Notes

Synthesis of an Se-Bridged Triiron Acyl Cluster Complex and the Fischer-Type Carbene Complex Derived from It: Isolation of Rotational Isomers

Minghuey Shieh,* Horng-Sun Chen, Hsin-Hung Chi, and Chuen-Her Ueng

Department of Chemistry, National Taiwan Normal University, 88, Sec. 4, Tingchow Road, Taipei 116, Taiwan, Republic of China

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Introduction

The interaction of reactive organic intermediates with metal surfaces in metal-catalyzed organic reactions attracts both inorganic and organic chemists.[1] Nevertheless, little was known in the area of main group transition metal clusters with organic species, and the roles of main group elements and transition metals have been even less exploited.[2,3] To better understand the influence of main group transition metal clusters on organic fragments, we explored the reaction of the tetrahedral cluster[4] $[SeFe_3(CO)_9]^{2-}$ with propargyl bromide. We describe in this paper the synthesis of the novel acyl cluster anion $[(\mu_3\text{-Se})Fe_3(CO)_9(\mu_3\text{-}\eta^1,\eta^1,\eta^3\text{-C(O)CHCCH}_2)]^-$ (**1**) and the isolation of the trans and cis isomers of the Fischer-type cluster carbenes $(\mu_3\text{-Se})Fe_3(CO)_9(\mu_3\text{-}\eta^1,\eta^1,\eta^3\text{-C(OMe)CHCCH}_2)$, **2** and **3**.

Although the isomerization of Fischer-type mononuclear carbene complexes is a well-known phenomenon,[5−7] the isolation of both cis/trans rotamers of the alkoxycarbene complexes in the solid state has been inaccessible because of the rapid exchanging rate about the $C_{carbene}\text{-O}$ bond.[8] As for Fischer-type cluster carbene complexes, this issue remains unexplored because there have been relatively few examples of metal clusters containing heteroatom-substituted carbene ligands.[9] The isolation of **2** and **3** in this work exhibits a pronounced effect of the substituents of the carbene-carbon on the rotation of the C−O bond of the methoxycarbene.

Experimental Section

All reactions were performed under an atmosphere of pure nitrogen using standard Schlenk techniques.[10] Solvents were purified, dried, and distilled under nitrogen prior to use. $Fe(CO)_5$ (Aldrich), SeO_2 (Strem), [Et₄N]Br (Merck), CF_3SO_3Me (Aldrich), and $HC\equiv CCH_2Br$ (Merck) were used as received without further purification. $[Et_4N]_2[SeFe_3(CO)_9]$[4] was prepared by the published method. Infrared spectra were recorded on a Perkin-Elmer Paragon 500 IR spectrometer as solutions in CaF_2 cells. ESI (electron spray ionization) mass spectra were obtained on a JMS D-300 mass spectrometer using MeCN as the solvent. The ¹H NMR and ¹³C 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 [Et₄N]₂[SeFe₃(CO)₉] with HC≡CCH₂Br. To a solution of 1.10 g (1.45 mmol) of $[Et_4N]_2[SeFe_3(CO)_9]$ in 40 mL of CH_2Cl_2 was added 0.13 mL (1.46 mmol) of $HC\equiv CCH_2Br$. The resulting solution was stirred at ambient tempeature for 27 h to give a yellowish-brown solution which was filtered, and the solvent was removed under vacuum. The residue was extracted with CH_2Cl_2, and the CH_2Cl_2 extract was washed with hexanes and then recrystallized with hexanes/CH_2-Cl_2 to give 0.540 g (0.776 mmol) of $[Et_4N][(\mu_3\text{-Se})Fe_3(CO)_9((\mu_3\text{-}\eta^1,\eta^1,\eta^3\text{-C(O)C(H)CCH}_2)]$ ([Et₄N][**1**]) (54% based on $[Et_4N]_2[SeFe_3(CO)_9]$). IR (ν_{CO}, ether): 2055 w, 2026 vs, 1922 s, 1956 s, 1940 m, 1924 w cm⁻¹. Negative ion (ESI-MS): m/z 566.7. Anal. Calcd (found) for [Et₄N][**1**]: C, 36.24 (36.26); H, 3.33 (3.13); N, 2.01 (2.06). ¹H NMR (400 MHz, DMSO-d_6, 299 K): δ 2.98 (s, CH), 2.94, 2.59 (2s, CH_2) (chemical shifts not given for [Et₄N]⁺). ¹³C NMR (100 MHz, DMSO-d_6, 299 K): δ 257.6 (Fe*C*≡O), 216.5, 212.8, 212.1, 211.6, 209.1, 209.0 (Fe*C*O), 109.0 (CH*C*CH₂), 87.4 (*C*H), 60.6 (CH_2) (chemical shifts not given for [Et₄N]⁺). The crystals of [Et₄N][**1**] suitable for X-ray analysis were grown from hexanes/ether at −20 °C.

Isolation of the Rotational Isomers of $(\mu_3\text{-Se})Fe_3(CO)_9(\mu_3\text{-}\eta^1,\eta^1,\eta^3\text{-C(OMe)CHCCH}_2)$, 2 and 3. To a solution of 0.91 g (1.31 mmol) of [Et₄N][**1**] in 30 mL of CH_2Cl_2 was added 0.25 mL (1.94 mmol) of CF_3SO_3Me in an ice−water bath. The resulting solution was stirred in the ice−water bath for 45 min to give a yellowish-green solution which was filtered, and the solvent was removed under vacuum. The residue was extracted with 60 mL of Et_2O, and the Et_2O extract was redissolved in 5 mL of CH_2Cl_2 and chromatographed with CH_2-Cl_2/hexanes (3:1) using a chromotron to give the first band of 0.08 g of the known complex $Se_2Fe_3(CO)_9$, the second red band of 0.06 g (0.103 mmol) of cis-$(\mu_3\text{-Se})Fe_3(CO)_9(\mu_3\text{-}\eta^1,\eta^1,\eta^3\text{-C(OMe)C(H)CCH}_2)$

* To whom all correspondence should be addressed.

(1) Grasselli, R. K.; Burrington, J. D. *Adv. Catal.* **1981**, *30*, 133.

(2) Shriver, D. F.; Kaesz, H. D.; Adams, R. D. *The Chemistry of Metal Cluster Complexes*; VCH Publishers: New York, 1990. (b) Roof, L. C.; Kolis, J. W. *Chem. Rev.* **1993**, *93*, 1037. (c) Whitmire, K. H. *Adv. Organomet. Chem.* **1997**, *42*, 1. (d) Mathur, P. *Adv. Organomet. Chem.* **1997**, *41*, 243. (e) Shieh, M. *J. Cluster Sci.* **1999**, *10*, 3.

(3) (a) Shieh, M.; Liou, Y.; Jeng, B.-W. *Organometallics* **1993**, *12*, 4926. (b) Shieh, M.; Shieh, M.-H. *Organometallics* **1994**, *13*, 920. (c) Shieh, M.; Chen, P.-F.; Tsai, Y.-C.; Shieh, M.-H.; Peng, S.-M.; Lee, G.-H. *Inorg. Chem.* **1995**, *34*, 2251. (d) Shieh, M.; Sheu, C.-m.; Ho, L.-F.; Cherng, J.-J.; Jang, L.-F.; Ueng, C.-H. *Inorg. Chem.* **1996**, *35*, 5504. (e) Shieh, M.; Tsai, Y.-C.; Cherng, J. J.; Shieh, M.-H.; Chen, H.-S.; Ueng, C.-H. *Organometallics* **1997**, *16*, 456.

(4) (a) Shieh, M.; Tsai, Y.-C. *Inorg. Chem.* **1994**, *33*, 2303. (b) Backman, R. E.; Whitmire, K. H. *Inorg. Chem.* **1994**, *33*, 2527.

(5) (a) Cardin, D. J.; Cetinkaya, B.; Lappert, M. F. *Chem. Rev.* **1972**, *72*, 545. (b) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1. (c) Fischer, E. O. *Rev. Pure Appl. Chem.* **1972**, *30*, 353.

(6) (a) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Mutiple Bonds*; Wiley-Interscience: New York, 1988. (b) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim: Germany, 1983. (c) Casey, C. P. *Transition Metal Organometallics in Organic Synthesis*; Alper, H., Ed.; Academic Press: New York, 1976; Vol. 1. (d) Casey, C. P.; Burkhart, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 5833. (e) Casey, C. P.; Albin, L. D.; Burkhart, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2533. (f) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.

(7) (a) Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1969**, *16*, 275. (b) Moser, E.; Fischer, E. O. *J. Organomet. Chem.* **1968**, *15*, 147.

(8) (a) Mills, O. S.; Redhouse, A. D. *Angew Chem., Int. Ed. Engl.* **1965**, *4*, 1082. (b) Mills, O. S.; Redhouse, A. D. *Chem. Commun.* **1966**, 814. (c) Kreiter, C. G.; Fischer, E. O. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 761. (d) Fischer, E. O.; Kreiter, C. G.; Kollmeier, H. J.; Müller, J.; Fischer, R. D. *J. Organomet. Chem.* **1971**, *28*, 237. (e) Spessard, G. O.; Miessler, G. L. *Organometallic Chemistry*; Prentice-Hall: New Jersey, 1996.

(9) (a) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159. (b) Adams, R. D. *Chem. Rev.* **1989**, *89*, 1703 and references therein. (c) Hahn, J. E. *Prog. Inorg. Chem.* **1984**, *31*, 205. (d) Knox, S. A. R. *Pure Appl. Chem.* **1984**, *56*, 81.

(10) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air Sensitive Compounds*; Wiley: New York, 1986.

Table 1. Crystallographic Data for
[Et$_4$N][(μ_3-Se)Fe$_3$(CO)$_9$((μ_3-η^1,η^1,η^3-C(O)C(H)CCH$_2$)]([Et$_4$N][**1**]),
trans-(μ_3-Se)Fe$_3$(CO)$_9$(μ_3-η^1,η^1,η^3-C(OMe)C(H)CCH$_2$) (**2**), and
cis-(μ_3-Se)Fe$_3$(CO)$_9$(μ_3-η^1,η^1,η^3-C(OMe)C(H)CCH$_2$) (**3**)

	[Et$_4$N][**1**]	**2**	**3**
empirical formula	C$_{21}$H$_{23}$Fe$_3$NO$_{10}$Se	C$_{14}$H$_6$Fe$_3$O$_{16}$Se	C$_{14}$H$_6$Fe$_3$O$_{16}$Se
fw	695.01	580.69	580.69
space group	*P*(1) (No.2)	*P*2$_1$/*c* (No.14)	*P*2$_1$/*n* (No.14)
a, Å	9.55(3)	9.552(3)	9.365(3)
b, Å	12.35(3)	16.221(2)	16.258(2)
c, Å	13.411(2)	12.574(3)	13.035(5)
α, deg	105.2(2)		
β, deg	101.96(2)	104.91(2)	106.21(3)
γ, deg	109.87(2)		
V, Å^3	1357.1(6)	1882.5(7)	1905.9(9)
Z	2	4	4
ρ(calc), g cm^{-3}	1.703	2.049	2.024
μ, cm^{-1}	29.7	42.6	42.1
radiation, λ (Å)	Mo Kα, 0.7107	Mo Kα, 0.7107	Mo Kα, 0.7107
temp, °C	25	25	25
residues: R^a; $R_w{}^a$	0.038; 0.032	0.026; 0.020	0.026; 0.020

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

(**3**) (8% based on [Et$_4$N][**1**]), and the third greenish-brown band of 0.057 g (0.098 mmol) of *trans*-(μ_3-Se)Fe$_3$(CO)$_9$(μ_3-η^1,η^1,η^3-C(OMe)C(H)-CCH$_2$) (**2**) (7.5% based on [Et$_4$N][**1**]). **2**: IR (ν_{CO}, CH$_2$Cl$_2$): 2079 w, 2052 vs, 2022 s, 1997 m, 1977 m, 1954 vw cm^{-1}. EI-MS: *m/z* 581.8. Anal. Calcd. (found) for **2**: C, 28.96 (28.94); H, 1.04 (0.98). ^{1}H NMR (400 MHz, CDCl$_3$, 295 K): δ 4.28 (s, OMe), 3.59 (s, CH), 3.14 (s, CH$_2$) 2.91 (s, CH$_2$). **3**: IR (ν_{CO}, CH$_2$Cl$_2$): 2073 w, 2048 vs, 2012 vs, 1995 s, 1978 m, 1954 w cm^{-1}. EI-MS: *m/z* 581.8. Anal. Calcd (found) for **3**: C, 28.96 (28.90); H, 1.04 (1.01). ^{1}H NMR (400 MHz, CDCl$_3$, 295 K): δ 5.58 (s, CH), 3.80 (s, OMe), 3.26 (d, CH$_2$, *J* = 8 Hz), 2.46 (d, CH$_2$, *J* = 8 Hz). Crystals of **2** and **3** suitable for X-ray analysis were grown from hexanes at −20 °C.

X-ray Structural Characterization of Complexes [Et$_4$N][1], 2, and 3. A summary of selected crystallographic data for [Et$_4$N][**1**], **2**, and **3** is given in Table 1. Data collection was carried out on a Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation at 25 °C employing the $\theta/2\theta$ scan mode. A ψ scan absorption correction was made.[11] All crystals were mounted on glass fibers with epoxy cement. Data reduction and structural refinement were performed using the NRCC-SDP-VAX packages,[12] and atomic scattering factors were taken from ref 13.

Structures of [Et$_4$N][1], 2, and 3. The crystal of [Et$_4$N][**1**] chosen for diffraction measurement was ca. 0.26 mm × 0.33 mm × 0.40 mm; crystal **2** had dimensions 0.40 mm × 0.36 mm × 0.32 mm; crystal **3** had dimension 0.23 mm × 0.27 mm × 0.34 mm. Cell parameters were obtained from 25 reflections with the 2θ angle in the range 22.86−33.88° for [Et$_4$N][**1**], 22.98° < 2θ < 30.52° for **2**, and 22.70° < 2θ < 32.54° for **3**. A total of 3197 reflections with $I > 2.5 \sigma(I)$ for [Et$_4$N][**1**] (2148 reflections with $I > 2.5 \sigma(I)$ for **2** and 2305 reflections with $I > 2.5 \sigma(I)$ for **3**) were refined by least-squares cycles. All the non-hydrogen atoms were refined with anisotropic temperature factors. Full-matrix, least-squares refinement led to convergence with $R = 3.8\%$ and $R_w = 3.2\%$ for [Et$_4$N][**1**], with $R = 2.6\%$ and $R_w = 2.0\%$ for **2**, and with $R = 2.6\%$ and $R_w = 2.0\%$ for **3**.

The selected bond distances and angles for [Et$_4$N][**1**], **2**, and **3** are presented in Tables 2, 3, and 4, respectively. Additional crystallographic data are available as Supporting Information.

Results and Discussion

When [Et$_4$N]$_2$[SeFe$_3$(CO)$_9$][4] was treated with propargyl bromide in MeCN, the novel acyl complex [Et$_4$N][**1**] was

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

(12) Gabe, E. J.; Le Page, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

(13) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.
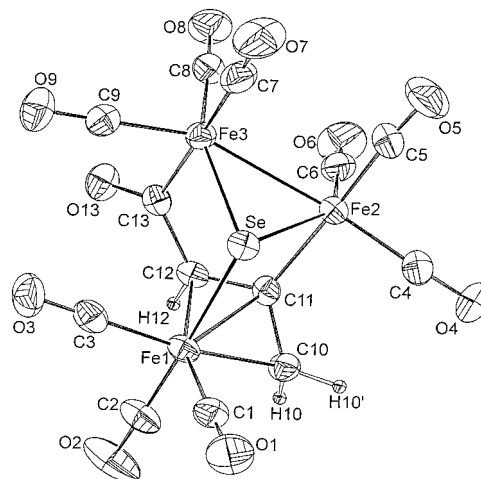
Figure 1. ORTEP diagram showing the structure and atom labeling for the anion **1**.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for [Et$_4$N][(μ_3-Se)Fe$_3$(CO)$_9$((μ_3-η^1,η^1,η^3-C(O)C(H)CCH$_2$)]([Et$_4$N][**1**])

		(A) Distances		
Se−Fe(1)	2.454(1)		Se−Fe(2)	2.33(1)
Se−Fe(3)	2.366(1)		Fe(3)−C(13)	2.015(6)
C(10)−C(11)	1.419 (8)		C(11)−C(12)	1.401(9)
C(12)−C(13)	1.500(8)			

		(B) Angles		
Fe(1)−Se−Fe(2)	97.09(4)		Fe(1)−Se−Fe(3)	103.73(4)
Fe(2)−Se−Fe(3)	69.65(4)		Fe(1)−C(11)−C(10)	70.9(3)
Fe(1)−C(11)−C(12)	69.2(3)		Fe(3)−C(13)−O(10)	124.5(4)
Fe(3)−C(13)−C(12)	117.3(4)			

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for *trans*-(μ_3-Se)Fe$_3$(CO)$_9$(μ_3-η^1,η^1,η^3-C(OMe)C(H)CCH$_2$) (**2**)

		(A) Distances		
Se−Fe(1)	2.456(1)		Se−Fe(2)	2.324(1)
Se−Fe(3)	2.388(1)		Fe(3)−C(13)	1.924(5)
C(10)−C(11)	1.403(6)		C(11)−C(12)	1.426(6)
C(12)−C(13)	1.456(6)		O(10)−C(13)	1.323(5)

		(B) Angles		
Fe(1)−Se−Fe(2)	95.72(3)		Fe(1)−Se−Fe(3)	101.25(3)
Fe(2)−Se−Fe(3)	69.86(3)		Fe(1)−C(11)−C(10)	72.2(3)
Fe(1)−C(11)−C(12)	70.1(2)		Fe(3)−C(13)−O(10)	130.1(3)
Fe(3)−C(13)−C(12)	122.9(3)			

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for *cis*-(μ_3-Se)Fe$_3$(CO)$_9$(μ_3-η^1,η^1,η^3-C(OMe)C(H)CCH$_2$) (**3**)

		(A) Distances		
Se−Fe(1)	2.4608(9)		Se−Fe(2)	2.3287(9)
Se−Fe(3)	2.373(1)		Fe(3)−C(13)	1.936(4)
C(10)−C(11)	1.401(9)		C(11)−C(12)	1.436 (6)
C(12)−C(13)	1.431(6)		O(10)−C(13)	1.323(5)

		(B) Angles		
Fe(1)−Se−Fe(2)	94.89(3)		Fe(1)−Se−Fe(3)	101.08(3)
Fe(2)−Se−Fe(3)	69.89(3)		Fe(1)−C(11)−C(10)	73.5(3)
Fe(1)−C(11)−C(12)	69.9(2)		Fe(3)−C(13)−O(10)	116.3(3)
Fe(3)−C(13)−C(12)	124.4(3)			

obtained (eq 1). The X-ray analysis (Figure 1) shows that the anion **1** consists of three Fe centers with one Fe−Fe bond, in which three Fe atoms are capped on the opposite sides by a Se atom and by an allylcarbonyl ligand C(O)CHCCH$_2$ in the fashion of μ_3-η^1,η^1,η^3. Cluster **1** can be considered as a CO insertion product, which is supported by the fact that the yield of **1** is significantly increased (54−85%) when the reaction is performed under an atmosphere of CO. In terms of electron counting, the C(O)CHCCH$_2$ ligand acts as a 5e$^-$ donor and the apical Se atom contributes 4e$^-$ in bonding, which gives a total

of 52e⁻ for the anion **1**, consistent with one Fe–Fe bond in this Fe₃ cluster anion.

The π-allyl complexes are well-known; however, those containing α-allylcarbonyl ligand are rare.[14–16] To our best knowledge, this type of μ_3-η^1,η^1,η^3-allylcarbonyl bonding mode is unusual and unprecedented. In **1**, the bond distances of C–C bonds in the allyl ligand are 1.401(9) and 1.419(8) Å, indicative of the double-bond character,[17] and are close to those (1.417 and 1.434 Å) in the related complex Fe₂(CO)₅Cp(μ-η^1,η^4-C(O)-CPhCCH₂).[16] Further, the presence of an acyl CO in **1** is spectroscopically indicated by an IR band at 1560 cm⁻¹ and by a ¹³C NMR resonance at δ 257.6.[18,16] The ¹³C–¹H COSY measurement unambiguously showed that the ¹H NMR resonances at δ 2.98 and 2.94, 2.59 correspond to the absorptions of the CH and the CH₂ of the allyl group, respectively.
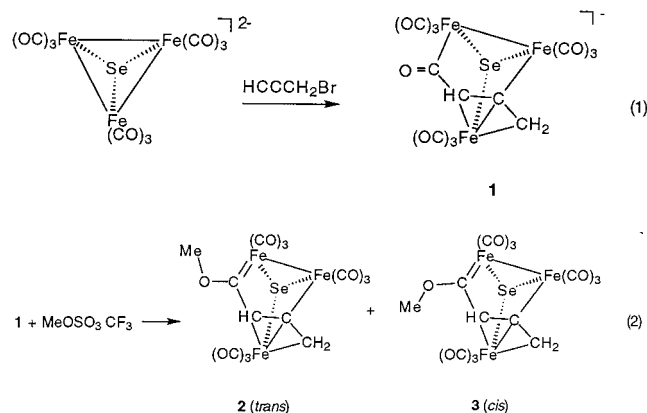
Since **1** is an acylate complex, the rational synthesis of a Fischer-type iron cluster carbene by O-alkylation was therefore attempted. It was found that the reaction could succeed with CF₃SO₃Me but not with MeI in CH₂Cl₂ to form two isomeric cluster carbene complexes (eq 2). Surprisingly, they could be separated by chromatotron chromatography on silica gel with the eluent of CH₂Cl₂/ether (3:1) and were fully characterized by spectroscopic methods and single-crystal X-ray analysis to be *trans*-(μ₃-Se)Fe₃(CO)₉(μ₃-η^1,η^1,η^3-C(OMe)CHCCH₂) (**2**) (Figure 2) and *cis*-(μ₃-Se)Fe₃(CO)₉(μ₃-η^1,η^1,η^3-C(OMe)CHCCH₂) (**3**) (Figure 3). The isomers **2** and **3** are also 52e⁻ species, which is in agreement with one Fe–Fe bond in these triiron clusters.

Complexes **2** and **3** equilibrate quickly in the solution, and the ratio is 2:1 at 25 °C. The ¹H NMR spectrum of **2** can be detected directly and gives absorptions at δ 3.59, 4.28, and 3.14, 2.91, assignable to those of CH, OMe, and CH₂, respectively. On the other hand, the ¹H NMR spectrum of **3** unambiguously showed the corresponding resonances at δ 5.58, 3.80, and two
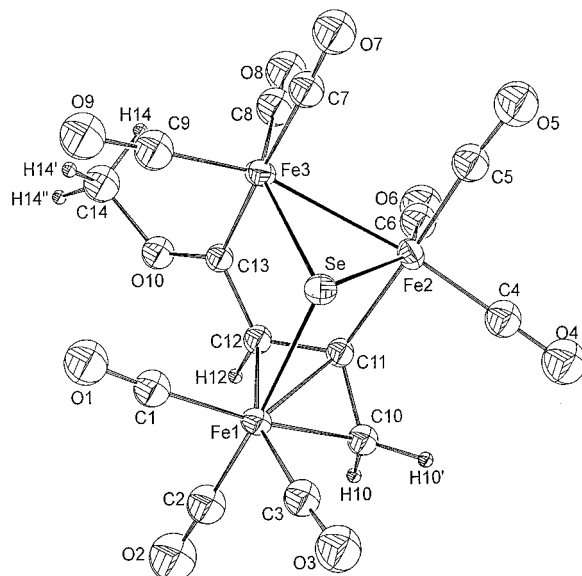

Figure 2. ORTEP diagram showing the structure and atom labeling for **2**.
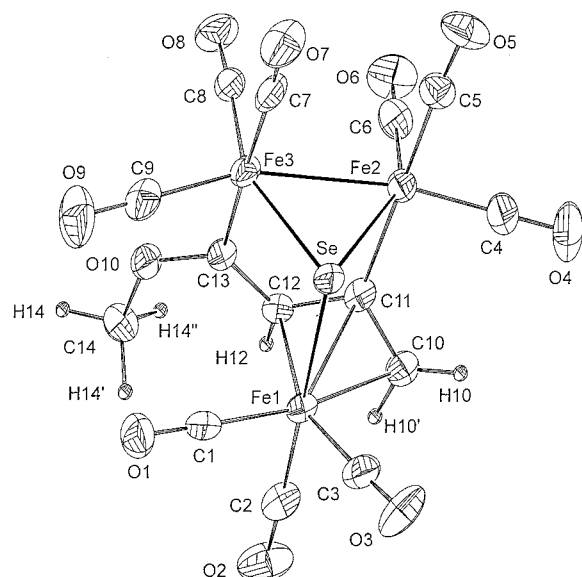

Figure 3. ORTEP diagram showing the structure and atom labeling for **3**.

doublets at δ 3.26, 2.46 having J = 8 Hz. This result confirms that the O–methyl group of the cis isomer is more strongly shielded by the CH group than that in the trans isomer, which was assumed previously for the interpretation of the isomerization of some mononuclear heterocarbene complexes.[7,8]

Complexes **2** and **3** both show the continuous conjugated double-bonding character in the O–C_carbene, C_carbene–Fe, and C_carbene–allyl bonds. As Fischer-type carbene complexes, **2** and **3** have a C_carbene–O bond distance of 1.323(5) Å, comparable to the typical C–O distances (1.29–1.35 Å) in terminally coordinated alkoxycarbene complexes.[6b] Further, the bond lengths of Fe–C_carbene in **2** and **3** are 1.924(5) and 1.936(4) Å, respectively, which are somewhat longer than that (1.856(5) Å) in the cluster carbene Fe₃(μ₃-NPh)₂(CO)₈{C(OEt)Ph}[19] but significantly shorter than the sum (2.02 Å) of the covalent radii for Fe and C atoms for a single bond.[17] In addition, the C_carbene–

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

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

(16) (a) Shuchart, C. E.; Young, G. H.; Wojcicki, A.; Calligaris, M.; Nardin, G. *Organometallics* **1990**, *9*, 2417. (b) Wojcicki, A.; Shuchart, C. E. *Coord. Chem. Rev.* **1990**, *105*, 35. (c) Amouri, H. E.; Gruselle, M. *Chem. Rev.* **1996**, *96*, 1077.

(17) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*; Harper Collins College Publishers: New York, 1993.

(18) Engel, P. F.; Pfeffer M. *Chem. Rev.* **1995**, *95*, 2281 and references therein.

(19) Williams, G. D.; Whittle, R. R.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 3936.

CH$_{allyl}$ distances (1.456(6) and 1.431(6) Å) in **2** and **3** are indicative of double-bond character as well.[17]

The rotation energy of the C$_{carbene}$−O bond was reported to be more effectively affected by solvents or steric effects for mononuclear chromium carbene complexes.[5,7,8] In this study, the presence of the Se−Fe−CO cluster moiety and the extended organic network should have a crucial influence on the rotation of the C−O bond of the methoxycarbene. The line shape analysis of the VT NMR spectra[20] gave the rotational energy of this cis/trans conversion, approximately 22.6 kcal/mol (94.6 kJ/mol),[21] which is greater than those (11.5−13.8 kcal/mol) for

the chromium methoxycarbene complexes[8] and allowed for the isolation of **2** and **3** at room temperature.

In summary, the novel Se−Fe−CO cluster anion [(μ_3-Se)-Fe$_3$(CO)$_9$(μ_3-η^1,η^1,η^3-C(O)CHCCH$_2$)]$^-$ has been synthesized and the subsequent methylation led to the first isolation of the rotational isomers of a Fischer-type alkoxycarbene complex in the solid state. Our finding clearly demonstrates the pronounced effect of substituents on the stabilization of the C$_{carbene}$−O bond of carbene ligands. Continuing investigation of the effect of other main group transition metal clusters on this issue is underway.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of [Et$_4$N][(μ_3-Se)Fe$_3$-(CO)$_9$((μ_3-η^1,η^1,η^3-C(O)C(H)CCH$_2$)] ([Et$_4$N][**1**]), *trans*-(μ_3-Se)Fe$_3$(CO)$_9$-(μ_3-η^1,η^1,η^3-C(OMe)C(H)CCH$_2$) (**2**), and *cis*-(μ_3-Se)Fe$_3$(CO)$_9$(μ_3-η^1,η^1,η^3-C(OMe)C(H)CCH$_2$) (**3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) (a) Rogers, M. T.; Woodbrey, J. C. *J. Phys. Chem.* **1962**, *66*, 540. (b) Drago, R. S. *Physical Methods in Chemistry*; Saunders: Philadelphia, 1977. (c) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; John Wiley & Sons: New York, 1988.

(21) Due to the thermal instability of **2** and **3**, the line shape analysis of the VT NMR spectra was carried out in the lower temperature ranges, which gave exchange rates of approximately 3.13, 10.8, 19.3, 37.7, 51.4, and 60.9 for the temperatures of 27.8, 32.8, 37.8, 42.8, 47.8, and 52.8 °C, respectively. The Arrhenius relation calculation showed that the rotational energy of this cis/trans conversion is about 22.6 kcal/mol (94.6 kJ/mol).