

Synthesis and Structure of a Novel Cluster with Trigonal-bipyramidal Ge_2Ru_3 Core[†]

ZHANG, Yong-Qiang^a (张永强) WANG, Bai-Quan^{*,a,b} (王佰全) XU, Shan-Sheng^a (徐善生)
 ZHOU, Xiu-Zhong^a (周秀中)

^a Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China

^b State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

When $t\text{-BuC}_5\text{H}_4\text{Me}_2\text{GeGeMe}_2\text{C}_5\text{H}_4\text{Bu-}t$ and $\text{Ru}_3(\text{CO})_{12}$ were refluxed in nonane, a novel germanium-ruthenium cluster with a trigonal-bipyramidal Ge_2Ru_3 core $\{(\mu^3\text{-Ge})[\text{Ru}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_4\text{Bu-}t)]\}_2\text{Ru}_3(\text{CO})_9$ (1) and a dinuclear ruthenium complex $[(\text{Me}_2\text{Ge})(\eta^5\text{-C}_5\text{H}_3\text{Bu-}t)\text{Ru}_2(\text{CO})_6]$ (2) were obtained. The structures of 1 and 2 were fully characterized by ¹H NMR, ¹³C NMR, IR spectra and elemental analysis, and 1 has also been determined by X-ray diffraction analysis.

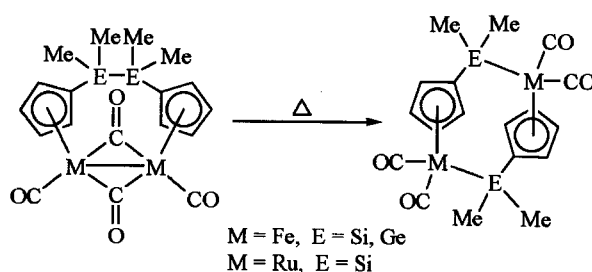
Keywords cluster, ruthenium, germanium, crystal structure

Introduction

We recently reported an intramolecular thermal rearrangement between Si—Si and Fe—Fe bonds in the dinuclear iron complex $\{(\text{Me}_2\text{SiSiMe}_2)[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2(\mu\text{-CO})_2]\}$ (Scheme 1).¹⁻⁵ The thermal rearrangement was later extended to germanium-iron and silicon-ruthenium analogues.⁶⁻⁸ The replacement of the Si—Si bond by a Ge—Ge bond greatly accelerated the rearrangement reaction due to the weaker Ge—Ge bond.

When the tetramethyldigermyl bridged cyclopentadiene $\text{C}_5\text{H}_5\text{Me}_2\text{GeGeMe}_2\text{C}_5\text{H}_5$ reacted with $\text{Ru}_3(\text{CO})_{12}$ in refluxing heptane, no corresponding dinuclear ruthenium was obtained, but the corresponding rearrangement prod-

Scheme 1



uct $[(\text{Me}_2\text{Ge})(\eta^5\text{-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2$, and the degemination products $[(\text{Me}_2\text{Ge})(\eta^5\text{-C}_5\text{H}_4)\text{Ru}_2(\text{CO})_6]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2$ were isolated (Scheme 2).⁹ However, when the tetramethyl-substituted cyclopentadienyl ligand $\text{C}_5\text{Me}_4\text{HMe}_2\text{GeGeMe}_2\text{C}_5\text{Me}_4\text{H}$ and $\text{Ru}_3(\text{CO})_{12}$ were refluxed similarly in boiling octane or decalin resulted in the unexpected formation of the germanium-ruthenium cluster with a trigonal-bipyramidal Ge_2Ru_3 core $\{(\mu^3\text{-Ge})[\text{Ru}(\text{CO})_2(\eta^5\text{-C}_5\text{Me}_4\text{H})]\}_2\text{Ru}_3(\text{CO})_9$ and the dinuclear ruthenium complex $[(\text{Me}_2\text{Ge})(\eta^5\text{-C}_5\text{Me}_4)\text{Ru}_2(\text{CO})_6]$ (Scheme 3).⁹

In order to further understand the effect of the substituents of cyclopentadienyl ring on the products, in this work, we study the reaction of $t\text{-BuC}_5\text{H}_4\text{Me}_2\text{GeGeMe}_2\text{C}_5\text{H}_4\text{Bu-}t$ with $\text{Ru}_3(\text{CO})_{12}$.

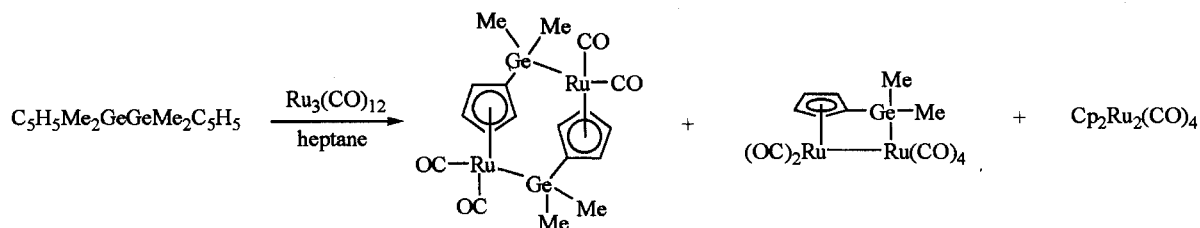
* E-mail: bqwang@nankai.edu.cn; Fax: 86-22-23502458

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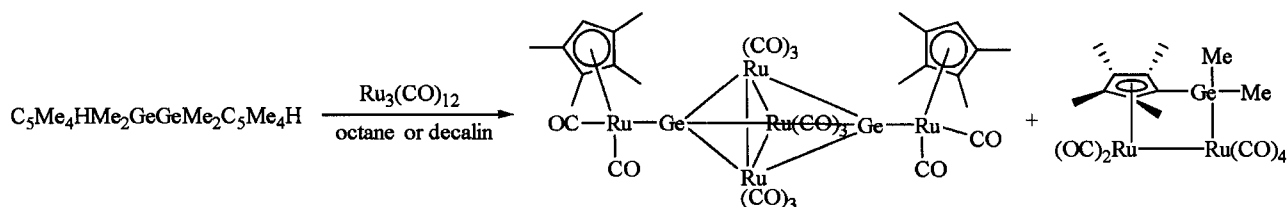
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[†]Dedicated to Professor HUANG YAO-Zeng on the occasion of his 90th birthday.

Scheme 2



Scheme 3



Experimental

General

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. ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker AC-P 200 spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C instrument. Infrared spectra were obtained as KBr disks on a Nicolet 5DX FT-IR spectrometer. $\text{Ru}_3(\text{CO})_{12}$ was purchased from Strem Co., *t*- $\text{BuC}_5\text{H}_4\text{Me}_2\text{GeGeMe}_2\text{C}_5\text{H}_4\text{Bu-}t$ was prepared according to the reported method.⁸

*Reaction of t-BuC₅H₄Me₂GeGeMe₂C₅H₄Bu-*t* with Ru₃(CO)₁₂*

A solution of $\text{Ru}_3(\text{CO})_{12}$ (1.00 g, 1.56 mmol) and *t*- $\text{BuC}_5\text{H}_4\text{Me}_2\text{GeGeMe}_2\text{C}_5\text{H}_4\text{Bu-}t$ (1.05 g, 2.35 mmol) in nonane (50 mL) was refluxed for 6 h. The solvent was removed under vacuum, and the residue was placed in an Al_2O_3 column. Elution with petroleum ether developed a yellow band, which was collected and, after solvent removal, afforded a yellow oily product. Further purification by recrystallization from pentane yielded complex 2 as yellow crystals (120 mg, 9%). M. p. 84–85 °C, ^1H NMR (CDCl_3 , 200 MHz) δ : 0.68 (s, 3H, GeMe), 0.70 (s, 3H, GeMe), 1.25 (s, 9H, CMe_3), 4.24

(brs, 1H, C_5H_3), 4.32 (brs, 1H, C_5H_3), 5.68 (brs, 1H, C_5H_3); ^{13}C NMR (CDCl_3 , 200 MHz) δ : 1.16 (GeMe), 31.1 (CMe_3), 31.8 (CMe_3), 77.6 ($\text{C}_5\text{H}_3\text{Ge}$), 80.6, 81.3, 90.1 (C_5H_3), 132.2 ($\text{C}_5\text{H}_3\text{-Bu-}t$), 197.1 (CO), 198.8–200.1 (m, CO); IR (KBr) ν_{co} : 2082, 2026, 1991, 1975, 1955, 1940 cm^{-1} . Anal. calcd for $\text{C}_{17}\text{H}_{18}\text{GeO}_6\text{Ru}_2$: C 34.24, H 3.04; found C 34.25, H 3.04.

Elution with CH_2Cl_2 developed another yellow band, which was collected and, after solvent removal, afforded a yellow product. Further purification by preparative TLC yielded complex 1 as orange crystals (50 mg, 4%). M. p. 196 °C (dec.), ^1H NMR (CDCl_3 , 200 MHz) δ : 1.29 (s, 18H, CMe_3), 5.38–5.46 (m, 8H, C_5H_4); ^{13}C NMR (CDCl_3 , 200 MHz) δ : 30.9 (CMe_3), 31.8 (CMe_3), 83.3, 87.8 (C_5H_4), 127.6 ($\text{C}_5\text{H}_4\text{Bu-}t$), 197.9 (CO), 201.7 (CO); IR (KBr) ν_{co} : 2054, 2016, 2001, 1986, 1964, 1946, 1937 cm^{-1} . Anal. calcd for $\text{C}_{31}\text{H}_{26}\text{Ge}_2\text{O}_{13}\text{Ru}_5$: C 29.62, H 2.08; found C 29.45, H 1.86.

Crystallography

Crystals suitable for X-ray diffraction were obtained from dichloromethane/hexane. All data were collected on an Enraf-Nonius CAD4 diffractometer with Mo $\text{K}\alpha$ radiation. Empirical absorption correction was applied. The structures were solved by direct method using the SDP-PLUS, SHELXS-86 and SHELXS-93 program on PDP 11/44 and Pentium 586/166 computer. The full-matrix

least-squares method was employed for refinement. Crystal data and refinement parameters are given in Table 1. Selected bond lengths and bond angles are listed in Table 2.

Table 1 Crystal data and refinement parameters for **1**

Empirical formula	C ₃₁ H ₂₆ Ge ₂ O ₁₃ Ru ₅
Formula weight	1257.08
Crystal system	Monoclinic
Space group	<i>P</i> ₂ ₁ / <i>c</i>
Unit cell dimensions	
<i>a</i> (nm)	0.9951(2)
<i>b</i> (nm)	1.8288(4)
<i>c</i> (nm)	2.1524(4)
β (°)	96.64(3)
<i>V</i> (nm ³)	3.891(2)
<i>Z</i>	4
<i>D</i> _{calc.} (g·cm ⁻³)	2.146
μ (mm ⁻¹)	3.4159
Crystal size (mm)	0.25 × 0.25 × 0.3
<i>F</i> (000)	2400
Temperature (K)	299(1)
<i>R</i> _{int}	0.031
Radiation (nm)	Mo K α (0.071073)
Data collection method	ω -2 θ
Max. 2 θ (°)	46
Total no. of observations	5754
No. of unique data [<i>I</i> ≥ 3 σ (<i>I</i>)]	3432
Final no. of variables	460
<i>R</i>	0.033
<i>wR</i>	0.040
Goodness-of-fit	1.23

Table 2 Selected bond distances (nm) and bond angles (°) of **1**

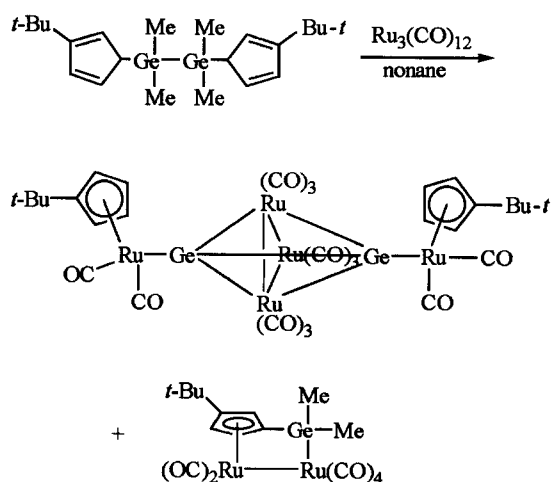
Ru(4)—Ge(1)	0.2418(1)	Ru(5)—Ge(2)	0.2425(1)
Ru(1)—Ru(2)	0.2890(1)	Ru(1)—Ru(3)	0.2941(1)
Ru(2)—Ru(3)	0.2882(1)	Ru(1)—Ge(1)	0.2475(1)
Ru(1)—Ge(2)	0.2496(1)	Ru(2)—Ge(1)	0.2555(1)
Ru(2)—Ge(2)	0.2499(1)	Ru(3)—Ge(1)	0.2482(1)
Ru(3)—Ge(2)	0.2503(1)		
Ru(2)-Ru(1)-Ru(3)	59.2(1)	Ge(1)-Ru(1)-Ge(2)	96.6(1)
Ru(1)-Ru(2)-Ru(3)	61.3(1)	Ge(1)-Ru(2)-Ge(2)	94.5(1)
Ru(1)-Ru(3)-Ru(2)	59.5(1)	Ge(1)-Ru(3)-Ge(2)	96.2(1)

Results and discussion

When *t*-BuC₅H₄Me₂GeGeMe₂C₅H₄Bu-*t* and Ru₃(CO)₁₂ were refluxed in nonane for 6 h, a novel germani-

um-ruthenium cluster with a trigonal-bipyramidal Ge₂Ru₃ core $\{(\mu^3\text{-Ge})[\text{Ru}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_4\text{Bu-}t)]\}_2\text{Ru}_3(\text{CO})_9$ (**1**) (4% yield), and a dinuclear ruthenium complex $[(\text{Me}_2\text{Ge})(\eta^5\text{-C}_5\text{HBu-}t)\text{Ru}_2(\text{CO})_6]$ (**2**) (9% yield) (Scheme 4) were obtained. Both **1** and **2** are yellow crystals and could be separated by preparative TLC. Their structures were fully characterized by ¹H NMR, ¹³C NMR, IR spectra and elemental analysis, and **1** has also been determined by X-ray diffraction analysis. The ¹H NMR spectrum of **1** exhibits only the resonances of the cyclopentadienyl rings at δ 5.41 and 5.44, and *t*-butyl groups at δ 1.29. The ¹³C NMR spectrum shows the two different resonances at δ 197.9 and 201.7 for CO groups, indicating two different types of ruthenium atoms exist in each molecule. Complex **2** shows the resonances of the cyclopentadienyl rings, *t*-butyl groups and germanium methyl groups in ¹H NMR spectrum. Its ¹³C NMR spectrum shows a singlet at δ 197.1 and multiple at δ 198.8—200.1 for CO groups. The IR spectrum exhibits six peaks for carbonyl absorption.

Scheme 4



When heptane was utilized as a refluxing solvent instead of nonane, no reaction was observed except for a slight decomposition of Ru₃(CO)₁₂. When the reaction was taken in refluxing octane, only complex **2** was obtained and the yield of **2** is nearly as the same as that in nonane, indicating that in high temperature it is favor to form the cluster complex **1**. This is very different from the reaction of C₅Me₄HMe₂GeGeMe₂C₅Me₄H with Ru₃(CO)₁₂, which gave a mixture of the cluster $\{(\mu^3\text{-Ge})-$

$[\text{Ru}(\text{CO})_2(\eta^5\text{-C}_5\text{Me}_4\text{H})]_2\text{Ru}_3(\text{CO})_9$ and the dinuclear ruthenium complex $[(\text{Me}_2\text{Ge})(\eta^5\text{-C}_5\text{Me}_4)\text{Ru}_2(\text{CO})_6]$ in boiling octane.⁹ This indicates that the steric effect, which makes all Ge—C bonds broken more easily, is the determinant factor for the formation of the cluster complexes. The more bulky four methyls on the cyclopentadienyl ring make the formation of the cluster complex more easier than one *tert*-butyl.

The single-crystal structure of **1** is presented in Fig. 1. Similar to the tetramethylcyclopentadienyl analogue, the molecule of **1** consists of an equatorial triangular cluster $\text{Ru}_3(\text{CO})_9$, capped on both sides by the apical fragment of $\{(\mu^3\text{-Ge})[\text{Ru}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_4\text{Bu-}t)]\}$. The $[(\eta^5\text{-C}_5\text{H}_4\text{Bu-}t)\text{Ru}(\text{CO})_2\text{Ge}]$ units occupy the axial sites in the cluster, while the $\text{Ru}(\text{CO})_3$ units occupy the equatorial sites. Each of the ruthenium atoms in the triangular cluster $\text{Ru}_3(\text{CO})_9$ is bonded to three CO groups, one being nearly in the Ru_3 plane and the other two pointing to the two sides of the plane. The ¹³C NMR spectrum shows only one resonance for the nine CO groups, thereby indicating the nine CO groups are chemically equivalent to one another. It is apparent that a free rotation of three carbonyl groups on each ruthenium atom should result in the equivalence of the nine CO groups. Each germanium atom is σ -bonded with four ruthenium atoms, one of which is chemically different from the other three. The two *t*-butyls take a *trans* configuration. The Ge—Ru bonds lie in the range of 0.2425—0.2555 nm, and the Ru—Ge bond distances at the end of $[\text{Ru}(\text{CO})_2(\eta^5\text{-C}_5\text{Me}_4\text{H})]$ (mean 0.2422 nm) are much shorter than those at the end of $\text{Ru}_3(\text{CO})_9$ (mean 0.2502 nm), possibly due to the difference of electronic effect. The Ru—Ru bond distances (mean 0.2904 nm) are close to those found in $\text{Ru}_3(\text{CO})_{12}$ (0.2854 nm)¹⁰ and $[\text{Ru}$

$(\text{CO})_3]_3(\mu\text{-GeMe}_2)_3$ (0.2926 nm),¹¹ but much longer than those in dinuclear ruthenium complexes; *e. g.* 0.2735 nm in *trans*- $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2]_2$,¹² 0.2821 nm in $[(\eta^5, \eta^{5'}\text{-C}_{10}\text{H}_8)\text{Ru}_2(\text{CO})_4]$ ¹³ and 0.2700—0.2766 nm in bridged diruthenium complexes $\text{E}[(\eta^5\text{-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2$ ($\text{E} = \text{CH}_2, \text{Me}_2\text{Si}, \text{Me}_2\text{Ge}, \text{Me}_2\text{SiSiMe}_2, \text{Me}_2\text{SiOSiMe}_2\text{OSiMe}_2$).^{6,14-17} The dihedral angle between two cyclopentadienyl rings is 47.9°.

Although there are several known clusters containing a *closo*- E_2M_3 core, where E is an element of group 14, almost all of them are involved in only iron metal in their E_2M_3 core.¹⁸⁻²⁵ Since there only the ligand *t*- $\text{BuC}_5\text{H}_4\text{-Me}_2\text{GeGeMe}_2\text{C}_5\text{H}_4\text{Bu-}t$ was employed in the reaction, it is fairly apparent that the production of the naked germanium atom should be accompanied by the cleavage of all of Ge—C bonds in the ligand. Although there are two reports about the cleavage of the Ge—C bond occurring in the formation of the cluster $[\text{Ru}(\text{CO})_3]_3(\mu\text{-GeMe}_2)_3$ via thermal decomposition of $\text{Me}_3\text{Ge}_2\text{Ru}(\text{CO})_4$,¹¹ and in the reaction of MeGeH_3 with $\text{Fe}(\text{CO})_5$ to generate a naked Ge atom in the cluster $\text{Ge}[\text{Fe}_2(\text{CO})_8]_2$,²⁵ the formation of naked germanium atoms via tie cleavage of all of Ge—C bonds is still relatively unusual. We have been unable to determine, up to date, the fate of these dissociated methyl groups. Complex **2** possesses a novel four-membered heterocyclic ring. Its formation is obviously involved in the cleavage of the Ge—Ge bond. However, a further detailed study on the relatively stable intermediate transients is needed to explore the reaction mechanism.

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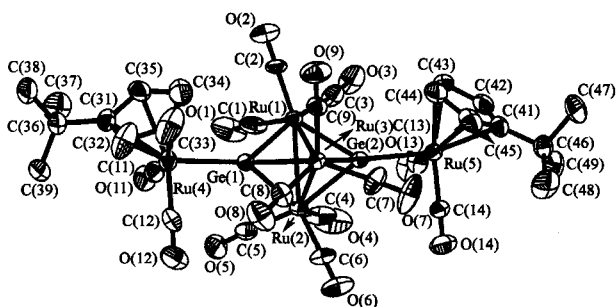


Fig. 1 Molecular structure of $\{(\mu^3\text{-Ge})[\text{Ru}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_4\text{Bu-}t)]\}_2\text{Ru}_3(\text{CO})_9$ (**1**).

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