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Unusual Formation of Vinyl Ether Derivatives in the Reaction of Tributyltin Hydride with Fischer Carbene Complexes Anchored on a Chalcogen-Stabilized Iron Carbonyl Cluster

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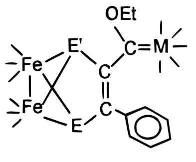
Summary: Treatment of $Fe_2(CO)_6\{\mu\text{-}EC(Ph){=}C(E')[C(OEt){=}M(CO)_5]\}$ (**1**: *E, E′ = Se; M = Cr.* **2**: *E, E′ = Se; M = W.* **3**: *E = S; E′ = Te; M = W) with excess* Bu_3SnH *in hexane at 0 °C produces enol ether derivatives:* $(CO)_6Fe_2\{\mu\text{-}EC(Ph)(H){-}C(E'){=}C(H)(OEt)\}$ *((Z)-**4a**: E, E′ = Se. (E)-**4b**: E, E′ = Se. (Z)-**5a**: E = S; E′ = Te. (E)-**5b**: E = S; E′ = Te). For E, E′ = Se, using 1 equiv of* Bu_3SnH*, the α-alkoxyallylstannane complex,* $(CO)_6Fe_2\{\mu\text{-}Se(Ph)C{=}C(Se){-}C(OEt)(H)SnBu_3\}$ *(**6**), was isolated. The molecular structure of (E)-**4b** was confirmed by X-ray analysis.*

Introduction

In continuation of our interest in preparing chalcogen-stabilized clusters with organic functional appendages, we have been exploring the chemistry of adducts of general formula $Fe_2(CO)_6\{\mu\text{-}EC(Ph){=}C(E')[C(OEt){=}M(CO)_5]\}$ (Figure 1) (**1**: M = Cr; E, E′ = Se. **2**: M = W; E, E′ = Se. **3**: M = W; E = S; E′ = Te), under different reaction conditions.[1]

Fischer carbene complexes participate in many interesting and remarkable transformations and have been extensively used in many organic syntheses.[2] The Fischer carbene moiety in complexes $Fe_2(CO)_6\{\mu\text{-}EC(Ph){=}C(E')[C(OEt){=}M(CO)_5]\}$ (**1**, **2**, or **3**) is a potential organic functional group. For example, it can be readily transformed to an amino carbene group, an ester, or an orthoester.[1b] Such functionality permits attachment of a metal cluster unit to organic residues of biological significance. For instance, an alkoxystannane functional group is a masked carbanion which can react with electrophiles like aldehyde or ketone with high diastereoselectivity.[3] Bu_3SnH is known to displace the pentacarbonylmetal moiety from the carbene carbon of a Fischer carbene complex to afford alkoxystannane derivatives under mild conditions.[4] We have examined this transformation using the cluster-supported Fischer carbene complexes under similar conditions and we report herein the formation of enol ether derivatives, from the reaction of **1**−**3** with excess Bu_3SnH and an alkoxystannane complex from **1** and **2** when equimolar quantity of Bu_3SnH was used.



	M	E	E'
1	Cr	Se	Se
2	W	Se	Se
3	W	S	Te

Figure 1.

Results and Discussion

The reaction of complexes $Fe_2(CO)_6\{\mu\text{-}EC(Ph){=}C(E')[C(OEt){=}M(CO)_5]\}$ (**1**: E, E′ = Se; M = Cr. **2**: E, E′ = Se; M = W. **3**: E = S; E′ = Te; M = W) with >2-fold excess of Bu_3SnH, in presence of 3−4 equiv of pyridine, at 0 °C yielded enol ether derivatives (mixture of *E*/*Z* isomers): $(CO)_6Fe_2\{\mu\text{-}EC(H)PhC(E'){=}C(H)(OEt)\}$ ((*Z*)-

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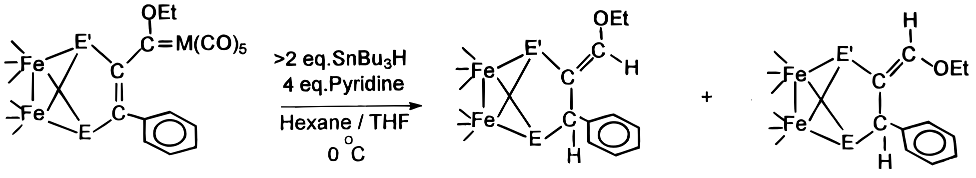
Scheme 1

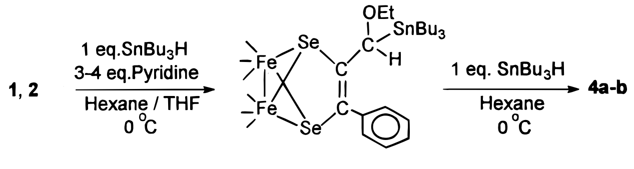


1: M = Cr; E, E' = Se
2: M = W; E, E' = Se
3: M = W; E = S; E' = Te

Z- **4a**: E, E' = Se
Z- **5a**: E = S; E' = Te

E-**4b**: E, E = Se
E-**5b**: E = S; E' = Te

Scheme 2



6

4a: E, E′ = Se. (*E*)-**4b**: E, E′ = Se. (*Z*)-**5a**: E = S; E′ = Te. (*E*)-**5b**: E = S; E′ = Te) as the only isolable, metal-containing products in reasonable yield (Scheme 1).

When an equimolar amount of Bu_3SnH was used, complexes **1** and **2** furnished an alkoxystannane derivative, $(CO)_6Fe_2\{\mu\text{-Se(Ph)C{=}C(Se)}\text{—}C(OEt)(H)SnBu_3\}$ (**6**) as a new, minor product in addition to the isomeric mixture of enol ether derivatives **4a**,**b**. It was observed that complex **6** could be converted to the enol ether derivatives on treatment with equimolar amount of Bu_3SnH albeit after a relatively extended period of time (12 h) in hexane at 0 °C (Scheme 2). The slow rate of this conversion suggests that complex **6** is a stable byproduct rather than the intermediate on route to the enol ether products. An analogous complex was not obtained from reaction of complex **3**, presumably because of unfavorable steric interaction between bulky tellurium and tin moieties.

All products were characterized by IR and ^{1}H, ^{13}C, ^{77}Se, or ^{125}Te NMR spectroscopy. The structure of (*E*)-**4b** was established by single-crystal X-ray diffraction methods. Identification of (*Z*)-**4a** was therefore based on comparison of its spectral features with that of (*E*)-**4b**. Similarly, (*E*)-**5b** was identified by comparison of its spectral features with that of (*Z*)-**5a**.

The structure of complex **6** was deduced on the basis of its spectral and analytical data. The infrared spectrum of **6** exhibits a carbonyl stretching pattern typical of the $Fe(CO)_3$ unit only, indicating loss of the $M(CO)_5$ fragment. In the aliphatic region of the ^{1}H NMR spectrum, three signals are observed: a singlet for the C*H* proton, a multiplet for the CH_2 protons of ethoxy group, indicating nonequivalence of the methylene protons due to attachment to a chiral center, and a triplet for the CH_3 group. The ^{13}C NMR spectrum displays signals for the butyl and ethoxy carbon atoms in the expected regions. From the coupling patterns and the coupling constant ($J_{C-H} = 182.5$ Hz), the peak at δ 142.9 ppm has been assigned to the chiral carbon (*C*(H)-$SnBu_3$) and the peak at δ 143.9 ppm has been assigned to the *C*(Ph) carbon. The ^{77}Se NMR spectrum of **6** shows two signals for the two nonequivalent Se atoms, one of which shows a Se—H coupling of 7.6 Hz.

The structure of (*E*)-**4b** was established by single-crystal X-ray diffraction methods, and its molecular structure is shown in Figure 2. It consists of a Fe_2Se_2 butterfly core and a vinylic ether unit, attached to the wing-tip selenium atoms.

The olefinic bond distance in (*E*)-**4b**, 1.28(1) Å, is smaller than the C═C distance of 1.331(7) Å in $\{(CO)_6Fe_2\{\mu\text{-SeC(Ph)═C(H)Se}\}$, but the C—C single bond distance of 1.52(2) Å is slightly longer than the corresponding C—C bond distance of 1.48(1) Å in $\{(CO)_6Fe_2\{\mu\text{-Se})_2\}$-CPh—C(H).[5] The Se(1)—C(7)—C(9) bond angle of 105.9(8)° in (*E*)-**4b** is 13° larger than the corresponding angle in $\{(CO)_6Fe_2(\mu\text{-Se})_2\}$CPh—C(H). The representative structure of (*E*)-**4b** helped to establish that isomeric products were in fact *E*/*Z* isomers pertaining to enol ether configuration.

The infrared spectra of (*Z*)-**4a**, **5a** and (*E*)-**4b**, **5b** exhibit carbonyl stretching patterns typical of the $Fe(CO)_3$ unit only, and their ^{1}H NMR spectra showed characteristic differences in chemical shift values of distinct signals. Between the *E* and *Z* isomeric pair of complexes, the methyl protons of the ethoxyl group are shielded in *E* compared to *Z*; methylene protons are shielded, albeit marginally, in *E* compared to *Z*; benzylic proton is shielded in *Z* compared to *E*; and olefinic proton is shielded in *Z* compared to *E* isomer. Similar differences are observed in ^{13}C NMR spectra of (*Z*)-**4a**, **5a** and (*E*)-**4b**, **5b** as well. 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 the *Z* isomer. The ^{77}Se NMR signals of (*Z*)-**4a** are shielded (443 and 622 ppm) compared to (*E*)-**4b** (521 and 628 ppm). ^{125}Te signal of (*Z*)-**5a** appears 109 ppm upfield of the signal observed for the *E* isomer.

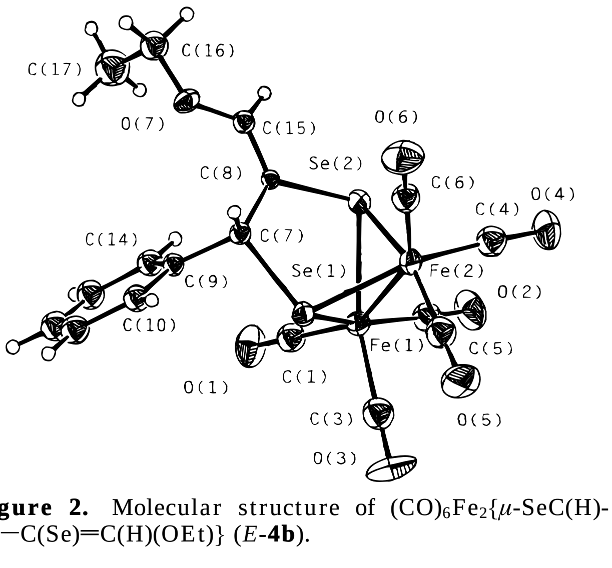


Figure 2. Molecular structure of $(CO)_6Fe_2\{\mu\text{-SeC(H)-Ph—C(Se)═C(H)(OEt)}\}$ (*E*-**4b**).

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Experimental Section

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 Nicolet-Impact 400 FTIR spectrometer as an *n*-hexane solution 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 the 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, tungsten hexacarbonyl, and phenylacetylene were purchased from Aldrich Chemical Co, and these were used without further purification. Bu_3SnH was purchased from Fluka Chemika. The homochalcogenide and mixed-chalcogenide iron carbonyl clusters $Fe_2(\mu\text{-}Se_2)(CO)_6$,[6] $Fe_2(\mu\text{-}STe)(CO)_6$,[7] α,β-unsaturated mixed-chalcogenide and homochalcogenide alkenylcarbene complexes $[(CO)_6Fe_2STe\{\mu\text{-}PhC{=}CC(OEt)\}Cr(CO)_5]$ and $[(CO)_6Fe_2Se_2\{\mu\text{-}PhC{=}CC(OEt)\}Cr(CO)_5]$[1] and the alkynyl Fischer carbene complexes $[(CO)_5M{=}C(OEt)(C{\equiv}CPh)]$ (M = Cr, W)[8] were prepared as previously reported.

General Procedure for Reaction of Bu_3SnH and $Fe_2(CO)_6\{\mu\text{-}EC(Ph){=}C(E')[C(OEt){=}M(CO)_5]\}$ (1, 2, or 3). In a typical preparation, into a freshly prepared solution of 1 equiv of **1**, **2**, or **3** in THF/hexane (5:95 v/v) (10 mL), 2−3 equiv of Bu_3SnH was added. The solution was stirred about 40 min (for **2** and **3**) and 4 h (for **1**) at 0 °C in presence of 3−4 equiv of pyridine. The reaction mixture was kept at −10 °C for 2 h to precipitate the (pyridine) pentacarbonyltungsten/chromium byproduct. 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 major yellow bands. The yellow band eluting first was characterized spectroscopically as (Z)-$(CO)_6Fe_2\{\mu\text{-}EC(H)Ph{-}C(E'){=}C(H)(OEt)\}$ ((Z)-**4a**, **5a**) and the second yellow band characterized spectroscopically as (E)-$(CO)_6Fe_2$ $\{\mu\text{-}EC(H)Ph{-}C(E'){=}C(H)(OEt)\}$ ((E)-**4b**, **5b**).

Complex (Z)-4a: yellow, yield 23 (from **1**) and 39% (from **2**). IR: 2067 (vs), 2029 (vs), 1997 (vs), 1998 (s), 1977 (m). ^{1}H NMR (δ, $CDCl_3$): 1.28 (t, J = 7.1 Hz, CH_3), 3.87 (q, J = 7.0 Hz, CH_2), 4.30 (d, $^{3}J_{H-H}$ = 2.1 Hz, $^{2}J_{Se-H}$ = 15.4 Hz, C(H)Se), 5.92 (d, $^{3}J_{H-H}$ = 1.5 Hz, $^{3}J_{Se-H}$ = 8.4 Hz), C(H)(OEt)), 7.12−7.32 (m, C_6H_5). ^{13}C NMR (δ, $CDCl_3$): 15.4 (t, CH_3), 50.4 (d, J_{C-H} = 144.7, CH(Ph)), 69.5 (q, J_{C-H} = 145.8, OCH$_2$), 127.8−129.1 (m, C_6H$_5$), 140.9 (s, =CSe), 151.3 (d, J_{C-H} = 178 Hz, =CH), 209.6 (s, Fe(CO)$_3$). ^{77}Se NMR (δ, $CDCl_3$): 443 (d, $^{3}J_{Se-H}$ = 8.4 Hz, =CSe), 622 (d, $^{2}J_{Se-H}$ = 15.2 Hz, C(H)(Ph)Se). Mp: 96−98 °C.

Complex (E)-4b: yellow, yield 37 (from **1**) and 44% (from **2**). IR: 2067 (vs), 2030 (vs), 1997 (vs), 1992 (s), 1979 (m). ^{1}H NMR (δ, $CDCl_3$): 0.97 (t, J = 7.1 Hz, CH_3), 3.72 (m, OCH_2), 4.77 (d, $^{3}J_{H-H}$ = 1.5 Hz, $^{2}J_{Se-H}$ = 20.4 Hz, C(H)Se), 6.80 (d, $^{3}J_{H-H}$ = 1.8 Hz, $^{3}J_{Se-H}$ = 7.6 Hz, =C(H)(OEt)), 7.10−7.24 (m, C$_6H_5$). ^{13}C NMR (δ, $CDCl_3$): 15.2 (t, CH$_3$), 47.8 (d, J_{C-H} = 149.6 Hz, CH(Ph)), 69.1 (q, J_{C-H} = 144.7, OCH$_2$), 127.1−128.3 (m, C_6H$_5$), 139.4 (s, =CSe), 146.6 (d, J_{C-H} = 180.2 Hz, =CH), 209.7 (s, Fe(CO)$_3$), 209.5 (s, Fe(CO)$_3$). ^{77}Se NMR (δ, $CDCl_3$): 521 (dd, $^{3}J_{Se-H}$ = 2.3 Hz, $^{3}J_{Se-H}$ = 6.8 Hz, =CSe), 628 (d, $^{2}J_{Se-H}$ = 19.8 Hz, C(H)(Ph)Se). Mp: 98−100 °C. Anal. Calcd (Found) for $Fe_2Se_2C_{17}O_7H_{12}$: C, 34.13 (34.38); H, 2.00 (2.30).

Table 1. Crystallographic Data for (E)-4b

empirical formula	$C_{17}H_{12}Fe_2O_7Se_2$
formula weight	597.89
space group	$P1$ (No. 2)
unit cell dimensions	a = 11.809(7) Å; α = 98.33(5)° b = 13.318(6) Å; β = 107.48(6)° c = 7.814(4) Å; γ = 111.27(4) °
U/Å^3	1046(1)
Z	2
D_c/g cm^{-3}	1.90
μ(Mo Kα)/mm^{-1}	48.96
F_{000}	580.00
2θ max/deg	50
$[F_o^2 \geq 3\sigma(Fo)^2]$, No	
no. of parameters refined, Np	168
largest electron density peak/e Å^3	0.36
R^a	0.0379
R'^b	0.0322
goodness of fit,^{c} S	1.53

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R' = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2}$, where $w = 1/\sigma^2(F_o)$. [c] $S = [\sum(|F_o| - |F_c|)/\sigma]/(No - Np)$.

Complex (Z)-5a: yellow, yield 25% (from **3**). IR: 2065 (s), 2027 (vs), 1997 (s), 1985 (m). ^{1}H NMR (δ, $CDCl_3$): 1.25 (t, J = 7.0 Hz, CH_3), 3.87 (q, J = 7.1 Hz, OCH_2), 4.02 (d, $^{3}J_{H-H}$ = 1.8 Hz, C(H)S), 5.77 (d, $^{3}J_{H-H}$ = 2.1 Hz, =C(H)(OEt)), 7.11−7.34 (m, C_6H_5). ^{13}C NMR (δ, $CDCl_3$): 15.5 (q, J_{C-H} = 126.9 Hz, CH$_3$), 62.6 (d, J_{C-H} = 146.4 Hz, CH(Ph)), 69.1 (t, J_{C-H} = 144.6 Hz, OCH$_2$), 128.2−129 (m, C_6H$_5$), 141.4 (s, =CTe), 154.8 (d, J_{C-H} = 178.2 Hz, =CH), 210.1 (s, Fe(CO)$_3$). ^{125}Te NMR (δ, $CDCl_3$): 628 (d, $^{3}J_{Te-H}$ = 7.7 Hz, =CTe). Mp: 102−104 °C. Anal. Calcd (Found) for $Fe_2STeC_{17}O_7H_{12}$: C, 34.04 (34.32); H, 2.00 (2.29).

The second yellow band was tentatively identified as (E)-**5b** (53%), based on similarity of spectral pattern and elemental analysis.

Preparation of $(CO)_6Fe_2\{\mu\text{-}SeC(Ph){=}C(Se){-}C(OEt)(H)SnBu_3\}$ (6). The complex **2** (1 g, 1.08 mmol) and Bu_3SnH (0.28 mL, 1.08 mmol) in hexane (10 mL) was stirred at 0 °C for 6 h in presence of 4 equiv of pyridine, and the reaction mixture was kept at −10 °C for 2 h to precipitate the (pyridine)pentacarbonyltungsten byproduct. The solution was filtered through Celite, and the solvent was removed in vacuo. The residue was chromatographed on silica gel column. Elution with hexane yielded a yellow band of **6** (0.24 g, 26%) followed by $(CO)_6Fe_2\{\mu\text{-}SeC(H)Ph{-}C(Se){=}C(H)(OEt)\}$ (**4a**,**b**) (0.26 g, 41%).

For 6. IR: 2064 (vs), 2028 (vs), 1994 (vs), 1974 (m). ^{1}H NMR (δ, $CDCl_3$): 0.84 (12H, t, J = 7.1 H, CH_3), 0.92 (6H, m, CH_2CH$_3$), 1.24 (6H, sextet, J = 7.1 Hz, CH_2CH$_2$CH$_3$), 1.41 (6H, m, CH_2CH$_2$CH$_2$CH_3), 3.89 (2H, m, OCH_2), 6.95 (1H, s, CH), 6.96−7.19 (5H, m, C$_6H_5$). ^{13}C NMR (δ, $CDCl_3$): 13.6 (t, CH$_2$$CH_3$), 15.4 (t, OCH$_2$$CH_3$), 27.5 (m, CH$_2CH_3$), 29.1 (m, CH$_2$-CH$_2CH_3$), 29.8 (m, CH$_2CH_2$ CH$_2$CH$_3$), 69.3 (q, OCH$_2$), 117.2 (s, =CCSe), 125, 128 (m, C_6H$_5$), 142.9 (d, J_{C-H} = 182.5 Hz, CHSnBu$_3$), 143.9 (s, C(Ph)Se)), 209.6 (s, Fe(CO)$_3$), 209.9 (s, Fe-(CO)$_3$). ^{77}Se NMR (δ, $CDCl_3$): δ 570 (d, $^{3}J_{Se-H}$ = 7.6, SeCC-(OEt)), 702 (s, SeC(Ph)). Mp: 76−78 °C. Anal. Calcd (Found) for $Fe_2SnSe_2C_{29}O_7H_{38}$: C, 39.24 (39.57); H, 4.28 (4.49).

Compound **6** (16%) was also obtained from the reaction of **1** and 1 equiv of Bu_3SnH in the presence of 4 equiv of pyridine under similar conditions.

Preparation of $(CO)_6Fe_2\{\mu\text{-}SeC(H)Ph{-}C(Se){=}C(H)(OEt)\}$ ((Z)-4a, (E)-4b) from 6. In a typical preparation, equimolar amounts of **6** (0.3 g, 0.33 mmol) and Bu_3SnH (0.09 mL, 0.33 mmol) were stirred at 0 °C in hexane for 12 h and allowed to come at room temperature. The solution was filtered through Celite, the solvent was removed, and the residue was subjected to chromatographic work up on thin-layer silica gel plates. Elution with hexane yielded two very

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for (*E*)-4b

Fe(1)−Se(1)	2.372(3)	Fe(1)−Fe(2)	2.551(3)
Fe(1)−Se(2)	2.373(3)	Se(1)−C(7)	2.03(1)
Fe(2)−Se(1)	2.367(3)	C(7)−C(8)	1.52(2)
Fe(2)−Se(2)	2.369(3)	C(8)−C(15)	1.28(1)

Fe(1)−Fe(2)−Se(1)	57.52(8)	Se(1)−Fe(1)−Se(2)	81.65(9)
Fe(1)−Fe(2)−Se(2)	57.39(7)	Se(1)−Fe(2)−Se(2)	81.68(8)
Fe(2)−Fe(1)−Se(2)	57.51(7)	Fe(1)−Se(1)−C(7)	103.3(4)
Fe(2)−Fe(1)−Se(1)	57.35(8)	Fe(2)−Se(2)−C(8)	102.8(4)
Fe(1)−Se(1)−Fe(2)	65.13(8)	Se(2)−C(8)−C(15)	118(1)
Fe(1)−Se(2)−Fe(2)	65.09(8)	Se(1)−C(7)−C(8)	111.2(9)

closely spaced yellow bands. The first yellow band to elute was characterized spectroscopically as (*Z*)-**4a**) (0.07 g, 38%) and the second band as (*E*)-**4b**) (0.09 g, 47%).

Crystal Structure Determination of (*E*)-4b. An orange red crystal of (*E*)-**4b** was selected and mounted on a glass fiber and sealed with epoxy glue. Data were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation operating at 50 kV and 35 mA. Cell constants and an orientation matrix for data collection were obtained from 25 carefully centered reflections in the range $11.00° < 2\theta < 23.43°$. Pertinent crystallographic data for (*E*)-**4b** are given in Table 1 and selected bond angle and bond distance are given in Table 2.

The data were collected at a temperature of 23 ± 1 °C using $\omega-2\theta$ scan technique to a maximum 2θ value of 50.0°. Scans were made at a speed of 8.0°/min (in ω). The structure was solved by direct methods.[9] Non-hydrogen atoms except carbon were refined anisotropically. The final cycle of the full-matrix least-squares refinement[10] was based on 983 observed reflections ($I > 3.00\sigma(I)$) and 168 variable parameters and converged (largest parameter shift was 0.001 times its ESD) with unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.0379$; $R' = [(\sum w(|F_o| - |F_c|)^2/\sum w F_o^2)]^{1/2} = 0.0322$.

The maximum and the minimum peaks on the final differences Fourier map corresponded to 0.36 and −38 e Å^3, respectively. Neutral atom scattering factors were taken from Cromer and Waber.[11] All calculations were performed using the Texsan crystallographic software package of Molecular Structure Corp.[12]

Conclusion

We have described an unusual formation of enol ether products from Fischer carbene complexes anchored to chalcogen-stabilized iron carbonyl clusters by reaction with excess Bu_3SnH. A stable alkoxystannane derivative has been isolated in some instances, which reacts slowly with added Bu_3SnH to yield the enol ether products eventually. These results once again illustrate how substituents influence and alter chemical reactivity pattern of Fischer carbene complexes.

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Supporting Information Available: Crystallographic details including complete tables of atomic coordinates, bond lengths and bond angles, and anisotropic displacement parameters for (*E*)-**4b** (6 pages). Ordering information is given on any current masthead page.

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[9] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

[10] Least-squares, function minimized: $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2(F_o^2)$; $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/(Lp)^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, Lp Lorentz−polarization factor, and $p = p$ factor.

[11] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*, Kynoch Press: Birmingham, U.K., 1974; Vol. 4, Table 2.2A.

[12] TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corporation, Texas, TX, 1985 and 1992.

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