

Synthesis, spectroscopic and structural characterisation of $(\text{CO})_6\text{Fe}_2\text{EE}'\{\mu\text{-C}(\text{H})(\text{CH}_3)\}_2$ and $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC}(\text{H})(\text{CH}_3)\text{E}'\}$ (E, E' = S, Se, Te)

Pradeep Mathur^{a,*}, Bala. Manimaran^a, C.V.V. Satyanarayana^b, Babu Varghese^c

^a Department of Chemistry, Indian Institute of Technology, Powai, Bombay, 400 076, India

^b Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Powai, Bombay, 400 076, India

^c Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras, 600 036, India

Received 20 April 1996; revised 19 June 1996

Abstract

Room temperature reaction of $(\text{CO})_6\text{Fe}_2(\mu\text{-EE}')$ (E ≠ E'; E, E' = S, Se, Te; E = E' = S, Se, Te) with diazoethane yielded two types of compound: $(\text{CO})_6\text{Fe}_2\text{EE}'\{\mu\text{-C}(\text{H})(\text{CH}_3)\}_2$ (1, 27%, E = E' = S; 2, 24%, E = S, E' = Se; 3, 21%, E = E' = Se; 5, 19%, E = S, E' = Te; 7, 12%, E = Se, E' = Te) and $(\text{CO})_6\text{Fe}_2\{\mu\text{-EC}(\text{H})(\text{CH}_3)\text{E}'\}$ (4, 13%, E = E' = Se; 6, 16%, E = S, E' = Te; 8, 22%, E = Se, E' = Te; 9, 28%, E = E' = Te). Compounds 1–9 were characterised by IR and ¹H, ¹³C, ⁷⁷Se and ¹²⁵Te NMR spectroscopy. Structures of 1, 3, 5, 8, and 9 were established by crystallographic methods. Compounds 1, 3, and 5 are isomorphic and isostructural and their structure consists of a distorted rhombus in which Fe and E (E = S, Se, Te) occupy adjacent corners. Two C(H)(CH₃) moieties bridge opposite Fe–E bonds and give roughly a chair conformation. Compounds 8 and 9 are isomorphic and isostructural and their structure consists of an Fe₂TeE (E = Se, Te) tetrahedral butterfly core containing a C(H)(CH₃) group as bridge between two wing-tips of chalcogen atoms.

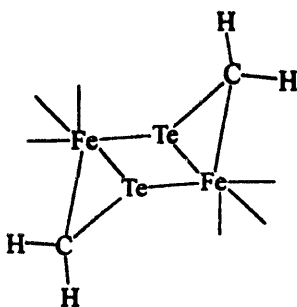
Keywords: Iron; Chalcogen; Diazoethane; Carbonyl; Crystal structure

1. Introduction

Metal alkylidene complexes have evinced considerable interest because they have been implicated as intermediates in many catalytic processes such as Fischer–Tropsch synthesis [1], olefin metathesis [2], alkene [3] and alkyne polymerisation [4], cyclopropanation of olefins [5] and methylenation of carbonyl compounds [6]. The possible involvement of methylene groups in carbon monoxide reduction on metal surfaces has led to interest in the synthesis of metal complexes containing bridging methylene groups [7]. Diazomethane is a convenient source of the CH₂ group, which can insert into a metal–metal bond by a process involving donation of the M–M bonding electron pair to the CH₂ of diazomethane and simultaneous loss of N₂ [8]. We have investigated the reaction of the metal–ditelluride com-

ound $(\text{CO})_6\text{Fe}_2(\mu\text{-Te}_2)$ with diazomethane and the structure of $(\text{CO})_6\text{Fe}_2(\mu\text{-TeCH}_2\text{Te})$ has been reported [9]. Insertion of the methylene group into the Te–Te bond of $(\text{CO})_6\text{Fe}_2(\mu\text{-Te}_2)$ is one of numerous examples of insertion of organic and inorganic moieties across the chalcogen–chalcogen bonds of $(\text{CO})_6\text{Fe}_2(\mu\text{-E}_2)$ (E = S, Se or Te) compounds, indicating that of the three types of bond in the Fe₂E₂ core, Fe–Fe, Fe–E and E–E, it is the E–E bond which is most susceptible to insertion. Convenient synthesis of the mixed-chalcogenide compounds $(\text{CO})_6\text{Fe}_2(\mu\text{-EE}')$ in recent times has provided the opportunity to investigate the reactivities of Fe–Fe, E–E', Fe–E and Fe–E' bonds in these compounds [10]. The reaction of $(\text{CO})_6\text{Fe}_2(\mu\text{-STe})$ with diazomethane yields, in addition to the expected $(\text{CO})_6\text{Fe}_2(\mu\text{-SCH}_2\text{Te})$, small amounts of another product resulting from a formal insertion of a methylene group into the Fe–Te bond, $\{(\text{CO})_3\text{Fe}(\mu\text{-CH}_2)\text{Te}\}_2$ (Fig. 1) [11]. In this paper we report on the reaction of diazoethane with the homochalcogenide compounds $(\text{CO})_6\text{Fe}_2(\mu\text{-E}_2)$ (E

* Corresponding author.

Fig. 1. $((\text{CO})_3\text{Fe}(\mu\text{-CH}_2)\text{Te})_2$.

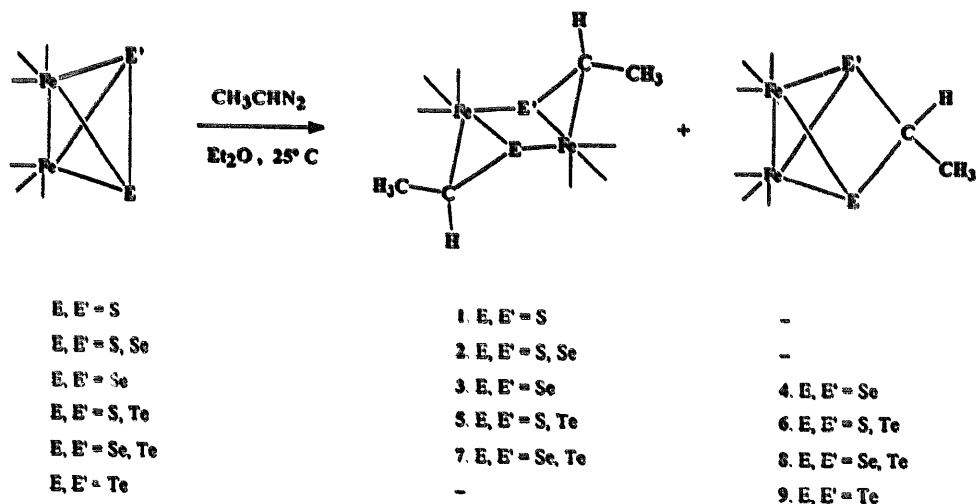
= S, Se, Te) and the mixed-chalcogenide compounds $(\text{CO})_6\text{Fe}_2(\mu\text{-EE}') (E \neq E'; E, E' = \text{S, Se, Te})$.

2. Results and discussion

When an ether solution containing $(\text{CO})_6\text{Fe}_2(\mu\text{-EE}') (E \neq E'; E, E' = \text{S, Se, Te}; E = E' = \text{S, Se, Te})$ was stirred at room temperature with diazoethane, two types of product were obtained: $(\text{CO})_6\text{Fe}_2\text{EE}'(\mu\text{-C(H)CH}_3)_2$ (1, $E, E' = \text{S}$; 2, $E = \text{S}, E' = \text{Se}$; 3, $E, E' = \text{Se}$; 5, $E = \text{S}, E' = \text{Te}$; 7, $E = \text{Se}, E' = \text{Te}$) and $(\text{CO})_6\text{Fe}_2(\mu\text{-EC(H)CH}_3)\text{E}'$ (4, $E, E' = \text{Se}$; 6, $E = \text{S}, E' = \text{Te}$; 8, $E = \text{Se}, E' = \text{Te}$; 9, $E, E' = \text{Te}$) (Scheme 1). All compounds are stable in solid form. In solution, compound 7 undergoes decomposition in dichloromethane over a period of hours, but the other compounds are stable. The products were characterised by IR and $^1\text{H}, ^{13}\text{C}, ^{77}\text{Se}$ and ^{125}Te NMR spectroscopy (Table 1). Compounds 1, 2, 3, 5 and 7 display an identical CO stretching pattern in their infrared spectra which is similar to that observed for the previously reported and structurally characterised $((\text{CO})_3\text{Fe}(\mu\text{-CH}_2)\text{Te})_2$ [11]. Similarly, 4, 6, 8 and 9 display a CO stretching pattern similar to that of $(\text{CO})_6\text{Fe}_2(\mu\text{-TeCH}_2\text{Te})$ [9]. ^{77}Se and ^{125}Te NMR spectra display Se–H and Te–H couplings

consistent with the bonding of a C(H)CH_3 group to these chalcogens. Assignment of ^{77}Se and ^{125}Te NMR signals is based on previous observations that the ^{125}Te NMR signal for the Fe–Te addition product $((\text{CO})_3\text{Fe}(\mu\text{-CH}_2)\text{Te})_2$ ($\delta -767$ ppm) is highfield relative to the signals for the E–Te inserted products $(\text{CO})_6\text{Fe}_2(\mu\text{-SCH}_2\text{Te})$ ($\delta 39$ ppm), $(\text{CO})_6\text{Fe}_2(\mu\text{-SeCH}_2\text{Te})$ ($\delta 146$ ppm) and $(\text{CO})_6\text{Fe}_2(\mu\text{-TeCH}_2\text{Te})$ ($\delta 336$ ppm). The ^{77}Se NMR signals between $\delta -276$ ppm and $\delta -304$ ppm can be assigned to the first type of compound $(\text{CO})_6\text{Fe}_2\text{SeE}(\mu\text{-C(H)CH}_3)_2$ (2, $E = \text{S}$; 3, $E = \text{Se}$; 7, $E = \text{Te}$) and the downfield signals appearing at $\delta 195$ ppm and $\delta 312$ ppm for the second type of compound $(\text{CO})_6\text{Fe}_2(\mu\text{-SeC(H)CH}_3)\text{E}$ (4, $E = \text{Se}$; 8, $E = \text{Te}$). Similarly, the highfield ^{125}Te NMR signals at $\delta -685$ ppm and $\delta -681$ ppm can be assigned to the compounds $(\text{CO})_6\text{Fe}_2\text{TeE}(\mu\text{-C(H)CH}_3)_2$ (5, $E = \text{S}$; 7, $E = \text{Se}$) and the downfield signals between $\delta 219$ ppm and $\delta 509$ ppm can be assigned to the compounds $(\text{CO})_6\text{Fe}_2(\mu\text{-EC(H)CH}_3)\text{E}$ (6, $E = \text{S}$; 8, $E = \text{Se}$; 9, $E = \text{Te}$).

Single crystals of 1, 3, 5, 8 and 9 were obtained and subjected to X-ray structural analysis. ORTEP representations (50% probability ellipsoids) of 1, 3, 5, 8 and 9 are shown in Figs. 2–6 respectively. Compounds 1, 3 and 5 are essentially isomorphous and isostructural; the core geometry consists of a heavy atom rhombus in which the Fe and chalcogen atoms occupy alternate corners. Each Fe atom is bonded to two chalcogen atoms, one C(H)CH_3 group and three terminal CO groups, which gives a distorted octahedral geometry around it. Two opposite Fe–chalcogen edges are bridged by a C(H)CH_3 group each, one on each side of the plane defined by the heavy atoms. Both methyl substituents in each molecule are oriented equatorially with respect to the FeEFeE plane. The iron, chalcogen and carbon six-membered structure assumes a chair conformation in compounds 1, 3 and 5. In each compound, the bridged Fe–chalcogen



Scheme 1. Formation of 1–9.

bonds are shorter than those which are unbridged. The E–Fe–E bond angles (79.7 to 82.1°) are smaller than the Fe–E–Fe angles (90.7 to 107.7°).

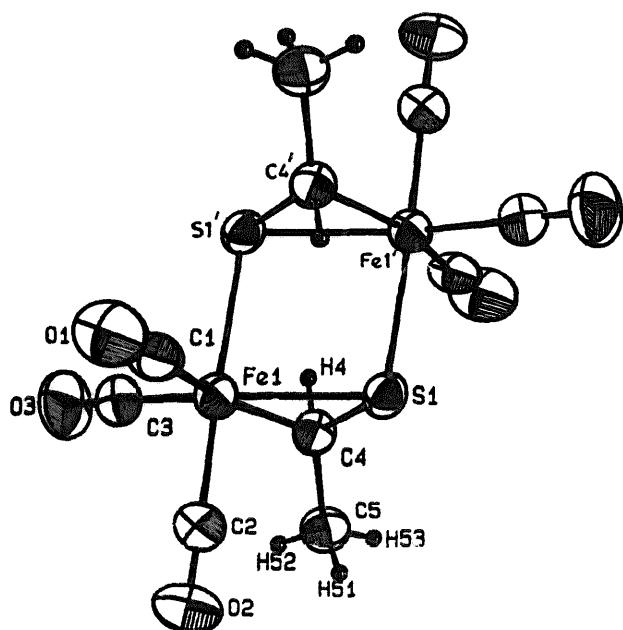
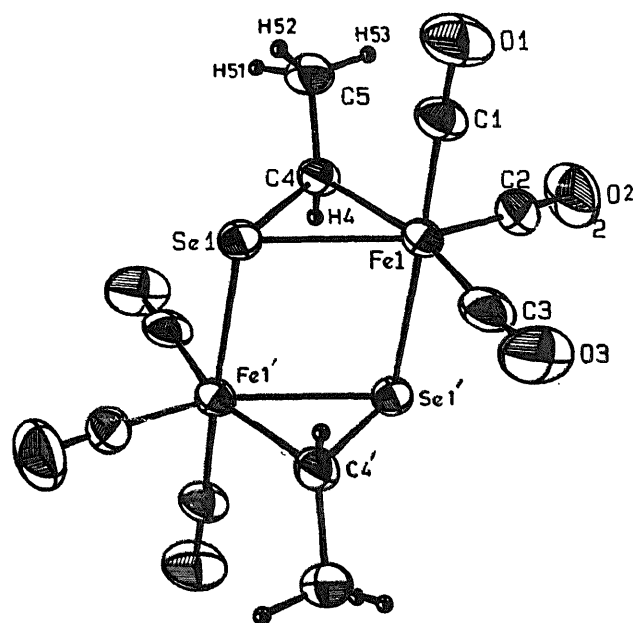
Compounds **8** and **9** are isomeric and isostructural. The core geometry in these compounds can be described as an open Fe₂EE butterfly tetrahedron, in which the chalcogen atoms are located at the wing-tips. The open edge of the Fe₂EE tetrahedron is bridged by a C(H)CH₃ group. Three terminally bonded carbonyl groups, the bridging chalcogen atoms and the Fe–Fe bond define a distorted octahedral geometry of each Fe

atom. Overall, the structures of **8** and **9** are similar to the previously reported methylene-bridged compounds (CO)₆Fe₂(μ-SeCH₂Te) [**10**] and (CO)₆Fe₂(μ-TeCH₂Te) [**9**]. The bond matrices of **8** and **9** are also similar to those of (CO)₆Fe₂(μ-SeCH₂Te) and (CO)₆Fe₂(μ-TeCH₂Te).

The formation of **1**, **2**, **3**, **5** and **7** formally occurs by the addition of C(H)CH₃ groups to the opposite Fe–E edges, and there is a cleavage of the Fe–Fe and E–E bonds. Since a chair conformation is obtained, the C(H)CH₃ groups approach the two wings of the Fe₂E₂

Table 1
Spectroscopic data for 1–9

Compound	IR (cm ⁻¹ , hexane)	¹ H NMR (δ, CDCl ₃)	¹³ C NMR (δ, CDCl ₃)	⁷⁷ Se NMR (δ, CDCl ₃)	¹²⁵ Te NMR (δ, CDCl ₃)
1	2068(w), 2053(s), 2048(m), 1998(s), 1963(w).	2.01 (CH ₃) d, J _{H-H} = 6.9 Hz; 5.06 (CH) q, J _{H-H} = 6.9 Hz.	27.5 (CH ₃) q, J = 128 Hz; 69.5 (CH) d, J = 164.5 Hz; 204.7, 207.5, 210.4 (CO)	—	—
2	2070(w), 2051(s), 1997(s), 1990(m), 1962(w).	2.02 (CH ₃) d, J _{H-H} = 6.6 Hz; 2.22(CH ₃) d, J _{H-H} = 7.2 Hz; 5.21(CH) q, J _{H-H} = 6.6 Hz; 5.88(CH) q, J _{H-H} = 7.5 Hz.	28.5 (CH ₃) q, J _{C-H} = 128 Hz; 29.4 (CH ₃) q, J _{C-H} = 127 Hz; 68.5(CH) d, J _{C-H} = 164 Hz; 76.9(CH) d, J _{C-H} = 163 Hz; 204.5, 205.2, 207.6, 208.6, 208.7, 211.5 (CO)	- 304.3, m	—
3	2064(w), 2050(s), 2044(m), 1994(s), 1958(w).	2.21 (CH ₃) d, J _{H-H} = 6.9 Hz; 6.05 (CH) q, J _{H-H} = 6.9 Hz.	30.1 (CH ₃) q, J = 128 Hz; 75.9 (CH) d, J = 163 Hz; 204.6, 208.8, 209.5 (CO)	- 300.5, m	—
4	2071(m), 2038(s), 2031(s), 2000(s), 1990(s), 1978(m), 1950(w).	1.9 (CH ₃) d, J _{H-H} = 6.9 Hz; 4.6 (CH) q, J _{H-H} = 6.9 Hz.	30.8 (CH ₃) q, J _{C-H} = 129 Hz; 45.2 (CH) d, J _{C-H} = 159.6 Hz 209.6, 209.8, (CO)	195.9, p, ³ J _{Se-H} = 10.6 Hz	—
5	2067(w), 2053(m), 2046(s), 1998(s), 1992(s), 1982(m).	1.99 (CH ₃) d, J _{H-H} = 6.6 Hz; 2.38 (CH ₃) d, J _{H-H} = 7.5 Hz; 5.31 (CH) q, J _{H-H} = 6.6 Hz; 6.69 (CH) q, J _{H-H} = 7.5 Hz.	29.7 (CH ₃) q, J _{C-H} = 129 Hz; 31.4 (CH ₃) q, J _{C-H} = 128 Hz; 66.2 (CH) d, J _{C-H} = 164 Hz; 74.5 (CH) d, J _{C-H} = 158 Hz, 203.4, 205.7, 206.3, 208.6, 210.2, 213.0 (CO)	—	- 684.7, m
6	2069(m), 2028(s), 2000(s), 1987(s), 1981(m), 1975(m), 1947(w).	1.83 (CH ₃) d, J _{H-H} = 6.9 Hz; ³ J _{Te-H} = 18.1 Hz; 4.15 (CH) q, J _{H-H} = 6.9 Hz. ² J _{Te-H} = 28.5 Hz	24.7 (CH) d, J _{C-H} = 158.1 Hz; 30.3 (CH ₃) q, J _{C-H} = 129.2 Hz; 209.9, 210.2 (CO)	—	219.7, qd, ³ J _{Te-H} = 18.3 Hz; ² J _{Te-H} = 29.4 Hz;
7	2064(w), 2049(m), 2046(s), 1993(s), 1984(m), 1958(w).	2.20 (CH ₃) d, J _{H-H} = 6.9 Hz; 2.39 (CH ₃) d, J _{H-H} = 7.5 Hz; 6.17 (CH) q, J _{H-H} = 6.9 Hz; 6.89 (CH) q, J _{H-H} = 5.7 Hz.	31.71 (CH ₃) q, J _{C-H} = 128 Hz; 32.41 (CH ₃) q, J _{C-H} = 128 Hz; 73.7 (CH) d, J _{C-H} = 162 Hz; 74.0 (CH) d, J _{C-H} = 158 Hz; 203.4, 205.9, 205.9, 209.9, 210.5, 211.2 (CO)	- 276.2, m	- 681.0, m
8	2066(m), 2026(s), 1997(s), 1986(s), 1977(m), 1973(m), 1944(w).	1.96 (CH ₃) d, J _{H-H} = 6.9 Hz; ³ J _{Te-H} = 20.4 Hz; 3.97 (CH) q, J _{H-H} = 6.9 Hz; ² J _{Te-H} = 29.4 Hz;	5.67 (CH) d, J _{C-H} = 158.3 Hz; 30.45 (CH ₃) q, J _{C-H} = 129.2 Hz; 210.6, 210.8 (CO)	312.8 p, ³ J _{Se-H} = 11.4 Hz;	330.3, qd, ³ J _{Te-H} = 20.6 Hz; ² J _{Te-H} = 29.3 Hz
9	2060(m), 2021(s), 1993(s), 1982(s), 1970(m), 1942(w).	2.06 (CH ₃) d, J _{H-H} = 7.2 Hz; ³ J _{Te-H} = 22.4 Hz; 3.26 (CH) q, J _{H-H} = 7.2 Hz; ² J _{Te-H} = 28.8 Hz;	- 37.3 (CH) d, J _{C-H} = 156.3 Hz; 30.2 (CH ₃) q, J _{C-H} = 129.2 Hz; 211.8, 212.1 (CO)	—	509.3, qd, ³ J _{Te-H} = 22.9 Hz; ² J _{Te-H} = 28.9 Hz

Fig. 2. Molecular structure of $(\text{CO})_6\text{Fe}_2\text{S}_2(\mu\text{-C(H)CH}_3)_2$ 1.Fig. 3. Molecular structure of $(\text{CO})_6\text{Fe}_2\text{Se}_2(\mu\text{-C(H)CH}_3)_2$ 3.

butterfly structure from opposite sides. The formation of 4, 6, 8 and 9 formally involves the cleavage of the E–E bond and addition of one C(H)CH₃ group across the open E–E edge of the Fe₂E₂ butterfly tetrahedron. Although the exact mechanistic information is not known at present, contrast in the reactivities of Fe–chalcogen and chalcogen–chalcogen bonds is apparent from our present study. For the smaller chalcogen combination, i.e. E, E' = S, S or S, Se, insertion of the C(H)CH₃ group into the chalcogen–chalcogen bonds is not observed, whereas for the larger chalcogen combi-

nation, i.e. E, E' = Te, Te, addition of the C(H)CH₃ group to the Fe–Te bonds is not observed. Further studies are currently in progress to provide an insight into the two types of addition reaction reported here.

3. Experimental

3.1. General procedures

All reactions and other manipulations were performed using standard Schlenk techniques under an

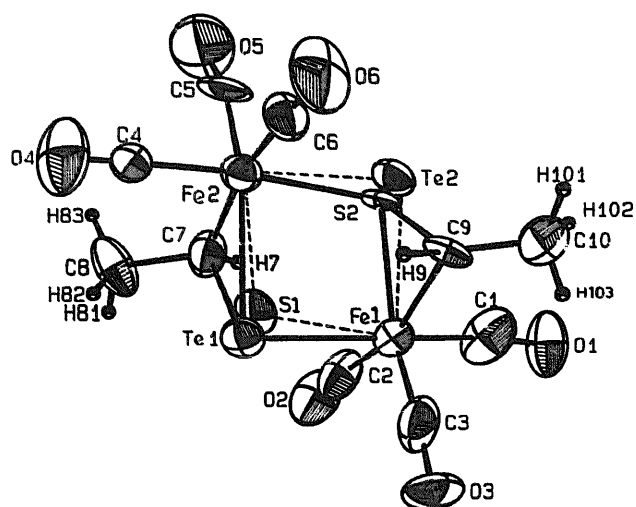
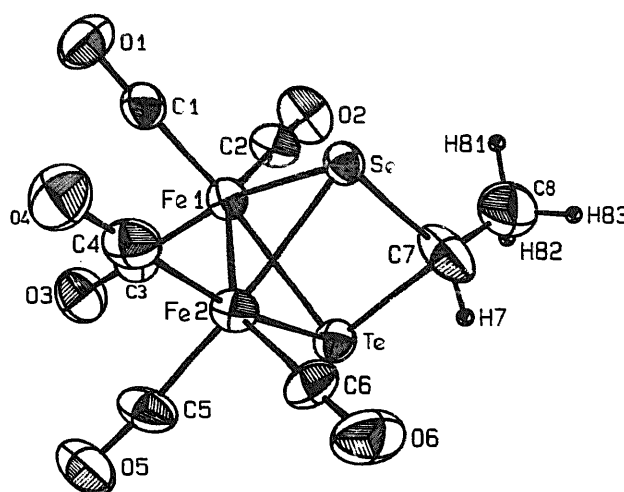
Table 2

Preparation of $(\text{CO})_6\text{Fe}_2\text{EE}'(\mu\text{-C(H)CH}_3)_2$ (E ≠ E'; E, E' = S, Se, Te; E = E' = S, Se) and $(\text{CO})_6\text{Fe}_2(\mu\text{-EC(H)CH}_3)_2$ (E ≠ E'; E = S, Se and E' = Te; E = E' = Se, Te)

Compound	$(\text{CO})_6\text{Fe}_2(\mu\text{-EE}')$ (mg (mmol))	Product	Colour	Yield (mg (%))	Analysis ^a		M.p. (°C)
					C	H	
1	$(\text{CO})_6\text{Fe}_2(\mu\text{-S}_2)$ 250 (0.727)	$(\text{CO})_6\text{Fe}_2\text{S}_2(\mu\text{-C(H)CH}_3)_2$	Yellow–orange	80 (27)	30.0 (29.9)	2.00 (1.96)	131–133 ^b
2	$(\text{CO})_6\text{Fe}_2(\mu\text{-SSe})$ 250 (0.639)	$(\text{CO})_6\text{Fe}_2\text{SSe}(\mu\text{-C(H)CH}_3)_2$	Light orange	70 (24)	26.9 (26.6)	1.79 (1.62)	124–126 ^b
3	$(\text{CO})_6\text{Fe}_2(\mu\text{-Se}_2)$ 250 (0.571)	$(\text{CO})_6\text{Fe}_2\text{Se}_2(\mu\text{-C(H)CH}_3)_2$	Orange	60 (21)	24.3 (24.6)	1.62 (1.71)	135–137 ^b
4	$(\text{CO})_6\text{Fe}_2(\mu\text{-Se}_2)$ 250 (0.571)	$(\text{CO})_6\text{Fe}_2(\mu\text{-SeC(H)CH}_3)\text{Se}$	Orange	35 (13)	20.6 (20.8)	0.85 (0.91)	76–78
5	$(\text{CO})_6\text{Fe}_2(\mu\text{-STe})$ 250 (0.569)	$(\text{CO})_6\text{Fe}_2\text{STe}(\mu\text{-C(H)CH}_3)_2$	Dark orange	55 (19)	24.2 (24.1)	1.61 (1.58)	121–123 ^b
6	$(\text{CO})_6\text{Fe}_2(\mu\text{-STe})$ 250 (0.569)	$(\text{CO})_6\text{Fe}_2(\mu\text{-SC(H)CH}_3)\text{Te}$	Dark orange	45 (16)	20.5 (20.7)	0.85 (0.94)	82–84
7	$(\text{CO})_6\text{Fe}_2(\mu\text{-SeTe})$ 250 (0.514)	$(\text{CO})_6\text{Fe}_2\text{SeTe}(\mu\text{-C(H)CH}_3)_2$	Orange–red	35 (12)	22.1 (22.3)	1.47 (1.54)	128–130 ^b
8	$(\text{CO})_6\text{Fe}_2(\mu\text{-SeTe})$ 250 (0.514)	$(\text{CO})_6\text{Fe}_2(\mu\text{-SeC(H)CH}_3)\text{Te}$	Orange–red	60 (22)	18.7 (18.9)	0.77 (0.79)	99–101
9	$(\text{CO})_6\text{Fe}_2(\mu\text{-Te}_2)$ 250 (0.467)	$(\text{CO})_6\text{Fe}_2(\mu\text{-TeC(H)CH}_3)\text{Te}$	Orange–red	75 (28)	17.1 (17.4)	0.71 (0.78)	106–108

^a Calculated values are given in parentheses.

^b With decomposition.

Fig. 4. Molecular structure of $(\text{CO})_6\text{Fe}_2\text{STe}(\mu\text{-C(H)CH}_3)_2$ 5.Fig. 5. Molecular structure of $(\text{CO})_6\text{Fe}_2[\mu\text{-SeC(H)CH}_3]\text{Te}$ 8.

atmosphere of pre-purified dry argon. The solvents were purified, dried and distilled under nitrogen atmosphere prior to use. Infrared spectra were recorded on a Nicolet Impact 400 FT spectrometer as hexane solutions in

0.1 mm pathlength NaCl cells. NMR spectra were 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 acquisition time and the spectra were referenced to

Table 3
Crystal data and details of measurements for 1, 3, 5, 8 and 9

Compound	1	3	5	8	9
Formula	$\text{C}_{10}\text{H}_8\text{Fe}_2\text{S}_2\text{O}_6$	$\text{C}_{10}\text{H}_8\text{Fe}_2\text{Se}_2\text{O}_6$	$\text{C}_{10}\text{H}_8\text{Fe}_2\text{STeO}_6$	$\text{C}_8\text{H}_4\text{Fe}_2\text{SeTeO}_6$	$\text{C}_8\text{H}_4\text{Fe}_2\text{Te}_2\text{O}_6$
FW	399.99	493.79	495.53	514.37	563.01
Crystal system	triclinic	triclinic	triclinic	monoclinic	monoclinic
<i>a</i> (Å)	6.412(2)	6.552(1)	6.635(1)	6.813(2)	6.938(4)
<i>b</i> (Å)	7.269(1)	7.249(2)	7.327(2)	13.264(5)	13.370(2)
<i>c</i> (Å)	8.841(2)	8.878(2)	8.853(2)	15.194(8)	15.170(6)
α (deg)	65.91(2)	113.14(2)	112.74(2)	—	—
β (deg)	77.25(2)	99.07(2)	99.26(1)	95.67(3)	95.28(4)
γ (deg)	84.75(2)	94.84(2)	95.28(2)	—	—
<i>V</i> (Å ³)	366.88(16)	377.92(40)	386.10(36)	1366.33(9)	1401.3(9)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
<i>Z</i>	1	1	1	4	4
D_{calc} (g cm ⁻³)	1.810	2.170	2.131	2.500	2.669
$F(000)$	200	236	236	952	1024
Crystal size dimensions (mm ³)	$0.3 \times 0.2 \times 0.2$	$0.3 \times 0.2 \times 0.3$	$0.3 \times 0.3 \times 0.2$	$0.2 \times 0.3 \times 0.2$	$0.2 \times 0.2 \times 0.3$
μ (cm ⁻¹)	22.7	67.1	38.8	68.7	61.8
<i>hkl</i> ranges	0 to 7, -8 to 8, -10 to 10	0 to 7, -8 to 8, -10 to 10	0 to 7, -8 to 8, -10 to 10	0 to 8, 0 to 15, -18 to 17	0 to 8, 0 to 15, -18 to 17
Unique observed reflections	1423	1457	1488	2606	2796
Maximum transmission factor (%)	99.90	95.70	99.92	97.20	100.00
Minimum transmission factor (%)	78.05	58.50	46.30	63.40	43.89
Unique observed reflections with $[F_o^2 \geq 3\sigma(F_o^2)]$	1336	1272	1344	1441	2230
No. of refined parameters	91	92	196	163	163
Final difference electron density (e Å ⁻³)	0.2	0.4	0.2	0.5	0.2
Maximum shift/error	0.03	0.02	1.43	0.99	0.03
<i>R</i>	0.024	0.040	0.029	0.048	0.028
<i>wR</i>	0.041	0.052	0.043	0.064	0.048

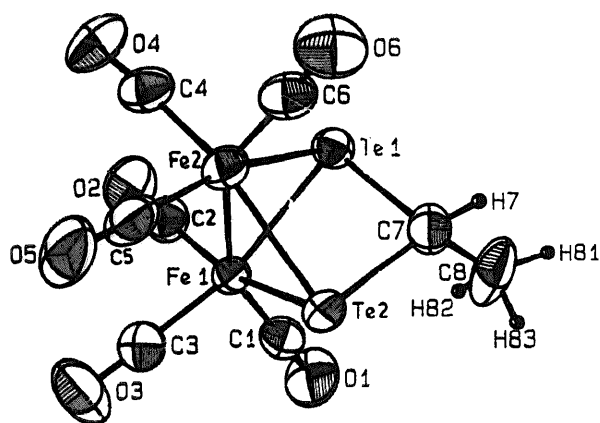


Fig. 6. Molecular structure of $(\text{CO})_6\text{Fe}_2(\mu\text{-TeC}(\text{H})\text{CH}_3)\text{Te}$ 9.

Me_2Se ($\delta = 0$). ^{125}Te NMR spectra were referenced to an external standard of Me_2Te ($\delta = 0$) and the spectra were obtained at an operating frequency of 94.6 MHz using 90° pulses with 1.0 s delay and 1.0 s acquisition time. Elemental analyses were carried out using a Carlo

Table 4
Atomic coordinates and isotropic displacement coefficients for 1

Atom	x	y	z	$B(\text{\AA}^2)$
Fe(1)	0.2000(4)	0.38968(3)	0.39307(2)	2.614(6)
S(1)	0.14397(8)	0.67781(6)	0.44112(5)	2.743(9)
O(1)	0.3478(3)	0.0362(3)	0.6613(2)	5.90(5)
O(2)	0.6420(3)	0.4709(3)	0.2089(2)	5.00(4)
O(3)	0.1014(3)	0.2319(2)	0.1614(2)	6.17(4)
C(1)	0.2881(4)	0.1738(3)	0.5613(2)	3.71(5)
C(2)	0.4703(3)	0.4412(3)	0.2799(2)	3.35(4)
C(3)	0.1412(4)	0.2873(3)	0.2546(2)	3.68(4)
C(4)	0.1102(3)	0.6752(3)	0.2506(2)	2.85(4)
C(5)	0.2509(4)	0.8098(3)	0.0888(2)	3.89(5)

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

Table 5
Atomic coordinates and isotropic displacement coefficients for 3

Atom	x	y	z	$B(\text{\AA}^2)$
Se(1)	0.15383(7)	0.36933(6)	0.55617(5)	2.450(9)
Fe(1)	0.2003(1)	0.72534(8)	0.61618(7)	2.35(1)
O(1)	0.6381(6)	0.8205(6)	0.7955(5)	5.0(1)
O(2)	0.1004(7)	1.1058(5)	0.8469(5)	5.6(1)
O(3)	0.3345(7)	0.8168(6)	0.3471(4)	5.4(1)
C(1)	0.4655(8)	0.7809(7)	0.7264(5)	3.2(1)
C(2)	0.1389(8)	0.9614(7)	0.7553(6)	3.4(1)
C(3)	0.2790(8)	0.7775(7)	0.4481(6)	3.5(1)
C(4)	0.1113(7)	0.5782(6)	0.7574(5)	2.60(9)
C(5)	0.2478(9)	0.6070(7)	0.9205(5)	3.5(1)

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

Table 6
Atomic coordinates and isotropic displacement coefficients for 5

Atom	x	y	z	$B(\text{\AA}^2)$
Te(1)	0.574	0.408	0.836	3.33(2)
Te(2)	0.2257(1)	0.7136(1)	0.72392(9)	3.37(2)
Fe(1)	0.2023(1)	0.3340(1)	0.6617(1)	3.19(2)
Fe(2)	0.5975(1)	0.7849(1)	0.89900(9)	3.25(2)
S(1)	0.5315(4)	0.4530(5)	0.8399(4)	3.71(6)
S(2)	0.2693(5)	0.6610(3)	0.7258(3)	3.17(6)
O(1)	-0.2302(8)	0.2645(9)	0.4972(7)	6.9(2)
O(2)	0.065(1)	0.255(1)	0.9278(7)	8.3(2)
O(3)	0.306(1)	-0.0313(9)	0.4171(7)	7.2(2)
O(4)	1.0278(8)	0.9008(8)	1.0939(6)	5.6(1)
O(5)	0.499(1)	1.1590(6)	1.1195(8)	7.8(2)
O(6)	0.7246(9)	0.8907(7)	0.6295(5)	6.0(1)
C(1)	-0.061(1)	0.2797(9)	0.5505(8)	4.5(1)
C(2)	0.113(1)	0.2885(9)	0.8306(6)	4.0(1)
C(3)	0.277(1)	0.0996(8)	0.5187(7)	3.7(1)
C(4)	0.858(1)	0.843(1)	1.0115(7)	4.6(2)
C(5)	0.553(1)	1.010(1)	1.031(1)	6.2(2)
C(6)	0.664(1)	0.850(1)	0.736(1)	5.2(2)
C(7)	0.5166(7)	0.6306(7)	1.0317(6)	2.7(1)
C(8)	0.655(1)	0.6526(8)	1.1971(6)	4.9(1)
C(9)	0.299(1)	0.4752(7)	0.5145(7)	3.8(1)
C(10)	0.165(1)	0.447(1)	0.359(1)	5.6(2)

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

Atoms Te(1), Te(2), S(1), S(2) have 50% site occupancy each. The Te(1) position is not refined for fixing the origin in the $P1$ system.

Erba automatic analyser. $(\text{CO})_6\text{Fe}_2(\mu\text{-EE}') (E \neq E'; E, E' = \text{S, Se, Te and } E, E' = \text{S, Se, Te})$ were prepared as reported in the literature [12].

Table 7
Atomic coordinates and isotropic displacement coefficients for 8

Atom	x	y	z	$B(\text{\AA}^2)$
Te	0.1875(1)	0.80712(8)	0.26921(7)	4.21(2)
Se	-0.2408(2)	0.7746(1)	0.20381(9)	3.31(3)
Fe(1)	-0.0021(3)	0.8616(1)	0.1252(1)	3.33(4)
Fe(2)	0.0319(3)	0.6738(1)	0.1658(1)	3.51(4)
O(1)	-0.254(2)	0.8484(9)	-0.0417(7)	6.4(3)
O(2)	-0.061(2)	1.0721(8)	0.1657(8)	7.0(3)
O(3)	0.351(1)	0.878(1)	0.0320(8)	7.4(3)
O(4)	-0.181(2)	0.5897(9)	0.0051(8)	6.4(3)
O(5)	0.407(1)	0.6176(9)	0.1023(8)	7.0(3)
O(6)	0.003(2)	0.5100(8)	0.2932(8)	6.7(3)
C(1)	-0.156(2)	0.854(1)	0.024(1)	4.4(3)
C(2)	-0.038(2)	0.9883(9)	0.148(1)	4.3(3)
C(3)	0.214(2)	0.874(1)	0.069(1)	4.5(3)
C(4)	-0.099(2)	0.623(1)	0.068(1)	4.7(3)
C(5)	0.262(2)	0.638(1)	0.132(1)	5.2(4)
C(6)	0.015(2)	0.574(1)	0.2421(9)	4.1(3)
C(7)	-0.096(2)	0.803(1)	0.323(1)	6.7(4)
C(8)	-0.154(3)	0.888(2)	0.367(1)	8.4(5)

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

Table 8
Atomic coordinates and isotropic displacement coefficients for 9

Atom	x	y	z	B(Å ²)
Te(1)	0.25696(5)	0.27280(3)	0.29605(3)	3.292(8)
Te(2)	-0.17839(6)	0.30568(3)	0.23346(2)	3.305(8)
Fe(1)	0.0052(1)	0.36170(6)	0.37759(5)	3.01(2)
Fe(2)	-0.0304(1)	0.17260(6)	0.33773(6)	3.23(2)
O(1)	0.0648(9)	0.5719(4)	0.3356(4)	6.9(1)
O(2)	0.2535(9)	0.3506(5)	0.5430(3)	6.4(1)
O(3)	-0.3443(8)	0.3781(5)	0.4692(4)	7.6(2)
O(4)	0.1771(8)	0.0916(4)	0.4996(4)	6.4(1)
O(5)	-0.3995(8)	0.1195(4)	0.4023(4)	7.5(1)
O(6)	-0.0061(9)	0.0111(4)	0.2094(4)	6.2(1)
C(1)	0.044(1)	0.4894(5)	0.3514(4)	4.3(1)
C(2)	0.157(1)	0.3544(5)	0.4790(4)	4.1(1)
C(3)	-0.209(1)	0.3736(5)	0.4323(5)	4.5(2)
C(4)	0.100(1)	0.1233(5)	0.4362(5)	4.3(1)
C(5)	-0.256(1)	0.1423(5)	0.3773(5)	4.6(1)
C(6)	-0.0156(9)	0.0734(5)	0.2591(4)	4.0(1)
C(7)	0.090(1)	0.3069(5)	0.1723(4)	4.1(1)
C(8)	0.141(1)	0.3965(7)	0.1263(5)	16.9(2)

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

3.2. Typical preparation of $(CO)_6Fe_2EE'\{\mu-C(H)CH_3\}_2$ ($E \neq E'$; $E, E' = S, Se, Te$; $E = E' = S, Se$) and $(CO)_6Fe_2\{\mu-EC(H)(CH_3)E'\}$ ($E \neq E'$; $E = S, Se$; $E' = Te$ and $E = E' = Se, Te$)

N-ethyl-N-nitroso-p-toluene sulphonamide was prepared by the action of ethyl amine and nitrous acid on toluene-p-sulphonyl chloride. Diazoethane was prepared by dissolving 2.28 g of N-ethyl-N-nitroso-p-toluene sulphonamide in 30 ml of diethyl ether. The solution

Table 9
Bond distances (Å) and bond angles (deg) for 1

Fe(1)–S(1)	2.2841(6)	S(1)–C(4)	1.753(2)
Fe(1)–S(1Y)	2.3318(5)	O(1)–C(1)	1.134(2)
Fe(1)–C(1)	1.816(2)	O(2)–C(2)	1.131(2)
Fe(1)–C(2)	1.787(2)	O(3)–C(3)	1.135(3)
Fe(1)–C(3)	1.787(3)	C(4)–C(5)	1.505(2)
Fe(1)–C(4)	2.047(2)		
S(1)–Fe(1)–S(1Y)	81.07(2)	C(2)–Fe(1)–C(3)	91.9(1)
S(1)–Fe(1)–C(1)	115.17(8)	C(2)–Fe(1)–C(4)	90.72(8)
S(1)–Fe(1)–C(2)	96.92(7)	C(3)–Fe(1)–C(4)	93.32(8)
S(1)–Fe(1)–C(3)	139.52(6)	Fe(1)–S(1)–Fe(1Y)	98.93(2)
S(1)–Fe(1)–C(4)	47.35(6)	Fe(1)–S(1)–C(4)	59.22(6)
S(1Y)–Fe(1)–C(1)	87.07(7)	Fe(1)–S(1Y)–C(4Y)	102.62(7)
S(1Y)–Fe(1)–C(2)	175.56(7)	Fe(1)–C(1)–O(1)	177.1(2)
S(1Y)–Fe(1)–C(3)	92.16(7)	Fe(1)–C(2)–O(2)	179.0(2)
S(1Y)–Fe(1)–C(4)	90.80(5)	Fe(1)–C(3)–O(3)	176.5(2)
C(1)–Fe(1)–C(2)	90.24(9)	Fe(1)–C(4)–S(1)	73.43(6)
C(1)–Fe(1)–C(3)	104.2(1)	Fe(1)–C(4)–C(5)	122.4(1)
C(1)–Fe(1)–C(4)	162.5(1)	S(1)–C(4)–C(5)	118.2(2)

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

Table 10
Bond distances (Å) and bond angles (deg) for 3

Se(1)–Fe(1)	2.4025(7)	Fe(1)–C(4)	2.055(5)
Se(1Y)–Fe(1)	2.4458(7)	O(1)–C(1)	1.151(6)
Se(1)–C(4)	1.914(4)	O(2)–C(2)	1.123(6)
Fe(1)–C(1)	1.782(5)	O(3)–C(3)	1.142(7)
Fe(1)–C(2)	1.797(4)	C(4)–C(5)	1.504(6)
Fe(1)–C(3)	1.813(6)		
Fe(1)–Se(1)–Fe(1Y)	97.87(3)	C(1)–Fe(1)–C(2)	93.0(2)
Fe(1)–Se(1)–C(4)	55.5(1)	C(1)–Fe(1)–C(3)	91.1(2)
Fe(1)–Se(1Y)–C(4Y)	100.7(1)	C(1)–Fe(1)–C(4)	91.3(2)
Se(1)–Fe(1)–Se(1Y)	82.13(2)	C(2)–Fe(1)–C(3)	105.0(2)
Se(1)–Fe(1)–C(1)	95.8(2)	C(2)–Fe(1)–C(4)	92.0(2)
Se(1)–Fe(1)–C(2)	141.1(2)	C(3)–Fe(1)–C(4)	162.8(2)
Se(1)–Fe(1)–C(3)	112.6(1)	Fe(1)–C(1)–O(1)	178.0(5)
Se(1)–Fe(1)–C(4)	50.1(1)	Fe(1)–C(2)–O(2)	177.2(5)
Se(1Y)–Fe(1)–C(1)	175.2(1)	Fe(1)–C(3)–O(3)	177.2(4)
Se(1Y)–Fe(1)–C(2)	91.3(2)	Se(1)–C(4)–Fe(1)	74.4(2)
Se(1Y)–Fe(1)–C(3)	85.7(1)	Se(1)–C(4)–C(5)	117.9(3)
Se(1Y)–Fe(1)–C(4)	90.7(1)	Fe(1)–C(4)–C(5)	121.7(3)

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

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 directly into the reaction flask [13] (the procedure given for the preparation of precursor of diazomethane was adopted in the diazoethane precursor preparation with appropriate reagents and conditions). Conditions used for the preparation of 1–9 are summarized in Table 2. In a typical preparation, to a solution of $(CO)_6Fe_2(\mu-EE')$ ($E \neq E'$; $E, E' = S, Se, Te$; $E = E' = S, Se, Te$) in dry diethyl ether was added dropwise an ethereal solution of diazoethane. Addition of diazoethane was continued until TLC and IR indicated total consumption of the starting material $(CO)_6Fe_2(\mu-EE')$. The reaction mixture was stirred at room temperature for a further 10 min. The solution was filtered through Celite and the solvent was evaporated in vacuo. The mixture was redissolved in hexane and subjected to chromatographic work-up on silica gel TLC plates to yield pure products. When E, E' combinations were S, S or S, Se, in each case only one product was obtained, $(CO)_6Fe_2S_2\{\mu-C(H)CH_3\}_2$ (1) and $(CO)_6Fe_2SSe\{\mu-C(H)CH_3\}_2$ (2) respectively. When the E, E' combination was Te, Te, again a single product was obtained, $(CO)_6Fe_2\{\mu-TeC(H)(CH_3)Te\}$ (9). For other chalcogen combinations, two products were obtained in each case; the first band to elute was $(CO)_6Fe_2EE'\{\mu-C(H)CH_3\}_2$ and the second band $(CO)_6Fe_2\{\mu-EC(H)(CH_3)E'\}$.

3.3. Crystal structure determination of 1, 3, 5, 8 and 9

Crystals of 1, 3, 5, 8 and 9 suitable for X-ray diffraction analysis were grown from a dichloromethane and hexane solvent mixture by slow evaporation of the

solvent mixture at 0°C. The data were measured at 300 K on an Enraf–Nonius CAD4 diffractometer generating Mo K α ($\lambda = 0.71073 \text{ \AA}$) radiation in the range

Table 11
Bond distances (\AA) and bond angles (deg) for 5

Te(1)–Fe(1)	2.5769(8)	Fe(2)–C(4)	1.773(7)
Te(1)–Fe(2)	2.5814(9)	Fe(2)–C(5)	1.701(7)
Te(1)–C(7)	1.987(4)	Fe(2)–C(6)	1.79(1)
Te(2)–Fe(1)	2.602(1)	Fe(2)–C(7)	2.016(6)
Te(2)–Fe(2)	2.582(1)	S(1)–C(7)	1.719(5)
Te(2)–C(9)	2.161(6)	S(2)–C(9)	1.895(6)
Fe(1)–S(1)	2.344(2)	O(1)–C(1)	1.123(8)
Fe(1)–S(2)	2.220(2)	O(2)–C(2)	1.07(1)
Fe(1)–C(1)	1.788(6)	O(3)–C(3)	1.091(8)
Fe(1)–C(2)	1.825(7)	O(4)–C(4)	1.179(8)
Fe(1)–C(3)	1.863(5)	O(5)–C(5)	1.194(9)
Fe(1)–C(9)	2.091(7)	O(6)–C(6)	1.21(1)
Fe(2)–S(1)	2.264(3)	C(7)–C(8)	1.539(8)
Fe(2)–S(2)	2.325(3)	C(9)–C(10)	1.45(1)
Fe(1)–Te(1)–Fe(2)	90.73(3)	S(1)–Fe(1)–C(3)	94.2(2)
Fe(1)–Te(1)–C(7)	93.8(1)	S(1)–Fe(1)–C(9)	88.9(2)
Fe(2)–Te(1)–C(7)	50.3(2)	S(2)–Fe(1)–C(1)	99.6(2)
Fe(1)–Te(2)–Fe(2)	90.13(4)	S(2)–Fe(1)–C(2)	110.7(2)
Fe(1)–Te(2)–C(9)	51.0(2)	S(2)–Fe(1)–C(3)	137.6(2)
Fe(2)–Te(2)–C(9)	91.8(2)	S(2)–Fe(1)–C(9)	52.1(2)
Te(1)–Fe(1)–Te(2)	89.40(3)	C(1)–Fe(1)–C(2)	89.1(3)
Te(1)–Fe(1)–S(1)	8.95(8)	C(1)–Fe(1)–C(3)	95.5(3)
Te(1)–Fe(1)–S(2)	81.74(8)	C(1)–Fe(1)–C(9)	92.1(3)
Te(1)–Fe(1)–C(1)	176.5(2)	C(2)–Fe(1)–C(3)	108.9(3)
Te(1)–Fe(1)–C(2)	87.4(2)	C(2)–Fe(1)–C(9)	162.7(2)
Te(1)–Fe(1)–C(3)	85.6(2)	C(3)–Fe(1)–C(9)	88.2(3)
Te(1)–Fe(1)–C(9)	91.2(2)	Te(1)–Fe(2)–Te(2)	89.74(3)
Te(2)–Fe(1)–S(1)	81.06(9)	Te(1)–Fe(2)–S(1)	7.51(7)
Te(2)–Fe(1)–S(2)	7.94(8)	Te(1)–Fe(2)–S(2)	79.73(7)
Te(2)–Fe(1)–C(1)	91.8(2)	Te(1)–Fe(2)–C(4)	92.8(2)
Te(2)–Fe(1)–C(2)	109.2(2)	Te(1)–Fe(2)–C(5)	145.2(4)
Te(2)–Fe(1)–C(3)	141.3(2)	Te(1)–Fe(2)–C(6)	114.2(2)
Te(2)–Fe(1)–C(9)	53.5(1)	Te(1)–Fe(2)–C(7)	49.4(1)
S(1)–Fe(1)–S(2)	73.5(1)	Te(2)–Fe(2)–S(1)	83.02(7)
S(1)–Fe(1)–C(1)	170.3(2)	Te(2)–Fe(2)–S(2)	10.22(6)
S(1)–Fe(1)–C(2)	87.1(2)	Te(2)–Fe(2)–C(4)	176.1(3)
Te(2)–Fe(2)–C(5)	89.6(3)	C(4)–Fe(2)–C(5)	90.0(4)
Te(2)–Fe(2)–C(6)	83.1(2)	C(4)–Fe(2)–C(6)	93.2(3)
Te(2)–Fe(2)–C(7)	93.3(1)	C(4)–Fe(2)–C(7)	90.6(3)
S(1)–Fe(2)–S(2)	73.15(9)	C(5)–Fe(2)–C(6)	100.2(4)
S(1)–Fe(2)–C(4)	99.6(2)	C(5)–Fe(2)–C(7)	96.0(4)
S(1)–Fe(2)–C(5)	141.2(4)	C(6)–Fe(2)–C(7)	163.3(3)
S(1)–Fe(2)–C(6)	116.4(2)	Fe(1)–S(1)–Fe(2)	105.6(1)
S(1)–Fe(2)–C(7)	46.9(1)	Fe(1)–S(1)–C(7)	110.4(2)
S(2)–Fe(2)–C(4)	171.0(2)	Fe(2)–S(1)–C(7)	58.9(2)
S(2)–Fe(2)–C(5)	98.9(3)	Fe(1)–S(2)–Fe(2)	107.7(1)
S(2)–Fe(2)–C(6)	85.5(2)	Fe(1)–S(2)–C(9)	60.5(2)
S(2)–Fe(2)–C(7)	88.2(1)	Fe(2)–S(2)–C(9)	107.8(2)
Fe(1)–C(1)–O(1)	171.5(5)	S(1)–C(7)–C(8)	122.7(4)
Fe(1)–C(2)–O(2)	176.9(7)	Te(1)–C(7)–Fe(2)	80.3(2)
Fe(1)–C(3)–O(3)	169.7(7)	Te(1)–C(7)–C(8)	111.64(4)
Fe(2)–C(4)–O(4)	173.4(6)	Te(2)–C(9)–Fe(1)	75.5(2)
Fe(2)–C(5)–O(5)	172.7(6)	Te(2)–C(9)–C(10)	110.9(4)
Fe(2)–C(6)–O(6)	174.7(6)	Fe(1)–C(9)–S(2)	67.5(2)
Fe(2)–C(7)–S(1)	74.1(3)	Fe(1)–C(9)–C(10)	120.0(5)
Fe(2)–C(7)–C(8)	122.4(4)	S(2)–C(9)–C(10)	122.7(5)
Te(2)–Fe(2)–S(1)	83.03(7)		

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

Table 12
Bond distances (\AA) and bond angles (deg) for 8

Te–Fe(1)	2.534(2)	Fe(2)–C(5)	1.76(1)
Te–Fe(2)	2.528(2)	Fe(2)–C(6)	1.78(1)
Te–C(7)	2.17(2)	O(1)–C(1)	1.15(2)
Se–Fe(1)	2.406(2)	O(2)–C(2)	1.16(2)
Se–Fe(2)	2.405(2)	O(3)–C(3)	1.14(2)
Se–C(7)	2.01(2)	O(4)–C(4)	1.14(2)
Fe(1)–Fe(2)	2.571(3)	O(5)–C(5)	1.16(2)
Fe(1)–C(1)	1.77(1)	O(6)–C(6)	1.15(2)
Fe(1)–C(2)	1.74(1)	C(1)–C(3)	2.56(2)
Fe(1)–C(3)	1.78(1)	C(4)–C(5)	2.57(2)
Fe(2)–C(4)	1.79(1)	C(7)–C(8)	1.38(3)
Fe(1)–Te–Fe(2)	61.04(6)	Te–Fe(2)–Fe(1)	59.61(6)
Fe(1)–Te–C(7)	86.3(5)	Te–Fe(2)–C(4)	157.6(5)
Fe(2)–Te–C(7)	83.3(5)	Te–Fe(2)–C(5)	92.0(5)
Fe(1)–Se–Fe(2)	64.59(7)	Te–Fe(2)–C(6)	99.7(4)
Fe(1)–Se–C(7)	93.5(5)	Se–Fe(2)–Fe(1)	57.71(7)
Fe(2)–Se–C(7)	90.0(5)	Se–Fe(2)–C(4)	94.3(5)
Te–Fe(1)–Se	75.30(7)	Se–Fe(2)–C(5)	161.7(5)
Te–Fe(1)–Fe(2)	59.36(6)	Se–Fe(2)–C(6)	99.1(4)
Te–Fe(1)–C(1)	159.6(5)	Fe(1)–Fe(2)–C(4)	98.0(5)
Te–Fe(1)–C(2)	99.9(5)	Fe(1)–Fe(2)–C(5)	104.5(5)
Te–Fe(1)–C(3)	93.6(5)	Fe(1)–Fe(2)–C(6)	150.7(5)
Se–Fe(1)–Fe(2)	57.69(7)	(4)–Fe(2)–C(5)	92.6(7)
Se–Fe(1)–C(1)	91.7(5)	C(4)–Fe(2)–C(6)	101.6(6)
Se–Fe(1)–C(2)	104.3(5)	C(5)–Fe(2)–C(6)	96.1(7)
Se–Fe(1)–C(3)	155.8(5)	Fe(1)–C(1)–O(1)	179.1(1)
Fe(2)–Fe(1)–C(1)	100.5(5)	Fe(1)–C(1)–C(3)	44.0(4)
Fe(2)–Fe(1)–C(2)	154.0(5)	O(1)–C(1)–C(3)	135.1(1)
Fe(2)–Fe(1)–C(3)	98.2(5)	Fe(1)–C(2)–O(2)	178.1(1)
C(1)–Fe(1)–C(2)	98.5(7)	Fe(1)–C(3)–O(3)	178.1(1)
C(1)–Fe(1)–C(3)	92.2(6)	Fe(1)–C(3)–C(1)	43.8(4)
C(2)–Fe(1)–C(3)	98.7(7)	O(3)–C(3)–C(1)	135.1(1)
Te–Fe(2)–Se	75.43(7)	Fe(2)–C(4)–O(4)	179.1(1)
Fe(2)–C(4)–C(5)	43.3(5)	Fe(2)–C(6)–O(6)	178.1(1)
O(4)–C(4)–C(5)	136.1(1)	Te–C(7)–Se	92.4(7)
Fe(2)–C(5)–O(5)	174.1(1)	Te–C(7)–C(8)	118.1(1)
Fe(2)–C(5)–C(4)	44.2(5)	Se–C(7)–C(8)	117.1(1)
O(5)–C(5)–C(4)	131.1(1)		

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

$2^\circ \leq \theta \leq 25^\circ$ using the ω - 2θ scan method. Intensity data were reduced for Lorentz and polarisation effects. The structures were solved by direct methods using SHELXS-86 programs. Fourier absorption corrections were applied using the program DIFABS [14]. Data processing and refinement were carried out with the MOLEN [15] package. All hydrogen atoms were located by difference Fourier maps and were not refined. The function minimised in least-square refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 4(F_o^2)/[\sigma(F_o^2)]^2 + [0.04(F_o^2)]^2$. Unlike 1 and 3, compound 5 is a non-centrosymmetric structure. For compound 5 structure solution gave two strong peaks for each chalcogen site. From bond distance criteria the peaks were identified as tellurium and sulfur. Refinement of site occupancy of the two disordered atoms showed that each atom possessed 50% occupancy. This kind of disorder can be interpreted as 50% of the unit cells of the mounted

Table 13
Bond distances (Å) and bond angles (deg) for 9

Te(1)–Fe(1)	2.5278(9)	Fe(2)–C(4)	1.798(7)
Te(1)–Fe(2)	2.530(1)	Fe(2)–C(5)	1.771(7)
Te(2)–Fe(1)	2.5401(9)	Fe(2)–C(6)	1.793(6)
Te(2)–Fe(2)	2.5344(9)	O(1)–C(1)	1.141(8)
Fe(1)–Fe(2)	2.606(1)	O(2)–C(2)	1.127(8)
Te(1)–C(7)	2.161(6)	O(3)–C(3)	1.135(9)
Te(2)–C(7)	2.158(7)	O(4)–C(4)	1.139(8)
Fe(1)–C(1)	1.779(7)	O(5)–C(5)	1.142(9)
Fe(1)–C(2)	1.787(6)	O(6)–C(6)	1.130(8)
Fe(1)–C(3)	1.777(7)	C(7)–C(8)	1.45(1)
Fe(1)–Te(1)–Fe(2)	62.03(3)	Te(2)–Fe(2)–Fe(1)	59.21(3)
Fe(1)–Te(2)–Fe(2)	61.80(3)	C(1)–Fe(1)–C(2)	99.0(3)
Te(1)–Fe(1)–Te(2)	75.80(3)	C(1)–Fe(1)–C(3)	99.7(3)
Te(1)–Fe(1)–Fe(2)	59.03(3)	C(2)–Fe(1)–C(3)	93.3(3)
Te(2)–Fe(1)–Fe(2)	58.99(3)	C(4)–Fe(2)–C(5)	91.4(3)
Te(1)–Fe(2)–Te(2)	75.85(3)	C(4)–Fe(2)–C(6)	103.1(3)
Te(1)–Fe(2)–Fe(1)	58.94(3)	C(5)–Fe(2)–C(6)	99.4(3)
Fe(1)–Te(1)–C(7)	89.2(2)	Fe(1)–C(3)–O(3)	177.4(6)
Fe(2)–Te(1)–C(7)	87.5(2)	Fe(2)–C(4)–O(4)	177.9(7)
Fe(1)–Te(2)–C(7)	89.1(2)	Fe(2)–C(5)–O(5)	177.0(6)
Fe(2)–Te(2)–C(7)	87.6(2)	Fe(2)–C(6)–O(6)	180.0(10)
Te(1)–Fe(1)–C(1)	102.5(2)	Te(1)–Fe(2)–C(4)	93.2(2)
Te(1)–Fe(1)–C(2)	90.9(2)	Te(1)–Fe(2)–C(5)	161.0(2)
Te(1)–Fe(1)–C(3)	156.5(3)	Te(1)–Fe(2)–C(6)	97.5(2)
Te(2)–Fe(1)–C(1)	99.5(2)	Te(2)–Fe(2)–C(4)	157.0(2)
Te(2)–Fe(1)–C(2)	159.2(2)	Te(2)–Fe(2)–C(5)	93.0(2)
Te(2)–Fe(1)–C(3)	93.1(2)	Te(2)–Fe(2)–C(6)	98.6(2)
Fe(2)–Fe(1)–C(1)	153.2(2)	Fe(1)–Fe(2)–C(4)	97.8(2)
Fe(2)–Fe(1)–C(2)	100.5(2)	Fe(1)–Fe(2)–C(5)	102.2(2)
Fe(2)–Fe(1)–C(3)	97.3(2)	Fe(1)–Fe(2)–C(6)	149.5(2)
Fe(1)–C(1)–O(1)	178.3(7)	Te(1)–C(7)–Te(2)	92.3(2)
Fe(1)–C(2)–O(2)	179.4(6)		

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

specimen having structure Fe(1)–Te(1)–Fe(2)–S(2) and the other 50% having structure Fe(1)–S(1)–Fe(2)–Te(2) (Fig. 4). Compound 5 is assigned the non-centrosymmetric space group $P1$. To find the absolute configuration of the molecule, the structure was refined with η parameter value +1 and –1 separately. The refinement showed almost the same R factor. The structure as well as its enantiomorph were refined using the SHELX 93 computer program, and found to have Flack parameter nearly zero in both cases. This result is not unexpected. The structure of compound 5 (including Te, S disorder) is fully centrosymmetric with crystallographic centrosymmetry at the midpoint of the Fe(1)–Fe(2) vector (or the midpoint of the vector joining any other corresponding atom set). However, one cannot justify assigning the space group as $P\bar{1}$ for the following reason. In an individual unit cell only one molecule exists where a Te atom cannot be inverted to the position of the S atom. The measured X-ray structure is a property averaged over all unit cells of the sample mounted. Crystal-

lographic data and details of measurements for all the structures are given in Table 3. Tables 4–8 list the atomic coordinates of 1, 3, 5, 8 and 9 respectively. Tables 9–13 list the bond distances and bond angles for 1, 3, 5, 8 and 9 respectively.

Acknowledgements

P.M. is grateful to the European Economic Community for a financial grant.

References

- [1] R.C. Brady and R. Pettit, *J. Am. Chem. Soc.*, 102 (1980) 6181.
- [2] R.H. Grubbs, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Vol. 9, Pergamon, Oxford, 1982, Chap. 54, p. 499.
- [3] L.R. Gilliom and R.H. Grubbs, *J. Am. Chem. Soc.*, 108 (1986) 733; W.J. Feast, V.C. Gibson, K.J. Ivin, A.M. Kenwright and E. Khosravi, *J. Chem. Soc., Chem. Commun.*, (1994) 1399.
- [4] T.J. Katz and S.J. Lee, *J. Am. Chem. Soc.*, 102 (1980) 422; A.F. Dyke, S.A.R. Knox, P.J. Naish and G.E. Taylor, *J. Chem. Soc., Chem. Commun.*, (1980) 203.
- [5] M. Brookhart, J.R. Tucker and G.R. Hush, *J. Am. Chem. Soc.*, 105 (1983) 258.
- [6] L.F. Cannizo and R.H. Grubbs, *J. Org. Chem.*, 50 (1985) 2316; L.E. Clawson, S.L. Buchwald and R.H. Grubbs, *J. Am. Chem. Soc.*, 25 (1984) 5733.
- [7] C. Zheng, Y. Apeloig and R. Hoffmann, *J. Am. Chem. Soc.*, 110 (1988) 749; C.P. Casey and J.D. Audett, *Chem. Rev.*, 86 (1986) 339; J.E. Hahn, *Prog. Inorg. Chem.*, 31 (1984) 205.
- [8] R.J. Puddephatt, *Polyhedron*, 7 (1988) 767.
- [9] P. Mathur and V.D. Reddy, *J. Organomet. Chem.*, 387 (1990) 193; P. Mathur, V.D. Reddy and R. Bohra, *J. Organomet. Chem.*, 401 (1991) 339.
- [10] P. Mathur, Md.M. Hossain, S. Umbarkar, C.V.V. Satyanarayana, S.S. Tavale and V.G. Puranik, *Organometallics*, 14 (1995) 959; P. Mathur, P. Sekar, C.V.V. Satyanarayana and M.F. Mahon, *Organometallics*, 14 (1995) 2115; 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, R. Kondru, S.N. Datta and M.M. Bhadbhade, *Organometallics*, 13 (1994) 2532.
- [11] P. Mathur, B. Manimaran, M.M. Hossain, C.V.V. Satyanarayana, V.G. Puranik and S.S. Tavale, *J. Organomet. Chem.*, 493 (1995) 251.
- [12] L.E. Bogan, D.A. Lesch and T.B. Rauchfuss, *J. Organomet. Chem.*, 250 (1983) 429; P. Mathur, D. Chakrabarty, Md.M. Hossain, R.S. Rashid, V. Rugmini and A.L. Rheingold, *Inorg. Chem.*, 31 (1992) 1106; D.A. Lesch and T.B. Rauchfuss, *Inorg. Chem.*, 20 (1981) 3583; P. Mathur, D. Chakrabarty, Md.M. Hossain and R.S. Rashid, *J. Organomet. Chem.*, 420 (1991) 79; P. Mathur, D. Chakrabarty and Md.M. Hossain, *J. Organomet. Chem.*, 401 (1991) 167.
- [13] A.I. Vogel, *Textbook of Practical Organic Chemistry*, ELBS, Longman, 4 edn., 1984, p. 289.
- [14] N. Walker and D. Stewart, *Acta Crystallogr.*, A 39 (1983) 158.
- [15] MolEN, *An Interactive Structure Solution Procedure*, Enraf-Nonius, Delft, Netherlands, 1990.