN [10]. The structures were solved by SIR92 [11]. Tables 2, 4 and 6 list the atomic coordinates of **1**, **3** and **4** respectively. Tables 3, 5 and 7 list the selected bond distances and bond angles of compounds **1**, **3** and **4** respectively. For all compounds thermal parameters and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

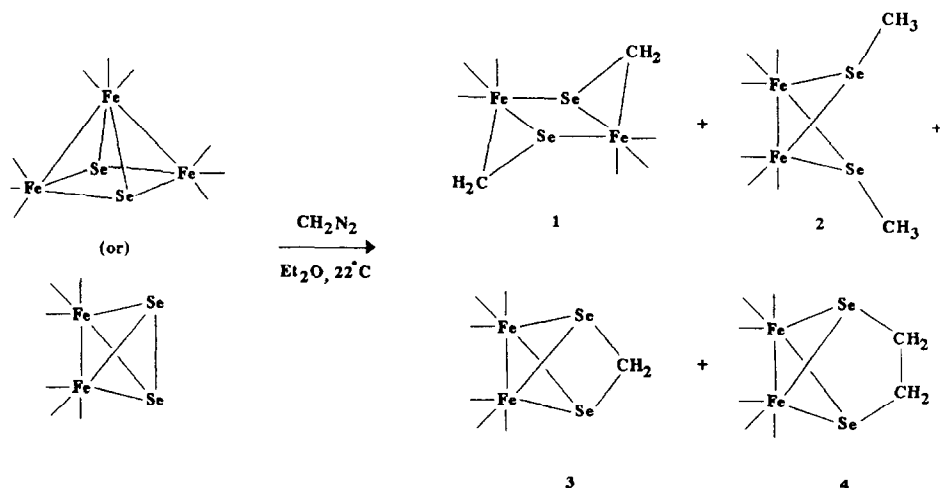
3. Results and discussion

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

When an ether solution containing $(\text{CO})_9\text{Fe}_3(\mu_3\text{-Se})_2$ or $(\text{CO})_6\text{Fe}_2(\mu\text{-Se}_2)$ was stirred with diazomethane at room temperature, the following four products were isolated: $\{(\text{CO})_3\text{Fe}(\mu\text{-CH}_2)\text{Se}\}_2$ (**1**), $(\text{CO})_6\text{Fe}_2(\mu\text{-SeCH}_3)_2$ (**2**), $(\text{CO})_6\text{Fe}_2(\mu\text{-SeCH}_2\text{Se})$ (**3**) and $(\text{CO})_6\text{Fe}_2(\mu\text{-SeCH}_2\text{CH}_2\text{Se})$ (**4**) (Scheme 1). Com-

pounds **1–4** were separated and isolated in pure form by chromatographic work-up and were found to be stable in solid form. Compound **2** has been reported previously and was identified by comparison of its IR and ^1H NMR spectra with that reported [12]. The new compounds **1**, **3**, and **4** were characterised by IR and ^1H , ^{13}C and ^{77}Se NMR spectroscopy. Their compositions were confirmed by elemental analysis.

The infrared spectra of **1**, **3** and **4** indicated the presence of only terminally bonded carbonyl ligands. The ^1H NMR spectrum of **1** showed two doublets for the CH_2 groups. Its proton-decoupled ^{13}C NMR spectrum showed a single peak, whereas the proton-coupled ^{13}C NMR spectrum showed a doublet of doublets. These features are consistent with the presence of non-equivalent H atoms on each CH_2 group of **1**. The ^{13}C NMR spectrum of **1** also displayed three peaks for the CO ligands, indicating that at room temperature CO rearrangement at each Fe center is slow on the NMR timescale. The ^{77}Se NMR spectrum of **1** displayed a single signal with a complex splitting pattern due to



Scheme 1.

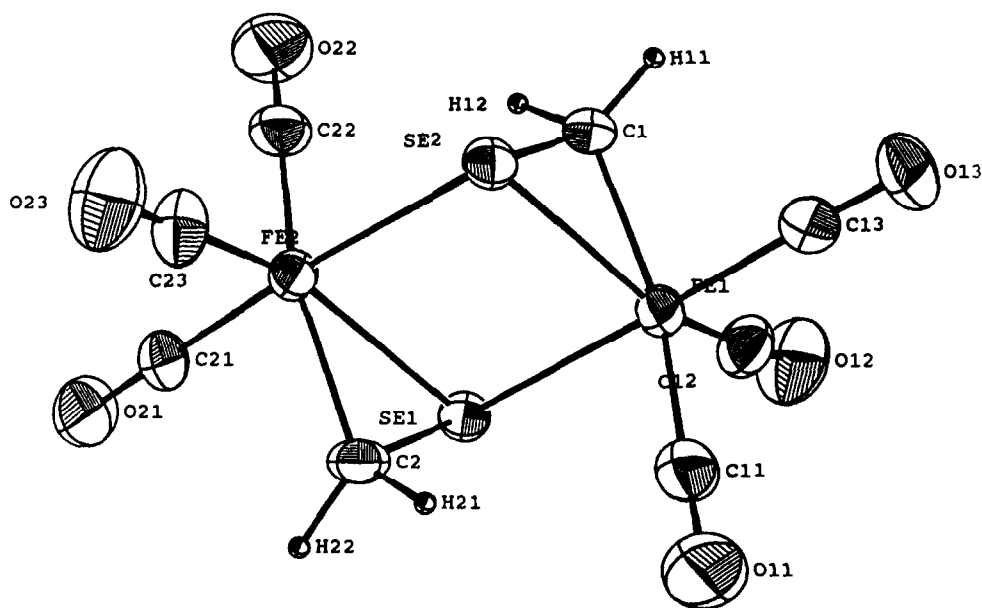


Fig. 1. ORTEP drawing of the molecular structure of **1** with thermal ellipsoids drawn at 50% probability.

short range and long range coupling with the non-equivalent protons of the two CH_2 groups.

The ^1H NMR spectrum of **3** showed a singlet, with ^{77}Se satellites, for the CH_2 group. Its proton coupled ^{13}C NMR spectrum displayed a triplet for the CH_2 group and a single peak due to the CO groups. The ^{77}Se NMR spectrum showed a triplet due to the coupling of Se atoms with CH_2 protons.

The ^1H NMR spectrum of **4** showed a singlet due to the CH_2 groups. Its proton coupled ^{13}C NMR spectrum displayed a triplet for the CH_2 group and a single peak due to the CO groups. The ^{77}Se NMR spectrum showed

a multiplet indicating the short range and long range Se–H coupling.

3.2. Molecular structures of **1**, **3** and **4**

Dark red crystals of **1**, **3** and **4** were grown from their hexane/ CH_2Cl_2 solutions at 0°C and X-ray structure analyses were carried out. The molecular structure of **1** is shown in Fig. 1. The structure consists of a planar arrangement of FeSeFeSe in which each Fe–Se bond is bridged by CH_2 groups, one on either side of the Fe_2Se_2 plane. Three carbonyl groups are terminally bonded to each Fe atom. The bonding of each Fe atom

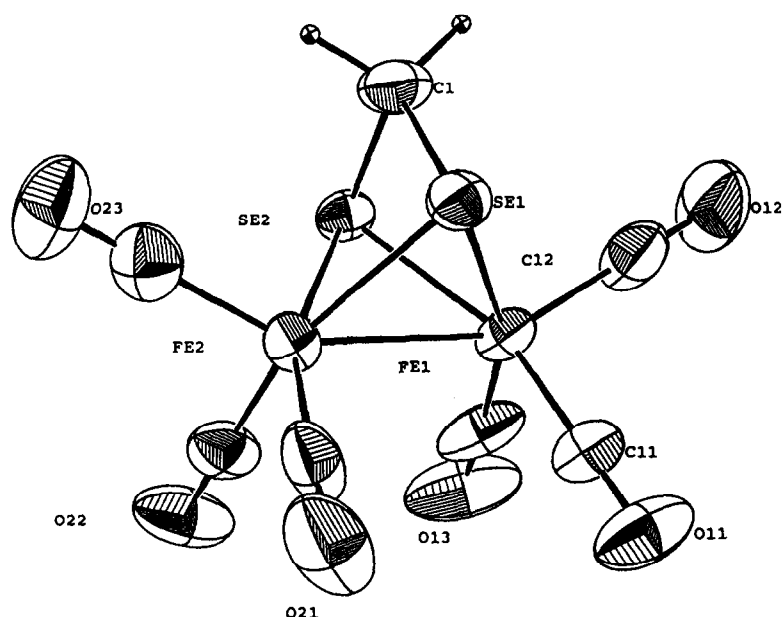


Fig. 2. ORTEP drawing of the molecular structure of **3** with thermal ellipsoids drawn at 50% probability.

to two Se atoms, one CH₂ group and three CO groups gives a distorted octahedral geometry around it. The Fe–Se bonds in **1** which are bridged by CH₂ groups, (Fe(1)–Se(2) = 2.3981(9) Å, Fe(2)–Se(1) = 2.3984(9) Å) are shorter than the unbridged Fe–Se bonds, (Fe(1)–Se(1) = 2.439(1) Å, Fe(2)–Se(2) = 2.437(1) Å). The average Fe–Se–Fe angle in compound **1** (98.3°) is larger than the average Fe–Se–Fe angle in (CO)₆Fe₂{μ-SeC(Ph)=C(H)Se} (63.6°), {(CO)₆Fe₂(μ-Se₂)₂-C(Ph)–C(H)} (64.5°), (CO)₆Fe₂(μ-SeCH₃)₂ (65.1°), (CO)₆Fe₂Se₂Pt(PPh₃)₂ (63.7°) [13].

The molecular structure of **3** is shown in Fig. 2. The structure consists of an Fe₂Se₂ butterfly core, and the CH₂ group is bridged between the wingtips of two Se atoms. Each Fe atom has three terminal carbonyl groups. Overall the structure of **3** is similar to that of (CO)₆Fe₂(μ-TeCH₂Te) and (CO)₆Fe₂(μ-SCH₂S) [6]. The average Fe–Se bond distance in **3** (2.379 Å) is somewhat longer than the average Fe–Se bond distances in {(CO)₆Fe₂(μ-Se₂)₂C(Ph)–C(H)} (2.368 Å) and shorter than the average Fe–Se bond distances in (CO)₆Fe₂{μ-SeC(Ph)=C(H)Se} (2.385 Å), {(CO)₅-Fe₂(μ-Se₂)₂C(Ph)–C(H)}(μ-dppe) (2.394 Å) [14], and (CO)₆Fe₂(μ-Se₂)Pt(PPh₃)₂ (2.401 Å). The average Fe–Se–Fe angle (64.1°) is larger than the average Fe–Te–Fe angle in (CO)₆Fe₂(μ-TeCH₂Te) (61.1°), (CO)₆Fe₂{μ-TeC(Ph)=C(H)Te} (61.3°) [15], (CO)₆Fe₂(μ-TeCH₃)₂ (62.3°) [16], and (CO)₆Fe₂(μ-Te(CH₂)₂Te) (62.6°) [17], indicating a larger degree of opening of the Fe₂Se₂ butterfly in **3**. The Se–C–Se bridging angle in **3** is

94.2(2)°, which is, similar to the S–C–S angle of 94.6(3)° reported for (CO)₆Fe₂(μ-SCH₂S) and more than the Te–C–Te angle of 92.1(4)° reported for (CO)₆Fe₂(μ-TeCH₂Te). The two bridging Se atoms, three carbonyl groups and the Fe–Fe bond define a distorted octahedral geometry around each Fe atom.

Fig. 3 shows the molecular structure of compound **4**. Its geometry can be described as consisting of an Fe₂Se₂ butterfly core with a CH₂–CH₂ group inserted between the Se atoms. Each Fe has three terminal carbonyl groups. The average Fe–Se bond distance in **4** (2.36 Å) is shorter than the average Fe–Se bond distance in {(CO)₆Fe₂(μ-Se₂)₂C(Ph)–C(H)} (2.37 Å) and (CO)₆Fe₂{μ-SeC(Ph)–C(H)Se} (2.3836 Å). The average Se–C bond length in **4** (1.965 Å) is slightly shorter than the average Se–C bond distance in {(CO)₆Fe₂(μ-Se₂)₂-C(Ph)–C(H)} (2.016 Å), but similar to the average Se–C bond distance in (CO)₆Fe₂{μ-SeC(Ph)=C(H)Se} (1.963 Å). The C–C bond distance in **4** (1.47 Å) is shorter than the C–C bond distance in (CO)₆Fe₂(μ-Te(CH₂)₂Te) (1.494 Å) and the average C–C bond distance in (CO)₆Fe₂(μ-Te(CH₂)₃Te) (1.483 Å). All other bond metrics are unexceptional.

4. Conclusion

The reaction of (CO)₉Fe₃(μ₃-Se₂) and (CO)₆Fe₂(μ-Se)₂ with the organic intermediate CH₂N₂ has been studied. In the reaction with diazomethane, four prod-

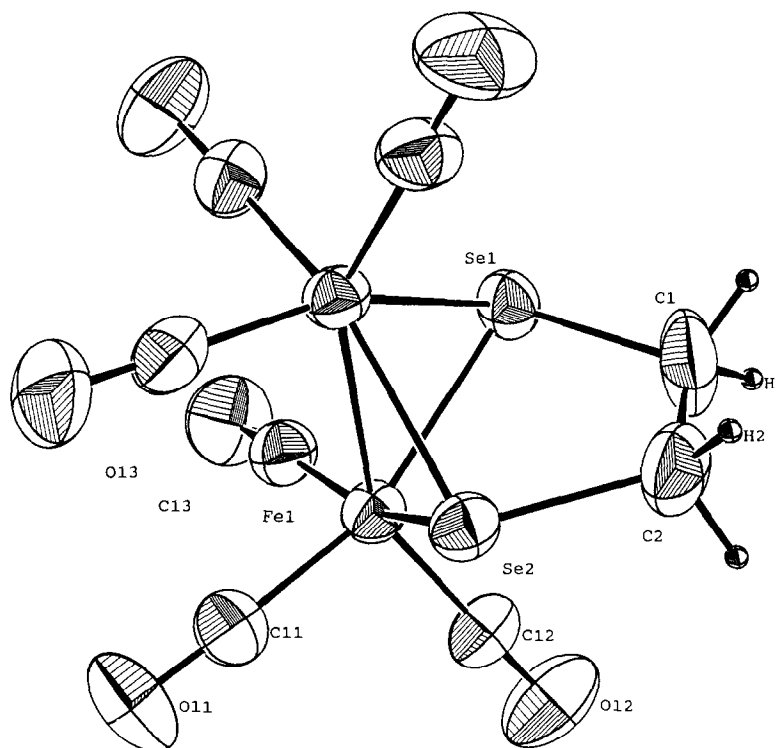


Fig. 3. ORTEP drawing of the molecular structure of **4** with thermal ellipsoids drawn at 50% probability.

ucts could be isolated, of which compound **1** represents the first example of an Fe–Se bond bridged by a methylene group. Although the coupling of methylene groups with alkynes on cluster compounds is well known [18], the coupling of two methylene groups in the formation of compound **4** is unusual [19].

Acknowledgments

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