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Isolation and characterization of $[Fe_2(CO)_6Se_2\{\mu\text{-}(CO)_3Cr(\eta^5\text{-}C_5(H)(CH_2Ph)(Ph)(OEt)\}]$, $[(CO)_6Fe_2\{\mu\text{-}EC(Ph){=}C(E')C(H)(OEt)\}]_2$ and $[(CO)_6Fe_2\{\mu\text{-}SC(H)(Ph)C(Te){=}C(H)(OEt)\}]$ from the thermolysis of Fischer carbene adducts $[(CO)_6Fe_2EE'\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$ (E, E′ = Se and E = S, E′ = Te)

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Abstract

Thermolysis of the trimetallic adducts $[(CO)_6Fe_2EE'\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$ **1a,b** (**1a**: E = E′ = Se; **1b**: E = S, E′ = Te) in refluxing THF yield the following complexes: $[Fe_2(CO)_6EE'\{\mu\text{-}(CO)_3Cr(\eta^5\text{-}C_5(H)(CH_2Ph)(Ph)(OEt)\}]$, (**2**: E = E′ = Se); $[(CO)_6Fe_2\{\mu\text{-}EC(Ph){=}C(E')C(H)(OEt)\}]_2$, (**3a**: E = E′ = Se; **3b**: E = S, E′ = Te) and $[(CO)_6Fe_2\{\mu\text{-}EC(H)(Ph)C(E'){=}C(H)(OEt)\}]$, (**4**: E = S, E′ = Te), where the product formation depends on the nature of chalcogen atoms present in the trimetallic adducts **1a** and **1b**. All products have been characterized by IR and ^{1}H-, ^{13}C-, ^{77}Se- and ^{125}Te-NMR spectroscopy and structural types were unequivocally established by X-ray crystallographic analysis of compounds **3a** and **4**. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Iron; Carbene; Cluster; X-ray diffraction

1. Introduction

We recently reported that the chalcogen stabilized diiron compounds $[Fe_2(\mu\text{-}EE')(CO)_6]$ (where E or E′ = S, Se or Te) add almost instantly to the triple bond of carbene complexes, $[(CO)_5M{=}C(OEt)(C{\equiv}CPh)$ (where M=Cr, W) [1]. In case of mixed chalcogen compounds (E ≠ E′), such addition to the acetylenic triple bond of the Fischer carbene complex is highly regioselective ([1]a). The metal–carbene fragment remains intact in the trimetallic adduct $[(CO)_6Fe_2EE'\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$ (E = S, Se; E′ = Se, Te), and so does the cluster unit. As a result of *cis*-addition, the resultant olefin has a fixed geometry where the phenyl ring resides close to the Fischer carbene function. Such spatial disposition of phenyl group may facilitate dissociation of a CO ligand from Cr or W, leading to coordinatively unsaturated intermediates. In order to explore possible generation and fate of such reactive intermediates, thermolysis of these adducts is under study. In a preliminary report, we described the isolation and structural characterisation of an unusual annulated product

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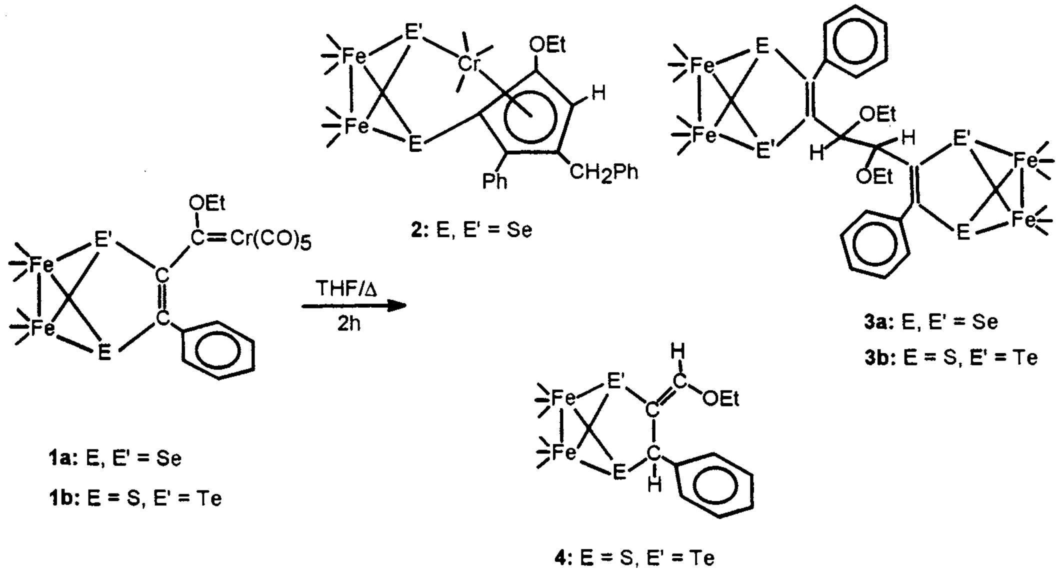

Scheme 1.

$[Fe_2(CO)_6Se_2\{\mu\text{-}(CO)_3Cr(\eta^5\text{-}C_5(H)(CH_2Ph)(Ph)(OEt)\}]$ obtained from the thermolysis reaction of $[(CO)_6Fe_2Se_2\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$ [2]. In this report, we describe in detail all the products obtained from the thermolysis of $[(CO)_6Fe_2Se_2\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$ (**1a**) and $[(CO)_6Fe_2STe\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$ (**1b**).

2. Results and discussion

The preparation and characterisation of the starting materials $[(CO)_6Fe_2EE'\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$ (**1a**, **b**) (**1a**: E, E′ = Se; **1b**: E = S; E′ = Te) have been described in detail earlier [1]. Thermolysis of individual complexes **1a** and **1b** are carried out by refluxing their THF solutions for 2 h, leading to the formation of known $[Fe_2(CO)_6Se_2\{\mu\text{-}(CO)_3Cr(\eta^5\text{-}C_5H(CH_2Ph)(Ph)(OEt)\}]$ (**2**) [2] and $[(CO)_6Fe_2\{\mu\text{-}SeCPh{=}CSeC(H)(OEt)\}]_2$ (**3a**) from **1a**, and of $[(CO)_6Fe_2\{\mu\text{-}(S)CPh{=}CTeC(H)(OEt)\}]_2$ (**3b**) and $[(CO)_6Fe_2\{\mu\text{-}SC(H)(Ph)C(Te){=}C(H)(OEt)\}]$ (**4**) from **1b** (Scheme 1).

Identification of **2** is based on comparison of its spectral features with those reported earlier [2]. Compounds **3a**, **3b**, and **4** have been characterised by IR and ^{1}H-, ^{13}C-, ^{77}Se- and ^{125}Te-NMR spectroscopy, and structures of **3a** and **4** have been established crystallographically. The IR spectra of all four products show bands due to terminal carbonyls only; the ν(CO) stretching patterns for **3a** and **3b** are identical.

The ^{1}H-NMR spectrum of compound **3a** features a non-exchangeable singlet at δ 3.16 ppm and signals in the aliphatic region due to ethoxy group. The methylene protons of the ethoxy group appear as two distinct doublet of quartets typical of an ethoxy group attached to a chiral centre. The ^{13}C-NMR spectrum indicates absence of any olefinic carbon, the most downfield of aliphatic carbon signals is shown to be attached to a hydrogen (presumably the proton at δ 3.16 ppm). Though both ^{1}H- and ^{13}C-NMR spectra suggest a symmetrical dimeric structure, an unambiguous assignment is based on the crystal structure analysis of **3a**.

Red crystals of **3a** were grown from hexane solvent at −4°C and a single crystal X-ray diffraction analysis was carried out. Its molecular structure is shown in Fig. 1.

The crystal structure reveals that, it is in essence, a symmetrical, dimeric compound derived from two molecules of the starting material. The two chiral centres have a *R*/*S* relationship. Among the selenium-carbon bond distances, the phenyl carbon forms a longer bond (C(13)–Se(2) (1.972 (5) Å) than the other carbon

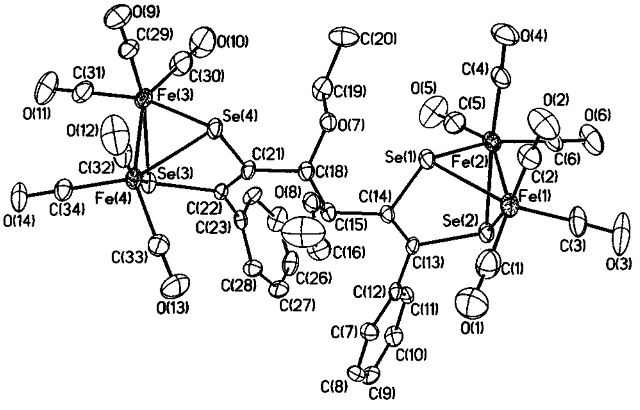

Fig. 1. Molecular structure of $[(CO)_6Fe_2\{\mu\text{-}SeC(Ph){=}C(Se)C(H)(OEt)\}]_2$ (**3a**).

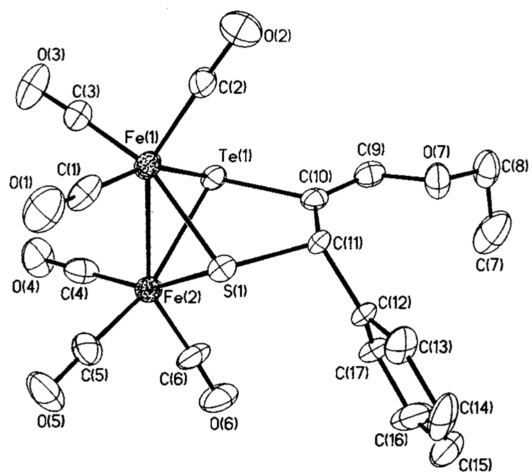

Fig. 2. Molecular strructure of [(CO)$_6$Fe$_2${μ-SC(H)Ph-C(Te)=C(H)(OEt)}] (**4**).

attached to the second Se atom of the rare Fe$_2$Se$_2$ unit, C(21)–Se(4) (1.929(5) Å).

A normal carbene dimerization reaction would have resulted in a tetrasubstituted, symmetrical olefin, [3] and therefore, the novel product obtained here can be viewed as a formal hydrogenated derivative of such an olefin. The symmetry of its structure explains the highly symmetrical ^{13}C-NMR spectrum of this compound, each signal represents two carbons of the molecule. The chirality of the saturated carbon is responsible for the diastereotopicity of the ethoxy methylene protons as observed in the ^{1}H-NMR spectrum. Interestingly, the chemical shift difference of these geminally non-equivalent methylene protons in complex **3b**, is not very large, and the signal therefore appears as a complex multiplet. The ^{13}C-NMR spectrum of complex **3b** also reflects its symmetrical dimeric structure, each signal representing two carbons. The origin of hydrogen atoms in these complexes is unclear at present.

The ^{77}Se-NMR spectrum of compound **3a** shows two signals, a singlet and a doublet with Se–H coupling, consistent with a three-bond coupling with the hydrogen atom. The ^{125}Te-NMR spectrum of **3b** shows a single peak, in the region normally associated with μ_3-Te ligand.

Also obtained from the thermolysis of **1b** is [(CO)$_6$Fe$_2${μ-SC(H)(Ph)C(Te)=C(H)(OEt)}] (**4**). The ^{1}H-NMR spectrum shows four signals, a triplet and a quartet for the ethoxy protons and two doublets, for the C(*H*)Ph and C(*H*)OEt) protons. The more downfield of these two also shows ^{125}Te satellites and therefore can be assigned to C(*H*)(OEt) proton. The ^{13}C- and ^{125}Te-NMR spectra are consistent with the structure of **4**. For an unambiguous structure elucidation, red crystals of **4** were grown from hexane solvent at 5°C and a single crystal X-ray diffraction analysis was carried out. There are three independent molecules of the complex in the asymmetric unit of **4**. The molecular structure of one molecule of **4** is shown in Fig. 2.

The crystal structure reveals an exocyclic enol ether function anchored to the chalcogenide cluster. The ethoxy group occupies a *syn* position with respect to the phenyl ring. It consists of a Fe$_2$STe butterfly core and a vinylic ether unit, attached to the wing-tip selenium and sulphur atom. The olefinic bond distance in **4**, (C(9)–C(10) 1.33(2) (Å) is somewhat longer than the corresponding olefinic bond distance of 1.28(1) (Å) in [(CO)$_6$Fe$_2${μ-SeC(Ph)(H)C(Se)=C(H)(OEt)}] [4]. The S(1)–C(11)–C(12) bond angle in **4**, 107.3(10)° is similar to the corresponding bond angle, Se(1)–C(7)–C(9) of 105.9(8)° in [(CO)$_6$Fe$_2${μ-SeC(Ph)(H)C(Se)=C(H)-(OEt)}] [4].

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

	3a	**4**
Formula	$C_{34}H_{22}Fe_4O_{14}Se_4$	$C_{17}H_{12}Fe_2O_7Ste$
Formula weight	1193.76	599.63
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	15.831 (5)	7.781 (3)
b (Å)	16.142 (6)	20.148 (9)
c (Å)	16.573 (7)	20.44 (2)
α (°)	—	86.13 (6)
β (°)	95.26 (2)	82.09 (5)
γ (°)	—	82.99 (5)
V (Å^3)	4217 (2)	3146 (3)
Z	4	6
$D_{calc.}$ (g cm^3)	1.880	1.899
μ(Mo–K$_\alpha$) (cm^{-1})	48.62	28.80
F(000)	2312	1740
Crystal size (mm)	0.40 × 0.30 × 0.10	0.30 × 0.20 × 0.10
2θ range for data collection (°)	48	48
Limiting indices	$-1\leq h\leq 18$, $-1\leq k\leq 19$, $-19\leq l\leq 19$	$-8\leq h\leq 8$, $-21\leq k\leq 21$, $-1\leq l\leq 21$
Reflections collected	8805	10 409
Independent reflections	7340 ($R_{int}=0.0558$)	8232 ($R_{int}=0.1405$)
Temp (K)	244 (2)	248 (2)
Absorption correction	Semiempirical	Empirical
T(max)/T(min)	1.000/0.813	1.000/0.647
Diffractometer	Siemens P4	
Radiation (Mo–K$_\alpha$) (Å)	$\lambda = 0.71073$	
Goodness-of-fit on F^2	0.801	1.029
Largest diff. peak and hole	0.519 and −0.702 eÅ^{-3}	1.467 and −1.317 eÅ^{-3}
$R(F)$, %^{a}	3.85	6.76
$R(wF^2)$, %^{a}	9.65	14.22

^{a} Quantity minimized = $R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o - Fc)|$.

3. Experimental section

All reactions and other manipulations were carried out under an argon or nitrogen atmosphere, using standard Schlenk techniques. Solvents were deoxygenated immediately prior to use. Reactions were monitored by FT-IR spectroscopy and thin-layer chromatography. Infrared spectra were recorded on a Nicolet-Impact 400 FTIR spectrometer as n-hexane solutions in sodium chloride cell at 0.1 mm path length. Elemental analyses were performed using a Carlo Erba 1106 automatic analyzer. ^{1}H-, ^{13}C-, ^{77}Se- and ^{125}Te-NMR spectra were recorded on a Varian VXR 300S spectrometer in $CDCl_3$ at 25°C. The operating frequency for ^{77}Se-NMR was 57.23 MHz with a pulse width of 15 μs and a delay of 1.0 s and operating frequency for ^{125}Te was 94.70 MHz with pulse width of 9.5 μs and a delay of 1 s. ^{77}Se-NMR spectra were referenced to Me_2Se ($\delta = 0$ ppm) and ^{125}Te-NMR spectra were referenced to Me_2Te ($\delta = 0$ ppm).

Chromium hexacarbonyl and phenylacetylene were purchased from Aldrich and these were used without further purification. The homo- and mixed-chalcogenide iron carbonyl clusters $[Fe_2(\mu\text{-}Se_2)(CO)_6]$ [5] and $[Fe_2(\mu\text{-}STe)(CO)_6]$, [6] α,β-unsaturated mixed chalcogenide carbene complexes $[(CO)_6Fe_2EE'\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$, (**1a**: E = E′ = Se; **1b**: E = S, E′ = Te) [1] and the alkynyl Fischer carbene complexes $[(CO)_5M{=}C(OEt)(C{\equiv}CPh)]$ (M=Cr, W) [7] were prepared as previously reported.

3.1. Thermolysis of $[(CO)_6Fe_2Se_2\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$

A solution of $[(CO)_6Fe_2Se_2\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$ (**1a**) (1 g, 1.26 mmol) in THF (10 ml) was refluxed for 2 h. The reaction was monitored by TLC, and refluxing stopped when all the starting material was consumed. The solution was filtered through Celite to remove the insoluble materials. After removal of solvent from the filtrate, the residue was subjected to chromatographic work-up using silicagel TLC plates. Elution with hexane/dichloromethane (9:1 v/v) mixture afforded the following compounds, in order of polarity: brown $[Fe_2(CO)_6Se_2\{\mu\text{-}(CO)_3Cr(\eta^5\text{-}C_5H(CH_2Ph)(Ph)(OEt)\}]$ (**2**) [2] (0.26 g, 25%) and red $[(CO)_6Fe_2\{\mu\text{-}SeCPh{=}CSeC(H)(OEt)\}]_2$ (**3a**) (0.28 g, 19%).

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times 10^3$) for **3a**

Atom	*x*	*y*	*z*	U_{eq}^{a}
Fe(1)	14 955.8(5)	6676.6(6)	3417.0(5)	47(1)
Fe(2)	14 789.4(5)	7818.5(6)	2377.0(6)	44(1)
Fe(3)	8988.4(5)	7953.4(6)	1441.9(5)	42(1)
Fe(4)	9030.1(5)	6566.3(6)	2127.8(5)	37(1)
Se(1)	13 622.6(4)	7289.9(4)	3002.2(4)	39(1)
Se(2)	14 919.4(4)	6413.3(4)	2008.9(4)	42(1)
Se(3)	9216.0(4)	6725.2(4)	724.9(4)	39(1)
Se(4)	10 206.5(3)	7476.7(4)	2256.1(4)	39(1)
O(1)	14 385(4)	5091(4)	4000(4)	116(2)
O(2)	15 034(3)	7667(3)	4895(3)	81(2)
O(3)	16 787(3)	6423(4)	3612(3)	114(3)
O(4)	14 639(3)	9297(3)	3364(3)	85(2)
O(5)	14 001(4)	8494(4)	853(3)	102(2)
O(6)	16 576(3)	8101(4)	2176(3)	98(2)
O(7)	12 071(2)	7883(3)	1892(2)	38(1)
O(8)	11 869(2)	6440(2)	2842(2)	38(1)
O(9)	8505(3)	8850(3)	2854(3)	81(2)
O(10)	9820(4)	9205(4)	529(4)	106(2)
O(11)	7302(3)	8077(4)	550(3)	97(2)
O(12)	8758(3)	6913(4)	3806(3)	92(2)
O(13)	9884(3)	4976(3)	2364(4)	95(2)
O(14)	7250(3)	6106(3)	1784(3)	62(1)
C(1)	14 624(5)	5713(6)	3787(5)	72(2)
C(2)	14 995(4)	7283(4)	4322(4)	55(2)
C(3)	16 074(4)	6539(5)	3533(4)	65(2)
C(4)	14 714(4)	8718(4)	2979(4)	48(2)
C(5)	14 304(5)	8235(5)	1433(5)	64(2)
C(6)	15 877(4)	7977(4)	2250(4)	61(2)
C(7)	13 186(3)	4674(4)	1459(3)	36(2)
C(8)	13 107(4)	4001(4)	953(4)	43(2)
C(9)	13 447(4)	4017(4)	2123(4)	45(2)
C(10)	13 828(4)	4724(4)	−23(4)	44(2)
C(11)	13 909(3)	5405(4)	478(3)	27(2)
C(12)	13 588(3)	5381(4)	1231(3)	32(2)
C(13)	13 718(3)	6092(4)	1796(3)	32(2)
C(14)	13 172(3)	6491(3)	2199(3)	28(1)
C(15)	12 222(3)	6424(4)	2090(3)	32(2)
C(16)	12 028(4)	5707(4)	3309(4)	51(2)
C(17)	11 694(6)	5828(5)	4120(4)	103(3)
C(18)	11 824(3)	7105(4)	1562(3)	35(2)
C(19)	11 969(4)	8532(4)	1310(4)	53(2)
C(20)	12 191(5)	9334(4)	1708(4)	71(2)
C(21)	10 864(3)	7028(4)	1435(3)	34(2)
C(22)	10 453(3)	6718(4)	777(3)	30(1)
C(23)	10 871(3)	6388(4)	91(3)	33(2)
C(24)	11 056(45)	6895(4)	−541(3)	45(2)
C(25)	11 586(4)	6620(5)	−1107(4)	59(2)
C(26)	11 918(4)	5862(5)	−1047(4)	55(2)
C(27)	11 719(4)	5338(4)	−456(4)	48(2)
C(28)	11 192(4)	5593(4)	122(4)	40(2)
C(29)	8698(4)	8515(4)	2287(5)	56(2)
C(30)	9504(5)	8715(5)	892(5)	69(2)
C(31)	7954(5)	8029(4)	911(4)	56(2)
C(32)	8857(4)	6782(5)	3151(4)	58(2)
C(33)	9546(4)	5580(4)	2280(4)	57(2)
C(34)	7941(4)	6285(4)	1900(4)	43(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalised *Uij* tensor.

3a: IR (cm^{-1}): 2067 (s), 2031 (vs), 1999 (s), 1989 (s), 1978 (w), 1949 (w). ^{1}H-NMR (ppm): δ 1.44 (6H, t, C*H*$_3$), 3.16 (2H, s, C*H*), 3.22 (2H, dq, $J = 6.9$, 1.5 Hz, OC*H*$_2$), 3.42 (2H, dq, $J = 7$, 1.5 Hz, OC*H*$_2$), 6.62–7.30 (10H, m, 2C$_6$*H*$_5$). ^{13}C-NMR (ppm): δ 15.4 (CH_3, $J_{C-H} = 127.4$ Hz), 65.6 (O*C*H$_2$, $J_{C-H} = 140$ Hz), 80.7 (*C*H(OEt), $J_{C-H} = 143.6$ Hz), 125.8–129.3 (*C*$_6$H$_5$), 136.2 (quat *C* in phenyl ring), 147.2 (Se*C*C(OEt), 150

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times 10^5$) for **4**

Atom	*x*	*y*	*z*	U_{eq}^{a}
Te(1)	7284(1)	4559(1)	847(1)	41(1)
Fe(1)	7161(3)	5149(1)	1908(1)	43(1)
Fe(2)	4427(3)	5163(1)	1347(1)	44(1)
S(1)	5022(5)	4501(2)	2229(2)	41(1)
O(1)	5781(18)	5941(7)	3051(7)	82(4)
O(2)	10 124(17)	4350(7)	2408(7)	82(4)
O(3)	8845(17)	6277(6)	1154(7)	90(4)
O(4)	4963(17)	6277(6)	375(6)	78(4)
O(5)	1950(17)	6026(6)	2233(7)	83(4)
O(6)	1943(16)	4508(7)	733(6)	77(4)
O(7)	7642(14)	2477(5)	1365(5)	58(3)
C(1)	6281(23)	5652(9)	2595(9)	59(5)
C(2)	8981(22)	4667(8)	2222(9)	52(4)
C(3)	8213(21)	5792(8)	1458(9)	55(4)
C(4)	4735(20)	5825(9)	757(9)	60(5)
C(5)	2937(23)	5690(8)	1888(9)	60(5)
C(6)	2930(23)	4749(9)	961(9)	61(5)
C(7)	6710(30)	1789(11)	593(12)	108(8)
C(8)	8159(25)	1928(8)	954(9)	69(5)
C(9)	7711(19)	3088(8)	1051(8)	49(4)
C(10)	6923(18)	3635(7)	1343(7)	41(4)
C(11)	5844(18)	3638(6)	1990(8)	43(4)
C(12)	4318(18)	3247(7)	2075(8)	38(4)
C(13)	3716(22)	3000(8)	2711(7)	55(5)
C(14)	2269(30)	2645(9)	2807(10)	80(7)
C(15)	1472(27)	2520(10)	2291(13)	86(7)
C(16)	2049(23)	2748(10)	1683(12)	85(7)
C(17)	3514(20)	3093(8)	1580(10)	62(5)
Te(11)	3417(1)	1319(1)	7620(1)	41(1)
Fe(11)	3383(3)	1758(1)	8752(1)	42(1)
Fe(12)	635(3)	1920(1)	8189(1)	41(1)
S(101)	1162(5)	1128(2)	8987(2)	43(1)
O(101)	6325(18)	910(7)	9237(8)	98(5)
O(102)	5255(15)	2855(6)	8151(7)	75(4)
O(103)	2110(18)	2513(6)	9931(7)	78(4)
O(104)	1367(17)	3121(6)	7386(6)	76(4)
O(105)	−1687(18)	2712(6)	9186(7)	84(4)
O(106)	−1976(15)	1505(6)	7462(6)	76(4)
O(107)	3472(15)	−792(5)	7874(6)	70(4)
C(101)	5200(23)	1224(8)	9033(9)	53(4)
C(102)	4559(20)	2431(8)	8382(9)	56(5)
C(103)	2624(20)	2202(9)	9482(10)	57(5)
C(104)	1064(21)	2636(8)	7706(8)	51(4)
C(105)	−781(22)	2392(8)	8801(8)	51(4)
C(106)	−957(20)	1650(9)	7749(9)	56(5)
C(107)	2438(43)	−1355(13)	7009(13)	56(5)
C(108)	3887(29)	−1288(9)	7391(12)	95(8)
C(109)	3674(21)	−157(7)	7626(9)	51(4)
C(110)	2951(18)	342(8)	7978(7)	41(4)
C(111)	1827(9)	300(7)	8629(7)	41(4)
C(112)	203(19)	−51(7)	8645(7)	42(4)
C(113)	−573(19)	−49(8)	8074(9)	57(5)
C(114)	−2040(22)	−364(10)	8084(9)	67(5)
C(115)	−2778(22)	−672(10)	8645(11)	73(6)
C(116)	−2010(24)	−688(9)	9214(11)	74(6)
C(117)	−487(19)	−368(6)	9199(8)	44(4)
Te(21)	11 546(1)	2121(1)	5929(1)	43(1)
Fe(21)	9428(3)	1488(1)	5469(1)	43(1)
Fe(22)	12 563(3)	1489(1)	4898(1)	43(1)
S(201)	10 235(5)	2119(2)	4559(2)	39(1)
O(201)	14 471(17)	471(6)	5699(7)	81(4)
O(202)	12 562(17)	596(6)	3821(7)	83(4)
O(203)	15 420(17)	2252(6)	4325(7)	85(4)
O(204)	10 105(19)	400(6)	6435(6)	86(4)
O(205)	8072(17)	576(7)	4645(7)	83(4)
O(206)	6111(17)	2151(7)	6139(7)	86(4)
O(207)	10 939(13)	4187(5)	5375(5)	50(3)
C(201)	13 692(22)	884(8)	5379(9)	54(5)
C(202)	12 527(19)	934(8)	4260(9)	54(5)
C(203)	14 305(22)	1936(9)	4542(10)	67(5)
C(204)	9808(21)	849(8)	6067(8)	52(4)
C(205)	8576(22)	956(8)	4967(9)	56(5)
C(206)	7412(24)	1891(8)	5851(8)	55(4)
C(207)	9076(30)	4867(11)	6158(10)	94(7)
C(208)	10 807(28)	4746(8)	5789(9)	72(6)
C(209)	11 159(16)	3592(6)	5682(9)	72(6)
C(210)	10 911(17)	3035(6)	5418(7)	34(3)
C(211)	10 323(19)	3006(7)	4782(7)	44(4)
C(212)	8555(18)	3379(6)	4674(7)	36(3)
C(213)	8223(24)	3561(8)	4041(9)	63(5)
C(214)	6611(27)	3922(8)	3947(10)	71(6)
C(215)	5398(26)	4077(9)	4478(14)	80(7)
C(216)	5715(25)	3873(10)	5098(12)	82(6)
C(217)	7331(20)	3525(8)	5212(9)	55(4)

[a] U_{eq} is defined as one third of the trace of the orthogonalised *Uij* tensor.

(S*C*Ph), 209.3 {Fe(*C*O)$_3$}. ^{77}Se-NMR (ppm): δ 534 (d, $J_{Se-H} = 6.1$ Hz, *Se*C(H)(OEt), 542 {s, *Se*C(Ph)}. M.p. 170–172°C. Anal. Calc. (Found) for $Fe_4Se_4C_{34}O_{14}H_{22}$: C, 34.19 (34.22), H, 1.84 (1.85%).

3.2. Thermolysis of [(CO)$_6$Fe$_2$STe{μ-C(Ph)=C–C(OEt)=Cr(CO)$_5$}]

A solution of [(CO)$_6$Fe$_2$STe{μ-C(Ph)=C–C(OEt)=Cr(CO)$_5$}] (**1b**) (0.7 g, 0.88 mmol) in THF (10 ml) was refluxed for 2 h. The reaction was monitored by TLC, and refluxing was stopped when all the starting material was consumed. The solution was filtered through Celite to remove the insoluble materials. After removal of solvent from the filtrate, the residue was subjected to chromatographic work-up using silicagel TLC plates. Elution with hexane/dichloromethane (9:1 v/v) mixture afforded the following compounds, in order of polarity: red [(CO)$_6$Fe$_2${μ-(5)CPh=CTeC(H)(OEt)}]$_2$ (**3b**) (0.09 g, 9%) and yellow [(CO)$_6$Fe$_2${μ-SC(H)(Ph)C(Te)=C(H)(OEt)}] (**4**) (0.08 g, 17%).

3b: IR (cm^{-1}): 2064 (s), 2028 (vs), 1998 (s) 1986 (s), 1973 (w), 1943 (w). ^{1}H-NMR (ppm): δ 1.41 (6H, t, C*H*$_3$), 2.77 (2H, s, C*H*), 3.23 (4H, m, OC*H*$_2$), 6.62–7.38 (10H, m, 2C$_6$*H*$_5$). ^{13}C-NMR (ppm): δ 15.7 (CH$_3$, $J_{C-H} = 127.4$ Hz), 65.1 (OCH$_2$, $J_{C-H} = 141$ Hz), 80.74 (*C*H(OEt), $J_{C-H} = 143.6$ Hz), 126.1–129.1 (*C*$_6$H$_5$), 132.3 (*C*Te), 136.8 (quat C in phenyl ring), 164 (*C*S(Ph), 209.7 {Fe(*C*O)$_3$}. ^{125}Te-NMR (ppm): δ 804.

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

Bond length (Å)			
Fe(1)–Fe(2)	2.521(2)	Se(1)–C(14)	1.942(5)
Fe(3)–Fe(4)	2.509(2)	Se(4)–C(21)	1.929(5)
Fe(1)–Se(1)	2.3751(12)	C(15)–O(8)	1.413(6)
Fe(2)–Se(1)	2.3590(12)	C(13)–C(14)	1.310(7)
Fe(3)–Se(4)	2.3779(12)	C(15)–C(18)	1.507(7)
Fe(4)–Se(4)	2.3666(12)	C(22)–C(21)	1.317(7)
Bond angle (°)			
Fe(1)–Se(1)–Fe(2)	64.35(4)	Se(4)–C(21)–C(18)	118.0(4)
Fe(2)–Se(2)–Fe(1)	64.41(4)	Fe(1)–Se(2)–C(13)	99.2(2)
Fe(3)–Fe(4)–Se(3)	57.50(3)	Se(1)–C(14)–C(15)	115.5(4)
Fe(3)–Se(4)–Fe(4)	63.86(4)	Fe(4)–Se(4)–C(21)	100.1(2)

M.p. 178–180°C. Anal. Calc. (Found) for $Fe_4Se_2Te_2C_{34}O_{14}H_{22}$: C, 34.14 (34.30), H, 1.84 (2.10%).

4: IR (cm^{-1}): 2066 (s), 2029 (vs), 1998 (s), 1989 (m). ^{1}H-NMR (ppm, $CDCl_3$): δ 0.96 (3H, t, CH_3), 3.74 (2H, q, OCH_2), 4.49 (1H, d, C(*H*)S), 6.62 (1H, d, $J_{Te-H} =$ 11.8 Hz, =C(*H*)(OEt)), 7.10–7.28 (5H, m, C_6H_5). ^{13}C-NMR (ppm, $CDCl_3$): δ 15.3 (*C*H_3, $J_{C-H} = 127.$ Hz), 60.1 (*C*H(Ph), $J_{C-H} = 144$ Hz), 69.1 (OCH_2, $J_{C-H} =$ 145.6 Hz), 127.5–128.3 (C_6H_5), 139.6 (s, =*C*Te), 150.1 (=*C*H, $J_{C-H} = 180.6$ Hz), 209.8 (Fe(*C*O)$_3$). ^{125}Te-NMR (ppm, $CDCl_3$): δ 737 (d, $^3J_{Te-H} = 12.2$ Hz, =C*Te*). M.p. 104–106°C. Anal. Calc. (Found) for $Fe_2STeC_{17}O_7H_{12}$: C, 34.04 (34.30); H, 2.00 (2.24%).

*3.3. Crystal structure determination of **3a** and **4***

Red crystals of **3a** and **4** were selected and mounted with epoxy cement to glass fibres. Single crystal X-ray data were collected on Siemans P4 diffractometer by using Mo–K$_\alpha$ radiation. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ($20 \leq 2\theta \leq 25°$). Pertinent crystallographic data of **3a** and **4** are summarized in Table 1. The systematic absences in the diffraction data of **3a** and **4** are uniquely consistent for the reported space groups. The asymmetric unit of **4** consists of three crystallographically-independent, but chemically identical molecules. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. Empirical absorption corrections for **4** was applied by using program DIFABS [8]. All non-H atoms were refined with anisotropic displacement coefficients and H atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHELXTL (5.3) program library (G. Sheldrick, Siemans XRD, Madison, WI). Final fractional atomic coordinates, selected bond lengths and bond angles for **3a** and **4** are listed in Tables 2–5.

Table 5
Selected bond distances (Å) and bond angles (°) for one of the independent molecule in the assymetric unit of **4**

Bond length (Å)			
Fe(1)–Te(1)	2.528(3)	Fe(2)–S(1)	2.237(5)
Fe(1)–S(1)	2.240(4)	Te(1)–C(10)	2.091(13)
Fe(2)–Te(1)	2.520(3)	C(10)–C(11)	1.47(2)
Fe(1)–Fe(2)	2.549(3)	C(9)–C(10)	1.33(2)
Fe(1)–S(1)	2.240(4)	C(11)–C(12)	1.49(2)
Bond angle (°)			
Fe(2)–Te(1)–Fe(1)	60.65(8)	Fe(2)–Te(1)–C(10)	95.84(4)
Te(1)–Fe(1)–Fe(2)	59.53(8)	Fe(1)–Te(1)–C(10)	93.2(4)
Te(1)–Fe(2)–S(1)	81.74(13)	Te(1)–C(10)–C(9)	117.4(11)
Fe(2)–S(1)–Fe(1)	69.42(13)	S(1)–C(11)–C(12)	107.3(10)
Te(1)–Fe(2)–Fe(1)	59.82(8)	Te(1)–C(10)–C(11)	117.6(11)
Fe(2)–Fe(1)–S(1)	55.24(12)	C(9)–C(10)–C(11)	124.9(13)
Te(1)–Fe(1)–S(1)	81.52(13)	S(1)–C(11)–C(10)	111.6(10)

4. Supplementary material available

Crystallographic details including fractional atomic coordinates for hydrogen atoms, bond lengths and bond angles and anisotropic displacement parameters and the structure factor tables for **3a** and **4** are available, upon request, from the authors.

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