

# Photoreaction of Silyliron(II) Complex $\text{Cp}^*\text{Fe}(\text{CO})_2\text{SiMe}_3$ ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) in the Presence of *p*-Tolylgermane

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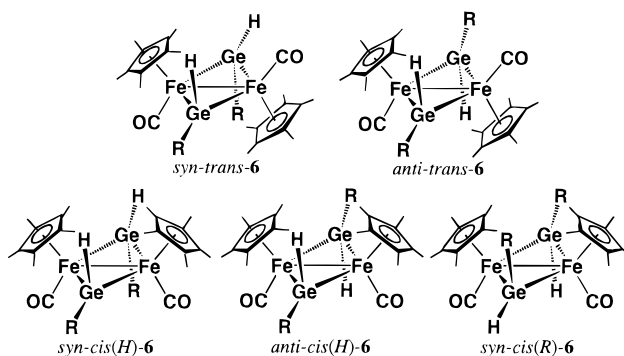
Photolysis of  $\text{Cp}^*\text{Fe}(\text{CO})_2\text{SiMe}_3$  (**3**) in the presence of *p*-TolGeH<sub>3</sub> (**4**) gave a mixture of *cis* and *trans* mono(germylene)-bridged diiron complexes,  $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Ge}p\text{-TolH})$  (*cis*-**5**, *trans*-**5**), a mixture of two kinds of *trans* bis(germylene)-bridged diiron complexes,  $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-Ge}p\text{-TolH})_2$  (*syn-trans*-**6**, *anti-trans*-**6**), and a complex with two  $\text{Fe}\cdots\text{H}\cdots\text{Ge}$  3-center 2-electron bonds,  $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-Ge}p\text{-TolH}_2)_2$  (**7**). A *cis* isomer of complex **6** (*syn-cis(H)*-**6**) was formed as the sole product by the thermolysis of complex **7**. Photolysis of **7** or *syn-cis(H)*-**6** resulted in the conversion to a mixture of *syn-trans*-**6** and *anti-trans*-**6**. Reversible thermal and photochemical interconversion between *cis* and *trans* isomers of complex **5** was observed. The molar ratio of the *cis* and *trans* isomers of complex **5** in  $\text{C}_6\text{D}_6$  was 7:93 at thermal equilibrium at 55 °C and 84:16 at the photostationary state at 6 °C.

## Introduction

The oxidative addition of Si–H bonds to low-valent transition metal centers is one of the most important reactions in the formation of transition metal to silicon bonds. Many silyl(transition metal) complexes<sup>1</sup> and several complexes with  $\text{M}\cdots\text{H}\cdots\text{Si}$  3-center 2-electron bonds<sup>2</sup> have been characterized. On the other hand, very little is known about analogous complexes possessing a  $\text{M}\cdots\text{H}\cdots\text{Ge}$  3-center 2-electron bond.<sup>3</sup> Recently, we prepared the first fully characterized complex with two  $\text{Fe}\cdots\text{H}\cdots\text{Ge}$  3-center 2-electron bonds,  $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-Ge}t\text{-BuH}_2)_2$  (**1**),<sup>4</sup> which may be an intermediate in the formation of the bis(germylene)-bridged diiron complex via H<sub>2</sub> expulsion.<sup>4</sup> These complexes (bis(germylene)-bridged diiron) can adopt five different geometries (two *trans* and three *cis*, Figure 1).

Recently, we reported the photochemical interconversion between the *cis* and *trans* isomers of  $\text{Cp}^*_2\text{Fe}(\text{CO})_2(\mu\text{-Ge}p\text{-TolH})_2$ .<sup>5</sup> The isomers of complexes of type  $\text{Cp}_2\text{M}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-ER}_2)$  (E = group 14 elements) can undergo either thermal or photochemical interconversion. The interconversion between these isomers has been reported for  $\text{Cp}_2\text{M}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CR}_2)$  (M = Fe, Ru; R = H, alkyl, alkenyl, Ph, SR, etc.),<sup>6a–c</sup>  $\text{Cp}_2\text{M}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-C=CHR})$  (M = Fe, Ru; R = H, alkyl, Ph),<sup>6g–i</sup>  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-SiHMe})$ ,<sup>7</sup>  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-SiX}t\text{-Bu})$  (X = Cl, Br, I, Me),<sup>8</sup>  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-GeMe}_2)$ ,<sup>9</sup> and  $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Si}p\text{-TolH})$  (**2**).<sup>10</sup>

Here we report the synthesis of the second diiron complex with two  $\text{Fe}\cdots\text{H}\cdots\text{Ge}$  3-center 2-electron bonds by photolysis of  $\text{Cp}^*\text{Fe}(\text{CO})_2\text{SiMe}_3$  (**3**) in the presence of *p*-TolGeH<sub>3</sub> (**4**). Through photolysis and thermolysis



**Figure 1.** Five possible geometric isomers of  $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-GeRH})_2$  (**6**).

of this 3-center 2-electron bond containing complex, we isolated three isomers of a bis(germylene)-bridged diiron complex among the five possible isomers of this complex. Also, thermal and photochemical interconversion between the *cis* and *trans* isomers of a mono(germylene)-bridged diiron complex was studied.

## Experimental Section

All manipulations were performed under an inert atmosphere using standard Schlenk techniques. Reagent-grade benzene, diethyl ether, hexane, pentane, and tetrahydrofuran

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(THF) were distilled from sodium–benzophenone ketyl immediately before use. Deuterated NMR solvents were stored over molecular sieves 4A under N<sub>2</sub>. Cp\*Fe(CO)<sub>2</sub>SiMe<sub>3</sub><sup>11</sup> was prepared according to the published procedure. *p*-Chlorotoluene was distilled over P<sub>2</sub>O<sub>5</sub> immediately prior to use. Germanium tetrachloride was stored under N<sub>2</sub> in a refrigerator. Other chemicals were used without further purification.

Photolysis was performed with an Ushio UM-452 450 W medium-pressure Hg lamp placed in a water-cooled, quartz jacket. Sample solutions were irradiated in Pyrex tubes.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker AC-300 spectrometer. Variable-temperature <sup>1</sup>H NMR spectra were recorded also on the Bruker AC-300 spectrometer. IR spectra were obtained on a Horita FT-200 spectrometer. Mass spectra were taken on a Hitachi M-52 or JEOL JMS-HX 110 mass spectrometer, and high-resolution mass spectra, on a JEOL JMS-HX 110 mass spectrometer. UV–visible spectra were recorded on a Shimadzu UV-260 UV-visible recording spectrophotometer connected to a TCC-260 temperature-controlled cell holder.

**Preparation of *p*-Tolylgermane.** (*p*-Tolyl)magnesium chloride was prepared by a solution of a solution of *p*-chlorotoluene (50.6 g, 0.400 mol) dissolved in THF (100 mL) into a flask containing Mg turnings (10 g, 0.42 mol) in THF (10 mL) over 70 min (Note: Mg was stirred and heated at 80 °C for 1–2 days, under a gentle flow of N<sub>2</sub>, in order to activate it). The mixture in the flask was stirred well during the addition and then for an additional 2 h at 45 °C. To a vigorously stirred solution of GeCl<sub>4</sub> (64.8 g, 0.300 mol) dissolved in Et<sub>2</sub>O (100 mL) was added the Grignard reagent over 90 min. The mixture was then gently refluxed for 2 h, MgCl<sub>2</sub> was filtered off over Celite, and the mixture was washed twice with 100 mL Et<sub>2</sub>O. All solvents were removed to yield a yellow solution. A fractional distillation of the latter solution afforded trichloro-*p*-tolylgermane, *p*-TolGeCl<sub>3</sub>, as a colorless liquid (27 g, 0.10 mol) in 33% yield (bp 60 °C, 0.6 mmHg) (lit. bp 129–131 °C, 24 mmHg<sup>12</sup>). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.85 (3H, s, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 6.72, 7.26 (2H × 2, d, J<sub>HH</sub> = 7.81 Hz, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 21.7 (C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 130.1, 131.2, 131.7, 143.9 (C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>). MS: *m/z* 270 (41, M<sup>+</sup>). Dichlorodi-*p*-tolylgermane<sup>13</sup> was also obtained in 28% yield.

To a well-stirred suspension of LiAlH<sub>4</sub> (3.2 g, 88 mmol) in Et<sub>2</sub>O (50 mL) was added a solution of the above trichloro-*p*-tolylgermane (27 g) in Et<sub>2</sub>O (30 mL) over 50 min. The mixture was then gently refluxed for 4 h. Excess LiAlH<sub>4</sub> was destroyed by the slow addition of 10% H<sub>2</sub>SO<sub>4</sub>. The reaction mixture was extracted with Et<sub>2</sub>O. The organic layer was dried over anhydrous MgSO<sub>4</sub>. Fractional distillation afforded *p*-tolylgermane, *p*-TolGeH<sub>3</sub> (**4**), as a colorless liquid (12.6 g, 0.075 mol) in 75% yield (bp 40 °C, 0.6 mmHg). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 2.05 (3H, s, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 4.26 (3H, s, GeH), 6.94, 7.27 (2H × 2, d, J<sub>HH</sub> = 7.69, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 22.0 (C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 128.0, 129.7, 136.0, 139.4 (C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>). IR (benzene solution): 2071 (s) (ν<sub>GeH</sub>) cm<sup>-1</sup>. MS: *m/z* 168 (21, M<sup>+</sup>). Anal. Found: C, 50.61; H, 5.78. Calcd for C<sub>7</sub>H<sub>10</sub>Ge: C, 50.42; H, 6.04.

**Photolysis of Cp\*Fe(CO)<sub>2</sub>SiMe<sub>3</sub> (**3**) in the Presence of *p*-TolGeH<sub>3</sub> (**4**).** Cp\*Fe(CO)<sub>2</sub>SiMe<sub>3</sub> (**3**) (670 mg, 2.09 mmol) and *p*-TolGeH<sub>3</sub> (**4**) in a small excess (550 mg, 3.30 mmol) in pentane (30 mL) were irradiated at 6 °C for 100 min. Evolution of carbon monoxide was observed, and the color of the solution changed from pale orange to dark red during the photolysis. Evaporation of volatile materials and subsequent flash chromatographic separation of the residue (silica gel, eluent hexane:benzene = 3:1) gave (1) a red mixture of *cis* and *trans* mono(germylene)-bridged diiron complexes Cp\*<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>(μ-CO)(μ-Gep-TolH) (**5**) (281 mg, 0.450 mmol, 32%, *cis*:*trans* = 21:79), (2) a violet mixture of two kinds of *trans* bis(germylene)-bridged diiron complexes Cp\*<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>(μ-Gep-

TolH)<sub>2</sub> (**6**) (224 mg, 0.29 mmol, 21%, *syn-trans*:*anti-trans* = 61:39), and (3) an orange complex Cp\*<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>(μ-Gep-TolH)<sub>2</sub> (**7**) (243 mg, 0.320 mmol, 23%). **5**: MS *m/z* 631 (3, M<sup>+</sup>), 603 (23, M<sup>+</sup> – CO), 540 (55, M<sup>+</sup> – *p*-Tol). Anal. Found: C, 57.48; H, 6.51. Calcd for C<sub>30</sub>H<sub>38</sub>O<sub>3</sub>Fe<sub>2</sub>Ge: C, 57.11; H, 6.07. *cis*-**5**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 1.60 (30H, s, 2Cp\*), 2.12 (3H, s, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 7.24, 8.36 (2H × 2, d, J<sub>HH</sub> = 7.74 Hz, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 8.62 (H, s, GeH); IR (KBr) 1994 (w) (ν<sub>GeH</sub>), 1942 (vs), 1903 (m) (ν<sub>COterm</sub>), 1731 (s) (ν<sub>CObrid</sub>) cm<sup>-1</sup>. *trans*-**5**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 1.61, 1.67 (30H, 2s, 2Cp\*), 2.20 (3H, s, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 7.24, 8.20 (2H × 2, d, J<sub>HH</sub> = 7.59 Hz, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 8.42 (H, s, GeH); IR (KBr) 1992 (w) (ν<sub>GeH</sub>), 1932 (m), 1901 (vs) (ν<sub>COterm</sub>), 1747 (s) (ν<sub>CObrid</sub>) cm<sup>-1</sup>. **6**: MS *m/z* 766 (43, M<sup>+</sup>), 738 (16, M<sup>+</sup> – CO), 618 (10, M<sup>+</sup> – 2CO – *p*-Tol). Anal. Found: C, 56.05; H, 5.84. Calcd for C<sub>36</sub>H<sub>44</sub>O<sub>2</sub>Fe<sub>2</sub>Ge<sub>2</sub>: C, 56.48; H, 5.79. *syn-trans*-**6**: <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO) δ 1.57, 1.62 (30H, 2s, 2Cp\*), 2.41 (6H, s, 2C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 7.32, 7.93 (4H × 2, d, J<sub>HH</sub> = 7.52 Hz, 2C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>; see Results and Discussion), 8.04 (2H, s, GeH); IR (KBr) 1930 (m), 1889 (s) (ν<sub>COterm</sub>) cm<sup>-1</sup>. *anti-trans*-**6**: <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO) δ 1.55 (30H, s, 2Cp\*), 2.38 (6H, s, 2C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 7.28, 7.87 (4H × 2, d, 2C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>; see Results and Discussion), 7.95 (2H, s, GeH); IR (KBr) 1876 (vs) (ν<sub>COterm</sub>) cm<sup>-1</sup>. **7**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ –12.74 (2H, s, 2FeH), 1.51 (30H, s, 2Cp\*), 2.18 (6H, s, 2C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 3.81 (2H, s, 2GeH), 7.13, 8.02 (4H × 2, d, J<sub>HH</sub> = 7.78 Hz, 2C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ 10.1 (CH<sub>3</sub>, Cp\*), 21.4 (C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 90.9 (Cp\*, ring C), 128.6, 135.6, 137.2, 141.6 (C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 222.9 (CO); IR (KBr) 1998 (w) (ν<sub>GeH</sub>), 1930 (vs), 1921 (vs) (ν<sub>COterm</sub>), 1898 (m) (ν<sub>Ge–H–Fe</sub>) cm<sup>-1</sup>; MS *m/z* 768 (10, M<sup>+</sup>), 697 (13, M<sup>+</sup> – Me – 2CO). Anal. Found: C, 55.98; H, 6.50. Calcd for C<sub>36</sub>H<sub>48</sub>O<sub>2</sub>Fe<sub>2</sub>Ge<sub>2</sub>: C, 56.33; H, 6.04.

**Thermolysis of Cp\*<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>(μ-Gep-TolH)<sub>2</sub> (**7**).** A solution of **7** (85 mg, 0.11 mmol) in benzene (30 mL) was refluxed at 70 °C for 3 h. The color of the solution changed gradually from orange to red during thermolysis. Removal of volatile materials from the reaction mixture followed by flash chromatographic separation of the residue in the dark (silica gel, eluent hexane:benzene = 3:1) gave two different bands. The first yellow band was a decomposed material. From the second red band, a *syn-cis*(*H*)-**6** isomer of bis(germylene)-bridged diiron complex Cp\*<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>(μ-Gep-TolH)<sub>2</sub> (**6**) (20 mg, 26 mmol, 25%) was obtained as a red powder. Further purification for this complex was unsuccessful because of the light sensitivity. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.58 (30H, s, 2Cp\*), 2.15 (6H, s, 2C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 7.29, 8.48 (4H × 2, d, J<sub>HH</sub> = 7.66 Hz, 2C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 8.67 (2H, s, GeH). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 11.0 (CH<sub>3</sub>, Cp\*), 21.5 (C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 91.6 (Cp\*, ring C), 129.0, 136.1, 138.0, 149.4 (C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 215.6 (CO). IR (KBr): 1921 (s), 1894 (m) (ν<sub>COterm</sub>) cm<sup>-1</sup>. MS: *m/z* 766 (9, M<sup>+</sup>), 738 (14, M<sup>+</sup> – CO). Exact mass: found: 768.0473; calcd for C<sub>36</sub>H<sub>44</sub>O<sub>2</sub>Fe<sub>2</sub>Ge<sub>2</sub>, 768.0464.

**Photolysis of Cp\*<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>(μ-Gep-TolH)<sub>2</sub> (**7**).** Photolysis of a benzene-*d*<sub>6</sub> solution of **7** in an NMR tube at 6 °C for 10 min was monitored by <sup>1</sup>H NMR spectroscopy. A *trans* mixture of **6** (molar ratio of *syn-trans*-**6** to *anti-trans*-**6** was 61:39) was observed with some decomposed materials and H<sub>2</sub>.

**Photolysis of Cp\*<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>(μ-Gep-TolH)<sub>2</sub> (*syn-cis*(*H*)-**6**).** The monitoring of the photolysis of a benzene-*d*<sub>6</sub> solution of *syn-cis*(*H*)-**6** in an NMR tube at 6 °C for 1 min by <sup>1</sup>H NMR spectroscopy showed a quantitative conversion from *syn-cis*(*H*)-**6** to the mixture of *syn*- and *anti-trans*-**6** with molar ratio 61:39.

**Kinetic Study of the Interconversion of *cis* and *trans* Isomers of Complex **5**.** The change of the UV–visible spectrum of a mixture of *cis* and *trans* isomers of complex **5** with molar ratio 84:16 in benzene was monitored in a quartz cell, at five different temperatures between 25.0 and 55.0 °C. Before the reaction, the mixture showed an absorption peak at 544 nm, which over time shifted to slightly longer wavelength, and an isobestic point was observed at 505 nm. The values of equilibrium constants at different temperatures were determined by the integration of <sup>1</sup>H NMR spectra of Cp\* groups. Plots of ln(A<sub>∞</sub> – A<sub>t</sub>/A<sub>∞</sub> – A<sub>0</sub>) vs time were linear (A<sub>∞</sub> = absorption at equilibrium; A<sub>t</sub> = absorption at time *t*; A<sub>0</sub> =

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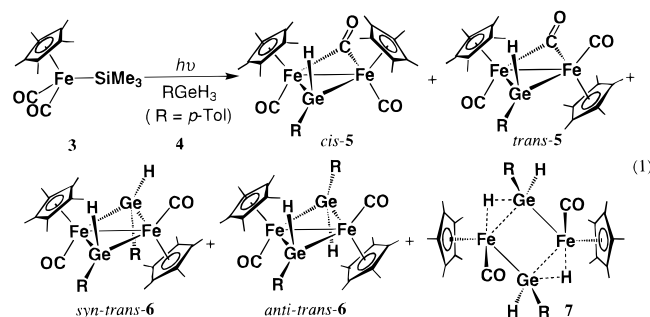
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initial absorption), and least-squares analyses gave correlation coefficients of  $>0.98$  (with a minimum of eight data points). The activation parameters were determined from five data points using the Kaleida Graph, and least-squares analyses gave correlation coefficients of  $>0.98$ .

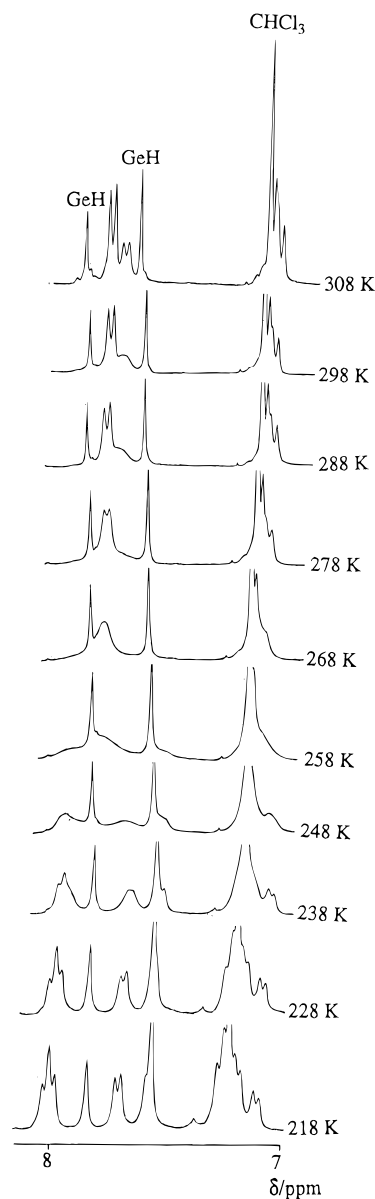
## Results and Discussion

**Photolysis of  $\text{Cp}^*\text{Fe}(\text{CO})_2\text{SiMe}_3$  (3) in the Presence of  $p\text{-TolGeH}_3$  (4).** Irradiation of  $\text{Cp}^*\text{Fe}(\text{CO})_2\text{SiMe}_3$  (3) in the presence of  $p\text{-TolGeH}_3$  (4) in pentane for 100 min afforded mono- and bis(germylene)-bridged diiron complexes and a complex with two  $\text{Fe}\cdots\text{H}\cdots\text{Ge}$  3-center 2-electron bonds (eq 1). The major product was



the mono(germylene)-bridged diiron complex  $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Ge}p\text{-TolH})$  (5) that was isolated as two fractions by flash chromatography with the total yield of 32%. The *cis* and *trans* isomers were separated in the column. However the  $^1\text{H}$  NMR spectra showed the *cis* isomer fraction contained 16% of the *trans* isomer, and the *trans* isomer fraction contained 5% of the *cis* isomer. This is attributable to the thermal isomerization between *cis* and *trans* isomers even at room temperature. The  $^1\text{H}$  NMR spectrum of the *trans* isomer showed two  $\text{Cp}^*$  signals, while that of the *cis* isomer showed only one. Both isomers showed one methyl signal of the *p*-tolyl group, two doublet signals in the aromatic region, and a singlet due to the  $\text{Ge-H}$  proton. In the IR spectrum of the *trans* isomer, the  $\nu_{\text{COasym}}$  band is stronger than  $\nu_{\text{COsym}}$ , while in the *cis* isomer this relationship is reversed. These data were found to be very similar to those of the analogous silylene complex  $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Si}p\text{-TolH})$  (2)<sup>10</sup> except for a small shift of the  $\text{GeH}$  protons (8.62 ppm for *cis* and 8.42 ppm for *trans* in  $\text{C}_6\text{D}_6$ ) toward low field relative to the  $\text{SiH}$  protons (7.44 ppm for *cis* and 7.01 ppm for *trans* in cyclohexane- $d_{12}$ ) in the  $^1\text{H}$  NMR spectra and the difference in the molar ratio between *cis* and *trans* isomers. The thermal and photochemical interconversion between *cis* and *trans* isomers of complex 5 will be discussed in detail in a later section of this paper.

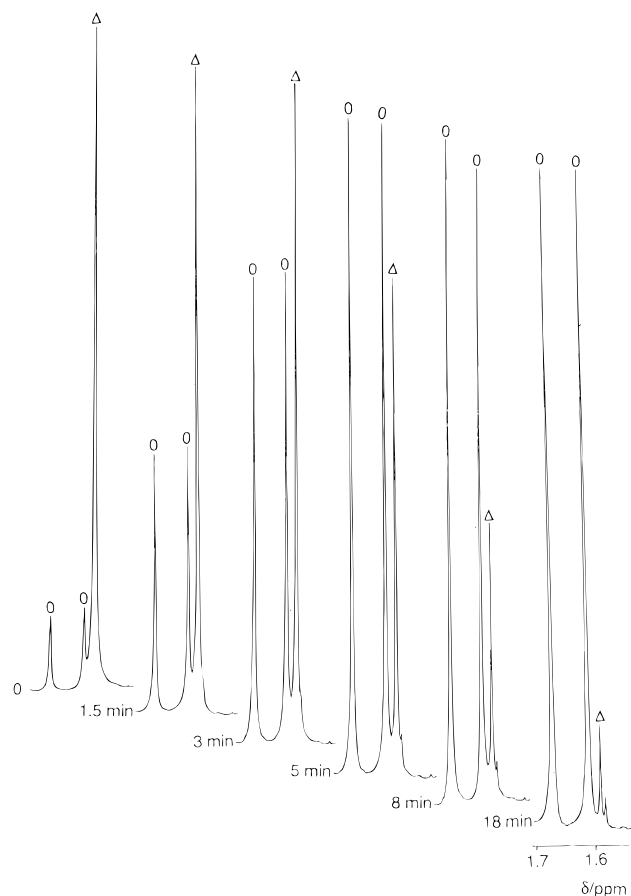
The second product was the bis(germylene)-bridged diiron complex  $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-Ge}p\text{-TolH})_2$  (6). Five geometric isomers are possible for complex 6 as shown in Figure 1. We have previously found that the bulkiness of the germanium substituents plays an important role in determining the geometry of the isomer.<sup>4,14</sup> Thus, the analogous complex  $\text{Cp}_2\text{Fe}(\text{CO})_2(\mu\text{-Ge}t\text{-BuH})_2$ <sup>14</sup> was isolated as an *anti-trans* isomer, while  $\text{Cp}^*_2\text{Fe}_2$



**Figure 2.** Temperature-dependent  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ) of the *syn*- and *anti-trans-6* mixture in the aromatic signal region.

$(\text{CO})_2(\mu\text{-Ge}t\text{-BuH})_2$ <sup>4</sup> exclusively adopted the *syn-cis(H)* configuration. This time, using a moderately sterically hindered *p*-tolyl group as a substituent on germanium, a violet mixture of *syn*- and *anti-trans* isomers of complex 6 was isolated in 21% yield with the ratio of *syn-trans-6*:*anti-trans-6* = 61:39. The characterization of these two isomers was based on the  $^1\text{H}$  NMR and IR spectra. In the  $^1\text{H}$  NMR spectrum, *syn-trans-6* showed two singlet signals in the area of  $\text{Cp}^*$ . Among the five possible geometric isomers of 6, the only isomer that can show two signals in the  $^1\text{H}$  NMR spectrum for  $\text{Cp}^*$  is the *syn-trans* one. Another piece of evidence for that structure is the IR spectrum that showed a medium band assigned to a symmetric  $\nu_{\text{CO}}$  at  $1930\text{ cm}^{-1}$ , while the asymmetric stretch at  $1889\text{ cm}^{-1}$  was found to be a strong band. The  $^1\text{H}$  NMR spectrum of the other isomer in this mixture showed only one signal for  $\text{Cp}^*$ , one methyl signal of *p*-tolyl groups, two doublet signals in the aromatic region, and one signal for  $\text{GeH}$ ; i.e., *syn-cis(H)*, *anti-trans*, and *syn-cis(p-Tol)* isomers were candidates for the other isomer in this mixture because all

(14) Kawano, Y.; Sugawara, K.; Tobita, H.; Ogino, H. *Chem. Lett.* **1994**, 293.



**Figure 3.** <sup>1</sup>H NMR spectral changes in the Cp\* signal region in C<sub>6</sub>D<sub>6</sub> on thermolysis of complex **5** at 55 °C: (Δ) *cis*-**5**, (O) *trans*-**5**.

of them can show this <sup>1</sup>H NMR spectrum. In the IR spectrum, *syn-cis(H)* and *syn-cis(p-Tol)* isomers must show both symmetric and asymmetric modes, while the *anti-trans* isomer must show only the asymmetric mode of the terminal carbonyl. Experimentally only one strong band for ν<sub>CO</sub> was observed at 1876 cm<sup>-1</sup>. Thus we assigned the other complex in this mixture as *anti-trans-6*.

The <sup>1</sup>H NMR signals of the aromatic protons of *syn-trans-6* and *anti-trans-6* complexes were found to be temperature-dependent, as shown in Figure 2. The spectrum at 218 K (in CDCl<sub>3</sub>) appeared to show all the eight doublet resonances of the aromatic protons of *p*-tolyl groups for the two isomers. By a gradual increasing of the temperature, the eight doublet resonances converted to four doublet resonances. The missing of one doublet in both cases is attributable to the overlapping with the solvent peak, which also did not allow us to assign each signal to which complex, especially at low temperature. Such behavior apparently results from the hindered rotation of *p*-tolyl groups in the presence of the adjacent bulky Cp\* groups.

The third product was Cp\*<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>(μ-Ge*p*-TolH<sub>2</sub>)<sub>2</sub> (**7**) with two Fe···H···Ge 3-center 2-electron bonds that was isolated in 23% yield. In the <sup>1</sup>H NMR spectrum of **7** in C<sub>6</sub>D<sub>6</sub>, the signals for bridging hydrides and terminal Ge–H's appear as two singlets with equal intensity at –12.74 and 3.81 ppm, respectively. The unusual high-field shift of the latter signal is attributable to the ring current effect of Cp\* ligands. The IR spectrum of **7**

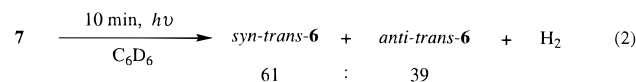
**Table 1.** Values of the Equilibrium Ratio, Equilibrium Constant (*K*), and Rate Constants (*k*<sub>1</sub>, *k*<sub>-1</sub>) of *cis* → *trans* Isomerization of Complex **5** at 298.2, 308.2, 313.2, 318.2, and 328.2 K

temp/K	<i>cis</i> / <i>trans</i>	<i>K</i>	<i>k</i> <sub>1</sub> /s <sup>-1</sup>	<i>k</i> <sub>-1</sub> /s <sup>-1</sup>
298.2	5.4:94.6	17.5	8.74 × 10 <sup>-5</sup>	4.99 × 10 <sup>-6</sup>
308.2	5.6:94.4	16.9	1.49 × 10 <sup>-4</sup>	8.84 × 10 <sup>-6</sup>
313.2	5.8:94.2	16.2	2.23 × 10 <sup>-4</sup>	1.37 × 10 <sup>-5</sup>
318.2	6.1:93.9	15.4	3.26 × 10 <sup>-4</sup>	2.12 × 10 <sup>-5</sup>
328.2	6.7:93.3	13.9	7.90 × 10 <sup>-4</sup>	5.68 × 10 <sup>-5</sup>

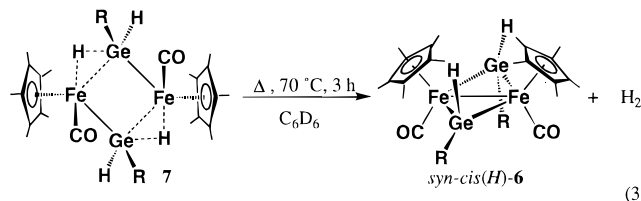
exhibits two weak bands at 1998 and 1898 cm<sup>-1</sup> that can be assigned to ν<sub>GeH</sub> and ν<sub>Ge–H–Fe</sub>, respectively, besides two intense bands of ν<sub>CO</sub> at 1930 and 1921 cm<sup>-1</sup>. Both the <sup>1</sup>H NMR and IR spectrum of complex **7** were found to be very similar to those of the analogous complex **1**,<sup>4</sup> which was characterized by X-ray crystallography.

These results differ markedly from the analogous reaction of Cp\*Fe(CO)<sub>2</sub>SiMe<sub>3</sub> (**3**) in the presence of *p*-TolSiH<sub>3</sub> that afforded only the mono(silylene)-bridged diiron complex Cp\*<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>(μ-CO)(μ-Si*p*-TolH) (**2**) as a *cis*–*trans* mixture.<sup>10</sup>

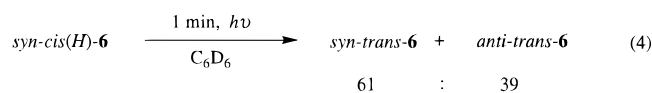
**Thermolysis and Photolysis of Complex 7.** Unlike complex **1** that shows the same behavior during either thermolysis or photolysis, affording only one isomer of Cp\*<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>(μ-Ge*t*-BuH)<sub>2</sub> (*syn-cis(H)*) with evolution of H<sub>2</sub> gas, the behavior of complex **7** in thermolysis is different from the photolysis reaction. As expected, the photolysis of complex **7** afforded a mixture of *syn-trans-6* and *anti-trans-6* complexes (eq 2) with



the same molar ratio as in the original reaction shown in eq 1. In contrast, thermolysis of complex **7** afforded the third isomer of complex **6** which adopted the *syn-cis(H)-6* configuration (eq 3). So far, the mechanism of



this dehydrogenation reaction is not clear. But if the thermal reaction is an intramolecular concerted process, the *syn-cis(H)* configuration of the product is consistent. The photolysis of *syn-cis(H)-6* isomer afforded a mixture of *syn*- and *anti-trans-6* with the molar ratio of 61:39 (eq 4). This isomerization was found to proceed relatively rapidly even under the usual fluorescent light.



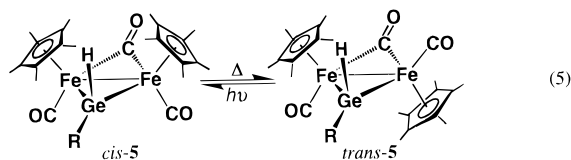
**Reversible Thermal and Photochemical Interconversion between *cis* and *trans* Isomers of the Germylene-Bridged Diiron Complex Cp\*<sub>2</sub>Fe<sub>2</sub>(CO)<sub>2</sub>(μ-CO)(μ-Ge*p*-TolH) (**5**).** The *cis* and *trans* isomers of complex **5** were found to undergo interconversion either

**Table 2. Activation Parameters  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$ , and  $\Delta G^\ddagger$  for the Isomerization of Complexes **5** and **2****

	<i>cis</i> - <b>5</b> $\rightarrow$ <i>trans</i> - <b>5</b>	<i>trans</i> - <b>5</b> $\rightarrow$ <i>cis</i> - <b>5</b>	<i>cis</i> - <b>2</b> $\rightarrow$ <i>trans</i> - <b>2</b> <sup>a</sup>	<i>trans</i> - <b>2</b> $\rightarrow$ <i>cis</i> - <b>2</b> <sup>a</sup>
$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$55.5 \pm 5.8$	$62.3 \pm 6.4$	$71.1 \pm 6.4$	$80.6 \pm 9.1$
$\Delta S^\ddagger/\text{J K}^{-1} \text{ mol}^{-1}$	$-137.2 \pm 18.6$	$-138.4 \pm 20.6$	$-90.3 \pm 20.5$	$-90.0 \pm 30.7$
$\Delta G^\ddagger_{298}/\text{kJ mol}^{-1}$	$96.4 \pm 12.2$	$103.6 \pm 13.5$	$98.0 \pm 12.5$	$107.4 \pm 18.2$

<sup>a</sup> Data are taken from ref 15.

thermally or photochemically (eq 5). This behavior is



closely analogous to that of the silicon analogue of **5** which we reported previously,<sup>15</sup> but the rate of the interconversion in **5** apparently is faster. The complexes with formula  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-ER}_2)$  (E = C, Si, or Ge; R = H, aliphatic, or aromatic groups) are known to exist usually as a mixture of *cis* and *trans* isomers in solution as in the cases of  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CMeH})$ ,<sup>6c</sup>  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-SiMeH})$ ,<sup>7</sup> and  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Ge}(p\text{-Tol})_2)$ ,<sup>5</sup> and it is rare to find only one isomer in solution as in the case of  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Si}t\text{-BuH})$ .<sup>10</sup> Figure 3 shows the <sup>1</sup>H NMR spectral change in the area of the Cp\* signals accompanying the thermal isomerization of complex **5** at 55 °C. Starting from the photostationary state mixture with the *cis:trans* ratio of 84:16, the *cis:trans* ratio changed gradually with time during thermolysis, where the signals of the *trans* isomer slowly increased in parallel with the decrease in the signals of the *cis* isomer, and the final (equilibrium) ratio of *cis:trans* became 7:93. At room temperature, a benzene-*d*<sub>6</sub> solution of complex **5** reached equilibrium after 24 h. The equilibrium ratios, the equilibrium constants (*K*), and the rate constants (*k*<sub>1</sub>,

*k*<sub>-1</sub>) are summarized in Table 1. A benzene solution of complex **5** (with molar ratio of *cis* and *trans* isomers of 84:16) was used to study the thermal isomerization by monitoring the electronic spectral changes of this mixture at 25.0, 35.0, 40.0, 45.0, and 55.0 °C. Table 2 shows the parameters of activation of both *cis*  $\rightarrow$  *trans* and *trans*  $\rightarrow$  *cis* isomerization. These results indicate that the *trans* isomer is thermodynamically more stable than the *cis* isomer, apparently due to the large steric repulsion between the two Cp\* rings with the *p*-tolyl group in the latter as in the case of the isostructural silylene complex  $\text{Cp}^*_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-Si}p\text{-TolH})$  (**2**).<sup>15</sup> The large negative entropies of activation imply participation of solvent which has been also proposed for the *cis*  $\rightarrow$  *trans* isomerization of  $\text{Cp}_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CH}_2)$ <sup>6a,b</sup> and **2**.<sup>15</sup> In comparison with the analogous silylene complex **2**, the  $\Delta H^\ddagger$  values of the isomerization of complex **5** are lower. The proportion of the *cis* isomer in equilibrium is larger in **5** (5%) than in the silicon analogue **2** (2%), apparently due to the longer Fe–Ge bond compared to the Fe–Si bond.<sup>10,14</sup> It must be also noted that a benzene-*d*<sub>6</sub> solution of complex **5** (the molar ratio of *cis:trans* equals 5:95) reached the photostationary state (*cis:trans* = 84:16) only after 1 min of irradiation. This is significantly faster than the corresponding process of **2**, which takes ca. 20 min.<sup>15</sup>

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