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Coupling Reactions of Ferrocenylacetylene with Mononuclear Metal Carbonyls $Fe(CO)_5$ and $M(CO)_6$ (M = Mo, W): Synthesis and Characterization of $[Fe(CO)_2\{\eta^5\text{-}2,5\text{-}Fc_2C_5H_2CO\}C(Fc){=}CH]$, $[Fe(CO)_2\{\eta^2{:}\eta^2\text{-}2,5\text{-}Fc_2C_4H_2Fe(CO)_3\}\text{-}\mu\text{-}CO]$, $[Fe(CO)_3\{\eta^2{:}\eta^2\text{-}2,5\text{-}Fc_2C_4H_2CO\}]$, 1,2,4-Triferrocenylbenzene, 2,5-Diferrocenylthiophene, and 2,5-Diferrocenylselenophene

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Thermolysis of a benzene solution containing $Fe(CO)_5$ and ferrocenylacetylene yielded three new compounds: $[Fe(CO)_2\{\eta^5\text{-}2,5\text{-}Fc_2C_5H_2CO\}C(Fc){=}CH]$ (**1**), $[Fe(CO)_2\{\eta^2{:}\eta^2\text{-}2,5\text{-}Fc_2C_4H_2\text{-}Fe(CO)_3\}\text{-}\mu\text{-}CO]$ (**2**), and $[Fe(CO)_3\{\eta^2{:}\eta^2\text{-}2,5\text{-}Fc_2C_4H_2CO\}]$ (**3**). When a benzene solution containing ferrocenylacetylene and $M(CO)_6$ (M = Mo, W) was refluxed, 1,2,4-triferrocenylbenzene (**4**) was formed. In contrast to the reaction of ferrocenylacetylene with $Fe(CO)_5$, which leads to cyclization with insertion of a CO molecule, in the reaction with $M(CO)_6$ no insertion of CO takes place during cyclization. However, if the reactions with $M(CO)_6$ are carried out in the presence of S_8-powder or Se-powder, insertion of these chalcogen atoms during cyclization does take place and 2,5-diferrocenylthiophene (**5**) and 2,5-diferrocenylselenophene (**6**) are formed respectively, along with **4**. All new compounds were characterized by IR and ^1H and ^{13}C NMR spectroscopy. Structures of **1**−**5** were established by single-crystal X-ray crystallography.

Introduction

Several studies have been carried out on the organometallic chemistry of alkynes since Reppe discovered the cyclomerization of acetylene to cyclooctatetraene, and interest in the reactions of $Fe(CO)_5$ with alkynes has continued since the pioneering work of Hübel.[1−6] Catalytic applications of Mo and W carbonyls have also been investigated for the ring-closing alkyne metathesis[7] and for the synthesis of macrocyclic compounds, for example, use of $W(CO)_5L$ (L = NCMe, thiirane, CO) for the preparation of cyclic polydisulfides from thiiranes.[8−10] Several research groups have been working on the use of alkynes as bridging ligands in cluster formation, preparation of metal acetylides, and subsequent investigation of acetylide coupling reactions on cluster frameworks.[11−14] In our earlier work on use of chalcogen-bridged metal carbonyl clusters for formation of new acetylide-incorporated mixed metal clusters, we have observed that the coupling of acetylides is strongly influenced by the nature of the metal atom present and the reaction conditions used.[15−19] In recent times we

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(1) Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Justus Liebigs Ann. Chem.* **1948**, *561*, 1.

(2) Cooke, J.; Takats, J. *J. Am. Chem. Soc.* **1997**, *119*, 11088.

(3) Young, F. R., III; O'Brien, D. H.; Pettersen, R. C.; Levenson, R. A.; Minden, D. L. V. *J. Organomet. Chem.* **1976**, *114*, 157

(4) Efraty, A.; Bystrek, R.; Geaman, J. A.; Huang, M. H. A.; Herber, R. H. *Synthesis* **1971**, *6*, 305.

(5) (a) Hübel, W. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1968; Vol. 1, p 273, and references therein. (b) Hübel, W.; Braye, E. H. *J. Inorg. Nucl. Chem.* **1959**, *10*, 250.

(6) Fehlhammer, W. R.; Stolzenberg, H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1983; Vol. 4, p 545, and references therein.

(7) Pschirer, N. G.; Fu, W.; Adams, R. D.; Bunz, H. F. *Chem. Commun.* **2000**, 87.

(8) Adams, R. D.; Queisser, J. A.; Yamamoto, J. H. *J. Am. Chem. Soc.* **1996**, *118*, 10674.

(9) Adams, R. D.; Yamamoto, J. H. *Organometallics* **1997**, *16*, 1430.

(10) Adams, R. D.; Perrin, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 3984.

(11) Shiu, C.-W.; Chi, Y.; Chung, C.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1998**, *17*, 2970.

(12) Akita, M.; Terada, M.; Moro-oka, Y. *Chem. Commun.* **1997**, 265.

(13) Sappa E. *J. Cluster Sci.* **1994**, *5*, 211 and 535.

(14) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 204.

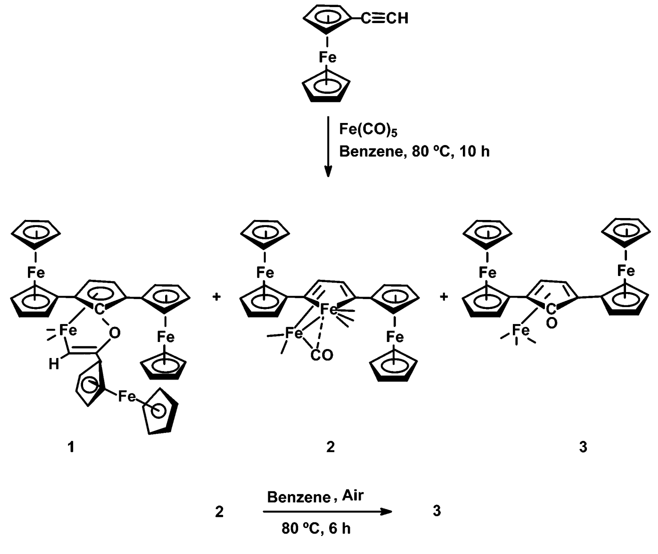
(15) Mathur, P.; Ahmed, M. O.; Dash, A. K.; Walawalkar, M. G.; Puranik, V. G. *J. Chem. Soc., Dalton Trans.* **2000**, 2916.

(16) Mathur, P.; Ahmed, M. O.; Dash, A. K.; Kalidas, J. H. *Organometallics* **2000**, *19*, 941.

(17) Mathur, P.; Ahmed, M. O.; Kalidas, J. H.; McGlinchey, M. J. *J. Chem. Soc., Dalton Trans.* **2002**, 619.

10.1021/om0504755 CCC: $30.25

Scheme 1



have focused our attention on investigation of reactions of acetylenes with metal acetylides and have found that bulky acetylenes, such as ferrocenylacetylene, introduce novel features in reactions with metal acetylides. Under photolytic conditions, reaction between ferrocenylacetylene and $Fe(CO)_5$ yields 2,5- and 2,6-diferrocenylquinones.[20] In this paper, we report on the reactions of ferrocenylacetylene with mononuclear metal carbonyls $Fe(CO)_5$ and $M(CO)_6$ (M = Mo, W) under thermolytic conditions and formation of $[Fe(CO)_2\{\eta^5\text{-}2,5\text{-}Fc_2C_5H_2\text{-}CO\}C(Fc){=}CH]$ (**1**), $[Fe(CO)_2\{\eta^2{:}\eta^2\text{-}2,5\text{-}Fc_2C_4H_2Fe(CO)_3\}\text{-}\mu\text{-}CO]$ (**2**), and $[Fe(CO)_3\{\eta^2{:}\eta^2\text{-}2,5\text{-}Fc_2C_4H_2CO\}]$ (**3**), 1,2,4-triferrocenylbenzene (**4**), 2,5-diferrocenylthiophene (**5**), and 2,5-diferrocenylselenophene (**6**).

Results and Discussion

Thermolysis of $Fe(CO)_5$ with Ferrocenylacetylene (FcC≡CH). When a benzene solution containing $Fe(CO)_5$ and FcC≡CH was subjected to reflux, under argon atmosphere for 10 h, the new compounds $[Fe(CO)_2\{\eta^5\text{-}2,5\text{-}Fc_2C_5H_2CO\}C(Fc){=}CH]$ (**1**), $[Fe(CO)_2\{\eta^2{:}\eta^2\text{-}2,5\text{-}Fc_2C_4H_2Fe(CO)_3\}\text{-}\mu\text{-}CO]$ (**2**), and $[Fe(CO)_3\{\eta^2{:}\eta^2\text{-}2,5\text{-}Fc_2C_4H_2CO\}]$ (**3**) were isolated from the reaction mixture (Scheme 1). Table 1 summarizes the conditions used for the preparation. Compounds **1**−**3** were characterized by IR and ^1H and ^{13}C NMR spectroscopy (Table 2). All three compounds are stable in the solid state, but compounds **1** and **2** decompose slowly in solution. When a benzene solution of **2** was subjected to reflux in air for 6 h, compound **3** was formed in 70% yield. The IR spectra of **1** and **3** show the presence of terminal carbonyls only, while that of **2** indicates the presence of semibridging CO in addition to the terminal carbonyl groups. ^1H and ^{13}C NMR spectra of compounds **1**−**3** confirm the presence of Cp rings of ferrocenyl groups and the presence of carbonyl groups. The per(ferrocenyl) analogues of **2** and **3** have been obtained earlier, in small amounts, from the reaction of differrocenylacetylene with $Fe_3(CO)_{12}$, and characterized spectroscopically. Crystals of **1**−**3**, suitable for X-ray analysis, were grown by slow evaporation of hexane/dichloromethane solvent mixtures at −5 °C, and we established their molecular structures by single-crystal X-ray analyses. ORTEP diagrams of **1**−**3** are shown in Figures 1−3, respectively.

The molecular structure of **1** consists of a (2,5-diferrocenyl)cyclopentadienone ring in which the two ferrocenyl units are mutually "*anti*". Attached to this is an $Fe(CO)_2C(H){=}C(Fc){-}$ unit; the Fe is π-bonded to the cyclopentadienone ring, and the carbon that is α to the ferrocenyl unit of $FcC{=}CH{-}Fe(CO)_2$ group is σ-bonded to the oxygen atom of the cyclopentadienone ring. The C−C bond distances in the cyclopentadienone ring range from 1.408(3) to 1.441(3) Å. The distances C(3)−C(7) (1.408(3) Å) and C(6)−C(7) (1.437(3) Å) of **1** are shorter than the corresponding distances of 1.497(9) and 1.495(9) Å in the η^4-cyclopentadienone unit of **3**. On the basis of a η^5-bonding mode of the cyclopentadienone unit to the iron atom, the 18-electron count is satisfied.

The molecular structure of **2** comprises a ferracyclopentadiene formed by a formal coupling of two ferrocenylacetylene molecules with an $Fe(CO)_3$ unit. This ferracyclopentadiene ring is η^4-bonded to another $Fe(CO)_3$ unit, which in turn is attached to the ring Fe through a direct Fe−Fe bond. The diene-bonded $Fe(CO)_3$ is rotated so as to achieve a staggered conformation with one CO group being significantly bent, Fe(1)−C(1)−O(1) = 166.2(4)°. The semibridging nature of this carbonyl is confirmed by IR spectroscopy (ν = 1896 cm^{-1}). The distances Fe(1)−Fe(2) (2.5138(8) Å) and Fe(2)−C(1) (2.472(5) Å) match well with other "non-sawhorse" type ferrole complexes reported earlier: $Fe(CO)_3[\eta^4\text{-}(OC)_3FeC_4H_4]$,[22] $Fe(CO)_3[\eta^4\text{-}(OC)_3FeC_4Ph_4]$,[23] $Fe(CO)_3[\eta^4\text{-}(OC)_3FeC_4(OH)_2Me_2]$,[24] and $Fe(CO)_3[\eta^4\text{-}(OC)_3FeC_4(OSiMe_3)_4]$.[25] One of the CO groups attached to the ring Fe is oriented nearly perpendicular to the ferracyclopentadiene ring, as also seen in the earlier reported structures. The two ferrocenyl groups attached to the ring are mutually perpendicular in **2**.

The molecular structure of **3** consists of an $Fe(CO)_3$ unit coordinated to an η^4-(2,5-diferrocenyl)cyclopentadienone resulting from a 2+2+1 coupling of two ferrocenylacetylene molecules with one CO molecule. In contrast to **1** and **2**, the ferrocenyl groups attached to the cyclopentadienone ring are "*syn*", opposite the $Fe(CO)_3$ unit. The cyclopentadienone ring is not planar, and the =CO unit is out of the plane with an angle of ~10°, indicating an anti-aromatic character of cyclopentadienone. The bond distances C(5)−C(6) (1.419(8) Å), C(6)−C(7) (1.388(9) Å), and C(7)−C(8) (1.436(8) Å) are indicative of delocalization of 4-π electrons over these four carbon atoms.

Thermolysis of Ferrocenylacetylene with $M(CO)_6$ (M = Mo, W). When a benzene solution containing ferrocenylacetylene and $M(CO)_6$ (M = Mo, W) was subjected to reflux, 1,2,4-triferrocenylbenzene (**4**) was formed. When a benzene solution containing FcC≡CH,

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[18] Mathur, P.; Mukhopadhyay, S.; Lahiri, G. K.; Chakraborty, S.; Thöne, C. *Organometallics* **2002**, *21*, 5209.

[19] Mathur, P.; Bhunia, A. K.; Srinivasu, C.; Mobin, S. M. *J. Organomet. Chem.* **2003**, *670*, 144.

[20] Mathur, P.; Bhunia, A. K.; Mobin, S. M.; Singh, V. K.; Srinivasu, C. *Organometallics* **2004**, *23*, 3694.

[21] Rosenblum, M.; Brawn, N.; King, B. *Tetrahedron. Lett.* **1967**, 4421.

[22] Dettlaf, G.; Weiss, E. *J. Organomet. Chem.* **1976**, *108*, 213.

[23] Riley, P. E.; Davis, R. E. *Acta Crystallogr. B* **1975**, *31*, 2928.

[24] Hock, A. A.; Mills, O. S. *Acta Crystallogr.* **1961**, *14*, 139.

[25] Dettlaf, G.; Behrens, U.; Eicher, T.; Weiss, E. *J. Organomet. Chem.* **1978**, *152*, 203.

Table 1. Experimental Conditions Used for the Preparation of 1–6

$Fe(CO)_5$/$Mo(CO)_6$ [mg (mmol)]	$FcC\equiv CH$) [mg (mmol) (used)] [mg (mmol) (recovered)]	S/Se [mg (mmol)]	product obtained	yield:[a] mg (%)	Anal: calcd (found)	mp/°C[b]
$Fe(CO)_5$	[210 (1.0)]		**1**	19 (12)	C, 60.77 (60.56)	188–192
[290 (1.48)]	[82 (0.39)]				H, 3.90 (3.88)	
			2	34 (16)	C, 51.47 (51.29)	211–215
					H, 2.85 (2.76)	
			3	41 (23)	C, 57.18 (56.80)	141–145
					H, 3.40 (3.38)	
$Mo(CO)_6$	[210 (1.0)]	S_8	**5**	37 (21)	C, 63.76 (63.52)	198–201
[53 (0.2)]	[47 (0.22)]	32 (0.13)			H, 4.43 (4.41)	
					S, 7.09 (6.95)	
			4	21 (13)	C, 68.62 (67.57)	245–247
					H, 4.76 (5.08)	
$Mo(CO)_6$	[210 (1.0)]	Se	**6**	44 (22)	C, 57.77 (58.09)	205–206
[53 (0.2)]	[45 (0.21)]	79 (1.0)			H, 4.01 (3.93)	
			4	23 (14)		
W(CO)6	[210 (1.0)]	S_8	**5**	41 (23)		
[70 (0.2)]	[44 (0.21)]	32 (0.13)	**4**	23 (14)		
W(CO)6	[210 (1.0)]	Se	**6**	42 (21)		
[70 (0.2)]	[42 (0.20)]	79 (1.0)	**4**	27 (16)		
$Mo(CO)_6$	[210 (1.0)]		**4**	31 (20)		
[53 (0.2)]	[53 (0.25)]					
$W(CO)_6$	[210 (1.0)]		**4**	28 (18)		
[70 (0.2]	[57 (0.27)]					

[a] Based on amount of $FcC\equiv CH$ consumed. [b] All with decomposition.

Table 2. Spectroscopic Data for Compounds 1–6

compound	IR [ν(CO), cm^{-1}, hexane]	^1H NMR (δ, $CDCl_3$)	^{13}C NMR (δ, $CDCl_3$)
1	2030 (vs), 1996 (s)	4.05 (s, 15H, (η^5-C_5H_5)), 3.98–4.09 (m, 12H, (η^5-C_5H_4)), 4.23 (s, 1H, –FeC(*H*)C(Fc)O–), 6.48 (s, 2H, –(Fc)CC(*H*)C(*H*)C(Fc)–)	66.74–69.77 (m, (η^5-C_5H_4)), 70.00 (s, (η^5-C_5H_5)), 71.32 (s, HCC(H)C(Fc)), 96.00 (s, (Fc)CC(O)), 108.26 (s, FeC(H)═C(O)(Fc)), 175.97 (Fc)C═C(H)Fe), 206.79 (s, (Fc)CC(O)), 210.85, 213.18 (Fe–CO)
2	2020 (vs), 1971 (vs), 1896 (s, br), 1777 (m)	4.17 (s, 10H, (η^5-C_5H_5)), 4.28–4.48 (m, 8H, (η^5-C_5H_4)), 4.93 (s, 2H, –(Fc)CC(*H*)C(*H*)C(Fc)–)	67.23–69.26 (m, (η^5-C_5H_4)), 69.41 (s, (η^5-C_5H_5)), 74.01 (s, HCC(H)C(Fc)), 128.16 (FcCFe$(CO)_4$), 198.62, 202.39, 208.32 (Fe-CO)
3	2065 (vs), 2010 (vs), 1996 (s), 1657 (s, br)	4.18 (s, 10H, (η^5-C_5H_5)), 4.31–4.33 (m, 4H, (η^5-C_5H_4)), 4.39–4.40 (m, 4H, (η^5-C_5H_4)), 5.48 (s, 2H, –(Fc)CC(*H*)C(*H*)C(Fc)–)	65.31–70.44 (m, (η^5-C_5H_4)), 75.98 (s, (η^5-C_5H_5)), 76.50 (s, HCC(H)C(Fc)), 86.05 (s, (Fc)CC(O)), 167 (s, ═CO), 208 (s, Fe–CO)
4		4.05–4.16 (m, 15H, (η^5-C_5H_5)), 4.37 (t, 6H, (η^5-C_5H_4)), 4.72 (t, 6H, (η^5-C_5H_4)), 7.34–7.87 (m, 3H, aromatic C*H*)	66.42–71.19 (m, Cp carbons), 128.86–136.89 (m, aromatic carbons)
5		4.15 (s, 10H, (η^5-C_5H_5)), 4.35 (t, 4H, (η^5-C_5H_4)), 4.64 (t, 4H, (η^5-C_5H_4)), 6.66 (s, 2H, –(Fc)CC(*H*)C(*H*)C(Fc)–)	66.54 (s, (η^5-C_5H_4)), 69.07 (s, C3,4 (η^5-C_5H_4)), 70.46 (s, (η^5-C_5H_5)), 81.65 (s, (η^5-C_5H_5)), 122.66 (s, C–C), 141.7 (s, C–S).
6		4.08 (s, 10H, (η^5-C_5H_5)), 4.24 (t, 4H, (η^5-C_5H_4)), 4.51 (t, 4H, (η^5-C_5H_4)), 6.95 (s, 2H, –(Fc)CC(*H*)C(*H*)C(Fc)–)	53.95 (s, (η^5-C_5H_4)), 67.4 (s, (η^5-C_5H_4)), 68.92 (s, (η^5-C_5H_5)), 70.10 (s, (η^5-C_5H_5)), 124.2 (s, C–C), 146.68 (s, C–Se).

$M(CO)_6$ (M = Mo and W), and E-powder (E = S, Se) was refluxed, 2,5-diferrocenylthiophene (**5**, E = S) and 2,5-diferrocenylselenophene (**6**, E = Se) were obtained, in addition to smaller amounts of **4** (Scheme 2). In the absence of $M(CO)_6$, and on extended thermolysis, we did not observe any formation of **5** and **6**, although small amounts of **4** were observed to be formed.

The experimental conditions used for these transformations are given in Table 1. Compounds **4**–**6** were characterized by IR and ^1H and ^{13}C NMR spectroscopy (Table 2). All three compounds are stable in solution under inert atmosphere and decompose slowly in air. The ^1H NMR spectra of these compounds confirmed the presence of Cp protons of ferrocenyl groups along with the aromatic protons expected for each structure. The cyclotrimerization of ferrocenylacetylene to give **4** is similar to the trimerization of phenylacetylene mediated by $[Co(CO)_4]_2Hg$.[26] Triferrocenylarenes have been synthesized by using the Ni- and Pd-catalyzed cross-coupling reactions of ferrocenylzinc chloride with trihalogenoarenes.[27] Cyclotrimerization of ferrocenylacetylene has been reported to be mediated by $[Ni(CO)_2(PPh_3)_2]$[28] or by Ziegler type catalysts.[29] By using $TaCl_5$ as catalyst, a mixture of 1,3,5-triferrocenylbenzene and its 1,2,4-subsituted isomer (**4**) is obtained.[30] Although small amounts of the pure 1,3,5-isomer could be separated and its molecular structure established crystallographically, that of the other isomer remained unreported. Compound **4** has also been obtained earlier from the reflux of dioxane solution containing ferrocenyl-

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(26) Hübel, W.; Hoogzand, C. *Chem. Ber.* **1960**, *93*, 103.

(27) Iyoda, M.; Kondo, T.; Okabe, T.; Matsuyama, H.; Sasaki, S.; Kuwatani, Y. *Chem. Lett.* **1997**, 35.

(28) Pittman, C. U., Jr.; Smith, L. R. *J. Organomet. Chem.* **1975**, *90*, 203.

(29) Nakashima, T.; Kunitake, T.; Aso, C. *Makromol Chem.* **1972**, *157*, 73.

(30) Stepmicka, P.; Cisarova, I.; Sedlacek, J.; Vohlidal, J.; Polasek, M. *Collect. Czech. Chem. Commun.* **1997**, *62*, 1577.

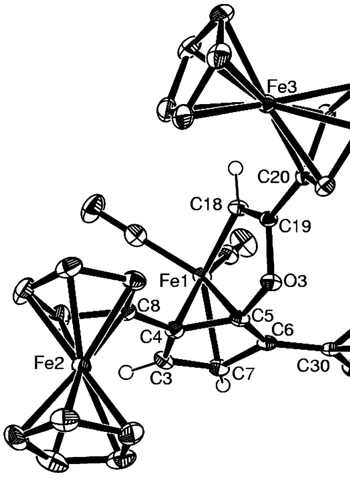


Figure 1. ORTEP diagram of $[\mathrm{Fe(CO)_2\{\eta^5\text{-}2,5\text{-}Fc_2C_5H_2\text{-}CO\}C(Fc){=}CH}]$ (**1**) with 50% probability ellipsoids. Selected bond lengths (Å) and bond angles (deg): Fe(1)−C(3) = 2.096(2), Fe(1)−C(4) = 2.117(2), Fe(1)−C(5) = 2.081(2), Fe(1)−C(6) = 2.134(2), Fe(1)−C(7) = 2.108(2), Fe(1)−C(18) = 1.979(2), C(3)−C(4) = 1.441(3), C(4)−C(5) = 1.429(3), C(5)−C(6) = 1.427(3), C(6)−C(7) = 1.437(3), C(3)−C(7) = 1.408(3), C(18)−C(19) = 1.339(3), O(3)−C(5) = 1.379(2), O(3)−C(19) = 1.417(2); C(7)−C(3)−C(4) = 108.70(18), C(5)−C(4)−C(3) = 105.57(17), C(3)−C(7)−C(6) = 109.55(19), C(6)−C(5)−C(4) = 110.82(18), C(5)−C(6)−C(7) = 105.32(18), C(19)−C(18)−Fe(1) = 118.20(16), C(18)−C(19)−C(20) = 130.2(2), C(5)−O(3)−C(19) = 108.67(16).

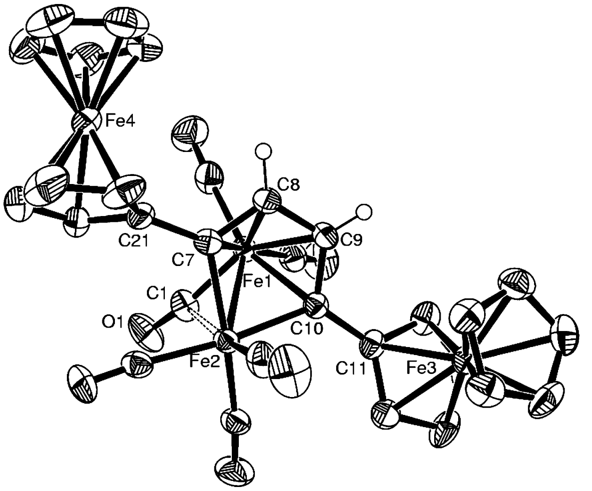


Figure 2. ORTEP diagram of $[\mathrm{Fe(CO)_2\{\eta^2{:}\eta^2\text{-}2,5\text{-}Fc_2C_4H_2\text{-}Fe(CO)_3\}\text{-}\mu\text{-}CO}]$ (**2**) with 50% probability ellipsoids. Selected bond lengths (Å) and bond angles (deg): Fe(1)−Fe(2) = 2.5138(8), Fe(1)−C(1) = 1.783(5), Fe(1)−C(7) = 2.110(4), Fe(1)−C(8) = 2.126(4), Fe(1)−C(9) = 2.125(4), Fe(1)−C(10) = 2.144(4), Fe(2)−C(7) = 1.989(4), Fe(2)−C(10) = 1.974(4), Fe(2)−C(1) = 2.472(5), O(1)−C(1) = 1.153(5), C(7)−C(8) = 1.408(6), C(8)−C(9) = 1.415(6), C(9)−C(10) = 1.412(6); Fe(1)−C(1)−O(1) = 166.2(4), Fe(2)−C(1)−O(1) = 123.5(3), Fe(1)−C(1)−Fe(2) = 70.32(15), C(10)−Fe(2)−C(7) = 82.00(17), C(8)−C(7)−Fe(2) = 113.7(3), C(9)−C(10)−Fe(2) = 113.7(3).

acetylene and $Co_2(CO)_8$, but its identification is based solely on elemental analysis and its oxidation by permanganate to trimellitic acid.[21] From the workup of our reaction mixtures, we were able to grow single crystals of **4** and **5** by slow evaporation of hexane/dichloromethane solvent mixtures at −5 °C, and single-crystal

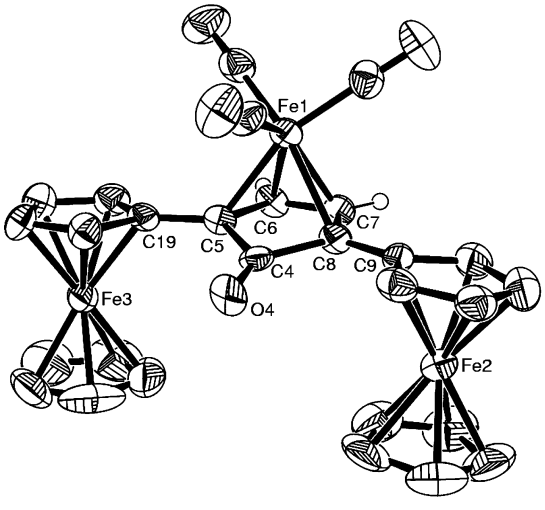
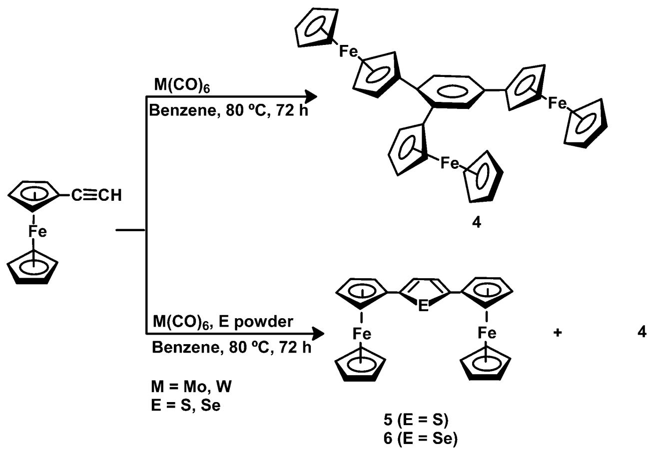


Figure 3. ORTEP diagram of $\mathrm{Fe(CO)_3[\eta^4\text{-}C_5H_2\{(\eta^5\text{-}C_5H_4)\text{-}Fe(\eta^5\text{-}C_5H_5)\}_2O]}$ (**3**), with 50% probability ellipsoids. Selected bond lengths (Å) and bond angles (deg): Fe(1)−C(4), = 2.414(5), Fe(1)−C(5) = 2.124(6), Fe(1)−C(6) = 2.051(6), Fe(1)−C(7) = 2.050(7), Fe(1)−C(8) = 2.155(7), C(4)−C(5) = 1.497(9), C(4)−C(8) = 1.495(9), C(5)−C(6) = 1.419(8), C(6)−C(7) = 1.388(9), C(7)−C(8) = 1.436(8), C(8)−C(9) = 1.447(9), C(5)−C(19) = 1.453(8), O(4)−C(4) = 1.218(7); C(7)−C(8)−C(9) = 126.6(6), C(7)−C(8)−C(4) = 106.7(6), C(5)−Fe(1)−C(8) = 66.6(2), C(7)−Fe(1)−C(5) = 66.6(3), C(6)−Fe(1)−C(5) = 39.7(2), C(8)−C(4)−C(5) = 103.4(6), C(6)−C(5)−C(4) = 107.6(6), C(4)−C(5)−Fe(1) = 81.7(4), C(7)−C(6)−C(5) = 109.4(6), C(7)−C(6)−Fe(1) = 70.2(4), C(5)−C(6)−Fe(1) = 72.9(4), C(6)−C(7)−C(8) = 109.9(6).

Scheme 2



X-ray analyses were undertaken. ORTEP diagrams of **4** and **5** are shown in Figures 4 and 5, respectively.

The molecular structure of **4** is essentially a trisubstituted benzene ring with ferrocenyl groups at the 1, 2, and 4 positions, their orientation being such as to minimize steric hindrance, otherwise expected for such a trisubstituted benzene molecule. We did not observe any other isomer of **4** in our reaction mixture. The C−C bond distances in the six-membered ring 1.374(5)−1.407(5) Å lie within the range typical of an aromatic ring system. The bond angles, C(2)−C(1)−C(7) = 124.7(4)°, C(3)−C(4)−C(27) = 121.0(4)°, and C(1)−C(2)−C(17) = 122.7(4)°, also indicate that the acetylenic bond in FcC≡CH is formally reduced as a result of the cyclotrimerization.

The molecular structure of **5** consists of a thiophene ring with ferrocenyl substituents at the 2 and 5 posi-

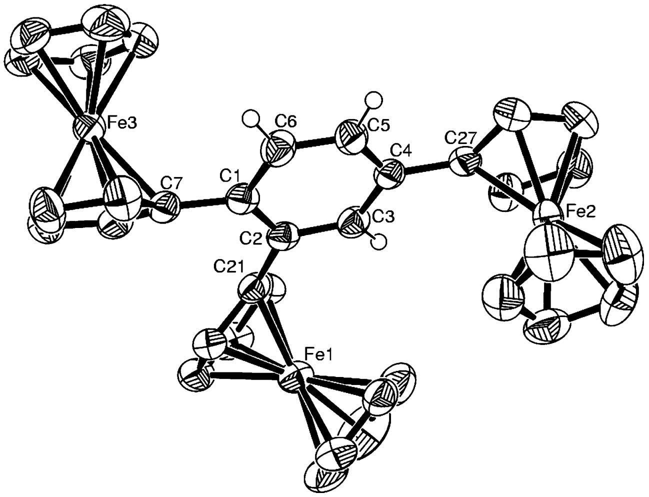


Figure 4. ORTEP diagram of [1,2,4-{(η^5-C_5H_4)Fe(η^5-C_5H_5)}$_3$$C_6H_3$] (**4**) with 50% probability ellipsoids. Selected bond lengths (Å) and bond angles (deg): C(1)−C(2) = 1.400(5), C(1)−C(6) = 1.407(5), C(1)−C(7) = 1.482(5), C(2)−C(3) = 1.399(5), C(2)−C(17) = 1.483(5), C(3)−C(4) = 1.383(5), C(4)−C(5) = 1.390(5), C(4)−C(27) = 1.479(5), C(5)−C(6) = 1.374(5); C(2)−C(1)−C(6) = 117.3(3), C(2)−C(1)−C(7) = 124.4(3), C(1)−C(2)−C(3) = 119.0(3), C(1)−C(2)−C(17) = 122.9(3), C(3)−C(2)−C(17) = 118.1(3), C(4)−C(3)−C(2) = 123.2(3), C(3)−C(4)−C(5) = 117.4(3), C(3)−C(4)−C(27) = 121.1(3), C(5)−C(4)−C(27) = 121.5(3), C(6)−C(5)−C(4) = 120.4(3), C(5)−C(6)−C(1) = 122.6(4), C(6)−C(1)−C(7) = 118.4(3).

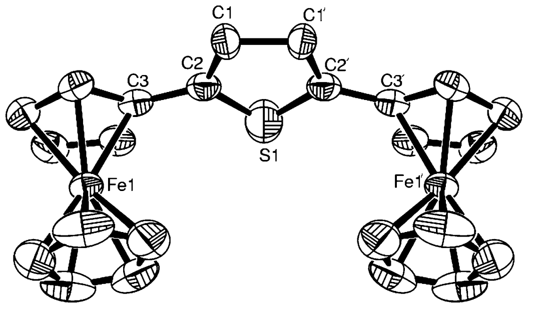


Figure 5. ORTEP diagram of [2,5-{(η^5-C_5H_4)Fe(η^5-C_5H_5)}$_2$$C_4H_2S$] (**5**) with 50% probability ellipsoids. Selected bond lengths (Å) and bond angles (deg): S(1)−C(2) = 1.714(5), S(1)−C(2)′ = 1.714(5), C(1)−C(1)′ = 1.497(9), C(1)−C(2) = 1.496(7), C(2)−C(3) = 1.464(7); C(2)′−S(1)−C(2) = 91.0(3), C(2)−C(1)−C(1)′ = 108.5(2), C(3)−C(2)−C(1) = 125.9(4), C(3)−C(2)−S(1) = 118.1(4), C(1)−C(2)−S(1) = 116.0(3).

tions. Both the ferrocenyl groups are oriented toward one side (*syn*) of the thiophene ring. The bond distances C(1)−C(2) (1.496(7) Å) and C(1)−C(1′) (1.497(9) Å) are longer than corresponding bond distances in **3** (1.419(8) and 1.388(9) Å, respectively). However, the bond distance C(2)−C(3) (1.464(7) Å) is closer to the corresponding bond distance C(5)−C(19) (1.453(8) Å) in **3**. The C(2)−S(1) (1.714(5) Å) lies between C−S single and double bond distances and indicates a bond order of 1.5 for this bond.

The structure of **6** was confirmed by ^{1}H and ^{13}C NMR and elemental analyses. The proton NMR spectrum of **6** has a singlet for two protons at δ 6.95 ppm and signals for Cp protons. ^{13}C NMR has signals for selenophene ring carbons at δ 124.2 and 146.68 ppm.

Experimental Section

General Procedures. All reactions and manipulations were carried out under an inert atmosphere of dry, prepurified argon or nitrogen using standard Schlenk line techniques. 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 hexane solutions in 0.1 mm path lengths NaCl cell and NMR spectra on a Varian VXRO-300S spectrometer in $CDCl_3$. Elemental analyses were performed on a Carlo-Erba automatic analyzer. TLC plates were purchased from Merck (20 × 20 cm, silica gel 60 F_{254}). FcC≡CH was prepared using a reported method.[31] $Fe(CO)_5$ was purchased from Fluka and $Mo(CO)_6$ and $W(CO)_6$ were from Strem, and were used without further purification. Details of quantities of starting materials used and yields of products obtained are given in Table 1.

Thermolysis of FcC≡CH with $Fe(CO)_5$. To a solution of FcC≡CH (210 mg, 1 mmol) in dry benzene (25 mL) was added $Fe(CO)_5$ (0.2 mL, 1.48 mmol), and the mixture was refluxed with stirring for 10 h. The solvent was removed in vacuo, and the residue was subjected to chromatographic workup using silica gel TLC plates. Use of 98:2 v/v hexane/acetone solvent mixture as eluant separated the following, in order of elution: a yellow band of unreacted FcC≡CH (82 mg) followed by a light orange band of **1** (13 mg, 8%), yellow band of **2** (28 mg, 13%), and red band of **3** (41.5 mg, 23%).

Thermolysis of FcC≡CH with $M(CO)_6$. A benzene solution (30 mL) containing $M(CO)_6$ (M = Mo, W) and FcC≡CH (in a molar ratio of 1:5, see Table 1) was heated at reflux for 72 h. The solution was cooled to room temperature and solvent removed in vacuo. The resulting residue was dissolved in dichloromethane and subjected to chromatographic workup using silica gel TLC plates. Use of 80:20 v/v hexane/dichloromethane solvent mixture as eluant separated the yellow band of unreacted FcC≡CH from another yellow band of 1,2,4-$Fc_3C_6H_3$ (**4**).

Thermolysis of FcC≡CH with $M(CO)_6$ and E-Powder (M = Mo, W and E = S, Se). A benzene solution (30 mL) containing $M(CO)_6$ (M = Mo, W), FcC≡CH, and E-powder (E = S_8, Se) (in a molar ratio of 1:5:5, see Table 1) was heated at reflux for 72 h. The solution was cooled to room temperature and solvent removed in vacuo. The resulting residue was dissolved in dichloromethane and subjected to chromatographic workup using silica gel TLC plates. With the use of 80:20 v/v hexane/dichloromethane solvent mixture as eluant the following were obtained in order of elution: a yellow band of unreacted FcC≡CH followed by yellow bands of 2,5-$Fc_2C_4H_2E$ (E = S, **5**; E = Se, **6**) and 1,2,4-$Fc_3C_6H_3$ (**4**).

Crystal Structure Determination of 1−5. Suitable X-ray quality crystals of **1**−**5** were grown by slow evaporation of dichloromethane/*n*-hexane solvent mixture at −5 °C, and X-ray crystallographic data were collected from single-crystal samples of **1** (0.33 × 0.23 × 0.14 mm^3), **2** (0.28 × 0.15 × 0.05 mm^3), **3** (0.40 × 0.08 × 0.08 mm^3), **4** (0.30 × 0.20 × 0.20 mm^3), and **5** (0.30 × 0.30 × 0.25 mm^3). Relevant crystallographic data and structure refinement details are listed in Table 3. A Bruker Smart 1000CCD area detector diffractometer equipped with an LT-2 low-temperature attachment was used for the cell determination and intensity data collection for compound **1**. For crystals of **2**−**5** a Nonius MACH3 diffractometer was used for the cell determination and intensity data collection. Monochromated Mo Kα radiation (λ = 0.71073 Å) was used for the measurements. The unit cell parameters for **2**−**5** were derived and refined by using randomly selected reflections in the θ range 6.3800−13.6000° (**2**), 7.1900−13.4700° (**3**), 6.6600−12.5100° (**4**), and 5.3300−12.4700° (**5**). Appropriate empirical absorption corrections using the programs SADABS (for **1**) or

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[31] Doisneau, G.; Balavonie, G.; Khan, T. F. *J. Organomet. Chem.* **1992**, *425*, 113.

Table 3. Crystal Data and Structure Refinement Parameters for 1, 2, 3, 4, and 5

	1	**2**	**3**	**4**	**5**
formula	$C_{39}H_{30}Fe_4O_3$	$C_{30}H_{20}Fe_4O_6$	$C_{28}H_{20}Fe_3O_4$	$C_{36}H_{30}Fe_3$	$C_{12}H_{11}FeS_{0.50}$
mol wt	770.03	699.86	587.99	630.15	227.09
temp	133(2) K	293(2)	293(2)	293(2)	293(2)
cryst syst	triclinic	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2_1/a$	$Pnma$
a, Å	7.3919(8)	7.8400(12)	35.321(3)	11.9320(12)	8.0620(9)
b, Å	11.0879(11)	11.9950(8)	6.4260(7)	12.4940(11)	24.1030(7)
c, Å	18.6596(18)	14.4890(8)	24.8580(18)	18.1790(14)	9.9580(17)
α, deg	97.989(5)	94.442(5)			90
β, deg	91.177(5)	93.843(8)	121.848(6)	95.373(8)	90
γ, deg	99.269(5)	105.805(8)			90
V, Å^3	1493.3(3)	1301.6(2)	4792.7(7)	2698.2(4)	1935.0(4)
Z	2	2	8	4	8
density(calcd), Mg/m^{-3}	1.713	1.786	1.630	1.551	1.559
abs coeff, mm^{-1}	1.945	2.230	1.825	1.616	1.613
F(000)	784	704	2384	1296	936
cryst size, mm	0.33 × 0.23 × 0.14	0.28 × 0.15 × 0.05	0.40 × 0.08 × 0.08	0.30 × 0.20 × 0.20	0.30 × 0.30 × 0.25
θ range, deg	1.88 to 28.39	1.41 to 24.94	1.35 to 24.93	1.12 to 24.92	1.69 to 24.93
index ranges	$-9 \le h \le 9$, $-14 \le k \le 14$, $0 \le l \le 24$	$-9 \le h \le 0$, $-13 \le k \le 14$, $-17 \le l \le 17$	$-35 \le h \le 41$, $0 \le k \le 7$, $-29 \le l \le 0$	$-14 \le h \le 14$, $0 \le k \le 14$, $0 \le l \le 21$	$0 \le h \le 9$, $0 \le k \le 28$, $0 \le l \le 11$
no. of rflns collected/ unique	9903/9903 [R(int) = 0.0000]	4928/4562 [R(int) = 0.0217]	4241/4127 [R(int) = 0.0431]	5019/4730 [R(int) = 0.0238]	1578/1578 [R(int) = 0.0000]
no of data/restraints/ params	9903/0/416	4562/0/437	4127/0/316	4730/0/468	1578/0/124
goodness-of-fit on F^2	1.104	1.020	0.972	0.919	1.075
final R indices [$I>2\sigma(I)$]	R1 = 0.0290 wR2 = 0.0753	R1 = 0.0390 wR2 = 0.0894	R1 = 0.0535 wR2 = 0.0989	R1 = 0.0342 wR2 = 0.0803	R1 = 0.0481 wR2 = 0.1490
R indices (all data)	R1 = 0.0376 wR2 = 0.0775	R1 = 0.0780 wR2 = 0.1031	R1 = 0.1855 wR2 = 0.1262	R1 = 0.0736 wR2 = 0.0968	R1 = 0.0556 wR2 = 0.1567
largest diff peak and hole, e Å^{-3}	0.484 and −0.322	0.542 and −0.625	0.604 and −0.550	0.319 and −0.249	0.603 and −1.035

ψ-scan (for **2**−**5**) were applied. The structures were solved by direct methods (SHELXS) and refined by full-matrix least squares against F^2 using SHELXL-97 (SHELX-TL for **1**) software.[32] Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model.

Conclusion

Although the formation of the cyclotrimerization product **4** from the thermolytic reaction of ferrocenylacetylene with molybdenum or tungsten hexacarbonyl is not unexpected, the formation of the ferrocenyl-substituted derivatives of thiophene (**5**) and selenophene (**6**) result from convenient single-pot reactions (albeit in somewhat modest yields). A significant contrast is seen in the thermolytic reaction of ferrocenylacetylene with iron pentacarbonyl. Compound **1** is the first structurally characterized example containing a η^5-bonded metal to a cyclopentadienone moiety. The formation of the cyclopentadienone unit of both **1** and **3** can be thought to arise from a formal coupling of two ferrocenylacetylene molecules with a CO; however introduction of excess CO in our reaction did not lead to an increase in the yields of these products. Compound **2** is an intermediate to **3**; however, our initial assumption that compound **1** may be formed from **3** by a formal insertion of a ferrocenylacetylene to the $Fe(CO)_3$ unit and the oxygen atom of the cyclopentadienone of **3** was incorrect, as we have not been able to obtain **1** from **3**, either by thermolysis or by photolysis.

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Supporting Information Available: Details of the structure determination for **1**−**5** including tables listing full bond length, bond angles, and torsion angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0504755

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(32) Sheldrick, G. M. *SHELX 97*, Program for crystal structure solution and refinement; University of Göttingen, 1997.