Silyl(silylene)–Iron Complexes

Direct Evidence for Extremely Facile 1,2- and 1,3-Group Migrations in an $FeSi_2$ System**

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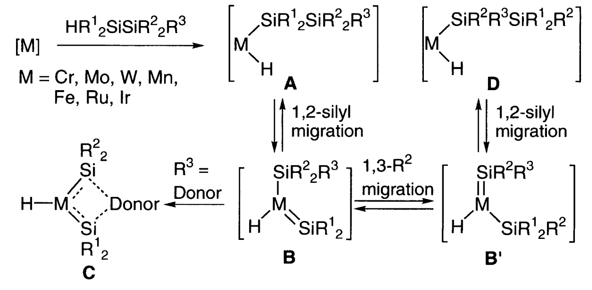
The formation and high reactivity of transition-metal–element multiple bonds plays an important role in transition-metal-catalyzed reactions, in particular, by facilitating the cleavage and formation of usually robust bonds. Olefin metathesis is a typical and very useful example of this type of reaction, in which carbene complexes, which have a metal–carbon double bond, are not only key intermediates but may also act as high-performance catalysts.[1] In contrast to metal–carbon multiple bonds, metal–element multiple bonds, where the element is from the third or subsequent row of the periodic table, have been much less widely investigated. Among them, silylene complexes, which possess a metal–silicon double bond, have been the most extensively studied,[2–9] but the mechanisms of their reactions remain rather unclear.

Both ourselves and Pannell's group have insisted, through the generation of silyl(silylene) complexes with transition metals from groups 6 to 9 and the preparation of their donor-stabilized forms, that 1,2- and 1,3-group migrations of these systems (Scheme 1) occur very easily under mild conditions, and cause the metal-catalyzed oligomerization/deoligomerization, isomerization, and redistribution of organosilicon



Scheme 1. Illustrating the 1,2- and 1,3-group migrations in silyl(silylene) complexes with metals of groups 6 to 9.

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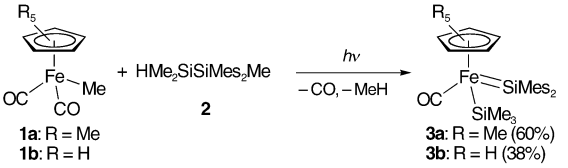
compounds.[2,3,10–12] In fact, this mechanism was notably successful in explaining the redistribution reactions of various organosilicon, -germanium, and -phosphorus systems.[13–15] We have previously given direct experimental evidence for 1,2-silyl-migration from Si to the metal M (**A**→**B** or **D**→**B′**) via isolating complexes of the type **B′** or **C**, which are formed in reactions of complexes of type **A** or **D**.[2,3,16] Furthermore, we have observed fluxional behavior in the 1,3-migration of methyl groups on an externally donor-stabilized silyl(silylene)iron complex [Cp(CO)Fe(=$SiMe_2$←HMPA)$SiMe_3$] (HMPA = hexamethyl phosphoramide) by variable-temperature NMR spectroscopy.[17] In this process, we assumed that the coordinated HMPA dissociates at elevated temperatures to generate a donor-free silyl(silylene) complex. We now give direct evidence for 1,3-alkyl migration (**B**→**B′** and vice versa) and 1,2-silyl migration from M to Si (**B**→**A** or **B′**→**D**) by employing newly synthesized, donor-free silyl(silylene)iron complexes.

Photolysis of [Cp′Fe$(CO)_2$Me] (**1a**: Cp′ = η^5-C_5Me_5 (Cp*); **1b**: Cp′ = η^5-C_5H_5 (Cp)) in the presence of $HSiMe_2SiMes_2Me$ (**2**; Mes = mesityl (2,4,6-trimethylphenyl)) produced the first donor-free silyl(silylene)iron complexes [Cp′Fe(CO)(=$SiMes_2$)$SiMe_3$] (**3a**: Cp′ = Cp*, 60%; **3b**: Cp′ = Cp, 38% yield, calculated by NMR spectroscopy [Eq. (1)]). Complex **3a** could be isolated as orange crystals in 40% yield, whereas isolation of **3b** was unsuccessful because of its extreme instability. We have previously synthesized the tungsten analogue of **3a** by a similar method, but the chemistry has not been thoroughly investigated.[16]



(1)

The molecular structure of **3a** is shown in Figure 1.[18] The two mesityl groups are on the silylene ligand, while all of the three methyl groups are on the silyl ligand. The iron–silylene bond (Fe–Si(1) 2.154(1) Å) is about 9% shorter than the iron–silyl bond (Fe–Si(2) 2.343(2) Å) and is the shortest reported bond of this type.[19] The silylene silicon atom is tricoordinate and its geometry is almost planar (sum of the three bond angles around Si(1) = 359.3 (2)°). No intermolecular bonding interaction was found. The ^{29}Si NMR spectra of **3a** and **3b** show signals for the dimesitylsilylene ligand at extremely low field (365.8 ppm for **3a** and 372.0 ppm for **3b**), which is characteristic of the donor-free dialkyl- or diarylsilylene complexes.[5,16] Also present are the resonances for the trimethylsilyl ligand (28.4 ppm for **3a** and 31.0 ppm for **3b**). These data unambiguously demonstrate the donor-free silyl(silylene)iron structures. In each of the ^{1}H NMR spectra of **3a** and **3b**, all the four *o*-Me groups, four *m*-H atoms, and two *p*-Me groups in two mesityl groups are inequivalent at room temperature. Apparently, the extremely congested structures of **3a** and **3b** lead to hindered rotation around both the Fe=Si and the Si–C(mesityl) bonds.

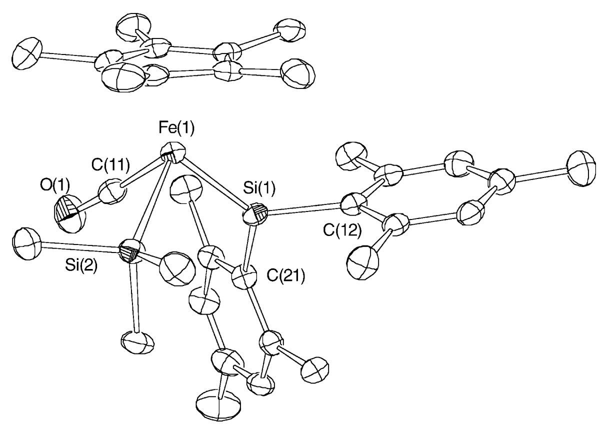
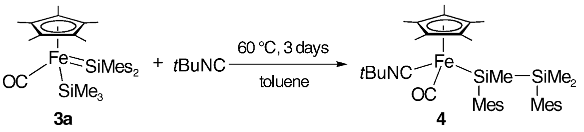


Figure 1. ORTEP drawing of **3a** showing thermal ellipsoids at the 50% probability level. Selected bond lengths [Å] and angles [°]: Fe(1)-Si(1) 2.154(1), Fe(1)-Si(2) 2.343(1), Fe(1)-C(11) 1.724(4); Si(1)-Fe(1)-Si(2) 93.15, Fe(1)-Si(1)-C(12) 127.8(1), Fe(1)-Si(1)-C(21) 127.2(1), C(12)-Si(1)-C(21) 104.3(2).

Sharma and Pannell previously reported that the photolysis of linear oligosilanyl–[Fe$(CO)_2$Cp] complexes containing more than three silicon atoms produces highly branched, tris(silyl)silyl iron complexes in high yields, for example, [{$Me_3Si(Me_2Si)_3$}Fe$(CO)_2$Cp] is converted to [$(Me_3Si)_3$Si–Fe$(CO)_2$Cp] on irradiation.[12] In this reaction, the 1,2-silyl migration from the Fe center to the silylene silicon atom on the silyl(silylene) iron intermediates (corresponding to **B**→**A** or **B′**→**D**; Scheme 1) could play an important role.

To confirm this hypothesis, thermolysis of **3a** in the presence of several two-electron-donor ligands was carried out. As a result, when **3a** was heated to 80 °C for 6 h in the presence of *t*BuNC, a disilanyl complex [Cp*Fe(CO)(CN*t*Bu)SiMesMeSiMesMe$_2$] (**4**) was isolated as a main product in 25% yield [Eq. (2)]. The ^{29}Si NMR signals of **4** appear in the normal range of disilanyl iron complexes (9.5 ppm for Fe–Si and −11.2 ppm for terminal Si atoms). The molecular structure of **4** is shown in Figure 2.[18] A *t*BuNC molecule is terminally coordinated to the iron center, and each of the α- and β-Si atoms of the disilanyl ligand is coordinated to a mesityl group. The Fe–Si(1) and Si(1)–Si(2) bond lengths are 2.4107(7) and 2.4004(9) Å, respectively, which are normal values for single bonds.



(2)

A mechanism that can rationalize the reactions in Equations (1) and (2) is illustrated in Scheme 2. From **1a**, successive CO dissociation, oxidative addition of **1**, methane reductive elimination, 1,2-silyl migration, and 1,3-methyl migration occur to afford **3a**. Three isomeric donor-free silyl(silylene) complexes (**3a**, **3a′**, and **3a″**) are in rapid

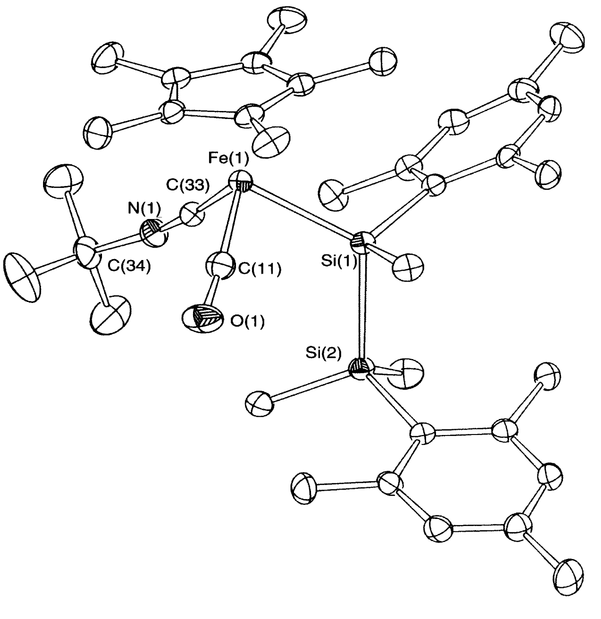
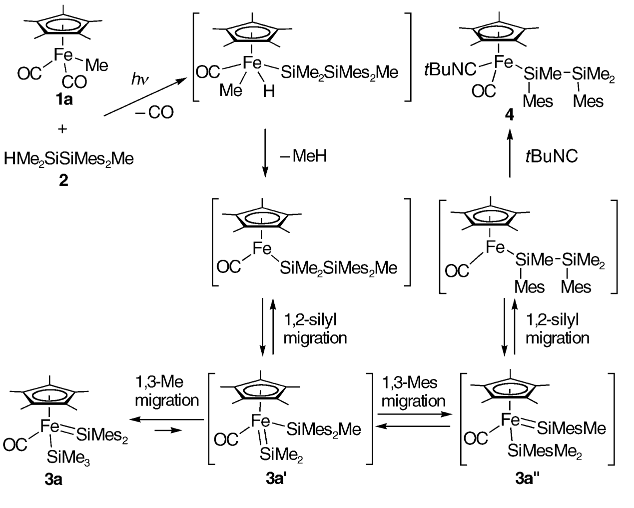


Figure 2. ORTEP drawing of **4** showing thermal ellipsoids at the 50% probability level. Selected bond lengths [Å] and angles [°]: Fe(1)-Si(1) 2.4107(7), Fe(1)-C(11) 1.732(2), Fe(1)-C(33) 1.808(2), Si(1)-Si(2) 2.4004(9), N(1)-C(33) 1.174(3); Fe(1)-Si(1)-Si(2) 118.74(3), Si(1)-Fe(1)-C(11) 84.23(9), Si(1)-Fe(1)-C(33) 94.92(7), C(11)-Fe(1)-C(33) 92.5(1), Fe(1)-C(33)-N(1) 173.4(2), C(33)-N(1)-C(34) 162.0(3).



Scheme 2. A mechanism for the formation of [Cp*Fe(CO)(=SiMes$_2$)-SiMe$_3$] (**3a**) and [Cp*Fe(CO)(CN*t*Bu)SiMesMeSiMesMe$_2$] (**4**).

equilibrium at room temperature, where **3a** is the major and only observable isomer. When this equilibrium mixture is heated in the presence of *t*BuNC, 1,2-migration of the silyl ligand onto the silylene ligand followed by coordination of *t*BuNC to the unsaturated iron center occurs to produce **4**. It should be noted that both **3a** and **4** take the structures that obviously minimize the steric repulsion between the bulky groups, namely, the two mesityl groups and a pentamethylcyclopentadienyl group. In other words, **3a** and **4** are the thermodynamically controlled products. Both the formation of **3a** and its conversion to **4** involves 1,2-silyl migration and 1,3-alkyl and/or aryl migration processes. These are considered to be concerted processes with low energy barriers.[20] Importantly, through the latter process, usually robust Si–C bonds readily cleave under extremely mild conditions: The typical bond dissociation energy of the Si–C single bond is 301 kJ mol^{-1}, which is comparable to that of the C–C single bond (346 kJ mol^{-1}).[21]

In this paper, we have provided the most straightforward evidence for extremely facile 1,2- and 1,3-group migrations in silyl(silylene) complex systems. These observations clearly show how organosilicon species bound to a transition-metal center can change their structures in an amazingly dynamic fashion through extremely facile Si–C and Si–Si bond fission and formation processes. A more detailed elucidation of the dynamic behavior is underway.

Experimental Section

3a: A pentane solution (3 mL) of [Cp*Fe(CO)$_2$Me] (**1a**; 1.02 g, 3.89 mmol) and HSiMe$_2$SiMes$_2$Me (**2**; 1.01 g, 2.96 mmol) in a pyrex sample tube with a teflon vacuum valve was irradiated for 80 min with a 450 W medium-pressure Hg lamp immersed in a water bath (4 °C). The reaction mixture was degassed every 20 min by a conventional freeze-pump-thaw cycle on a vacuum line. The reaction mixture was filtered through a glass filter and volatiles were removed from the filtrate under reduced pressure. The residue was recrystallized from pentane at –30 °C to afford orange crystals of [Cp*Fe(CO)-(=SiMes$_2$)SiMe$_3$] (**3a**) in 40% yield (0.660 g, 1.18 mmol). ^{1}H NMR (300 MHz, [D$_6$]benzene): $\delta = 0.59$ (s, 9H, SiMe$_3$), 1.56 (s, 15H, C$_5$Me$_5$), 2.05 (s, 3H, *o*-Me), 2.10 (s, 3H, *o*-Me), 2.12 (s, 3H, *o*-Me), 2.15 (s, 3H, *o*-Me), 2.74 (s, 3H, *p*-Me), 3.05 (s, 3H, *p*-Me), 6.51 (s, 1H, *m*-H), 6.56 (s, 1H, *m*-H), 6.79 (s, 1H, *m*-H), 6.86 ppm (s, 1H, *m*-H); ^{13}C{^{1}H} NMR (75.5 MHz, [D$_6$]benzene): $\delta = 9.5$ (SiMe$_3$), 10.1 (C$_5$*Me*$_5$), 21.1 (*p*-Me), 23.7 (*o*-Me), 24.0 (*o*-Me), 24.7 (*o*-Me), 24.9 (*o*-Me), 93.7 (*C*$_5$Me$_5$), 128.7 (*C*$_6$H$_2$Me$_3$), 129.2 (*C*$_6$H$_2$Me$_3$), 138.7 (*C*$_6$H$_2$Me$_3$), 138.9 (*C*$_6$H$_2$Me$_3$), 139.2 (*C*$_6$H$_2$Me$_3$), 139.3 (*C*$_6$H$_2$Me$_3$), 142.5 (*C*$_6$H$_2$Me$_3$), 142.8 (*C*$_6$H$_2$Me$_3$), 145.3 (*C*$_6$H$_2$Me$_3$), 145.6 (*C*$_6$H$_2$Me$_3$), 220.2 ppm (CO); ^{29}Si{^{1}H} NMR (59.6 MHz, [D$_6$]benzene): $\delta = 28.4$ (SiMe$_3$), 365.8 ppm (SiMes$_2$); IR ([D$_6$]benzene solution): $\tilde{\nu} = 1905$ cm^{-1} (s, ν_{CO}); MS (EI, 70 eV) 558 (M^+, 8), 543 (M^+–CH$_3$, 30), 515 (M^+–CH$_3$-CO, 12), 73 (SiMe$_3$, 100); elemental analysis calcd (%) for C$_{32}$H$_{46}$FeOSi$_2$: C 68.79, H 8.30; found: C 69.07, H 8.41.

4: A toluene solution (5 mL) of **3a** (0.103 g, 0.184 mmol) and *t*BuNC (0.0730 g, 0.878 mmol) in a pyrex tube with a teflon vacuum valve was heated to 80 °C for 6 h. After removal of volatiles, the yellow residue was recrystallized from toluene/hexane to afford yellow crystals of [Cp*Fe(CO)(CN*t*Bu)SiMesMeSiMesMe$_2$] (**4**) in 25% yield (0.030 g, 0.047 mmol). ^{1}H NMR (300 MHz, [D$_6$]benzene): $\delta = 0.69$ (s, 3H, SiMes*Me*$_2$), 0.97 (s, 3H, SiMes*Me*$_2$), 1.09 (s, 3H, SiMes*Me*), 1.46 (s, 15H, C$_5$Me$_5$), 2.15 (s, 3H, *p*-Me), 2.23 (s, 3H, *p*-Me), 2.45 (s, 6H, *o*-Me), 2.52 (s, 3H, *o*-Me), 2.64 (s, 3H, *o*-Me), 6.78 (s, 2H, *m*-H), 6.84 (s, 1H, *m*-H), 6.88 ppm (s, 1H, *m*-H); ^{13}C{^{1}H} NMR (75.5 MHz, [D$_6$]benzene): $\delta = 6.4$ (Si*Me*), 6.7 (Si*Me*), 9.9 (C$_5$*Me*$_5$), 11.7 (Si*Me*), 21.1 (C$_6$H$_2$*Me*$_3$), 25.8 (C$_6$H$_2$*Me*$_3$), 26.8 (C$_6$H$_2$*Me*$_3$), 28.0 (C$_6$H$_2$*Me*$_3$), 31.2 (C*Me*$_3$), 56.3 (*C*Me$_3$), 92.7 (*C*$_5$Me$_5$), 128.9 (*C*$_6$H$_2$Me$_3$), 129.1 (*C*$_6$H$_2$Me$_3$), 129.3 (*C*$_6$H$_2$Me$_3$), 130.1 (*C*$_6$H$_2$Me$_3$), 136.3 (*C*$_6$H$_2$Me$_3$), 136.9 (*C*$_6$H$_2$Me$_3$), 137.2 (*C*$_6$H$_2$Me$_3$), 140.3 (*C*$_6$H$_2$Me$_3$), 144.5 (*C*$_6$H$_2$Me$_3$), 145.3 (*C*$_6$H$_2$Me$_3$), 176.6 (Fe*C*N), 222.3 ppm (CO); ^{29}Si{^{1}H} NMR (59.6 MHz, [D$_6$]benzene): $\delta = -11.2$ (SiMesMe$_2$), 9.5 ppm (SiMesMe); IR ([D$_6$]benzene solution): $\tilde{\nu} = 1907$ cm^{-1} (s) (ν_{CO}); MS (EI, 70 eV) 641 (M^+, 0.3), 626 (M^+–Me, 0.6), 556 (M^+–CO–*t*Bu, 4), 515 (M^+–CO–CN*t*Bu–Me, 7), 464

(M^+−CO−2Me−Mes, 100); elemental analysis calcd (%) for $C_{37}H_{55}FeONSi_2$: C 69.24, H 8.64, N 2.18; found: C 69.31, H 8.66, N 2.28.

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[18] **3a**: monoclinic; $P2_1/c$; $a = 10.4593(2)$, $b = 18.3566(6)$, $c = 16.0338(4)$ Å, $\beta = 96.5724(7)°$; $V = 3058.2(1)$ Å^3; $Z = 4$; $C_{32}H_{46}FeOSi_2$; $T = 150$ K, 26965 reflections, 6692 independent ($R_{int} = 0.043$); $R1 = 0.046$ ($I > 3\sigma(I)$), $Rw = 0.106$; $\mu = 5.93$ cm^{-1}; Full-matrix least-squares on F^2. **4**: monoclinic; $P2_1$; $a = 8.8296(2)$, $b = 20.6795(5)$, $c = 9.9852(2)$ Å, $\beta = 99.970(1)°$; $V = 1795.68(7)$ Å^3; $Z = 2$; $C_{37}H_{55}FeNOSi_2$; $T = 150$ K, 17660 reflections, 4233 independent ($R_{int} = 0.036$); $R1 = 0.027$ ($I > 2\sigma(I)$), $Rw = 0.063$; $\mu = 5.14$ cm^{-1}; Full-matrix least-squares on F^2. CCDC-215618 (**3a**) and CCDC-215619 (**4**) contains 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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