Photoreaction of Silyliron(II) Complex Cp*Fe(CO)₂SiMe₃ $(Cp^* = \eta^5 - C_5 Me_5)$ in the Presence of *p*-Tolylgermane

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Photolysis of $Cp*Fe(CO)_2SiMe_3$ (3) in the presence of *p*-TolGeH₃ (4) gave a mixture of *cis* and trans mono(germylene)-bridged diiron complexes, Cp*₂Fe₂(CO)₂(u-CO)(u-Gep-TolH) (cis-5, trans-5), a mixture of two kinds of trans bis(germylene)-bridged diiron complexes, $Cp*_2Fe_2(CO)_2(\mu$ -Gep-TolH)₂ (syn-trans-**6**, anti-trans-**6**), and a complex with two Fe···H···Ge 3-center 2-electron bonds, $Cp_{2}^{*}Fe_{2}(CO)_{2}(\mu$ -Gep-TolH₂)₂ (7). A cis isomer of complex **6** (syncis(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 C_6D_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 silvl(transition metal) complexes¹ and several complexes with M···H···Si 3-center 2-electron bonds² have been characterized. On the other hand, very little is known about analogous complexes possessing a M···H···Ge 3-center 2-electron bond.³ Recently, we prepared the first fully characterized complex with two Fe---H---Ge 3-center 2-electron bonds, Cp*2Fe2(CO)2- $(\mu$ -Ge*t*-BuH₂)₂ (**1**),⁴ which may be an intermediate in the formation of the bis(germylene)-bridged diiron complex via H₂ expulsion.⁴ 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 Cp*₂Fe(CO)₂- $(\mu$ -Ge*p*-Tol₂)₂.⁵ The isomers of complexes of type Cp₂M₂- $(CO)_2(\mu$ -CO) $(\mu$ -ER₂) (E = group 14 elements) can undergo either thermal or photochemical interconversion. The interconversion between these isomers has been reported for $Cp_2M_2(CO)_2(\mu$ -CO)(μ -CR₂) (M = Fe, Ru; R = H, alkyl, alkenyl, Ph, SR, etc.), $^{6a-i}$ Cp₂M₂(CO)₂(μ -CO)- $(\mu$ -C=CHR) (M = Fe, Ru; R = H, alkyl, Ph),^{6g-i} $Cp_2Fe_2(CO)_2(\mu-CO)(\mu-SiHMe)$,⁷ $Cp_2Fe_2(CO)_2(\mu-CO)(\mu-CO)(\mu-CO)(\mu-CO)(\mu-CO))$ SiXt-Bu) (X = Cl, Br, I, Me),⁸ Cp₂Fe₂(CO)₂(μ -CO)(μ -GeMe₂),⁹ and Cp*₂Fe₂(CO)₂(μ -CO)(μ -Sip-TolH) (**2**).¹⁰

Here we report the synthesis of the second diiron complex with two Fe···H···Ge 3-center 2-electron bonds by photolysis of Cp*Fe(CO)₂SiMe₃ (3) in the presence of *p*-TolGeH₃ (4). Through photolysis and thermolysis



Figure 1. Five possible geometric isomers of Cp*₂Fe₂- $(CO)_2(\mu$ -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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^{Abstract published in} *Advance ACS Abstracts*, October 1, 1950.
(1) Aylett, B. J. *Adv. Inorg. Radiochem.* 1982, *25*, 1.
(2) (a) Hart-Davis, A. J.; Graham, W. A. G. *J. Am. Chem. Soc.* 1971, *94*, 4388. (b) Schubert, U.; Scholz, G.; Müller, J.; Ackermann, K; Worle, B. *J. Organomet. Chem.* 1986, *306*, 303. (c) Schubert, U.; Müller, J.; Alt, H. G. Organometallics **1987**, *6*, 469. (d) Luo, X.-L.; Crabtree, R. H. J. Am. Chem. Soc. **1987**, *111*, 2527.

⁽³⁾ Carre, F.; Colomer, E.; Corriu, R. J. P.; Vioux, A. Organometallics 1984, 3, 1272.

⁽⁴⁾ Submitted for publication.

⁽⁵⁾ El-Maradny, A.; Tobita, H.; Ogino, H. Chem. Lett. 1996, 83.

^{(6) (}a) Korswagen, R.; Alt, R.; Speth, D.; Ziegler, M. L. Angew. Chem., Int. Ed. Engl. **1981**, 20, 1049. (b) Altbach, M. I.; Muedas, C. A.; Korswagen, R. P. J. Organomet. Chem. **1986**, 306, 375. (c) Dyke, A. F.; Knox, S. A. R.; Morris, M. J.; Naish, P. J. J. Chem. Soc., Dalton Trans. 1983, 1417. (d) Davies, D. L.; Knox, S. A. R.; Mead, K. A.; Morris, M. J.; Woodward, P. J. Chem. Soc., Dalton Trans. 1984, 2293. (e) Gracey, B. P.; Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G. J. Chem. Soc., Dalton Trans. 1985, 1935. (f) Colborn, R. E.; Dyke, A. F.; Knox, S. S. A. R.; Mead, K. A.; Woodward, P. J. Chem. Soc., Dalton Trans. **1983**, 2099. (g) Colborn, R. E.; Davies, D. L.; Dyke, A. F.; Endesfelder, A.; Knox, S. A. R. *J. Chem. Soc., Dalton Trans.* **1983**, 2661. (h) Schoeder, N. C.; Funchess, R.; Jacobson, R. A.; Angelici, R. J. Organometallics 1989, 8, 521. (i) Casey, C. P.; Austin, E. Ă. J. Am. Chem. Soc. 1988, 110, 7106.

⁽⁷⁾ Malisch, W.; Ries, W. Angew. Chem., Int. Ed. Engl. 1978, 17, 120.

⁽⁸⁾ Tobita, H.; Kawano, Y.; Ogino, H. *Chem. Lett.* **1989**, 2155.
(9) Job, R. C.; Curtis, M. D. *Inorg. Chem.* **1973**, *12*, 2514.

⁽¹⁰⁾ Kawano, Y.; Tobita, H.; Ogino, H. J. Organomet. Chem. 1992, 428 125

(THF) were distilled from sodium-benzophenone ketyl immediately before use. Deuterated NMR solvents were stored over molecular sieves 4A under N₂. Cp*Fe(CO)₂SiMe₃¹¹ was prepared according to the published procedure. p-Chlorotoluene was distilled over P2O5 immediately prior to use. Germanium tetrachloride was stored under N₂ 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.

¹H NMR and ¹³C NMR spectra were recorded on a Bruker AC-300 spectrometer. Variable-temperature ¹H 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 temperaturecontrolled cell holder.

Preparation of p-Tolylgermane. (p-Tolyl)magnesium chloride was prepared by the addition of a solution of pchlorotoluene (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 N₂, 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 GeCl₄ (64.8 g, 0.300 mol) dissolved in Et₂O (100 mL) was added the Grignard reagent over 90 min. The mixture was then gently refluxed for 2 h, MgCl₂ was filtered off over Celite, and the mixture was washed twice with 100 mL Et₂O. All solvents were removed to yield a yellow solution. A fractional distillation of the latter solution afforded trichloro-p-tolylgermane, p-TolGeCl₃, as a colorless liquid (27 g, 0.10 mol) in 33% yield (bp 60 °C, 0.6 mmHg) (lit. bp 129-131 °C, 24 mmHg¹²). ¹Ĥ NMR (C₆D₆): δ 1.85 (3H, s, $C_6H_4CH_3$), 6.72, 7.26 (2H × 2, d, $J_{HH} = 7.81$ Hz, $C_6H_4CH_3$). ¹³C NMR (CDCl₃): δ 21.7 (C₆H₄CH₃), 130.1, 131.2, 131.7, 143.9 $(C_6H_4CH_3)$. MS: m/z 270 (41, M⁺). Dichlorodi-*p*-tolylgermane¹³ was also obtained in 28% yield.

To a well-stirred suspension of LiAlH₄ (3.2 g, 88 mmol) in Et₂O (50 mL) was added a solution of the above trichloro-ptolylgermane (27 g) in Et₂O (30 mL) over 50 min. The mixture was then gently refluxed for 4 h. Excess LiAlH₄ was destroyed by the slow addition of 10% H_2SO_4 . The reaction mixture was extracted with Et₂O. The organic layer was dried over anhydrous MgSO₄. Fractional distillation afforded p-tolylgermane, p-TolGeH₃ (4), as a colorless liquid (12.6 g, 0.075 mol) in 75% yield (bp 40 °C, 0.6 mmHg). ¹H NMR (C₆D₆): δ 2.05 (3H, s, C₆H₄CH₃), 4.26 (3H, s, GeH), 6.94, 7.27 (2H \times 2, d, $J_{\rm HH} = 7.69, C_6 H_4 CH_3$). ¹³C NMR (CDCl₃): δ 22.0 (C₆H₄CH₃), 128.0, 129.7, 136.0, 139.4 (C₆H₄CH₃). IR (benzene solution): 2071 (s) (ν_{GeH}) cm⁻¹. MS: m/z 168 (21, M⁺). Anal. Found: C, 50.61; H, 5.78. Calcd for C₇H₁₀Ge: C, 50.42; H, 6.04.

Photolysis of Cp*Fe(CO)₂SiMe₃ (3) in the Presence of p-TolGeH₃ (4). Cp*Fe(CO)₂SiMe₃ (3) (670 mg, 2.09 mmol) and p-TolGeH₃ (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*2Fe2-(CO)₂(*u*-CO)(*u*-Ge*p*-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*2Fe2(CO)2(u-Gep-

 $TolH_{2}$ (6) (224 mg, 0.29 mmol, 21%, syn-trans:anti-trans = 61:39), and (3) an orange complex Cp*₂Fe₂(CO)₂(µ-Gep-TolH₂)₂ (7) (243 mg, 0.320 mmol, 23%). 5: MS m/z 631 (3, M⁺), 603 (23, $M^+ - CO$), 540 (55, $M^+ - p$ -Tol). Anal. Found: C, 57.48; H, 6.51. Calcd for C₃₀H₃₈O₃Fe₂Ge: C, 57.11; H, 6.07. cis-5: ¹H NMR (C₆D₆) δ 1.60 (30H, s, 2Cp*), 2.12 (3H, s, C₆H₄CH₃), 7.24, 8.36 (2H \times 2, d, $J_{\rm HH}$ = 7.74 Hz, C₆H₄CH₃), 8.62 (H, s,-GeH); IR (KBr) 1994 (w) (v_{GeH}), 1942 (vs), 1903 (m) (v_{COterm}), 1731 (s) (ν_{CObrid}) cm⁻¹. trans-5: ¹H NMR (C₆D₆) δ 1.61, 1.67 (30H, 2s, 2Cp*), 2.20 (3H, s, C₆H₄CH₃), 7.24, 8.20 (2H \times 2, d, $J_{\rm HH} = 7.59$ Hz, C₆ H_4 CH₃), 8.42 (H, s, GeH); IR (KBr) 1992 (w) (ν_{GeH}) , 1932 (m), 1901 (vs) (ν_{COterm}) , 1747 (s) (ν_{CObrid}) cm⁻¹. 6: MS m/z 766 (43, M⁺), 738 (16, M⁺ – CO), 618 (10, M⁺ – 2CO - p-Tol). Anal. Found: C, 56.05; H, 5.84. Calcd for C₃₆H₄₄O₂Fe₂Ge₂: C, 56.48; H, 5.79. syn-trans-6: ¹H NMR ((CD₃)₂CO) δ 1.57, 1.62 (30H, 2s, 2Cp*), 2.41 (6H, s, 2C₆H₄CH₃), 7.32, 7.93 (4H \times 2, d, $J_{\rm HH}$ = 7.52 Hz, 2C₆H₄CH₃; see Results and Discussion), 8.04 (2H, s, GeH); IR (KBr) 1930 (m), 1889 (s) (ν_{COterm}) cm⁻¹. anti-trans-6: ¹H NMR ((CD₃)₂CO) δ 1.55 (30H, s, 2Cp*), 2.38 (6H, s, 2C₆H₄CH₃), 7.28, 7.87 (4H × 2, d, 2C₆H₄CH₃; see Results and Discussion), 7.95 (2H, s, GeH); IR (KBr) 1876 (vs) (ν_{COterm}) cm⁻¹. 7: ¹H NMR (C₆D₆) δ -12.74 (2H, s, 2FeH), 1.51 (30H, s, 2Cp*), 2.18 (6H, s, 2C₆H₄CH₃), 3.81 (2H, s, 2GeH), 7.13, 8.02 (4H × 2, d, J_{HH} = 7.78 Hz, 2C₆H₄-CH₃); ¹³C NMR (C₆D₆) δ 10.1 (CH₃, Cp*), 21.4 (C₆H₄CH₃), 90.9 (Cp*, ring C), 128.6, 135.6, 137.2, 141.6 (C₆H₄CH₃), 222.9 (CO); IR (KBr) 1998 (w) (v_{GeH}), 1930 (vs), 1921 (vs) (v_{COterm}), 1898 (m) ($\nu_{\text{Ge-H-Fe}}$) cm⁻¹; MS m/z 768 (10, M⁺), 697 (13, M⁺ – Me – 2CO). Anal. Found: C, 55.98; H, 6.50. Calcd for C₃₆H₄₈O₂Fe₂Ge₂: C, 56.33; H, 6.04.

Thermolysis of Cp*₂Fe₂(CO)₂(µ-Gep-TolH₂)₂ (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 $Cp_{2}^{*}Fe_{2}(CO)_{2}(\mu$ -Gep-TolH₂)₂ (6) (20 mg, 26 mmol, 25%) was obtained as a red powder. Further purification for this complex was unsuccessful because of the light sensitivity. ¹H NMR (C₆D₆): δ 1.58 (30H, s, 2Cp*), 2.15 (6H, s, $2C_6H_4CH_3$) 7.29, 8.48 (4H × 2, d, J_{HH} = 7.66 Hz, $2C_6H_4$ -CH₃), 8.67 (2H, s, GeH). ¹³C NMR (C₆D₆): δ 11.0 (CH₃, Cp*), 21.5 (C₆H₄CH₃), 91.6 (Cp*, ring C), 129.0, 136.1, 138.0, 149.4 (C₆H₄CH₃), 215.6 (CO). IR (KBr): 1921 (s), 1894 (m) (v_{COterm}) cm⁻¹. MS: m/z 766 (9, M⁺), 738 (14, M⁺ – CO). Exact mass: found: 768.0473; calcd for $C_{36}H_{44}O_2Fe_2Ge_2$, 768.0464.

Photolysis of Cp*2Fe2(CO)2(µ-Gep-TolH2)2 (7). Photolysis of a benzene- d_6 solution of 7 in an NMR tube at 6 °C for 10 min was monitored by ¹H 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 H₂.

Photolysis of Cp*2Fe2(CO)2(µ-Gep-TolH)2 (syn-cis(H)-**6).** The monitoring of the photolysis of a benzene- d_6 solution of *syn-cis(H)*-6 in an NMR tube at 6 °C for 1 min by ¹H NMR spectroscopy showed a quantitative conversion from syncis(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 isosbestic point was observed at 505 nm. The values of equilibrium constants at different temperatures were determined by the integration of ¹H NMR spectra of Cp* groups. Plots of $\ln(A_{\infty} - A_t/A_{\infty} - A_0)$ vs time were linear ($A_{\infty} =$ absorption at equilibrium; A_t = absorption at time t; A_0 =

⁽¹¹⁾ Randolph, C. L.; Wrighton, M. S. Organometallics 1987, 6, 365.
(12) Seyferth, D.; Hetflejs, J. J. Organomet. Chem. 1968, 11, 253.
(13) Mochida, K.; Matsushige, N.; Hamashima, M. Bull. Chem. Soc. Jpn. 1985, 55, 1443.

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 Cp*Fe(CO)₂**SiMe**₃ (3) in the Presence of *p*-TolGeH₃ (4). Irradiation of Cp*Fe(CO)₂-SiMe₃ (3) in the presence of *p*-TolGeH₃ (4) in pentane for 100 min afforded mono- and bis(germylene)-bridged diiron complexes and a complex with two Fe···H···Ge 3-center 2-electron bonds (eq 1). The major product was



the mono(germylene)-bridged diiron complex Cp*2Fe2- $(CO)_2(\mu$ -CO)(μ -Gep-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 ¹H 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 ¹H NMR spectrum of the trans isomer showed two 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 Ge-H proton. In the IR spectrum of the trans isomer, the $v_{\rm COasym}$ band is stronger than $v_{\rm COsym}$, while in the *cis* isomer this relationship is reversed. These data were found to be very similar to those of the analogous silylene complex Cp*₂Fe₂(CO)₂(µ-CO)(µ-Sip-TolH) (2)¹⁰ except for a small shift of the GeH protons (8.62 ppm for cis and 8.42 ppm for trans in C₆D₆) toward low field relative to the SiH protons (7.44 ppm for cis and 7.01 ppm for *trans* in cyclohexane- d_{12}) in the ¹H 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 $Cp^*{}_2Fe(CO)_2(\mu$ -Ge*p*-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.^{4,14} Thus, the analogous complex $Cp_2Fe(CO)_2(\mu$ -Ge*t*-BuH)₂¹⁴ was isolated as an *anti-trans* isomer, while $Cp^*_2Fe_2$ -



Figure 2. Temperature-dependent ¹H NMR spectra (CDCl₃) of the *syn-* and *anti-trans-***6** mixture in the aromatic signal region.

 $(CO)_2(\mu$ -Ge*t*-BuH)_2⁴ 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 ¹H NMR and IR spectra. In the ¹H NMR spectrum, *syn-trans*-6 showed two singlet signals in the area of Cp*. Among the five possible geometric isomers of 6, the only isomer that can show two signals in the ¹H NMR spectrum for 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 $\nu_{\rm CO}$ at 1930 cm⁻¹, while the asymmetric stretch at 1889 cm⁻¹ was found to be a strong band. The ¹H NMR spectrum of the other isomer in this mixture showed only one signal for Cp*, one methyl signal of *p*-tolyl groups, two doublet signals in the aromatic region, and one signal for GeH; i.e., syncis(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. ¹H NMR spectral changes in the Cp* signal region in C₆D₆ on thermolysis of complex **5** at 55 °C: (Δ) *cis*-**5**, (0) *trans*-**5**.

of them can show this ¹H 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_{CO} was observed at 1876 cm⁻¹. Thus we assigned the other complex in this mixture as *anti-trans*-**6**.

The ¹H NMR signals of the aromatic protons of *syntrans*-**6** and *anti-trans*-**6** complexes were found to be temperature-dependent, as shown in Figure 2. The spectrum at 218 K (in CDCl₃) 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 $Cp_2Fe_2(CO)_2(\mu$ -Gep-TolH₂)₂ (7) with two Fe···H···Ge 3-center 2-electron bonds that was isolated in 23% yield. In the ¹H NMR spectrum of 7 in C₆D₆, 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_1 , k_{-1}) of *cis* \rightarrow *trans* Isomerization of Complex 5 at 298.2, 308.2, 313.2, 318.2, and 328.2 K

temp/K	cis/trans	K	k_1/s^{-1}	k_{-1}/s^{-1}
298.2	5.4:94.6	17.5	$8.74 imes 10^{-5}$	$4.99 imes10^{-6}$
308.2	5.6:94.4	16.9	$1.49 imes10^{-4}$	$8.84 imes10^{-6}$
313.2	5.8:94.2	16.2	$2.23 imes10^{-4}$	$1.37 imes10^{-5}$
318.2	6.1:93.9	15.4	$3.26 imes10^{-4}$	$2.12 imes10^{-5}$
328.2	6.7:93.3	13.9	$7.90 imes10^{-4}$	$5.68 imes10^{-5}$

exhibits two weak bands at 1998 and 1898 cm⁻¹ that can be assigned to ν_{GeH} and $\nu_{Ge-H-Fe}$, respectively, besides two intense bands of ν_{CO} at 1930 and 1921 cm⁻¹. Both the ¹H NMR and IR spectrum of complex 7 were found to be very similar to those of the analogous complex 1,⁴ which was characterized by X-ray crystallography.

These results differ markedly from the analogous reaction of Cp*Fe(CO)₂SiMe₃ (**3**) in the presence of *p*-TolSiH₃ that afforded only the mono(silylene)-bridged diiron complex Cp*₂Fe₂(CO)₂(μ -CO)(μ -Si*p*-TolH) (**2**) as a *cis*-*trans* mixture.¹⁰

Thermolysis and Photolysis of Complex 7. Unlike complex **1** that shows the same behavior during either thermolysis or photolysis, affording only one isomer of $Cp*_2Fe_2(CO)_2(\mu$ -Ge*t*-BuH)_2 (*syn-cis(H)*) with evolution of H₂ 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 *syncis*(*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.

$$syn-cis(H)-6 \xrightarrow[C_6D_6]{1 min, hv} syn-trans-6 + anti-trans-6 \qquad (4)$$

Reversible Thermal and Photochemical Interconversion between *cis* and *trans* **Isomers of the Germylene-Bridged Diiron Complex** $Cp*_2Fe_2(CO)_2$ -(μ -CO)(μ -Gep-TolH) (5). The *cis* and *trans* isomers of complex 5 were found to undergo interconversion either

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Table 2.	Activation	Parameters ΔH	[♯] , Δ <i>S</i> [♯]	, and ΔG	[‡] for the	Isomerization	of Com	plexes 5	and 2	;
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	cis-5 → $trans$ -5	$trans-5 \rightarrow cis-5$	cis - $2 \rightarrow trans$ - 2^a	$trans-2 \rightarrow cis-2^a$
$\Delta H^{\ddagger}/\text{kJ mol}^{-1}$ $\Delta S^{\ddagger}/\text{J K}^{-1} \text{ mol}^{-1}$ $\Delta C^{\ddagger}/k \text{ I mol}^{-1}$	$55.5 \pm 5.8 \ -137.2 \pm 18.6 \ 06.4 \pm 12.2$	$\begin{array}{c} 62.3\pm 6.4 \\ -138.4\pm 20.6 \\ 102.6\pm 12.5 \end{array}$	$71.1 \pm 6.4 \\ -90.3 \pm 20.5 \\ 98.0 \pm 12.5$	80.6 ± 9.1 -90.0 \pm 30.7 107.4 \pm 18.2

^a 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,15 but the rate of the interconversion in 5 apparently is faster. The complexes with formula $Cp_2Fe_2(CO)_2(\mu$ -CO)(μ -ER₂) (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 $Cp_2Fe_2(CO)_2(\mu$ -CO)(μ -CMeH),^{6c} Cp₂Fe₂(CO)₂(µ-CO)(µ-SiMeH),⁷ and Cp₂Fe₂(CO)₂(µ-CO)- $(\mu$ -Ge(p-Tol $)_2$),⁵ and it is rare to find only one isomer in solution as in the case of $Cp_2Fe_2(CO)_2(\mu-CO)(\mu-Sit-$ BuH).¹⁰ Figure 3 shows the ¹H 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_6 solution of complex 5 reached equilibrium after 24 h. The equilibrium ratios, the equilibrium constants (K), and the rate constants (k_1, \ldots, k_n)

(15) Kawano, Y.; Tobita, H.; Ogino, H. Organometallics 1992, 11, 499.

 k_{-1}) 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 Cp*₂Fe₂(CO)₂(µ-CO)(µ-Sip-TolH) (2).¹⁵ The large negative entropies of activation imply participation of solvent which has been also proposed for the $cis \rightarrow trans$ isomerization of Cp₂Fe₂(CO)₂(μ -CO)(μ - CH_2)^{6a,b} and **2**.¹⁵ In comparison with the analogous silylene complex **2**, the ΔH^{\sharp} 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.^{10,14} It must be also noted that a benzene- d_6 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.¹⁵

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