Synthesis, Structure, and Properties of Three- and Six-Membered Metallacycles Composed of Iron, Germanium, and Sulfur Atoms

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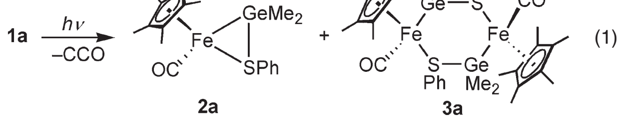
Ultraviolet irradiation of Cp*(CO)$_2$FeGeMe$_2$SPh in the presence of acetone afforded *trans*-[Cp*Fe(CO){μ-κ^2*Ge*,*S*-GeMe$_2$SPh}]$_2$, while the introduction of a bulkier substituent on the sulfur atom allowed selective formation of the three-membered metallacycle Cp*(CO)Fe{κ^2*Ge*,*S*-GeMe$_2$SMes} (Mes = 2,4,6-C$_6$H$_2$Me$_3$).

Three-membered metallacycles composed of one transition metal and two main-group typical elements have attracted much attention in view of their unique bonding modes, strained molecular structures, and novel reactivities.[1–4] Recently, we reported that photolysis of Cp*(CO)$_2$FeSiMe$_2$TePh in the presence of acetone afforded Cp*(CO)Fe{κ^2*Si*,*Te*-SiMe$_2$OCMe$_2$TePh}.[3] The reaction can be explained by the insertion of acetone into the silicon–tellurium bond of the transient three-membered metallacycle Cp*(CO)Fe{κ^2*Si*,*Te*-SiMe$_2$TePh}. Attempts to isolate the three-membered metallacyle failed due to its instability. Tilley et al. succeeded in the synthesis and X-ray characterization of [Cp*(Me$_3$P)Ir{κ^2*Si*,*S*-Si(S^{t}Bu)$_2$S^{t}Bu}](OTf).[4] We report here the photochemistry of Cp*(CO)$_2$FeGeMe$_2$SAr, leading to the formation of two novel metallacycles, *trans*-[Cp*Fe(CO){μ-κ^2*Ge*,*S*-GeMe$_2$SPh}]$_2$ and Cp*(CO)Fe{κ^2*Ge*,*S*-GeMe$_2$SAr} [Ar = Ph, 2,4,6-C$_6$H$_2$Me$_3$ (Mes)], depending on the substituents on the sulfur atom.

At $-45\,°$C, a THF solution of Cp*(CO)$_2$FeGeMe$_2$Cl was treated with NaSAr [Ar = Ph, 2,4,6-C$_6$H$_2$Me$_3$ (Mes)], which was freshly prepared by the reaction of ArSH and NaH in THF. Workup of the reaction mixture and recrystallization of the residue afforded yellow crystals of Cp*(CO)$_2$FeGeMe$_2$SAr in moderate yields [Ar = Ph (**1a**, 70%), Mes (**1b**, 55%)]. Elemental analysis, spectroscopic data, and X-ray diffraction studies[5] confirm the formation of **1**.

Ultraviolet ($\lambda > 300$ nm) irradiation of **1a** in benzene-d_6 gave a mixture of Cp*(CO)Fe{κ^2*Ge*,*S*-GeMe$_2$SPh} (**2a**) and *trans*-[Cp*Fe(CO){μ-κ^2*Ge*,*S*-GeMe$_2$SPh}]$_2$ (**3a**) (eq 1). The formation yields of **2a** and **3a** achieved maxima after 1.5 min (**2a**, 56%) and 4 min (**3a**, 29%), respectively. Further irradiation resulted in decomposition of **2a** and **3a**, giving several unidentified products. It was difficult to isolate **2a** and **3a** from the reaction mixture.



2a **3a**

Irradiation of a benzene-d_6 solution of **1a** in the presence of acetone suppressed the formation of **2a**, giving **3a** in 51% NMR yield. A large-scale experiment allowed the isolation of **3a** as brown crystals in 25% yield. The molecular structure of **3a** is depicted in Figure 1.[5] Complex **3a** contains an unprecedented Fe$_2$Ge$_2$S$_2$ six-membered ring, in which the conformation is best described as a twisted boat. The two Cp* ligands are in a mutually trans relationship. The most striking feature of **3a** is the exceptionally long Ge–S bonds (2.3919(19) and 2.379(2) Å), which are longer than that of **1a** (2.2850(7) Å) by 0.1 Å, and much longer than typical Ge–S bond lengths (2.16–2.30 Å).[6] This lengthening is likely to be attributable to steric repulsion between the phenyl groups on S and the methyl groups on Ge; the interatomic distances of C3···C13 (3.126(11) Å) and C5···C7 (3.490(12) Å) are significantly shorter than the sum (3.7 Å) of the effective van der Waals radii of the methyl groups (2.0 Å) and the half-thickness of the phenyl π-electron clouds (1.7 Å). In contrast to **3a**, related six-membered metallacycles Fe$_2$Si$_2$P$_2$ are known to exist as a mixture of twisted boat and chair forms.[2a]

The ^{1}H NMR spectrum of **3a** exhibits three singlet signals at δ 0.77 (6H, GeMe), 1.23 (6H, GeMe), and 1.30 (30H, Cp*). A significant low-energy shift is observed in ν_{CO} (1896 cm^{-1}) compared with **1a** (1925, 1979 cm^{-1}), which is consistent with the replacement of a carbonyl ligand with a more electron-donating SPh moiety.

Introduction of a bulkier substituent on the sulfur atom allowed selective formation of the three-membered metallacycle Cp*(CO)Fe{κ^2*Ge*,*S*-GeMe$_2$SMes} (**2b**) as green crystals in 72% isolated yield (eq 2). Formation of the corresponding six-membered Fe$_2$Ge$_2$S$_2$ metallacycle was not observed throughout the reaction even in the presence of acetone probably due to the steric reason. The ^{1}H NMR spectrum of **2b** exhibits singlet signals at δ 0.36 (3H, GeMe), 1.14 (s, 3H, GeMe), 1.68 (15H, Cp*), 2.01 (3H, *p*-ArMe), 2.53 (6H, *o*-ArMe), and 6.71 (2H, *m*-ArH), supporting the formation of a three-membered metallacycle. The IR spectrum shows a ν_{CO} band at 1900 cm^{-1}.

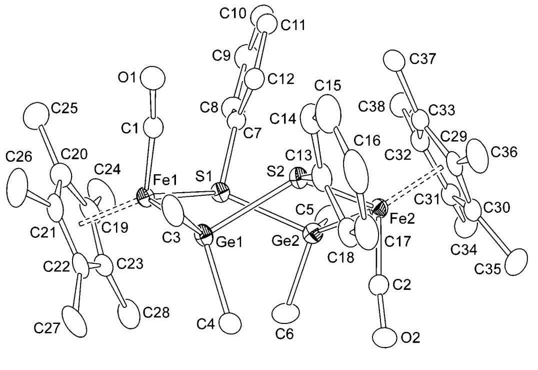


Figure 1. ORTEP drawing of **3a** with 30% thermal ellipsoids.

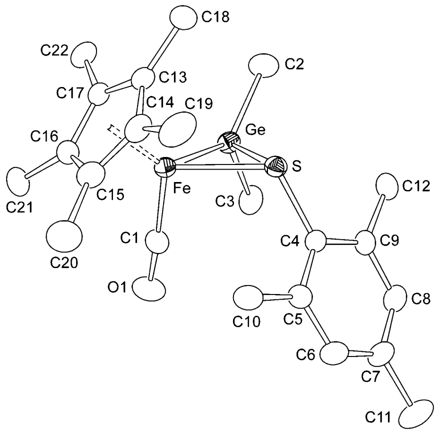
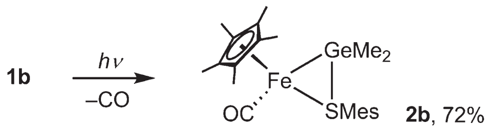
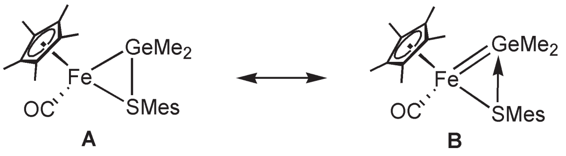


Figure 2. ORTEP drawing of **2b** with 50% thermal ellipsoids.



(2)

The ORTEP drawing of **2b** is shown in Figure 2.[5] Complex **2b** adopts a novel three-membered metallacycle structure composed of Fe, S, and Ge atoms. The Fe–Ge bond distance (2.2688(5) Å) is near the shorter limit of iron–germanium complexes previously reported (2.24–2.50 Å)[6,7] and lies in the range observed for germyleneiron complexes (2.24–2.37 Å),[7] indicating the unsaturated character of the iron–germanium bond. The sum of the bond angles for three bonds around the Ge atom (not including the Ge–S bond) is 359.9°, which is consistent with sp^2 hybridization of the Ge center. Another characteristic feature is the long Ge–S bond (2.3555(7) Å), compared with **1a** (2.2850(7) Å), which probably reflects the dative bond character of the Ge–S bond in **2b**.[8] These structural features suggest a significant contribution by the internally base-stabilized thiolato(germylene) complex **B** as a canonical structure (eq 3).



(3)

Although the role of acetone in the selective formation of **3a** has not been clarified, we believe that acetone catalyzes the dimerization process: nucleophilic attack by acetone toward the electron-deficient germanium atom in **2a** cleaves the Ge–S bond and generates an acetone-stabilized thiolato(germylene) intermediate, which easily dimerizes to give **3a**. A related mechanism has been postulated for the formation of the $Fe_2Si_2P_2$ metallacycles.[2a] At this time there is no direct evidence available to rule out the mechanism involving the dimerization of coordinatively unsaturated Cp*Fe(CO){κ^1*Ge*-GeMe$_2$SMes} formed through the dissociation of the sulfur part and stabilized by acetone.

Complex **2b** is the first three-membered metallacycle composed of one transition metal atom and Ge and S atoms in which the Me$_2$Ge–SMes fragment donates three electrons to the metal center.[9] The reactivity of this species is of great interest. A preliminary reactivity study of **2b** was carried out with MeOH. Addition of 2.5 equiv. of MeOH to a benzene-d_6 solution of **2b** at room temperature resulted in disproportionation, giving Cp*(CO)$_2$FeSMes (**4**) in 27% NMR yield accompanied by the formation of several unidentified products with low intensity in the ^{1}H NMR spectrum. When **1b** was irradiated in the presence of MeOH, **4** and HGeMe$_2$OMe were formed almost quantitatively. Compound **4** was isolated from the reaction mixture as brown crystals in 67% yield. Since complex **1b** is stable to alcohol under mild conditions, **2b** should react with MeOH quantitatively in the presence of CO. A possible mechanism involves nucleophillic attack by MeOH of the electron-deficient germanium atom in **2b** to generate Cp*(CO)FeH(GeMe$_2$OMe)(SMes) (**C**). Intermediate **C** then undergoes reductive elimination of HGeMe$_2$OMe followed by coordination of CO to give the product **4**. Formation of methoxyhydrosilanes from silylene complexes and methanol have been well documented.[10]

In summary, we succeeded in the synthesis and X-ray characterization of novel three- and six-membered metallacycles composed of iron, germanium, and sulfur atoms. The reactivity of these metallacycles toward various substrates is currently under active investigation.

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11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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