Reactions of a Silyl(silylene)iron Complex with Nitriles: Carbon−Carbon Bond Cleavage of Nitriles by the Transiently Generated Disilanyliron(II) Intermediate

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A silyl(silylene) iron complex, Cp*Fe(CO)(=SiMes$_2$)SiMe$_3$ (**1**), which was prepared by the photoreaction of Cp*Fe(CO)$_2$Me (**2**) with hydrodisilane Mes$_2$MeSiSiMe$_2$H (**3**), reacted with nitriles RCN (R = Ph, Me) at 80 °C to afford a mixture of a disilanyl isocyanide complex Cp*Fe(CO)(R)(CNSiMe$_2$SiMes$_2$Me) (**5a**, R = Ph; **5b**, R = Me) and a pair of diastereomers of Cp*Fe(CO)(R)(CNSiMesMeSiMesMe$_2$) (**6a**, R = Ph; **6b**, R = Me). The molecular structure of **5a** was determined by X-ray crystallography. On the other hand, when the photoreaction of **2** with **3** was performed in the presence of benzonitrile, acetonitrile, or acetonitrile-d_3, at ca. 5 °C, only the disilanyl isocyanide complex **5a**, **5b**, or **5b-d_3** was obtained as a single product. The formation of these disilanyl isocyanide complexes is understood by the action of coordinatively unsaturated disilanyliron(II) intermediates Cp*Fe(CO)SiMe$_2$SiMes$_2$Me, etc., which are transiently generated by thermal isomerization of **1** or photoreaction of **2** with **3**, to incoming nitriles. The C−C bond of the nitrile ligand is activated through migration of the disilanyl group to the nitrogen atom of nitriles.

Introduction

Silyl(silylene) complexes are regarded as key intermediates in various reactions involving organosilicon compounds, and 1,2- and 1,3-group migrations on these complexes have been postulated to cause the metal-catalyzed oligomerization/deoligomerization, isomerization, and redistribution of organosilicon compounds.[1] Recently, we succeeded in giving direct experimental evidence for the 1,3-alkyl migration between two silicon atoms and 1,2-silyl migration from Fe to Si on a donor-free silyl(silylene)iron complex, Cp*Fe(CO)(=SiMes$_2$)SiMe$_3$ (**1**, Mes = mesityl), which was synthesized by the photoreaction of Cp*Fe(CO)$_2$Me (**2**) with hydrodisilane Mes$_2$MeSiSiMe$_2$H (**3**).[2] Thus, the reaction of **1** with ^{t}BuNC afforded the disilanyl complex Cp*Fe(CO)(CN^{t}Bu)(SiMesMeSiMesMe$_2$) (**4**) via 1,2- and 1,3-group migrations. With our continuing interest in the reactivity of the silyl(silylene) complex, we have investigated the reactivity of **1** toward nitriles, which were expected to act as a two-electron donor to the metal center or to the silicon

atom of the silylene ligand.[3] Against our expectations, reactions of **1** with nitriles did not produce the simple nitrile analogues of **4** or the base-stabilized forms of **1**, but gave disilanyl isocyanide complexes Cp*Fe(CO)(R)(CNSiMe$_2$SiMes$_2$Me) and Cp*Fe(CO)(R)(CNSiMeMesSiMesMe$_2$) (R = Ph, Me). The formation of these disilanylisocyanide complexes implies that the C−C bond cleavage of nitriles took place after 1,2- and 1,3-group migration reactions in the organosilicon moieties.

The C−C bond activation of unstrained nitriles using transition metal complexes is usually difficult, but some interesting C−C bond cleavages of unstrained nitriles have been demonstrated in reactions involving complexes of Ni,[4a−d,5,6] Pd,[4a] Pt,[4a] Mo,[4e] Rh,[7] Ir,[8] and Fe.[9] Especially, very recently some silyl complexes have been demonstrated to cleave the C−C bonds of nitriles. Bergman, Brookhart, et al. reported that the reaction of [Cp*(PMe$_3$)Rh(SiPh$_3$)(ClCH$_2$Cl)]$^+$ with RCN produced [Cp*(PMe$_3$)RhR(CNSiPh$_3$)]$^+$ (R = alkyl and aryl groups).[7]

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Tilley et al. found that a similar activation of nitrile occurred using a cationic Ir(III) silyl complex.[8] Nakazawa et al. also reported the related C−C bond cleavage of nitrile using an Fe(II) silyl complex[9a] and its application to catalytic aryl−CN bond cleavage reaction[9b] as well as catalytic silylcyanation of aldehydes and ketones.[9c] In these examples, it is suggested that nitrile-coordinated silyl complexes are key intermediates, and the following silyl migration to the nitrile nitrogen and subsequent C−C bond cleavage afford silyl isocyanide complexes.

We report here the details of the formation of disilanyl isocyanide complexes by the reaction of silyl(silylene)iron complex **1** with nitriles RCN (R = Ph, Me) and also by the photoreaction of **2** and **3** in the presence of nitriles. The X-ray crystal structure of one of the disilanyl isocyanide complexes, Cp*Fe(CO)(Ph)(CNSiMe$_2$SiMes$_2$Me) (**5a**), and possible reaction mechanisms are also discussed.

Results and Discussion

Thermal Reaction of Cp*Fe(CO)(=SiMes$_2$)SiMe$_3$ (1) with Nitriles. Silyl(silylene)iron complex **1** was heated in toluene at 80 °C for 5 h with an excess of benzonitrile to afford a 3:2 mixture of Cp*Fe(CO)(Ph)(CNSiMe$_2$SiMes$_2$Me) (**5a**) and a pair of diastereomers of Cp*Fe(CO)(Ph)(CNSiMesMeSiMesMe$_2$) (**6a**) in 40% combined yield (eq 1). Similar heating of **1** in acetonitrile as a solvent at 80 °C for 6 h afforded an approximately 5:6 mixture of disilanyl isocyanide complexes, Cp*Fe(CO)(Me)(CNSiMe$_2$SiMes$_2$Me) (**5b**) and a pair of diastereomers of Cp*Fe(CO)(Me)(CNSiMesMeSiMesMe$_2$) (**6b**) in 31% combined yield (eq 1). Monitoring of the reactions by ^{1}H NMR spectroscopy shows that each reaction proceeds almost quantitatively. Their low isolated yields are mainly attributable to their instabilities; the products slowly decompose in solution to give Cp*$_2$Fe$_2$(CO)$_4$, which disturbs purification of the products by recrystallization. Although the characterization of these products was difficult only from their spectroscopic data, the structure of **5a** was successfully confirmed by the X-ray crystal structure determination. Other complexes (**5b**, **6a**, and **6b**) were characterized on the basis of the similarity of their spectroscopic data with those of **5a** (see Experimental Section).

(1)

5a (R = Ph)
5b (R = Me)

6a (R = Ph)
6b (R = Me)
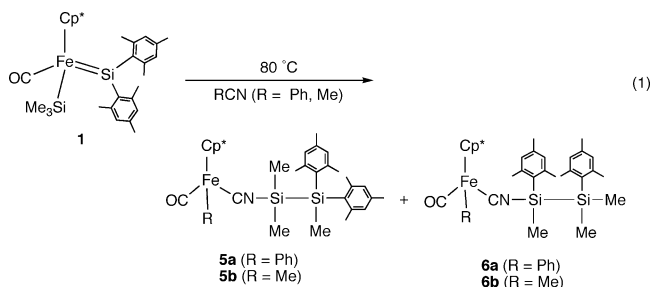
X-ray Crystal Structure Determination of 5a. The ORTEP drawing of **5a** is depicted in Figure 1 with the selected bond lengths (Å) and bond angles (deg). The X-ray crystal structure analysis of **5a** clearly reveals that **5a** is a disilanyl isocyanide complex having an unprecedented Fe−C−N−Si−Si linkage. The iron atom adopts a typical three-legged piano-stool structure, which consists of Cp*, carbonyl, phenyl, and disilanyl isocyanide ligands. Therefore, the iron atom becomes a chiral center and the crystal consists of the enantiomers. The Fe(1)−C(12) (1.79(1) Å), C(12)−N(1) (1.18(2) Å), and N(1)−Si(1) (1.76(1) Å) bond lengths are comparable with the Fe−C (1.790(5) Å), C−N (1.181(7) Å), and N−Si (1.701(6) Å) bond lengths of Cp*Fe(PPh$_3$)(CNSiPh$_3$)Me,[9a] typical of iron isocyanide complexes.[10]
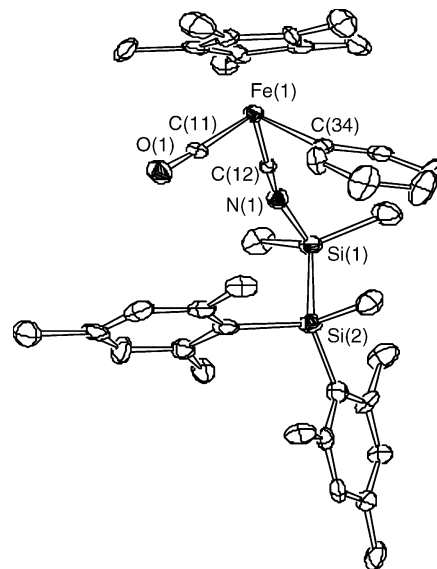
Figure 1. ORTEP drawing of **5a**, showing 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Fe(1)−C(12) 1.79(1), C(12)−N(1) 1.18(2), N(1)−Si(1) 1.76(1), Si(1)−Si(2) 2.364(5), Fe(1)−C(34) 2.01(1), Fe(1)−C(11) 1.78(1), C(11)−O(1) 1.13(2); Fe(1)−C(12)−N(1) 177(1), C(12)−N(1)−Si(1) 166(1), N(1)−Si(1)−Si(2) 99.0(4).

Photochemical Reaction of 2 and 3 in the Presence of Nitriles. Interestingly, the photoreaction of **2** and **3** in the presence of nitriles also produced the same type of disilanyl isocyanide complexes but only as a single product. Thus, irradiation of a toluene solution of **2** and **3** containing a slight excess of benzonitrile in a Pyrex glass tube at ca. 5 °C afforded Cp*Fe(CO)(Ph)(CNSiMe$_2$SiMes$_2$Me) (**5a**) as yellow crystals in 77% isolated yield (eq 2). In a similar manner, **5b** was isolated as a yellow solid in 22% yield by employing acetonitrile as a solvent. This low yield of **5b** is mainly due to its high instability. In an NMR experiment using acetonitrile-d_3 as a solvent, **5b-d_3** formed as a single product in 82% NMR yield. Complex **6a** or **6b** was not observed in every case of these photochemical reactions.

(2)

5a (R = Ph)
5b (R = Me)
5b-d_3 (R = CD$_3$)
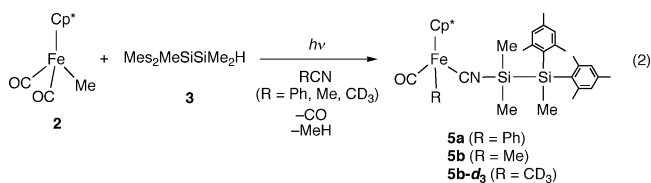
A Possible Mechanism for the Formation of 5 and 6. The fact that **5** and **6** have a disilanyl isocyanide ligand and an R group (from nitrile RCN) on the iron center indicates that the C−C bond of nitriles is activated by the insertion of the iron fragment into the C−C bond and simultaneous migration of the disilanyl group to the nitrogen of nitriles. In addition, as mentioned in the Introduction, **1** reacted with isocyanide ^{t}BuNC at 60 °C to produce mainly the disilanyl complex Cp*Fe(CO)(CN^{t}Bu)(SiMesMeSiMesMe$_2$) (**4**). This result suggests that an unsaturated disilanyl intermediate is generated from **1** at the initial stage under heating conditions and can be trapped by a two-electron donor such as ^{t}BuNC. Taking these results into consideration, a possible mechanism for the formation of disilanyl isocyanide complexes in the reaction of **1** with nitriles

(10) Based on a search of the Cambridge Structural Database, CSD version 5.25 (November 2003).

Scheme 1. A Possible Mechanism for the Formation of 5 and 6
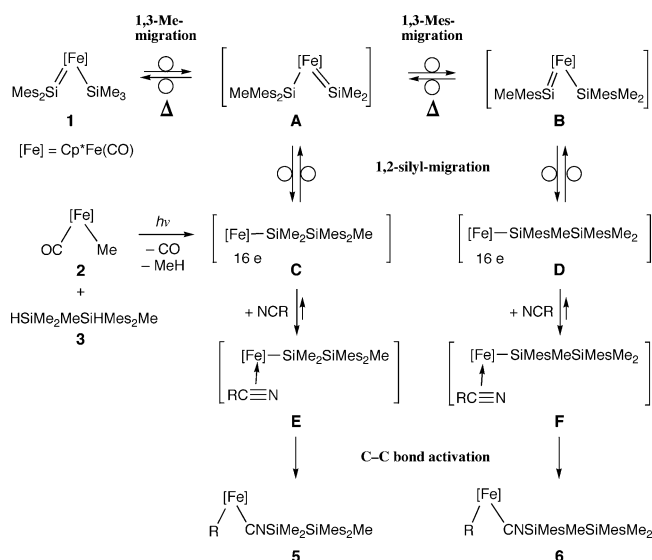
is illustrated in Scheme 1. The mechanism consists of (1) 1,3-migration of a methyl group followed by a mesityl group on **1** to produce other isomeric silyl(silylene) complexes **A** and **B**, (2) 1,2-silyl migration from **A** and **B** to generate 16e disilanyl complexes **C** and **D**, respectively, (3) coordination of nitriles to **C** and **D** to produce **E** and **F**, respectively, and (4) disilanyl group migration from Fe to N and subsequent oxidative addition of a C−C bond of the resulting η^2-iminoacyl ligand to the iron center to produce **5** and **6**. The final path is thought to be irreversible, while the other paths are reversible. Although we could not observe any intermediates, Jones observed the formation of an η^2-nitrile complex and subsequent oxidative addition to produce (dippe)Ni(Ph)(CN) (dippe = diisopropyl-phosphinoethane) in the reaction of [(dippe)NiH]$_2$ with PhCN.[5] Bergman and Brookhart also observed an η^1-nitrile intermediate as well as an η^2-iminoacyl intermediate, [Cp*(PMe$_3$)Rh(η^2-C(4-(OMe)C$_6$H$_4$)=N(SiPh$_3$))]$^+$, which was isolated and structurally confirmed, in the reaction of [Cp*(PMe$_3$)Rh(SiPh$_3$)(ClCH$_2$Cl)]$^+$ with MeOC$_6$H$_4$CN.[7b] Nakazawa et al. also suggested a mechanism involving η^2-nitrile- and η^2-iminoacyl-coordinated species for their C−C bond activation of acetonitrile using an Fe(II) silyl complex based on DFT calculation.[9a] Probably, the step of C−C bond cleavage of nitriles in our system would also proceed via a similar mechanism involving η^2-nitrile (**E** and **F**) and/or η^2-iminoacyl intermediates.

Exclusive formation of **5** in the photoreaction of **2** and **3** in the presence of nitriles is explained as follows. In this case, the initial product is the 16e disilanyl complex **C**. At low temperature, 1,2-silyl migration from **C** to **A** is suppressed, while coordination of nitriles to **C** and the following C−C bond activation process of nitriles (**C** → **E** → **5**) still occurs smoothly to give only **5**.

It should be pointed out again here that the product ratio of **5** to **6** in the thermal reaction was different depending on the nitriles employed: When benzonitrile was used, the ratio of **5a** to **6a** was 3:2, while when acetonitrile was used, that of **5b** to **6b** was 5:6. However, as demonstrated in the previous paragraph, if the C−C bond activation process of nitriles (**C** → **E** → **5** and also **D** → **F** → **6**) is faster than the processes before that, the ratio of the products **5** and **6** must be independent of the nitriles. A plausible explanation is the existence of the interaction between a nitrile molecule and silyl(silylene) complexes **A** and **B**. It is well known that silylene complexes are stabilized by coordination of bases including nitriles. The stability of the adduct must depend on the steric interaction between the nitrile and silylene ligand, and the largest steric interaction is expected to the adduct between benzonitrile and **B** having a mesityl(methyl)silylene ligand, which is apparently the least stable. Therefore, the ratio of **A** to **B** is predicted to be higher in the adducts of bulkier benzonitrile than in those of acetonitrile. The above-mentioned ratios of **5** to **6**, which are considered to reflect the ratios of **A** to **B**, are consistent with this hypothesis. We recently demonstrated through the thermal reaction of **1** with CO that disilanyl complex **D** forms preferably to **C** due to the steric repulsion among two mesityl groups and other parts of the molecule, which is less in **B** than **A**.[2b] This is retained in the acetonitrile adducts of **A** and **B**, while reversed in the corresponding benzonitrile adducts.

Conclusions

We found that not only 1,2-silyl migration but also C−C bond activation of nitriles occur in the reaction of the silyl(silylene) iron complex Cp*Fe(CO)(=SiMes$_2$)SiMe$_3$ (**1**) with nitriles at 80 °C to produce disilanylisocyanide complexes Cp*Fe(CO)-(R)(CNSiMe$_2$SiMes$_2$Me) (**5**) and Cp*Fe(CO)(R)(CNSiMesMe-SiMesMe$_2$) (**6**). Complex **5** was also produced as a single product by the photoreaction of Cp*Fe(CO)$_2$Me (**2**) with Mes$_2$-MeSiSiMe$_2$H (**3**) in the presence of nitriles at low temperature. We proposed a reaction mechanism involving the transient formation of unsaturated disilanyliron complexes Cp*Fe(CO)-(SiMe$_2$SiMes$_2$Me) (**C**) and Cp*Fe(CO)(SiMesMeSiMesMe$_2$) (**D**). Coordination of nitriles to **C** or **D** followed by migration of the disilanyl group from Fe to N and addition of C−C bond of nitriles gives **5** (and **6**).

Experimental Section

General Procedures. All manipulations were carried out under argon using standard Schlenk or vacuum line techniques. Benzene-d_6, toluene, hexane, pentane, acetonitrile, and acetonitrile-d_3 were dried over calcium hydride and distilled before use. Benzonitrile was dried over 4 Å molecular sieves before use. Cp*Fe(CO)-(=SiMes$_2$)SiMe$_3$ (**1**),[2] Cp*Fe(CO)$_2$Me (**2**) (Cp* = η^5-C$_5$Me$_5$),[11] and Mes$_2$MeSiSiMe$_2$H (**3**)[12] were synthesized according to the previously reported procedures. ^{1}H, ^{13}C{^{1}H}, ^{29}Si{^{1}H}, and ^{1}H−^{29}Si-{^{1}H} COLOC NMR spectra were recorded on a Bruker ARX-300, a Bruker AVANCE-300, or a JEOL ECA-600 spectrometer. ^{1}H NMR chemical shifts ware referenced to the residual ^{1}H NMR signal of the deuterated solvents. ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR chemical shifts were referenced to an external standard of TMS. Infrared spectra were obtained using a HORIBA FT-730 spectrophotometer. Mass spectra were recorded on a Shimadzu GCMS-QP5000 mass spectrometer operating in electron impact (EI) mode. Exact mass spectra were recorded on a Bruker Daltonics APEX-(III) mass spectrometer operating in electrospray ionization (ESI) mode. Elemental analyses were performed at the Instrumental Analysis Center for Chemistry, Tohoku University.

Thermal Reaction of Cp*Fe(CO)(=SiMes$_2$)SiMe$_3$ (1) with PhCN. A toluene (5 mL) solution of **1** (109 mg, 0.195 mmol) and benzonitrile (94 mg, 0.91 mmol) was heated at 80 °C for 5 h. After removal of volatiles, the residue was recrystallized from pentane (3 mL) to afford yellow crystals of an isomeric mixture of Cp*Fe-(CO)(Ph)(CNSiMe$_2$SiMes$_2$Me) (**5a**) and Cp*Fe(CO)(Ph)(CNSiMes-MeSiMesMe$_2$) (**6a**) (**5a:6a** = 3:2) in 40% combined yield (52 mg, 0.079 mmol). **5a** and **6a** were not separated even by repeated

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Chart 1
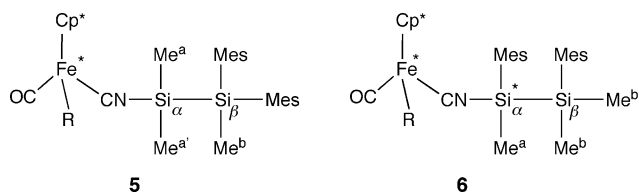
recrystallization from the mixture, but pure **5a** was isolated from the reaction of Cp*Fe(CO)$_2$Me (**2**) and Mes$_2$MeSiSiMe$_2$H (**3**) in the presence of benzonitrile (vide infra). Complex **6a** was found to be a mixture of two diasteromers and was characterized by ^{1}H, ^{29}Si{^{1}H}, and ^{1}H–^{29}Si{^{1}H} COLOC NMR (see Supporting Information). Data of **6a** (a mixture of two diastereomers): ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.47, 0.53, 0.54, 0.60 (s, SiMes*Me*$_2$), 0.75, 0.78 (s, SiMes*Me*), 1.53, 1.55 (s, C$_5$Me$_5$), 1.986, 1.992, 2.03, 2.04 (s, *p*-Me), 2.16, 2.22, 2.23, 2.28 (s, *o*-Me), 6.56–6.60 (*m*-H), 7.06–7.22 (m, *p*-H or *m*-H of FePh), 7.73–7.80 (m, *o*-H of FePh). ^{13}C{^{1}H} NMR (75.5 MHz, C$_6$D$_6$): δ 2.4, 2.5, 4.75, 4.81 (SiMe), 9.78, 9.81 (C$_5$*Me*$_5$), 21.0 (*p*-Me), 24.52, 24.55, 25.2, 25.3 (*o*-Me), 94.2 (*C*$_5$Me$_5$), 112.9, 119.0, 127.1, 128.8, 128.9, 129.6, 131.9, 139.6, 143.9, 144.1, 144.6, 165.0, 165.5 (*C*$_6$H$_2$Me$_3$ or Fe*C*$_6$H$_5$), 207.2 (FeCNSi), 221.4 (CO). Some of these carbon signals seem to be overlapped. ^{29}Si{^{1}H} NMR (59.6 MHz, C$_6$D$_6$): δ −22.0 (β-Si), −21.9 (β-Si), −16.7 (α-Si), −16.5 (α-Si, see Chart 1). Exact mass (ESI) for the isomeric mixture of **5a** and **6a**: calcd for C$_{39}$H$_{51}$FeNOSi$_2$+Na 684.2751, found 684.2753.

Thermal Reaction of Cp*Fe(CO)(=SiMes$_2$)SiMe$_3$ (1) with MeCN. An isomeric mixture of Cp*Fe(CO)(Me)(CNSiMe$_2$SiMes$_2$-Me) (**5b**) and Cp*Fe(CO)(Me)(CNSiMesMeSiMesMe$_2$) (**6b**) (**5b**: **6b** = 5:6) was obtained in 31% combined yield (52 mg, 0.079 mmol) in a procedure similar to that for **5a** and **6a** by heating (80 °C for 6 h) an acetonitrile (5 mL) solution of **1** (213 mg, 0.381 mmol). Pure **5b** was prepared by the photoreaction of **2** and **3** in acetonitrile (vide infra). Data of **6b** (a mixture of two diastereomers): ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.22, 0.23 (s, FeMe), 0.30, 0.59, 0.61, 0.66, 0.67, 0.74 (s, SiMe), 1.630, 1.635 (s, C$_5$Me$_5$), 2.00, 2.04 (s, *p*-Me), 2.26, 2.29, 2.34, 2.35 (s, *o*-Me), 6.60, 6.64 (s, *m*-H). ^{13}C{^{1}H} NMR (75.5 MHz, C$_6$D$_6$): δ −12.4, −12.0 (FeMe), 1.4, 2.5, 4.7, 4.9 (SiMe), 9.6, 9.7 (C$_5$*Me*$_5$), 21.0 (*p*-CH$_3$), 24.75, 24.77, 25.2, 25.3 (*o*-CH$_3$), 92.74, 92.83 (*C*$_5$Me$_5$), 128.76, 128.79, 129.3, 129.6, 130.4, 138.6, 139.5, 144.0, 144.6 (*C*$_6$H$_2$Me$_3$), 209.7 (FeCNSi), 222.1, 222.3 (CO). Some of these carbon signals seem to be overlapped. ^{29}Si{^{1}H} NMR (59.6 MHz, C$_6$D$_6$): δ −22.7 (β-Si), −21.9 (β-Si), −17.8 (α-Si), −17.6 (α-Si). Exact mass (ESI) for the isomeric mixture of **5b** and **6b**: calcd for C$_{34}$H$_{49}$FeNOSi$_2$ 599.2697, found 599.2699.

Photoreaction of 2 and 3 in the Presence of Benzonitrile: Isolation of Cp*Fe(CO)(Ph)(CNSiMe$_2$SiMes$_2$Me) (5a). A toluene solution (5 mL) of Cp*Fe(CO)$_2$Me (**2**) (90.6 mg, 0.346 mmol), Mes$_2$MeSiSiMe$_2$H (**3**) (119 mg, 0.349 mmol), and PhCN (46 mg, 0.45 mmol) in a Pyrex sample tube with a Teflon vacuum valve was irradiated for 2 h with a 450 W medium-pressure Hg lamp immersed in a water bath (ca. 5 °C). The reaction mixture was degassed every 20 min of irradiation by a conventional freeze–pump–thaw cycle on a vacuum line. After removal of volatiles, the residue was recrystallized from acetonitrile to afford yellow crystals of **5a** in 77% yield (176 mg, 0.266 mmol). Data of **5a**: ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.32 (s, 3H, SiMe$_2$), 0.33 (s, 3H, SiMe$_2$), 0.79 (s, 3H, SiMes$_2$*Me*), 1.52 (s, 15H, C$_5$Me$_5$), 2.05 (s, 3H, *p*-Me), 2.06 (s, 3H, *p*-Me), 2.226 (s, 6H, *o*-Me), 2.232 (s, 6H, *o*-Me), 6.64 (s, 2H, *m*-H), 6.65 (s, 2H, *m*-H), 7.10 (d, J_{HH} = 7.2 Hz, 1H, *p*-H of FePh), 7.19 (t, J_{HH} = 7.2 Hz, 2H, *m*-H of FePh), 7.75 (d, J_{HH} = 7.2 Hz, 2H, *o*-H of FePh). ^{13}C{^{1}H} NMR (75.5 MHz, C$_6$D$_6$): δ 1.4 (α-SiMe), 1.5 (α-SiMe), 2.8 (β-SiMe), 9.7 (C$_5$*Me*$_5$), 21.0 (*p*-Me), 24.7 (*o*-Me), 94.1 (*C*$_5$Me$_5$), 122.1, 127.2, 129.5, 129.6, 132.5, 133.0, 138.6, 143.2, 143.3, 143.7, 165.3 (*C*$_6$H$_2$Me$_3$ or Fe*C*$_6$H$_5$),

207.5 (FeCNSi), 221.3 (CO). ^{29}Si{^{1}H} NMR (59.6 MHz, C$_6$D$_6$): δ −27.6 (SiMes$_2$Me), −8.6 (SiMe$_2$). IR (C$_6$D$_6$): 1924 (ν$_{CO}$), 2017 (ν$_{CN}$) cm^{-1}. MS (EI, 70 eV): 661 (M$^+$, 13), 633 (M$^+$ − CO, 21), 618 (M$^+$ − CO − Me, 4), 421 (M$^+$ − Cp* − CO − Ph, 100). Anal. Calcd for C$_{39}$H$_{51}$FeNOSi$_2$: C, 70.77; H, 7.77; N, 2.12. Found: C, 70.50; H, 7.77; N, 2.06.

Photoreaction of 2 and 3 in the Presence of Acetonitrile: Isolation of Cp*Fe(CO)(Me)(CNSiMe$_2$SiMes$_2$Me) (5b). Cp*Fe-(CO)(Me)(CNSiMe$_2$SiMes$_2$Me) (**5b**) was prepared as a relatively unstable yellow solid in 22% yield (60 mg, 0.10 mmol) by a procedure similar to that for **5a** employing an acetonitrile solution (5 mL) of **2** (144 mg, 0.549 mmol) and **3** (156 mg, 0.458 mmol). Data of **5b**: ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.19 (s, 3H, FeMe), 0.287 (s, 3H, α-SiMe$_2$), 0.293 (s, 3H, α-SiMe$_2$), 0.88 (s, 3H, SiMes$_2$*Me*), 1.62 (s, 15H, C$_5$Me$_5$), 2.07 (s, 6H, *p*-Me), 2.315 (s, 6H, *o*-Me), 2.324 (s, 6H, *o*-Me), 6.68 (s, 4H, *m*-H). ^{13}C{^{1}H} NMR (75.5 MHz, C$_6$D$_6$): δ −12.0 (FeMe), 1.4 (α-SiMe), 1.6 (α-SiMe), 2.8 (β-SiMe), 9.7 (C$_5$*Me*$_5$), 21.1 (*p*-Me), 24.8 (*o*-Me), 92.7 (*C*$_5$-Me$_5$), 130.0 (*C*$_6$H$_2$Me$_3$), 133.0 (*C*$_6$H$_2$Me$_3$), 138.9 (*C*$_6$H$_2$Me$_3$), 143.4 (*C*$_6$H$_2$Me$_3$), 210.0 (FeCNSi), 222.1 (CO). ^{29}Si{^{1}H} NMR (59.6 MHz, C$_6$D$_6$): δ −27.7 (SiMes$_2$Me), −10.2 (SiMe$_2$). IR (C$_6$D$_6$): 1909 (ν$_{CO}$), 2003 (ν$_{CN}$) cm^{-1}. MS (EI): 599 (M$^+$, 9), 571 (M$^+$ − CO, 21), 556 (M$^+$ − CO − Me, 27), 421 (M$^+$ − Cp* − CO − Me, 100). Anal. Calc for C$_{34}$H$_{49}$FeONSi$_2$: C, 68.09; H, 8.23; N, 2.34. Found: C, 67.95; H, 8.27; N, 2.28.

Photoreaction of 2 and 3 in the Presence of Acetonitrile-d_3. In a procedure similar to that of **5b**, Cp*Fe(CO)(CD$_3$)(CNSiMe$_2$-SiMes$_2$Me) (**5b-d_3**) was obtained in 82% NMR yield by irradiation of an acetonitrile-d_3 solution (0.5 mL) containing **2** (10 mg, 0.037 mmol), **3** (10 mg, 0.030 mmol), and an internal standard, Si(SiMe$_3$)$_4$ (1 mg, 0.003 mmol). The spectral data of **5b-d_3** were essentially identical to those of **5b** except the signals for the CD$_3$ group. Data of **5b-d_3**: ^{1}H NMR (300 MHz, CD$_3$CN): δ 0.327 (s, 3H, α-SiMe$_2$), 0.337 (s, 3H, α-SiMe$_2$), 0.81 (s, 3H, SiMes$_2$*Me*), 1.64 (s, 15H, C$_5$-Me$_5$), 2.22 (s, 6H, *p*-Me), 2.24 (s, 12H, *o*-Me), 6.80 (s, 4H, *m*-H). ^{29}Si{^{1}H} NMR (59.6 MHz, CD$_3$CN): δ −28.0 (SiMes$_2$Me), −9.4 (SiMe$_2$).

X-ray Crystal Structure Determination of 5a. The yellow crystals of **5a** suitable for X-ray crystal structure determination were grown by keeping a mixture of hexane and toluene containing **5a** at −30 °C. One of the crystals was mounted on a glass fiber. The intensity data for **5a** were collected on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation to a maximum 2θ value of 55.0 at 150 K. A total of 44 images, corresponding to 220.0° oscillation angles, were collected with two different goniometer settings. Exposure time was 5.0 min per degree. Readout was performed in the 0.100 mm pixel mode. Numerical absorption collections were applied on the crystal shape. The structure of **5a** was solved by the heavy-atom method (DIRDIF94 PATTY)[13] and refined by the block-diagonal least-squares method with individual anisotropic thermal parameters for non-hydrogen atoms. The positions of all hydrogen atoms were calculated and fixed. The final residue R_1 for reflections (3316) with $I > 4σ(I)$ was R_1 = 0.099. All calculations were performed using the teXsan crystal structure analysis package.[14] Crystallographic information has been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 215874 (**5a**)).

(13) Beurskens, P. T.; Admireal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Isreal, R.; Smits, J. M. M. *The DIRDIF-94 program system*; Technical Report of the Crystallography Laboratory; University of Nijimegen: The Netherlands, 1994.

(14) *teXsan*, Crystal Structure Analysis Package; Molecular Structure Corporation, 1985 and 1999.