Formation of vinyl ether derivatives in the reaction of tributyltin hydride with cluster supported Fischer carbene complexes: structural characterisation of $[(CO)_6Fe_2Te_2\{\mu\text{-}PhC{=}CC(OEt)\}W(CO)_5]$

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Abstract

Treatment of the complex $[(CO)_6Fe_2EE'\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}M(CO)_5\}]$, (**1**: $E = S$, $E' = Se$; $M = Cr$; **2**: $E = S$, $E' = Se$; $M = W$; **3**: $E = E' = Te$; $M = Cr$ and **4**: $E = E' = Te$; $M = W$), with excess Bu_3SnH in hexane at 0°C produces enol ether derivatives: $(CO)_6Fe_2\{\mu\text{-}EC(Ph)(H)\text{-}C(E'){=}C(H)(OEt)\}$ (*E*/*Z*-**5**: $E = S$, $E' = Se$ and *E*/*Z*-**6**: $E = E' = Te$). All the compounds have been characterised by IR and ^1H-, ^{13}C- or ^{77}Se-NMR spectroscopy. The structure of $[(CO)_6Fe_2Te_2\{\mu\text{-}(Ph)C{=}CC(OEt)\}W(CO)_5]$ has been established crystallographically.

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

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1. Introduction

In continuation of our studies of chalcogen-stabilised clusters with organic functional appendages, we have been exploring the chemistry of adducts of general formula $[(CO)_6Fe_2EE'\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}M(CO)_5\}]$, (where $M = Cr$ or W and E, $E' = S$, Se or Te) [1].

The Fischer carbene moiety in $[(CO)_6Fe_2EE'\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}M(CO)_5\}]$ is a potential organic functional group which can be readily transformed to an amino carbene group, an ester or an *ortho*ester [1b]. The alkynyl Fischer carbene complexes participate in many interesting and remarkable transformations and have been extensively used in many organic syntheses [2]. Tributyltinhydride is known to displace the pentacarbonylmetal moiety from the carbene carbon of $[(CO)_5M{=}C(OEt)(C \equiv CPh)]$ ($M = Cr$, W) under mild conditions to provide 1,1-hydrostannation alkoxystannane derivatives [3].

In the course of our study on the reactivity of $Fe_2(\mu\text{-}EE')(CO)_6$ (E, $E' = S$, Se, Te) clusters with the acetylenic triple bond, we have observed that the triple bond in alkynyl Fischer carbene complexes, $(CO)_5M{=}C(OEt)(C{\equiv}CPh)$ ($M = Cr$, W), instantly adds to the bridging chalcogen–chalcogen bond in $Fe_2(\mu\text{-}EE')(CO)_6$ (E, $E' = S$, Se, Te) to give adducts, $[(CO)_6Fe_2EE'\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}M(CO)_5\}]$, (E, $E' =$ S, Se, Te; $M = Cr$, W). In the case of mixed-chalcogenide systems, $[Fe_2(\mu\text{-}EE')(CO)_6]$ ($E \neq E'$), the addition of the bridged chalcogen atoms to the acetylenic triple bond is highly regioselective.

Crystal structures of the trimetallic adducts, $[(CO)_6Fe_2EE'\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}M(CO)_5\}]$ [1a], ($EE' = SSe$, $M = W$; $EE' = STe$, $M = Cr$ and $EE' = SeTe$, $M = W$) reveal that the metal-carbene fragment, and the phenyl ring are *cis* to each other, which on thermolysis, could assist in removing a CO ligand from the metal pentacarbonyl unit to create a coordinatively unsaturated, reactive species, or a stable, η^6-arene–

metal coordinated complex, as obtained by Merlic [4]. When the thermolysis of the chromium trimetallic adducts, $[(CO)_6Fe_2EE'\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$, (EE′ = SSe, SeSe, STe) was carried out in THF at reflux temperature, formation of a formal η^6-arene–chromium complex was not obtained. Some unusual annulated products, $[Fe_2(CO)_6EE'\{\mu\text{-}(CO)_3Cr(\eta^5\text{-}C_5H\text{-}(CH_2Ph)(Ph)(OEt)\}]$ (EE′ = SeSe), $[(CO)_6Fe_2EE'\{\mu\text{-(indanone)}\}]$ (EE′ = SSe and SeSe), $[(CO)_6Fe_2\{\mu\text{-}EE'\text{(2-ethoxy-1-naphthol)}\}]$ (EE′ = SSe, SeSe and STe), $[(CO)_6Fe_2\{\mu\text{-}EC(H)Ph{-}C(E'){=}C(H)(OEt)\}]$ (EE′ = STe) and $[(CO)_6Fe_2\{\mu\text{-}EC(Ph){=}C(E')C(H)(OEt)\}]_2$ (EE′ = SeSe and EE′ = STe) [5], were formed. Formation of the products was found to be influenced by the nature of the bridging chalcogen atoms present in the trimetallic adducts, $[(CO)_6Fe_2\text{-}EE'\{\mu\text{-}(Ph)C{=}C{-}C(OEt)\}Cr(CO)_5]$, (EE′ = SSe, EE′ = STe, and EE′ = SeSe). The above annulated products were not observed when the thermolysis of $[(CO)_6Fe_2EE'\{\mu\text{-}PhC{=}C{-}C(OEt)\}W(CO)_5]$, (EE′ = SSe, EE′ = STe, and EE′ = SeSe) complexes was carried out. It has also been observed previously that the reactivity of Te-bridged compounds, very often contrasts, quite markedly, from those which contain other chalcogen bridges. We have therefore carried out a structural characterisation of an adduct containing two Te-ligands and a tungsten pentacarbonyl moiety to see if any structural differences could be observed from the other related adduct, previously characterised by X-ray methods. We have also investigated the reactions of some adducts, $[(CO)_6Fe_2EE'\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}M(CO)_5\}]$, (**1**: E = S, E′ = Se; M = Cr; **2**: E = S, E′ = Se; M = W; **3**: E = E′ = Te; M = Cr and **4**: E = E′ = Te; M = W), with Bu_3SnH to form enol ether derivatives.

2. Results and discussion

2.1. Molecular structure of $[(CO)_6Fe_2Te_2\{\mu\text{-}PhC{=}C{-}C(OEt)\}W(CO)_5]$ (4)

An ORTEP plot of the molecular structure of **4** is shown in Fig. 1. The structure consists of a Fe_2Te_2 butterfly core, with the alkenyl carbene unit attached to the wing-tip of chalcogen atoms of the butterfly, such that the C(Ph) and C(carbene moiety) groups are bonded to the tellurium atoms. The $W(CO)_5$ unit and the phenyl group on the β-carbon atom of the alkenyl moiety are *cis* to each other, and therefore, in this respect the structure is similar to that observed earlier for $[(CO)_6Fe_2EE'\text{-}\{\mu\text{-}PhC{=}C{-}C(OEt)\}M(CO)_5]$, (EE′ = SSe, M = W; EE′ = STe, M = Cr and EE′ = SeTe, M = W) [1a]. The acetylenic C–C bond distance of 1.348(8) Å in complex **4** is slightly longer than the corresponding C–C bond distance in the phenylacetylene adducts, $[(CO)_6Fe_2\{\mu\text{-}TeC{-}(H){=}C(Ph)Se\}]$ (1.32(1) Å) [6] and in the mixed-chalcogenide trimetallic adduct, $[(CO)_6Fe_2SeTe\{\mu\text{-}C(Ph){=}CC(OEt){=}W(CO)_5\}]$ (1.324(11) Å) [1a]. The metal–carbene bond distance in complex **4** is not significantly different from those reported for simple carbene complexes, $(CO)_5M{=}C(OEt)(C\equiv CPh)$ (M = Cr, W) [7]. The Fe(1)–Fe(2) bond distance of 2.5989(13) Å is slightly longer than the earlier reported trimetallic adducts, $[(CO)_6Fe_2EE'\{\mu\text{-}C(Ph){=}CC(OEt){=}W(CO)_5\}]$ (EE′ = SSe, 2.507 (2) Å and EE′ = SeTe, 2.572(2) Å) [1a].

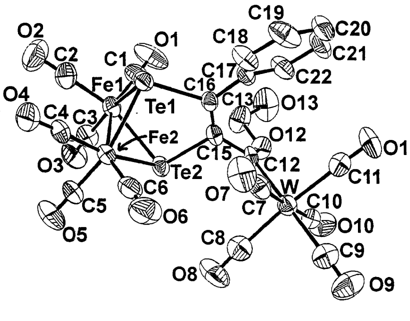
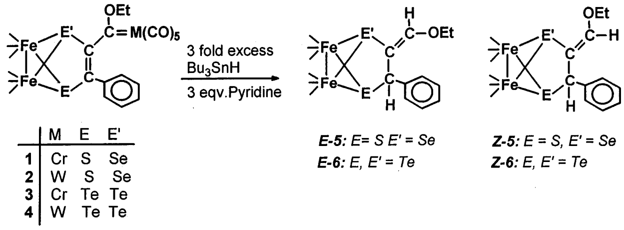


Fig. 1. Molecular structure of $[(CO)_6Fe_2Te_2\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}W(CO)_5\}]$ **4**.



	M	E	E′
1	Cr	S	Se
2	W	S	Se
3	Cr	Te	Te
4	W	Te	Te

Scheme 1.

2.2. Synthesis and characterisation of enol ether derivatives, $(CO)_6Fe_2\{\mu\text{-}EC(H)Ph{-}C(E'){=}C(H)(OEt)\}$ (5, EE′ = SSe; 6, EE′ = TeTe)

The reaction of complexes $[(CO)_6Fe_2EE'\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}M(CO)_5\}]$, (**1**: E = S, E′ = Se; M = Cr; **2**: E = S, E′ = Se; M = W; **3**: E = E′ = Te; M = Cr and **4**: E = E′ = Te; M = W) with a 3-fold excess of Bu_3SnH, in the presence of three equivalents of pyridine at 0°C, yielded the enol ether derivatives (mixture of *E*/*Z* isomers): $(CO)_6Fe_2\{\mu\text{-}EC(H)Ph{-}C{-}(E'){=}C(H)(OEt)\}$ (*E*/*Z*-**5**: E = S, E′ = Se; *E*/*Z* -**6**: E, E′ = Te) as the only isolatable, metal-containing products (Scheme 1).

Recent studies on the reaction of cluster supported Fischer carbene complexes, $[(CO)_6Fe_2EE'\{\mu\text{-}C(Ph){=}CC(OEt){=}M(CO)_5\}]$ (M = Cr or W; EE′ = STe, SeSe) with Bu_3SnH showed that in the case when E, E′ = Se, Se; the carbene complexes of both chromium and tungsten form α-(alkoxy)stannane derivative $[(CO)_6Fe_2\{\mu\text{-}SCPh{=}C(Se)C\text{-}(OEt)(H)SnBu_3\}]$, [8], which on treatment with one equivalent of Bu_3SnH, forms, very slowly, the enol ether derivative, $(CO)_6Fe_2\{\mu\text{-}SeC(H)Ph{-}C(Se){=}C(H)(OEt)\}$ at 0°C. The slow rate of this conversion suggests that the α-(alkoxy) stannane derivative is a stable by-product rather than an intermediate en-route to the enol ether products.

When the reaction of complexes, $[(CO)_6Fe_2Te_2\{\mu\text{-}C(Ph){=}CC(OEt){=}M(CO)_5\}]$ (**3**: M = Cr and **4**: M = W) was carried out with one equivalent of Bu_3SnH, formation of α-(alkoxy)stannanes derivative $[(CO)_6Fe_2\{\mu\text{-}TeCPh{=}C(Te)C(OEt)(H)SnBu_3\}]$ was not observed. This reaction underscores the importance of chalcogen atoms in determining reaction pathways in these complexes. This would also suggest that the putative α-(alkoxy)stannane intermediate for complex **3** or **4** is too unstable to permit isolation, presumably because of unfavourable steric interaction between bulky tellurium and tin moieties.

Compounds **5** and **6** have been characterised by IR and ^{1}H-, ^{13}C- or ^{77}Se-NMR spectroscopy. Identification of *E* and *Z* isomers is based on comparison of the spectral features with that of earlier reported compounds $E/Z\text{-}(CO)_6Fe_2\{\mu\text{-}EC(H)Ph{-}C(E'){=}C(H)\ (OEt)\}$ (EE′ = SeSe and STe) [8]. The infrared spectra of compounds *Z*-**5**, **6** and *E*-**5**, **6** exhibit carbonyl stretching patterns typical of an $Fe(CO)_3$ unit only and the ^{1}H-NMR spectra of these two isomers showed characteristic differences in chemical shift values of distinct signals. The methyl and methylene protons in complexes **5** and **6** are more shielded in *E* than in *Z* isomers, whereas, the benzylic and olefinic protons are more shielded in *Z* than *E* isomers. In complex **5**, the $^3J_{Se-H}$ value in the *Z*-isomer (8.5 Hz) is higher than in the *E*-isomer (4.7 Hz), whereas in **6**, the $^2J_{Te-H}$ values in the *E*-isomer (23.4 Hz) and the *Z*-isomer (20.4 Hz) are somewhat similar. Similar trends are observed in ^{13}C-NMR spectra of compounds *Z*-**5**, **6** and *E*-**5**, **6**. While the quaternary olefinic carbon is less sensitive to *E*/*Z* configuration, the other olefinic carbon is shielded in *E* compared to *Z*. Also, the chiral carbon is shielded in *E* compared to *Z* isomer. The ^{77}Se-NMR signals of compound *Z*-**5** are shielded (389 ppm, $J_{Se-H} = 8.5$ Hz) compared to *E*-**5** (450 ppm, $J_{Se-H} = 4.7$ Hz).

3. Experimental

3.1. General procedures

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 solution in sodium chloride cell at 0.1 mm path length. Elemental analyses were performed using a Carlo Erba 1106 automatic analyser. ^{1}H-, ^{13}C- and ^{77}Se-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. ^{77}Se-NMR spectra were referenced to Me_2Se ($\delta = 0$ ppm).

Complexes **1**–**4** were prepared as previously reported [1].

3.2. General procedure for reaction of Bu_3SnH and $[(CO)_6Fe_2EE'\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}M(CO)_5\}]$ (**1**: $E = S$, $E' = Se$; $M = Cr$; **2**: $E = S$, $E' = Se$; $M = W$; **3**: $E = E' = Te$; $M = Cr$ and *4*: $E = E' = Te$; $M = W$)

In a typical preparation, into a freshly prepared solution of one equivalent of **1**–**4** in THF/hexane (5:95 v/v) (10 ml), 3-fold excess of Bu_3SnH was added. The solution was stirred for 4 h (for **1** and **3**) or 1.5 h (for **2** and **4**) at 0°C in the presence of three equivalents of pyridine. The reaction mixture was kept at −10°C for 1 h to precipitate the (pyridine)-pentacarbonyltungsten/chromium by-product. The solution was filtered through Celite and the solvent was removed in vacuo. The residue was subjected to chromatography on thin layer silica-gel plates. Elution with hexane yielded, in each case, two yellow bands. The first band was characterised spectroscopically as $Z\text{-}(CO)_6Fe_2\{\mu\text{-}EC(H)Ph{-}C(E'){=}C(H)\text{-}(OEt)\}$ (*Z*-**5**, **6**) and the second band characterised as $E\text{-}(CO)_6Fe_2\{\mu\text{-}EC(H)Ph{-}C(E'){=}C\text{-}(H)(OEt)\}$ (*E*-**5**, **6**).

3.2.1. Complex *Z*-**5**: yellow, yield 27% (from **1**), 36% (from **2**)

IR: 2070 (vs), 2032 (vs), 2000 (vs), 1979 (m), 1951(w). ^{1}H-NMR (δ, $CDCl_3$): 1.26 (t, $J = 7.1$ Hz, CH_3), 3.90 (q, $J = 7.0$ Hz, OCH_2), 4.13 (d, $J = 2.1$ Hz, C(H)S), 6.01 (d, $J = 1.5$ Hz, $J_{Se-H} = 8.5$ Hz), C(H)(OEt)), 7.14–7.36 (m, C_6H_5). ^{13}C-NMR (δ, $CDCl_3$): 15.4 (CH_3), 58.1 (d, $J_{C-H} = 145.2$, CH(Ph)), 69.5 (q, $J_{C-H} = 145.8$, OCH_2), 127.6–128.9 (m, C_6H_5), 140.5 (s, = CSe), 150.4 (d, $J_{C-H} = 179.2$ Hz, = CH(OEt)), 209 (s, $Fe(CO)_3$). ^{77}Se-NMR (δ, $CDCl_3$): 389 (d, $J_{Se-H} = 8.5$ Hz). m.p. 90–92°C.

3.2.2. Complex *E*-**5**: yellow, yield 32% (from **1**), 39% (from **2**)

IR: 2070 (vs), 2031 (vs), 2001 (vs), 1981 (m), 1951(w). ^{1}H-NMR (δ, $CDCl_3$): 0.99 (t, $J = 7.1$ Hz, CH_3), 3.70 (m, OCH_2), 4.45 (d, $J = 1.7$ Hz, C(H)S), 6.81 (d, $J = 1.5$ Hz, $J_{Se-H} = 4.7$ Hz, =C(H)(OEt)), 7.10–7.34 (m, C_6H_5). ^{13}C-NMR (δ, $CDCl_3$): 15.3 (CH_3), 55.6 (d, $J_{C-H} = 148.2$ Hz, CH(Ph)), 69.2 ($J_{C-H} = 144.7$, OCH_2), 126.2–128.7 (m, C_6H_5), 138.6 (s, = CSe), 145.6 (d, $J_{C-H} = 181.1$ Hz, = CH(OEt)), 208.8 (s, $Fe(CO)_3$). ^{77}Se-NMR (δ, $CDCl_3$): 450 (d, $J_{Se-H} = 4.7$ Hz). m.p. 94–

96°C. Anal. Calc. (Found) for $Fe_2SSeC_{17}O_7H_{12}$: C, 37.04 (37.36); H, 2.17 (2.35).

3.2.3. *Complex Z-**6**: yellow, yield 22% (from **3**), 28% (from **4**)*

IR: 2056 (s), 2020 (vs), 1999 (w), 1988 (s), 1970 (w). ^{1}H-NMR (δ, $CDCl_3$): 1.24 (t, $J = 7.0$ Hz, CH_3), 3.85 (q, $J = 7.1$ Hz, OCH_2), 4.75 (d, $J = 1.7$ Hz, $J_{Te-H} = 20.4$ Hz, C(H)Te), 5.56 (d, $J = 2.1$ Hz, = C(H)(OEt)), 7.02–7.26 (m, C_6H_5). ^{13}C-NMR (δ, $CDCl_3$): 15.5 ($J_{C-H} = 126.9$ Hz, CH_3), 48.2 (d, $J_{C-H} = 146.4$ Hz, CH(Ph)), 68.9 ($J_{C-H} = 144.6$ Hz, OCH_2), 126.4–129.3 (m, C_6H_5), 140.8 (s, = CTe), 149.7 (d, $J_{C-H} = 179.4$ Hz, = CH(OEt)), 210.8 (s, $Fe(CO)_3$). m.p. 106–108 °C.

3.2.4. *Complex E-**6**: yellow, yield 27% (from **3**), 35% (from **4**)*

IR: 2057 (s), 2021 (vs), 1997 (w), 1986 (s), 1970 (w). ^{1}H-NMR (δ, $CDCl_3$): 0.98 (t, $J = 7.0$ Hz, CH_3), 3.72 (q, $J = 7.1$ Hz, OCH_2), 5.58 (d, $J = 1.8$ Hz, $J_{Te-H} = 23.4$, C(H)Te), 6.49 (d, $J = 2.1$ Hz, = C(H)(OEt)), 7.04–7.28 (m, C_6H_5). ^{13}C-NMR (δ, $CDCl_3$): 15.2 ($J_{C-H} = 126.9$ Hz, CH_3), 45.5 (d, $J_{C-H} = 145.1$ Hz, CH(Ph)), 68.4 ($J_{C-H} = 144.6$ Hz, OCH_2), 126.2–128.8 (m, C_6H_5), 138.2 (s, = CTe), 147.4 (d, $J_{C-H} = 180.4$ Hz, = CH(OEt)), 210.7 (s, $Fe(CO)_3$). m.p. 112–114°C. Anal. Calc. (Found) for $Fe_2Te_2C_{17}O_7H_{12}$: C, 29.35 (29.67); H, 1.72 (1.98).

Table 1
Crystal data and structure refinement for[$(CO)_6Fe_2Te_2$\{μ-PhC=C–C(OEt)\}–$W(CO)_5$] (**4**)

Identification code	**4**
Empirical formula	$C_{22}H_{10}Fe_2O_{12}Te_2W$
Formula weight	1017.05
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	11.4670(15)
b (Å)	15.650(3)
c (Å)	16.358(2)
α (°)	90
β (°)	102.595(10)
γ (°)	90
V (Å^3)	2865.0(7)
Z	4
$D_{calc.}$ (g cm^{-3})	2.358
Absorption coefficient (mm^{-1})	7.057
F(000)	1872
Theta range for data collection (°)	2.24–24.97
Index ranges	$0 \leq h \leq 13$, $0 \leq k \leq 18$, $-19 \leq l \leq 18$
Reflections collected	5274
Independent reflections	5009 [$R_{int} = 0.0175$]
Completeness to theta = 24.97	99.9%
Absorption correction	Psi-scan
Max/min transmission	0.9996, 0.6816
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5009/0/353
Goodness-of-fit on F^2	1.139
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0283$, $wR_2 = 0.0504$
R indices (all data)	$R_1 = 0.0510$, $wR_2 = 0.0631$
Extinction coefficient	0.00025(4)
Largest difference peak and hole (e Å^{-3})	0.992 and −0.525

Table 2
Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [Å $\times 10^3$] for **4**

Atom	x	y	z	U_{eq} [a]
W	7884(1)	6147(1)	2058(1)	41(1)
Te(1)	3857(1)	8534(1)	1374(1)	38(1)
Te(2)	4709(1)	6997(1)	209(1)	41(1)
Fe(1)	3326(1)	8255(1)	−197(1)	41(1)
Fe(2)	2911(1)	7118(1)	863(1)	38(1)
O(12)	7833(4)	7441(3)	683(3)	50(1)
C(16)	5716(5)	8193(4)	1659(4)	34(1)
C(12)	7219(5)	7181(4)	1226(3)	35(1)
O(7)	5981(5)	6623(4)	3128(3)	74(2)
C(15)	6068(6)	7596(4)	1170(4)	39(2)
O(5)	1559(5)	5969(4)	−407(3)	78(2)
O(10)	9749(5)	5815(4)	908(4)	73(2)
O(4)	722(5)	7701(4)	1321(4)	73(2)
C(7)	6674(6)	6440(5)	2748(4)	47(2)
C(17)	6521(5)	8614(4)	2374(4)	37(1)
O(11)	9842(5)	7334(4)	3207(4)	92(2)
C(8)	6711(8)	5308(5)	1387(5)	61(2)
C(10)	9081(7)	5919(4)	1321(5)	51(2)
O(3)	2475(6)	7375(4)	−1794(3)	85(2)
C(4)	1575(6)	7486(5)	1134(5)	50(2)
C(9)	8566(8)	5161(5)	2828(5)	69(2)
O(6)	3579(6)	5970(4)	2306(4)	82(2)
C(11)	9130(7)	6920(5)	2789(5)	58(2)
O(8)	6059(7)	4812(4)	1028(4)	102(2)
C(1)	4223(8)	9044(5)	−565(5)	60(2)
O(1)	4770(7)	9544(4)	−811(4)	94(2)
O(2)	1115(6)	9226(5)	−368(4)	98(2)
C(19)	6924(8)	9099(5)	3801(5)	66(2)
O(9)	8945(7)	4613(4)	3263(4)	106(2)
C(20)	8062(7)	9307(5)	3769(5)	62(2)
C(6)	3341(7)	6417(5)	1744(5)	52(2)
C(18)	6143(7)	8767(5)	3107(4)	53(2)
C(2)	1975(8)	8846(6)	−281(5)	61(2)
C(3)	2785(7)	7727(5)	−1174(4)	55(2)
C(5)	2100(7)	6411(5)	87(5)	52(2)
C(22)	7672(6)	8839(5)	2343(5)	55(2)
C(13)	7417(7)	8138(6)	79(5)	67(2)
C(21)	8444(7)	9187(5)	3043(5)	70(2)
C(14)	8452(9)	8551(7)	−122(6)	99(4)

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

3.3. *Crystal structure determination of [$(CO)_6Fe_2Te_2$\{μ-PhC=C–C(OEt)\}$W(CO)_5$] (**4**)*

Red crystals of **2** were grown from hexane solutions at −4°C and were used for data collection. Data was collected on an Enraf-Nonius CAD4 diffractometer with Mo–K$_\alpha$ ($\lambda = 0.71073$ Å) radiation at room tem-

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

Bond length (Å)			
W–C(12)	2.145(6)	Te(2)–Fe(1)	2.5239(11)
W–C(10)	2.046(8)	Fe(1)–C(1)	1.794(9)
Te(1)–C(16)	2.148(6)	Fe(1)–Fe(2)	2.5989(13)
Te(1)–Fe(2)	2.5285(10)	O(12)–C(12)	1.313(7)
Te(1)–Fe(1)	2.5463(10)	C(16)–C(15)	1.348(8)
Te(2)–C(15)	2.171(6)	C(16)–C(17)	1.478(8)
Te(2)–Fe(2)	2.5275(10)	C(12)–C(15)	1.456(8)
Bond angles (°)			
Fe(2)–Te(1)–Fe(1)	61.61(3)	C(11)–W–C(12)	91.8(3)
C(15)–Te(2)–Fe(1)	99.44(18)	C(16)–Te(1)–Fe(2)	100.81(16)
C(15)–Te(2)–Fe(2)	100.62(17)	C(16)–Te(1)–Fe(1)	100.58(15)
Fe(1)–Te(2)–Fe(2)	61.93(3)	C(1)–Fe(1)–Te(2)	104.6(3)
Te(2)–Fe(1)–Te(1)	82.56(3)	Te(2)–Fe(2)–Fe(1)	58.97(3)
Te(2)–Fe(1)–Fe(2)	59.10(3)	C(15)–C(16)–Te(1)	117.1(4)
Te(1)–Fe(1)–Fe(2)	58.86(3)	C(17)–C(16)–Te(1)	118.7(4)
Te(1)–Fe(2)–Te(2)	82.84(3)	C(16)–C(15)–C(12)	131.1(5)
Te(1)–Fe(2)–Fe(1)	59.53(3)	C(16)–C(15)–Te(2)	117.9(5)

perature using the ω-2θ scan method. Other relevant crystallographic data are listed in Table 1. Unit cell parameters were refined using 25 machine centred reflections. The structure was solved by SHELXS-97 program using direct methods and refined using SHELXL-97. All the non-hydrogen atoms were refined anisotropically and the refinement converged to $R = 0.0283$ for unique reflections with $I > 2\sigma(I)$. Hydrogen atoms were geometrically constrained and refined using a riding model as contained in SHELXL-97. Tables 2 and 3 list the fractional atomic coordinates and selected bond lengths/angles for **4**, respectively.

4. Conclusions

We have described the formation of enol ether products from the cluster supported Fischer carbene complexes, $[(CO)_6Fe_2EE'\{\mu\text{-PhC=CC(OEt)}\}M(CO)_5]$ ($M =$ Cr or W; $EE' =$ SSe or TeTe) by reaction with an excess of Bu_3SnH in presence of pyridine. Though the intermediate α-(alkoxy)stannane derivative $[(CO)_6Fe_2\{\mu\text{-SeCPh=C(Se)C(OEt)(H)SnBu}_3\}]$ has been isolated in the case of $[(CO)_6Fe_2Se_2\{\mu\text{-PhC=CC(OEt)}\}M(CO)_5]$ using one equivalent of Bu_3SnH, the corresponding α-(alkoxy)stannane derivative $[(CO)_6Fe_2\{\mu\text{-TeCPh=C(Te)C-(OEt)(H)SnBu}_3\}]$ for $EE' =$ TeTe is not observed. In the case of mixed-chalcogenide systems formation of α-(alkoxy)stannane derivatives $[(CO)_6Fe_2\{\mu\text{-ECPh=C(E')C(OEt)(H)SnBu}_3\}]$, is not observed. These results once again illustrate how substituents influence and alter the chemical reactivity pattern of cluster supported Fischer carbene complexes.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 103128. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK

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