Chemical Modification of the Metal−Carbene Appendage in New, Trimetallic Adducts of $Fe_2(CO)_6(\mu$-EE′) (E = S, Se and E′ = Se, Te) and Alkynyl Fischer Carbene Complexes $(CO)_5M$=C(OEt)(C≡CPh) (M = Cr, W)

Pradeep Mathur* and Sundargopal Ghosh

Chemistry Department, Indian Institute of Technology, Powai, Bombay 400076, India

Amitabha Sarkar

Division of Organic Chemistry (Synthesis), National Chemical Laboratory, Pune 411008, India

C. V. V. Satyanarayana

Regional Sophisticated Instrumentation Center, Indian Institute of Technology, Powai, Bombay 400 076, India

Vedavati G. Puranik

Division of Physical Chemistry, National Chemical Laboratory, Pune 411008, India

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From the room temperature reaction of the transition metal alkynyl Fischer carbene complexes $(CO)_5M$=C(OEt)(C≡CPh) (M = Cr, W) with the homochalcogenide compounds $Fe_2(CO)_6(\mu$-$E_2)$ (E = S, Se, Te), the following new trimetallic adducts were obtained: [$(CO)_6$-$Fe_2E_2\{\mu$-PhC=CC(OEt)$\}M(CO)_5$] (**1**−**5**; **1**, 30%, E = S, M = Cr; **2**, 85%, E = Se, M = Cr; **3**, 85%, E = Se, M = W; **4**, 28%, E = Te, M = Cr; **5**, 25%, E = Te, M = W). Alkoxy groups are readily replaced by amino groups in adducts **2**, **3**, and **5** at room temperature as *syn*- and *anti*-isomers, [$(CO)_6Fe_2E_2\{\mu$-PhC=CCN(H)R$\}M(CO)_5$] (*syn*-**8a**−**f** and *anti*-**8a**−**f**; where R = CH_3, CH_2Ph, CH_2CH=CH_2), in 70−90% yield. When a methanolic solution of [$(CO)_6Fe_2$-EE′$\{\mu$-PhC=CC(OEt)$\}M(CO)_5$] (E ≠ E′; E = S, Se; E′ = Se, Te; M = Cr, W) was stirred at room temperature for 1−2 days, the ester and ortho ester derivatives $(CO)_6Fe_2\{\mu$-EC(Ph)=C(CO)(OR)E′$\}$ (**12**−**15**) and $(CO)_6Fe_2\{\mu$-EC(Ph)=CC(OR)$(OMe)_2$E′$\}$ (**16**−**19**) (R = CH_3, C_2H_5) were formed. All compounds were characterized by IR and ^{1}H, ^{13}C, ^{77}Se, and ^{125}Te NMR spectroscopies. Crystallographic analysis of the compound $Fe_2(CO)_6\{\mu$-SC-(Ph)=CC$(OCH_3)_2(OC_2H_5)$Te$\}$ (**17**) established its structure as a Fe_2STe tetrahedral butterfly core containing the ortho ester unit, C(Ph)=C−C$(OCH_3)_2(OC_2H_5)\}$ as a bridge between the two wing-tip chalcogens.

Introduction

In recent years cluster compounds incorporating single-atom ligands have received considerable attention, largely because of their utility in the synthesis of high-nuclearity clusters; this activity has been particularly high for metal−chalcogen clusters.[1] We recently reported that $Fe_2(\mu$-EE′$)(CO)_6$ (where E or E′ = S, Se, or Te) readily adds to monosubstituted alkynes to form adducts $Fe_2(CO)_6\{\mu$-EC(H)=C(R)E′$\}$ (where R = Ph, CH_2OH, and H).[2] Though addition to a disubstituted alkyne was not feasible under similar conditions, we now find that mixed chalcogenide derivatives, $Fe_2(\mu$-EE′$)(CO)_6$ (where E or E′ = S, Se, or Te), add almost instantly to the triple bond of alkynyl Fischer carbene complexes $(CO)_5M$=C(OEt)(C≡CPh) (where M = Cr, W).[3] In these adducts, the metal−carbene fragment may be chemically modified by oxidation, substitution, etc. to incorporate the desired organic molecule or spacer subsequently. It is also of interest to explore the modified reactivity of a Fischer carbene complex where the carbene carbon is attached to a styrene linkage from which a metal cluster is suspended. An annulation reaction, for instance, can lead to functionally attractive organic appendages to the diiron cluster. In this report, we describe the results of our initial explorations, *viz*, (a) facile aminolysis to form aminocarbene derivatives, (b) formation of ortho ester derivatives at the carbene carbon with expulsion of the metal carbonyl, and (c) clean and selective oxidation of the metal−carbene fragment to carboxylate groups.

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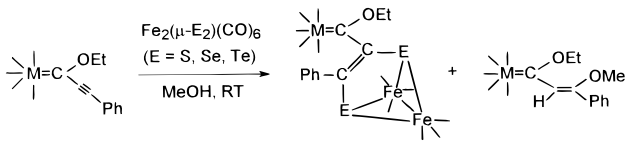
Scheme 1



M = Cr, W

	M	E	Yield (%)
1	Cr	S	30
2	Cr	Se	85
3	W	Se	85
4	Cr	Te	28
5	W	Te	25

6. M = Cr
7. M = W

Results and Discussion

Synthesis of $[(CO)_6Fe_2E_2\{\mu$-PhC═CC(OEt)$\}M(CO)_5]$. The iron carbonyl homochalcogenide compounds $Fe_2(\mu$-EE$)(CO)_6$ readily added to the reactive triple bond of the alkynyl Fischer carbene complexes $(CO)_5M$═C(OEt)(C≡CPh) (M = Cr, W) to provide trimetallic adducts in moderate to high yields (Scheme 1, Table 1). In a typical preparation, a freshly prepared methanol solution of $Fe_2(\mu$-EE$)(CO)_6$ (E = S, Se, Te) was added to an equimolar amount of the solid Fischer carbene complex. After the reaction mixture was stirred at room temperature for 40−50 min, the trimetallic $[(CO)_6Fe_2E_2\{\mu$-PhC═CC(OEt)$\}M(CO)_5]$ (E = S, Se, Te and M = Cr, W) (**1**−**5**) was isolated by chromatography over silica gel and purified by crystallization from hexane at −4 °C to afford air-stable, red, crystalline solids in 30−85% yield. In each case, a trace amount of the Fischer carbene complex $(CO)_5$M═C(OEt){CH═C-(OMe)Ph} (**6**, M = Cr; **7**, M = W) was obtained as a side product and identified on the basis of a comparison of its IR and ^{1}H NMR spectral data with that reported in the literature.[4]

The characterization of compounds **1**−**5** is based on a comparison of their spectroscopic features with those of the recently reported and stucturally characterized trimetallic adducts $Fe_2(CO)_6\{\mu$-EC(Ph)═C(E′)[(OEt)C═M-$(CO)_5]\}$ (E = S, Se; E′ = Se, Te; M = Cr, W).[3] The spectroscopic features of **1**−**5** are summarized in Table 2. The infrared spectra of compounds **1**−**5** exhibit almost identical carbonyl stretching patterns typically observed for compounds containing $Fe(CO)_3$ and $M(CO)_5$ (M = Cr, W) units. The ^{13}C NMR spectra of all of the compounds display two peaks between δ 133 and 157 ppm. The downfield signal has been assigned to *C*(Ph) and the upfield signal to *C*(C═M), in line with previous reports.[5] We observe three signals in the CO region corresponding to the CO groups attached to the Fe atom and to the *cis*- and *trans*-CO groups in the $M(CO)_5$ (M = Cr, W) unit. The most deshielded signal at δ 311−337 ppm is assigned to the carbene carbon, M═*C*. The ^{77}Se NMR spectra of **2** and **3** show two broad peaks at δ 550−600 ppm. Similarly, the ^{125}Te NMR spectra of **4** and **5** show two broad peaks at δ 960−1200 ppm.

Aminolysis of 2, 3, and 5. Displacement of the alkoxy group of a carbene complex by an amine is well-known.[6] Such a reaction permits the attachment of diverse organic molecules to a metal carbene complex.[7] On stirring diethyl ether solutions of **2**, **3**, or **5** with the amines RNH_2 (R = CH_2CH═CH_2, CH_2Ph, or CH_3) at room temperature, the aminocarbene derivatives $[(CO)_6$-$Fe_2E_2\{\mu$-PhC═CCN(H)R$\}$ $M(CO)_5]$ (*syn*- or *anti*-**8a**−**f**) were formed in high yield (Scheme 2). These compounds were characterized by IR and ^{1}H, ^{13}C, ^{77}Se, and ^{125}Te NMR spectroscopies. The IR spectra show six bands in the terminal CO region, a pattern similar to that observed for **1**−**5** but with the bands in **8a**−**f** shifted to lower frequencies. Due to high barrier to C−N bond rotation, two sets of compounds (with a *syn* and *anti* relationship of the N-substituent with respect to chromium or tungsten) were observed, and it was possible to separate the *syn* and *anti* isomers of each of **8a**−**f** with the *syn* isomer being predominant. Identification of the *syn* and *anti* isomers was made by ^{1}H NMR spectroscopy; in the *syn* isomer, the signals for the −NCH_2− and −NCH_3 protons appear upfield relative to the signals in the *anti* isomer, in line with previous reports in the literature.[8] On aminolysis, the ^{13}C resonance of the carbene carbon is shifted upfield as expected. ^{13}C, ^{77}Se, and ^{125}Te NMR spectroscopy also aids in distinguishing the two isomers. A difference of 2−3 ppm is observed between the ^{13}C NMR signals for the carbene carbon atoms in the two isomers, with the more downfield signal belonging to the *anti* isomer. Although rotational isomers were separated and individually identified, it is noted that any single isomer in solution slowly attains equilibrium with the other at room temperature over a period of 6−8 weeks. The ^{77}Se NMR spectra of compounds **8a**−**e** show two signals at δ 550−600 ppm; the more deshielded signal is assigned to the Se atom attached to the β carbon. Similarly, the ^{125}Te NMR spectrum of **8f** shows two signals at δ 960−1200 ppm. For *anti*-**8b**−**c**, the two ^{77}Se NMR signals are very closely spaced, but for *anti*-**8a** and **8e**, which have allylamino groups, the difference in the chemical shifts is somewhat larger. In both the ^{77}Se and ^{125}Te NMR spectra, the signals for the *syn* isomers appear more downfield relative to the corresponding signals for the *anti* isomers.

Formation of Ester and Ortho Ester Derivatives $(CO)_6Fe_2\{\mu$-EC(Ph)═C(CO)(OR)E′$\}$ and $(CO)_6Fe_2\{\mu$-EC(Ph)═CC(OR)$(OMe)_2$E′$\}$. Rapid oxidation of the trimetallic adducts $[(CO)_6Fe_2EE'\{\mu$-PhC═CC(OEt)$\}$-$M(CO)_5]$ with 1 equiv of TMNO in dichloromethane resulted in the clean formation of carboxylic ester derivatives $(CO)_6Fe_2\{\mu$-EC(Ph)═C(CO)(OR)E′$\}$ (**12**, 68%, E = E′ = Se, R = C_2H_5; **13**, 62%, E = S, E′ = Te, R = C_2H_5; **15**, 63%, E = Se, E′ = Te, R = C_2H_5) (Scheme 3). When the trimetallic adducts were allowed to stir in methanol for 1−2 days, in addition to the $(CO)_6Fe_2\{\mu$-EC(Ph)═C(CO)(OR)E′$\}$ (**12**, 35%, E = E′ = Se, R = C_2H_5; **13**, 30%, E = S, E′ = Te, R = C_2H_5; **14**, 12%, E = Se, E′

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Table 1. Experimental Conditions Used for Preparation of $[(CO)_6Fe_2E_2\{\mu\text{-PhC=CC(OEt)}\}M(CO)_5]$ (M = Cr, W and E = S, Se, Te) (1-5)

$(CO)_5M{=}C(OEt)(C{\equiv}CPh)$ (g, mmol)	$(CO_6Fe_2(\mu\text{-}E_2)$ (g, mmol)	reaction time (min)	product	yield (g (%))	anal. found (calcd)	mp (°C)
$(CO)_5Cr{=}C(OEt)(C{\equiv}CPh)$ (0.15, 0.42)	$(CO_6Fe_2(\mu\text{-}S_2)$ (0.14, 0.42)	50	**1**	0.09 (30)	C, 37.8 (38.0); H, 1.25 (1.44)	124−126 (dec)
$(CO)_5Cr{=}C(OEt)(C{\equiv}CPh)$ (0.13, 0.38)	$(CO)_6Fe_2(\mu\text{-}Se_2)$ (0.17, 0.38)	40	**2**	0.25 (85)	C, 33.3 (33.5); H, 1.12 (1.26)	130−132 (dec)
$(CO)_5W{=}C(OEt)(C{\equiv}CPh)$ (0.27, 0.57)	$(CO)_6Fe_2(\mu\text{-}Se_2)$ (0.25, 0.57)	40	**3**	0.44 (85)	C, 28.5 (28.7); H, 0.9 (1.08)	138−140 (dec)
$(CO)_5Cr{=}C(OEt)(C{\equiv}CPh)$ (0.08, 0.24)	$(CO)_6Fe_2(\mu\text{-}Te_2)$ (0.13, 0.24)	50	**4**	0.06 (28)	C, 29.6 (29.8); H, 1.0 (1.13)	140−142 (dec)
$(CO)_5W{=}C(OEt)(C{\equiv}CPh)$ (0.17, 0.37)	$(CO)_6Fe_2(\mu\text{-}Te_2)$ (0.2, 0.37)	50	**5**	0.09 (25)	C, 25.6 (25.9); H, 0.85 (0.98)	148−150 (dec)

= Te, R = CH_3; **15**, 17%, E = Se, E′ = Te, R = C_2H_5) compounds, the ortho ester derivatives $(CO)_6Fe_2\{\mu\text{-EC(Ph)=CC(OR)(OMe)}_2E'\}$ (**16**, 40%, E = E′ = Se, R = C_2H_5; **17**, 35%, E = S, E′ = Te, R = C_2H_5; **18**, 10%, E = Se, E′ = Te, R = CH_3; **19**, 15%, E = Se, E′ = Te, R = C_2H_5) were also obtained (Scheme 3). Formation of the latter involves a formal replacement of the $M(CO)_5$ fragment in the adduct by two methoxy groups. When the trimetallic adduct used was $[(CO)_6Fe_2SeTe\{\mu\text{-PhC=CC(OEt)}\}W(CO)_5]$ (**11**), a mixture of ester and ortho ester derivatives were formed with −C(CO)(OMe), −C(CO)(OEt), −$C(OMe)_3$, and −C(OEt)$(OMe)_2$ functions (**14**, **15**, **18**, **19**, respectively). It is possible that an alkoxide exchange preceded the formation of the ortho ester in this case.

Formation of an ortho ester from a metal−carbene complex is rather curious. A bimolecular reaction for the introduction of the third alkoxy group is unlikely on steric grounds. This would suggest that an incipient carbenium ion develops by a neighboring group participation of a chalcogen atom and is eventually trapped by a MeOH molecule. The stabilization of a carbenium ion is, thus, reminiscent of the stabilization of a propargyl cation[9] when the alkyne is complexed to $Co_2(CO)_6$. This reaction does not take place with simple Fischer carbene complexes such as Ph−C(OMe)=$M(CO)_5$ (M = Cr, W) under similar condition.

The spectral features of **12**−**19** are summarized in Table 2. The ^{13}C NMR peak due to M=*C* was absent in all of the spectra. The ester function was confirmed by the IR band at 1725−1730 cm^{-1}, the ^{13}C NMR peak at 160−165 ppm, and the ^1H NMR spectra. The ^{77}Se and ^{125}Te NMR spectra of these carboxylic esters also display two peaks between 500 and 700 and 770 and 970 ppm, respectively. The presence of the alkoxy group of the ortho esters is evident in the ^1H NMR spectra. The ^{13}C NMR peak of the ortho ester carbon appears at 155−160 ppm. The ^{77}Se and ^{125}Te NMR signals for the ortho ester derivatives appear more downfield by 22−24 and 28−40 ppm, respectively, relative to the corresponding signals observed for the ester derivatives. The ^{77}Se and ^{125}Te NMR signals for the ester derivatives were found to shift upfield, and for ortho ester derivatives they shift downfield relative to the corresponding signals in the trimetallic adducts. The structure of a representative ortho ester product, **17**, has been confirmed by single-crystal X-ray diffraction.

Molecular Structure of 17. Deep red, air-stable crystals of **17** were obtained from a hexane solution at −4 °C, and an X-ray diffraction study was undertaken. An ORTEP diagram of the molecular structure of **17** is shown in Figure 1. The structure consists of an Fe_2STe butterfly core, and the ortho ester molecule is attached to the wing-tip S and Te atoms of the butterfly, such that the CPh group is bonded to the S atom and the −$CC(OMe)_2(OEt)$ group to the Te atom. Each Fe atom has three terminally bonded carbonyl groups. The attachment of the ortho ester groups to the Fe_2STe core in **17** is similar to the attachment of phenylacetylene to the Fe_2Se_2 and Fe_2STe cores, respectively, in $(CO)_6Fe_2\{\mu\text{-SeC(H)=C(Ph)Se}\}$[10] and $(CO)_6Fe_2\{\mu\text{-SC(H)=C (Ph)Te}\}$.[2a] The acetylenic C−C bond distance of 1.337(9) Å in **17** is comparable with the corresponding bond distance of 1.330(6) Å in the trimetallic adduct $[(CO)_6Fe_2STe\{\mu\text{-PhC=CC(OEt)}\}Cr(CO)_5]$. The Fe(1)-Fe(2) bond distance of 2.5289(14) Å in **17** is shorter than the corresponding bond distance of 2.571(4) Å in $(CO)_6Fe_2\{\mu\text{-TeC(H)=C(Ph)Te}\}$ and 2.5445(13) Å in $[(CO)_6Fe_2STe\{\mu\text{-PhC=CC(OEt)}\}Cr(CO)_5]$ but comparable to those in other related Te-containing acetylenic derivatives: $(CO)_6Fe_2\{\mu\text{-SeC(H)=C(Ph)Te}\}$, 2.539(5) Å, and $(CO)_6Fe_2\{\mu\text{-SC(H)=C(Ph)Te}\}$, 2.526(2) Å. The Fe−Te−Fe bond angle of 59.56(4)° is similar to the corresponding bond angles in $(CO)_6Fe_2\{\mu\text{-SC(H)=C(Ph)Te}\}$, 59.47(4)°, and $(CO)_6Fe_2\{\mu\text{-SeC(H)=C(Ph)Te}\}$, 59.95(13)°, but smaller than the Fe−S−Te bond angle of 68.12 (16)° in **17** itself. All other parameters are unexceptional.

Experimental Section

General Procedures. All reactions and other manipulations were carried out under an argon or nitrogen atmosphere, using standard Schlenk techniques unless otherwise mentioned. 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 *n*-hexane solutions in a sodium chloride cell with a 0.1 mm path length. Elemental analyses were performed using a Carlo Erba 1106 automatic analyzer. ^1H, ^{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 NMR was 94.70 MHz with a 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, primary amines, and phenylacetylene were purchased from Aldrich Chemical Co., and these compounds were used without further purification. The homochalcogenide iron carbonyl clusters $Fe_2(\mu\text{-}S_2)(CO)_6$,[11] $Fe_2(\mu\text{-}Se_2)(CO)_6$,[12] and $Fe_2(\mu\text{-}Te_2)(CO)_6$,[13] α,β-unsaturated mixed chalcogenide alkenyl carbene complexes $[(CO)_6Fe_2EE'\{\mu\text{-PhC=CC(OEt)}\}M(CO)_5]$ (M = Cr, W; E = S,

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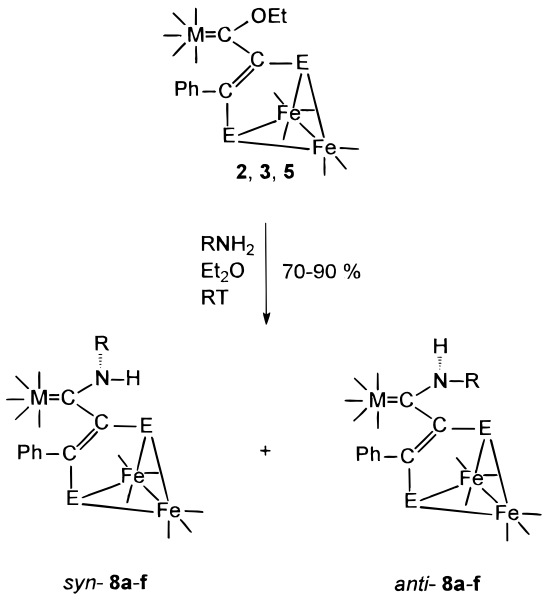
Table 2. Spectroscopic Data for Compounds 1−5 and 12−19

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	2081 (m), 2061 (vs), 2045 (vs), 2008 (vs), 1991 (m), 1962 (br, s)	1.62 (3H, t, J = 6.9 Hz, CH_3), 4.50 (2H, q, J = 7 Hz, CH_2), 6.91−7.25 (C_6H_5)	14.1 (q, CH_3, J_{C-H} = 129 Hz), 76.0 (t, OCH_2, J_{C-H} = 147 Hz), 127−129 (C_6H_5), 133.1 (s, α carbon), 142.0 (s, β carbon), 207.0 (s, *C*O (Fe)), 214.8 (s, *cis*-*C*O (Cr)), 222.8 (s, *trans*-*C*O (Cr)), 336.2 (s, Cr=*C*)		
2	2077 (m), 2060 (vs), 2040 (vs), 2005 (vs), 1986 (m), 1962 (br, s)	1.65 (3H, t, J = 6.9 Hz, CH_3), 4.52 (2H, q, J = 7 Hz, CH_2), 6.97−7.29 (C_6H_5)	14.3 (q, CH_3, J_{C-H} = 129 Hz), 76.1 (t, OCH_2, J_{C-H} = 147 Hz), 127−129 (C_6H_5), 134.0 (s, α carbon), 143.0 (s, β carbon), 208.4 (s, *C*O (Fe)), 215.0 (s, *cis*-*C*O (Cr)), 223.0 (s, *trans*-*C*O (Cr)), 337.2 (s, Cr=*C*)	560.8, 595.6	
3	2079 (m), 2066 (vs), 2040 (vs), 2003 (vs), 1983 (m), 1965 (br, s)	1.65 (3H, t, J = 7 Hz, CH_3), 4.51 (2H, q, J = 7 Hz, CH_2), 7.05−7.3 (C_6H_5)	14.6 (q, CH_3, J_{C-H} = 129 Hz), 76.1 (t, OCH_2, J_{C-H} = 146 Hz), 125−129 (C_6H_5), 135.0 (s, α carbon), 141.0 (s, β carbon), 195 (s, *cis*-*C*O (W)), 202.6 (s, *trans*-*C*O (W)), 208.4 (s, *C*O (Fe)), 311.6 (s, W=*C*)	518.3, 560.4	
4	2070 (m), 2056 (vs), 2030 (vs), 1997 (vs), 1977 (m), 1961 (br, s)	1.69 (3H, t, J = 7.1 Hz, CH_3, 4.46 (2H, q, J = 7 Hz, CH_2), 6.97−7.3 (C_6H_5)	14.8 (q, CH_3, J_{C-H} = 129.5 Hz), 75.6 (t, OCH_2, J_{C-H} = 147 Hz), 127−129 (C_6H_5), 139 (s, α carbon), 147.0 (s, β carbon), 211 (s, *C*O (Fe)), 215.2 (s, *cis*-*C*O (Cr)), 223.0 (s, *trans*-*C*O (Cr)), 338 (s, Cr=*C*)		1141.2, 1233.3
5	2074 (m), 2059 (vs), 2030 (vs), 1995 (vs), 1978 (m), 1964 (br, s)	1.65 (3H, t, J = 6.9 Hz, CH_3), 4.52 (2H, q, J = 7 Hz, CH_2), 6.97−7.29 (C_6H_5)	14.6 (q, CH_3, J_{C-H} = 128 Hz), 77.0 (t, CH_2, J_{C-H} = 149 Hz), 128−129 (C_6H_5), 139.0 (s, α carbon), 148.1 (s, β carbon), 196 (s, *cis*-*C*O (W)), 202.5 (s, *trans*-*C*O (W)), 210.9 (s, *C*O (Fe)), 313 (s, W=*C*)		1138.8, 1226.9
12	2073 (vs), 2039 (vs), 2003 (vs), 1987 (m), 1726 (m)	1.01 (3H, t, J = 7.05 Hz, CH_3), 3.97 (2H, q, J = 7.2 Hz, CH_2), 7.06−7.35 (C_6H_5)	13.6 (q, CH_3, J_{C-H} = 128 Hz), 61.9 (t, OCH_2, J_{C-H} = 147 Hz), 125−129 (C_6H_5), 117.0 (*C*−CO), 136.9 (*C*Ph), 163.1 (C−*C*O), 208.6 (*C*O (Fe))	554.5, 510.6	
13	2070 (vs), 2035 (vs), 2002 (m), 1996 (m), 1727 (m)	1.01 (3H, t, J = 7.13 Hz, CH_3), 3.95 (2H, q, J = 7.1 Hz, CH_2), 7.07−7.34 (C_6H_5)	13.6 (q, CH_3, J_{C-H} = 127 Hz), 61.9 (t, OCH_2, J_{C-H} = 148 Hz), 126−129 (C_6H_5), 116.8 (*C*−CO), 137.3 (*C*Ph), 165.2 (C−*C*O), 209.0 (*C*O (Fe))		773.9
14	2067 (vs), 2032 (vs), 1997 (vs), 1984 (m), 1730 (m)	3.52 (3H, s, OCH_3), 7.05−7.35 (C_6H_5)	52.7 (q, OCH_3, J_{C-H} = 147 Hz), 117.4 (*C*−CO), 126−129 (C_6H_5), 117.4 (*C*−CO), 138.5 (*C*Ph), 165.0 (*C*−CO), 209.8 (*C*O (Fe))	641.7	931.3
15	2067 (vs), 2032 (vs), 1994 (vs), 1983 (m), 1725 (m)	1.00 (3H, t, J = 7 Hz, CH_3), 3.95 (2H, q, J = 7.1 Hz, OCH_2), 7.04−7.36 (C_6H_5)	13.7 (q, CH_3, J_{C-H} = 127 Hz), 62.1 (t, OCH_2, J_{C-H} = 148 Hz), 126−129 (C_6H_5), 118.7 (*C*−CO), 138.7 (*C*Ph), 165.5 (C−*C*O), 209.9 (*C*O (Fe))	645.2	935.5
16	2069 (vs), 2032 (vs), 1995 (m), 1992 (m), 1980 (m)	0.97 (3H, t, J = 7.05 Hz, CH_3), 3.09 (6H, s, OCH_3), 3.29 (2H, q, J = 6.9 Hz, OCH_2), 7.08−7.27 (C_6H_5)	14.3 (q, CH_3, J_{C-H} = 128 Hz), 49.6 (q, OCH_3, J_{C-H} = 144 Hz), 58.0 (t, OCH_2, J_{C-H} = 147 Hz), 114.6 (s, *C*−C(OCH_3), 125−128 (C_6H_5), 142 (*C*Ph), 151 (s, −*C*(OCH_3)$_2$), 209 (*C*O)Fe	578.8, 537.4	
17	2067 (vs), 2035 (m), 2029 (vs), 1999 (vs), 1989 (m), 1975 (m)	0.98 (3H, t, J = 7.05 Hz, CH_3), 3.07 (6H, s, OCH_3), 3.27 (2H, q, J = 7 Hz, OCH_2), 7.11−7.28 (C_6H_5)	14.3 (q, CH_3, J_{C-H} = 128 Hz), 49.6 (q, OCH_3, J_{C-H} = 144 Hz), 58.0 (t, OCH_2, J_{C-H} = 147 Hz), 115.0 (s, *C*−C(OCH_3)$_2$), 209 (*C*O (Fe))		811.6
18	2063 (vs), 2026 (vs), 1995 (vs), 1987 (vs), 1973 (m)	3.06 (9H, s, OCH_3), 7.06−7.28 (C_6H_5)	49.7 (q, OCH_3, J_{C-H} = 146 Hz), 115.9 (s, *C*−C(OCH_3), 125−128 (C_6H_5), 138.3 (*C*Ph), 160.2 (s, −*C*(OCH_3)$_2$), 210.5 (*C*O Fe))	666.4	961.7
19	2063 (vs), 2026 (vs), 1994 (vs), 1986 (vs), 1972 (m)	0.99 (3H, t, J = 7.10 Hz, CH_3), 3.08 (6H, s, OCH_3), 3.30 (2H, q, J = 7 Hz, OCH_2), 7.10−7.29 (C_6H_5)	14.3 (q, CH_3, J_{C-H} = 129 Hz), 49.7 (q, OCH_3, J_{C-H} = 145 Hz), 58.1 (t, OCH_2, J_{C-H} = 148 Hz), 116 (s, *C*−C(OCH_3), 126−128.5 (C_6H_5), 141 (*C*Ph), 152.0 (s, −*C*(OCH_3)$_2$), 210 (*C*O (Fe))	669.2	964.4

Scheme 2



	M	E	R
8a	Cr	Se	CH_2=$CHCH_2$
8b	W	Se	CH_2Ph
8c	Cr	Se	CH_3
8d	Cr	Se	CH_2Ph
8e	W	Se	CH_2=$CHCH_2$
8f	W	Te	CH_2Ph

Se; E′ = Te),[3] and the alkynyl Fischer carbene complexes [$(CO)_5$M=C(OEt)(C≡CPh)][14] (M = Cr, W) were prepared as previously reported.

Preparation of [$(CO)_6Fe_2E_2${μ-PhC=CC(OEt)}M$(CO)_5$] (1−5) (E = S, Se, Te and M = Cr, W). Table 1 summarizes the conditions used for the preparation of **1**−**5**. In a typical preparation, equimolar amounts of a solution of $(CO)_6Fe_2${μ-E_2) and $(CO)_5$M=C(OEt)(C≡CPh) in methanol were stirred at room temperature for 35−50 min. The stirring was stopped when all of the $(CO)_6Fe_2${μ-E_2) had been consumed, as monitored by TLC. The solvent was removed in vacuo, and the residue was chromatographed on silica gel column. Elution with hexane yielded, in each case, a major red band followed by trace amounts of a yellow band. The red band eluting first was characterized spectroscopically as [$(CO)_6Fe_2E_2${μ-PhC=CC(OEt)}M$(CO)_5$] (**1**−**5**), and the second band was identified as the corresponding alkenyl Fischer carbene complex [$(CO)_5$M=C(OEt){CH=C(OMe)Ph] (M = Cr, W) (**6** and **7**).[4]

Preparation of $(CO)_6Fe_2${μ-EC(Ph)=C(C(OMe)$_2$(OR))E′} and $(CO)_6Fe_2${μ-EC(Ph)=C(CO)(OR)E′} (where E = S, Se; E′ = Se, Te; R = CH_3, C_2H_5) (12−19). The experimental conditions used for the preparation of **12**−**19** are summarized in Table 3. In a typical preparation, a methanolic solution of [$(CO)_6Fe_2$EE′{μ-PhC=C C(OEt)}M$(CO)_5$] was stirred for 1−2 days in the presence of air. The reaction was monitored by TLC. The solvent was removed in vacuo, and the residue was subjected to chromatographic workup using silica gel TLC plates with hexane/CH_2Cl_2 (80:20) as the eluent. A red band, eluting first, was characterized as $(CO)_6Fe_2${μ-EC(Ph)=C(CO)(OR)E′} (**12**−**15**). The second band was characterized spectroscopically as $(CO)_6Fe_2${μ-EC(Ph)=C C(OMe)$_2$(OR)E′} (**16**−**19**).

Oxidation of [$(CO)_6Fe_2$EE′{μ-PhC=CC(OEt)}M$(CO)_5$] (M = Cr, W; E = S, Se; E′ = Se, Te) by TMNO. To a solution of [$(CO)_6Fe_2$EE′{μ-PhC=CC(OEt)}M$(CO)_5$] in 8 mL of CH_2Cl_2 was added dropwise 1 equiv of freshly sublimed TMNO dissolved in 5 mL of CH_2Cl_2. The color of the solution changed from red to orange red. The solution was filtered through Celite to remove any insoluble materials, and after removal of the solvent, the residue was subjected to chromatography on a silica gel column using hexane/CH_2Cl_2 (70:30) as the eluent. A simple orange-red band was collected, and the product was identified as $(CO)_6Fe_2${μ-EC(Ph)=C(CO)(OEt)E′}.

Preparation of Aminocarbene Complexes [$(CO)_6Fe_2E_2$-{μ-PhC=CCN(H)R}M$(CO)_5$] (8a−f) (where M = Cr, W; R = CH_3, CH_2Ph, CH_2CH=CH_2; E = Se, Te). To a solution of freshly prepared [$(CO)_6Fe_2E_2${μ-PhC=CC(OEt)}M$(CO)_5$] (**2**−**3**, **5**) in dry diethyl ether (8 mL) was added a 1.5−2-fold excess of RNH_2 (R = CH_3, CH_2Ph, or CH_2CH=CH_2), and the reaction mixture was stirred at room temperature for 15 min. The solution was filtered through Celite to remove any insoluble materials. The solvent was removed in vacuo, and the residue was subjected to chromatography on silica gel TLC plates. Elution with hexane/CH_2Cl_2 (60:40) yielded two closely moving red bands. The band eluting first was characterized as *syn*-[$(CO)_6Fe_2E_2${μ-PhC=CCN(H)R}M$(CO)_5$] (*syn*-**8a**−**f**), and the second red band was characterized as *anti*-[$(CO)_6Fe_2E_2${μ-PhC=CCN(H)R}M$(CO)_5$] (*anti*-**8a**−**f**).

Complex 8a: Red solid (90%), *syn:anti* 60:40. IR (ν(CO), cm^{-1}): 2075 (vs), 2056 (s), 2039 (vs), 2005 (vs), 1980 (m), 1942 (br, s). *syn*-**8a**: ^{1}H NMR (δ, ppm) 4.50 (2H, dd, J = 5.7 Hz, NCH_2), 5.36 (2H, dd, ^2J = 12.5 Hz, ^3J = 2.2 Hz, =CH_2), 5.88 (1H, m, HC−CH_2), 7.10−7.28 (5H, m, C_6H_5), 7.99 (1H, br, NH). ^{13}C NMR (δ, ppm): 54.9 (NCH_2), 120.9 (CH=CH_2), 127−130 (C_6H_5), 129.3 CH=CH_2), 137.8 (α-C, NCCSe), 150.2 (β-C, CPh), 208.6 (CO (Fe)), 215.8 (*cis*-(CO)(Cr)), 221.5 (*trans*-(CO)(Cr)), 274.9 (Cr=C). ^{77}Se NMR (δ, ppm): 592 and 563. *anti*-**8a**: ^{1}H NMR (δ, ppm) 4.20 (2H, m, NCH_2), 5.47 (2H, dd, ^2J = 11.7 Hz, ^3J = 2.1 Hz, =CH_2), 5.97 (1H, m, HC−CH_2), 7.06−7.35 (5H, m, C_6H_5), 8.50 (1H, br, NH). ^{13}C NMR (δ, ppm): 52.2 (NCH_2), 119.4 (CH=CH_2), 127−130 (C_6H_5), 128.8 (CH=CH_2), 137.5 (α-C, NCCSe), 149.4 (β-C, CPh), 208.8 (CO(Fe)), 215.7 (*cis*-(CO)(Cr)), 221.2 (*trans*-(CO)(Cr), 276.6 (Cr=C). ^{77}Se NMR (δ, ppm): 589 and 560. Mp: 108−110 °C. Anal. Calcd (Found) for $C_{23}H_{11}Fe_2CrNO_{11}Se_2$: C, 34.5 (34.4); H, 1.37 (1.22); N, 1.75 (1.60).

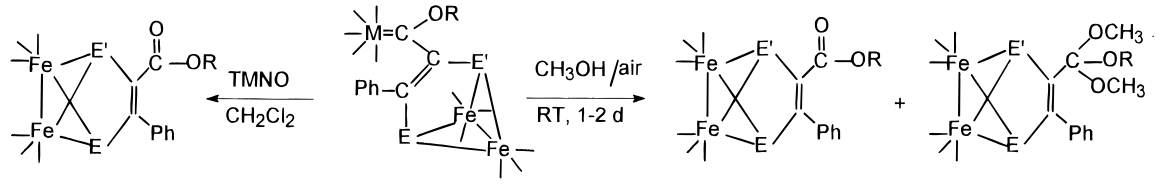
Complex 8b: Red solid (86%), *syn:anti* 54:46. IR (ν(CO), cm^{-1}): 2076 (vs), 2062 (s), 2039 (vs), 2005 (vs), 1980 (m), 1939 (br, s) *syn*-**8b**: ^{1}H NMR (δ, ppm) 4.84 (2H, d, J = 5.5 Hz, NCH_2), 7.08−7.40 (10H, m, 2C_6H_5), 7.95 (1H, br, NH). ^{13}C NMR (δ, ppm): 59.1 (NCH_2), 127.4−129.5 (2C_6H_5), 133.2, 134.6 (*quat C* phenyl ring), 138 (α-C, NCCSe), 152.6 (β-C, CPh), 196.7 (*cis*-(CO)(W)), 200.7 (*trans*-(CO)(W)), 208.6 (CO(Fe)), 251.8 (W=C). ^{77}Se NMR (δ, ppm): 583 and 557. *anti*-**8b:** ^{1}H NMR (δ, ppm) 4.57 (1H, d of part of an ABq, ^2J = 15 Hz, ^3J = 5.7 Hz, NCH_2), 4.31 (1H, d of part of an ABq, ^2J = 15 Hz, ^3J = 5.7 Hz, NCH_2), 7.11−7.51 (10H, m, 2C_6H_5), 8.47 (1H, br, NH). ^{13}C NMR (δ, ppm): 56.3 (NCH_2), 127.5−129.6 (2C_6H_5), 132.7, 134.9 (*quat C* phenyl ring), 136.6 (α-C, NCCSe), 147 (β-C, CPh), 197.1 (*cis*-(CO)(W)), 200.7 (*trans*-(CO)(W)), 208.1, 208.7 (CO(Fe)), 252.4 (W=C). ^{77}Se NMR (δ, ppm): 576 and 555. Mp: 92−94 °C Anal. Calcd (Found) for $C_{27}H_{13}Fe_2WNO_{11}Se_2$: C, 33.0 (32.9); H, 1.32 (1.23); N, 1.42 (1.30).

Complex 8c: Red solid (74%), *syn:anti* 52:48. IR (ν(CO), cm^{-1}): 2075 (vs), 2055 (s), 2039 (vs), 2005 (vs), 1984 (m), 1949 (br, s). *syn*-**8c**: ^{1}H NMR (δ, ppm) 3.56 (d, J = 5.1 Hz, NCH_3), 7.11−7.30 (m, C_6H_5), 8.22 (1H, br, NH). ^{13}C NMR (δ, ppm): 39.8 (NCH_3), 127−129 (C_6H_5), 135.8 (α-C, NCCSe), 142.6 (β-C, CPh), 208.6 (CO(Fe)), 216 (*cis*-(CO)(Cr)), 222.1 (*trans*-(CO)(Cr)), 274.6 (Cr=C). ^{77}Se NMR (δ, ppm): 593 and 562. *anti*-**8c**: ^{1}H NMR (δ, ppm) 3.20 (d, J = 4.8 Hz, NCH_3), 7.04−7.22 (5H, m, C_6H_5), 8.56 (1H, br, NH). ^{13}C NMR (δ, ppm): 37.9 (NCH_3), 127−129.2 (C_6H_5), 135.1 (α-C, NCCSe), 142 (β-C, CPh), 208.2 (CO(Fe)), 216 (*cis*-(CO)(Cr)), 221.2 (*trans*-(CO)-

(13) Bogan, L. E.; Lesch, D. A.; Rauchfuss, T. B. *J. Organomet. Chem.* **1983**, *250*, 429.

(14) Fischer, E. O.; Kreissl, F. R. *J. Organomet. Chem.* **1972**, *35*, C47−C51.

Scheme 3



	M	E	E'	R
2	Cr	Se	Se	C_2H_5
3	W	Se	Se	C_2H_5
9	Cr	S	Te	C_2H_5
10	W	S	Te	C_2H_5
11	W	Se	Te	C_2H_5

	E	E'	R
12, 16	Se	Se	C_2H_5
13, 17	S	Te	C_2H_5
14, 18	Se	Te	CH_3
15, 19	Se	Te	C_2H_5

Table 3. Experimental Conditions Used for Preparation of $Fe_2(CO)_6\{\mu$-EC(Ph)=C(CO)(OR)E′$\}$ (12−13) and $Fe_2(CO)_6\{\mu$-EC(Ph)=CC$(OCH_3)_2$(OR)E′$\}$ (E = S, Se; E′ = Se, Te; R = CH_3, C_2H_5 (16−19)

starting material (g, mmol)	reaction time (h)	product	yield (g (%))	anal. found (calcd)	mp, °C
$[(Co)_6Fe_2Se_2\{\mu$-PhC=CC(OEt)$\}W(CO)_5]$ (**3**) (0.2, 0.21)	30	**12**	0.04 (35)	C, 33.2 (33.3); H, 1.5 (1.63)	oil
		16	0.05 (40)	C, 34.5 (34.6); H, 2.35 (2.43)	102−104
$[(CO)_6Fe_2STe\{\mu$-PhC=CC(OEt)$\}Cr(CO)_5]$ (**9**) (0.3, 0.38)	44	**13**	0.07 (30)	C, 33.1 (33.2); H, 1.52 (1.63)	oil
		17	0.08 (35)	C, 34.4 (34.5); H, 2.3 (2.42)	104−106
$[(CO)_6Fe_2SeTe\{\mu$-PhC=CC(OEt)$\}W(CO)_5]$ (**11**) (0.4, 0.41)	42	**14**	0.03 (12)	C, 29.5 (29.7); H, 1.1 (1.23)	oil
		15	0.04 (17)	C, 30.8 (30.9); H, 1.4 (1.5)	oil
		18	0.03 (10)	C, 31.0 (31.2); H, 1.9 (2.02)	110−112
		19	0.04 (15)	C, 32.0 (32.2); H, 2.1 (2.26)	112−114

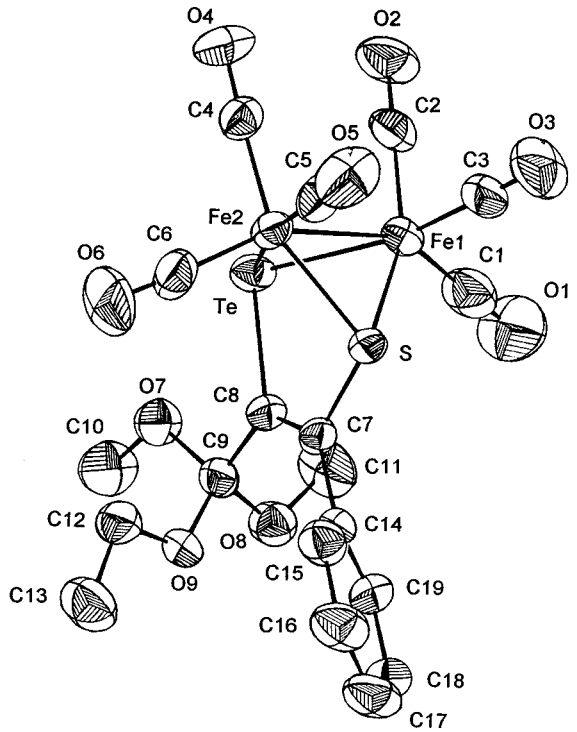


Figure 1. Molecular structure of $(CO)_6Fe_2\{\mu$-SC(Ph)=CC$(OC_2H_5)(OMe)_2$Te$\}$ (**17**).

(Cr)), 276.5 (Cr=*C*). ^{77}Se NMR (*δ*, ppm): 570 and 558. Mp: 118−120 °C (decomp). Anal. Calcd (Found) for $C_{21}H_9Fe_2CrNO_{11}Se_2$: C, 32. 6 (32.5); H, 1.16 (1.03); N, 1.81 (1.65).

Complex 8d: Red solid (88%), *syn:anti* 57:43. IR (*ν*(CO), cm^{-1}): 2075 (vs), 2055 (s), 2039 (vs), 2005 (vs), 1984 (m), 1939 (br, s). *syn*-**8d**: ^{1}H NMR (*δ*, ppm) 4.99 (2H, d, *J* = 5.4 Hz, NCH_2), 7.04−7.42 (10H, m, 2C$_6H_5$), 8.06 (1H, br, N*H*). ^{13}C NMR (*δ*, ppm): 57.2 (NCH_2), 127.1−129.6 (2C_6H_5), 133.4, 134.9 (*quat C* phenyl ring), 37.3 (α-C, NC*C*Se), 150.7 (*β*-C, *C*Ph), 208.6 (*C*O(Fe)), 215.9 (*cis*-(*C*O)(Cr)), 221.4 (*trans*-(*C*O)(Cr)), 273.6 (Cr=*C*). ^{77}Se NMR (*δ*, ppm): 586 and 562. *anti*-**8d**: ^{1}H NMR (*δ*, ppm) 4.64 (1H, d of part of an ABq, ^2J = 14.9 Hz, ^3J = 5.6 Hz, NCH_2), 4.38 (1H, d of part of an ABq, ^2J = 14.9 Hz, ^3J = 5.6 Hz, NCH_2), 7.10−7.50 (10H, m, 2C$_6H_5$), 8.51 (1H, br, N*H*). ^{13}C NMR (*δ*, ppm): 54.6 (NCH_2), 127.4−129.5 (2C_6H_5), 133.1, 134.2 (*quat C* phenyl ring), 136.2 (α-C, NC*C*Se), 149.2 (*β*-C, *C*Ph), 208.5 (*C*O(Fe)), 215.5 (*cis*-(*C*O)(Cr)), 221.3 (*trans*-(*C*O)(Cr)), 275.4 (Cr=*C*). ^{77}Se NMR (*δ*, ppm): 578 and 559 Mp: 86−88 °C. Anal. Calcd (Found) for $C_{21}H_9Fe_2CrNO_{11}Se_2$: C, 32.6 (32.5); H, 1.16 (1.03); N, 1.81 (1.65).

Complex 8e: Red solid (80%), *syn:anti* 62:38. IR (*ν* (CO), cm^{-1}): 2076 (vs), 2062 (s), 2039 (vs), 2005 (vs), 1983 (m), 1942 (br, s). *syn*-**8e**: ^{1}H NMR (*δ*, ppm) 4.35 (2H, dd, *J* = 5.5 Hz, NCH_2), 5.28 (2H, dd, ^2J = 12.5 Hz, ^3J = 2.2 Hz, =CH_2), 5.80 (1H, m, *H*C−CH_2), 7.1−7.26 (5H, m, C$_6H_5$), 7.5 (1H, br, N*H*). ^{13}C NMR (*δ*, ppm): 53.5 (NCH_2), 119.1 (CH=*C*H$_2$), 126.8−128.8 (C_6H_5), 129.4 (*C*H=CH$_2$), 136.8 (α-C, NC*C*Se), 149.8 (*β*-C, *C*Ph), 197.1 (*cis*-(*C*O)(W)), 200.2 (*trans*-(*C*O)(W)), 208.9 (*C*O(Fe)), 257.6 (W=*C*). ^{77}Se NMR (*δ*, ppm): 594 and 566. *anti*-**8e**: ^{1}H NMR (*δ*, ppm) 3.91 (2H, m, NCH_2), 5.41 (2H, dd, ^2J = 12.4 Hz, ^3J = 2.3 Hz, =CH_2), 5.90 (1H, m, *H*C−CH_2), 7.12−7.30 (5H, m, C$_6H_5$), 8.26 (1H, br, N*H*). ^{13}C NMR (*δ*, ppm): 51.7 (NCH_2), 118.4 (CH=*C*H$_2$), 126.9−129 (C_6H_5), 129.2 (*C*H=CH$_2$), 137 (α-C, NC*C*Se), 149.3 (*β*-C, *C*Ph), 197.2 (*cis*-(*C*O)(W)), 200 (*trans*-(*C*O)(W)), 208.3, 208.9 (*C*O(Fe)), 258.9 (W=*C*). ^{77}Se NMR (*δ*, ppm): 591 and 562. Mp: 126−128 °C. Anal. Calcd (Found) for $C_{23}H_{11}Fe_2WNO_{11}Se_2$: C, 29.7 (29.4); H, 1.18 (1.10); N, 1.15 (1.00).

Complex 8f: Red solid (76%), *syn:anti* 68:32. IR (*ν* (CO), cm^{-1}): 2068 (s), 2058 (s), 2029 (vs), 1996 (vs), 1974 (m), 1945 (br, s). *syn*-**8f**: ^{1}H NMR (*δ*, ppm) 4.74 (2H, d, *J* = 5.5 Hz, NCH_2), 7.0−7.39 (10H, m, 2C$_6H_5$), 7.97 (1H, br, N*H*). ^{13}C NMR (*δ*, ppm): 59.1 (NCH_2), 126.1−129.6 (2C_6H_5), 133.2, 134.4 (*quat C* phenyl ring), 139.6 (α-C, NC*C*Se), 149.8 (*β*-C, *C*Ph), 196.9

Table 4. Crystallographic Data and Structure Refinement for $Fe_2(CO)_6\{\mu$-SC(Ph)=C(C(OCH$_3$)$_2$(OC$_2$H$_5$))Te$\}$ (17)

empirical formula	$C_{19}H_{16}Fe_2O_9STe$
fw	659.68
temp	293 (2) K
wavelength	0.709 30 Å
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimens	a = 10.514(2) Å, a = 90°
	b = 17.681(3) Å, b = 96.63 (2)°
	c = 13.016(5), Å, g = 90°
volume	2403.5(11) Å^3
Z	4
density (calculated)	1.823 Mg/m^3
abs coeff	2.529 mm^{-1}
F(000)	1288
cryst size	0.4 ¥ 0.45 ¥ 0.8 mm
q range for data collection	1.95−23.43°
index ranges	$-11 \le h \le 11$,
	$0 \le k \le 19$, $0 \le l \le 14$
no. of reflns collected	3539
refinement method	full-matrix least-squares on F^2
no. of data/restraints/parameters	3539/0/289
goodness of fit on F^2	1.035
final R indices ($I > 2s(I)$)	R1 = 0.0687, wR2 = 0.1620
R indices (all data)	R1 = 0.0787, wR2 = 0.1706
largest diff peak and hole	2.916 and −1.809 e Å^3

(*cis*-(*C*O)(W)), 200.5 (*trans*-(*C*O)(W)), 211 (*C*O(Fe)), 255.3 (W=*C*). ^{125}Te NMR (δ, ppm): 1187 and 1132. *anti*-**8f**: ^{1}H NMR (δ, ppm) 4.43 (1H, d of part of an ABq, ^2J = 15 Hz, ^3J = 5.4 Hz, NCH_2), 4.30 (1H, d of part of an ABq, ^2J = 15 Hz, ^3J = 5.4 Hz, NCH_2), 7.07−7.51 (10H, m, 2C$_6H_5$), 8.38 (1H, br, N*H*). ^{13}C NMR (δ, ppm): 56.7 (N*C*H$_2$), 126.5−129.8 (2*C*$_6$H$_5$), 132.4, 134.1 (*quat C* phenyl ring), 138.8 (α-C, NC*C*Se), 149.9 (β-C, *C*Ph), 197.2 (*cis*-(*C*O)(W)), 200.5 (*trans*-(*C*O)(W)), 210.5, 211.3 (*C*O-(Fe)), 257.2 (W=*C*). ^{125}Te NMR (δ, ppm): 1189 and 1132. Mp: 98−100 °C. Anal. Calcd (Found) for $C_{27}H_{13}Fe_2WNO_{11}Se_2$: C, 30.0 (29.8); H, 1.20 (1.05); N, 1.29 (1.15).

Crystal Structure Determination of 17. Red crystals of **17** were grown from a hexane solution at −4 °C for the crystal structure determination. Single-crystal X-ray data were collected by the $\omega/2\theta$ scan mode with a scan speed of 1 deg/min on a PC-controlled Enraf-Nonius CAD-4 single-crystal X-ray diffractometer using Mo Kα (λ = 0.709 30 Å) radiation. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ($20° \le 2\theta \le 25°$). Pertinent crystallographic data for **17** are summarized in Table 4. The structure was solved by direct methods using the NRCVAX programs.[15] First the Te, S, and two Fe atoms were located, and subsequent difference Fourier maps revealed entire the structure. The structure was refined by full-matrix least-squares methods using SHELX-93[16] with R = 0.068 and R_w = 0.16 for 3539 [$F_o^2 \ge 2\sigma(F_o)^2$] reflections. Final ΔF synthesis shows no features above 2.9 e Å^{-3}. Selected bond lengths and bond angles for **17** are listed in Table 5.

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for 17

Fe(1)−Te	2.5417(13)	Fe(1)−Fe(2)	2.5289(14)
Fe(1)−S	2.260(2)	S−C(7)	1.818(6)
Fe(2)−Te	2.5499(11)	C(7)−C(8)	1.337(9)
Fe(2)−S	2.255(2)	Te−C(8)	2.137(6)
Fe(1)−C(1)	1.817(10)	C(8)−C(9)	1.531(9)
Fe(1)−Fe(2)−Te	60.06(3)	S−Fe(2)−Te	80.89(5)
Fe(1)−Fe(2)−S	56.04(5)	Fe(1)−S−C(7)	108.1(2)
Fe(2)−Fe(1)−Te	60.38(3)	Fe(2)−Te−C(8)	94.0(2)
Fe(2)−Fe(1)−S	55.84(5)	Fe(2)−S−C(7)	108.3(2)
Fe(1)−Te−Fe(2)	59.56(4)	Fe(1)−Te−C(8)	94.3(2)
Fe(1)−S−Fe(2)	68.12(6)	Te−C(8)−C(9)	117.9(4)
S−Fe(1)−Te	80.97(5)	S−C(7)−C(8)	118.1(5)

Conclusion

In this paper, we have demonstrated that iron carbonyl chalcogenide compounds (CO)$_6$Fe$_2$(μ-E$_2$) (E = S, Se, Te) add with excellent facility to the activated triple bond of an alkynyl Fischer carbene complex. A unique combination of three metal−carbonyl centers make these structurally defined molecules readily soluble in organic solvents, a useful criterion that permits systematic exploitation of their chemistry. The metal−carbene fragment present in these molecules is essentially a versatile, latent organic functional group. The C=M(CO)$_5$ function of the trimetallic adduct can be readily modified to an aminocarbene complex or organic derivatives such as a carboxylic ester or ortho ester under mild conditions that do not affect the rest of the molecule. Such functionalizations can be useful if one desires to append organic molecules with sensitive functional groups to metal clusters in order to investigate their biological significance or possible use in metalloimmunoassay.[17]

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Supporting Information Available: Tables of atomic coordinates, bond lengths and bond angles, and anisotropic displacement parameters, and hydrogen coordinates for **17** (6 pages). Ordering information is given on any current masthead page.

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