

## Isolation of a Reactive Iron Silyl Silylene by Complexation to Chromium Carbonyl: ( $\eta^5\text{-C}_5\text{R}_5$ )Fe(CO)SiMe<sub>2</sub>( $\eta^6\text{-C}_6\text{H}_5\text{Cr(CO)}_2$ )( $\mu\text{-SiMe}_2$ )

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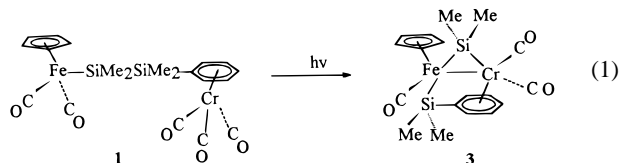
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The chemistry of the silicon–silicon bond in transition-metal-substituted oligosilanes has recently received considerable attention.<sup>1</sup> Oligosilanes substituted with the ( $\eta^5\text{-C}_5\text{H}_5$ )Fe(CO)<sub>2</sub>-(Fp-) system have been observed to exhibit silylene eliminations,<sup>2a–c</sup> migrations from the transition metal centers to ancillary ligands,<sup>2a</sup> and isomerizations.<sup>2d,e</sup> The photochemical isomerizations, and ultimate conversion of isomeric di- and trisilane-substituted iron complexes Fp(SiMe<sub>2</sub>)<sub>n</sub>SiR<sub>3</sub> (*n* = 1, 2)<sup>2c</sup> to the corresponding Fp-monosilanes, are proposed to occur *via* iron silyl silylene intermediates, e.g., ( $\eta^5\text{-C}_5\text{H}_5$ )Fe(CO)(=SiMe<sub>2</sub>)-SiR<sub>3</sub>, undergoing a series of 1,3-alkyl/aryl/silyl migrations.<sup>2</sup> Taking advantage of such chemistry, silylene formation from, and isomerization of, oligosilanes using FpSiMe<sub>3</sub> as catalyst has been demonstrated.<sup>3</sup> Recently, 1,3-migrations in metal silyl silylene intermediates were found to be involved in palladium-catalyzed isomerizations of alkoxyoligosilanes<sup>4a</sup> and the isomerization of tungsten<sup>4b</sup> and iridium-substituted<sup>4c</sup> oligosilanes.

Such silyl silylene intermediates have been observed spectroscopically in solution,<sup>5ab</sup> and intramolecularly alkoxy-stabilized iron silylene complexes were reported by the Ogino group.<sup>6</sup> However, these latter complexes exhibit no further photochemical reactivity. Since transition-metal silylene complexes are now well-established, both base-stabilized<sup>7</sup> and base-free,<sup>8</sup> including a recent platinum iron–silylene complex,<sup>8e</sup> the inability to isolate the reactive intermediate iron silyl silylene complexes posed a drawback to the proposed mechanisms.

We have synthesized bimetallic disilyl complexes containing iron and chromium, ( $\eta^5\text{-C}_5\text{R}_5$ )Fe(CO)<sub>2</sub>SiMe<sub>2</sub>SiMe<sub>2</sub>( $\eta^6\text{-C}_6\text{H}_5\text{Cr(CO)}_3$ ) (R = H (**1**), R = Me (**2**)), by a high-yield thermal reaction between the appropriate iron disilane complex and Cr(CO)<sub>6</sub> in a refluxing *n*-butyl ether/THF (80:20) solution.<sup>9</sup> The Cr(CO)<sub>3</sub> complexes are photochemically labile. Irradiation of a C<sub>6</sub>D<sub>6</sub> solution of **1** with medium-pressure Hg lamp in a sealed NMR tube resulted in the formation of a silylene-bridged binuclear complex [( $\eta^5\text{-C}_5\text{H}_5$ )Fe(CO)SiMe<sub>2</sub>( $\eta^6\text{-C}_6\text{H}_5\text{Cr(CO)}_2$ )-( $\mu\text{-SiMe}_2$ ) (**3**)], isolated in 45% yield, eq 1.<sup>9</sup>



Irradiation of the pentamethylcyclopentadienyl (Cp\*) analog **2** resulted in the formation of the corresponding silylene-bridged complex **4**. We have obtained crystals of **4** suitable for X-ray diffraction, and the resulting structure is illustrated in Figure 1.<sup>10</sup>

The coordination pattern illustrates a Fe–Si–Cr cyclic ring structure and the tendency of the Cr to bond preferentially to the Si end of the Fe–Si bond. The Fe–Si silylene bond of 2.352(3) Å is only marginally shorter than the other Fe–Si bond length of 2.368(3) Å, and both are longer than those of the intramolecularly base-stabilized Cp\*Fe(CO)SiMe<sub>2</sub>-OMe-SiMe<sub>2</sub>, 2.222 and 2.207 Å.<sup>6</sup> However, they are close to those of various dimeric bridging silylene iron complexes, which range from 2.251 to 2.421 Å.<sup>11,12</sup> The Cr–Si bond distance of 2.387(4) Å is similar to those of base-stabilized silylene chromium com-

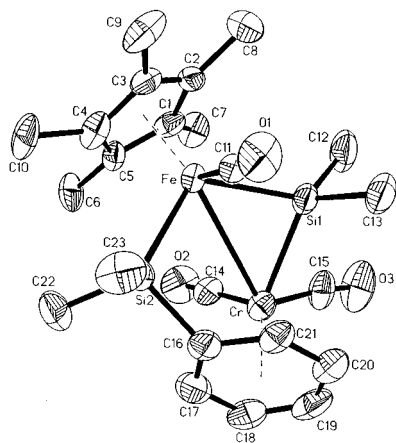
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- (9) Selected data for **1**. IR (hexane, cm<sup>-1</sup>): 2000.3, 1949.7 (Fe–CO); 1976.5, 1911.1 (Cr–CO). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.33, 0.40 (SiMe<sub>2</sub>); 3.99 (s,  $\eta^5\text{-C}_5\text{H}_5$ ); 4.05, 4.47, 4.90 (m,  $\eta^6\text{-C}_6\text{H}_5$ ). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ -3.0, 3.4 (SiMe<sub>2</sub>); 83.1 ( $\eta^5\text{-C}_5\text{H}_5$ ); 90.9, 94.7, 98.9, 101.8 ( $\eta^6\text{-C}_6\text{H}_5$ ); 215.3 (Fe–CO); 233.9 (Cr–CO). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>): δ 16.1 (Fe–Si); -10.1. Anal. Calcd for C<sub>20</sub>H<sub>22</sub>CrFeO<sub>5</sub>Si<sub>2</sub>: C, 47.43; H, 4.38. Found: C, 47.17; H, 4.74. Selected Data for **2**. IR (hexane, cm<sup>-1</sup>): 1980.0, 1928.4 (Fe–CO); 1973.3, 1906.4 (Cr–CO). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.37, 0.58 (SiMe<sub>2</sub>); 1.41 (s, CH<sub>3</sub>); 4.43, 4.64, 5.03 (m,  $\eta^6\text{-C}_6\text{H}_5$ ). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ -2.54, 2.62 (SiMe<sub>2</sub>); 9.73 (CH<sub>3</sub>); 90.9, 94.6, 94.9, 99.5, 103.4 (C<sub>5</sub>Me<sub>5</sub> +  $\eta^6\text{-C}_6\text{H}_5$ ); 217.6 (Fe–CO); 234.2 (Cr–CO). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>): δ 14.3 (Fe–Si); -10.0. Anal. Calcd for C<sub>25</sub>H<sub>32</sub>CrFeO<sub>5</sub>Si<sub>2</sub>: C, 52.08; H, 5.59. Found: C, 51.37; H, 5.75. Selected Data for **6**: IR (hexane, cm<sup>-1</sup>): 1979.4, 1927.7 (Fe–CO); 1975.2, 1910.4 (Cr–CO). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.72 (SiMe<sub>2</sub>); 1.30 (s, CH<sub>3</sub>); 4.29–4.72, 4.92, 5.36 (m,  $\eta^6\text{-C}_6\text{H}_5$ ). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 9.6 (SiMe<sub>2</sub>); 10.6 (CH<sub>3</sub>); 89.7, 94.9, 95.3, 98.4, 99.5 (C<sub>5</sub>Me<sub>5</sub> +  $\eta^6\text{-C}_6\text{H}_5$ ); 217.4 (Fe–CO); 234.3 (Cr–CO). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>): δ 39.5. Anal. Calcd for C<sub>23</sub>H<sub>26</sub>CrFeO<sub>5</sub>Si: C, 53.29; H, 5.05. Found: C, 52.73; H, 4.98. Selected data for **7**. IR (hexane, cm<sup>-1</sup>): 1983.8, 1931.9 (Fe–CO); 1971.9, 1907.8 (Cr–CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.28, (SiMe<sub>3</sub>); 0.62 (SiMe); 1.67 (CH<sub>3</sub>); 5.11, 5.45, 5.59 ( $\eta^6\text{-C}_6\text{H}_5$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 1.12, (SiMe<sub>3</sub>); 1.22 (SiMe); 10.1 (CH<sub>3</sub>); 89.7, 95.23, 99.13, 101.3, 110.3 (C<sub>5</sub>Me<sub>5</sub> +  $\eta^6\text{-C}_6\text{H}_5$ ); 217.0, 217.8 (Fe–CO); 233.8 (Cr–CO). <sup>29</sup>Si NMR (CDCl<sub>3</sub>): δ 17.5 (Fe–Si); -11.5. Selected data for **3**. IR (hexane, cm<sup>-1</sup>): 2000.0, 1976.3, 1946.8, 1910.2, 1855.9 (CO). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.44, 0.65 (SiMe<sub>2</sub>); 1.03, 1.23 ( $\mu\text{-SiMe}_2$ ); 4.11 (s,  $\eta^5\text{-C}_5\text{H}_5$ ); 4.21, 4.32, 5.12 (m,  $\eta^6\text{-C}_6\text{H}_5$ ). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ -2.44, 2.83 (SiMe<sub>2</sub>); 15.0, 15.3 ( $\mu\text{-SiMe}_2$ ); 83.8 ( $\eta^5\text{-C}_5\text{H}_5$ ); 90.5, 91.4, 95.5, 99.4, 100.1 ( $\eta^6\text{-C}_6\text{H}_5$ ); 215.1 (Fe–CO); 237.3, 242.4 (Cr–CO). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>): δ 231.0 ( $\mu\text{-SiMe}_2$ ); 30.2. HRMS: Calcd for C<sub>18</sub>H<sub>22</sub>CrFeO<sub>5</sub>Si<sub>2</sub> m/z 449.9862, found, m/z 449.9864. Selected data for **4**. IR (hexane, cm<sup>-1</sup>): 1979.0, 1927.8, 1901.1, 1855.5 (CO). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.65, 0.70 (SiMe<sub>2</sub>); 1.05, 1.33 ( $\mu\text{-SiMe}_2$ ); 1.53 (s, CH<sub>3</sub>); 3.73, 4.26, 4.37, 4.69, 5.13 (m,  $\eta^6\text{-C}_6\text{H}_5$ ). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.94, 4.47 (SiMe<sub>2</sub>); 11.0 (CH<sub>3</sub>); 15.9, 17.1 ( $\mu\text{-SiMe}_2$ ); 90.3, 92.1, 95.0, 100.0, 100.4 (C<sub>5</sub>Me<sub>5</sub> +  $\eta^6\text{-C}_6\text{H}_5$ ); 217.9 (Fe–CO); 238.6, 243.9 (Cr–CO). <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>): δ 233.9 ( $\mu\text{-SiMe}_2$ ); 28.8.

(10) Data collected from a black crystal using a Siemens R3m/V diffractometer and Mo K $\alpha$  radiation. Orthorhombic; space group *Pna*2<sub>1</sub>; *a* = 16.495(3) Å, *b* = 9.679(2) Å, *c* = 14.801(3) Å; *Z* = 4; *R* = 5.82; GOF = 1.39.

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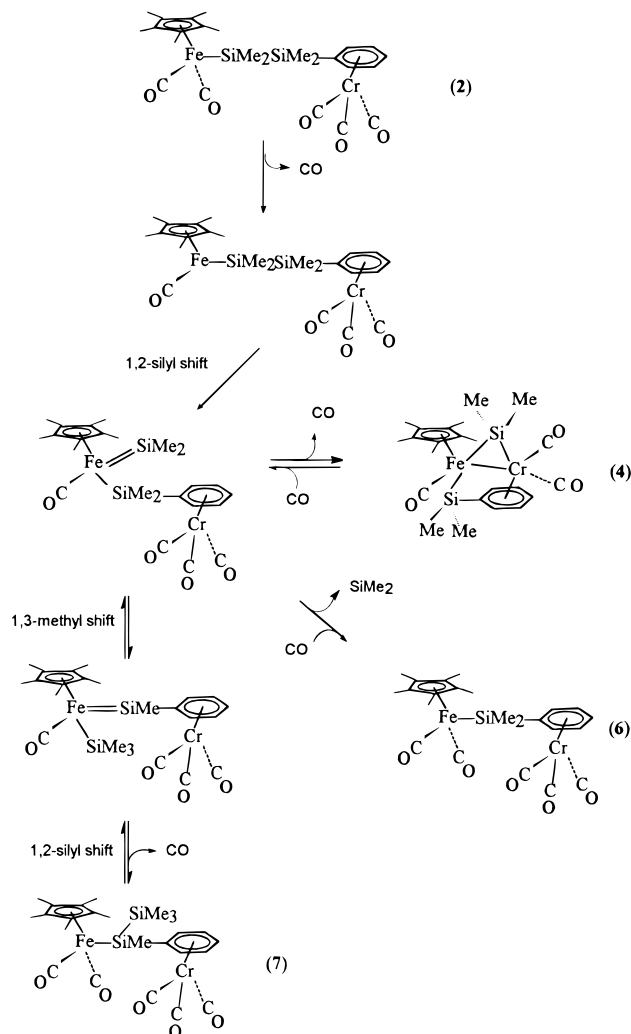


**Figure 1.** Structure of **4**. Selected bond lengths (Å): Fe–Si(1) = 2.352(3); Fe–Si(2) = 2.368(3); Fe–Cr = 3.095(4); Cr–Si = 2.387(4). Bond angles around Si(1) (deg): C(12)–Si–C(13) = 97.8(5); Fe–Si(1)–Cr = 81.5(1), Cr–Si(1)–C(12) = 122.3(4), Cr–Si(1)–C(13) = 116.0(4), Fe–Si(1)–C(12) = 122.1(4), Fe–Si(1)–C(13) = 119.0(3).

plexes which range from 2.342 to 2.527 Å.<sup>13</sup> The Fe–Cr bond length of 3.095(4) Å represents the longest such bond reported in the Cambridge Data Base, where the mean Cr–Fe bond length is 2.786 Å, with the longest values being 2.937,<sup>14</sup> 2.945,<sup>15</sup> and 2.969 Å.<sup>16</sup> The coordination about the silicon atom is a distorted tetrahedron, and the sum of the angles about Si (excluding the bonds to Cr) is 339°. This value does not approach that of the more planar Ogino–Tobita base-stabilized silylene complexes,<sup>6</sup> ~350°, but is similar to that of the base-stabilized silylene Cr complexes,<sup>13</sup> ~340°. All of these values are distinct from the value of 360° noted for planar Pt and Ru silylenes reported by the Tilley group.<sup>8</sup> The asymmetric coordination to Cr of the Fe–Si bond is also reflected by the Cr–Si–Fe and Cr–Fe–Si bond angles of 81.5(1)° and 48.7(1)°, respectively. The exact reasons for this asymmetric bonding are unclear, and any explanation must await further examples of this type of interaction. The solution NMR data for **3** and **4** are in accord with their structures.

The formation of silylene complexes **3** and **4** from the photolysis of complexes **1** and **2** agrees with the general mechanism proposed with respect to the chemistry of the Fp disilyl complexes, and the overall reaction process is illustrated in Scheme 1. A distinction between the alkoxy-donor-stabilized bis(silylene)iron complexes obtained by the Ogino group and chromium carbonyl silylene complexes **3** and **4** is the photolability of the latter. Continued irradiation of **3** or **4** in the presence of CO results in the transformation of the complexes to FpSiMe<sub>2</sub>(η<sup>6</sup>-C<sub>6</sub>H<sub>5</sub>Cr(CO)<sub>3</sub>) (**5**) and Fp\*SiMe<sub>2</sub>(η<sup>6</sup>-C<sub>6</sub>H<sub>5</sub>Cr-

**Scheme 1**



(CO)<sub>3</sub>) (**6**), respectively, with elimination of SiMe<sub>2</sub>. Therefore, **3** and **4** are true intermediates in the photochemical silylene-elimination/isomerization processes that are the signature chemistry of the oligosilyl Fp complexes. Finally, irradiation of the isomeric Fp\*SiMe(η<sup>6</sup>-C<sub>6</sub>H<sub>5</sub>Cr(CO)<sub>3</sub>)SiMe<sub>3</sub> (**7**) (where Fp\* = (η<sup>5</sup>-CH<sub>3</sub>)<sub>5</sub>C<sub>5</sub>)Fe(CO)<sub>2</sub>) also leads to the formation of **4** further validating the mechanism proposed for this chemistry. We are continuing our studies with respect to longer chain oligosilanes containing the η<sup>6</sup>-C<sub>6</sub>H<sub>5</sub>Cr(CO)<sub>3</sub> substituent as well as the properties of the new bimetallic complexes.

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**Supporting Information Available:** Listings of crystal data, data collection, solution and refinement, complete atomic coordinates, bond distances and angles, and anisotropic thermal parameters for **4** and synthetic details (10 pages). See any current masthead page for ordering and Internet access instructions.

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