CHEMISTRY LETTERS, pp. 293-296, 1994.

# Synthesis and Properties of Germylene-Bridged Diiron Complexes Using *t*-Butylgermane as a Precursor of Ligands

Yasuro KAWANO, Keiko SUGAWARA, Hiromi TOBITA, and Hiroshi OGINO*
Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980

Photolysis of $CpFe(CO)_2SiMe_3$ (Cp = $\eta$-$C_5H_5$) in the presence of a new alkylgermane $^tBuGeH_3$ afforded a mono($\mu$-germylene)diiron complex $Cp_2Fe_2(CO)_3(\mu$-$GeH^tBu)$ (**4**) and a bis($\mu$-germylene)diiron complex $Cp_2Fe_2(CO)_2(\mu$-$GeH^tBu)_2$ (**5**). The structure of **4** was determined by X-ray crystallography.

Hydrosilanes and hydrogermanes have been known to react with transition metal complexes at their E-H (E = Si or Ge) bonds and form the complexes having E-M bonds.1) Therefore, polyhydrosilanes and polyhydrogermanes, which have more than one E-H bond, can serve as precursors of bridging ligands .1)

Previously, we reported the photochemical reactions of an iron-carbonyl complex $CpFe(CO)_2SiMe_3$ (**1**) with *tertiary*-alkyl trihydrosilanes $RSiH_3$ (R = $^tBu$ or $H(CMe_2)_2$). These reactions gave silylene-bridged diiron complexes $Cp_2Fe_2(CO)_3(\mu$-SiHR) (**2a**: R = $^tBu$, **2b**: R = $H(CMe_2)_2$) exclusively in high yields.2) The complex **2** shows some conspicuous properties and reactivities: The bridging silicon in **2** exhibits a $^{29}Si$ NMR signal at the remarkably low field ($\delta$ 254-255 ppm).2b) The hydrogen atom on the bridging silicon in **2a** is readily converted into halogen atoms,3) and the resulting complex can be a precursor of the cationic $\mu$-silylyne (RSi) complex.4) These results prompted us to investigate the photoreactions using trihydrogermane instead of trihydrosilane. Here we report a photochemical reaction of **1** in the presence of $^tBuGeH_3$ (**3**), giving germylene-bridged complexes, and the characterization and properties of the products.

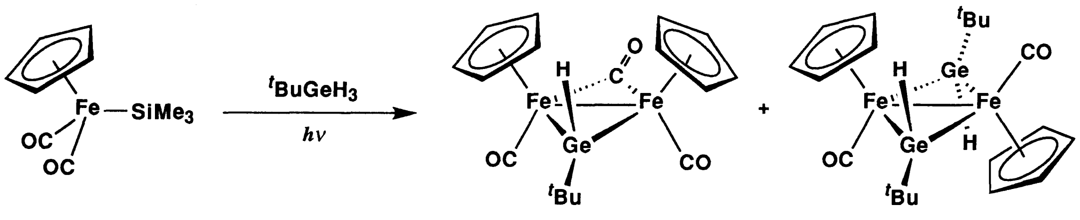
*t*-Butylgermane **3**, which is a new trihydrogermane, was prepared according to the reactions shown in Scheme 1 and was isolated as a colorless liquid in 98% yield by vacuum distillation at low temperature.5)

$$GeX_4 + {}^tBuMgCl \longrightarrow {}^tBuGeX_3 \qquad (X = Cl \text{ or } OEt)$$

$${}^tBuGeX_3 \xrightarrow[{}^nBu_2O]{LiAlH_4} {}^tBuGeH_3\ (\mathbf{3})$$

Scheme 1.

A mixture of **1** and **3** in a 2 : 1 molar ratio was irradiated in dry pentane using a 450 W medium pressure mercury lamp at 0 °C for 4 h. 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 chromatographic separation gave red crystals of a $\mu$-germylene complex $Cp_2Fe_2(CO)_3(\mu$-$GeH^tBu)$ (**4**) and a bis($\mu$-germylene) complex $Cp_2Fe_2(CO)_2(\mu$-$GeH^tBu)_2$ (**5**) in 40 and 11% yields, respectively (Eq. 1).



**1** **4** **5** (1)

Several geometric isomers are possible for both **4** and **5**. In fact, the complex **5** was obtained as a mixture of some isomers. By recrystallization of the isomeric mixture of **5** from $CH_2Cl_2$-hexane, we isolated pure *anti-trans* **5** (the isomer shown in Eq. 1).[6] As to **4**, only the *cis*(H) isomer (the isomer shown in Eq. 1) was obtained.[7]

The molecular structure of **4** was determined by X-ray crystallography; crystal data: triclinic, space group $P\bar{1}$, $a$ / Å = 9.090(1), $b$ / Å = 15.476(2), $c$ / Å = 6.776(1), $\alpha$ / deg = 102.13(1), $\beta$ / deg = 104.23(1), $\gamma$ / deg = 86.15(1), $V$ / Å$^3$ = 903.2(1), $R$ = 0.040, $R_w$ = 0.050. The structure of **4** closely resembles that of its silicon analogue **2a**.[2] As shown in Fig. 1, the two cyclopentadienyl rings are mutually *cis* and the *t*-butyl group is located on the opposite side to the Cp rings with respect to the $Fe_2GeC$ four-membered ring probably to avoid the steric congestion. The Fe(1)-Fe(2) distance (2.641(1) Å) is longer than those of $Cp_2Fe_2(CO)_3(\mu\text{-CHMe})$ (2.520(2) Å),[8] **2a** (2.614(1) Å),[2] and $Cp_2Fe_2(CO)_3(\mu\text{-GeMe}_2)$ (2.628(1) Å).[9] Clearly the Fe-Fe distance of $Cp_2Fe_2(CO)_3(\mu\text{-ERR'})$ (E = C, Si, Ge) depends on the size of the bridging unit ERR': The larger the bridging unit, the longer the Fe-Fe distance. The Ge-Fe distances (2.344(1) and 2.345(1) Å) are quite similar to those of $Cp_2Fe_2(CO)_3(\mu\text{-GeMe}_2)$ (2.345(1) and 2.347(1) Å).[9]

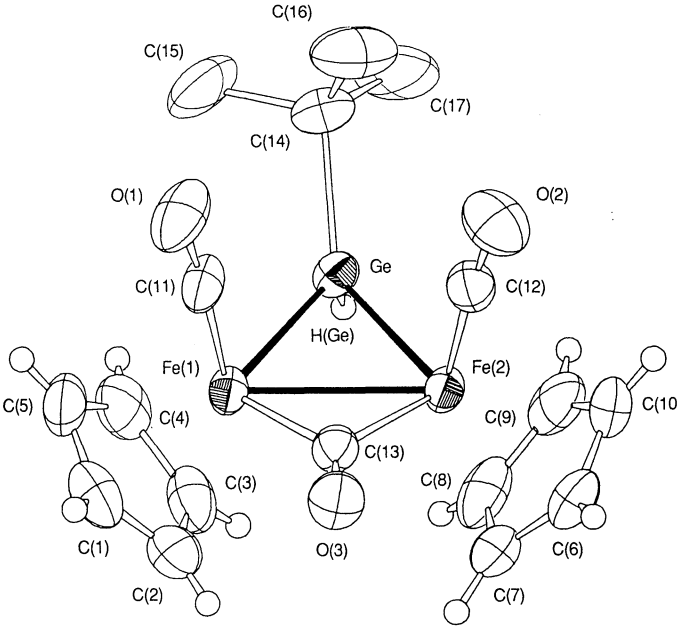


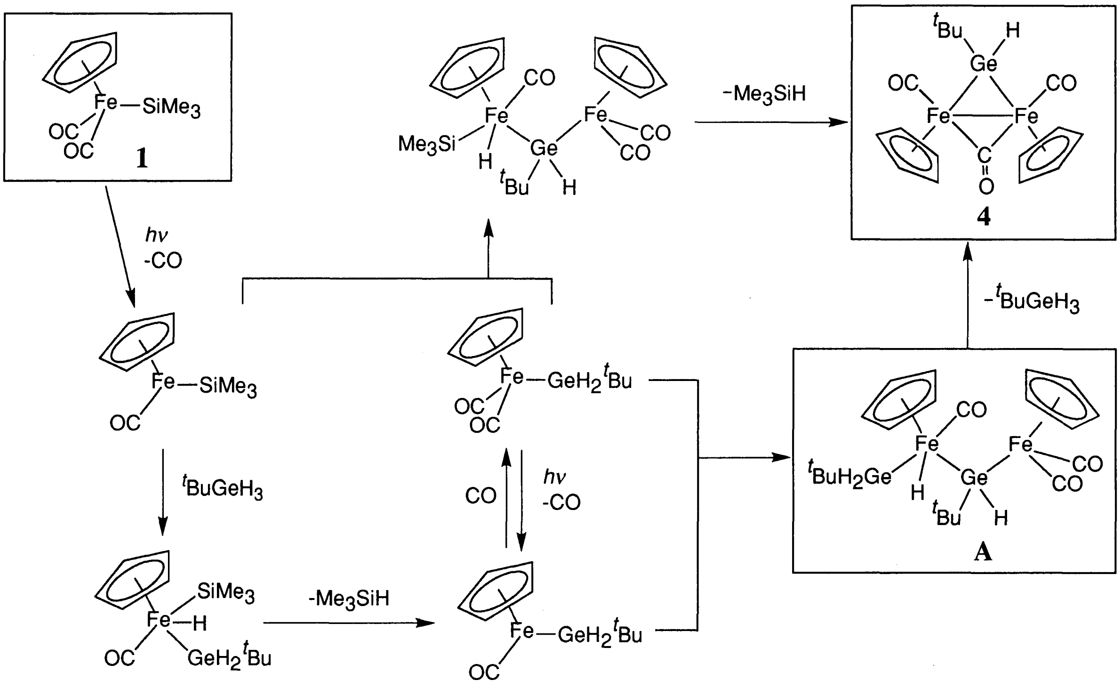
Fig. 1. ORTEP drawing of **4**. Thermal ellipsoids represent 50% probability level except for the hydrogen atoms.

The *cis* (H) configuration of **4** is retained when the crystals of **4** is dissolved in a cold solvent: In the $^1H$ or $^{13}C$ NMR spectrum in $CD_2Cl_2$ at −30 °C, only one singlet signal was observed for Cp ligands.[7] Furthermore, NOE was observed between the signals of Cp protons and Ge-H. However, when the solution was allowed to stand at ambient temperature for one day, new signals assigned to the *trans* isomer and the other *cis* isomer appeared.[10] This observation is in sharp contrast to the case of **2**, in which no geometrical isomerization was observed at ambient temperature.

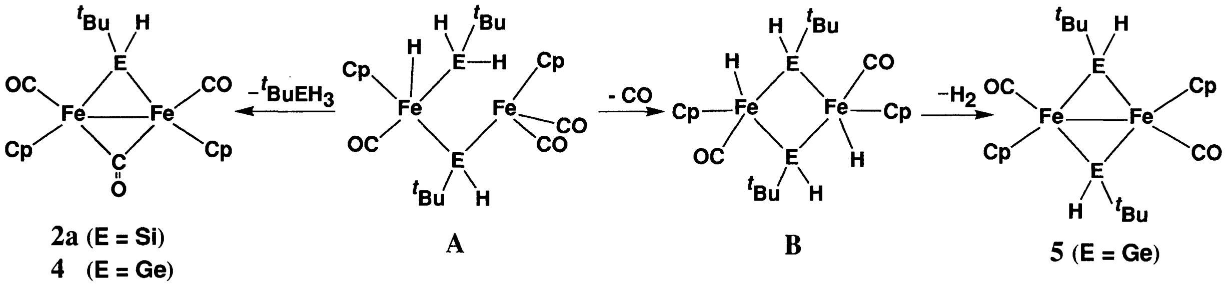
The geometry (*anti-trans*) of recrystallized bis($\mu$-germylene) complex **5** was determined on the basis of the spectral data:[6] In the IR spectrum of **5**, only an absorption assigned to the asymmetric vibration was observed in the $\nu$CO region. In the $^1H$ and $^{13}C$ NMR spectra, **5** exhibits only one Cp signal, respectively.

The Ge-H bond in **4** is highly activated. The hydrogen atom on the germylene-bridge of **4** is replaced by chlorine atom to give a $\mu$-chlorogermylene complex $Cp_2Fe_2(CO)_3(\mu\text{-GeCl}^t\text{Bu})$ (**6**) even in $CH_2Cl_2$, which does not react with usual hydrogermanes and the Si-H in the silylene-bridged complexes **2**.[11)]

The formation of **4** can be explained by essentially the same mechanism as that of the photoreaction of **1** with trihydrosilane,[2)] which includes oxidative addition of hydrogermanes to a photochemically generated 16 electron complex (Scheme 2).[12)] One might propose the reaction of **4** with $^t\text{BuGeH}_3$ as a pathway of the formation of **5**. However, irradiation of **4** in the presence of $^t\text{BuGeH}_3$ did not provide **5** at all. We propose a mechanism shown in Scheme 3 (E = Ge) for the formation of **5**: Dissociation of CO instead of $^t\text{BuGeH}_3$ from **A** results in the formation of **B**, which then eliminates $H_2$ to give **5**. Incidentally, this photoreaction gave a bis($\mu$-germylene)complex **5** as well as **4**, whereas the photoreaction of $^t\text{BuSiH}_3$ with **1** gave the mono($\mu$-silylene)complex **2a**, exclusively.[2)] This difference is attributable to the fact that germanium-metal bond is stronger than silicon-metal bond.[13)] Namely, in the case of E = Si in Scheme 3, only the reductive elimination of $^t\text{BuSiH}_3$ occurs to give **2a**, while in the case of E = Ge, reductive



Scheme 2.



Scheme 3.

elimination of $^t\mathrm{BuGeH_3}$ becomes harder to occur and a CO ligand dissociates competitively.

References

1) B. K. Nicholson, K. M. Mackay, and R. F. Gerlach, *Rev. Silicon, Germanium, Tin, Lead Compd.*, **5**, 67 (1981); B. J. Aylett, *Adv. Inorg. Chem. Radiochem.*, **25**, 1 (1982); T. D. Tilley, "The Chemistry of Organic Silicon Compounds," ed by S. Patai and Z. Rappoport, Wiley, New York (1989), Chap. 24; T. D.Tilley, "Silicon-Heteroatom Bond," ed by S. Patai and Z. Rappoport, Wiley, New York (1991), Chap. 9-10.

2) a) H. Tobita, Y. Kawano, M. Shimoi, and H. Ogino, *Chem. Lett.*, **1987**, 2247; b) Y. Kawano, H. Tobita, and H. Ogino, *J. Organomet. Chem.*, **428**, 125 (1992).

3) H. Tobita, Y. Kawano, and H. Ogino, *Chem. Lett.*, **1989**, 2155.

4) Y. Kawano, H. Tobita, and H. Ogino, *Angew. Chem., Int. Ed. Engl.*, **30**, 843 (1991).

5) Data for **3**: $^1$H NMR (200 MHz, $C_6D_6$) $\delta$ / ppm 1.04 (s, 9H, $^t$Bu), 3.72 (s, 3H, Ge-H). $^{13}$C NMR (22.5 MHz, $C_6D_6$) $\delta$ / ppm 20.8 ($CMe_3$), 30.2 ($CMe_3$). IR (neat, NaCl) 2060 $cm^{-1}$ (s, $\nu$GeH). MS (EI, 70 eV) $m/z$ 134 (100, $M^+$), 75 (23, $M^+ - {}^t$Bu). Anal. Found: C, 34.94; H, 8.27%. Calcd. for $C_4H_{12}Ge$: C,36.19; H, 9.11%.

6) Data for the *anti-trans* isomer of **5**: $^1$H NMR (90 MHz, $CD_2Cl_2$, –30 °C) $\delta$ / ppm 1.50 (d, $^4J$ = 0.5 Hz, 18H, $^t$Bu), 4.65 (s, 10H, Cp), 7.67 (decet, $^4J$ = 0.5 Hz, 2H, Ge*H*). $^{13}$C NMR (22.5 MHz, $CD_2Cl_2$, –30 °C) $\delta$ / ppm 30.9 ($CMe_3$), 41.4 ($CMe_3$), 78.1 (Cp), 219.0 (CO). IR (KBr) 1922 (m, $\nu$GeH), 1900 (s, $\nu CO_{term}$). MS (EI, 70 eV) $m/z$ 562 (39, $M^+$), 534 (20, $M^+$– CO), 506 (13, $M^+$– 2 CO). Exact mass Found: $m/z$ 561.9392, Calcd for $C_{20}H_{30}Fe_2Ge_2O_2$: 561.9379.

7) Data for **4** (*cis* (H) isomer): $^1$H NMR (90 MHz, $CD_2Cl_2$, –30 °C) $\delta$ / ppm 1.46 (d, $^4J$ = 0.8 Hz, 9H, $^t$Bu), 4.65 (s, 10H, Cp), 8.17 (decet, $^4J$, 1H, Ge*H*). $^{13}$C NMR (22.5 MHz, $CD_2Cl_2$, –30 °C) $\delta$ / ppm 29.4 ($CMe_3$), 38.9 ($CMe_3$), 83.1 (Cp), 212.4 ($CO_{term}$), 279.6 ($CO_{brid}$). IR (KBr) 1945 (vs), 1920 (m) ($\nu CO_{term}$), 1715 (s) ($\nu CO_{brid}$). MS (EI, 70 eV) $m/z$ 458 (49, $M^+$), 430 (15, $M^+$– CO), 402 (49, $M^+$– 2CO). Anal. Found: C, 44.08; H, 4.09%. Calcd for $C_{17}H_{20}Fe_2GeO_3$: C, 44.71; H, 4.40%.

8) A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, **1983**, 1427.

9) R. D. Adams, M. I. Bruce, and F. A. Cotton, *Inorg. Chem.*, **13**, 1080 (1974).

10) Data for *trans*-**4**: $^1$H NMR (90 MHz, $CD_2Cl_2$, r.t.) $\delta$ / ppm 1.68 (d, $^4J$ = 0.8 Hz, 9H, $^t$Bu), 4.78, 4.79 (s, 5H x 2, Cp). *cis* ($^t$Bu)-**4**: $^1$H NMR (90 MHz, $CD_2Cl_2$, r.t.) $\delta$ / ppm 1.74 (d, $^4J$ = 0.8 Hz, 9H, $^t$Bu), 4.67 (s, 10H, Cp). Ge*H* signals for these isomers were too weak to be observed.

11) Data for **6**: $^1$H NMR (90 MHz, $C_6D_6$, r.t.) $\delta$ / ppm 1.63 (s, 9H, $^t$Bu), 4.27 (s, 10H, Cp). $^{13}$C NMR (22.5 MHz, $C_6D_6$, r.t.) $\delta$ / ppm 29.1 ($CMe_3$), 51.2 ($CMe_3$), 85.9 (Cp), 211.6 ($CO_{term}$), 284.9 ($CO_{brid}$). IR (KBr) 1952 (vs), 1920 (m) ($\nu CO_{term}$), 1773 (s) ($\nu CO_{brid}$). MS (EI, 70 eV) $m/z$ 492 (42, $M^+$), 464 (59, $M^+$– CO). Anal. Found: C, 41.63; H, 3.99; Cl, 6.91%. Calcd for $C_{17}H_{19}ClFe_2GeO_3$: C, 41.58; H, 3.90; Cl, 7.23%.

12) Photo-generated $[(\eta\text{-}C_5Me_5)Fe(CO)SiMe_3]$ was isolated in a low-temperature matrix; C. L. Randolph and M. S. Wrighton, *J. Am. Chem. Soc.*, **108**, 3366 (1986).

13) For example, G. F. Bradley and S. R. Stobart, *J. Chem. Soc., Dalton Trans.*, **1974**, 264.

(Received November 1, 1993)