Photoreactions of Silyliron(II) Complexes Cp'Fe(CO)$_2$SiMe$_3$ (Cp' = η^5-C$_5$H$_5$, η^5-C$_5$Me$_5$) with Di-*p*-tolylgermane (*p*-Tol)$_2$GeH$_2$

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Photolysis of CpFe(CO)$_2$SiMe$_3$ (Cp = η^5-C$_5$H$_5$) in the presence of (*p*-Tol)$_2$GeH$_2$ afforded a mixture of *cis* and *trans* isomers of diiron complexes Cp$_2$Fe$_2$(CO)$_2$(μ-CO){μ-Ge(*p*-Tol)$_2$} and Cp$_2$Fe$_2$(CO)$_2${μ-Ge(*p*-Tol)$_2$}$_2$. The photostationary state with *cis* : *trans* = 85 : 15 was attained by the photolysis of either *cis* or *trans* isomer of the latter complex. In contrast, photoreaction of Cp*Fe(CO)$_2$SiMe$_3$ (Cp* = η^5-C$_5$Me$_5$) with (*p*-Tol)$_2$GeH$_2$ gave a monoiron complex Cp*Fe(CO)$_2$GeH(*p*-Tol)$_2$.

It is well known that the R$_2$E group, where R represents either an alkyl, aryl, or hydrogen and E is one of the group 14 elements, Si, Ge, or Sn, can function as a bridging unit across two metal atoms.[1] The first bis(germylene)-bridged diiron complex was reported by Job and Curtis:[2] The photolysis of an iron complex CpFe(CO)$_2$GeMe$_2$Cl gave a small amount of *cis*-bis(germylene)diiron complex Cp$_2$Fe$_2$(CO)$_2$(GeMe$_2$)$_2$ (**1**). Recently, we reported the photochemical reactions of iron-carbonyl complexes CpFe(CO)$_2$SiMe$_3$ (**2**) and Cp*Fe(CO)$_2$SiMe$_3$ (**3**) with *t*-butylgermane *t*-BuGeH$_3$.[3,4] In both reactions, bis(germylene)-bridged diiron complexes Cp'$_2$Fe$_2$(CO)$_2$(μ-GeH*t*-Bu)$_2$ (Cp' = Cp, Cp*) were obtained along with mono(germylene)-bridged diiron complexes Cp'$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-GeH*t*-Bu). Here we report the photochemical reactions of **2** and **3** with di-*p*-tolylgermane (*p*-Tol)$_2$GeH$_2$ (**4**) whose substituents are more sterically hindered than methyl and less sterically hindered than *t*-butyl.

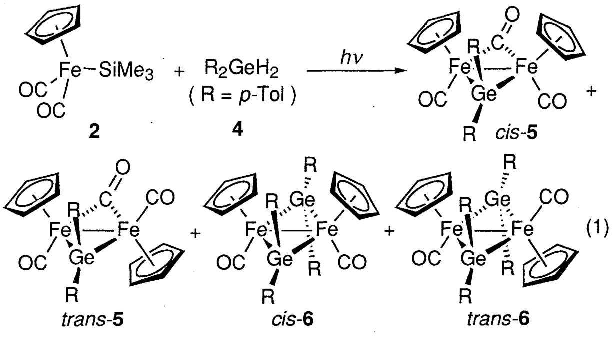
Di-*p*-tolylgermane (**4**) was prepared as described in the literature.[5] A mixture of **2** and **4** in a 1 : 1 molar ratio was irradiated in dry pentane using a 450 W medium pressure mercury lamp at 0 °C for 100 min. Evolution of carbon monoxide was observed and the color of the solution changed from pale yellow to deep red during the photolysis. Evaporation of volatile materials and subsequent flash chromatographic separation of the residue (silica gel, eluent hexane : benzene = 1 : 1) gave Cp$_2$Fe$_2$(CO)$_2$(μ-CO){μ-Ge(*p*-Tol)$_2$} (**5**), *cis*-Cp$_2$Fe$_2$(CO)$_2${μ-Ge(*p*-Tol)$_2$}$_2$ (*cis*-**6**), and *trans*-Cp$_2$Fe$_2$(CO)$_2${μ-Ge(*p*-Tol)$_2$}$_2$ (*trans*-**6**) (eq 1).

Complex **5** was obtained as a mixture of *cis* and *trans* isomers in 1 : 3 molar ratio, which was clearly shown in the ^{1}H NMR spectrum in a benzene-d_6 solution and the IR spectrum in a benzene solution:[6] The major isomer shows only one set of ^{1}H NMR signals for *p*-tolyl groups, and the stronger asymmetrical νCO_{term} band (with lower frequency) compared to the symmetrical one (with higher frequency). These spectroscopic properties are consistent with the structure of *trans*-**5**.

Interestingly, recrystallization of the *cis-trans* mixture of **5** from CH$_2$Cl$_2$-pentane resulted in red crystals of the minor isomer *cis*-**5** exclusively in 44% yield based on **2**. The IR spectrum of the recrystallized sample of **5** showed only two stretching bands for terminal CO ligands, in which the symmetrical stretching band (with higher frequency) is much stronger than the asymmetrical stretching band (with lower frequency). This result supports the *cis* configuration of molecules in the crystals.[7]

When crystals of *cis*-**5** was dissolved in benzene-d_6 at room temperature, the ^{1}H NMR spectrum showed both *cis* and *trans* isomers in 1 : 3 molar ratio. This indicates that, in solution, complex **5** is in a dynamic equilibrium between *cis* and *trans* isomers. A similar behavior has been observed for Cp$_2$Fe(CO)$_2$(μ-CO)(GeMe$_2$),[1] and Cp$_2$Fe(CO)$_2$(μ-CO)(GeH*t*-Bu),[3] but in these complexes the *cis* isomers are preferred over the *trans* isomers even in solution.

Pure *cis*-**6**[8] was obtained by recrystallization of the crude product from CH$_2$Cl$_2$-pentane as deep red crystals in 22% yield, and pure *trans*-**6**[9] from toluene as pink crystals in 10% yield. The geometry of *cis*-**6** and *trans*-**6** isomers was determined on



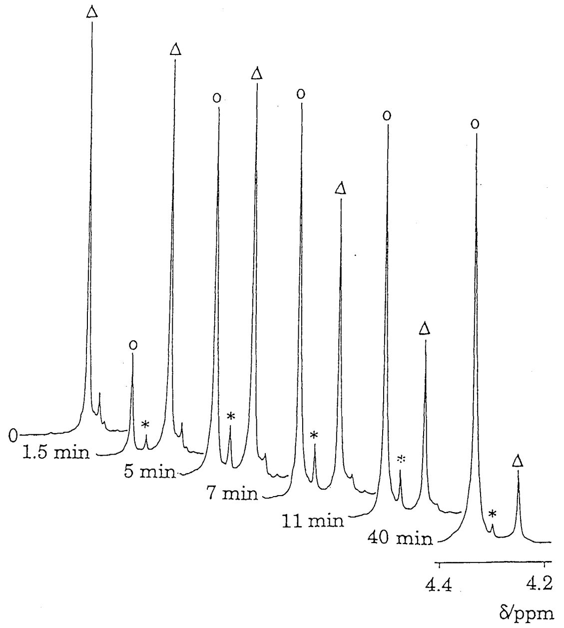
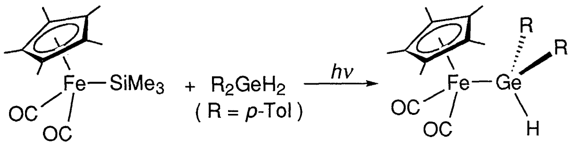


Figure 1. ^{1}H NMR spectral change in the Cp signal region in C$_6$D$_6$ on irradiation at 6 °C: (Δ) *trans*-**6**; (o) *cis*-**6**; (*) impurity.

the basis of the spectral data.[8,9] Unlike **5**, complex **6** did not show thermal *cis-trans* isomerization. However, when a benzene-d_6 solution of *trans*-**6** was irradiated, ^{1}H NMR spectra indicated decrease in signals of *trans* isomer and increase in signals of *cis* isomer. After 40 min, this reaction reached a photostationary state in which the ratio of *cis*-**6** to *trans*-**6** was 85 : 15 (Figure 1). The same ratio of *cis*-**6** to *trans*-**6** was obtained at the photostationary state, when a solution of *cis*-**6** was irradiated under the same conditions. The predominance of the *cis* isomer in the photochemical synthesis and in the photostationary state in the interconversion between *cis* and *trans* isomers implies that the *trans* → *cis* conversion is more efficient than *cis* → *trans* conversion under the photochemical conditions.

Irradiation of a mixture of $Cp^*Fe(CO)_2SiMe_3$ (**3**) and $(p\text{-Tol})_2GeH_2$ (**4**) under the same conditions for 3 hours gave no stable diiron complex except for $Cp^*{}_2Fe_2(CO)_4$ which was obtained in 5% yield, while the main product was a yellow monoiron complex $Cp^*Fe(CO)_2GeH(p\text{-Tol})_2$ (**7**)[10] obtained in 69% yield (eq 2).



(2)

3 **4** **7**

The absence of μ-germylenediiron complex in this reaction may be attributed to the steric bulkiness of the two *p*-tolyl groups and the pentamethylcyclopentadienyl ring in **7**, a possible intermediate toward μ-germylenediiron complex, which renders the germanium atom of **7** unfavorable to accept the second iron fragment. It was also noticed that a solution of complex **7** in benzene-d_6 was stable when irradiated alone for more than one hour.

In conclusion, *p*-tolyl substituents on germanium as a moderately sterically hindered group allow the formation of both *cis* and *trans* isomers of bis(germylene)-bridged diiron complex in case of **2** (Cp), while they are too sterically hindered in case of **3** (Cp*) to form any germylene-bridged diiron complex.

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6 Data for **5**: ^{1}H NMR (300 MHz, C_6D_6) (***cis***) δ = 2.163 (3H, s, CH_3), 2.166 (3H, s, CH_3), 4.26 (10H, s, Cp), 7.07, 7.23, 7.47, 7.81 (2H x 4, 4d, J_{HH} = 7.7 Hz, $C_6H_4CH_3$); (***trans***) δ = 2.15 (6H, s, CH_3), 4.30 (10H, s, Cp), 7.13, 7.84 (4H x 2, d, J_{HH} = 7.9 Hz, $C_6H_4CH_3$). IR (***cis***) (KBr) 1953 (vs), 1920 (m) (νCO_{term}), 1749 (s) (νCO_{brid}) cm^{-1}; (***trans***) (benzene soln) 1975 (m), 1927 (vs) (νCO_{term}), 1770 (s) (νCO_{brid}) cm^{-1}. MS (EI, 70 ev) *m/z* (582, M^+), (554, M^+-CO), (526, M^+- 2CO), (498, M^+-3CO). Anal. Found: C, 55.44; H 4.02%. Calcd for $C_{27}H_{24}Fe_2GeO_3$: C, 55.84; H, 4.17%.
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8 Data for *cis*-**6**: ^{1}H NMR (300 MHz, C_6D_6) δ = 2.18, 2.21 (12H, 2s, CH_3), 4.33 (10H, s, Cp), 7.11, 7.26, 7.33, 7.88 (4H x 4, d, J_{HH} = 7.8 Hz, $C_6H_4CH_3$). IR (KBr) 1955 (vs), 1945 (m) (νCO_{term}) cm^{-1}. MS (EI, 70ev) *m/z* (810, M^+), (780, M^+-CO), (752, M^+-2CO). Anal. Found: C, 60.71; H, 5.09%. Calcd for $C_{40}H_{38}Fe_2Ge_2O_2$: C, 59.92; H, 4.74%.
9 Data for *trans*-**6**: ^{1}H NMR (300 MHz, C_6D_6) δ = 2.17 (12H, s, CH_3), 4.25 (10H, s, Cp), 7.08,7.90 (8H x 2, d, J_{HH} = 7.8 Hz, $C_6H_4CH_3$). IR (KBr) 1905 (vs) (νCO_{term}) cm^{-1}. MS (EI, 70ev) *m/z* (811, M^++1), (780, M^+-CO), (751, M^+-2CO). Anal. Found: C, 59.56; H, 4.48%. Calcd for $C_{40}H_{38}Fe_2Ge_2O_2$: C, 59.92; H, 4.74%.
10 Data for **7**: ^{1}H NMR (300 MHz, C_6D_6) δ = 1.42 (15H, s, C_5Me_5), 2.10 (6H, s, $C_6H_4CH_3$), 5.38 (H, s, GeH), 7.06, 7.88 (4H x 2, 2d, J_{HH} = 7.7 Hz, $C_6H_4CH_3$). ^{13}C NMR (300 MHz, C_6D_6) δ = 9.4 (C_5Me_5), 21.3 ($C_6H_4CH_3$), 94.5 (ring carbons of Cp*), 128.9, 135.3, 137.2, 141.7 ($C_6H_4CH_3$), 217.8 (2CO). IR (KBr) : 1920 (vs), 1980 (vs) (νCO_{term}), 1932 (vs) (νGeH) cm^{-1}. MS (EI, 70ev) *m/z* (504, M^+), (476, M^+-CO), (448, M^+-2CO). Anal. Found: C, 62.06; H, 6.03%. Calcd for $C_{26}H_{30}FeGeO_2$: C, 62.09; H, 6.01%.