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

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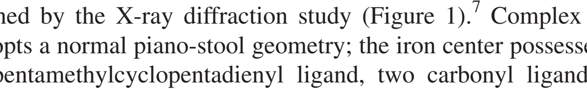
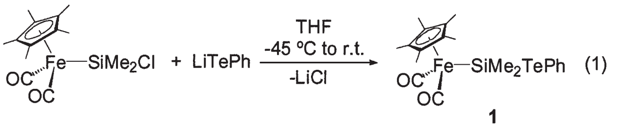
The tellurosilyliron complex $\mathrm{Cp^*(CO)_2FeSiMe_2TePh}$ (**1**) was synthesized by treatment of $\mathrm{Cp^*(CO)_2FeSiMe_2Cl}$ with LiTePh. Irradiation of complex **1** and acetone in toluene led to dissociation of a CO ligand and insertion of acetone into the silicon–tellurium bond to afford the five-membered metallacycle $\mathrm{Cp^*(CO)Fe\{\kappa^2(\mathit{Si},\mathit{Te})\text{-}Me_2SiOCMe_2TePh\}}$.

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 $\mathrm{L}_n\mathrm{MSiMe_2ER}_m$ 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 synthesis and photochemistry of a tellurosilyliron(II) complex $\mathrm{Cp^*(CO)_2FeSiMe_2TePh}$ (**1**).



Scheme 1.

A THF solution of $\mathrm{Cp^*(CO)_2FeSiMe_2Cl}$ was treated with LiTePh, which was freshly prepared by the reaction of $\mathrm{Ph_2Te_2}$ and $\mathrm{LiBEt_3H}$ 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 $\mathrm{L}_n\mathrm{FeSiR_3}$ (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 $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR spectrum shows a signal (δ 47.4) in the normal region of silyliron complexes.[1]



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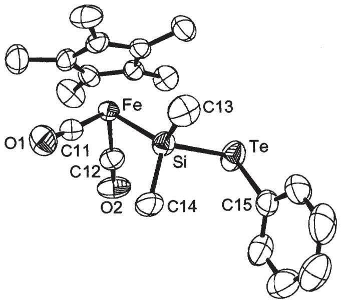
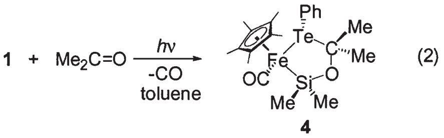


Figure 1. ORTEP drawing of **1**. Selected interatomic distances (Å) and bond angles (°): Fe–Si 2.311(2), Te–Si 2.568(2), Te–C15 2.123(9), Si–Fe–C11 82.9(2), Si–Fe–C12 85.5(3), C11–Fe–C12 98.9(4), Fe–Si–Te 110.42(8), Si–Te–C15 94.8(2), Fe· · ·Te 4.009(2).

UV ($\lambda > 300$ nm) irradiation of **1** in benzene-d_6 gave a complex mixture of $\mathrm{Cp^*(CO)_2FeTePh}$ (**2**),[10] $\mathrm{[Cp^*Fe(CO)_2]_2}$, and unidentified products, all of them being in low yields. Formation of **2** and $\mathrm{[Cp^*Fe(CO)_2]_2}$ could be explained by assuming the initial generation of three-membered metallacycle $\mathrm{Cp^*(CO)Fe\{\kappa^2(\mathit{Si},\mathit{Te})\text{-}Me_2SiTePh\}}$ (**3**). Intermediate **3** then releases the silylene moiety [$:\mathrm{SiMe_2}$], and the following coordination of CO affords **2**. Intermediate **3** can also release the tellurosilyl ligand $\mathrm{SiMe_2TePh}$ to give a [Cp*(CO)Fe] fragment, which is smoothly converted to $\mathrm{[Cp^*Fe(CO)_2]_2}$ through the coordination of CO and dimerization. In addition, Tilley et al. reported the synthesis and structure of thiasilairidacylcle $\mathrm{[Cp^*(PMe_3)Ir\{\kappa^2(\mathit{Si},\mathit{S})\text{-}Si(S^\mathit{t}Bu)_2S^\mathit{t}Bu\}](OTf)}$ by the reaction of $\mathrm{Cp^*(PMe_3)Ir(Me)OTf}$ with $\mathrm{HSi(S^\mathit{t}Bu)_3}$.[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 exess 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 ^{1}H NMR spectroscopy showed decrease of the peak of **4** on prolonged irradiation.



4

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 benzenetellurolato(silylene) form **A** in Figure 3.

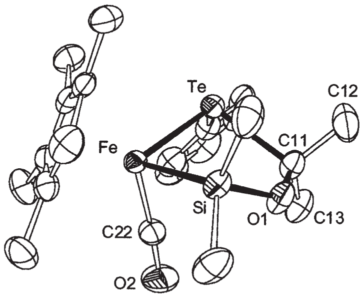
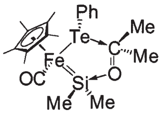


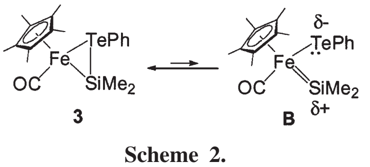
Figure 2. ORTEP drawing of **4**. Selected bond lengths (Å) and angles (°): Fe–Si 2.296(1), Fe–Te 2.4407(9), Fe–C22 1.727(4), O2–C22 1.158(5), Te–C11 2.280(5), O1–C11 1.387(6), Si–O1 1.708(4), Te–Fe–Si 82.34(4), Fe–Te–C11 98.0(1), Fe–Si–O1 108.3(1), Te–C11–O1 105.9(3), Si–O1–C11 125.4(3).



A

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 $^{29}Si\{^1H\}$ 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 ring[15] and/or to a significant contribution of its open-form, tellurolato(silylene) complex **B** (Scheme 2). The lone pair of acetone readily coordinates to the positively charged silylene silicon atom,[16] and then the lone pair of the intramolecular tellurolato ligand nucleophillically attacks the carbonyl carbon atom of acetone to form **4**.

References and Notes

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6 Data for **1**: ^1H NMR (300 MHz, benzene-d_6) δ 1.01 (s, 6H, SiMe$_2$), 1.50 (s, 15H, C$_5$Me$_5$), 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); ^{13}C NMR (75.5 MHz, benzene-d_6) δ 9.3 (SiMe$_2$), 9.8 (C$_5$*Me*$_5$), 95.8 (*C*$_5$Me$_5$), 108.8, 127.1, 129.0, 142.0 (Ph), 216.6 (CO); ^{29}Si NMR (59.6 MHz, benzene-d_6) δ 47.4; IR (KBr) 1981, 1930 cm^{-1} (ν_{CO}); Anal. Calcd. for $C_{20}H_{26}FeO_2SiTe$: C, 47.11; H, 5.14%. Found: C, 47.31; H, 5.12%.

7 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**: $C_{20}H_{26}FeO_2SiTe$, $M = 509.96$, monoclinic, $P2_1/c$ (#14), $a = 8.779(4)$ Å, $b = 8.976(5)$ Å, $c = 27.637(3)$ Å, $\beta = 92.42(2)°$, $V = 2175(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.557$ g cm^{-3}, μ(Mo Kα) = 20.71 cm^{-1}, R (R_w) = 0.045 (0.059) for 2324 unique data with $I > 3.0\sigma(I)$. Data for **4**: $C_{22}H_{32}FeO_2SiTe$, $M = 540.03$, monoclinic, $P2_1/n$ (#14), $a = 9.815(6)$ Å, $b = 16.164(6)$ Å, $c = 15.020(4)$ Å, $\beta = 99.52(3)°$, $V = 2350(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.526$ g cm^{-3}, μ(Mo Kα) = 19.22 cm^{-1}, R (R_w) = 0.033 (0.043) for 3696 unique data with $I > 3.0\sigma(I)$. 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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10 The tellurolato complex **2** was independently synthesized by refluxing the toluene solution of $[Cp^*Fe(CO)_2]_2$ and Ph_2Te_2. Green crystals of **2** were obtained in 63% isolated yield.

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12 Data for **4**: ^1H NMR (300 MHz, benzene-d_6) δ 0.67, 0.92 (s, 3H × 2, SiMe$_2$), 1.08, 1.93 (s, 3H × 2, CMe$_2$), 1.68 (s, 15H, C$_5$Me$_5$), 7.02–7.10 (m, 3H, *m,p*-Ph), 7.86 (m, 2H, *o*-Ph); ^{13}C NMR (75.5 MHz, benzene-d_6) δ 6.5, 11.6 (SiMe$_2$), 11.1 (C$_5$*Me*$_5$), 34.7, 38.4 (C*Me*$_2$), 79.9 (*C*Me$_2$), 90.3 (*C*$_5$Me$_5$), 114.6, 129.2, 129.4, 137.5 (Ph), 220.3 (CO); ^{29}Si NMR (59.6 MHz, benzene-d_6) δ 95.3; IR (KBr) 1880 (CO); Anal. Calcd. for $C_{22}H_{32}FeO_2SiTe$: C, 48.93; H, 5.97%. Found: C, 48.88; H, 5.73%.

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