

# Synthesis and Characterization of the Ferrio-Substituted Silicon(II) Compound $\text{Me}_5\text{C}_5(\text{CO})_2\text{FeSiC}_5\text{Me}_5^\dagger$

Peter Jutzi,\* Kinga Leszczyńska, Andreas Mix, Beate Neumann, Britta Rummel, Wolfgang Schoeller,<sup>†</sup> and Hans-Georg Stammler

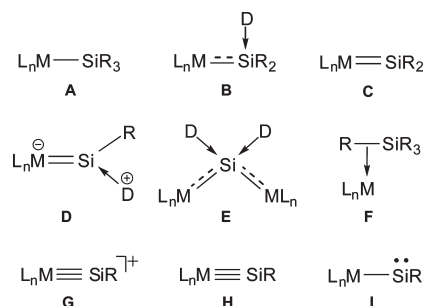
University of Bielefeld, Faculty of Chemistry, Universitätsstrasse 26, 33615 Bielefeld, FRG.. <sup>†</sup>Present address: University of California at Riverside, Department of Chemistry, Riverside, CA 92521-0403; e-mail wolfgang.schoeller@ucr.edu.

Received April 29, 2010

**Summary:** Reaction of the (pentamethylcyclopentadienyl)-silicon cation with the (pentamethylcyclopentadienyl)dicarbonylferrate anion leads to the formation of the crystalline, thermolabile silicon(II) compound  $[(\eta^5\text{-pentamethylcyclopentadienyl})\text{dicarbonylferrio}](\eta^3\text{-pentamethylcyclopentadienyl})\text{-silicon}$ . The singlet–triplet energy difference  $\Delta E_{ST}$  is calculated to be 25.4 kcal/mol.

During the last few decades, several types of molecules containing transition-metal–silicon bonds have been synthesized and structurally characterized, including compounds of the type **A–H** in Chart 1, which contain single,<sup>1</sup> double,<sup>1,2</sup> triple,<sup>1,4</sup> and electron-deficient bonds<sup>1,5</sup> between the transition-metal fragment  $\text{ML}_n$  and a silicon atom and in which silicon is present in different formal oxidation states.<sup>1,6</sup> Some of these species are regarded to be important intermediates in metal-catalyzed reactions in organosilicon chemistry. Only very recently the first stable neutral compound of type **H** containing a metal–silicon triple bond, the molybdenum silylidyne complex  $\text{Cp}(\text{CO})_2\text{MoSiC}_6\text{H}_3\text{-2,6-Trip}_2$  (Trip = 2,4,6-triisopropylphenyl), has been synthesized.<sup>4</sup> Interestingly, compounds of the type **I**, in which a transition-metal fragment is a substituent of a divalent silicon atom (“metallo-silicon(II) compounds”) are still unknown. The synthesis of a precursor molecule suitable for the preparation of the compound  $(\text{H}_5\text{C}_5)(\text{CO})_2\text{FeSiMe}$  has already been described by West et al., but only trapping reactions could be performed successfully.<sup>7</sup> Here, we report the synthesis, the X-ray crystal structure, some NMR data, and calculations of

**Chart 1. Classes of Compounds Containing a Transition-Metal–Silicon Bond<sup>a</sup>**



<sup>a</sup> Legend:  $\text{L}_n\text{M}$  = transition-metal fragment; R = monofunctional group; D = donor molecule.

the first member in this class. For the  $\text{RSi}$  component, we have chosen the (pentamethylcyclopentadienyl)silicon  $((\text{Me}_5\text{C}_5)\text{Si})$  unit. With the advent of the (pentamethylcyclopentadienyl)silicon cation,  $\text{Me}_5\text{C}_5\text{Si}^+$ ,<sup>8</sup> a novel route to neutral divalent silicon compounds is available, simply by the addition of anionic nucleophiles, as already shown by some examples.<sup>8,9</sup> For the anionic transition-metal component, we have chosen the (pentamethylcyclopentadienyl)dicarbonylferrate anion, due to the stabilizing effects of the  $\text{Me}_5\text{C}_5(\text{CO})_2\text{Fe}$  fragment exerted in comparable bonding situations.<sup>10</sup>

The salt  $[\text{Me}_5\text{C}_5\text{Si}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  (**1**) was reacted with the salt  $\text{Na}^+[\text{Fe}(\text{CO})_2\text{C}_5\text{Me}_5]^-$  (**2**) at  $-78^\circ\text{C}$  in two different solvents (see Scheme 1). In a mixture of dimethoxyethane and hexane, single-electron transfer (SET) took place exclusively to give the known  $\text{Fe–Fe}$  dimer  $[\text{Me}_5\text{C}_5(\text{CO})_2\text{Fe}]_2$  (**3**),<sup>11</sup> decamethylsilocene (**4**),<sup>12</sup> and elemental silicon, the last two species presumably as the result of a disproportionation of a reactive intermediate of the composition  $[\text{Me}_5\text{C}_5\text{Si}]_2$ .<sup>13</sup> In hexane as solvent and in the

<sup>†</sup> Part of the Dietmar Seyferth Festschrift. Dedicated to Professor Dietmar Seyferth, with sincere thanks for his longstanding helpful comments.

\*To whom correspondence should be addressed. E-mail: peter.jutzi@uni-bielefeld.de.

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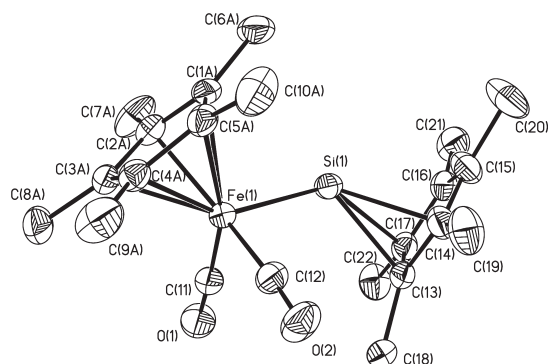
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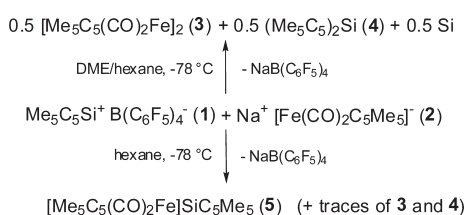
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**Figure 1.** ORTEP plot of the molecular structure of **5**. Thermal ellipsoids represent 50% probability. Hydrogen atoms are omitted for clarity; the disorder at the (Fe)Cp\* group is not shown (see the Supporting Information).

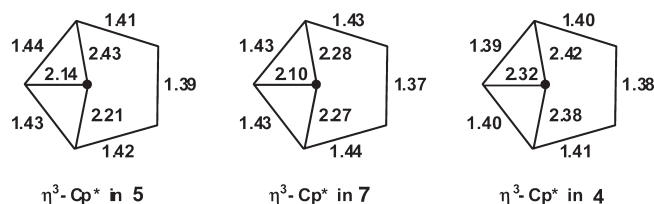
### Scheme 1. Synthesis of the Ferrosilicon(II) Compound **5**



presence of small amounts of diethyl ether, the title compound **5** was obtained in 48% yield after filtration and concentration of the remaining solution and after crystallization at  $-30^\circ\text{C}$  as air-sensitive, brown crystals. In addition to compound **5**, small amounts ( $\sim 3\%$ ) of the compounds **3** and **4** were detected by NMR spectroscopy in the remaining solution. In the solid state, compound **5** is stable at  $-30^\circ\text{C}$  for some weeks; at ambient temperature it rearranges to the insertion product **6** (vide infra). In solution it decomposes mainly to **6**, **3**, and **4**, as shown by NMR spectroscopy.

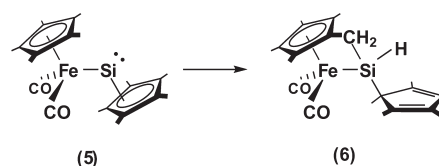
Despite the thermal instability of **5**, crystals could be grown from hexane solution at lower temperatures. The molecular structure was determined by single-crystal X-ray diffraction (Figure 1).<sup>14</sup> The structure analysis shows the presence of a monomeric species with two  $\text{Me}_5\text{C}_5$  (Cp\*) ligands, one  $\eta^5$ -bonded to iron and the other  $\eta^3$ -bonded to silicon. The Si–C distances of 2.136(2) (Si–C(13)), 2.210(2) (Si–C(14)), and 2.435(2) Å (Si–C(17)) in the latter correspond to an asymmetric  $\eta^3$  bonding. This bonding situation

(14) X-ray crystallography: single crystals of **5** were coated with a layer of hydrocarbon oil, attached to a glass fiber, and cooled to 100 K for data collection. Crystallographic data were collected with a Bruker Nonius KappaCCD diffractometer with Mo K $\alpha$  radiation (graphite monochromator,  $\lambda = 0.71073$  Å). Crystal data are as follows:  $\text{C}_{22}\text{H}_{30}\text{FeO}_2\text{Si}$ ;  $M_r = 410.40$ ; orthorhombic; *Pbca* (No. 61);  $a = 15.1433(7)$  Å;  $b = 9.2167(4)$  Å;  $c = 30.8421(15)$  Å;  $V = 4304.7(3)$  Å<sup>3</sup>;  $Z = 8$ ;  $D_c = 1.267$  Mg m<sup>-3</sup>;  $\mu(\text{Mo K}\alpha) = 0.769$  mm<sup>-1</sup>; brown fragment  $0.08 \times 0.29 \times 0.30$  mm<sup>3</sup>; 37 558 measured reflections,  $2\theta \leq 60^\circ$ ,  $R_1 = 0.0419$  for 4402 reflections with  $I > 2\sigma(I)$ ,  $wR_2 = 0.1144$  for all 6218 unique reflections, 268 parameters. Crystallographic programs used for structure solution and refinement were from SHELX-97. The structure was solved by direct methods and was refined by using full-matrix least squares on  $F^2$  of all unique reflections with anisotropic thermal parameters for all non-hydrogen atoms, except the disordered carbons with 0.16 occupancy. The Cp\* ring is disordered on two positions (84:16). Hydrogen atoms were included at calculated positions with  $U(\text{H}) = 1.5U_{\text{eq}}$  of the corresponding carbon atom. CCDC 774453 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



**Figure 2.** Si–C and C–C bond lengths in the ( $\eta^3$ -Cp\*)Si unit of compounds **5**, **7**, and **4**.

### Scheme 2. Rearrangement of **5** to **6**



is comparable to that found in the arylsilicon(II) compound [2,6-(Trip)<sub>2</sub>H<sub>3</sub>C<sub>6</sub>]( $\eta^3$ -Cp\*)Si (Trip = 2,4,6-*i*Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) (**7**)<sup>15</sup> and in the  $\eta^3$ -Cp\* unit in the sandwich compound Cp\*<sub>2</sub>Si (**4**) (see Figure 2). Thus, electron donation to the vacant orbital at silicon originates mainly from the Cp\* ring. As expected, the Fe–Si bond length of 2.3677(6) Å in **5** is greater than that in the silicon(IV) compound Cp\*(CO)<sub>2</sub>FeSiH<sub>3</sub> (2.287(2) Å).<sup>16</sup> Thus, this bond is regarded to be rather weak (see below for the calculations). The angle at silicon (Fe–Si–C(13)) is 112.8(1) $^\circ$  and differs from the respective angle in the arylsilicon compound **7** (101.98(7) $^\circ$ ). The geometry at the silicon atom may be qualitatively described on the basis of sp<sup>2</sup> hybridization, with one hybrid orbital representing the lone pair and the others engaged in bonding to the substituents. The remaining vacant p orbital at silicon interacts mainly with a filled  $\pi$  orbital at the Cp\* fragment.

The <sup>1</sup>H NMR spectrum of **5** is in accord with the constitution of the compound as derived from the X-ray crystal structure data. It shows sharp singlets for both the iron-bonded and the silicon-bonded pentamethylcyclopentadienyl (Cp\*) groups; the latter is slightly broadened on cooling to  $-50^\circ\text{C}$ , characteristic for the presence of a fluxional Cp\* system. Similarly, the <sup>13</sup>C NMR spectrum shows singlets for the ring carbon atoms and for the methyl groups both on the iron and on the silicon-bonded Cp\* group. In addition, a resonance signal for the CO groups is observed. The simplicity of the NMR spectra indicates the presence of a rather symmetric structure also in solution with a mirror plane along the Cp\*(centroid)–Fe–Si–Cp\*(centroid) vector. In the <sup>29</sup>Si NMR spectrum, the resonance signal for the divalent silicon atom is observed at  $\delta +316.7$  ppm. Thus, a downfield shift of 716.8 ppm takes place on going from **1** ( $-400.1$  ppm) to **5**.

The silicon(II) compound **5** rearranges easily to the silicon(IV) compound **6** by oxidative addition of a C–H unit from the Cp\* group at iron to the divalent silicon atom (see Scheme 2). The silicon(IV) compound **6** is characterized by a prochiral silicon atom and thus by several signals for the Cp\* group at silicon in the <sup>1</sup>H and <sup>13</sup>C NMR spectra (see the Experimental Section). The <sup>29</sup>Si NMR signal of **6** is observed at  $\delta -53.2$  ppm with  $^1J(\text{SiH}) = 205.4$  Hz.

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To get a deeper insight into the structure and bonding of **5**, calculations have been performed at a DFT level of theory.<sup>17</sup> The calculated equilibrium structure (RI-BP86/TZVP) is comparable to that found by X-ray crystallography and is presented in the Supporting Information together with the  $x, y, z$  atom coordinates. All investigated structures are ensured as energy minima on the electronic hypersurface by corresponding vibrational analyses. The structure **5** shows the expected symmetry (mirror plane) with a  $\eta^5$ -Cp\* iron unit and with a  $\eta^3$ -Cp\* silicon unit, the latter with Si–C distances of 2.165 (Si–C(1)), 2.344 (Si–C(2)), and 2.353 Å (Si–C(2')). The Fe–Si bond length is found to be 2.378 Å, and the Fe–Si–C<sub>1</sub> angle is calculated to be 113.2°. Calculated structural parameters of the insertion product **6** are provided in the Supporting Information. Compound **6** is calculated to be only 9.3 kcal/mol more stable (with ZPE correction) than compound **5** in its singlet state.

A population analysis, based on the NBO values and on the Wiberg bond indices, implicates that the bonding in **5** is best described as a resonance hybrid between the ferrosilicon(II) species Cp\*(CO)<sub>2</sub>Fe–SiCp\* and the donor–acceptor complex [Cp\*(CO)<sub>2</sub>Fe]<sup>–</sup>[SiCp\*]<sup>+</sup>, resulting in a weak (Wiberg bond order of 0.541) Fe–Si bond. The latter is mainly located (74.2%) at Fe (23.2% s, 76.5% d) and less (25.8%) at Si (4.9% s, 94.8% p), supporting the donor–acceptor formulation. Following the population analysis, a charge of +0.216 is remaining on the half-sandwich fragment Me<sub>5</sub>C<sub>5</sub>Si. For the  $\eta^3$ -Cp\*-Si interaction, the Wiberg bond order indices are as follows: Si–C(1), 0.353; Si–C(2), 0.262; Si–C(2'), 0.259; Si–C(3), 0.070; Si–C(3'), 0.068. In addition to the calculated Cp\*–Si  $\pi$  interaction, a rather weak Fe–Si  $\pi$  interaction is also conceivable, following arguments from MO theory.<sup>18</sup> This  $\pi$  contribution, involving the silicon-based p orbital and the Cp\*(CO)<sub>2</sub>Fe HOMO of a'' symmetry, is substantiated in a lower molecular orbital (HOMO-4). The HOMO ( $\sigma$  orbital at silicon) and the LUMO (p orbital at silicon) are mainly localized at the silicon atom and thus reveal the nature of a silylene (for a full table of the orbitals, see the Supporting Information).

The <sup>29</sup>Si NMR shift of **5** was calculated to be +295.5 ppm at the RI-BP86/TZVP level and +387.8 ppm at the B3LYP/TZVP level. The differences from the experimental value (+316.7 ppm) can be explained by strong paramagnetic contributions, which generally are not sufficiently recognized in calculations of this type. A strong paramagnetic contribution to the <sup>29</sup>Si NMR shift in the ground-state structure of **5** can be concluded from the calculated (adiabatic) singlet–triplet energy difference  $\Delta E_{ST}$  of 25.4 kcal/mol (ZPE included), which is not much larger than those calculated for SiH<sub>2</sub> ( $\Delta E_{ST}$  = 16.6 kcal/mol)<sup>19</sup> and SiMe<sub>2</sub> ( $\Delta E_{ST}$  = 23.0 kcal/mol).

The ferrosilicon(II) compound **5** might be a useful substrate for the preparation of a further species containing a metal–silicon triple bond.<sup>4</sup> In germanium chemistry, the metallocgermylene Cp(CO)<sub>3</sub>MoGeC<sub>6</sub>H<sub>3</sub>(2,6-Mes<sub>2</sub>) presumably has

been a reactive intermediate in the preparation of the compound Cp(CO)<sub>2</sub>MoGeC<sub>6</sub>H<sub>3</sub>(2,6-Mes<sub>2</sub>), the first stable species containing a metal–germanium triple bond.<sup>20</sup> On the other hand, the ferriogermynes CpFe(CO)<sub>2</sub>GeCH–(SiMe<sub>3</sub>)<sub>2</sub>, CpFe(CO)<sub>2</sub>GeMes\*, and Cp\*Fe(CO)<sub>2</sub>GeMes\* (Mes\* = C<sub>6</sub>H<sub>2</sub>(2,4,6-*i*Bu<sub>3</sub>)<sup>21</sup>) could not be transformed into stable iron–germanium triple-bond systems.<sup>22</sup>

**Experimental Section.** **Synthesis of 5.** Hexane (10 mL) and diethyl ether (0.2 mL) were added at –78 °C to a mixture of **1** (296 mg, 0.35 mmol) and **2** (95 mg, 0.35 mmol). The reaction mixture was stirred for 1 h at –78 °C and then warmed to –25 °C over 2 h and stirred for a further 3 h at –25 °C. At this temperature the resulting brown suspension was filtered. The remaining solid was extracted with cold hexane (5 mL). The combined hexane solutions were concentrated to ~1 mL and left to crystallize overnight at –30 °C. Compound **5** was isolated as brown crystals (69 mg, yield 48%). The remaining solution contained **5**, contaminated with small amounts of **3** and **4**, as checked by NMR spectroscopy.

Data for compound **5** are as follows. <sup>1</sup>H NMR (600.13 MHz, C<sub>6</sub>D<sub>6</sub>, TMS external,  $\delta$  (ppm)): 2.11 (Me<sub>5</sub>C<sub>5</sub>Si); 1.53 (Me<sub>5</sub>C<sub>5</sub>Fe). <sup>13</sup>C NMR (250 MHz, in C<sub>6</sub>D<sub>6</sub>, TMS internal,  $\delta$  (ppm)): 9.2, 96.1 (Me<sub>5</sub>C<sub>5</sub>Fe), 10.9, 119.9 (Me<sub>5</sub>C<sub>5</sub>Si), 218.6 (CO). <sup>29</sup>Si NMR (119.23 MHz, in C<sub>6</sub>D<sub>6</sub>, TMS external,  $\delta$  (ppm)): +316.7.

<sup>1</sup>H NMR for compounds **3** and **4** (in C<sub>6</sub>D<sub>6</sub>, TMS internal,  $\delta$  (ppm)): compound **3**, 1.59 (lit.<sup>11</sup> 1.62 (CS<sub>2</sub>)); compound **4**, 1.89 (identical with literature data<sup>12</sup>).

**Compound 6.** Compound **5** (32 mg) was stored for 1 week in a glovebox. A quantitative rearrangement to **6** (32 mg, orange solid) was observed.

Data for compound **6** are as follows. <sup>1</sup>H NMR (600.13 MHz, toluene-*d*<sub>8</sub>, 298 K, TMS external,  $\delta$  (ppm)): 1.48, 1.54, 1.66, 1.72 (4 s, Me<sub>4</sub>C<sub>5</sub>Fe), 1.90 (s, br, Me<sub>5</sub>C<sub>5</sub>Si), 1.84, 1.96 (2 dd, <sup>2</sup>J(H, H) = 14.0 Hz, <sup>3</sup>J(H, H) = 4.4 Hz) (CH<sub>2</sub>Me<sub>4</sub>C<sub>5</sub>Fe), 3.17 (t, <sup>3</sup>J(H, H) = 4.4 Hz) (Si–H). <sup>1</sup>H NMR (600.13 MHz, toluene-*d*<sub>8</sub>, 233 K, TMS external,  $\delta$  (ppm)): 1.38, 1.89, 2.00, 2.04, 2.23 (5 s, Me<sub>5</sub>C<sub>5</sub>Si), 1.41, 1.46, 1.60, 1.67 (4 s, Me<sub>4</sub>C<sub>5</sub>Fe), 1.86, 1.93 (2 dd, <sup>2</sup>J(H, H) = 13.5 Hz, <sup>3</sup>J(H, H) = 4.6 Hz) (CH<sub>2</sub>Me<sub>4</sub>C<sub>5</sub>Fe), 3.09 (s, br) (Si–H). <sup>13</sup>C NMR (150.90 MHz, toluene-*d*<sub>8</sub>, 233 K, TMS external,  $\delta$  (ppm)): 11.6, 11.8, 12.0, 12.3, 14.1, 53.1, 134.7, 134.9, 138.4, 138.9 (Me<sub>5</sub>C<sub>5</sub>Si), 9.0, 10.0, 10.1, 10.2, 84.0, 85.5, 88.1, 99.3, 100.3 (Me<sub>4</sub>C<sub>5</sub>Fe), 4.8 (CH<sub>2</sub>Si), 218.4, 219.8 (CO). <sup>29</sup>Si NMR (119.23 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS external,  $\delta$  (ppm)): –53.2 (<sup>1</sup>J(Si, H) = 205.4 Hz). IR (KBr pellet, cm<sup>–1</sup>):  $\nu$ (CO) 1967, 1913. HR MS (EI,  $m/z$ ): calcd for C<sub>22</sub>H<sub>30</sub>O<sub>2</sub>FeSi 408.1411, found 408.1369.

**Acknowledgment.** The financial support of the Deutsche Forschungsgemeinschaft, of the University of Bielefeld, and of the Fonds der Chemischen Industrie is gratefully acknowledged.

**Supporting Information Available:** Tables, figures, and a CIF file giving crystal structure data of **5**, calculated geometries and energies of **5** (singlet and triplet) and of **6**, and front orbitals (Kohn–Sham orbitals) for the singlet state of **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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