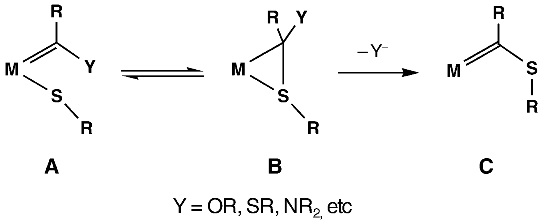
Carbene Complexes

Formation of an Iron(II) Carbene–Thiolato Complex by Insertion of Carbon Monoxide into an Si–C Bond**

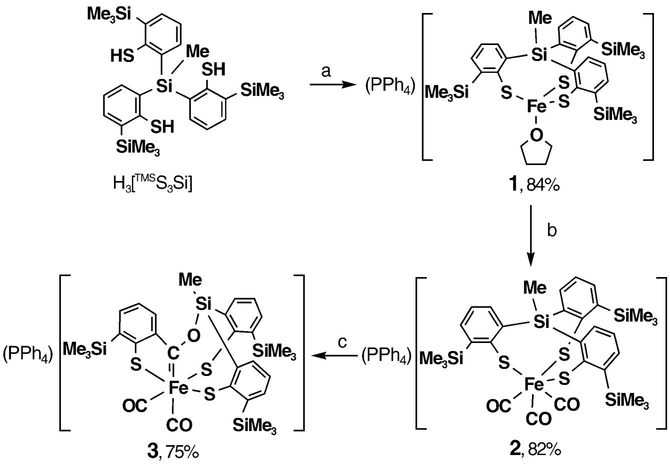
*Masahiro Yuki, Tsukasa Matsuo, and Hiroyuki Kawaguchi**

The carbene carbon atom in Fischer carbene complexes is well known to be susceptible to nucleophilic attack. Hence, complexes **A** bearing both Fischer carbene and thiolato ligands would be in equilibrium with the thiametalacyclopropane form **B**.[1] Although the existence of an equilibrium between **A** and **B** was supported by NMR spectroscopy and reactivity studies,[1a] such complexes are scarce.[2–4] A possible reason for this paucity lies in facile intramolecular nucleophilic substitution to form the RS-substituted carbene complex **C**.



In our studies of transition-metal complexes of thiolato ligands,[5] we designed and synthesized the tridentate ligand $[^{\text{TMS}}S_3Si]^{3-}$ ($H_3[^{\text{TMS}}S_3Si]$ = tris(3-trimethylsilyl-2-mercaptophenyl)methylsilane).[6] On attempting to carbonylate an iron(II) complex of $[^{\text{TMS}}S_3Si]^{3-}$, namely **1**, we encountered an unexpected formation of a stable Fischer carbene–thiolato complex **3** (Scheme 1). Intriguingly, **3** exhibits a bonding interaction of the Fischer carbene carbon atom with the thiolato ligand.[7]

Treatment of $[Fe(CF_3SO_3)_2(CH_3CN)_2]$ with 1 equiv of $Li_3(^{\text{TMS}}S_3Si)$ followed by cation exchange with PPh_4Br afforded $PPh_4[Fe(^{\text{TMS}}S_3Si)(thf)]$ (**1**). The magnetic moment of **1** is typical of tetrahedral Fe^{II} centers ($\mu_{\text{eff}} = 4.77\,\mu_B$). Despite line-broadening and a paramagnetic shift of the resonances, the ^{1}H NMR spectrum exhibits five signals ascribed to the $[^{\text{TMS}}S_3Si]^{3-}$ ligand, and this suggests that the solution structure is consistent with C_3 symmetry.



Scheme 1. Synthesis of **1**–**3**. a) 3 BuLi then $[Fe(CF_3SO_3)_2(CH_3CN)_2]$, THF; b) CO, THF, −48 °C; c) THF, RT.

An X-ray crystallographic study of **1** (Figure 1) showed that the iron atom is bound to the three sulfur donors and one THF molecule with an average Fe–S distance of 2.301 Å and an Fe–O distance of 2.130(2) Å.[8] The iron center has a tetrahedral environment with slight compression of the S-Fe-S angles (av 113.5°). The S-Fe-O angles average 104.7°. The bridging Si(1) atom assumes a tetrahedral geometry, and the atoms Fe and Si(1) are separated by 3.3701(9) Å. The strain in the eight-membered $\{FeS_2C_4Si\}$ ring of **1** is relieved by propeller twisting of the $[^{\text{TMS}}S_3Si]^{3-}$ ligand, which leads to average S-Fe-Si-C torsion angles of 41.9°.

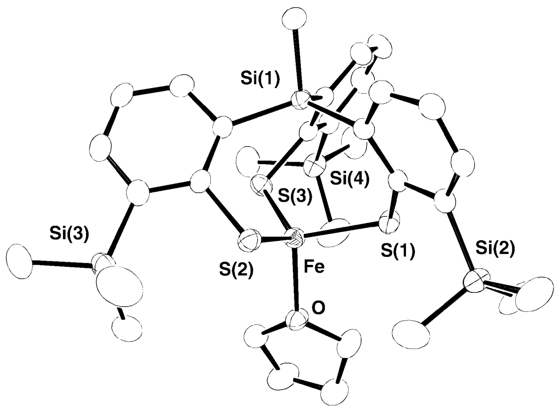


Figure 1. Structure of the anion of **1** with 50% ellipsoids. Selected bond lengths [Å] and angles [°]: Fe–S(1) 2.2798(9), Fe–S(2) 2.3097(9), Fe–S(3) 2.3129(9), Fe–O 2.130(2); S(1)-Fe-S(2) 106.02(3), S(1)-Fe-S(3) 112.00(3), S(2)-Fe-S(3) 122.62(3), S(1)-Fe-O 100.81(6), S(2)-Fe-O 110.13(7), S(3)-Fe-O 103.14(7).

Complex **1** smoothly reacted with 1 atm of CO in THF at −48 °C to give the diamagnetic carbonyl derivative $(PPh_4)[Fe(^{\text{TMS}}S_3Si)(CO)_3]$ (**2**). The ^{1}H NMR spectrum of **2** indicates that the symmetric coordination of the $[^{\text{TMS}}S_3Si]^{3-}$ ligand is retained. The $^{13}C\{^1H\}$ NMR resonance of the carbonyl ligands is found at $\delta = 209.6$ ppm. The IR spectrum of **2** displays two carbonyl stretching bands at 2052 and

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[*] Dr. M. Yuki, Dr. T. Matsuo, Prof. Dr. H. Kawaguchi
Coordination Chemistry Laboratories
Institute for Molecular Science
Myodaiji, Okazaki, 444-8585 (Japan)
Fax: (+81) 564-55-5245
E-mail: hkawa@ims.ac.jp

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1990 cm^{-1}, indicative of a facial tricarbonyl geometry. Complex **2** is stable at low temperature, but is unstable in solution at ambient temperature. On warming to room temperature, the red solution gradually turned green, and complete conversion to complex **3** occurred.

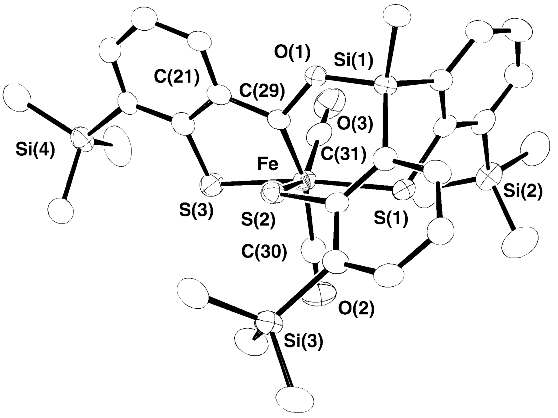
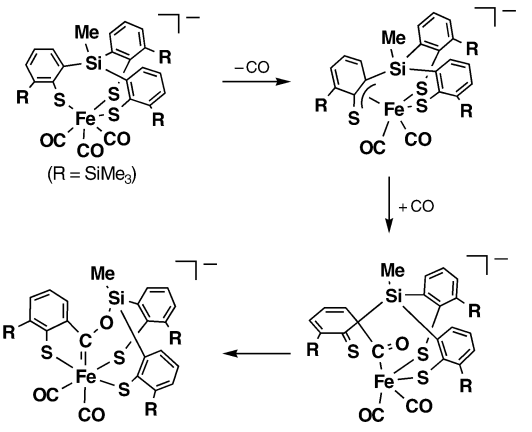


Figure 2. Structure of the anion of **3** with 50% ellipsoids. Selected bond lengths [Å] and angles [°]: Fe–S(1) 2.334(1), Fe–S(2) 2.299(1), Fe–S(3) 2.281(1), Fe–C(29) 1.981(4), Fe–C(30) 1.818(5), Fe–C(31) 1.745(5), S(2)–C(29) 1.872(4), Si(1)–O(1) 1.652(3), O(1)–C(29) 1.409(5), C(21)–C(29) 1.487(6); S(1)-Fe-S(2) 97.96(5), S(1)-Fe-S(3) 170.21(5), S(2)-Fe-S(3) 87.32(6), S(2)-Fe-C(29) 51.2(1), S(2)-Fe-C(30) 107.8(2), C(29)-Fe-C(31) 96.1(2), C(30)-Fe-C(31) 104.9(2), Fe-S(2)-C(29) 55.6(1), Fe-C(29)-S(2) 73.2(2), Fe-C(29)-O(1) 126.0(3), Fe-C(29)-C(21) 117.2(3), S(2)-C(29)-O(1) 114.8(3), S(2)-C(29)-C(21) 110.2(3), O(1)-C(29)-C(21) 109.5(3).

The crystal structure of **3** revealed an unprecedented Fischer carbene–thiolato complex (Figure 2).[8] The coordination environment of the iron center is best described as distorted octahedral, with two mutually *cis* carbonyl ligands and a new [$^{\text{TMS}}$S$_3$Si]-derived tetradentate ligand in which the original trithiolato ligand has been transformed into a carbene–trithiolato moiety by insertion of CO into an Si–C bond. The Fe–C(29) bond length of 1.981(4) Å is at the long end of known Fe–C(carbene) bonds,[9] and the C(29) atom has trigonal-planar geometry, as evidenced by the sum of angles at C(29) of 352.7°. The Fe–S bond lengths, which range from 2.299(1) to 2.334(1) Å, are typical of low-spin Fe$^{\text{II}}$ thiolato complexes.[10] It is noteworthy that the thiolato sulfur atom S(2) is in close proximity to the carbene carbon atom C(29), although the separation of 1.872(4) Å is longer than a normal C–S single bond (C(sp^3)–S 1.82 Å).[11] Longer C–S bonds (1.87–1.92 Å) have been observed for sulfur atoms bonded to spiro carbon atoms.[12] This structural feature suggests that substantial bonding interaction occurs between the vacant p orbital of the carbene carbon atom and the lone pair of the thiolato sulfur atom. This notion is also supported by the elongation of the C(29)–O(1) distance (1.409(5) Å) relative to those of Fischer carbene complexes.

Spectroscopic data of **3** are consistent with the solid-state structure. The ^{1}H NMR spectrum reveals a total lack of symmetry in solution, as evidenced by three SiMe$_3$ singlets. In the ^{13}C{^{1}H} NMR spectrum of **3**-^{13}C, prepared with ^{13}CO, the carbene carbon atom resonates at $\delta = 128.6$ ppm as a doublet of doublets ($^2J_{C,C} = 11$, 7 Hz) and is accompanied by two doublets of doublets ascribed to two terminal carbonyl ligands at $\delta = 213.6$ ($J = 11$, 2 Hz) and 220.1 ppm ($J = 7$, 2 Hz). The chemical shift of the carbene carbon atom shows that this center is shielded relative to typical Fischer carbene complexes (220–350 ppm),[13] a difference that may arise from the interaction between the carbene carbon atom and the thiolato sulfur atom. In the IR spectrum, the carbonyl bands of **3** (1993, 1928 cm^{-1}) are at lower wavenumber than those of **2** because of the higher σ-donor/π-acceptor ratio of the carbene ligand relative to CO.

Scheme 2 shows the likely sequence of events in the formation of **3** from **2**. This transformation is presumed to involve loss of one CO ligand and η^1/η^3 rearrangement of one of the arylthiolate groups, followed by migratory insertion of the CO ligand into an Si–C bond and subsequent capture of the liberated CO. This would yield an acyl intermediate with a dearomatized ring, which could then undergo a net [1,3]-silyl migration to give a carbene species due to the high oxophilicity of the silicon atom. In arylthiolato complexes π coordination at the aryl substituent is uncommon. However, our recent finding that the arylthiolato ligand SC$_6$H$_3$-2,6-(SiMe$_3$)$_2$ can bind to the metal center though the aryl moiety could provide support for the η^1/η^3 rearrangement of this proposed mechanism.[5] Although carbonylation of early transition-metal and actinide complexes is well known to produce enolate complexes via insertion of CO into Si–C bonds,[14] this kind of intramolecular transformation is rare for late-transition-metal complexes. Recently, it was reported that a platinum complex with Ph$_2$P=NSiMe$_3$ ligands underwent insertion of CO into the N–Si bond and subsequent migration of the SiMe$_3$ group to generate an N,O-substituted carbene.[15]



Scheme 2. Proposed mechanism for the transformation of **2** into **3**.

To gain some insight into the kinetics of the formation of **3**, we monitored the disappearance of CO stretching absorptions in the IR spectrum of **2** from 277 to 296 K. The resulting data gave first-order plots with excellent correlation coefficients ($R^2 > 0.997$). An Arrhenius plot yielded values of $\Delta H^{\neq} = 125.3 \pm 3.3$ kJ mol^{-1} and $\Delta S^{\neq} = 122 \pm 11$ J mol^{-1} K^{-1}. Together with the observation that the rate of the reaction is slower in the presence of CO, the positive entropy of activation suggests a rate-limiting step involving CO loss from **2**. The formation of **3** might be driven by strain in the large chelate rings in **2**.

Finally, preliminary reactivity studies were carried out with **3**. Treatment of **3** with 1 equiv of methyl iodide gave a mixture of three products in which one of the three thiolato donors of the $[^{TMS}S_3Si]^{3-}$ ligand was methylated according to NMR spectroscopic data. The carbene moiety remains intact during the course of the reaction, in which a dithio(thioether)carbene ligand is formed. On the other hand, complex **3** was inert toward nucleophiles such as PEt_3.

In summary, we have synthesized the novel iron(II) trithiolato complex **1** containing the tripodal $[^{TMS}S_3Si]^{3-}$ ligand. Carbene–thiolato complex **3** was prepared by reaction of **1** with CO, in which insertion of CO into an Si−C bond took place. Since the coordinated THF molecule of **1** is labile, the trithiolato complex **1** could be a useful reagent for exploring the chemistry of iron–sulfur compounds relevant to the active sites in metalloenzymes. We are currently investigating the reactivity of **1** and **3**.

Experimental Section

1: A solution of $Li_3[^{TMS}S_3Si]$, prepared by reaction of $H_3[^{TMS}S_3Si]$ (428 mg, 0.729 mmol) with BuLi (1.58 M, 1.42 mL, 2.21 mmol) in THF (10 mL), was added to $[Fe(CF_3SO_3)_2(CH_3CN)_2]$ (317 mg, 0.728 mmol). The mixture was stirred for 15 min at room temperature, and a solution of PPh_4Br (305 mg, 0.727 mmol) in CH_3CN (3.5 mL) was added. After removal of the solvent in vacuo, recrystallization of the residue from THF/Et_2O afforded pale-yellow rods of **1** (643 mg, 84 %); elemental analysis (%) calcd for $C_{56}H_{67}FeOPS_3Si_4$: C 63.97, H 6.42, S 9.15; found: C 63.83, H 6.53, S 8.67; ^1H NMR ($[D_8]$THF, 500 MHz, 23 °C): $\delta = 20.1$ (br, $w_{1/2} = 21$ Hz, 3H), 17.7 (br, $w_{1/2} = 40$ Hz, 3H), 8.35 (br, 8H, PPh_4^+), 8.09 (br, 12H, PPh_4^+), 6.99 (br, $w_{1/2} = 38$ Hz, 27H), −2.90 (br, $w_{1/2} = 27$ Hz, 3H), −25.3 ppm (br, $w_{1/2} = 24$ Hz, 3H); magnetic moment: $\mu_{eff} = 4.77\ \mu_B$.

2: A solution of **1** (368 mg, 0.35 mmol) in THF (3 mL) was treated with 1 atm of CO at −48 °C for 1 h. The red solution was concentrated and layered with Et_2O at −48 °C to give **2** (306 mg, 82 %) as red plates; elemental analysis (%) calcd for $C_{55}H_{59}FeO_3PS_3Si_4$: C 62.12, H 5.59, S 9.05; found: C 61.95, H 5.93, S 8.30; IR (KBr): $\tilde{\nu}(CO) = 2052$ (s), 1990 cm^{-1} (s); ^1H NMR ($[D_8]$THF, 500 MHz, −30 °C): $\delta = 8.0$–7.6 (br, 20H, PPh_4^+), 7.19 (d, $J = 7.3$ Hz, 3H, ArH), 7.14 ($J = 6.8$ Hz, 3H, ArH), 6.75 (dd, $J = 6.8$, 7.3 Hz, 3H, ArH), 0.40 (s, 3H, SiMe), 0.27 ppm (s, 27H, $SiMe_3$). $^{13}C\{^1H\}$ NMR ($[D_8]$THF, 125 MHz, −30 °C): $\delta = 209.6$ (CO). $^{29}Si\{^1H\}$ NMR ($[D_8]$THF, 99 MHz, −30 °C) $\delta = -7.6$ ($SiMe_3$), −18.9 ppm (SiMe).

3: A solution of **2** (306 mg, 0.288 mmol) in THF (7 mL) was stirred for 2 h at room temperature. The resulting green solution was evaporated to dryness. The residue was washed with Et_2O and recrystallized from THF/Et_2O to give **3** as green plates (229 mg, 75 %); elemental analysis (%) calcd for $C_{55}H_{59}FeO_3PS_3Si_4$: C 62.12, H 5.59, S 9.05; found: C 61.85, H 5.69, S 8.83; IR (KBr): $\tilde{\nu}(CO) = 1993$ (s), 1928 cm^{-1} (s); ^1H NMR ($[D_8]$THF, 500 MHz): $\delta = 8.0$–7.5 (m, 20H, PPh_4^+), 7.64 (d, $J = 7.3$ Hz, 1H), 7.34 (d, $J = 6.7$ Hz, 1H), 7.28 (d, $J = 6.7$ Hz, 1H), 7.19 (d, $J = 7.3$ Hz, 1H), 7.16 (d, $J = 7.3$ Hz, 1H), 6.89 (m, 2H), 6.83 (d, $J = 7.3$ Hz, 1H), 6.55 (m, 1H), 0.62 (s, 3H, SiMe), 0.331 (s, 9H, $SiMe_3$), 0.325 (s, 9H, $SiMe_3$), 0.28 ppm (s, 3H, $SiMe_3$); $^{13}C\{^1H\}$ NMR ($[D_8]$THF, **3**-^{13}C): $\delta = 219.8$ ($^2J_{C,C} = 11$, 2 Hz, CO), 213.3 ($J = 7$, 2 Hz, CO), 128.9 ppm ($J = 11$, 7 Hz, $C_{carbene}$); ^{29}Si NMR (DEPT, $[D_8]$THF, 99 MHz): $\delta = -5.0$, −6.3, −8.4 ($SiMe_3$), −15.1 ppm (SiMe).

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[8] Crystal data for **1**: $C_{56}H_{67}FeOPS_3Si_4$, $M_r = 1051.49$, crystal dimensions $0.40 \times 0.25 \times 0.10$ mm, $a = 26.090(5)$, $b = 14.900(3)$, $c = 29.470(6)$ Å, $\beta = 100.560(3)°$, $V = 11262(4)$ Å^3, monoclinic, $C2/c$ (no. 15), $Z = 8$, $\rho_{calcd} = 1.240\ g\,cm^{-3}$, $F(000) = 4448$, $\mu = 5.29\ cm^{-1}$, 42749 measured, 12534 independent, 9455 observed reflections ($F_o^2 > 2\sigma F_o^2$), R_1(observed data) = 0.054, wR_2(all data) = 0.137; Crystal data for **3**: $C_{55}H_{59}FeOPS_3Si_4$, $M_r = 1063.41$, crystal dimensions $0.45 \times 0.10 \times 0.03$ mm, $a = 18.717(7)$, $b = 15.436(6)$, $c = 20.571(8)$ Å, $\beta = 109.550(4)°$, $V = 5601(4)$ Å^3, monoclinic, $P2_1/n$ (no. 14), $Z = 4$, $\rho_{calcd} = 1.261\ g\,cm^{-3}$, $F(000) = 2232$, $\mu = 5.35\ cm^{-1}$, 44131 measured, 12801 independent, 7564 observed reflections ($F_o^2 > 2\sigma F_o^2$), R_1(observed data) = 0.075, wR_2(all data) = 0.189. Rigaku Saturn CCD system (**1**) or Murcury CCD system (**3**), $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å), graphite monochromator, $T = 173$ K; the structures were solved by direct methods and refined against F^2 for all independent reflections (heavy atoms with anisotropic temperature factors, H atoms located at calculated positions with isotropic temperature factors); CCDC-219529 (**1**) and -219530 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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