3536 *Organometallics* **1997,** *16,* 3536−3540

Regioselective Addition of Mixed-Chalcogenide Iron Carbonyl Clusters $Fe_2(CO)_6(\mu\text{-}EE')$ ($E \neq E'$, E, E' = S, Se, Te) to a Carbon−Carbon Triple Bond Activated by a Metal Carbene Fragment. Structural Characterization of New Trimetallic Adducts $Fe_2(CO)_6\{\mu\text{-}SC(Ph){=}C(Te)[(OEt)C{=}Cr(CO)_5]\}$, $Fe_2(CO)_6\text{-}\{\mu\text{-}SC(Ph){=}C(Se)[(OEt)C{=}W(CO)_5]\}$, and $Fe_2(CO)_6\{\mu\text{-}SeC(Ph){=}C(Te)[(OEt)C{=}W(CO)_5]\}$

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From the room-temperature reaction of the transition-metal alkynyl Fischer carbene complexes $(CO)_5M{=}C(OEt)(C{\equiv}CPh)$ (M = Cr, W) with the mixed-chalcogenide compounds $Fe_2(CO)_6(\mu\text{-}EE')$ ($E \neq E'$, E, E' = S, Se, Te), the following new trimetallic adducts were obtained: $Fe_2(CO)_6\{\mu\text{-}EC(Ph){=}C(E')[(OEt)C{=}M(CO)_5]\}$ **1**−**6** (**1**, 85%, E = S, E' = Se, M = Cr; **2**, 82%, E = S, E' = Se, M = W; **3**, 84%, E = S, E' = Te, M = Cr; **4**, 80%, E = S, E' = Te, M = W; **5**, 83%, E = Se, E' = Te, M = Cr; **6**, 81%, E = Se, E' = Te, M = W). In addition, trace amounts of the corresponding alkenyl Fischer carbene complexes $(CO)_5M{=}C(OEt)\text{-}\{(CH{=}C(OMe)Ph\}$ **7**−**8** (**7**, M = Cr; **8**, M = W) were also formed in each case. Compounds **1**−**6** were characterized by IR and ^1H, ^{13}C, ^{77}Se, and ^{125}Te NMR spectroscopy. Crystallographic analyses of the compounds **2**, **3**, and **6** were carried out. The structures of **2**, **3**, and **6** can be described as Fe_2EE' (E, E' = S, Se, Te) tetrahedral butterfly cores containing the alkynyl Fischer carbene as a bridge between the two wingtip chalcogens with three terminally bonded carbonyl groups on each Fe atom.

Introduction

In the course of our investigations on the addition of inorganic and organic species to $Fe_2(\mu\text{-}EE')(CO)_6$ (where E or E' = S, Se, or Te), we prepared, under facile conditions, the acetylene adducts $Fe_2(CO)_6\{\mu\text{-}EC(H){=}C(R)E'\}$ (where R = Ph, CH_2OH, and H).[1,2] The addition of the C−C triple bonds across the reactive E−E' bonds was found to depend on the E, E' combination in $Fe_2(\mu\text{-}EE')(CO)_6$ (where E or E' = S, Se, or Te). Bonding and reactivity studies of alkynes attached to metal centers is of current interest because of the potential of the coordinated alkynes to be transformed into useful organic species.[3] In contrast to the large number of reports on the different types of acetylene bonding modes to transition metals, relatively little is known about the addition of acetylenes on main group elements.[4] The use of certain main group elements as bridging and stabilizing ligands in designed cluster growth reactions has been extensively demonstrated in recent years.[5]

The compounds $Fe_2(\mu\text{-}EE')(CO)_6$ are highly reactive species, and different combinations of the chalcogen ligands in these provide versatility in their reactions with organic and inorganic moieties. Reaction between phenylacetylene and these clusters leads to the formation of regioisomeric products. Diaryl, alkylaryl, or dialkylacetylenes did not undergo similar addition reaction. Initially, it appeared that the steric factor alone precluded the addition to disubstituted alkynes, but use

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Table 1. Experimental Conditions Used for Preparation of $Fe_2(CO)_6\{\mu\text{-}EC(Ph){=}C(E')[(OEt)C{=}M(CO)_5]\}$ ($M = Cr$, W and $E \neq E'$; E = S, Se; E′ = Se, Te) (1−6)

$(CO)_5M{=}C(OEt)(C{\equiv}CPh)$ [g, (mmol)]	$(CO)_6Fe_2(\mu\text{-}EE')$ [g, (mmol)]	reaction time (min)	product	yield, g (%)	anal. calcd (found)	mp, °C
$(CO)_5Cr{=}C(OEt)(C{\equiv}CPh)$ [0.14, (0.40)]	$(CO)_6Fe_2(\mu\text{-}SSe)$ [0.20, (0.51)]	35	**1**	0.25 (85)	C, 35.6 (35.7); H, 1.35 (1.44)	128−130 dec
$(CO)_5W{=}C(OEt)(C{\equiv}CPh)$ [0.14, (0.30)]	$(CO)_6Fe_2(\mu\text{-}SSe)$ [0.15, (0.38)]	35	**2**	0.21 (82)	C, 30.2 (30.4); H, 1.14 (1.26)	136−138 dec
$(CO)_5Cr{=}C(OEt)(C{\equiv}CPh)$ [0.16, (0.47)]	$(CO)_6Fe_2(\mu\text{-}STe)$ [0.24, (0.54)]	40	**3**	0.31 (84)	C, 33.4 (33.6); H, 1.26 (1.38)	132−134 dec
$(CO)_5W{=}C(OEt)(C{\equiv}CPh)$ [0.23, (0.48)]	$(CO)_6Fe_2(\mu\text{-}STe)$ [0.23, (0.52)]	45	**4**	0.35 (80)	C, 28.6 (28.8); H, 1.08 (1.18)	142−144 dec
$(CO)_5Cr{=}C(OEt)(C{\equiv}CPh)$ [0.13, (0.37)]	$(CO)_6Fe_2(\mu\text{-}SeTe)$ [0.19, (0.39)]	45	**5**	0.25 (83)	C, 31.5 (31.7); H, 1.03 (1.10)	138−140 dec
$(CO)_5W{=}C(OEt)(C{\equiv}CPh)$ [0.18, (0.38)]	$(CO)_6Fe_2(\mu\text{-}SeTe)$ [0.20, (0.41)]	40	**6**	0.29 (81)	C, 27.2 (27.4); H, 1.03 (1.16)	146−148 dec

Table 2. Crystallographic Data for $C_{22}H_{10}Fe_2O_{12}SeTeW$ (6), $C_{22}H_{10}Fe_2O_{12}S_{0.7}Se_{1.3}W$ (2), and $C_{22}H_{10}CrFe_2O_{12}STe$ (3)

	6	**2**	**3**
formula	$C_{22}H_{10}Fe_2O_{12}SeTeW$	$C_{22}H_{10}Fe_2O_{12}S_{0.7}Se_{1.3}W$	$C_{22}H_{10}CrFe_2O_{12}STe$
fw	968.41	886.94	789.66
space group	*Pbca*	*Pbca*	*Pbca*
a, Å	13.797(2)	13.910(3)	13.713(5)
b, Å	18.742(3)	18.444(4)	18.309(7)
c, Å	21.490(2)	21.289(2)	21.427(1)
V, Å^3	5557(1)	5462(1)	5380(4)
Z	8	8	8
cryst color/habit	deep red block	deep red block	deep red block
D(calc), g cm^{-3}	2.315	2.157	1.950
(Mo Kα), cm^{-1}	75.58	70.96	26.62
T, K	240(2)	240(2)	244(2)
T(max)/*T*(min)	0.275/0.214	0.284/0.169	0.889/0.560
radiation		Mo Kα ($\lambda = 0.710\ 73$ Å)	
$R(F)[I > 2\sigma(I)]$,[a] %	4.26	4.23	3.86
$R(wF^2)[I > 2\sigma(I)]$,[a] %	7.46	10.11	18.51

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

Table 3. Selected Bond Distances (Å) and Bond Angles (Deg) for 2, 3, and 6

	2, M = W	**3**, M = Cr	**6**, M = W
Fe(1)−Fe(2)	2.507(2)	2.5445(13)	2.572(2)
Fe(2)−S/Se	2.304(2)		
C(7)−C(8)	1.316(11)	1.330(6)	1.324(11)
Fe(1)−Te		2.5272(12)	2.5322(14)
Fe(2)−Te		2.5226(10)	2.5291(13)
Fe(1)−Se	2.383(2)		2.365(2)
Fe(2)−Se	2.373(2)		2.375(2)
Fe(1)−S		2.249(2)	
Fe(2)−S		2.255(2)	
W−C(9)	2.161(9)		2.152(8)
Cr−C(9)		2.014(5)	
Se−C(8)	1.965(9)		
Te−C(8)		2.165(4)	2.186(8)
Fe(1)−Se−Fe(2)	63.63(6)		65.73(5)
Fe(1)−Fe(2)−Se	58.38(5)		56.95(5)
Fe(2)−Fe(1)−Se	57.99(5)		57.32(4)
Fe(1)−Fe(2)−Te		59.83(3)	59.51(4)
Fe(1)−Te−Fe(2)		60.51(3)	61.09(4)
Cr−C(9)−C(8)		125.8(3)	
Fe(1)−S−Fe(2)		68.78(4)	
Fe(1)−Fe(2)−S		55.50(4)	
Te−C(8)−C(7)		114.2(3)	
Se−C(7)−C(8)			118.1(6)
W−C(9)−C(8)	124.2(6)		124.3(6)
Se−Fe(2)−S/Se	81.73(7)		
Fe(1)−S/Se−Fe(2)	65.95(7)		

of a highly polarized carbon−carbon triple bond in alkynyl Fischer carbene complexes dispelled this apprehension. Addition of $Fe_2(\mu\text{-}EE')(CO)_6$ ($E \neq E'$ and E, E′ = S, Se, or Te) occurred on this C−C triple bond with high facility and yield to provide highly regioselective trimetallic adducts. This paper describes the preparation and structural characterization of these new, functional metal clusters.

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 a Nicolet-Impact 400 FTIR spectrometer as an *n*-hexane solution in a sodium chloride cell at 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 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, and phenylacetylene were purchased from Aldrich Chemical Co., and these were used without further purification. The mixed chalcogenide iron carbonyl clusters $Fe_2(\mu\text{-}SSe)(CO)_6$, $Fe_2(\mu\text{-}STe)(CO)_6$, and $Fe_2(\mu\text{-}SeTe)(CO)_6$[6] and the alkynyl Fischer carbene complexes were prepared as previously reported.[7]

Preparation of $Fe_2(CO)_6\{\mu\text{-}EC(Ph){=}C(E')[C(OEt){=}M(CO)_5\}]$ (1−6) (E = S, Se; E = Se, Te and M = Cr, W). Table 1 summarizes the conditions used for the preparation of **1**−**6**. In a typical preparation, equimolar amounts of a solution of $(CO)_6Fe_2(\mu\text{-}EE')$ and $(CO)_5M{=}C(OEt)(C{\equiv}CPh)$ in methanol were stirred at room temperature for 35−45 min. The stirring was stopped when all the $(CO)_6Fe_2(\mu\text{-}EE')$ had been consumed, as monitored by TLC. The solvent was removed in vacuo, and the residue was chromatographed on a 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

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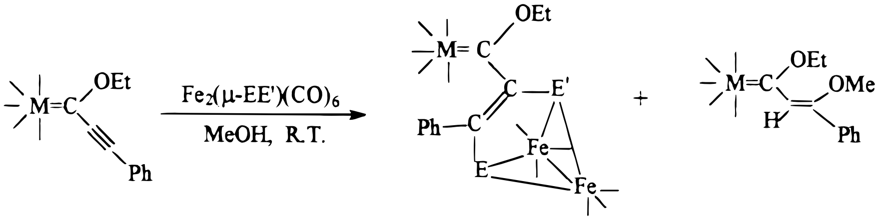
Scheme 1. Formation of Compounds 1−6



	M	E	E'
1.	Cr	S	Se
2.	W	S	Se
3.	Cr	S	Te
4.	W	S	Te
5.	Cr	Se	Te
6.	W	Se	Te

7. M = Cr
8. M = W

eluting first was characterized spectroscopically as $Fe_2(CO)_6$-{μ-EC(Ph)=C(E′)[C(OEt)=M(CO)$_5$]} (**1**−**6**), and the second band was identified as the corresponding alkenyl Fischer carbene complex [(CO)$_5$M=C(OEt){CH=C(OMe)Ph] (**7**, M = Cr; **8**, M = W).[8]

Crystal Structure Determination of 2, 3, and 6. Red crystals of **2**, **3**, and **6** were selected and mounted with epoxy cement to glass fibers. Single-crystal X-ray data were collected on a Siemens P4 diffractometer using Mo Kα 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 **2**, **3**, and **6** are summarized in Table 2. The systematic absences in the diffraction data for **2**, **3**, and **6** are uniquely consistent for the space group *Pbca*. The structures were solved using direct methods and completed by subsequent difference Fourier syntheses and by full-matrix least-squares procedures. Semiempirical ellipsoid absorption corrections were applied. The S atom in **2** is compositionally disordered with selenium 70/30 and is refined as an oversized sulfur atom. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions. The largest remaining peaks in the difference map (1.01−1.47 e Å^{-3} for **6**) and (1.10−1.12 e Å^{-3} for **2**) occur at a chemically unreasonable positions (0.75−0.97 Å from tungsten for **6** and 1.10−1.12 Å from tungsten for **2**) and were considered as noise.

All software and sources of the scattering factors are contained in the SHELXTL (5.3) program library (Sheldrick, G. Siemens XRD, Madision, WI). Selected bond lengths and bond angles for **2**, **3**, and **6** are listed in Table 3.

Results and Discussion

Synthesis of 1−6. The alkynyl Fischer carbene complexes of tungsten and chromium were prepared following reported procedures.[7] In a typical reaction, a freshly prepared solution of $Fe_2(\mu$-EE′)(CO)$_6$ (E ≠ E′, E, E′ = S, Se, Te) in methanol was added to an equimolar amount of solid Fischer carbene complex under a blanket of argon at room temperature. On stirring at room temperature for 30−45 min, the adduct $Fe_2(CO)_6$-{μ-EC(Ph)=C(E′)[(OEt)C=M(CO)$_5$]} (E ≠ E′, E = S, Se, E′ = Se, Te, and M = Cr, W) was obtained as an air-stable solid in 80−85% yield (Scheme 1). The products were isolated as single regioisomers by chromatography over silica gel followed by crystallization from hexane at −4 °C. The chromium-containing complexes (**1**, **3**, and **5**) were obtained as deep red crystals, while the tungsten derivatives (**2**, **4**, and **6**) were orange-red crystalline solids. In each case, trace amounts of the corresponding known alkenyl Fischer carbene complexes (CO)$_5$M=C(OEt){CH=C(OMe)Ph} (**7**, M = Cr; **8**, M = W) were also obtained, and these were identified on the basis of comparison with IR and ^{1}H NMR spectral data reported in the literature.[8]

General Trends. Unlike simple monosubstituted alkynes, addition of $Fe_2(\mu$-EE′)(CO)$_6$ (E ≠ E′, E, E′ = S, Se, Te) to the triple bond of the Fischer carbene complexes occurred readily and in high yield. Even with complexes like $Fe_2(\mu$-$S_2)(CO)_6$ and $Fe_2(\mu$-$Te_2)(CO)_6$ that are reluctant to add to alkynes, addition readily occurs to the triple bond of acetylenic carbene complexes.[9] Such facility of reaction can be attributed to the high reactivity of the acetylenic bond in alkynyl Fischer carbene complexes.[10] Owing to the strong electron-withdrawing M(CO)$_5$ fragment attached to the carbene carbon, the alkyne bond is considerably polarized. The ^{13}C chemical shift difference of more than 40 ppm between the α- and the β-alkynyl carbons[11a] would attest to this effect. While a consequence of such polarization of the alkyne bond is facile nucleophilic attack by the chalcogen atom, a strong regiochemical preference is also to be expected when two different chalcogenide atoms are present in the iron cluster. The smaller chalcogenide atom would accommodate a developing negative charge better and react preferentially at the electron-deficient β-acetylenic carbon. True to this expectation, with all the heterochalcogenide clusters, only one regioisomer of the product was obtained

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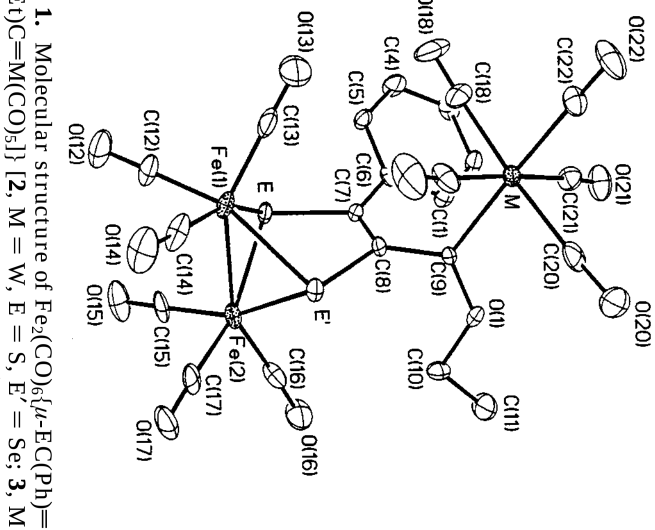

Figure 1. Molecular structure of $Fe_2(CO)_6\{\mu\text{-EC(Ph)=C-(E')[(OEt)C=M(CO)}_5]\}$ [**2**, M = W, E = S, E′ = Se; **3**, M = Cr, E = S, E′ = Te; **6**, M = W, E = Se, E′ = Te].

in each case.[11b] This result may be contrasted with our earlier finding that the room-temperature reaction of $Fe_2(\mu\text{-SeTe})(CO)_6$ with phenylacetylene in the presence of a trace amount of NaOAc gives rise to the formation of two regioisomers $Fe_2(CO)_6\{\mu\text{-Se(Ph)C=C(H)Te}\}$ and $Fe_2(CO)_6\{\mu\text{-Te(Ph)C=C(H)Se}\}$ in 23% and 21% yield, respectively.[1a]

These new complexes have a close structural resemblance with the dicobalt−alkyne complexes widely used in the Pauson−Khand reaction[12] and chemistry of stabilized propargylic cations.[13] However, in our molecules, the alkynes are not directly complexed with the metal carbonyl fragment; rather, they are linked to the chalcogenide atoms. The chemistry of such an unusual "heterocycle" is yet unexplored.

Molecular Structures of 2, 3, and 6. Crystal structure solutions for three representative complexes were carried out to confirm the stated regioselectivity pattern. It also enabled us to interpret the ^{77}Se and ^{125}Te NMR data with confidence. Red crystals of **2** and orange-red crystals of **3** and **6** were grown from hexane solutions at −4 °C for crystal structure determination. Despite the difference in chalcogenide elements present in different complexes, the complexes **2**, **3**, and **6** were found to be isomorphous. The molecular structures of **2**, **3**, and **6** are shown in Figure 1.

The structure consists of a Fe_2EE' (E ≠ E′ and E, E′ = S, Se and Te) butterfly core, and the alkynyl carbene unit is attached to the wingtip of chalcogen atoms. The acetylenic C−C bond distances of complexes **2**, **3**, and **6** are longer by at least 0.01 Å than in the corresponding phenylacetylene adducts.[1a,c] The metal−carbene bond

Table 4. Spectroscopic Data for Compounds 1−6

compd	IR (ν(CO) 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	2080 (m), 2075 (m), 2061 (s), 2042 (vs), 2008 (br, s), 1988 (m), 1962 (br, s)	1.68 (3H, t, J = 7.02 Hz, CH_3), 4.57 (2H, q, J = 7.02 Hz, CH_2), 7.06−7.30 (m, C_6H_5)	14.9 (q, J_{CH} = 129.3 Hz, CH_3), 76.1 (t, J_{CH} = 146.8 Hz, OCH_2), 127−129 (C_6H_5), 133.9 (s, α carbon), 147.5 (s, β carbon), 207.6 (s, CO (Fe)), 215.1 (s, *cis*-CO (Cr), 223.4 (s, *trans*-CO (Cr), 337.6 (s, Cr=C)	523	
2	2080 (m), 2067 (m), 2042 (vs), 2005 (s), 1992 (m), 1988 (m), 1966 (br, s)	1.63 (3H, t, J = 7.02 Hz, CH_3), 4.60 (2H, q, J = 6.9 Hz, CH_2), 7.08−7.28 (m, C_6H_5)	14.7 (q, J_{CH} = 129.1 Hz, CH_3), 77.3 (t, J_{CH} = 150.1 Hz, OCH_2), 127−129 (C_6H_5), 134.2 (s, α carbon), 148.3 (s, β carbon), 195.7 (s, *cis*-CO (W), 202.5 (s, *trans*-CO (W), 207.8 (s, CO (Fe), 310.9 (s, W=C)	518	
3	2076 (m), 2059 (s), 2039 (vs), 2006 (s), 2002 (m), 1971 (m), 1959 (br, s)	1.68 (3H, t, J = 7.14 Hz, CH_3), 4.44 (2H, q, J = 7.09 Hz, CH_2), 7.04−7.30 (C_6H_5)	14.8 (q, J_{CH} = 129.2 Hz, CH_3), 75.5 (t, J_{CH} = 146.2 Hz, OCH_2) 127−129 (C_6H_5), 135.4 (s, α carbon), 154.1 (s, β carbon), 208.7 (s, CO (Fe)), 215.2 (s, *cis*-CO (Cr), 223.5 (s, *trans*-CO (Cr), 337.6 (s, Cr=C)		974
4	2077 (m), 2065 (s), 2038 (vs), 2004 (s), 1999 (m), 1964 (br, s)	1.64 (3H, t, J = 7 Hz, CH_3), 4.52 (2H, q, J = 7.14 Hz, CH_2), 7.08−7.29 (m, C_6H_5)	14.6 (q, J_{CH} = 128.7 Hz, CH_3), 77.4 (t, J_{CH} = 150.5 Hz, OCH_2) 127−129 (C_6H_5), 135.6 (s, α carbon), 155.2 (s, β carbon), 195.8 (s, *cis*-CO (W), 202.4 (s, *trans*-CO (W), 208.8 (s, CO (Fe), 311.2 (s, W=C)		965
5	2073 (m), 2058 (s), 2036 (vs), 2001 (s), 1985 (m), 1960 (br, s)	1.69 (3H, t, J = 7.14 Hz, CH_3), 4.45 (2H, q, J = 7.02 Hz, CH_2), 7.02−7.29 (C_6H_5)	14.9 (q, J_{CH} = 129.4 Hz, CH_3), 75.7 (t, J_{CH} = 146.8 Hz, OCH_2), 127−129 (C_6H_5), 136.7 (s, α carbon), 148.2 (s, β carbon), 209 (s, CO (Fe)), 215.3 (s, *cis*-CO (Cr), 223.2 (s, *trans*-CO (Cr), 338.7 (s, Cr=C)	645	1105
6	2076 (m), 2063 (s), 2035 (vs), 2000 (s), 1998 (m), 1964 (br, s)	1.64 (3H, t, J = 7.02 Hz, CH_3), 4.53 (2H, q, J = 7.32 Hz, CH_2), 7.06−7.28 (C_6H_5)	14.6 (q, J_{CH} = 128.8 Hz, CH_3), 77.2 (t, J_{CH} = 150.6, Hz OCH_2), 127−129 (C_6H_5), 136.9 (s, α carbon), 148.5 (s, β carbon), 195.8 (s, *cis*-CO (W), 202.5 (s, *trans*-CO (W), 209.6 (s, CO (Fe), 311.2 (s, W=C)	645	1098

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distances of these complexes are not significantly different from those reported for simple carbene complexes.[14]

The crystal structures clearly reveal that the carbene–metal fragment and the phenyl ring are *cis* to each other, which offers curious possibilities from the standpoint of metal–carbene chemistry.[15]

Spectral Characterization. Spectroscopic features of **1**–**6** are summarized in Table 4. The infrared spectra in hexane of compounds **1**–**6** exhibit almost identical carbonyl stretching patterns typically observed for compounds containing the $Fe(CO)_3$ and $M(CO)_5$ (M = Cr, W) units. For all six compounds, only terminally bonded carbonyl stretching frequencies are observed. Comparison of infrared spectra of compounds **1**–**6** with the previously reported related compounds $(CO)_6Fe_2\{\mu\text{-}EC(Ph){=}C(H)E'\}$[1a] (E ≠ E′ and E, E′ = S, Se, and Te) shows that there is a shift of bands to lower ν(CO) values in $Fe_2(CO)_6\{\mu\text{-}EC(Ph){=}C(E')[(OEt)C{=}M(CO)_5]\}$ (E ≠ E′ and E = S, Se, E′ = Se, Te) for the following combinations of EE′ ligands: SSe > STe > SeTe. The ^{1}H NMR spectra of compounds **1**–**6** show one triplet and one quartet for the ethoxy group attached to the carbene carbon. ^{13}C NMR spectra display two peaks between δ 133 and 156 ppm. The downfield signal has been assigned to *C*(Ph) and the upfield signal to *C*(C=M) in line with previous reports.[11a] The separation in chemical shifts of the two signals is at a maximum for compound **4** (19.6 ppm) and at a minimum for **5** (11.5 ppm). The spectra also displayed peaks for phenyl carbon atoms at δ 127–129 ppm. We observe three signals in the CO region: the signal at δ 207–211 ppm can be assigned to two $Fe(CO)_3$ units, while the other two correspond to *cis* CO and *trans* CO in $M(CO)_5$ (M = Cr, W) unit. The most deshielded signals at δ 337–338 ppm for **1**, **3**, and **5** and δ 312–310 ppm for **2**, **4**, and **6** were assigned to the carbene carbon atom.

The ^{77}Se NMR spectra of compounds $Fe_2(CO)_6\{\mu\text{-}SC(Ph){=}C(Se)[(OEt)C{=}M(CO)_5]\}$ (M = Cr, W) show a singlet at δ 523 and 518 ppm, respectively, whereas compounds $Fe_2(CO)_6\{\mu\text{-}SeC(Ph){=}C(Te)[(OEt)C{=}M(CO)_5]\}$ show a singlet at δ 645 (M = Cr, W). Examination of the ^{77}Se NMR spectra for the above series of compounds shows that the signal shifts downfield when the site of attachment of the Se atom changes from an α to a β carbon. The ^{125}Te NMR spectra of compounds **3**–**6** showed a singlet each at δ 965–1105 ppm.

Conclusions

We have demonstrated that mixed chalcogenide clusters like $Fe_2(\mu\text{-}EE')(CO)_6$ (E,E′ = S, Se, or Te) can readily add to the activated carbon–carbon triple bond attached to the carbene carbon in a Fischer carbene complex to yield regioisomerically pure adducts. Crystal structure determination of representative complexes established the identity of the new trimetallic products beyond doubt and led to unequivocal assignment of ^{77}Se and ^{125}Te NMR spectral patterns. 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 which provides handle to covalently link a metal cluster to an organic molecule or a biopolymer.[16] Relevant functional group transformations will be reported in due course.

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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 **2**, **3**, and **6** (18 pages). Ordering information is given on any current masthead page.

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