Thermal Ring Contraction of 1,2-Digermacyclohexadienes Coordinated with Iron Tricarbonyl Fragment

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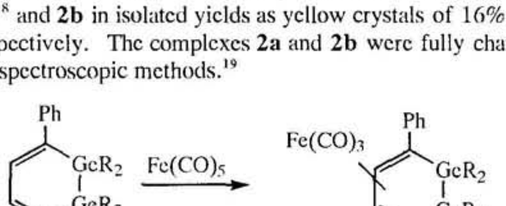
1,1,2,2-Tetraalkyl-3,6-diphenyl-1,2-digermacyclohexa-3,5-dienes (**1**) reacted with iron pentacarbonyl to give the corresponding tricarbonyl(η^4-1,1,2,2-tetraalkyl-3,6-diphenyl-1,2-digermacyclohexa-3,5-diene)iron (**2**). Heating **2** caused extrusion of dialkylgermylenes to give (η^4-1,1-dialkyl-2,5-diphenyl-1-germacyclopenta-2,4-diene)tricarbonyliron (**3**). The structures of the (diene)iron tricarbonyls were detecrimined by X-ray crystal structure analysis.

Recently, considerable interest has been focussed on complexes having transition metal-group 14 element bonds as important intermediates in a number of transition metal-catalyzed transformations of group 14 element compounds.[1-14] Examination of reactivities of group 14 element compounds coordinated with transition metals is expected to provide important information on the mechanisms of transformation of the group 14 metal compounds catalyzed by transition metal complexes. In the course of our studies to understand the mechanisms of reactions of organogermanium compounds having Ge-Ge bonds with alkynes in the presence of iron pentacarbonyl[15] we have prepared new π-complexes of 1,2-digermacyclohexadienes coordinated with an iron carbonyl fragment. We describe herein the properties of the iron-bound cyclic digermanes involving the ring contraction together with the structures of the isolated η^4-diene-iron complexes containing the cyclic germanes.

When a degassed toluene-d_8 solution of 1,1,2,2-tetraalkyl-3,6-diphenyl-1,2-digermacyclohexa-3,5-dienes (**1a**, **b**)[16,17] was heated at 130 °C for 13.5 h with iron pentacarbonyl in a Pyrex NMR tube, tricarbonyl(η^4-1,1,2,2-tetraalkyl-3,6-diphenyl-1,2-digermacyclohexa-3,5-diene)iron (**2a**, **b**) was obtained in 96 and 22% NMR yields, respectively, as the sole products. The tricarbonyl(diene)iron (**2a**, **b**) were isolated and purified with TLC with silica followed by recrystallization from ethanol to give **2a**[18] and **2b** in isolated yields as yellow crystals of 16% and 9%, respectively. The complexes **2a** and **2b** were fully characterized by spectroscopic methods.[19]



(1)

1a: R=Me, **b**: R=Et

2a: R=Me, 16%
b: R=Et, 9%

The molecular structure of **2a** is shown in Figure 1. The cyclic diene **1a** is puckered with a dihedral angle of 157° between the two planes Ge(1)-Ge(2)-C(1)-C(2) and Ge(1)-C(4)-C(3)-C(2).[20] The intramolecular distances in the tricarbonyl(diene)iron **2a** indicate bonding of the $Fe(CO)_3$ fragment with the two double bonds of 1,2-digermacyclohexa-3,5-diene. This interaction results in a bending of the ring with a dihedral angle of 136° between the two planes C(1)-Ge(2)-Ge(1)-C(4) and C(1)-C(2)-C(3)-C(4). The C(2)-C(3) bond length (1.416(6) Å) of **2a** is shorter than that of **1a** (1.48(2) Å). The Ge(1) and Ge(2) bond length (2.381(9) Å) in **2a** is similar to that of **1a** (2.40(2) Å).

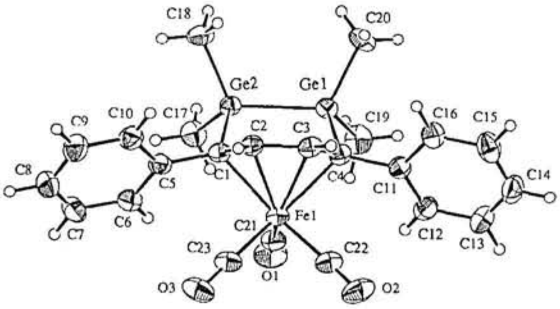


Figure 1. Molecular structure of **2a**. Selected bond lengths [Å] and angles [°]: Ge(1)-Ge(2) 2.381 (8), Ge(2)-C(1) 1.975 (4), C(1)-C(2) 1.429 (5), C(2)-C(3) 1.416 (6), C(3)-C(4) 1.427 (5), Ge(1)-C(4) 1.974 (3), Ge(1)-C(19) 1.953 (4), Ge(1)-C(20) 1.941 (5), Ge(2)-C(17) 1.954 (4), Ge(2)-C(18) 1.962 (4), C(1)-C(5) 1.502 (5), Fe(1)-C(1) 2.174 (4), Fe(1)-C(2) 2.070 (4), Fe(1)-C(3) 2.061 (4), Fe(1)-C(4) 2.177 (4), Ge(1)-Ge(2)-C(1) 98.5 (1), Ge(2)-C(1)-C(2) 121.0 (3), C(1)-C(2)-C(3) 122.4 (3), C(2)-C(3)-C(4) 123.9 (3), C(4)-Ge(2)-C(19) 111.4 (2), C(4)-Ge(2)-C(20) 106.3 (2), Ge(1)-Ge(2)-C(4) 98.8 (1), Ge(2)-C(1)-C(5) 112.0 (2), C(2)-C(1)-C(5) 116.1 (3), C(1)-Fe(1)-C(2) 39.3 (1), C(1)-Fe(1)-C(3) 72.1 (1), C(1)-Fe(1)-C(4) 86.3 (1)Ge(2)-C(1)-Fe(1) 115.1 (2).

Heating a degassed toluene-d_8 solution of the isolated **2a** at 130 °C for 9 h caused expulsion of a germylene unit to give (η^4-1,1-dimethyl-2,5-diphenyl-1-germacyclopenta-2,4-diene)tricarbonyliron (**3a**)[21] in 18% yield. The reaction was accompanied by liberation of the digermacyclohexadiene (**1a**) in 13% yield as well as 1,1-dimethyl-2,5-diphenyl-1-germacyclopenta-2,4-diene (**4a**) in a yield of 12% as established by comparison of their ^{1}H-NMR and MS spectra with those of authentic samples.[22,23] The germylene unit expelled was found to be converted into mixtures of unidentified oligo(dimethylgermylenes)s showing ^{1}H-NMR signals at δ 0.1-0.5 ppm. Attempts of trapping the released dimethylgermylene with CCl_4,[24] known as a good germylene trapping agent, was unsuccessful. The germole-coordinated tricarbonyliron complex **3a** was independently prepared by the reaction of **4a** with iron pentacarbonyl. Since the cyclic diene **1a** and (diene)tricarbonyliron **3a** are thermally stable under the experimental conditions employed, formation of **3a** and **4a** is considered to be caused by thermal reaction of **1a** activated on coordination to the iron tricarbonyl fragment.

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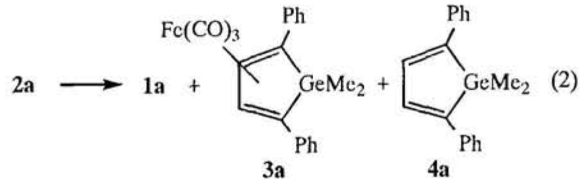

3a **4a**

The structure of (diene)tricarbonyliron **3a** is shown in Figure 2. The $Fe(CO)_3$ fragment of **3a** is bonded with the two double bonds of the planar 1-germacyclopenta-2,4-diene ring. The C(2)-C(3) bond length (1.412(5) Å) in **3a** is similar to that in **2a** (1.416(6) Å).

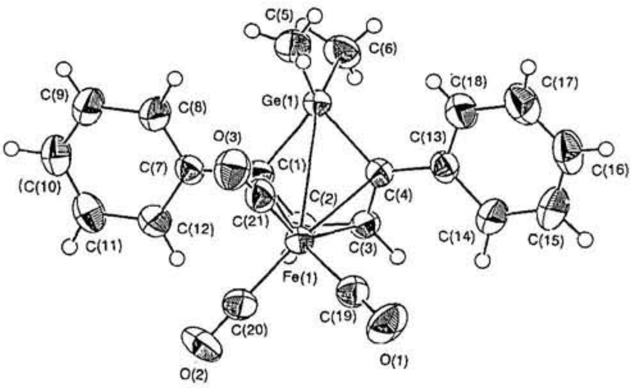

Figure 2. Molecular structure of **3a**. Selected bond lengths [Å] and angles [°]: Ge(1)-C(1) 1.964 (4), C(1)-C(2) 1.426 (5), C(2)-C(3) 1.412 (5), C(3)-C(4) 1.428 (5), Ge(1)-C(4) 1.958 (5), Ge(1)-C(5) 1.945 (5), Ge(1)-C(6) 5), Fe(1)-C(1) 2.194 94), Fe(1)-C(2) 2.056 (4), Fe(1)-C(3) 2.068 (4), Fe(1)-C(4) 2.213 (4), C(1)-Ge(1)-C(4) 84.0 (2), Ge(1)-C(1)-C(2) 105.6 (2), C(1)-C(2)-C(3) 115.5 (3), C(2)-C(3)-C(4) 114.8 (3), C(3)-C(4)-Ge(1) 106.1 (3), C(1)-Fe(1)-C(2) 39.1 (2), C(1)-Fe(1)-C(3) 68.5 (2), C(1)-Fe(1)-C(4) 73.1 (2), C(2)-Fe(1)-C(3) 40.0 (2), C(2)-Fe(1)-C(4) 68.0 (2), C(3)-Fe(1)-C(4) 38.8 (2), Ge(1)-C(1)-Fe(1) 92.4 (2), Fe(1)-C(1)-C(2) 65.2 (2), Fe(1)-C(2)-C(3) 70.4 (2), Fe(1)-C(2)-C(1) 75.7 (2).

The reaction of 1,1,2,2-tetramethyl-3,4,5,6-tetraphenyl-1,2-digermacyclohexa-3,5-diene with iron pentacarbonyl did not occur at 130 °C presumably due to steric hindrance of the four phenyl groups attached on the diene unit.

Sakurai and co-workers have reported that disilanyliron complexes afford highly unstable silyl(silylene)iron complexes which undergo extrusion of silylenes to give silyliron complexes for the ring contraction reaction of tricarbonyl(η^4-1,1,2,2-tetramethyl-3,6-diphenyl-1,2-disilacyclohexa-3,5-diene)iron.[25] The present ring contraction reaction of **1** bound with iron carbonyl fragment may also proceed through a similar germyl(germylene)-iron complex as a key intermediate. To support the participation of (diene)iron tricarbonyl for the ring contraction reaction, a degassed toluene-d_8 solution of a large amount of **1a** and **2a** was heated at 130 °C for 13 h. The yields of **3a** (50%) and **4a** (40%) significantly increased. Failure to detect germyl(germylene)iron complex by NMR is attributed to its instability.[26-28]

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