Iron Complexes of (*E*)- and (*Z*)-1,2-Dichlorodisilenes

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Olefin transition-metal complexes have been studied extensively as important reactive intermediates in various catalytic reactions,[1] and their structures and bonding nature are well understood on the basis of the Dewar−Chatt−Duncanson model.[2] In contrast, very few studies have been reported on the synthesis, structure, and reactions of the silicon congeners of olefin complexes, transition-metal complexes of η^2-disilenes[3−6] and η^2-silaethenes.[7] We herein report the synthesis and unique isomerization of iron complexes of (*E*)- and (*Z*)-1,2-dichlorodisilenes, **1E** and **1Z**, respectively, which constitute not only the first disilene complexes with *E*,*Z*-isomerism but also the first complexes with halogen-substituted disilene ligands.[8]

Disilene iron complexes **1E** and **1Z** were synthesized by the reaction of the corresponding 2,2,3,3-tetrachlorotetrasilane **2** with an excess amount of $K_2Fe(CO)_4$[9] in DME at room temperature for 2 days (eq 1). Separation by flash column chromatography and then recrystallization afforded pure **1E** and **1Z** as yellow crystals in 28 and 9% yields, respectively.[10]

(1)
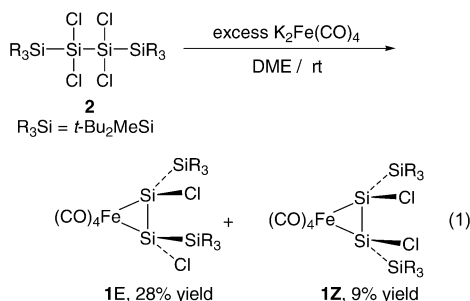
Disilene complexes **1E** and **1Z** were characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopies and X-ray crystallography.[11] The molecular structure of **1Z** is shown in Figure 1. Complexes **1E** and **1Z** have (*E*)- and (*Z*)-1,2-dichlorodisilenes as η^2-ligands, respectively, and adopt approximate octahedral geometry around the iron center. The averaged distance between iron and silicon in **1Z** is 2.436(9) Å, which is longer than the Si−Fe distances in the reported silyl−iron complexes (2.197−2.422 Å).[12] The Si1−Si2 bond distance is 2.2726(7) Å, which is ∼0.1 Å longer than that of the reported (*E*)-1,2-dichlorodisilene (2.163(4) Å)[8] but shorter than those of the usual Si−Si single bonds (2.335−2.697 Å).[13]

The extent of the pyramidalization at Si1 and Si2 is also characteristic in disilene complex **1Z**. The substituents of the disilene ligand are significantly bent away from the iron; the bent angle defined as an angle between Cl1−Si1−Si3 plane and the plane perpendicular to the Fe−Si1−Si2 plane in **1Z** is ∼30°. On the basis of the structural parameters, **1Z** is characterized as a metallacyclopropane rather than a disilene π complex.[14] A similar metallacyclopropane structure was observed for **1E**.[11]

When the reaction of **2** with $K_2Fe(CO)_4$ in DME was monitored by ^1H NMR spectroscopy, the complete consumption of the starting tetrasilane **2** was observed at the reaction time of 22 h. During the
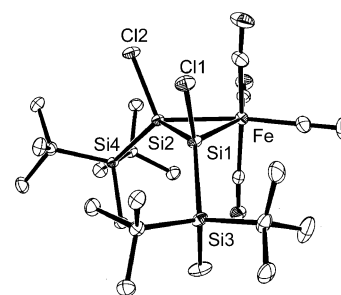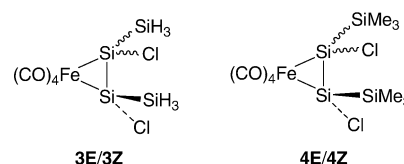

Figure 1. Molecular structure of (*Z*)-disilene complex **1Z** determined by X-ray crystallography (30% thermal probability ellipsoid). Hydrogen atoms are omitted for clarity: Selected bond lengths (Å) and bond angles (deg): Fe−Si1 2.4447(5), Fe−Si2 2.4269(7), Si1−Si2 2.2726(7), Si1−Cl1 2.1013-(7), Si2−Cl2 2.0949(6), Si3−Si1−Cl1 106.00(3), Si2−Si1−Si3 133.42-(3), Cl1−Si1−Si2 109.00(3).

Chart 1

reaction times between 4 (45% conversion) and 12 h (88% conversion), the isomer ratio **1Z**/**1E** changed from 10 to 5.0, while the total yield of **1E** and **1Z** was almost constant (73−76% yields). The results indicate that the reaction gives preferably **1Z** at the initial stage but **1Z** isomerizes slowly to more stable isomer **1E**.

A kinetic study of the isomerization from **1Z** to **1E** was performed using pure **1Z** (eq 2) in detail in THF-d_8 and benzene-d_6. In THF-d_8, the isomerization obeyed the first-order kinetics between 296 and 323 K; the rate constant (k_1) was 3.34×10^{-4} s^{-1} at 323 K and the activation enthalpy ($\Delta H^\ddagger$) and activation entropy ($\Delta S^\ddagger$) were determined to be 20.2 kcal mol^{-1} and −7.4 cal mol^{-1} K^{-1}, respectively. The isomerization was very slow in benzene-d_6 with $k_1 = 4.66 \times 10^{-7}$ s^{-1} at 323 K.

$$\mathbf{1Z} \xrightarrow[\text{THF-}d_8]{\Delta, \, k_1} \mathbf{1E} \qquad (2)$$

Since **1Z** was not detected in the ^1H NMR spectrum at the end of the isomerization, **1E** should be >3 kcal mol^{-1} more stable than **1Z**. Theoretical calculations for model iron−disilene complexes **3E**/**3Z** and **4E**/**4Z** (Chart 1) at the DFT/B3LYP level[15] showed that **4E** is 1.5 kcal mol^{-1} more stable than **4Z**, while **3E** is 0.49 kcal mol^{-1} less stable than **3Z**, suggesting that the relative stability is affected by the steric bulkiness of the silyl substituents. The relative stability estimated for **1E**/**1Z** would be reasonable on this basis.

A mechanism involving silylene−iron complex **5** as a key intermediate is proposed for the preferable formation of **1Z** during the synthetic reaction (eq 1) as shown in Scheme 1. In silylene

Scheme 1
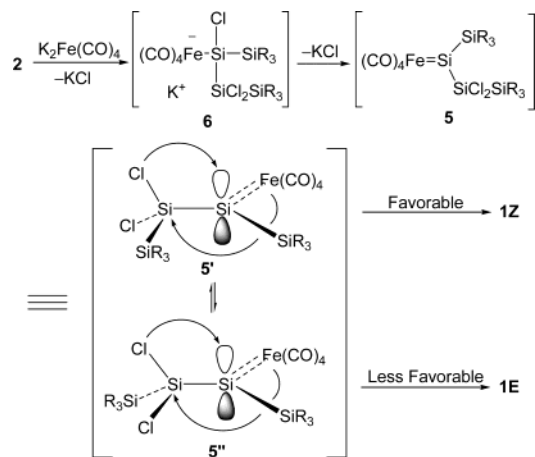
complex **5**, β-chlorine migration may take place from conformation **5′** or **5″** having coplanar geometry between the migrating chlorine atom and a pπ-type orbital of α-silicon atom. The dyotropic rearrangement of **5′** to **1Z** would be sterically more favorable than that of **5″** to **1E**, because the severe steric repulsion between a trialkylsilyl group and Fe(CO)$_4$ group is caused during the latter rearrangement. A straightforward mechanism involving the formation of the corresponding 1,2,2-trichlorodisilanyliron anionic complex **6** followed by the nucleophilic attack of the anionic iron to the β-silicon atom cannot explain the observed diastereoselectivity in the synthetic reaction.

In accord with the above mechanism, it has been reported that the reaction of Na$_2$Fe(CO)$_4$ with bis(*tert*-butoxy)dichlorosilane gives the corresponding silylene–iron complex coordinated by tetrahydrofuran[16] and that the reaction of Na$_2$Fe(CO)$_4$ with 1,2-dichlorotetramethyldisilane afforded the corresponding 2-chlorodisilanyliron anionic complex instead of the corresponding ferradisilacyclopropane.[17] Since silylene–iron complex **5** can be stabilized by complexation to a Lewis base such as THF and DME, the isomerization of **5** to **1Z/1E** would be accelerated in THF.

While the reverse reaction of **1Z** to **5′** followed by the rotation to **5″** and then the dyotropic rearrangement would lead to the thermodynamically favorable isomer **1E**, some other possible mechanisms emerge for the *Z*-to-*E* isomerization. The isomerization may occur (1) during the dissociation–association equilibrium between the corresponding disilene and Fe(CO)$_4$,[18] (2) during the removal of one CO from **1Z** and then Si–Si bond cleavage forming the corresponding bis-silylene complex followed by the reverse Si–Si bond formation, and (3) during the heterolytic Fe–Si bond cleavage forming the corresponding zwitterionic intermediate and then recombination. However, preliminary theoretical calculations have shown that any of the reactions 1–3 is unlikely.[19]

Supporting Information Available: X-ray structural information on **1E** and **1Z** (CIF) and the details of the theoretical calculations, synthesis, and kinetics for the isomerization. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) For the details of the synthesis of **1E** and **1Z**, see the Supporting Information. **1E**: yellow crystals; ^{1}H NMR (400 MHz, C$_6$D$_6$, δ) 0.22 (s, 6H), 1.26 (s, 18H), 1.27 (s, 18H); ^{13}C NMR (100 MHz, C$_6$D$_6$, δ) −5.3, 22.5, 22.8, 29.5, 29.6, 206.4; ^{29}Si NMR (79 MHz, C$_6$D$_6$, δ) 21.8 [*Si*Me(*t*-Bu)$_2$], 27.4 (*Si*–Fe). HRMS calcd for C$_{22}$H$_{42}$Cl$_2$FeO$_4$Si$_4$ − CO: 580.0931. Found: 580.0932. MS (EI, 70 eV): *m/z* 580 (M$^+$ − CO, 2.3), 524 (M$^+$ − CO − ^{t}Bu, 10.9), 213 (100). **1Z**: yellow crystals; ^{1}H NMR (400 MHz, C$_6$D$_6$, δ) 0.03 (s, 6H), 1.21 (s, 18H), 1.26 (s, 18H); ^{13}C NMR (100 MHz, C$_6$D$_6$, δ) −5.8, 22.4, 22.7, 29.5, 29.7, 206.4; ^{29}Si NMR (79 MHz, C$_6$D$_6$, δ) 19.2 [*Si*Me(*t*-Bu)$_2$], 29.0 (*Si*–Fe).

(11) The refinement of the structure of **1E** was achieved only with the *R* value of 0.149, because the recrystallization of **1E** with various solvents always gave thin scales. The analysis, however, was sufficient for assigning atom connectivity and the structural characteristics of **1E**. Crystal data for **1Z** (173 K): C$_{22}$H$_{42}$Cl$_2$FeO$_4$Si$_4$; FW 609.67; monoclinic; space group $P2_1/c$ (No. 14); $a = 15.376(3)$ Å, $b = 11.174(2)$ Å, $c = 18.510(3)$ Å, $β = 100.535(2)°$, $V = 3126.7(10)$ Å^3, Density (calcd) 1.295 Mg/m^3, $Z = 4$. Final R indices $R = 0.035$, $R_w = 0.118$ for all data, 6983 unique reflections. For the details of the X-ray analysis of **1E** and **1Z**, see the Supporting Information.

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(19) The dissociation of **3Z** to the corresponding disilene and Fe(CO)$_4$ and the removal of one CO from **3Z** are 34.0 and 43.5 kcal mol^{-1} endothermic, respectively, at the B3LYP/LanL2DZ//RHF/LanL2DZ level, while the reaction energy for the proposed dyotropic rearrangement is only +10.5 kcal mol^{-1}. No minimum is observed for the zwitterionic intermediate formed via the process (3). The energy for a related reaction of (CO)$_4$Fe(SiH$_3$)$_2$ forming [(CO)$_4$FeSiH$_3$]$^-$ and SiH$_3$$^+$ is 152 kcal mol^{-1}, suggesting that the process (3) will be improbable even if the solvation is taken into account. To elucidate the detailed mechanisms, more sophisticated calculations including a search for the transition states will be required. Details of the present calculations are given in the Supporting Information.

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