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Synthesis and Characterization of Ferrocenylchalcogenopropargyl Complexes [Fe(η^5-$C_5H_4E^ICH_2C{\equiv}CH)_2$] ($E^I$ = Se, S) and Their Reactions To Form Unusual Ferrocenyl-Containing Metal Clusters with Eclipsed Cp Rings and New Five-Membered $FeE^ICH{=}CCH_2$ Ring Ligand System[†]

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The new bis(chalcogenopropargyl)ferrocene complexes [Fe(η^5-$C_5H_4E^ICH_2C{\equiv}CH)_2$] ($E^I$ = Se, **1**; E^I = S, **2**) have been prepared by treatment of the dilithiated [Fe(η^5-$C_5H_4Li)_2$] with Se or S powder, followed by reaction with propargyl bromide. Reaction of **1** and **2** with [Fe_2M(μ_3-E)$_2$(CO)$_9$] (E = S, Se and M = Fe, Ru) forms new clusters which feature an unusual five-membered $FeE^ICH{=}CCH_2$ ring with a π bond between the olefinic unit and the Fe atom, and the Cp rings adopt an eclipsed arrangement. The structures of **1** and [Fe(η^5-$C_5H_4E^ICH_2C{\equiv}CH$)(η^5-C_5H_4{$Fe_2M(CO)_8$(μ-E)(μ_3-E)(E^ICHCCH_2)})] (M = Fe, E = Se, E^I = Se, **3**; M = Fe, E = S, E^I = Se, **4**; M = Ru, E = S, E^I = Se, **7**) have been determined crystallographically.

1. Introduction

In the past we have reported on the reactions of different types of chalcogen-bridged metal carbonyl clusters with mononuclear acetylide complexes. Several new mixed-metal clusters stabilized by bridging chalcogens and acetylide ligands have been obtained by this method, and in many cases coupling of acetylide ligands is observed, with the type of acetylide coupling being strongly influenced by the nature of chalcogens present in the starting complex and by the reaction conditions adopted.[1−5] Substituted ferrocenes have attracted considerable interest in the past few years as possible synthons for polyferrocenylenes and related compounds, for useful properties such as electrical conductivity and in the preparation of metal-containing polymers.[6−10] Use of bulky ferrocenylacetylene adds an additional variant to the type of product obtainable from reactions carried out in the presence of free acetylenes. Recently we reported on the photochemical reaction of ferrocenylacetylene with iron pentacarbonyl to form 2,5- and 2,6-diferrocenylquinone.[11] Formation of the quinones was shown to proceed via an intermediate, tetracarbonyl(2-ferrocenylmaleoyl)iron. With less bulky acetylenes, we were unable to obtain other substituted quinones. The contrast between ferrocenylacetylene and phenylacetylene has also been observed in their reactions with mixtures of [$Fe_3(CO)_9$(μ_3-S)$_2$] and [(η^5-C_5H_5)M(CO)$_3$(CCPh)] (M = Mo, W). For instance, photochemical reactions of [$Fe_3(CO)_9$(μ_3-S)$_2$] with [(η^5-C_5H_5)M(CO)$_3$(CCPh)] (M = Mo, W) in the presence of added HCCR (R = Ph, n-Bu) gives mixed-Fe_3M clusters bearing μ_3-CCPh and μ_3-C(H)=C(R)S ligands; when the reaction is carried out in the presence of ferrocenylacetylene (FcCCH), a rare “acetylide-flip” occurs with formation of a {SC(H)CFc} ligand in the new mixed-metal cluster isolated.[12]

Our interest in bulky acetylenes extends to investigation of the reactivity of ferrocenyldiacetylenes with the

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10.1021/om049226r CCC: $30.25

Table 1. Spectroscopic Data for Compounds 1−7

compd	IR (ν(CO), cm^{-1}; hexane]	^{1}H NMR (δ; $CDCl_3$)	^{13}C NMR (δ; $CDCl_3$)
1	3316 (m), 2080 (m)	2.23 (t, 2H, $HC{\equiv}C$), 3.22 (d, 4H, CH_2), 4.28 (t, 4H, HCCSe), 4.44 (t, 4H, HCCHCSe)	13.66 (s, CH_2), 70.77 (s, $HC{\equiv}C$), 71.36 (s, $C{\equiv}CH$), 71.66 (s, HCCHCSe), 76.48 (s, HCCSe), 81.35 (s, CSe)
2	3318 (m), 2078 (m)	2.21 (t, 2H, $HC{\equiv}C$), 3.29 (d, 4H, CH_2), 4.29 (t, 4H, HCCS), 4.44 (t, 4H, HCCHCS)	25.69 (s, CH_2), 71.26 (s, $HC{\equiv}C$), 71.57 (s, $C{\equiv}CH$), 75.31 (s, HCCHCS), 79.39 (s, HCCS), 80.61 (s, CS)
3	2064 (s), 2037 (vs), 2026 (m), 2002 (s), 1991 (m), 1967 (m)	1.92 (t, 1H, $HC{\equiv}C$), 2.81 (d, 2H, CH_2), 3.71−3.79 (m, 4H, sub η^5-C_5H_4), 3.77 (s, 2H, CH_2Fe), 4.13−4.28 (m, 4H, unsub η^5-C_5H_4), 5.85 (s, 1H, $HC{=}C$)	14.1 (s, CH_2), 62.3 (s, CH_2Fe), 71.5 (s, $HC{\equiv}C$), 71.6−78.1 (m, $(\eta^5\text{-}C_5H_4)_2Fe$), 81.5 ($HC{=}C$), 88.1 ($C{\equiv}CH$), 137.3 (s, $C{=}CH$), 209.3−215.8 (CO)
4	2060 (s), 2036 (vs), 2013 (w), 2001 (m), 1987 (w), 1960 (m)	1.91 (t, 1H, $HC{\equiv}C$), 2.80 (d, 2H, CH_2), 3.75−3.79 (m, 4H, sub η^5-C_5H_4), 3.75 (s, 2H, CH_2Fe), 4.11−4.17 (m, 4H, unsub η^5-C_5H_4), 5.93 (s, 1H, $HC{=}C$)	13.7 (s, CH_2), 63.2 (s, CH_2Fe), 71.2 (s, $HC{\equiv}C$), 71.4−77.6 (m, $(\eta^5\text{-}C_5H_4)_2Fe$), 81.1 ($HC{=}C$), 86.7 ($C{\equiv}CH$), 147.6 (s, $C{=}CH$), 208.1−211.3 (CO)
5	2057 (s), 2030 (vs), 1994 (m), 1981 (s), 1957 (m)	1.89 (t, 1H, $HC{\equiv}C$), 2.86 (d, 2H, CH_2), 3.66−3.83 (m, 4H, sub η^5-C_5H_4), 3.76 (s, 2H, CH_2Fe), 4.11−4.36 (m, 4H, unsub η^5-C_5H_4), 5.72 (s, 1H, $HC{=}C$)	12.9 (s, CH_2), 61.9 (s, CH_2Fe), 70.2 (s, $HC{\equiv}C$), 71.3−76.9 (m, $(\eta^5\text{-}C_5H_4)_2Fe$), 81.8 ($HC{=}C$), 86.3 ($C{\equiv}CH$), 136.6 (s, $C{=}CH$), 208.7−214.8 (CO)
6	2053 (s), 2026 (vs), 2013 (m), 1989 (w), 1976 (s), 1955 (m)	1.91 (t, 1H, $HC{\equiv}C$), 2.80 (d, 2H, CH_2), 3.74−3.78 (m, 4H, sub η^5-C_5H_4), 3.75 (s, 2H, CH_2Fe), 4.12−4.14 (m, 4H, unsub η^5-C_5H_4), 5.98 (s, 1H, $HC{=}C$)	14.1 (s, CH_2), 58.4 (s, CH_2Fe), 71.6 (s, $HC{\equiv}C$), 71.7−77.8 (m, $(\eta^5\text{-}C_5H_4)_2Fe$), 80.6 ($HC{=}C$), 88.0 ($C{\equiv}CH$), 138.2 (s, $C{=}CH$), 209.8−217.8 (CO)
7	2064 (s), 2036 (vs), 2001 (s), 1991 (w), 1966 (s), 1895 (m)	1.91 (t, 1H, $HC{\equiv}C$), 2.80 (d, 2H, CH_2), 3.71−3.80 (m, 4H, sub η^5-C_5H_4), 3.76 (s, 2H, CH_2Fe), 4.12−4.21 (m, 4H, unsub η^5-C_5H_4), 5.94 (s, 1H, $HC{=}C$)	14.3 (s, CH_2), 62.8 (s, CH_2Fe), 71.6 (s, $HC{\equiv}C$), 71.9−77.8 (m, $(\eta^5\text{-}C_5H_4)_2Fe$), 81.9 ($HC{=}C$), 88.3 ($C{\equiv}CH$), 148.2 (s, $C{=}CH$), 209.2−216.81 (CO)

hope of preparing new types of organometallic polymers containing the ferrocenylacetylene units as bridges between chalcogen-bridged metal carbonyl cluster units. Although the diacetylene $[Fe(C_5H_4C{\equiv}CH)_2]$ is known, it is very reactive and undergoes rapid polymerization, preventing isolation of the type of chalcogen-bridged clusters of interest to us.[13] In our quest to obtain a ferrocene derivative with two acetylenic bonds and a compound which would be relatively stable to work with under thermal and photochemical conditions without undergoing decomposition or polymerization, we have developed the synthesis of chalcogenopropargyl derivatives of ferrocene, $[Fe(\eta^5\text{-}C_5H_4E^IH_2CC{\equiv}CH)_2]$ (E = Se, S). This paper describes the synthesis, structural characterization, and some reactivity studies with chalcogen-bridged metal carbonyl clusters.

Results and Discussion

Synthesis and Characterization of the Ferrocenylchalcogenopropargyl Complexes $[Fe(\eta^5\text{-}C_5H_4E^I\text{-}H_2CC{\equiv}CH)_2]$ (E^I = Se, 1; E^I = S, 2). The synthesis of chalcogenopropargyl complexes **1** and **2** is summarized in Scheme 1. The adduct $[Fe(\eta^5\text{-}C_5H_4ELi)_2]$ was formed by the reaction of $[Fe(\eta^5\text{-}C_5H_4Li)_2{\cdot}TMEDA]$ and chalcogen powder at low temperature, and it was treated with propargyl bromide to form **1** and **2** in yields of 36 and 25%, respectively. The new 1,1′-disubstituted ferrocenylchalogenopropargyl complexes were characterized by IR and ^{1}H and ^{13}C NMR spectroscopy (Table 1).

The infrared spectra of both compounds confirm the presence of the acetylenic $C{\equiv}C$ (ca. 2100 cm^{-1}) and CH groups (ca. 3300 cm^{-1}). The ^{1}H NMR spectra show four signals for each compound, a triplet for the acetylenic proton, a doublet for the methylene protons, and a pair of symmetrical triplets (AA′XX′ pattern) for the cyclopentadienyl rings, indicating the nonequivalent nature of the η^5-C_5H_4 protons. On the basis of NOESY experiments, the upfield triplet is assigned to the pair of protons H(2,5) and H(2′,5′) and the downfield triplet to the protons H(3,4) and H(3′,4′). Crystals of **1** were grown from a hexane/dichloromethane solvent mixture at −5 °C, and a single-crystal X-ray analysis was undertaken. An ORTEP diagram of **1** is shown in Figure 1.

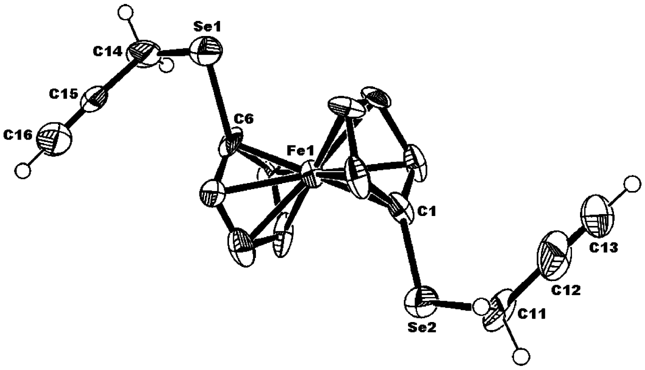

Figure 1. ORTEP diagram of **1** with 50% probability ellipsoids.

Scheme 1

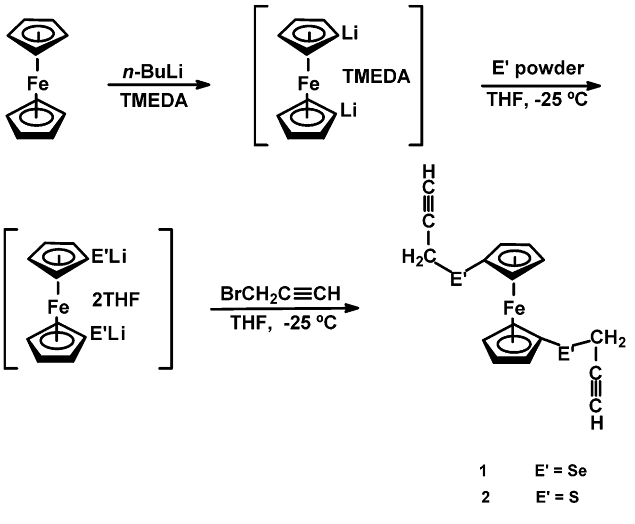

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 1, 3, 4, and 7

	1	**3**	**4**	**7**
Bond Lengths				
M−Fe(3)		2.554(4)	2.497(2)	2.573(2)
M−E(1)		2.371(3)	2.257(3)	2.353(4)
M−E(2)		2.391(3)	2.268(3)	2.358(3)
Fe(3)−E(1)		2.366(3)	2.257(3)	2.322(4)
Fe(3)−E(2)		2.392(3)	2.279(3)	2.331(4)
Fe(2)−E(2)		2.413(8)	2.287(3)	2.295(4)
Fe(2)−Se(1)		2.414(3)	2.409(19)	2.406(2)
Fe(2)−C(14)		2.048(15)	2.031(10)	2.046(13)
Fe(2)−C(15)		2.051(15)	2.046(11)	2.056(13)
E(1)-C(15)		1.998(16)	1.790(11)	1.804(16)
Se(1)−C(14)		1.908(16)	1.885(12)	1.911(15)
C(14)−C(15)	1.42(3)	1.35(2)	1.390(15)	1.33(18)
C(15)−C(16)	1.20(4)	1.42(2)	1.430(17)	1.4(2)
Se(2)−C(11)	1.978(12)	1.941(16)	1.978(13)	1.973(18)
C(11)−C(12)	1.50(4)	1.43(3)	1.43(2)	1.4(3)
C(12)−C(13)	1.11(4)	1.13(3)	1.11(2)	1.15(3)
Bond Angles				
C(11)−C(12)−C(13)	177(3)	178.0(3)	177.9(18)	177.0(2)
C(12)−C(11)−Se(2)	112.7(14)	112.3(15)	112.0(10)	113.8(14)
C(15)−C(14)−Se(1)	113.0(14)	113.7(13)	116.3(9)	116.3(12)
C(14)−C(15)−C(16)	176(3)	122.0(15)	117.3(11)	118.1(14)
C(15)−C(16)−Fe(2)		68.0(8)	67.3(7)	68.8(7)
C(16)−C(15)−E(1)		118.1(12)	121.2(9)	120.8(11)
C(6)−Se(1)−C(14)	100.7(8)	99.2(7)	99.2(5)	99.2(6)
C(1)−Se(2)−C(11)	98.4(7)	97.3(8)	97.1(5)	97.2(8)
E(1)−M−E(2)		83.64(9)	82.01(10)	80.08(12)
E(2)−Fe(2)−C(16)		98.5(5)	98.0(4)	98.8(4)

The molecular structure of **1** consists of a ferrocenylene unit in a staggered geometry (35°), and the rings are inclined at an angle of ca. 1.5°. Each ring bears a $SeCH_2C{\equiv}CH$ group oriented in a mutually trans disposition with minimum interacetylenic interaction. Angles subtended at the two Se atoms are slightly different (C(6)−Se(1)−C(14) = 100.7(8)°, C(1)−Se(2)−C(11) = 98.4(7)°) and are greater than the C−Se−C angle of 96.6(3)° observed in $[(C_4H_4S)SeCH_2CH_2OPh]$.[14] Selected bond lengths and bond angles are listed in Table 2 and require no further discussion here.

Reactivity of 1 and 2 toward $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ and $[Fe_2Ru((CO)_9(\mu_3\text{-}E)_2]$ (E = Se, S). The orientation of the two acetylenic units in **1** and **2** suggested to us that each would be capable of reacting independently with a metal carbonyl unit. When a benzene solution containing equimolar amounts of **1** or **2** and $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ or $[Fe_2Ru(CO)_9(\mu_3\text{-}E)_2]$ (E = Se, S) was subjected to reflux, the unusual clusters **3**−**7** could be isolated from the reaction solutions (Scheme 2). When an excess amount of the Fe_3E_2 or Fe_2RuE_2 reactant was used, **3**−**7** were obtained in similar yields and no other new products were observed in the reactions. The new clusters were characterized by IR and ^1H and ^{13}C NMR spectroscopy, and the molecular structures of **3**, **4**, and **7** were established crystallographically. ORTEP diagrams of **3**, **4**, and **7** are shown in Figures 2−4 respectively, and selected bond lengths and bond angles are listed in Table 2.

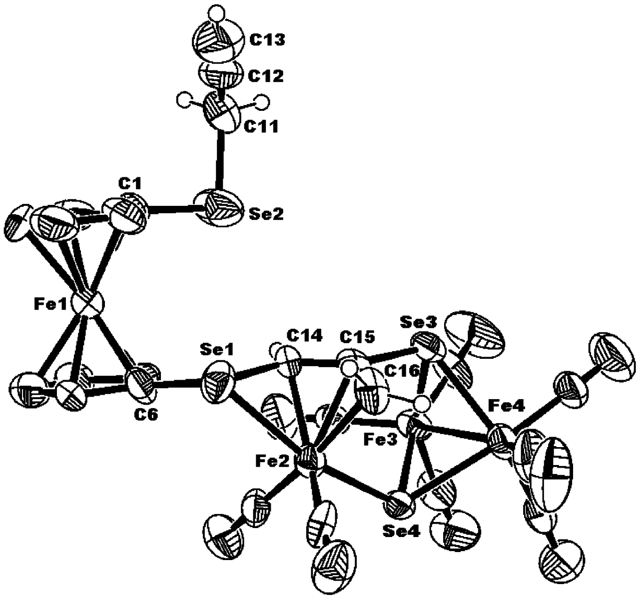
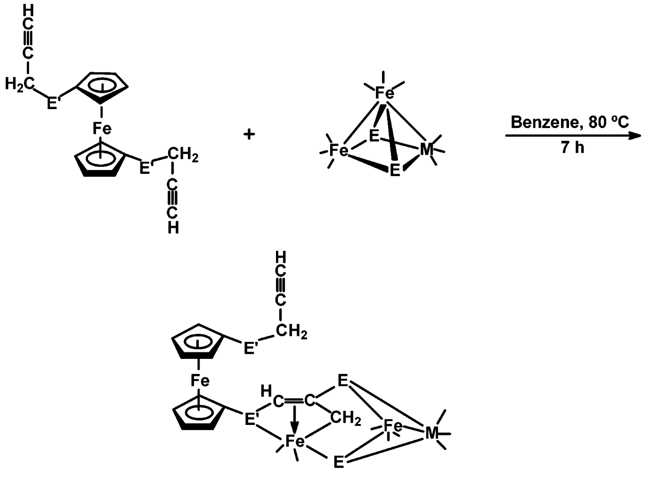


Figure 2. ORTEP diagram of **3** with 50% probability ellipsoids.

Scheme 2



Compound	M	E	E'
3	Fe	Se	Se
4	Fe	S	Se
5	Fe	Se	S
6	Ru	Se	Se
7	Ru	S	Se

The molecular structure of each consists of a butterfly Fe_2E_2 (**3** and **4**) or $FeRuS_2$ (**7**) unit attached to an $FeSeC(H){=}CCH_2$ five-membered ring. The Se atom of this ring is bonded to the C_5H_4 ring of a $(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_4SeCH_2C{\equiv}CH)Fe$ unit. The two metal atoms in the butterfly unit bear three terminal carbonyls each, while the Fe atom in the five-membered ring has two carbonyls. To satisfy electron counting at this Fe atom, we believe that there must exist a π bond between the $C(H){=}C$ and the $Fe(CO)_2$ groups of the ring. Indeed, the C(olefin)−Fe distances in **3**, **4**, and **7** (average C(14)−Fe(2) = 2.042 Å and average C(15)−Fe(2) = 2.051 Å) compare well with the average distances observed between the coordinated olefinic carbons and the iron atom in $[Fe(CO)_4(\eta^2\text{-}CH_2CHCN)]$[15] (2.10 Å), $[Fe(CO)_4(\eta^2\text{-}C_6H_8)]$[16] (2.15 Å), and $[Fe(CO)_3\{\eta^2\text{-}C_6H_4(CH{=}CH_2)(PPh_2)\}]$[17] (2.05 Å). However, the C=C bond distance of 1.35−1.39 Å in **3**, **4**, and **7** is somewhat shorter than the C−C bond distances reported in other iron−olefin

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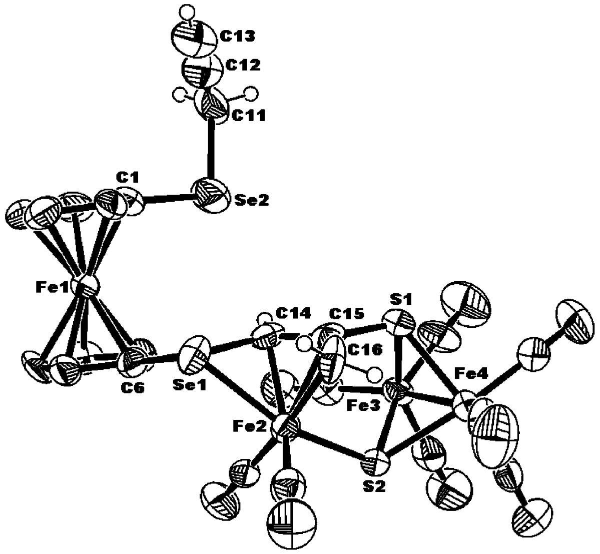

Figure 3. ORTEP diagram of **4** with 50% probability ellipsoids.

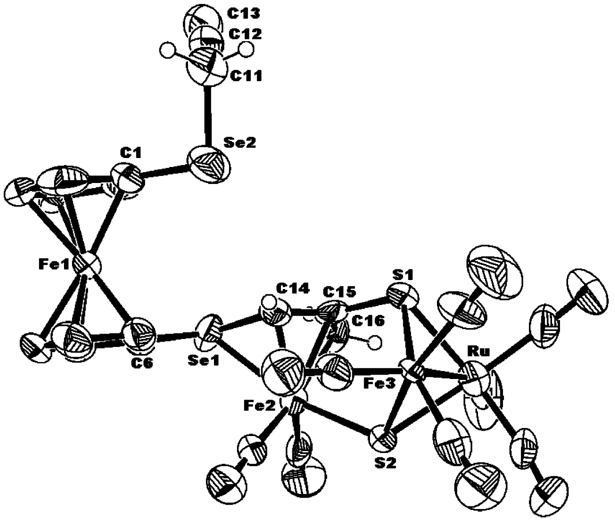

Figure 4. ORTEP diagram of **7** with 50% probability ellipsoids.

complexes, $[Fe(CO)_4(\eta^2\text{-}CH_2CHCN)]$ (1.40(2) Å), $[Fe(CO)_4(\eta^2\text{-}C_6H_8)]$ (1.421(5) Å), and $[Fe(CO)_3\{\eta^2\text{-}C_6H_4(CH{=}CH_2)(PPh_2)\}]$ (1.45 Å), suggesting that perhaps the π interaction is rather weak and the bond between the two carbon atoms retains much of its olefinic character.

The two C_5H_4 rings in the ferrocene unit are only marginally staggered (by 5−8°), and the two rings also show a slight tilt (ca. 2−8°). The C−S, C−Se, and C−C bond distances are all within the expected range. The C≡C bond distances of the uncoordinated propargylic group in **3**, **4**, and **7** (1.43 Å) are equal and marginally shorter than the corresponding bond distance in **1** (1.50(4) Å). The second propargylic group undergoes a formal "flip" from a E^ICH_2CCH group in **1** and **2** to a E^I-$CHCCH_2$ group on formation of **3**, **4**, and **7**. Second, formation of the clusters also involves a formal rotation of one of the ferrocene rings such that the two rings are almost eclipsed and the two propargylic groups are in a mutually cis configuration. Although the exact mechanistic details are difficult to establish, such a rotation of the rings would suggest that the chalcogens of both the chalcogenopropargyl groups take part in the initial attack on the $Fe_2ME_2(CO)_9$ cluster. This would be followed by a flip of one of the propargyl groups and its incorporation into the five-membered $FeSeC(H){=}CCH_2$ ring. An intact Fe−Ru bond in **7** suggests that the formation of **3**−**7** involves a formal cleavage of the Fe_{basal}−Fe_{apical} bond and incorporation of the basal Fe atom into the five-membered $FeE'CHCCH_2$ ring. We attempted to add a second cluster unit to the pendant propargylic group of **3**−**7** by carrying out a thermolysis reaction of **3**−**7** with an excess of $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ or $[Fe_2Ru(CO)_9(\mu_3\text{-}E)_2]$. In all cases we could isolate only the unreacted starting materials from the reaction mixture and no new products were obtained.

3. Conclusion

Preparation of the thio- or selenopropargyl derivatives of ferrocene, **1** and **2**, respectively, provides an opportunity to investigate the reactivity at the two acetylenic units of these complexes. Reactions of **1** and **2** with the chalcogen-bridged metal carbonyl clusters of the type $[Fe_2M(CO)_9(\mu_3\text{-}E)_2]$ gives rise to clusters **3**−**7**, which display a number of unusual features. The most prominent is the eclipsed rings of the ferrocenylene unit. Although we are unable to establish the driving force for the staggered to eclipsed change on reaction of **1** and **2** to form **3**−**7**, we speculate that, at some stage in the mechanism of formation of the products, both of the chalcogenopropargyl units must be attached to the adding chalcogen-bridged cluster moiety. Second, the formation of the new five-membered $FeE'CH{=}CCH_2$ ring, in which the olefin bonds to the metal atom, is unprecedented.

4. Experimental Section

General Procedure. Reactions and manipulations were performed using standard Schlenk techniques under an atmosphere of prepurified argon. Solvents were purified, dried, and distilled under an argon atmosphere prior to use. Infrared spectra were recorded on a Nicolet Impact 400 FT spectrometer as dichloromethane solutions in 0.1 mm path length NaCl cells and NMR spectra on a Varian VXRO-300S spectrometer in $CDCl_3$. Elemental analyses were performed on a Carlo-Erba automatic analyzer. The compounds $[Fe_2M(CO)_9(\mu_3\text{-}E)_2]$ (M = Fe, Ru; E = S, Se) were prepared as reported earlier.[18] Iron pentacarbonyl and ferrocene were purchased from Fluka, and propargyl bromide was purchased from Merck, and these were used without further purification.

Preparation of Ferrocenylchalcogenopropargyl Complexes $[Fe(\eta^5\text{-}C_5H_4E^ICH_2C{\equiv}CH)_2]$ (E^I = Se, 1; E^I = S, 2). To a rapidly stirred hexane (2 mL) slurry of ferrocene (850 mg, 4.57 mmol) was added a 1.6 M hexane solution of *n*-butyllithium (7.5 mL, 12 mmol,). Freshly distilled *N,N,N′,N′*-tetramethylethylenediamine (TMEDA; 0.89 mL, 5.5 mmol) was added dropwise over a period of 1 h. During the addition, the reaction mixture became quite warm (ca. 50 °C) and the reaction mixture attained a deep cherry red color. After 14 h of constant stirring at room temperature, 20 mL of THF was added to dissolve the dilithiated product and the reaction flask was cooled to −25 °C. To this was added a suspension of chalcogen powder (E^I = Se, 632 mg, 8 mmol; E^I = S, 260 mg, 8 mmol) in 15 mL of THF. The temperature of the mixture was slowly brought to room temperature over a

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(18) (a) Mathur, P.; Chakrabarty, D.; Hossain, M. M.; Rashid, R. S.; Rugmini, V.; Rheingold, A. L. *Inorg. Chem.* **1992**, *31*, 1106. (b) Mathur, P. Hossain, M. M.; Rashid, R. S. *J. Organomet. Chem.* **1993**, *460*, 83.

Table 3. Experimental Conditions Used for the Preparation of 3−7

$[Fe_2M(CO)_9(\mu_3\text{-}E)_2]$ [mg (mmol) used] {mg (mmol) recovered}	$[Fe(\eta^5\text{-}C_5H_4E^ICH_2C{\equiv}CH)_2]$ [mg (mmol) used] {mg (mmol) recovered}	product obtained	yield:[a] mg (%)	anal. calcd (found)	mp, °C[b]
$[Fe_3(CO)_9(\mu_3\text{-}Se)_2]$ [100 (0.17)] {20 (0.03)}	$[Fe(\eta^5\text{-}C_5H_4SeCH_2C{\equiv}CH)_2]$ [73 (0.17)] {18 (0.04)}	**3**	42 (31)	C, 29.58 (29.73); H, 1.45 (1.56)	156−158
$[Fe_3(CO)_9(\mu_3\text{-}S)_2]$ [100 (0.21)] {12 (0.02)}	$[Fe(\eta^5\text{-}C_5H_4SeCH_2C{\equiv}CH)_2]$ [87 (0.21)] {20 (0.05)}	**4**	38 (24)	C, 32.82 (33.04); H, 1.61 (1.74)	164−166
$[Fe_3(CO)_9(\mu_3\text{-}Se)_2]$ [100 (0.17)] {22 (0.04)}	$[Fe(\eta^5\text{-}C_5H_4SCH_2C{\equiv}CH)_2]$ [56 (0.17)] {18 (0.06)}	**5**	25 (21)	C, 32.82 (32.61); H, 1.61 (1.43)	172−174
$[Fe_2Ru(CO)_9(\mu_3\text{-}Se)_2]$ [100 (0.16)] {15 (0.02)}	$[Fe(\eta^5\text{-}C_5H_4SeCH_2C{\equiv}CH)_2]$ [67 (0.16)] {19 (0.05)}	**6**	32 (23)	C, 28.25 (28.56); H, 1.38 (1.49)	141−143
$[Fe_2Ru(CO)_9(\mu_3\text{-}S)_2]$ [100 (0.19)] {10 (0.02)}	$[Fe(\eta^5\text{-}C_5H_4SeCH_2C{\equiv}CH)_2]$ [79 (0.19)] {21 (0.05)}	**7**	28 (18)	C, 31.18 (30.97); H, 1.52 (1.38)	146−148

[a] Based on amount of $[Fe_2M(CO)_9(\mu_3\text{-}E)_2]$ consumed. [b] All with decomposition.

Table 4. Crystal Data and Structure Refinement Parameters for 1, 3, 4, and 7

	1	**3**	**4**	**7**
formula	$C_{16}H_{14}FeSe_2$	$C_{24}H_{14}Fe_4O_8Se_4$	$C_{24}H_{14}Fe_4O_8S_2Se_2$	$C_{24}H_{14}Fe_3RuO_8S_2Se_2$
mol wt	420.04	969.59	875.79	921.01
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P1$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	6.0550(6)	11.2890(7)	11.2860(11)	11.4021(17)
b, Å	6.8540(6)	10.9700(12)	10.8070(15)	10.8602(17)
c, Å	10.0860(8)	24.1500(17)	23.9350(10)	24.127(4)
α, deg	105.771(7)			
β, deg	101.616(7)	96.531(6)	96.608(6)	97.031(3)
γ, deg	104.784(9)			
V, Å^3	372.64(6)	2971.3(4)	2899.9(5)	2965.1(8)
Z	1	4	4	4
density (calcd), Mg/m^3	1.872	2.167	2.006	2.063
abs coeff, mm^{-1}	5.878	6.858	4.661	4.578
F(000)	204	1848	1704	1776
temp, K	293(2)	293(2)	293(2)	293(2)
cryst size, mm	0.40 × 0.35 × 0.30	0.15 × 0.10 × 0.05	0.25 × 0.225 × 0.20	0.30 × 0.16 × 0.01
θ range, deg	2.19−24.92	1.69−24.92	1.71−24.93	1.70−25.00
index ranges	$-7 \le h \le 6$, $0 \le k \le 8$, $-11 \le l \le 11$	$0 \le h \le 13$, $0 \le k \le 13$, $-28 \le l \le 28$	$0 \le h \le 13$, $0 \le k \le 12$, $-28 \le l \le 28$	$-13 \le h \le 13$, $-12 \le k \le 12$, $-28 \le l \le 28$
no. of rflns collected/unique	1430/1430 (R(int) = 0.0000)	3723/3723 (R(int) = 0.0000)	3859/3859 (R(int) = 0.0000)	27 318/5226 (R(int) = 0.1202)
no. of data/restraints/params	1430/0/177	3723/0/361	3859/0/393	5226/15/361
goodness of fit on F^2	1.110	1.041	1.055	1.129
final R indices ($I > 2\sigma(I)$)	R1 = 0.0527, wR2 = 0.1291	R1 = 0.0672, wR2 = 0.1475	R1 = 0.0584, wR2 = 0.1314	R1 = 0.0836, wR2 = 0.2079
R indices (all data)	R1 = 0.0649, wR2 = 0.1385	R1 = 0.1276, wR2 = 0.1803	R1 = 0.0928, wR2 = 0.1538	R1 = 0.1506, wR2 = 0.2452
largest diff peak, hole, e Å^{-3}	1.328, 1.720	1.317, −1.180	1.174, −0.827	2.630, −0.920

period of 5 h. A deep orange suspension was obtained. The reaction mixture containing the reactive intermediate $[Fe(\eta^5\text{-}C_5H_4E^ILi)_2]\cdot 2THF$ (E = Se, S) was again cooled to −25 °C. Propargyl bromide (0.36 mL, 4 mmol) was added dropwise using a syringe through a rubber septum into the reaction mixture. The reaction mixture was warmed to room temperature and was stirred for another 5 h. The reaction mixture was then filtered through a Celite pad and the solvent removed from the filtrate. The orange solid obtained was dissolved in dichloromethane and was chromatographed through a silica gel column. Petroleum ether eluted traces of unreacted ferrocene, while a 1:3 v/v mixture of dichloromethane/petroleum ether eluted the required products $Fe(\eta^5\text{-}C_5H_4E^ICH_2C{\equiv}CH)_2$ (E^I = Se, **1**; E^I = S, **2**). Data for **1** are as follows. Yield: 690 mg (36%). Mp: 180−182 °C dec. Anal. Calcd for $C_{16}H_{14}FeSe_2$: C, 45.71; H, 3.33. Found: C, 45.66; H, 3.26. Data for **2** are as follows. Yield: 372 mg (25%). Mp: 196−198 °C dec. Anal. Calcd for $C_{16}H_{14}FeS_2$: C, 58.92; H, 4.29. Found: C, 58.86; H, 4.20.

Preparation of $[Fe(\eta^5\text{-}C_5H_4E^ICH_2C{\equiv}CH)(\eta^5\text{-}C_5H_4\{Fe_2M(CO)_8(\mu\text{-}E)(\mu_3\text{-}E)(E^ICHCCH_2)\})]$ (M = Fe, E = Se, E^I = Se, 3; M = Fe, E = S, E^I = Se, 4; M = Fe, E = Se, E^I = S, 5; M = Ru, E = Se, E^I = Se, 6; M = Ru, E = S, E^I = Se, 7). In a typical preparation, a mixture of $[Fe_2M(CO)_9(\mu_3\text{-}E)_2]$ (M = Fe, Ru; E = S, Se) and $[Fe(\eta^5\text{-}C_5H_4E^ICH_2C{\equiv}CH)_2]$ (E^I = S, Se) in 30 mL of benzene was heated to reflux temperature for 7 h. After it was cooled to room temperature, the reaction mixture was filtered through Celite and the solvent was removed in vacuo. The residue was dissolved in dichloromethane and subjected to chromatographic workup on silica gel TLC plates. Elution with a 2/98 v/v acetone/*n*-hexane mixture yielded the following in order of elution: purple $[Fe_2M(CO)_9(\mu_3\text{-}E)_2]$, yellow $[Fe(\eta^5\text{-}C_5H_4E^ICH_2C{\equiv}CH)_2]$, and reddish-brown $[Fe(\eta^5\text{-}C_5H_4E^ICH_2C{\equiv}CH)(\eta^5\text{-}C_5H_4\{Fe_2M(CO)_8(\mu\text{-}E)(\mu_3\text{-}E)(E^ICHCCH_2)\})]$ (M = Fe, E = Se, E^I = Se, **3**; M = Fe, E = S, E^I = Se, **4**; M = Fe, E = Se, E^I = S, **5**; M = Ru, E = Se, E^I = Se, **6**; M = Ru, E = S, E^I = Se, **7**). Some other bands were also observed, but these were of insufficient amounts to facilitate their isolation and identification.

Details of the quantities of starting materials used, microanalytical data, melting points, and yields of products obtained are given in Table 3.

Crystal Structure Determinations of 1, 3, 4, and 7. Our success in obtaining reasonable quality crystals of the new compounds has been limited. Poor-quality single crystals for X-ray diffraction were obtained by slow evaporation of dichloromethane/*n*-hexane solvent mixtures of **1** and **7** at 0 °C and from toluene solutions of **2** and **3** at −30 °C. Relevant crystallographic data and structure refinement details are listed in Table 4. A Nonius MACH 3 diffractometer equipped with graphite-monochromated Mo Kα radiation was used for the cell determination and intensity data collection for **1**, **3**, and **4**. Unit cell dimensions were obtained using 25 centered reflections in the θ range 5.17−12.37 for **1**, **3**, and **4**. A Bruker SMART APEX CCD diffractometer equipped with graphite-monochromated Mo Kα radiation with a fine focus tube at 50 kV and 40 mA was used for the cell determination and intensity data collection for **7**: crystal to detector distance, 6.05 cm; 512 × 512 pixels/frame, hemisphere data acquisition; total scans, 3; total frames, 1271; oscillation/frame, −0.3°; exposure/frame, 30.0 s/frame; maximum detector swing angle, −30°; beam center, (260.2, 252.5); in-plane spot width, 1.24; SAINT integration. All the data were corrected by Lorentzian, polarization, and absorption effects. The structures were solved by direct methods (SHELXS) and refined by full-matrix least squares on F^2.[19] Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and refined using a riding model.

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Supporting Information Available: Details of the structure determinations as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049226R

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[19] Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Solution and Refinement; University of Göttingen, Göttingen, Germany, 1997.