

Novel Rearrangement Reactions. 5. Thermal Rearrangement of Digermyl-Bridged Biscyclopentadienyl Diiron Complexes

(Me₂GeGeMe₂)[(η⁵-C₅R₄)Fe(CO)]₂(μ-CO)₂ (R = H and Me)

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Complexes (Me₂GeGeMe₂)[(η⁵-C₅R₄)Fe(CO)]₂(μ-CO)₂ (R = H, **1**; Me, **3**) **1** and **3**, prepared by the reaction of C₅R₄HMe₂GeGeMe₂C₅R₄H with Fe(CO)₅ in refluxing xylene, underwent a novel thermal reaction between their Ge–Ge and Fe–Fe bonds, forming corresponding rearrangement products with new cyclic structures, [Me₂Ge(η⁵-C₅R₄)Fe(CO)]₂ (R = H, **2**; Me **4**). Compared with the case of silicon, the weaker Ge–Ge bond resulted in an easier rearrangement reaction. Reactions of **1** with iodine and sodium amalgam were examined. Molecular structures of **1**, **2**, **3**, and **4** were determined by X-ray diffraction.

Introduction

Considerable attention has been focused on the synthesis and chemical behavior of a variety of bridged binuclear metal–metal-bonded transition-metal complexes.¹ These systems are suitable for studying interactions between two metal reaction sites that are in close proximity. In particular, we have been interested in bridged biscyclopentadienyl tetracarbonyl diiron complexes in which two cyclopentadienyl ligands are linked together by certain alkyl or silyl groups.² Compared to their nonbridged analogues, these complexes exhibit unique characteristics in both their structures and reactivity.³

We recently reported a novel rearrangement of the Si–Si and Fe–Fe bonds in a binuclear iron complex (Me₂SiSiMe₂)[(η⁵-C₅H₄)Fe(CO)]₂(μ-CO)₂ (Scheme 1).⁴ An alternative mechanism was subsequently proposed based on detailed investigation of the rearrangement stereospecificity, reaction intermediate, and crossover reac-

tions.⁵ The similarity between silicon and germanium led us to synthesize the related germyl-bridged analogues and to examine the corresponding rearrangement reaction between Ge–Ge and Fe–Fe bonds.

Results and Discussion

Synthesis of (Me₂GeGeMe₂)[(η⁵-C₅R₄)Fe(CO)]₂(μ-CO)₂ and Its Rearrangement Reaction. 1,2-Bis-(cyclopentadienyl)tetramethyldigermane, C₅H₅Me₂GeGeMe₂C₅H₅, which was prepared by reaction of 1,2-dichlorotetramethyldigermane, ClMe₂GeGeMe₂Cl, and cyclopentadienyllithium, was treated with Fe(CO)₅ in xylene under reflux for 10 h. After workup, preparative thin-layer chromatography (TLC) afforded purple crystals of **1** in 12% yield, as well as a yellow product, which was later confirmed to have the structure of **2** (Scheme 2). To illuminate the relationship between **1** and **2**, a xylene solution of isolated pure **1** was refluxed for 6 h. It was found that, despite some decomposition, **1** was entirely converted into **2**. This suggested that **2** was formed via a thermal rearrangement reaction between the Ge–Ge and Fe–Fe bonds of **1**, similar to its sila-bridged analogue.⁴

It is worth noting that even at a considerably lower temperature (110 °C for 24 h in refluxing toluene), the reaction still proceeded readily. In contrast, there was hardly any rearrangement observed for the silicon analogue under the same conditions. Apparently, the weakness of the Ge–Ge bond (relative to the Si–Si bond) facilitated the rearrangement.

Similarly, when the tetramethyl-substituted ligand C₅Me₄HMe₂GeGeMe₂C₅Me₄H was treated with Fe(CO)₅ in refluxing xylene for 8 h, complex **3** was obtained in 27% yield, and its rearrangement product **4** in 12% yield. A small amount of degermylation product [η⁵-C₅HMe₄Fe(CO)]₂(μ-CO)₂ was also isolated at the same

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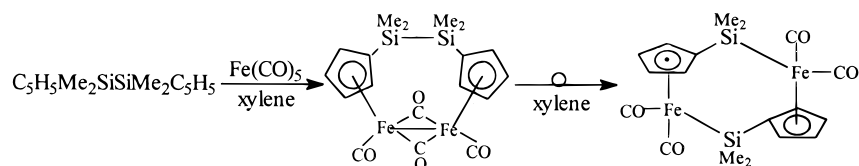
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Scheme 1



Scheme 2

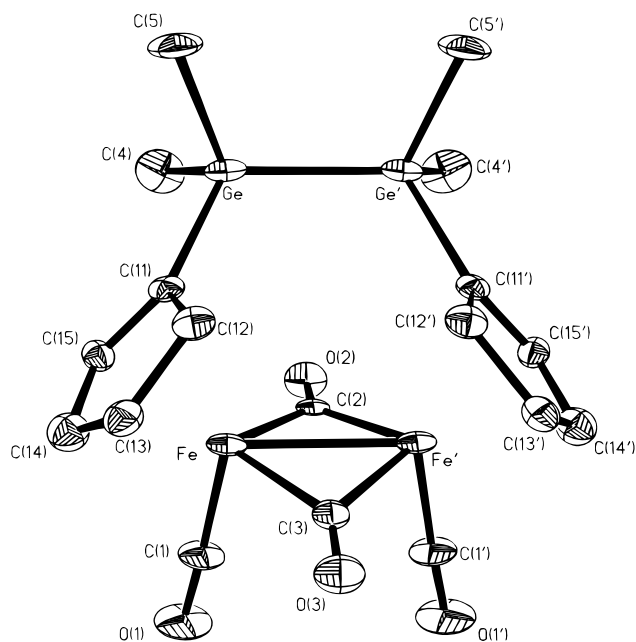
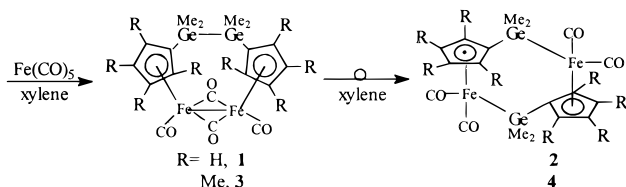


Figure 1. Molecular structure of $(\text{Me}_2\text{GeGeMe}_2)[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2]_2$ (**1**). Hydrogen atoms are omitted for clarity.

time. A sample of pure complex **3** was then refluxed in xylene for 10 h. **4** was isolated in 32% yield accompanied by some decomposition. This was very different from the Si-Si bridged analogue, which underwent rearrangement with great difficulty, affording the rearrangement product in very low yield.⁶

A significant difference between **1** and **2** or **3** and **4** was presented in their IR spectra. While **1** and **3** both have absorptions for terminal and bridged carbonyl groups, **2** and **4**, in accordance with their structures as determined by X-ray diffraction analysis, show only terminal CO ligands. The molecular structures of all complexes were confirmed by single-crystal X-ray diffraction.

Molecular Structures of 1, 2, 3, and 4. The molecular structure of **1** is presented in Figure 1. Table 1 provides the selected bond distances and angles. The molecule of **1** has mirror symmetry. This is different from its silicon analogue, which was found to be unsymmetrical.⁶ In **1**, two germanium atoms and two iron

Table 1. Selected Bond Distances (Å) and Angles (deg) for **1** and **3**

	1	3
Fe-Fe'	2.544(3)	2.581(5)
Ge-Ge'	2.408(2)	2.390(4)
Ge-C(11)	2.009(6)	1.974(16)
Fe-C(11)	2.141(5)	2.129(16)
Fe'-Fe-C(11)	110.3(5)	109.6(4)
Ge'-Ge-C(11)	113.8(4)	113.6(5)
Ge-C(11)-Fe	128.6(7)	134.8(8)
PL-PL' ^a	93.99	107.12

^a PL = the plane of the Cp ring.

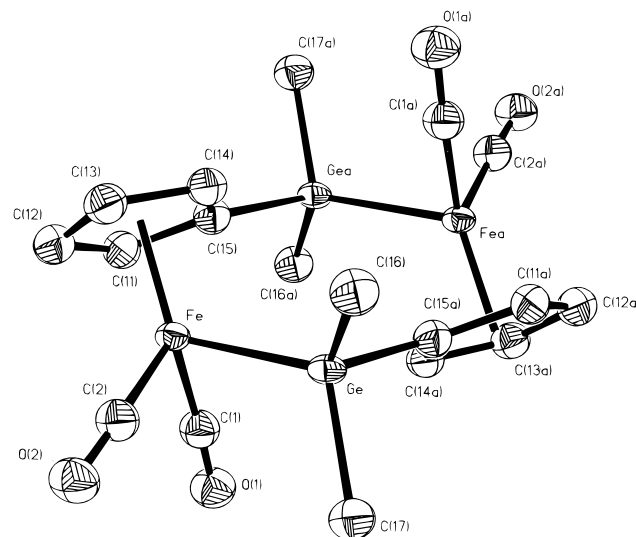


Figure 2. Molecular structure of $[\text{Me}_2\text{Ge}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2]_2$ (**2**). Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **2**

Bond Distances			
Fe-Ge	2.379(2)	Fe-C(15)	2.123(5)
Ge-C(15a)	1.955(6)		
Bond Angles			
Ge-Fe-C(15)	100.1(2)	C(1)-Fe-C(2)	91.3(3)
Fe-Ge-C(15a)	112.1(2)	C(16)-Ge-C(17)	106.3(3)

atoms are planar. The six-membered ring formed by germanium, iron, and the bridgehead carbon atoms of the cyclopentadienyl rings takes a standard boat conformation, which results in certain molecular strain. The Fe-Fe distance [2.544(3) Å] is longer than that in its silicon analogue [2.526(2) Å]. The Ge-Ge bond length is 2.408(2) Å, and the dihedral angle between the two cyclopentadienyl ring planes is 93.99°.

The molecular structure of **2** is illustrated in Figure 2. Selected bond distances and angles are listed in Table 2. The molecule of **2** consists of two $[\text{Me}_2\text{Ge}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2]$ moieties linked to each other by two Ge-Fe bonds. Like many analogues,^{4,6,7} **2** has C_i symmetry. The six-membered ring Fe-Ge-C(15a)-Fe(a)-Ge(a)-

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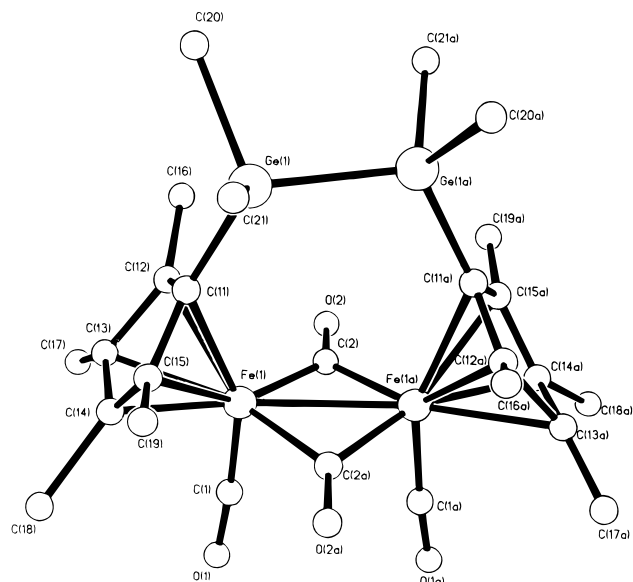


Figure 3. Molecular structure of $(\text{Me}_2\text{GeGeMe}_2)[(\eta^5\text{-C}_5\text{-Me}_4)\text{Fe}(\text{CO})]_2(\mu\text{-CO})_2$ (**3**).

C(15), constituting its molecular framework, adopts precisely a stable chair conformation. The Fe–Ge distance [2.379(2) Å] is slightly longer than the Fe–Si bond [2.315(2) Å] in its silicon analogue. It is noteworthy that whereas the six-membered rings in related Fe–Fe complexes (for both silicon and germanium analogues) may be in twisted boat or boat conformation, the corresponding rings in the rearrangement products always take a standard chair conformation,^{4–7} a structural characteristic of the products. It appears that such chair conformations, which are highly symmetrical, are preferred in energy, while the molecular strain in the substrates is likely to be the driving force of the rearrangement reaction.

The molecular structure of **3** is presented in Figure 3. Table 1 provides selected bond distances and angles. Similar to its silicon analogue, the molecule of **3** has C_2 symmetry. The corresponding six-membered ring also takes a twist boat conformation. As in its silicon analogue,⁶ the Fe–Fe distance [2.581(5) Å] is longer than that in the parent complex **1** [2.544(3) Å], while the Ge–Ge bond length [2.390(4) Å] is slightly shorter than in **1** [2.408(2) Å]. This may be attributed to the steric effect of the crowded methyl groups. The steric repulsion results in a slight stretch of the Fe–Fe bond and a compression of the Si–Si bond, to reduce unfavorable nonbonded interactions. The dihedral angle [107.12°] between the two cyclopentadienyl ring planes is much larger than in **1** [93.99°]. The Ge atoms deviate from the linked cyclopentadienyl rings by 0.3857 Å.

The molecular structure of **4** is illustrated in Figure 4. Selected bond distances and angles are listed in Table 3. There are two independent molecules with the ratio of 1/2 (A/B) in the unit cell: one (A) being unsymmetrical, and the other (B) having C_i symmetry. The dihedral angle between the two Cp rings is 2.29° for A, while the two Cp planes are parallel to each other for B. Like complex **2**, B has C_i symmetry, and the

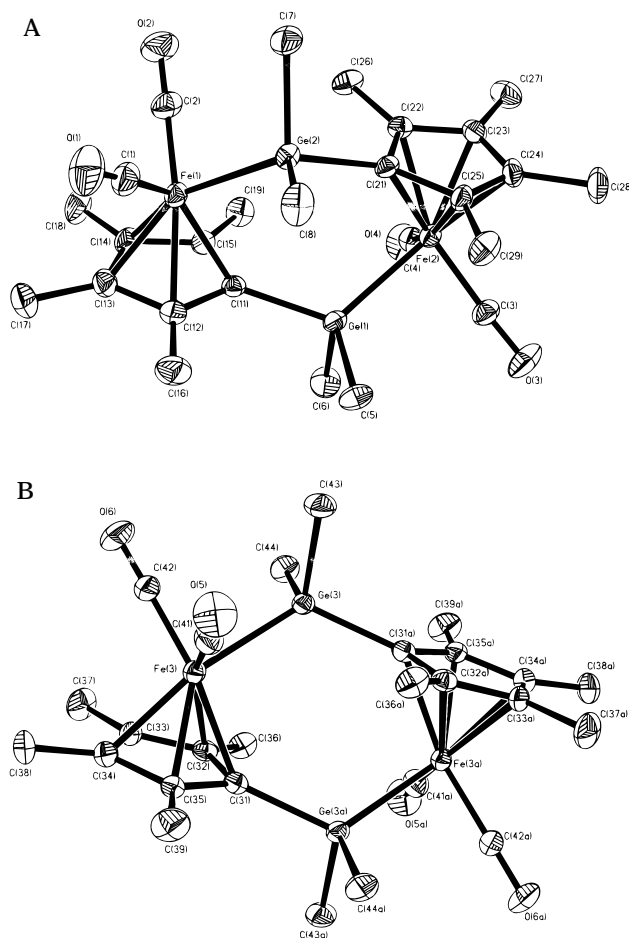


Figure 4. Molecular structure of $[\text{Me}_2\text{Ge}(\eta^5\text{-C}_5\text{Me}_4)\text{Fe}(\text{CO})]_2$ (**4**), showing labeling scheme for the two independent molecules present as a ratio of 1/2 (A/B) in the crystal structure.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **4**

Bond Distances			
Fe(1)–Ge(2)	2.403(1)	Fe(1)–C(11)	2.109(7)
Fe(2)–Ge(1)	2.401(1)	Fe(2)–C(21)	2.128(6)
Fe(3)–Ge(3)	2.395(1)	Fe(3)–C(31)	2.118(7)
Ge(1)–C(11)	1.988(8)	Ge(2)–C(21)	1.992(7)
Ge(3)–C(31a)	1.986(7)		
Bond Angles			
Ge(2)–Fe(1)–C(11)	89.8(2)	Fe(1)–C(11)–Ge(1)	137.1(3)
Ge(1)–Fe(2)–C(21)	89.0(2)	Fe(2)–C(21)–Ge(2)	137.1(3)
Ge(3)–Fe(3)–C(31)	99.0(2)	Fe(3)–C(31)–Ge(3a)	134.5(3)
Fe(2)–Ge(1)–C(11)	120.0(2)	Fe(1)–Ge(2)–C(21)	120.5(2)
Fe(3)–Ge(3)–C(31a)	119.1(2)		

corresponding six-membered ring adopts a standard chair conformation. The Fe–Ge distance [2.401(1) Å for A; 2.395(1) Å for B] is slightly longer than those in **2** (2.379(2) Å), presumably due to the repulsion of methyl groups.

Reactivity of 1. Experiments were conducted to examine if there were any special features about the reactivity of **1**, the first example of a dinuclear Fe–Fe complex containing a Ge–Ge bond, arising from the introduction of the germyl bridge. Reaction of **1** with iodine in CHCl_3 gave a normal Fe–Fe cleaved product, **5** (Scheme 3). No other product was detected. This indicated that although the Ge–Ge bond is liable to cleavage by halogens (Cl_2 , and Br_2 in some instances), and although it seemed somehow activated in **1** (in that

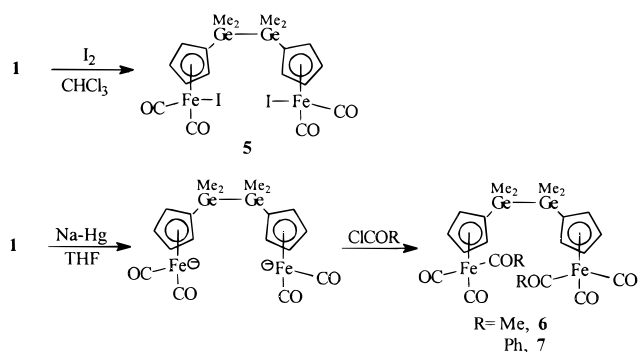
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Table 4. Summary of X-ray Diffraction Data

	1	2	3	4
formula	C ₁₈ H ₂₀ Fe ₂ Ge ₂ O ₄	C ₁₈ H ₂₀ Fe ₂ Ge ₂ O ₄	C ₂₆ H ₃₆ Fe ₂ Ge ₂ O ₄	C ₂₆ H ₃₆ Fe ₂ Ge ₂ O ₄
fw	557.26	557.23	669.45	669.45
space group	P2 ₁ /m	P2 ₁ /n	P-4	P-1
cryst syst	monoclinic	monoclinic	tetragonal	triclinic
Z	2	2	2	3
a (Å)	7.095(5)	9.046(1)	11.073(2)	8.821(2)
b (Å)	15.455(3)	10.606(2)	11.073(2)	9.610(2)
c (Å)	9.126(3)	10.704(3)	11.243(2)	26.328(5)
α (deg)				81.02(3)
β (deg)	92.35(4)	96.57(2)		87.29(3)
γ (deg)				69.78(3)
volume (Å ³)	1000(1)	1020.1(6)	1738.5(9)	2068(1)
d _{calc} (g cm ⁻³)	1.78	1.864	1.613	1.612
crystal size (mm)	0.2 × 0.3 × 0.3	0.2 × 0.3 × 0.2	0.2 × 0.3 × 0.4	0.1 × 0.2 × 0.5
radiation (Å ³)	MoKα(0.71073)	MoKα(0.71073)	MoKα(0.71073)	MoKα(0.71073)
μ (cm ⁻¹)	43.77	42.94	31.92	31.91
data collection method	ω/2θ	ω/2θ	ω/2θ	ω/2θ
max 2θ (deg)	46.0	46.0	46.0	46.0
total no. of observns	1543	1598	2154	5898
no. of unique data, I > 3σ(I)	981	1157	1697	3838
final no. of variables	136	118	154	460
R ^a	0.045	0.038	0.10	0.046
R _w ^b	0.049	0.045	0.12	0.050
goodness-of-fit	2.58	2.033	2.27	0.88

^a $\sum ||F_o - F_c|| / \sum |F_o|$. ^b $[\sum w(|F_o - F_c|)^2 / \sum w F_o^2]^{1/2}$.

Scheme 3



it reacted with the Fe–Fe bond), it remained inactive as usual to iodine. Treatment of **1** with sodium amalgam in THF showed that the Ge–Ge bridge did not affect either the neutral reduction of the Fe–Fe bond or the subsequent nucleophilic reaction of the anion.

Experimental Section

General Procedures. Schlenk and vacuum line techniques were employed for all manipulations of air- and moisture-sensitive compounds. Reaction solvents were distilled from appropriate drying agents under argon before use. Tetrahydrofuran, heptane, and xylene were distilled from sodium/benzophenone ketyl and purged with argon prior to use. ¹H NMR spectra were recorded on a JEOL FX-90Q or BRUKER AC-P200 spectrometer, whereas infrared spectra were recorded on a Nicolet 5DX FT-IR spectrometer as a KBr disk. Elemental analyses were performed by a Perkin-Elmer 240C analyzer. 1,2-Dichlorotetramethyldigermane was prepared from GeMe₄ by literature methods.⁸

Preparation of C₅H₅Me₂GeGeMe₂C₅H₅. A solution of ClMe₂GeGeMe₂Cl (1.8 g, 6.5 mmol) in 10 mL of THF was added to 13 mmol of cyclopentadienyllithium in 30 mL of THF. After 5 h of stirring at room temperature, solvent was removed under vacuum. The residue was extracted with CH₂Cl₂ and

filtered through a short Al₂O₃ column (5 × 3 cm). Removal of solvent yielded 1.9 g of a pale yellow oil. This was used without further purification. ¹H NMR (90 MHz, CDCl₃): δ 0.20(s, 12H, 2GeMe₂), 2.90(s, 2H, α-H), 5.80–6.80(m, 8H, 2C₅H₄).

Preparation of (Me₂GeGeMe₂)[(η⁵-C₅H₄)Fe(CO)]₂(μ-CO)₂ (1**) and [Me₂Ge(η⁵-C₅H₄)Fe(CO)₂]₂ (**2**).** A 1.9 g (5.7 mmol) sample of C₅H₅Me₂GeGeMe₂C₅H₅ and 2.4 mL of Fe(CO)₅ were heated in 50 mL of xylene under reflux for 10 h. After removal of excess of Fe(CO)₅ and solvent under vacuum, preparative TLC afforded first a yellow band, then a red one, from which yellow crystals of **2** (0.24 g, 10%) and dark red crystals of **1** (0.29 g, 12%) were obtained, respectively. For **1**: Anal. Calcd for C₁₈H₂₀Fe₂Ge₂O₄: C, 38.80; H, 3.62. Found: C, 38.45; H, 3.50. IR (ν_{CO}, cm⁻¹): 1753.5, 1794.5, 1942.2, 1975.0. ¹H NMR (90 MHz, CDCl₃): δ 0.48(s, 12H, 2GeMe₂), 4.36(s, 4H, 2C₅H₂), 5.32(s, 4H, 2C₅H₂). For **2**: Anal. Calcd for C₁₈H₂₀Fe₂Ge₂O₄: C, 38.80; H, 3.62. Found: C, 38.61; H, 3.55. IR (ν_{CO}, cm⁻¹): 1934.0, 1975.0. ¹H NMR (200 MHz, CDCl₃): δ 0.56(s, 12H, 2GeMe₂), 4.96(d, 8H, 2C₅H₄).

Rearrangement Reaction of Complex 1. A 0.15 g sample of **1** was heated in refluxing xylene (20 mL) for 6 h. The originally dark red solution turned orange-yellow. After removal of solvent, the residue was extracted with CH₂Cl₂ and filtered through a short Al₂O₃ column (7 × 3 cm). From the filtrate, 0.1 g (67%) of yellow crystals of **2** was obtained.

Preparation of C₅Me₄HMe₂GeGeMe₂C₅Me₄H. A solution of ClMe₂GeGeMe₂Cl (2.25 g, 8.2 mmol) in 20 mL of THF was added to 16.4 mmol of tetramethylcyclopentadienyllithium in 30 mL of THF. After 12 h of stirring at room temperature, 30 mL of water was added. The aqueous layer was separated and extracted twice with 20 mL of ether. The organic and ether extracts were combined and dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure. The residue was recrystallized from pentane and afforded 1.2 g (33%) of white crystals. ¹H NMR (90 MHz, CDCl₃): δ 0.16(s, 12H, 2GeMe₂), 1.72(s, 12H, 2C₅Me₂), 1.76(s, 12H, 2C₅Me₂), 2.90(m, 2H, 2α-H).

Preparation of (Me₂GeGeMe₂)[(η⁵-C₅Me₄)Fe(CO)]₂(μ-CO)₂ (3**) and [Me₂Ge(η⁵-C₅Me₄)Fe(CO)₂]₂ (**4**).** A 1.1 g (2.5 mmol) sample of C₅Me₄HMe₂GeGeMe₂C₅Me₄H and 1.5 mL of Fe(CO)₅ were heated in 50 mL of xylene under reflux for 8 h. After removal of excess of Fe(CO)₅ and solvent under vacuum, preparative TLC afforded first a yellow band, then two red

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bands, from which yellow crystals of **4** (0.19 g, 12%), dark red crystals of **3** (0.46 g, 27%), and dark red crystals of $[(\eta^5\text{-C}_5\text{-Me}_4\text{H})\text{Fe}(\text{CO})]_2(\mu\text{-CO})_2$ (55 mg) were obtained. For **3**: Anal. Calcd for $\text{C}_{26}\text{H}_{36}\text{Fe}_2\text{Ge}_2\text{O}_4$: C, 46.65; H, 5.42. Found: C, 46.62; H, 5.54. IR (ν_{CO} , cm^{-1}): 1748.2, 1925.2, 1973.1. ^1H NMR (200 MHz, CDCl_3): δ 0.37(s, 12H, 2GeMe₂), 1.84(s, 12H, 2C₅Me₂), 1.95(s, 12H, 2C₅Me₂). For **4**: Anal. Calcd for $\text{C}_{26}\text{H}_{36}\text{Fe}_2\text{Ge}_2\text{O}_4$: C, 46.65; H, 5.42. Found: C, 46.63; H, 5.41. IR (ν_{CO} , cm^{-1}): 1932.0, 1968.6. ^1H NMR (200 MHz, CDCl_3): δ 0.55(s, 12H, 2GeMe₂), 1.88(s, 12H, 2C₅Me₂), 1.96(s, 12H, 2C₅Me₂). For $[(\eta^5\text{-C}_5\text{Me}_4\text{H})\text{Fe}(\text{CO})]_2(\mu\text{-CO})_2$:⁹ Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{Fe}_2\text{O}_4$: C, 56.69; H, 5.62. Found: C, 57.01; H, 5.80. IR (ν_{CO} , cm^{-1}): 1734.2, 1753.5, 1942.2, 1975.0. ^1H NMR (90 MHz, CDCl_3): δ 1.69(s, 12H, 2C₅Me₂), 1.72(s, 12H, 2C₅Me₂), 3.83(s, 2H, Cp-H).⁹

The Rearrangement Reaction of Complex 3. Similar to the rearrangement of **1**, 0.28 g of **3** was refluxed in 30 mL of xylene for 10 h; 0.09 g (32%) of **4** was obtained.

Reaction of 1 with I₂. A 0.17 g (0.30 mmol) sample of **1** and 0.08 g (0.30 mmol) of I₂ were stirred in CHCl_3 (15 mL) for 3 h. Excess I₂ was removed by washing with a $\text{Na}_2\text{S}_2\text{O}_3$ solution. The organic layer was dried and chromatographed on an Al_2O_3 column (220 cm, CH_2Cl_2) to give dark brown crystals of $(\text{Me}_2\text{GeGeMe}_2)[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{I}]_2$ (**5**) (0.13 g, 53%). Anal. Calcd. For $\text{C}_{18}\text{H}_{20}\text{Fe}_2\text{Ge}_2\text{I}_2\text{O}_4$: C, 26.60; H, 2.49. Found: C, 26.64; H, 2.42. IR (ν_{CO} , cm^{-1}): 2018.8, 1976.4. ^1H NMR (90 MHz, CDCl_3): δ 0.61(s, 12H, 2GeMe₂), 4.81(m, 4H, 2C₅H₂), 5.02(m, 4H, 2C₅H₂).

Reaction of 1 with Na/Hg. A 0.33 g (0.60 mmol) sample of **1** was treated with an excess of 1% sodium amalgam in THF. The dark red color of the solution changed to yellow-brown within 20 min. After 1 h, the resulting solution was divided into two equal portions, which were treated, respectively, with acetyl chloride (0.8 mmol) and benzoyl chloride (0.8 mmol). After 3 h of stirring, 0.09 g (45%) of $(\text{Me}_2\text{GeGeMe}_2)[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{C}(\text{O})\text{Me}]_2$ (**6**) and 0.12 g (52%) of $(\text{Me}_2\text{GeGeMe}_2)$

$[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{C}(\text{O})\text{Ph}]_2$ (**7**) were isolated, as yellow crystals from the respective reaction mixtures by column chromatography. For **6**: Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{Fe}_2\text{Ge}_2\text{O}_6$: C, 41.07; H, 4.07. Found: C, 40.85; H, 4.22. IR (ν_{CO} , cm^{-1}): 2010.1, 1952.6. ^1H NMR (90 MHz, CDCl_3): δ 0.48(s, 12H, 2GeMe₂), 4.69(s, 4H, 2C₅H₂), 5.00(s, 4H, 2C₅H₂). For **7**: Anal. Calcd for $\text{C}_{32}\text{H}_{30}\text{Fe}_2\text{Ge}_2\text{O}_6$: C, 50.08; H, 3.94. Found: C, 50.20; H, 4.12. IR (ν_{CO} , cm^{-1}): 2016.0, 1955.4. ^1H NMR (90 MHz, CDCl_3): δ 0.51(s, 12H, 2GeMe₂), 4.88(s, 4H, 2C₅H₂), 5.08(s, 4H, 2C₅H₂).

Molecular Structure Determination. Crystals suitable for X-ray diffraction were obtained from hexane/dichloromethane solutions. All data sets were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo K α radiation. Empirical absorption corrections using the program DIFBAS were applied to intensity data. All calculations were performed on a PDP11/44 computer using the SDP-PLUS program system. The structures were solved by a direct phase determination method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. Neutral atom scattering factors were taken from the tabulation of Cromer and Waber.¹⁰ Selected bond distances and angles for **1**, **2**, **3**, and **4** are given in Tables 1, 2, and 3, respectively. A summary of the crystallographic results is presented in Table 4.

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Supporting Information Available: Supporting Information Available: Tables of final positional and thermal parameters of the non-hydrogen atoms, general temperature factors, calculated hydrogen atom positions, and bond distances and angles for **1**, **2**, **3**, and **4** (36 pages). Ordering information is given on any current masthead page.

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(10) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(9) Xu, S.; Zhong, X.; Zhou, X. *Nankai Daxue Xuebao* **1996**, *29* (3), 104–6 (in Chinese).