Annulation Reactions of Fischer Carbene Complexes Tethered on a Chalcogen-Stabilized Iron Carbonyl Cluster: Dependence of Reaction Pathway on Chalcogen Atom

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When a benzene solution containing the Fischer carbene complex $[(CO)_6Fe_2Se_2\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$ (**6**) and phenylacetylene, diphenylacetylene, 1-hexyne, or 3-hexyne is subjected to reflux, the substituted cyclopentadienylchromium complexes $[Fe_2(CO)_6Se_2\{\mu\text{-}(CO)_3Cr(\eta^5\text{-}C_5(R)(R')(Ph)(OEt)\}]$ (**8a** R = H, R′ = Ph; **8b** R, R′ = Ph; **8c** R = H, R′ = $(CH_2)_3CH_3$; and **8d** R, R′ = C_2H_5) are formed in 72−79% yield. The corresponding SSe analogue $[(CO)_6Fe_2SSe\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$ (**7**) reacts with phenylacetylene or diphenylacetylene to form $[Fe_2(CO)_6SSe\{\mu\text{-}C(H)C(O)C(H){=}C(\eta^6\text{-}C_6H_5Cr(CO)_3)C(Ph)\}]$ (**9a**) or $[Fe_2(CO)_6SSe\{\mu\text{-}C(H)C(O)C(Ph){=}C(\eta^6\text{-}C_6H_5Cr(CO)_3)C(Ph)\}]$ (**9b**) in high yields (82% and 85%). All new compounds have been characterized by IR and ^1H, ^{13}C, and ^{77}Se NMR spectroscopy, and structural types were unequivocally established by crystallographic analysis of compounds **8b** and **9b**.

Introduction

On the strength of diverse, synthetically useful reactivity, the Fischer-type carbene complexes[1] have been used extensively in organic synthesis either by thermal[2] or photochemical activation.[3] It has been widely reported that variations in the substituents of the carbene unit often lead to novel and unprecedented reactivity trends. In the course of our ongoing investigations on the reactivity modification of Fischer carbene complexes tethered on chalcogen-stabilized diiron clusters of the type $[(CO)_6Fe_2EE'\{\mu\text{-}C(Ph){=}C{-}C{-}(OEt){=}Cr(CO)_5\}]$ (where EE′ = SeSe, SSe, STe),[4] we have observed the formation of several unusual products: $[Fe_2(CO)_6Se_2\{\mu\text{-}(CO)_3Cr(\eta^5\text{-}C_5H(CH_2Ph)(Ph)(OEt)\}]$ (**1**), $[(CO)_6Fe_2\text{-}Se_2\{\mu\text{-}(indanone)\}]$ (**2**), $[(CO)_6Fe_2\{\mu\text{-}EE'(2\text{-ethoxy-1-naphthol})\}]$ (**3a**, EE′ = SeSe; **3b** EE′ = STe), $[(CO)_6Fe_2\{\mu\text{-}SC(H)Ph{-}C(Te){=}C(H)(OEt)\}]$ (**4**), and $[(CO)_6Fe_2\{\mu\text{-}EC(Ph){=}C{-}(E')C(H)(OEt)\}]_2$ (**5a**, EE′ = SeSe; **5b** EE′ = STe) (Chart 1).[5] These were primarily unimolecular thermal rearrangements, and it was clear that the reaction pathways were dependent, to a considerable extent, on the type and combination of chalcogen atoms. We find that the type of chalcogen atom present in the cluster also dictates reaction pathways in bimolecular annulation reactions with alkynes, an account of which is presented in this paper.

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[1] For reviews on the synthetic applications of Fischer carbene complexes, see: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag-Chemie: Deerfield Beach, FL, 1984. (b) *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic Publishers: Boston, MA, 1989.

[2] (a) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 5. (b) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press Inc.: Greenwich, CT, 1989; Vol.1. (c) Dötz, K. H. *Angew Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Dötz, K. H. In *Organometallics in Organic Synthesis*: *Aspects of a Modern Interdisciplinary Field*; tom Dieck, H., de Meijere, A., Eds.; Springer: Berlin, 1988.

[3] For photochemical reactions, see: (a) Hegedus, L. S. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Hegedus, L. S., Eds.; Pergamon Press: New York, 1995; Vol. 12, pp 549. (b) Merlic, C. A.; Xu, D.; Khan, S. I. *Organometallics* **1992**, *11*, 412. (c) Hegedus, L. S. *Acc. Chem. Res.* **1995**, *28*, 299.

[4] (a) Mathur, P.; Ghosh, S.; Sarkar, A.; Satyanarayana, C. V. V.; Rheingold, A. L.; Liable-Sands, L. M. *Organometallics* **1997**, *16*, 3536. (b) Mathur, P.; Ghosh, S.; Sarkar, A.; Satyanarayana, C. V. V.; Puranik, V. G. *Organometallics* **1997**, *16*, 4392.

[5] (a) Mathur, P.; Ghosh, S.; Sarkar, A.; Rheingold, A. L.; Guzei, I. A. *Organometallics* **1998**, *17*, 770. (b) Mathur, P.; Ghosh, S.; Sarkar, A.; Rheingold, A. L.; Guzei, I. A. *J. Organomet. Chem.*, in press.

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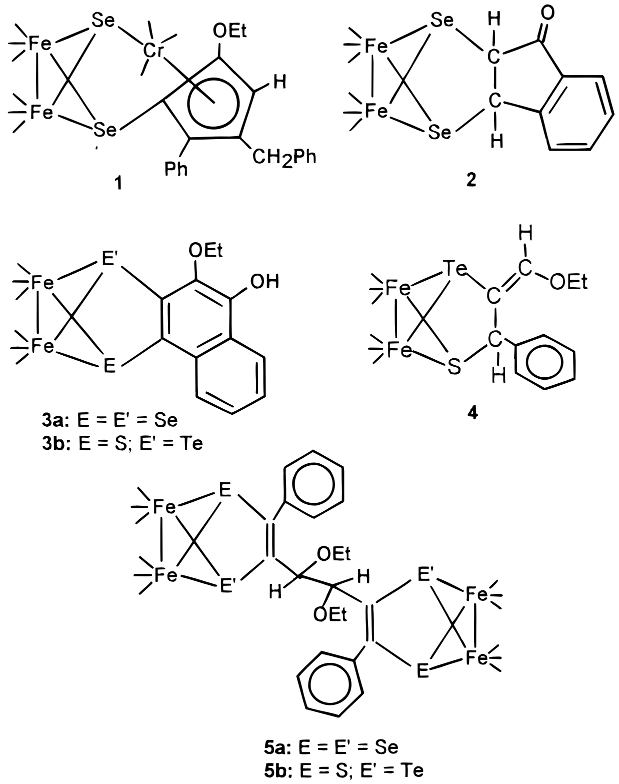
Chart 1



Results and Discussions

The benzannulation reaction described by Dötz[6] inspired the reaction of our cluster-supported carbene complexes $[(CO)_6Fe_2Se_2\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$ (**6**) and $[(CO)_6Fe_2SSe\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$ (**7**) with representative alkynes. Cyclopentadiene formation from alkenyl carbene complexes and alkynes has been previously documented by the group of de Meijere[7] as well by the group of Aumann.[8] Alkoxy carbene complexes of chromium with unsaturated substituents normally afford benzannulated products in good yields, while tungsten analogues and amino carbene complexes of chromium with similar substituents provide indane derivatives.[2] In the latter instance, insertion of a CO group from the metal carbonyl moiety does not take place during annulation. This fundamental observation has been at the starting point of several investigations. As described in the following passages, thermal reaction of unsaturated chromium carbene complexes (**6** and **7**) underwent annulation reactions with terminal and internal alkynes *without* CO insertion.

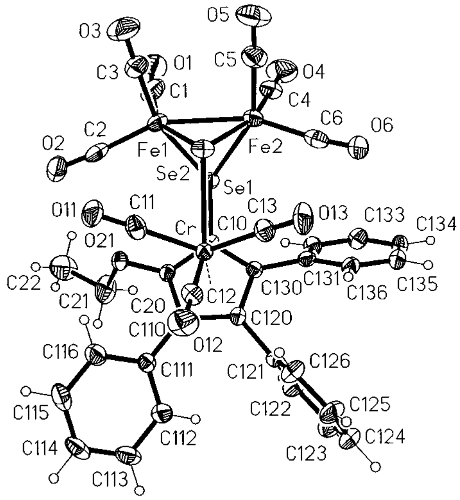
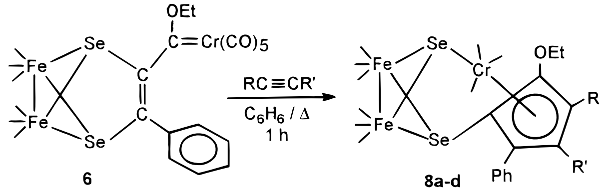


Figure 1. $[Fe_2(CO)_6Se_2\{\mu\text{-}(CO)_3Cr(\eta^5\text{-}C_5(Ph)_3(OEt)\}]$ (**8b**).

Synthesis of $[Fe_2(CO)_6Se_2\{\mu\text{-}(CO)_3Cr(\eta^5\text{-}C_5(R')(R)(Ph)(OEt)\}]$ (8a–d). On refluxing a benzene solution of trimetallic adduct $[(CO)_6Fe_2Se_2\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$ (**6**) with internal and terminal alkynes RC≡CR′ (where R = H, R′ = Ph; R, R′ = Ph; R = H, R′ = $(CH_2)_3CH_3$; R, R′ = Et), cyclopentaannulated products $[Fe_2(CO)_6Se_2\{\mu\text{-}(CO)_3Cr(\eta^5\text{-}C_5(R)(R')(Ph)(OEt)\}]$ (**8a** R = H, R′ = Ph; **8b** R, R′ = Ph; **8c** R = H, R′ = $(CH_2)_3CH_3$; and **8d** R, R′ = C_2H_5) were obtained in 72–79% yield (Scheme 1).

Scheme 1



	R	R'	yield (%)
8a	H	Ph	79
8b	Ph	Ph	74
8c	H	(CH2)3CH3	70
8d	C2H5	C2H5	72

Compounds **8a–d** were characterized by infrared and ^1H, ^{13}C, and ^{77}Se NMR spectroscopy. The infrared spectra of these compounds exhibit almost identical carbonyl stretching patterns, similar to those observed for $[Fe_2(CO)_6Se_2\{\mu\text{-}(CO)_3Cr(\eta^5\text{-}C_5H(CH_2Ph)(Ph)(OEt)\}]$.[5a] The diastereotopic methylene protons of the ethoxy group in **8a–d** showed two well-separated sets of doublets of quartets (J_{H-H} = 9.8–10.2 and 7–7.2 Hz). The chemical shifts of the geminally nonequivalent methylene protons in these complexes are well separated ($\Delta\nu$ = 0.2–0.7 ppm). The ^{13}C NMR spectra of compounds **8a–d** showed two very closely placed peaks between δ 67 and 68 ppm. From the coupling constant values (J_{C-H} = 180 Hz) and spectral patterns, the downfield signal has been assigned to the *C*H carbon in the cyclopentadiene ring and the upfield one to the O*C*H_2 carbon in the ethoxy group. ^{77}Se NMR spectra of compounds **8a–d** showed two signals each for the two nonequivalent Se atoms.

The structure of these complexes was further confirmed by the crystal structure solution of a representative complex **8b**. Its molecular structure, shown in Figure 1, can be described best as consisting of an open $(CO)_6Fe_2Se_2$ unit attached with a $(CO)_3Cr\{(\eta^5\text{-}C_5(Ph)_3(OEt)\}$ moiety. The Cr–Se bond distance, 2.6070 (8) Å, of **8b** is somewhat long as compared to the Cr–Se bond

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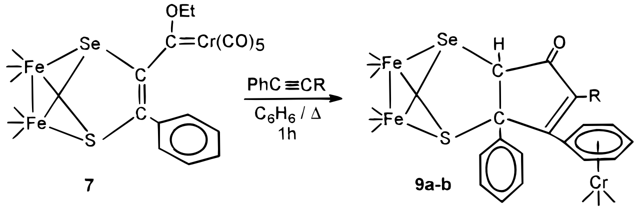
(7) (a) Stein, F.; Duetsch, M.; Lackmann, R.; Noltemeyer, M.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1658. (b) Duetsch, M.; Stein, F.; Lackmann, R.; de Meijere, A. *Synlett* **1991**, 324.

(8) (a) Aumann, R.; Heinen, H. *J. Organomet. Chem.* **1990**, *389*, C1. (b) Aumann, R. *Chem. Ber.* **1993**, *126*, 2325. (c) Aumann, R.; Jasper, B.; Fröhlich, R. *Organometallics* **1995**, *14*, 3167.

distances in [$CrFe_2(CO)_{10}Se_4$] (2.411(2) and 2.429(14) Å)[9] but comparable with the related compound [$Fe_2(CO)_6$-$Se_2\{\mu$-$(CO)_3Cr(\eta^5$-$C_5H(CH_2Ph)(Ph)(OEt)\}$] (**1**) (2.625(1) Å).[5a] The Fe−Fe and Fe−Se bond distances in **8b**, 2.5343(9) and 2.3777(8) Å (av), respectively, are comparable with other related molecules of the form [$(CO)_6Fe_2(\mu$-SeXSe)] (X = CH_2, 2.527(1) and 2.3741 (av) Å;[10] X = C(H)═C(Ph), 2.512(1) and 2.3837 (av) Å;[11] X = C(H)═C(C≡CMe), 2.507(2) and 2.3838 (av) Å).[12]

Synthesis of [$Fe_2(CO)_6SSe\{\mu$-C(H)C(O)C(R)═C-(η^6-$C_6H_5Cr(CO)_3$)C(Ph)}] (R = H and Ph) (9a,b). Refluxing a benzene solution of [$(CO)_6Fe_2SSe\{\mu$-C(Ph)═C−C−(OEt)═$Cr(CO)_5\}$] (**7**) with the alkynes PhC≡CR (R = H, Ph) led to the formation of arene−chromium complexes [$Fe_2(CO)_6SSe\{\mu$-C(H)C(O)C(R)═C(η^6-C_6H_5Cr-$(CO)_3$)C(Ph)}] (**9a** R = H; **9b** R = Ph) in 82% and 85% yield, respectively (Scheme 2).

Scheme 2



7

9a-b

9a: R = H (82 %)
9b: R = Ph (85 %)

Unlike complex **6**, complex **7** did not react with 1-hexyne and 3-hexyne. The infrared spectral pattern of **9a** and **9b** is identical; the spectra show signals corresponding to the presence of terminally bonded metal carbonyl groups and signals in the region 1709−1711 cm^{-1}, typical of a ketonic group. Since an aromatic ketone was the expected product, the high value of 1711 cm^{-1} suggested the presence of a five-membered cyclic ketone in this molecule. The ^1H NMR spectra of **9a** and **9b** showed one singlet, each associated with selenium satellites. From the chemical shift and coupling constant values (J_{Se-H} = 18 and 16.8 Hz for **9a** and **9b**, respectively), it is clear that the Se atom is attached with a saturated carbon. While the ^1H NMR spectrum of compound **9a** showed a singlet at δ 6.34 ppm, compound **9b** does not show any peak in this region, implying the presence of an olefinic proton in compound **9a**. In both, a set of signals in the region δ 5.16−5.81 ppm indicated the presence of a phenyl ring complexed with $Cr(CO)_3$. ^{77}Se NMR spectra of both compounds showed one doublet at δ 509 ppm (J_{Se-H} = 18.3 Hz) and δ 500 ppm (J_{Se-H} = 17.5 Hz), respectively.

To confirm the position of the phenyl ring, complexed with $Cr(CO)_3$, the NOE difference spectrum for **9a** (irradiating at 6.4 ppm) was recorded, and it is observed that there is a strong interaction (18.9% peak enhancement at 5.68 ppm) between the complexed phenyl protons and the olefinic proton. When the signal at 3.7 ppm was irradiated and the NOE difference spectrum recorded, we could observe a 12.75% peak enhancement on the uncomplexed phenyl ring at 7.4 ppm. This experiment allowed us to place the $Cr(CO)_3$ group attached to the phenyl ring as shown in the structure **9a**.

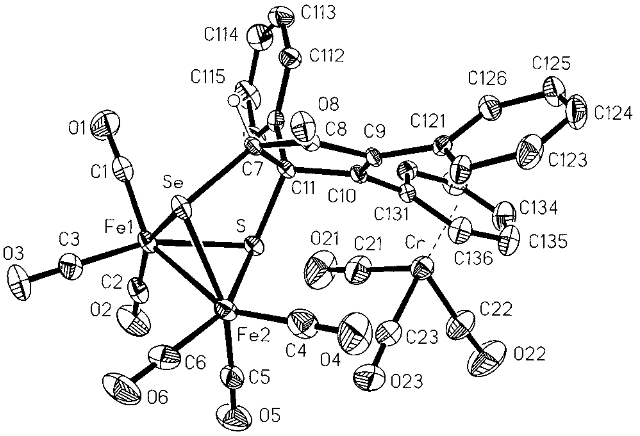


Figure 2. [$Fe_2(CO)_6SSe\{\mu$-C(H)C(O)C(Ph)═C(η^6-C_6H_5Cr-$(CO)_3$)C(Ph)}] (**9b**).

For unambiguous structure elucidation, a representative crystal structure determination was carried out. Single crystals of **9b** were grown by layering a CH_2Cl_2/EtOH solution with hexane at −4 °C, and an X-ray structure elucidation was carried out. Its molecular structure is shown in Figure 2. The structure can be described as consisting of an open $(CO)_6Fe_2SSe$ unit attached to a highly substituted cyclopentenone moiety.

The C(7)−C(11) bond distance of 1.545(5) (Å), which is attached to the S and Se atoms is slightly longer than the corresponding C−C bond distance of 1.502(6) Å, in the [$(CO)_6Fe_2\{\mu$-Se_2(indanone)}] (**2**) derivative.[13] The S−C(11)−C(10) bond angle of 110.4(2)° in **9b** is similar to the corresponding bond angle of 110.4(3)° in the related compound [$(CO)_6Fe_2\{\mu$-Se_2(indanone)}] (**2**). The Fe(2)−Se bond distance of 2.3609(8) Å is comparable to the corresponding bond distance of 2.3502 Å (av) in **2**, 2.3775 Å (av) in [$\{(CO)_6Fe_2(\mu$-$Se)_2\}_2$C(Ph)C(H)],[11] and 2.3475 Å (av) in [$\{(CO)_6Fe_2(\mu$-SSe$\}_2$C(Ph)C(H)].[14]

Although the exact mechanism of formation of **8a**−**d** and **9a**,**b** is not established at present, the fundamental difference in the two types of product formation stems from the difference in the reactivities of the Se−C and S−C bonds in the respective precursors, **6** and **7**. The formation of **8a**−**d** must involve the cleavage of the more polar Se−C bond in **6**, whereas the S−C bond in **7** is more stable and remains intact during the sequence of transformations leading to the formation of **9a**,**b**.

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 thin-layer chromatography and FT-IR spectroscopy. Infrared

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[9] Mathur, P.; Sekar, P.; Rheingold, A. L.; Liable-Sands, L. M. *Organometallics* **1997**, *16*, 142.

[10] Mathur, P.; Manimaran, B.; Trivedi, R.; Hossain, M. M.; Arabatti, M. *J. Organomet. Chem.* **1996**, *515*, 155.

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[12] Mathur, P.; Hossain, M. M.; Rheingold, A. L. *J. Organomet. Chem.* **1996**, *507*, 187.

[13] Mathur, P.; Ghosh, S.; Sarkar, A.; Rheingold, A. L.; Guzei, I. A. Unpublished results.

[14] Mathur, P.; Dash, A. K.; Hossain, M. M.; Chen, Y.-S.; Holt, E. M.; Rao, S. N. *J. Organomet. Chem.* **1996**, *526*, 379.

spectra were recorded on Nicolet-Impact 400 FTIR spectrometer as an *n*-hexane solution in a sodium chloride cell with a 0.1 mm path length. Elemental analyses were performed using a Carlo Erba 1106 automatic analyzer. ^{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 (δ = 0 ppm).

Chromium hexacarbonyl, phenylacetylene, diphenylacetylene, 1-hexyne, and 3-hexyne were purchased from Aldrich Chemical Co., and these were used without further purification. The homo- and mixed-chalcogenide iron carbonyl clusters $[Fe_2(\mu\text{-}Se_2)(CO)_6]$[15] and $[Fe_2(\mu\text{-}SSe)(CO)_6]$,[16] α,β-unsaturated homo- and mixed-chalcogenide carbene complexes $[(CO)_6Fe_2EE'\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$, (**6** E = E′ = Se; **7** E = S, E′ = Se),[4] and the alkynyl Fischer carbene complexes $[(CO)_5M{=}C(OEt)(C{\equiv}CPh)]$ (M = Cr, W)[17] were prepared as previously reported.

Thermolysis of $[(CO)_6Fe_2Se_2\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$ with $RC{\equiv}CR'$ (Where R = H, R′ = Ph; R, R′ = Ph; R = H, R′ = $(CH_2)_3CH_3$ and R, R′ = Et). In a typical preparation, a freshly prepared solution of 1 equiv of $[(CO)_6Fe_2Se_2\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$ (**6**) in benzene (10 mL) was refluxed with 3 equiv of $RC{\equiv}CR'$ (R = H, R′ = Ph; R, R′ = Ph; R = H, R′ = $(CH_2)_3CH_3$ and R, R′ = Et) for 1 h. The solution was filtered through Celite to remove the insoluble materials, and after removal of the solvent from the filtrate, the residue was subjected to chromatographic workup using silica gel TLC plates. Elution with a hexane/CH_2Cl_2 (8:2 v/v) mixture afforded a reddish-brown band $[Fe_2(CO)_6Se_2\{\mu\text{-}(CO)_3Cr(\eta^5\text{-}C_5(R')(R)(Ph)(OEt)\}]$ (**8a** R = H, R′ = Ph, 79%; **8b** R, R′ = Ph, 74%; **8c** R = H, R′ =$(CH_2)_3CH_3$, 70%; and **8d** R, R′ = C_2H_5, 72%).

8a. IR [(ν(CO), cm^{-1}]: 2066 (s), 2030 (s), 2012 (s), 1996 (s), 1981 (w), 1953 (m), 1947 (m). ^{1}H NMR (δ, ppm): 1.59 (t, 3H, C*H*$_3$), 4.06 (dq, 1H, *J* = 9.8 and 7.2 Hz, OC*H*$_2$), 4.24 (dq, 1H, *J* = 10 and 7.1 Hz, OC*H*$_2$), 4.77 (s, 1H, Cp ring), 6.98−7.57 (m, 10H, 2C$_6$*H*$_5$). ^{13}C NMR (δ, ppm): 14.4 (*C*H$_3$), 67.5 (*J* = 147.5 Hz, O*C*H$_2$), 68.6 (*J* = 180.2 Hz, *C*H), 98.7, 116.6, 128.2, 128.6, 129.1, 129.6, 130.4, 131.6, 132.5, 134.1, 149.6, 208.1 and 209.4 (CO in Fe(*C*O)$_3$), 235.5, 237.1, and 247.3 (*C*O in Cr(*C*O)$_3$). ^{77}Se NMR (δ, ppm): 395 and 209. Mp (°C): 114−116 (dec). Anal. Calcd (Found) for $C_{28}H_{16}CrFe_2O_{10}Se_2$: C, 40.30 (40.51); H, 1.91 (2.11).

8b. IR [(ν(CO), cm^{-1}]: 2067 (s), 2031 (s), 2011 (s), 1995 (s), 1980 (w), 1952 (m), 1948 (m). ^{1}H NMR (δ, ppm): 1.23 (t, 3H, C*H*$_3$), 3.74 (dq, 1H, *J* = 9.9 and 7 Hz OC*H*$_2$), 4.12 (dq, 1H, *J* = 9.8 and 6.8 Hz, OC*H*$_2$), 6.83−7.55 (m, 15H, 3C$_6$*H*$_5$). ^{13}C NMR (δ, ppm): 15.5 (*C*H$_3$), 72.4 (*J* = 145.5 Hz, O*C*H$_2$), 89.4, 97.6, 101.4, 115.7, 123.3, 128.3, 129.1, 129.5, 130.2, 130.8, 131.6, 132.9, 140.5, 145.9, 207.9 and 209.2 (CO in Fe(*C*O)$_3$), 235.9, 236.5, and 248.2 (CO in Cr(CO)$_3$). ^{77}Se NMR (δ, ppm): 382 and 210. Mp (°C): 118−120 (dec). Anal. Calcd (Found) for $C_{34}H_{20}CrFe_2O_{10}Se_2$: C, 44.85 (44.99); H, 2.19 (2.30).

8c. IR [(ν(CO), cm^{-1}]: 2067 (s), 2030 (s), 2011 (s), 1994 (s), 1980 (w), 1951 (m), 1948 (m). ^{1}H NMR (δ, ppm): 0.67 (t, 3H, CH$_2$C*H*$_3$), 1.05 (m, 2H, C*H*$_2$CH$_3$), 1.57 (q, 5H, OC*H*$_2$ and C*H*$_2$-CH$_2$CH$_3$), 1.82 (m, 2H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 2.40 (m, 2H, C*H*$_2$-CH$_2$ CH$_2$CH$_3$), 4.02 (dq, 1H, *J* = 10.1 and 7.2 Hz, OC*H*$_2$), 4.19 (dq, 1H, *J* = 10.2 and 7 Hz, OC*H*$_2$), 4.58 (s, 1H, Cp ring), 7.47−7.63 (m, 5H, C$_6$*H*$_5$). ^{13}C NMR (δ, ppm): 13.5 (CH$_2$CH$_2$*C*H$_3$), 14.4 (OCH$_2$*C*H$_3$), 22.1 (*C*H$_2$CH$_3$), 27.3 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 32.0 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 67.2, 67.3 (O*C*H$_2$ and *C*H in Cp ring), 96.3, 116.1, 128.7, 129.4, 129.7, 131.4, 135.9, 149.3, 208.2 and 209.5 (CO in Fe(*C*O)$_3$), 235.1, 237.3, and 247.2 (CO in Cr(*C*O)$_3$). ^{77}Se NMR (δ, ppm): 389 and 212. Mp (°C): 104−106 (dec). Anal. Calcd (Found) for $C_{26}H_{20}CrFe_2O_{10}Se_2$: C, 38.34 (38.51); H, 2.45 (2.60).

Table 1. Crystallographic Data for 8b and 9b

	8b	9b
formula	$C_{34}H_{20}CrFe_2O_{10}Se_2$	$C_{32}H_{16}CrFe_2O_{10}SSe$
fw	910.12	835.17
space group	$P2_1/c$	$P\bar{1}$
cryst syst	monoclinic	triclinic
a, Å	12.380(2)	10.2105(12)
b, Å	17.563(3)	11.4013(14)
c, Å	15.636(3)	13.695(2)
α, deg	90	94.553(12)
β, deg	90.07(2)	99.223(14)
γ, deg	90	93.975(8)
V, Å^3	3399.7(10)	1563.2(3)
Z	4	2
D(calc), Mg/m^3	1.778	1.774
$2\theta_{max}$, deg	50	50
F(000)	1792	828
abs coeff, mm^{-1}	3.354	2.547
goodness-of-fit on F^2	0.875	0.931
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0358	R1 = 0.0344
R indices (all data)	wR2 = 0.0756	wR2 = 0.0824

8d. IR [(ν(CO), cm^{-1}]: 2069(s), 2031 (s), 2010 (s), 1992 (s), 1982 (w), 1950 (m), 1946 (m). ^{1}H NMR (δ, ppm): 0.61 (t, 3H, *J* = 7.5 Hz, CH$_2$C*H*$_3$), 1.17 (t, 3H, *J* = 7.5 Hz, CH$_2$C*H*$_3$), 1.62 (t, 3H, *J* = 7.2 Hz, OCH$_2$C*H*$_3$), 1.84 (m, 1H, *J* = 7.5 Hz, C*H*$_2$), 2.03 (m, 1H, *J* = 7.5 Hz, C*H*$_2$), 2.39 (m, 1H, *J* = 7.2 Hz, C*H*$_2$), 2.53 (m, 1H, *J* = 7.2 Hz, C*H*$_2$), 3.99 (dq, 1H, *J* = 9.8 and 7.1 Hz, OC*H*$_2$), 4.67 (dq, 1H, *J* = 9.9 and 7.2 Hz, OC*H*$_2$), 7.48−7.67 (m, 5H, C$_6$*H*$_5$). ^{13}C NMR (δ, ppm): 14.01 (*C*H$_3$), 15.53 (*C*H$_3$), 15.86 (*C*H$_3$), 17.53 (*C*H$_2$), 18.53 (*C*H$_2$), 73.5 (O*C*H$_2$), 96.79, 98.79, 114.22, 128.89, 129.43, 130.06, 131.21, 143.26, 208.19 and 209.42 (CO in Fe(*C*O)$_3$), 234.12, 237.06, and 248.14 (CO in Cr(*C*O)$_3$). ^{77}Se NMR (δ, ppm): 384 and 214. Mp (°C): 108−110 (dec). Anal. Calcd (Found) for $C_{26}H_{20}CrFe_2O_{10}Se_2$: C, 38.34 (38.51); H, 2.45 (2.60).

Thermolysis of $[(CO)_6Fe_2SSe\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$ with $RC{\equiv}CPh$ (R = H and Ph). In a typical preparation, a freshly prepared solution of 1 equiv of $[(CO)_6Fe_2SSe\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$ (**7**) in benzene (10 mL) was refluxed with 2 equiv of $RC{\equiv}CPh$ (where R = H and Ph) for 1 h. The solution was filtered through Celite to remove the insoluble materials, and the residue was subjected to chromatographic workup using silica gel TLC plates. Elution with a hexane/CH_2Cl_2 (4:6 v/v) mixture afforded a red band $[Fe_2(CO)_6SSe\{\mu\text{-}\overline{C(H)C(O)C(R){=}C(\eta^6\text{-}C_6H_5Cr(CO)_3)C}(Ph)\}]$ (**9a** R = H, 82%; **9b** R = Ph, 85%).

9a. IR [(ν(CO), cm^{-1}]: 2076 (s), 2040 (vs), 2009 (s), 2000 (m), 1985 (s), 1930 (br, m), 1712 (m). ^{1}H NMR (δ, ppm): 3.70 (s, 1H, J_{Se-H} = 18 Hz, aliphatic proton in cyclopentenone ring), 5.10−5.80 (m, 5H, {η^6-C$_6$H$_5$Cr(CO)$_3$}), 6.34 (s, 1H, olefinic proton in cyclopentenone ring), 7.32−7.62 (m, 10H, 2C$_6$*H*$_5$). ^{13}C NMR (δ, ppm): 61.1 (J_{C-H} = 153.2 Hz, *C*(H)Se), 65.4 (*C*(Ph)S), 89.2−95.1 {η^6-*C*$_6$H$_5$Cr(CO)$_3$}, 114.5 (J_{C-H} = 158.1 Hz, α-*C* in cyclopentenone ring), 126.1, 126.9, 127.8, 128.5, 128.9, 129.2, 130.5, 136.4, 137.9, 143.3, 171.6 (*β*-*C* in cyclopentenone), 199.2 (*C*O in cyclopentenone), 207.8 (CO in Fe(*C*O)$_3$), 230.4 (CO in Cr(*C*O)$_3$). ^{77}Se NMR (δ, ppm): 509 (J_{Se-H} = 18.3 Hz). Mp (°C): 82−84. Anal. Calcd (Found) for $C_{26}H_{11}CrFe_2O_{10}SSe$: C, 41.12 (41.41); H, 1.58 (1.76).

9b. IR [(ν(CO), cm^{-1}: 2077 (s), 2039 (vs), 2011 (s), 1999 (m), 1980 (s), 1922 (br, m), 1711 (m).^{1}H NMR (δ, ppm): 3.92 (s, 1H, J_{Se-H} = 16.8 Hz, proton in cyclopentenone ring), 4.74−5.51 (m, 5H, {η^6-C$_6$*H*$_5$Cr(CO)$_3$}), 7.23−7.74 (m, 15H, 3C$_6$*H*$_5$). ^{13}C NMR (δ, ppm): 60.9 (*C*(H)Se, J_{C-H} = 152.6 Hz), 76.2 (*C*(Ph)S), 86.2−97.9 {η^6-*C*$_6$H$_5$Cr(CO)$_3$}, 127.7, 128.1, 129.1, 129.4, 129.7, 139.13, 141.1, 164.1 (*β*-*C* in cyclopentenone ring), 198.8 (*C*O in cyclopentenone), 208.1 (CO in Fe(*C*O)$_3$), 231.1 (CO in Cr(*C*O)$_3$). ^{77}Se NMR (δ, ppm): 500 (J_{Se-H} = 17.5 Hz).

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 8b

Cr−Cp (center)	1.838	Fe(1)−C(1)	1.780(6)
Fe(1)−Se(1)	2.3693(9)	Fe(1)−Se(2)	2.4035(9)
Fe(1)−Fe(2)	2.5343(9)	Fe(2)−C(5)	1.781(6)
Fe(2)−Se(2)	2.3777(8)	Fe(2)−Se(1)	2.3897(8)
Se(1)−C(10)	1.940(4)	Se(2)−Cr	2.6070(8)
Cr−C(12)	1.852(5)	Cr−C(13)	1.877(5)
Cr−C(11)	1.877(5)		
Se(1)−Fe(1)−Se(2)	84.19(3)	Se(1)−Fe(1)−Fe(2)	58.22(2)
Se(2)−Fe(1)−Fe(2)	57.50(2)	Se(2)−Fe(2)−Se(1)	84.31(3)
Se(2)−Fe(2)−Fe(1)	58.49(3)	Se(1)−Fe(2)−Fe(1)	57.43(2)
C(10)−Se(1)−Fe(1)	107.77(11)	C(10)−Se(1)−Fe(2)	107.38(11)
Fe(1)−Se(1)−Fe(2)	64.35(3)	Fe(2)−Se(2)−Fe(1)	64.01(3)
Fe(2)−Se(2)−Cr	112.15(3)	Fe(1)−Se(2)−Cr	110.35(3)
C(12)−Cr−Se(2)	123.72(14)	C(13)−Cr−Se(2)	74.14(14)
C(11)−Cr−Se(2)	70.03(14)		

Mp (°C): 88−90. Anal. Calcd (Found) for $C_{32}H_{16}CrFe_2O_{10}SSe$: C, 46.0 (46.21); H, 1.91 (2.08).

Crystal Structure Determination of 8b and 9b. Red crystals of **8b** and **9b** suitable for crystal structure determination were grown from a hexane/CH_2Cl_2 solution (**8b**) or by layering a CH_2Cl_2/EtOH solution with hexane (**9b**) at −4 °C. Red crystals of **8b** and **9b** were mounted on glass fibers and transferred to the cold gas stream (−100 °C) of a Siemens P4 diffractometer equipped with an LT-2 low-temperature attachment. Monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) was used for the measurements. Cell constants were refined from setting angles of 50 reflections in the 2θ range 6−25°. Appropriate absorption corrections based on ψ scans were applied. The crystal structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically using full-matrix least-squares methods based upon F^2 (SHELXL-93).[18] Hydrogens were included using a riding model. Pertinent crystallographic data **8b** and **9b** are summarized in Table 1. Selected bond lengths and bond angles for **8b** and **9b** are listed in Tables 2 and 3.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for 9b

Fe(1)−S	2.2609(11)	Cr−C(23)	1.833(5)
Fe(1)−Se	2.3582(8)	Fe(1)−Fe(2)	2.5219(9)
Fe(2)−C(5)	1.805(5)	Fe(2)−S	2.2354(11)
Fe(2)−Se	2.3609(8)	Se−C(7)	1.969(3)
S−C(11)	1.865(4)	C(8)−C(9)	1.476(5)
C(7)−C(11)	1.545(5)	C(9)−C(10)	1.353(5)
Cr−C(21)	1.857(5)	Cr−C(22)	1.840(5)
Cr−C(23)	1.833(5)		
S−Fe(1)−Se	81.01(3)	S−Fe(2)−Se	81.47(3)
C(7)−Se−Fe(1)	99.44(10)	C(7)−Se−Fe(2)	101.16(10)
Fe(1)−Se−Fe(2)	64.61(2)	C(11)−S−Fe(2)	109.58(12)
C(11)−S−Fe(1)	104.83(12)	Fe(2)−S−Fe(1)	68.23(3)
C(8)−C(7)−C(11)	106.4(3)	C(8)−C(7)−Se	109.2(2)
C(11)−C(7)−Se	114.1(2)	C(7)−C(11)−S	110.4(2)
C(10)−C(11)−S	110.4(2)	C(23)−Cr−C(21)	89.5(2)
C(21)−Cr−C(22)	91.1(2)	C(22)−Cr−C(23)	86.4(2)

Conclusions

In summary, we have reported an annulation reaction between Fischer carbene complexes tethered on chalcogen stabilized diiron clusters, $[(CO)_6Fe_2EE'\{\mu\text{-}C(Ph){=}C{-}C(OEt){=}Cr(CO)_5\}]$ (EE′ = SeSe and SSe), and alkynes. We observe that *no* CO insertion takes place in this case and different annulated products are formed, where formation of products are determined by the nature of the chalcogen atoms present.

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Supporting Information Available: Tables of atomic coordinates, all bond lengths and angles, and anisotropic displacement parameters for **8b** and **9b** (10 pages). Ordering information is given on any current masthead page.

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