Novel Types of Organic S−Fe−CO Complexes: Reaction of $[SFe_3(CO)_9]^{2-}$ with Propargyl Bromide

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We have synthesized a series of novel organic S−Fe−CO complexes from the reaction of the sulfur-capped triiron carbonyl cluster $[SFe_3(CO)_9]^{2-}$ with the bifunctional propargyl bromide and subsequent reactions. When $[SFe_3(CO)_9]^{2-}$ was treated with 2 equiv of propargyl bromide in MeCN, three new organo-bridged iron−sulfur carbonyl complexes, $[Et_4N][Fe_3(CO)_9(\mu_3\text{-}\eta^3{:}\eta^1{:}\eta^2\text{-}CH_2C(S)CHC(O))]$ ($[Et_4N]$-[**1**]), $(\mu_3\text{-}S)Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C(H){=}C(CH_3))$ (**2**), and $Fe_2(CO)_6(\mu_2\text{-}\eta^2{:}\eta^3\text{-}SC(O)C(CH_3)CH)$ (**3**), were obtained. The novel anionic acyl cluster **1** is a CO insertion product and can be considered to display a SFe_3 core bridged by an allylcarbonyl ligand, $H_2C{=}CCHC(O)$, in $\mu_2\text{-}\eta^3{:}\eta^1$ fashion. While cluster **2** can be seen to possess a SFe_3 core coordinated with a propyne ligand, $CH{\equiv}C(CH_3)$, complex **3** exhibits a SFe_2 core bridged by a α-methylvinylcarbonyl ligand, $C(O)C(CH_3){=}CH$. The anionic cluster **1** could transform to **2** and **3** upon treatment with excess propargyl bromide. When $[Et_4N]$[**1**] was reacted with the oxidizing agent $[Cu(MeCN)_4][BF_4]$, the neutral diiron complex $Fe_2(CO)_6(\mu_2\text{-}\eta^2{:}\eta^3\text{-}C(O)CHC(S)(CH_3))$ (**4**) was obtained as the major product. Complex **4** is seen to possess a SFe_2 core linked by a β-methylvinylcarbonyl ligand, $C(O)CH{=}C(CH_3)$. More interestingly, the methylation of the acyl cluster **1** with CF_3SO_3Me afforded a unique triiron cluster carbene, $Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^4{:}\eta^2\text{-}CH_2C(S)CHC(OCH_3))$ (**5**). This paper describes a rare example of the reaction of a sulfur-capped triiron cluster with the bifunctional propargyl bromide and related reactions, in which a new series of iron−sulfur carbonyl complexes coordinated with novel organic fragments results, and the relative stability of some resultant complexes is discussed on the basis of theoretical calculations.

Introduction

In recent years, sulfur-containing iron carbonyl complexes have drawn increased attention mainly due to their unusual structures and chemical reactivities as well as their potential usefulness in catalysis and material and life sciences.[1] The previous study showed that the interaction of anionic sulfur-bridged iron carbonyl complexes with electrophilic species was largely emphasized for those with some alkyl- or alkyl-like halides.[2−4] The direct reactions of S-bridged iron carbonyl clusters with unsaturated hydrocarbon species have remained scarce, and related studies were limited to only some diiron systems.[2,3,5] Quite a number of metal-alkyne systems have been reported to have versatile bonding modes and interesting transformations.[1,2,5−9] For example, Vahrenkamp and co-workers synthesized a series of heteronuclear metal complexes starting from mononuclear acetylide complexes $LnMC{\equiv}CR$.[6] Wojcicki and co-workers developed syntheses and reactivities of many binuclear and polynuclear transition metal−propargyl and/or −allenyl complexes.[7,8] More recently, some polynuclear metal carbonyl clusters with simple alkynes have been studied as well.[9] Nevertheless, the factors governing the selectivity of metal clusters with unsaturated organic species are not fully under-

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stood. As to main group−transition metal clusters, this issue has long remained little explored due to the complicated coupling effect of main group elements and transition metals.

We recently reported on the reaction of tellurium-capped and selenium-capped triiron carbonyl clusters $[\mathrm{EFe_3(CO)_9}]^{2-}$ (E = Te, Se) with propargyl bromide.[10] The acyl clusters of the type $[(\mu_3\text{-E})\mathrm{Fe_3(CO)_9}(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-C(O)CHCCH}_2)]^-$ and the Fischer-carbene clusters $(\mu_3\text{-E})\mathrm{Fe_3(CO)_9}(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-C(OMe)CHCCH}_2)$ (E = Te, Se) were obtained in both systems. However, the sulfur-capped triiron cluster $[\mathrm{SFe_3(CO)_9}]^{2-}$ is expected to behave differently with the bifunctional propargyl bromide due to the smaller size and the greater electronegativity of S vs Se and Te. To probe the effect of chalcogen atoms, reactivity patterns, and viable synthetic routes, we studied the reaction of $[\mathrm{SFe_3(CO)_9}]^{2-}$ with propargyl bromide and subsequent reactions. In this study, novel types of the acyl cluster and the Fischer-carbene cluster were discovered, the structural transformations in this sulfur−iron system were established, and the relative stability of some resultant complexes is discussed on the basis of theoretical calculations.

Experimental Section

General Procedures. All reactions were performed under an atmosphere of pure nitrogen using standard Schlenk techniques.[11] Solvents were purified, dried, and distilled under nitrogen prior to use. $\mathrm{HC{\equiv}CCH_2Br}$ (Merck) and $\mathrm{CF_3SO_3Me}$ (Aldrich) were used as received. $[\mathrm{Et_4N}]_2[\mathrm{SFe_3(CO)_9}]$[4a] and $[\mathrm{Cu(MeCN)_4}][\mathrm{BF_4}]$[12] were prepared by the published methods. Infrared spectra were recorded on a Perkin-Elmer Paragon 500 IR spectrometer as solutions in $\mathrm{CaF_2}$ cells. The ^{1}H and ^{13}C NMR spectra were taken on a JEOL 400 instrument at 399.78 and 100.53 MHz, respectively. Elemental analyses of C, H, and N were performed on a Perkin-Elmer 2400 analyzer at the NSC Regional Instrumental Center at National Taiwan University, Taipei, Taiwan.

Reaction of $[\mathrm{Et_4N}]_2[\mathrm{SFe_3(CO)_9}]$ with $\mathrm{HC{\equiv}CCH_2Br}$ (1:2). To a solution of 0.594 g (0.83 mmol) of $[\mathrm{Et_4N}]_2[\mathrm{SFe_3(CO)_9}]$ in 30 mL of MeCN was added 0.15 mL (1.69 mmol) of $\mathrm{HC{\equiv}CCH_2Br}$. The resulting solution was stirred at room temperature for 38 h to give a brown solution, which was filtered, and the solvent was removed under vacuum. The precipitate was extracted with hexane, and the hexane extract was chromatographed with hexane using a Chromotron to give the first, reddish-brown band of 0.01 g (0.02 mmol) of $(\mu_3\text{-S})\mathrm{Fe_3(CO)_9}(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-C(H)=C(CH}_3))$ (**2**) (2%, based on $[\mathrm{Et_4N}]_2[\mathrm{SFe_3(CO)_9}]$). IR ($\nu_{\mathrm{CO}}$, hexane): 2089 (w), 2057 (vs), 2039 (vs), 2019 (vs), 2005 (s), 2000 (s) cm^{-1}. Negative ion (ESI-MS): *m/z* 491.9. Mp: 74 °C dec. Anal. Calcd for **2**: C, 29.31; H, 0.82. Found: C, 29.41; H, 0.82. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 298 K): δ 2.96 (s; $\mathrm{CH_3}$), 8.70 (s; CH). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$, 298 K): δ 42.15 ($\mathrm{CH_3}$), 183.82 (CH), 214.35 (−C−), 201.44, 205.69, 206.26, 209.79 ($\mathrm{FeC{\equiv}O}$). Complex **2** is soluble in hexane, ether, $\mathrm{CH_2Cl_2}$, THF, and MeCN. The second, orange band of 0.01 g (0.03 mmol) of $\mathrm{Fe_2(CO)_6}(\mu_2\text{-}\eta^2{:}\eta^3\text{-SC(O)C(CH}_3\text{)CH})$ (**3**) was collected using $\mathrm{CH_2Cl_2}$/hexane (1:1) as eluent (3%, based on $[\mathrm{Et_4N}]_2[\mathrm{SFe_3(CO)_9}]$). IR ($\nu_{\mathrm{CO}}$, hexane): 2087 (s), 2054 (vs), 2020 (vs), 2016 (vs), 2002 (m), 1971 (w), 1706 (s) cm^{-1}. Negative ion (ESI-MS): *m/z* 380.0. Mp: 127 °C dec. Anal. Calcd for **3**: C, 31.62; H, 1.06. Found: C, 32.13; H, 1.11. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 298 K): δ 1.99 (s, $\mathrm{CH_3}$), 8.49 (s, CH). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$, 298 K): δ 20.47 ($\mathrm{CH_3}$), 103.94 (−C−), 162.39 (CH), 186.97 (C(O)), 206.78 ($\mathrm{FeC{\equiv}O}$). Complex **3** is soluble in hexane, ether, $\mathrm{CH_2Cl_2}$, THF, and MeCN. The residue was then extracted with $\mathrm{CH_2Cl_2}$, and the $\mathrm{CH_2Cl_2}$ extract was recrystallized from hexane/$\mathrm{CH_2Cl_2}$ to give 0.44 g (0.68 mmol) of $[\mathrm{Et_4N}][\mathrm{Fe_3(CO)_9}(\mu_3\text{-}\eta^3{:}\eta^1{:}\eta^2\text{-CH}_2\text{C(S)CHC(O)})]$ ($[\mathrm{Et_4N}]$[**1**]) (82%, based on $[\mathrm{Et_4N}]_2[\mathrm{SFe_3(CO)_9}]$). IR ($\nu_{\mathrm{CO}}$, $\mathrm{CH_2Cl_2}$): 2047 (s), 2008 (vs), 1983 (vs), 1946 (s), 1596 (w) cm^{-1}. Negative ion (ESI-MS): *m/z* 518.8. Anal. Calcd for $[\mathrm{Et_4N}]$[**1**]: C, 38.86; H, 3.57; N 2.16. Found: C, 38.93; H, 3.54; N 2.04. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ 2.39 (d, $\mathrm{CH_2}$, J = 4 Hz), 2.58 (d, $\mathrm{CH_2}$, J = 4 Hz), 2.33 (s, CH) (chemical shift not given for $[\mathrm{Et_4N}]^+$). ^{13}C NMR (100 MHz, DMSO-d_6, 298 K): δ 42.79 ($\mathrm{CH_2}$), 68.62 (CH), 89.37 ($\equiv$CS), 209.55, 210.45, 211.86, 214.90, 217.09, 217.43, 217.85, 222.16 ($\mathrm{FeC{\equiv}O}$), 258.32 (C(O)) (chemical shift not given for $[\mathrm{Et_4N}]^+$). Complex **1** is soluble in ether, $\mathrm{CH_2Cl_2}$, THF, and MeCN.

Reaction of $[\mathrm{Et_4N}]_2[\mathrm{SFe_3(CO)_9}]$ with $\mathrm{HC{\equiv}CCH_2Br}$ (1:16). Similar to the procedures for the reaction of 1:2 ratio in MeCN, the reaction solution was stirred at room temperature for 38 h. The residue was chromatographed with hexane to give the first, reddish-brown band of **2** (4%, based on $[\mathrm{Et_4N}]_2[\mathrm{SFe_3(CO)_9}]$), and chromatographed with $\mathrm{CH_2Cl_2}$/hexane (1:1) to yield the second, orange band of **3** (10%, based on $[\mathrm{Et_4N}]_2[\mathrm{SFe_3(CO)_9}]$).

Reaction of $[\mathrm{Et_4N}]$[1] with $\mathrm{HC{\equiv}CCH_2Br}$ (1:4). To a solution of 0.33 g (0.51 mmol) of $[\mathrm{Et_4N}]$[**1**] in 20 mL of MeCN was added 0.19 mL (2.14 mmol) of $\mathrm{HC{\equiv}CCH_2Br}$. The mixture was stirred at room temperature for 45 h. The residue was chromatographed with hexane to give the first, reddish-brown band of 0.01 g (0.02 mmol) of **2** (4%, based on $[\mathrm{Et_4N}]$[**1**]) and chromatographed with $\mathrm{CH_2Cl_2}$/hexane (1:1) to give the second, orange band of 0.02 g (0.05 mmol) of **3** (10%, based on $[\mathrm{Et_4N}]$[**1**]).

Reaction of $[\mathrm{Et_4N}]$[1] with $[\mathrm{Cu(MeCN)_4}][\mathrm{BF_4}]$ (at room temperature). To a mixture of 0.58 g (0.89 mmol) of $[\mathrm{Et_4N}]$[**1**] and 0.306 g (0.97 mmol) of $[\mathrm{Cu(MeCN)_4}][\mathrm{BF_4}]$ was added 30 mL of $\mathrm{CH_2Cl_2}$. The reaction mixture was stirred at room temperature for 36 h. The solution was filtered to remove Cu precipitate and some unidentified species, and the solvent was collected to obtain $\mathrm{Fe(CO)_5}$, confirmed by IR spectroscopy. The residue was extracted with THF, and the THF solvent was concentrated and then chromatographed with hexane to give the first, reddish-brown band of 0.02 g (0.04 mmol) of **2** (4%, based on $[\mathrm{Et_4N}]$[**1**]). The second, yellowish-brown band was collected to give 0.07 g (0.18 mmol) of $\mathrm{Fe_2(CO)_6}(\mu_2\text{-}\eta^2{:}\eta^3\text{-C(O)CHC(S)(CH}_3))$ (**4**) (20%, based on $[\mathrm{Et_4N}]$[**1**]). IR (ν_{CO}, hexane): 2084 (s), 2043 (vs), 2022 (vs), 2009 (vs), 1997 (s), 1967 (w), 1640 (m) cm^{-1}. Negative ion (ESI-MS): *m/z* 379.8. Mp: 84 °C dec. Anal. Calcd for **4**: C, 31.62; H, 1.06. Found: C, 31.61; H, 1.12. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 298 K): δ 2.70 (s, $\mathrm{CH_3}$), 4.47 (s, CH). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$, 298 K): δ 24.02 ($\mathrm{CH_3}$), 86.86 (CH), 130.70 ($\equiv$CS), 236.57 (FeC(O)), 209.73, 207.56, 205.54, 202.67 ($\mathrm{FeC{\equiv}O}$). Complex **4** is soluble in hexane, ether, $\mathrm{CH_2Cl_2}$, THF, and MeCN.

Reaction of $[\mathrm{Et_4N}]$[1] with $[\mathrm{Cu(MeCN)_4}][\mathrm{BF_4}]$ (in refluxing $\mathrm{CH_2Cl_2}$). A mixture of $[\mathrm{Et_4N}]$[**1**] and $[\mathrm{Cu(MeCN)_4}][\mathrm{BF_4}]$ with a molar ratio of 1:1.1 in $\mathrm{CH_2Cl_2}$ was heated to reflux for 36 h, which was then worked up as before. The residue was extracted with THF, and the THF solvent was concentrated, which was chromatographed with hexane to give the first, reddish-brown band of **2** (6%, based on $[\mathrm{Et_4N}]$[**1**]). The second, orange band was collected to give **3** (17%, based on $[\mathrm{Et_4N}]$[**1**]).

Reaction of $[\mathrm{Et_4N}]$[1] with $\mathrm{CF_3SO_3Me}$. To a solution of 0.29 g (0.45 mmol) of $[\mathrm{Et_4N}]$[**1**] in 20 mL of $\mathrm{CH_2Cl_2}$ was added 0.06 mL (0.53 mmol) of $\mathrm{CF_3SO_3Me}$ in an ice−water bath. The mixture was stirred in an ice−water bath for 1 h, then warmed to room temperature, and stirred for another 3 h. The resultant solution was filtered, and the solvent was removed under vacuum. The residue was extracted with $\mathrm{Et_2O}$ and was concentrated and chromatographed

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Table 1. Crystallographic Data for $[Et_4N][Fe_3(CO)_9(\mu_3\text{-}\eta^3:\eta^1:\eta^2\text{-}CH_2C(S)CHC(O))]$ ($[Et_4N][1]$), $(\mu_3\text{-}S)Fe_3(CO)_9(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C(H){=}C(CH_3))$ (2), $Fe_2(CO)_6(\mu_2\text{-}\eta^2:\eta^3\text{-}SC(O)C(CH_3)CH)$ (3), $Fe_2(CO)_6(\mu_2\text{-}\eta^2:\eta^3\text{-}C(O)CHC(S)(CH_3))$ (4), and $Fe_3(CO)_9(\mu_3\text{-}\eta^1:\eta:^4\eta^2\text{-}CH_2C(S)CHC(OCH_3))$ (5)

	[Et4N][**1**]	**2**	**3**	**4**	**5**
empirical formula	$C_{21}H_{23}Fe_3NO_{10}S$	$C_{12}H_4Fe_3O_9S$	$C_{10}H_4Fe_2O_7S$	$C_{10}H_4Fe_2O_7S$	$C_{14}H_6Fe_3O_{10}S$
fw	649.02	491.76	379.89	379.89	533.80
cryst syst	monoclinic	triclinic	triclinic	triclinic	omonoclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	Cc
cryst dimens, mm	0.61 × 0.53 × 0.12	0.50 × 0.40 × 0.35	0.45 × 0.35 × 0.15	0.15 × 0.08 × 0.05	0.45 × 0.20 × 0.15
a, Å	8.649(3)	9.166(6)	6.727(2)	7.165(2)	10.105(2)
b, Å	20.801(5)	13.309(6)	6.935(2)	8.389(2)	31.158(7)
c, Å	14.594(3)	14.537(8)	15.956(2)	12.369(1)	12.710(6)
α, deg		78.50(4)	89.434(2)	78.36(4)	
β, deg	91.90(2)	82.17(5)	84.290(1)	86.65(4)	108.06(2)
γ, deg		77.76(5)	66.166(2)	68.12(3)	
V, Å^3	2624(1)	1690(2)	677.2(3)	675.6(3)	3805(2)
Z	4	4	2	2	8
D(calcd), g cm^{-3}	1.643	1.933	1.863	1.867	1.864
μ, mm^{-1}	1.769	2.706	2.321	2.326	2.416
diffractometer	Nonius (CAD4)	Nonius (CAD4)	Nonius (CAD4)	Nonius (CAD4)	Nonius (CAD4)
radiation (λ), Å	0.71073	0.71073	0.71073	0.71073	0.71073
temp, K	298	298	298	298	298
θ range for data collecn, deg	1.70−24.93	1.59−24.98	2.56−24.91	1.68−27.41	2.13−24.92
T_{min}/T_{max}	0.72/0.81	0.22/0.39	0.53/0.70	0.73/0.89	0.64/0.69
no. of indep reflns ($I > 2\sigma(I)$)	4616 ($R_{int} = 0.0116$)	5937 ($R_{int} = 0.0219$)	2366 ($R_{int} = 0.0132$)	3093 ($R_{int} = 0.0135$)	3498 ($R_{int} = 0.0047$)
R1[a]/wR2[a]($I > 2\sigma(I)$)	0.032/0.086	0.052/0.139	0.024/0.066	0.032/0.075	0.025/0.066
R1[a]/wR2[a](all data)	0.054/0.095	0.063/0.151	0.032/0.070	0.101/0.094	0.034/0.070

[a] The functions minimized during least-squares cycles were $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

with hexane to give a purplish-red band of 0.09 g (0.17 mmol) of $Fe_3(CO)_9(\mu_3\text{-}\eta^1:\eta^4:\eta^2\text{-}CH_2C(S)CHC(OCH_3))$ (**5**) (38%, based on $[Et_4N]$[**1**]). IR (ν_{CO}, hexane): 2086 (s), 2055 (vs), 2021 (s), 2008 (vs), 2000 (s), 1959 (m) cm^{-1}. Negative ion (ESI-MS): *m/z* 533.5. Mp: 130 °C dec. Anal. Calcd for **5**: C, 31.50; H, 1.13. Found: C, 31.44; H, 1.11. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 2.40 (d, CH_2, $J = 8$ Hz), 2.87 (d, CH_2, $J = 8$ Hz), 3.79 (s, OCH_3), 5.15 (s, CH). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 8.69 (CH_2), 59.91 (OCH_3), 82.62 (CH), 125.43 (≡C(S)), 232.92 (FeC(OCH_3)), 207.67, 212.34 (FeC≡O). Complex **5** is soluble in hexane, ether, CH_2Cl_2, THF, and MeCN.

X-ray Structural Characterization of $[Et_4N]$[1] and 2−5. The selected crystallographic data for $[Et_4N]$[**1**] and **2**−**5** are given in Table 1. All crystals were mounted on glass fibers with epoxy cement. Data collection for $[Et_4N]$[**1**] and **2**−**5** was carried out on a Nonius (CAD-4) diffractometer using graphite-monochromated Mo Kα radiation at 298 K in the 2θ range 2.0−50° using $\theta-2\theta$ scans, and an empirical absorption correction by azimuthal (ψ) scans was applied.[13] The structures were solved by direct methods and were refined with SHELXL-97.[14] All non-hydrogen atoms were refined with anisotropic temperature factors. The space group of **5** is *Cc* with $Z = 8$, and its absolute structure was checked by Flack parameter 0.005(17).[15] There are two crystallographically independent molecules of **5** in the crystal lattice with very slight differences in bond distances and bond angles, and only one molecule is presented herein for the structural comparison. The selected distances and angles for $[Et_4N]$[**1**] and **2**−**5** are listed in Table 2. Additional crystallographic data as CIF files are available as Supporting Information.

Computational Details. The DFT functional B3LYP level calculation was carried out with the use of the Gaussian 98 package.[16] The 6-21G basis set was used for S, C, O, and H atoms, while the LanL2DZ basis set with the corresponding effective core potential (ECP) was employed for Fe. The geometries of complexes **3** and **4** are taken from the crystal structures, and no geometric optimization was employed. Calculations for cluster **5** (trans form) and its cis form were performed using the Discover Molecular Simulation Program, Version 2.95, and the input file for Discover was generated by Insight II.

Results and Discussion

Reaction of $[Et_4N]_2[SFe_3(CO)_9]$ with Propargyl Bromide. When $[Et_4N]_2[SFe_3(CO)_9]$[4a] was treated with 2 equiv of propargyl bromide in MeCN at room temperature for 38 h, the major product $[Et_4N][Fe_3(CO)_9(\mu_3\text{-}\eta^3:\eta^1:\eta^2\text{-}CH_2C(S)CHC(O))]$ ($[Et_4N]$[**1**]) and two minor products $(\mu_3\text{-}S)Fe_3(CO)_9(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C(H){=}C(CH_3))$ (**2**) and $Fe_2(CO)_6(\mu_2\text{-}\eta^2:\eta^3\text{-}SC(O)C(CH_3)CH)$ (**3**) were isolated. If the reaction was carried out with excess propargyl bromide in MeCN, the neutral products **2** and **3** were obtained (Scheme 1). Complexes $[Et_4N]$[**1**], **2**, and **3** are fully characterized on the basis of IR, ^{1}H NMR, ^{13}C NMR, elemental analysis, and single-crystal X-ray analysis.

The X-ray analysis shows that the anion **1** consists of three Fe centers with two Fe−Fe bonds, in which the three Fe centers are bridged by a sulfur-substituted allylcarbonyl ligand $CH_2{=}C(S)CHC(O)$ in the $\mu_3\text{-}\eta^3:\eta^1:\eta^2$ bonding mode (Figure 1). In terms of the electron count, the $CH_2{=}C(S)CHC(O)$ ligand acts as a 7*e* donor to give a total of 50*e* for anion **1**, consistent with

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(13) North, A. C. T.; Philips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

(14) Sheldrick, G. M. *SHELXL97*, version 97-2; University of Göttingen: Germany, 1997.

(15) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

(16) The DFT calculations were performed with the use of the Gaussian 98 package: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Rega, N.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomeperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN98*, revision A.11.3; Gaussian, Inc.: Pittsburgh, PA, 2002.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $[Et_4N][Fe_3(CO)_9(\mu_3\text{-}\eta^3:\eta^1:\eta^2\text{-}CH_2C(S)CHC(O))]$ ($[Et_4N][\mathbf{1}]$), $(\mu_3\text{-}S)Fe_3(CO)_9(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C(H){=}C(CH_3))$ (2), $Fe_2(CO)_6(\mu_2\text{-}\eta^2:\eta^3\text{-}SC(O)C(CH_3)CH)$ (3), $Fe_2(CO)_6(\mu_2\text{-}\eta^2:\eta^3\text{-}C(O)CHC(S)(CH_3))$ (4), and $Fe_3(CO)_9(\mu_3\text{-}\eta^1:\eta{:}^4\eta^2\text{-}CH_2C(S)CHC(OCH_3))$ (5)

	$[Et_4N][\mathbf{1}]$		
S−Fe(2)	2.218(1)	S−Fe(3)	2.2182(9)
Fe(1)−Fe(2)	2.8351(8)	Fe(2)−Fe(3)	2.7123(8)
S−C(11)	1.770(3)	Fe(1)−C(10)	2.136(4)
Fe(1)−C(11)	2.067(3)	Fe(1)−C(12)	2.108(3)
Fe(3)−C(13)	2.022(3)	C(10)−C(11)	1.396(5)
C(11)−C(12)	1.410(4)	C(12)−C(13)	1.483(4)
Fe(2)−S−Fe(3)	75.38(3)	Fe(1)−Fe(2)−Fe(3)	90.75(3)
Fe(2)−S−C(11)	92.0(1)	S−C(11)−C(10)	123.2(2)
S−C(11)−C(12)	115.5(2)	Fe(1)−C(10)−C(11)	68.0(2)
Fe(1)−C(11)−C(10)	73.3(2)	Fe(1)−C(11)−C(12)	71.8(2)
Fe(1)−C(12)−C(11)	68.7(2)	Fe(1)−C(12)−C(13)	111.7(2)
Fe(3)−C(13)−C(12)	115.5(2)	C(10)−C(11)−C(12)	120.5(3)
C(11)−C(12)−C(13)	119.3(3)		
	Compound **2**		
S−Fe(1)	2.203(2)	S−Fe(2)	2.262(2)
S−Fe(3)	2.198(2)	Fe(1)−Fe(2)	2.584(2)
Fe(2)−Fe(3)	2.585(2)	Fe(1)−C(11)	1.954(5)
Fe(2)−C(10)	2.122(4)	Fe(2)−C(11)	2.156(4)
Fe(3)−C(10)	1.932(5)	C(10)−C(11)	1.399(6)
C(11)−C(12)	1.515(6)		
Fe(1)−S−Fe(2)	70.71(6)	Fe(1)−S−Fe(3)	113.32(7)
Fe(2)−S−Fe(3)	70.82(6)	Fe(1)−Fe(2)−Fe(3)	90.68(6)
	Compound **3**		
S−Fe(1)	2.2345(8)	S−Fe(2)	2.2850(8)
Fe(1)−Fe(2)	2.5364(6)	S−C(10)	1.821(3)
Fe(1)−C(7)	1.937(2)	Fe(2)−C(7)	2.081(2)
Fe(2)−C(8)	2.185(3)	C(7)−C(8)	1.396(3)
C(8)−C(9)	1.502(4)	C(8)−C(10)	1.468(4)
Fe(1)−S−Fe(2)	68.27(2)	S−Fe(1)−Fe(2)	56.81(2)
S−Fe(2)−Fe(1)	54.92(2)	Fe(1)−C(7)−Fe(2)	78.19(9)
S−C(10)−C(8)	107.3(2)	S−C(10)−O(7)	123.3(2)
Fe(1)−C(7)−C(8)	123.3(2)	Fe(2)−C(7)−C(8)	75.0(1)
Fe(2)−C(8)−C(7)	66.9(1)	Fe(2)−C(8)−C(9)	126.0(2)
Fe(2)−C(8)−C(10)	87.8(2)	C(7)−C(8)−C(9)	124.5(2)
C(7)−C(8)−C(10)	116.2(2)	C(9)−C(8)−C(10)	117.8(2)
C(8)−C(10)−O(7)	129.0(3)		
	Compound **4**		
S−Fe(1)	2.234(1)	S−Fe(2)	2.208(1)
Fe(1)−Fe(2)	2.636(1)	S−C(9)	1.739(3)
Fe(1)−C(8)	2.167(4)	Fe(1)−C(9)	2.093(4)
Fe(2)−C(7)	1.992(4)	C(7)−C(8)	1.476(5)
C(8)−C(9)	1.385(5)	C(9)−C(10)	1.491(5)
Fe(1)−S−Fe(2)	72.81(5)	S−Fe(1)−Fe(2)	53.13(4)
S−Fe(2)−Fe(1)	54.05(4)	S−C(9)−C(8)	113.3(3)
S−C(9)−C(10)	121.1(3)	Fe(1)−C(8)−C(7)	94.4(2)
Fe(1)−C(8)−C(9)	68.2(2)	Fe(1)−C(9)−C(8)	73.9(2)
Fe(1)−C(9)−C(10)	126.9(3)	Fe(2)−C(7)−C(8)	110.5(3)
Fe(2)−C(7)−O(7)	128.6(3)	C(7)−C(8)−C(9)	120.1(3)
C(8)−C(9)−C(10)	125.5(3)	C(8)−C(7)−O(7)	120.6(3)
	Compound **5**		
S−Fe(2)	2.280(2)	S−Fe(3)	2.220(2)
Fe(1)−Fe(2)	2.709(1)	Fe(2)−Fe(3)	2.582(1)
S−C(11)	1.756(6)	Fe(1)−C(10)	2.119(6)
Fe(2)−C(11)	2.105(5)	Fe(2)−C(12)	2.144(5)
Fe(2)−C(13)	2.208(6)	Fe(3)−C(13)	1.907(6)
C(10)−C(11)	1.455(8)	C(11)−C(12)	1.413(8)
C(12)−C(13)	1.425(8)	O(10)−C(13)	1.371(7)
O(10)−C(14)	1.43(1)		
Fe(2)−S−Fe(3)	70.01(5)	S−Fe(2)−Fe(3)	53.89(5)
S−Fe(3)−Fe(2)	56.10(5)	Fe(1)−Fe(2)−Fe(3)	145.48(4)
S−C(11)−Fe(2)	71.8(2)	Fe(2)−C(13)−Fe(3)	77.3(2)
S−C(11)−C(10)	120.9(4)	S−C(11)−C(12)	112.9(4)
Fe(1)−C(10)−C(11)	97.1(3)	Fe(2)−C(11)−C(10)	117.7(4)
Fe(2)−C(11)−C(12)	72.1(3)	Fe(2)−C(12)−C(11)	69.1(3)
Fe(2)−C(12)−C(13)	73.3(3)	Fe(2)−C(13)−C(12)	68.5(3)
Fe(2)−C(13)−O(10)	129.9(5)	Fe(3)−C(13)−C(12)	121.7(4)
Fe(3)−C(13)−O(10)	119.5(4)	C(10)−C(11)−C(12)	125.7(5)
C(12)−C(13)−O(10)	118.6(5)	C(13)−O(10)−C(14)	120.7(5)

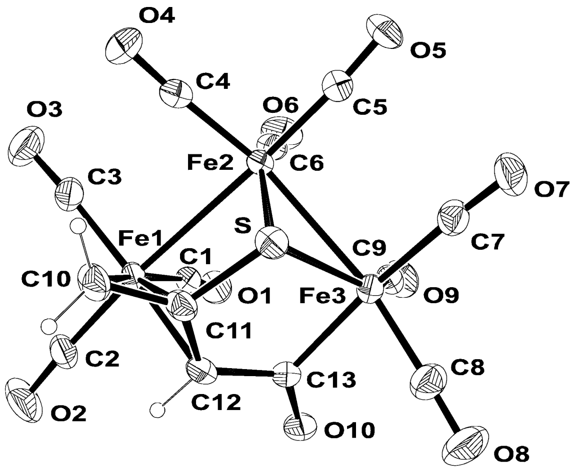

Figure 1. ORTEP diagram showing the structure and atom labeling for the anion **1**.

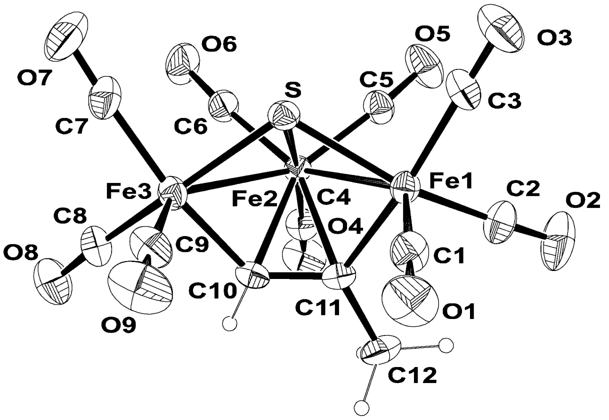

Figure 2. ORTEP diagram showing the structure and atom labeling for **2**.

two Fe−Fe bonds in this Fe_3 cluster. Although the π-allyl complexes are well known, those containing allylcarbonyl ligands are very few.[7,8b,10,17−19] To our best knowledge, there are no reports on complexes containing the sulfur-substituted allylcarbonyl ligand $CH_2{=}C(S)CHC(O)$, and anionic cluster **1** possesses the unprecedented $\mu_3\text{-}\eta^3:\eta^1:\eta^2\text{-}CH_2C(S)CHC(O)$ bonding mode. The existence of the acyl group of anion **1** was further identified by an IR absorption at 1596 cm^{-1} and by a ^{13}C NMR resonance at 258.32 ppm, which are compared to other acyl absorptions in the related complexes.[7,8b,18,20] The $^{13}C-^{1}H$ COSY measurements of anion **1** unambiguously show that the ^1H NMR resonances at δ 2.33 and 2.39, 2.58 correspond to the absorptions of the CH and the CH_2 of the allyl group, respectively. X-ray analysis shows that cluster **2** consists of three Fe centers with two Fe−Fe bonds, in which the three Fe atoms are capped on the opposite sides by the S atom and by a propyne ligand, $HC{\equiv}CCH_3$, as a 4*e* donor in $\mu_3\text{-}\eta^1:\eta^2:\eta^1$ fashion (Figure 2). On the other hand, complex **3** comprises an $Fe_2(CO)_6$ unit coordinated

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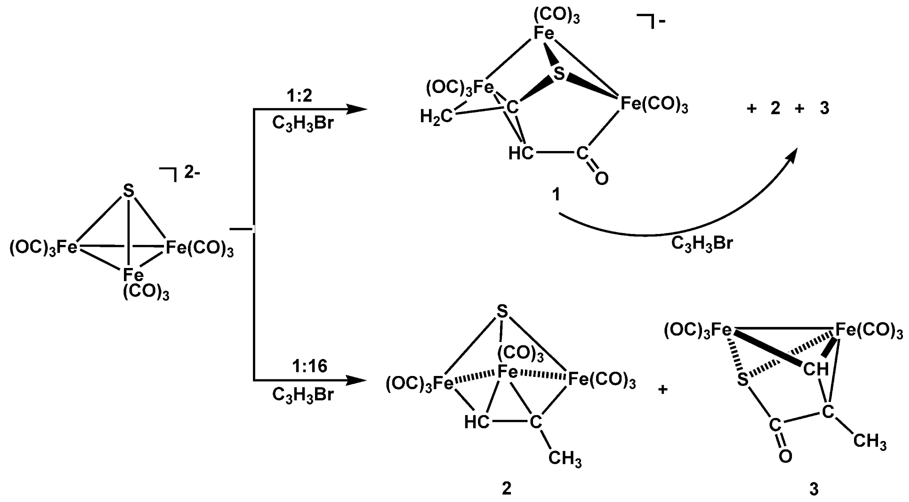
[17] (a) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press Ltd.: Elmsford, NY, 1982; Vols. 6 and 8. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (c) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. (d) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395.

[18] Amouri, H. E.; Gruselle, M. *Chem. Rev.* **1996**, *96*, 1077.

[19] (a) Binger, P.; Certinkaya, B.; Krüger, C. *J. Organomet. Chem.* **1978**, *159*, 63. (b) Bkouche-Waksman, I.; Ricci, J. S., Jr.; Koetzle, T. F.; Weichmann, J.; Herrmann, W. A. *Inorg. Chem.* **1985**, *24*, 1492.

[20] Engel, P. F.; Pfeffer, M. *Chem. Rev.* **1995**, *95*, 2281, and references therein.

Scheme 1



with a SC(O)C(CH$_3$)═CH fragment as a 6*e* donor in μ_2-η^2:η^3 fashion (Figure 3).

The formation of anion **1** can be viewed to result from the nucleophilic attack of [SFe$_3$(CO)$_9$]$^{2-}$ onto the propargyl bromide accompanied by one Fe−Fe and one S−Fe bond breakage, a series of bond formations, and a CO insertion. Contrary to those in the analogous Se and Te systems,[10] anion **1** shows the direct interaction of the chalcogen atom with the propargyl group mainly due to the smaller size of S vs Se or Te. Anion **1** is a CO insertion product, which can be supported by the fact that the yield of **1** was significantly increased (81−96%) if the reaction was conducted under an atmosphere of CO. In addition, the propargyl bromide could act as the oxidizing agent to convert anion **1** to neutral complexes **2** and **3**, as evidenced by the fact that anion **1** transformed to **2** and **3** upon treatment with excess propargyl bromide in MeCN. On the basis of their structural features, cluster **2** can be regarded to be derived from **1** by a CO loss and the capture of one hydrogen, and complex **3** can be viewed as a C$_4$-rearrangement product from **1** by the loss of one Fe(CO)$_3$ group and the capture of one hydrogen. If the reaction of **1** with propargyl bromide was carried out in the presence of H$_2$, the yields of **2** and **3** remained unchanged, which rules out the possibility of hydrogen abstraction from H$_2$ molecules. However, when the proton source HCl(aq) was provided to react with **1**, complexes **2** and **3** were obtained in better yields. On the basis of the lower yields of **2** and **3**, propargyl bromide could also act as a weak proton donor in the reaction with **1**; however, other proton sources under our reaction conditions cannot be excluded.

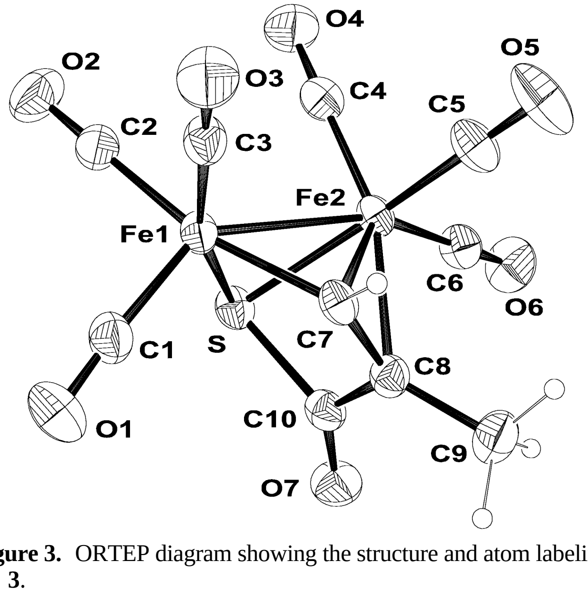
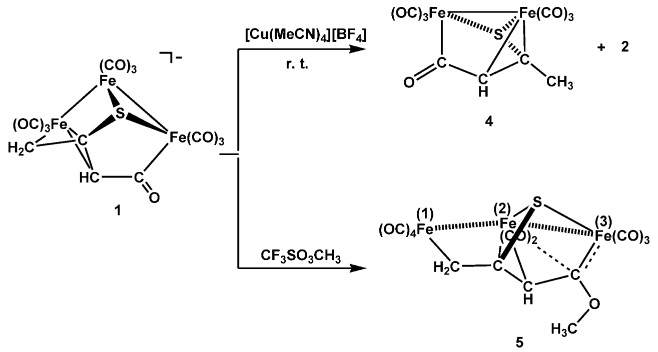


Figure 3. ORTEP diagram showing the structure and atom labeling for **3**.

Scheme 2



Reactions of [Et$_4$N][1] with [Cu(MeCN)$_4$][BF$_4$] and CF$_3$SO$_3$Me. To further explore reactivities of the acyl cluster **1**, reactions of [Et$_4$N][**1**] with [Cu(MeCN)$_4$][BF$_4$] and CF$_3$SO$_3$Me were performed (Scheme 2).

When [Et$_4$N][**1**] was treated with 1.1 equiv of the oxidizing agent [Cu(MeCN)$_4$][BF$_4$] in CH$_2$Cl$_2$, the diiron complex Fe$_2$(CO)$_6$(μ_2-η^2:η^3-C(O)CHC(S)(CH$_3$)) (**4**) was yielded with a small amount of **2**. X-ray analysis shows that complex **4** is composed of an Fe$_2$(CO)$_6$ unit bridged by the C(O)CH═C(S)(CH$_3$) moiety in μ_2-η^2:η^3 fashion (Figure 4). Complex **4** is an isomer of complex **3** but with the major difference of the arrangement of the methylvinylcarbonyl moiety. While complex **3** consists of a SFe$_2$ core bridged by a α-methylvinylcarbonyl ligand, complex **4** is composed of a SFe$_2$ core linked by a *β*-methylvinylcarbonyl moiety. Complex **3** can be considered as a C$_4$-rearrangement product, and complex **4** retains the C$_4$-arrangement. If [Et$_4$N][**1**] reacted with [Cu(MeCN)$_4$]BF$_4$ in refluxing CH$_2$Cl$_2$, complex **3** was produced along with a small amount of **2**, but complex **4** was not formed. While complex **4** was obtained at room temperature, complex **3** was produced at higher temperature. Therefore, complex **4** is a kinetically controlled product and complex **3** is a thermodynamically controlled product in this reaction.

Interestingly, careful methylation of the acyl cluster **1** with CF$_3$SO$_3$Me in CH$_2$Cl$_2$ led to the formation of a novel Fischer-type Fe$_3$ carbene complex, Fe$_3$(CO)$_9$(μ_3-η^1:η^4:η^2-CH$_2$C(S)CHC(OCH$_3$)) (**5**). The X-ray analysis shows that cluster **5** displays

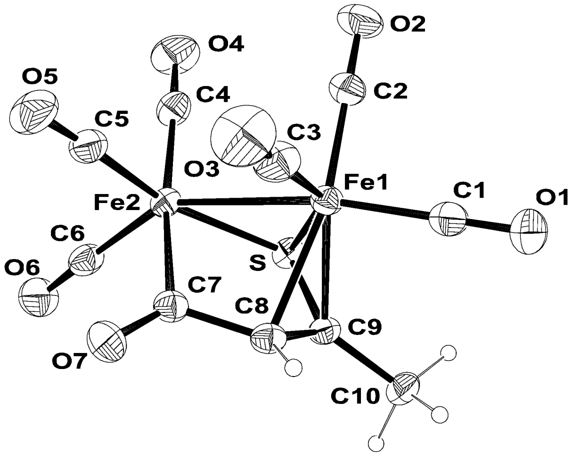


Figure 4. ORTEP diagram showing the structure and atom labeling for **4**.

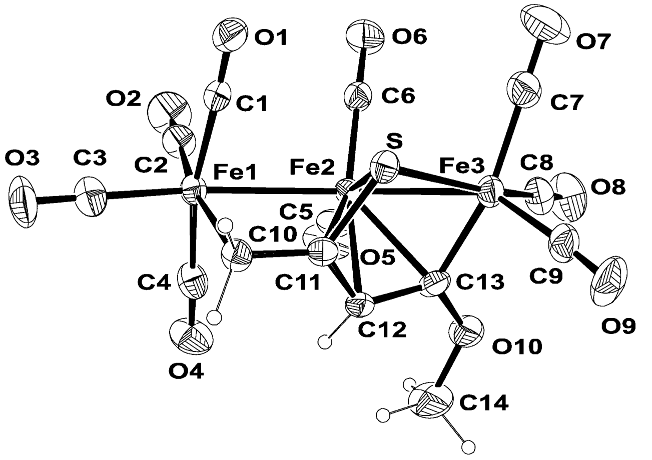


Figure 5. ORTEP diagram showing the structure and atom labeling for **5**.

an Fe_3 core linked with the $CH_2{=}C(S)CHC(OCH_3)$ ligand in μ_3-η^1:η^4:η^2 fashion (Figure 5), which is structurally related to the anion **1** but with the distinct bonding mode of the organic fragment to the Fe_3 framework. To the best of our knowledge, this μ_3-η^1:η^4:η^2-$CH_2{=}C(S)CHC(OMe)$ bonding mode is unprecedented. In **5**, the $CH_2{=}C(S)CHC(OCH_3)$ ligand contributes 8*e* to give a total of 50*e* for this Fe_3 carbene cluster with two Fe−Fe bonds. A close inspection of the structure of **5** reveals that the Fe−C(allyl) bonds range from 2.105(5) to 2.144(5) Å and the Fe(2)−$C_{carbene}$ bond (2.208(6) Å) is long but still considered to have weak single-bond interaction.[21] As a result, the Fe(3)−$C_{carbene}$ bond (1.907(6) Å)[22] should have partial double bond character. In addition, the ^1H NMR spectra of **5** gave resonances at δ 2.40 and 2.87; 3.79; and 5.15 corresponding to the absorptions of CH_2, OCH_3, and CH, respectively. DEPT experiments indicated that the ^{13}C resonances at δ 8.69, 59.91, 82.62, 125.43, and 232.92 were attributed to CH_2, OCH_3, CH, ≡CS, and C(OMe), respectively

Formation and Stability of Carbene Cluster 5. On the basis of structural features of anion **1** and **5**, one would assume that methylation of anion **1** proceeds not only via the direct O-alkylation driven by the Fe(3) atom but also via Fe(2)−C(13)$_{carbene}$ bond formation accompanied by Fe(1)−C(11) and Fe(1)−C(12) bond breakage, Fe(2)−C(11) and Fe(2)−C(12) bond formation, and a CO migration from Fe(2) to Fe(1). The CO migration is partially supported by the fact that the yield of complex **5** is significantly increased (38−48%) as the methylation is conducted under CO atmosphere.

Chart 1

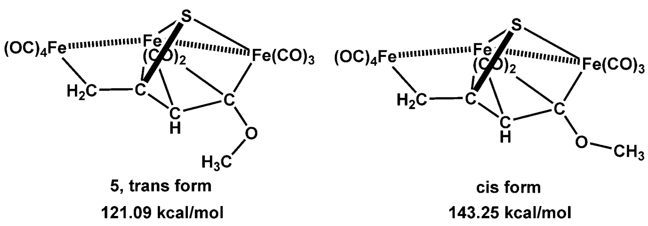


Table 3. Atomic Charges for $Fe_2(CO)_6(\mu_2\text{-}\eta^2{:}\eta^3\text{-}SC(O)C(CH_3)CH)$ (3) and $Fe_2(CO)_6(\mu_2\text{-}\eta^2{:}\eta^3\text{-}C(O)CHC(S)(CH_3))$ (4)

complex	atomic charges							
3	S	Fe1	Fe2	C7	C8	C9	C10	O7
	1.68	−0.27	−1.14	−0.12	0.27	−0.54	0.51	−0.28
4	S	Fe1	Fe2	C7	C8	C9	C10	O7
	1.61	−1.16	−0.25	0.85	0.30	−0.42	−0.53	−0.30

In theory, two rotational isomers (trans and cis forms) of the alkoxycarbene can be formed because of the slow rotation about the $C_{carbene}$−O bond.[23] The Insight II calculations show that the total energies of cluster **5** (trans form) and the cis form are 121.09 and 143.25 kcal/mol, respectively, in agreement with the fact that there is no observation of the cis form (Chart 1). This phenomenon is similar to the analogous Te system,[10b] but it is in contrast to the Se system, where the cis and trans forms are isolable due to the greater rotational energy.[10a] Contrary to that in the Se or Te system, the $C_{carbene}$(13)−Fe(3) bond in **5** has partial double bond character, as mentioned above, which would result in a higher degree of rotation about the $C_{carbene}$−O bond. Hence, the isolation of cluster **5** (trans form) is mainly due to its greater thermal stability.

Stability of Isomeric Complexes 3 and 4. The diiron complexes **3** and **4** are both oxidized products of anion **1**. As previously mentioned, **3** and **4** are geometrical isomers, and each exhibits the SFe_2-vinylcarbonyl-based geometry. DFT calculations show that the atomic charges (Table 3) for Fe(1) and Fe(2) in compound **3** are −0.27 and −1.14, respectively, and those for Fe(2) and Fe(1) in compound **4** are −0.25 and −1.16, indicative of similar degree of electron-cloud distribution between the two irons. However, DFT calculations show that complex **3** is lower in total energy than complex **4**. This is consistent with our experimental result that complex **3** is a thermodynamically controlled product in the reaction of **1** with $[Cu(MeCN)_4]BF_4$ in CH_2Cl_2.

Structures of $[Et_4N][1]$ and 5. The structures of anion **1** and **5** are depicted in Figures 1 and 5, respectively, and selected bond lengths and angles are given in Table 2. In anion **1**, the bond distances of the C−C bonds in the allylic moiety are 1.396(5) and 1.410(4) Å, indicative of double-bond character.[21] Of special interest in anion **1** is that there is a highly strained metallobicyclobutane C_3Fe ring in the framework with the dihedral angle of 130.97(2)° at the Fe−C crease, in which the bridgehead carbon is in an extremely distorted tetrahedral

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Table 4. Average Bond Distances (Å) for $[Et_4N][Fe_3(CO)_9(\mu_3\text{-}\eta^3{:}\eta^1{:}\eta^2\text{-}CH_2C(S)CHC(O))]$ ($[Et_4N]$[1]), $(\mu_3\text{-}S)Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C(H){=}C(CH_3))$ (2), $Fe_2(CO)_6(\mu_2\text{-}\eta^2{:}\eta^3\text{-}SC(O)C(CH_3)CH)$ (3), $Fe_2(CO)_6(\mu_2\text{-}\eta^2{:}\eta^3\text{-}C(O)CHC(S)(CH_3))$ (4), $Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta{:}^4\eta^2\text{-}CH_2C(S)CHC(OCH_3))$ (5), and Related Complexes

complex	S−Fe (Å)	Fe−Fe (Å)	ref
$[Et_4N][Fe_3(CO)_9(\mu_3\text{-}\eta^3{:}\eta^1{:}\eta^2\text{-}CH_2C(S)CHC(O))]$ ($[Et_4N]$[**1**])	2.218	2.7737	*a*
$(\mu_3\text{-}S)Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C(H)\text{-}C(CH_3))$ (**2**)	2.221	2.585	*a*
$Fe_2(CO)_6(\mu_2\text{-}\eta^2{:}\eta^3\text{-}SC(O)C(CH_3)CH)$ (**3**)	2.2598	2.5364(6)	*a*
$Fe_2(CO)_6(\mu_2\text{-}\eta^2{:}\eta^3\text{-}C(O)CHC(S)(CH_3))$ (**4**)	2.221	2.636(1)	*a*
$Fe_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^4{:}\eta^2\text{-}CH_2C(S)CHC(OCH_3))$ (**5**)	2.250	2.646	*a*
$(\mu\text{-}\sigma,\pi\text{-}HC{=}C(C(O)Me)C(O)S)Fe_2(CO)_6$	2.267	2.539(1)	2d
$[(\mu\text{-}CH_2{=}CHCH_2)Fe_2(CO)_6]_2[\mu\text{-}S(CH_2)_4S\text{-}\mu]$	2.2207	2.653(1)	3b
$[Fe_2(CO)_6]_2(\mu\text{-}S{-}S\text{-}\mu)[\mu\text{-}SCH_2(CH_2OCH_2)_2CH_2S\text{-}\mu]$	2.259	2.520	3b
$[Fe_2(CO)_6]_2[(\mu\text{-}SCH_2(CH_2OCH_2)_2CH_2S\text{-}\mu)]_2$	2.257	2.513(1)	3b
$[(\mu\text{-}\sigma,\pi\text{-}PhCH{=}CH)Fe_2(CO)_6]_2(\mu\text{-}S(CH_2)_4S\text{-}\mu)$	2.264	2.546	3b
$[\{Fe_2(\mu\text{-}MeCS_2)(CO)_6\}_2(\mu\text{-}SCH_2(CH_2OCH_2)_2CH_2S\text{-}\mu)]$	2.251	2.616(3)	3c
$(\mu\text{-}PhS)[\mu\text{-}Cp(CO)_2FeSC{=}S][Fe_2(CO)_6]_2(\mu_4\text{-}S)$	2.2634	2.5795	3d
$[Et_4N][SFe_3(\mu\text{-}H)(CO)_9]$	2.196	2.607	4a
$[Et_4N][CH_3SFe_3(CO)_9]$	2.126	2.637	4a
$(\mu\text{-}\sigma,\pi\text{-}HC{=}CHC(O)S)Fe_2(CO)_6$	2.267	2.532(3)	25a
$[Fe_2(CO)_4\{\mu\text{-}SCH{=}C(Ph)C(O)\}(\mu\text{-}dppm)]$	2.2307	2.6413(5)	26a
$[n\text{-}Bu_4N]_2[Fe_5(CO)_{14}(\mu_3\text{-}S)_2]$	2.180	2.601	27
$[Ph_4P]_2[\{Fe_2(CO)_6(\mu_3\text{-}S)_2\}_2Ni]\cdot CH_2Cl_2$	2.283	2.503(3)	27

[a] This work.

environment. Cluster **5** shows the continuous conjugated double bond character in the $O{-}C_{carbene}$, $C_{carbene}{-}Fe(3)$, and $C_{carbene}{-}$allyl bonds. As a Fischer-type carbene complex, **5** has a $C_{carbene}{-}O$ bond distance of 1.371(7) Å, comparable to the typical C−O distances (1.29−1.35 Å) in terminally coordinated alkoxycarbene complexes.[24]

Structures of 2−4. The structures of **2**−**4** are depicted in Figures 2−4, respectively, and selected bond lengths and angles are listed Table 2. It is noted that the Fe−Fe distance (2.5364(6) Å) and the Fe(1)−C(7) length (1.937(2) Å) in **3** are comparatively short and indicative of double-bond character in the $Fe{-}Fe{-}C_{vinyl}$ backbone. As a consequence, the extended conjugation from the vinylcarbonyl fragment to the diiron centers is evident in **3**, which also explains its greater stability vs **4**. In contrast, the Fe−Fe bond of **4** is 2.636(1) Å, indicative of single-bond character.[21] Complexes bridged by the $SC(O)CR_1{=}CR_2$ or $C(O)CR_3{=}C(S)R_4$ ligands are known to be labile, and these ligands are seen only in some diiron or dicobalt systems.[2d,25,26] Complexes **3** and **4** represent additional examples with possible combinations of different substituents.

Structural Comparison of [Et$_4$N][1] and 2−5. For comparison, the average S−Fe and Fe−Fe distances in complexes **1**−**5** and the related compounds are listed in Table 4. Basically, the S−Fe distances in **1**−**5** are in good agreement with the related S−Fe complexes.[2d,3b−d,4a,25a,26a,27] As listed in Table 4, it is of interest to note that the S−Fe and Fe−Fe bond lengths generally are increased as the organic moieties are introduced into the S−Fe skeletons due to the skeletal spanning by the organic linkers. Further, the S−Fe distances in complexes **3** (2.2598 Å) and **4** (2.221 Å) are close; however, the Fe−Fe distance in **3** (2.5364(6) Å) is significantly shorter than that in **4** (2.636(1) Å) probably due to the electron-withdrawing group C(O) adjacent to the iron center in **4**. Last, the average S−Fe and Fe−Fe bond distances of **1** (2.218 and 2.7737 Å) are a bit different from those in **5** (2.250 and 2.646 Å) probably owing to the differing organic moieties and charges.

Summary

In summary, a new series of organic S−Fe−CO complexes has been synthesized from the reaction of the sulfur-capped triiron cluster $[SFe_3(CO)_9]^{2-}$ with the bifunctional propargyl bromide and subsequent reactions. Contrary to Se and Te systems, new types of the acyl cluster and the Fischer-type cluster carbene are obtained due to the stronger affinity of the propargyl group with the S ligand. Moreover, the stability of the trans Fischer-type cluster carbene and the resultant diiron complexes is discussed on the basis of theoretical calculations.

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Supporting Information Available: X-ray crystallographic files in CIF format for $[Et_4N]$[**1**] and **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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