

Photochemistry of a Tellurosilyl(carbonyl)iron(II) Complex. Generation of a Novel Te–Si–Fe Three-membered Cyclic Intermediate

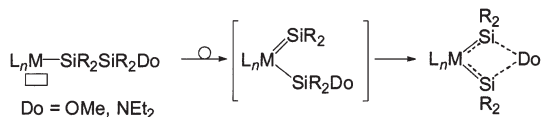
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The tellurosilyliron complex $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{TePh}$ (**1**) was synthesized by treatment of $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{Cl}$ with LiTePh . Irradiation of complex **1** and acetone in toluene led to dissociation of a CO ligand and insertion of acetone into the silicon–tellurium bond to afford the five-membered metallacycle $\text{Cp}^*(\text{CO})\text{Fe}\{\kappa^2(\text{Si},\text{Te})\text{-Me}_2\text{SiOCMe}_2\text{TePh}\}$.

Over the past few decades, a considerable number of studies have been made on the synthesis and properties of transition metal silyl complexes, which could participate in various transformation reactions of organosilicon compounds.¹ Although a large number of silyl complexes with alkyl and/or aryl substituents have been explored, little is known about the reactivity of heteroatom-substituted silyl complexes. Pannell and we reported that a coordinatively unsaturated disilanyl complex undergoes 1,3-migration of a terminal silyl group to generate a silyl-(silylene) complex.^{2,3} In particular, the photoreaction of disilanyl(carbonyl)metal complexes having an intramolecular donor such as alkoxy or amino group gives donor-bridged bis(silylene) complexes almost quantitatively (Scheme 1).⁴ Our recent interest has been focusing on the syntheses and reactivities of $\text{L}_n\text{MSiMe}_2\text{ER}_m$ compounds, in which the heteroatom (E) at the β -position possesses a lone electron pair and could be coordinated to an unsaturated metal center generated in the course of the reactions.⁵ We report here the syntheses and photochemistry of a tellurosilyliron(II) complex $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{TePh}$ (**1**).



Scheme 1.

A THF solution of $\text{Cp}^*(\text{CO})_2\text{FeSiMe}_2\text{Cl}$ was treated with LiTePh , which was freshly prepared by the reaction of Ph_2Te_2 and LiBEt_3H in THF (Eq 1). Workup of the mixture and crystallization from toluene/hexane at -30°C afforded yellow crystals of **1** in 69% isolated yield.⁶ The structure of **1** was determined by the X-ray diffraction study (Figure 1).⁷ Complex **1** adopts a normal piano-stool geometry; the iron center possesses a pentamethylcyclopentadienyl ligand, two carbonyl ligands, and a tellurosilyl ligand. The Fe–Si bond (2.311(2) Å) is significantly shorter than the typical iron–silicon bond (2.32–2.37 Å) in L_nFeSiR_3 (R = alkyl, aryl),¹ but is comparable to those of the silyliron complexes with electron-withdrawing groups or heteroatoms on the silicon atom (2.21–2.31 Å).¹ The shortening

is attributable to the back-donation from the iron d_{π} orbital to the σ^* orbital of the silicon–tellurium bond.^{5,8} Consistently, the bond length of Si–Te (2.568(2) Å) is close to the longer limit of the normal silicon–tellurium single bonds (2.47–2.57 Å).⁹ Various spectroscopic data also support the structure of **1**. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum shows a signal (δ 47.4) in the normal region of silyliron complexes.¹

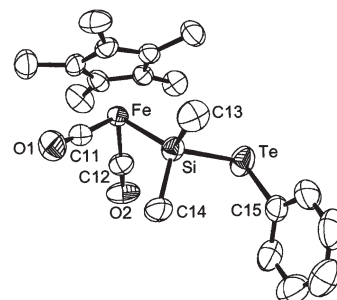
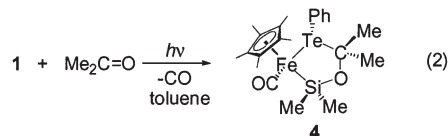
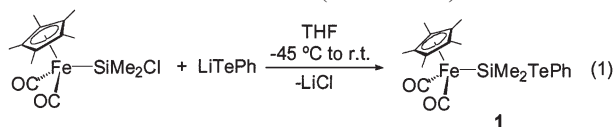


Figure 1. ORTEP drawing of **1**. Selected interatomic distances (Å) and bond angles ($^\circ$): Fe–Si 2.311(2), Te–Si 2.568(2), Te–C15 2.123(9), Si–Fe–C11 82.9(2), Si–Fe–C12 85.5(3), C11–Fe–C12 98.9(4), Fe–Si–Te 110.42(8), Si–Te–C15 94.8(2), Fe...Te 4.009(2).

UV ($\lambda > 300\text{ nm}$) irradiation of **1** in benzene- d_6 gave a complex mixture of $\text{Cp}^*(\text{CO})_2\text{FeTePh}$ (**2**),¹⁰ $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$, and unidentified products, all of them being in low yields. Formation of **2** and $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$ could be explained by assuming the initial generation of three-membered metallacycle $\text{Cp}^*(\text{CO})\text{-Fe}\{\kappa^2(\text{Si},\text{Te})\text{-Me}_2\text{SiTePh}\}$ (**3**). Intermediate **3** then releases the silylene moiety $[\text{SiMe}_2]$, and the following coordination of CO affords **2**. Intermediate **3** can also release the tellurosilyl ligand SiMe_2TePh to give a $[\text{Cp}^*(\text{CO})\text{Fe}]$ fragment, which is smoothly converted to $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$ through the coordination of CO and dimerization. In addition, Tilley et al. reported the synthesis and structure of thiasilairidacycle $[\text{Cp}^*(\text{PMe}_3)\text{Ir}\{\kappa^2(\text{Si},\text{S})\text{-Si}(\text{S}'\text{Bu})_2\text{S}'\text{Bu}\}](\text{OTf})$ by the reaction of $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Me})\text{OTf}$ with $\text{HSi}(\text{S}'\text{Bu})_3$.¹¹ This fact also supports the intermediate formation of the tellurasilametallacycle **3**.

To trap the intermediate **3**, the photolysis of **1** was performed in the presence of acetone. Thus, irradiation of **1** in the presence of a large excess of acetone for 5 min afforded the insertion product **4** (Eq 2). Crystallization of the residue from hexane afforded brown crystals of **4** in 26% isolated yield.¹² The low yield is due to the sensitivity of **4** to irradiation. In fact, monitoring the reaction by ^1H NMR spectroscopy showed decrease of the peak of **4** on prolonged irradiation.



The X-ray crystal structure analysis of **4** (Figure 2)⁷ revealed that the Fe–Si bond (2.296(1) Å) is slightly shorter than the normal iron–silicon single bonds (2.31–2.46 Å)¹ and is close to the values for base-stabilized silylene complexes (2.21–2.29 Å).¹ The Fe–Te bond (2.4407(9) Å) is considerably shorter than the previously reported Fe–Te bonds in telluroether complexes (2.53–2.59 Å).¹³ The bond lengths of Si–O1 and Te–C11 are 1.708(4) Å and 2.280(5) Å, respectively, and are both longer than the normal distances of the corresponding single bonds [Si–O (ca. 1.63 Å),¹⁴ Te–C (2.07–2.17 Å)¹³]. Furthermore, the bond distance of O1–C11 (1.387(6) Å) is significantly shorter than the normal C–O single bond (ca. 1.42 Å).¹⁴ These structural features suggest the significant contribution of the acetone-stabilized benzenetelluroolato(silylene) form **A** in Figure 3.

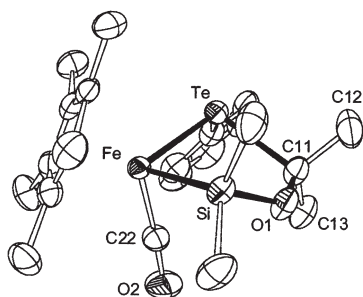


Figure 2. ORTEP drawing of **4**. Selected bond lengths (Å) and angles (°): Fe–Si 2.296(1), Fe–Te 2.4407(9), Fe–C22 1.727(4), O2–C22 1.158(5), Te–C11 2.280(5), O1–C11 1.387(6), Si–O1 1.708(4), Te–Fe–Si 82.34(4), Fe–Te–C11 98.0(1), Fe–Si–O1 108.3(1), Te–C11–O1 105.9(3), Si–O1–C11 125.4(3).

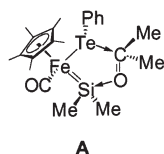
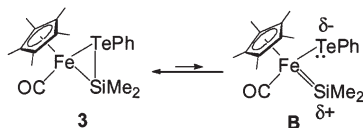


Figure 3.

The NMR spectroscopic features of **4** are consistent with the crystal structure. The signals of four Me groups on the five-membered metallacycle appear inequivalently at 0.67, 0.93, 1.08, and 1.93 ppm. The ²⁹Si{¹H} NMR spectrum shows a signal at 95.3 ppm. The chemical shift is characteristic of the base-stabilized silylene complexes,¹ supporting the contribution of **A**.



Scheme 2.

The formation of **4** can be considered to proceed through the insertion of the C=O bond of acetone into the Si–Te bond in tellurasilametallacycle **3**. Since the precursor **1** does not react with acetone at room temperature, this highly enhanced reactivity of **3** is attributable to the ring strain of the three-membered ring¹⁵ and/or to a significant contribution of its open-form, telluroolato(silylene) complex **B** (Scheme 2). The lone pair of ace-

tone readily coordinates to the positively charged silylene silicon atom,¹⁶ and then the lone pair of the intramolecular telluroolato ligand nucleophilically attacks the carbonyl carbon atom of acetone to form **4**.

References and Notes

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- Data for **1**: ¹H NMR (300 MHz, benzene-*d*₆) δ 1.01 (s, 6H, SiMe₂), 1.50 (s, 15H, C₅Me₅), 6.94 (*pseudo t*, *J* = 7 Hz, 2H, *m*-Ph), 7.05 (*t*, *J* = 7 Hz, 1H, *p*-Ph), 8.01 (*d*, *J* = 7 Hz, 2H, *o*-Ph); ¹³C NMR (75.5 MHz, benzene-*d*₆) δ 9.3 (SiMe₂), 9.8 (C₅Me₅), 95.8 (C₅Me₅), 108.8, 127.1, 129.0, 142.0 (Ph), 216.6 (CO); ²⁹Si NMR (59.6 MHz, benzene-*d*₆) δ 47.4; IR (KBr) 1981, 1930 cm^{−1} (ν_{CO}); Anal. Calcd. for C₂₀H₂₆FeO₂SiTe: C, 47.11; H, 5.14%. Found: C, 47.31; H, 5.12%.
- The structure was solved by direct methods (SIR92). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Data for **1**: C₂₀H₂₆FeO₂SiTe, *M* = 509.96, monoclinic, *P*₂/c (#14), *a* = 8.779(4) Å, *b* = 8.976(5) Å, *c* = 27.637(3) Å, β = 92.42(2)°, *V* = 2175(1) Å³, *Z* = 4, *D*_{calcd} = 1.557 g cm^{−3}, μ(Mo Kα) = 20.71 cm^{−1}, *R* (*R*_w) = 0.045 (0.059) for 2324 unique data with *I* > 3.0σ(*I*). Data for **4**: C₂₂H₃₂FeO₂SiTe, *M* = 540.03, monoclinic, *P*₂/n (#14), *a* = 9.815(6) Å, *b* = 16.164(6) Å, *c* = 15.020(4) Å, β = 99.52(3)°, *V* = 2350(1) Å³, *Z* = 4, *D*_{calcd} = 1.526 g cm^{−3}, μ(Mo Kα) = 19.22 cm^{−1}, *R* (*R*_w) = 0.033 (0.043) for 3696 unique data with *I* > 3.0σ(*I*). Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as no. CCDC-213434 for **1** and no. CCDC-213435 for **4**.
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- The telluroolato complex **2** was independently synthesized by refluxing the toluene solution of [Cp*Fe(CO)₂]₂ and Ph₂Te₂. Green crystals of **2** were obtained in 63% isolated yield.
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- Data for **4**: ¹H NMR (300 MHz, benzene-*d*₆) δ 0.67, 0.92 (s, 3H × 2, SiMe₂), 1.08, 1.93 (s, 3H × 2, CMe₂), 1.68 (s, 15H, C₅Me₅), 7.02–7.10 (m, 3H, *m*, *p*-Ph), 7.86 (m, 2H, *o*-Ph); ¹³C NMR (75.5 MHz, benzene-*d*₆) δ 6.5, 11.6 (SiMe₂), 11.1 (C₅Me₅), 34.7, 38.4 (CMe₂), 79.9 (CMe₂), 90.3 (C₅Me₅), 114.6, 129.2, 129.4, 137.5 (Ph), 220.3 (CO); ²⁹Si NMR (59.6 MHz, benzene-*d*₆) δ 95.3; IR (KBr) 1880 (CO); Anal. Calcd. for C₂₂H₃₂FeO₂SiTe: C, 48.93; H, 5.97%. Found: C, 48.88; H, 5.73%.
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