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Unexpected Formation of the Ruthenium Carbonyl Cluster with a Trigonal-Bipyramidal Ge_2Ru_3 Core Accompanied by Loss of Germanium Methyl Groups

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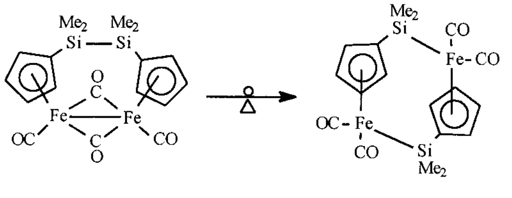
Summary: A novel trigonal-bipyramidal ruthenium carbonyl cluster, $[(\mu^3\text{-}Ge)\{Ru(CO)_2(\eta^5\text{-}C_5Me_4H)\}]_2Ru_3(CO)_9$ ***(3)****, was accidentally synthesized by thermal treatment of* $Ru_3(CO)_{12}$ *and* $C_5Me_4HMe_2GeGeMe_2C_5Me_4H$ *in boiling decalin, along with the dinuclear ruthenium complex* $[(Me_2Ge)(\eta^5\text{-}C_5Me_4)Ru_2(CO)_6]$ ***(4)****. Similar treatment of* $Ru_3(CO)_{12}$ *and* $C_5H_5Me_2GeGeMe_2C_5H_5$ *in boiling heptane afforded three different bimetallic complexes,* $[(Me_2Ge)(\eta^5\text{-}C_5H_4)Ru_2(CO)_6]$ ***(1)****,* $[(Me_2Ge)(\eta^5\text{-}C_5H_4)Ru(CO)_2]_2$ ***(2)****, and dimer* $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$*. Molecular structures of* ***2****,* ***3****, and* ***4*** *have been determined by single-crystal X-ray diffraction.*

Introduction

There is much attention on the synthesis and study of the transition metal complexes with multiple bonds between transition metals and "bare" main group elements mainly due to their implications in catalysis and material science.[1,2] Most of these complexes with novel structures result from accidental discoveries. A particular class of compounds with such bonds are transition metal carbonyl clusters containing a closo-E_2M_3 core, where E is a main group element and M is a transition metal.[3] Many of these clusters have been typically prepared by thermal treatment of transition metal carbonyl complexes and a wide range of ligand precursors containing group 14 elements in hydrocarbon solvents with high boiling points.

We recently reported an intramolecular thermal rearrangement between silicon−silicon and iron−iron bonds in the dinuclear iron complex $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)]_2(\mu\text{-}CO)_2]$ (eq 1).[4] An alternative mechanism involving intermediates containing iron and silicon free radicals was subsequently suggested.[5] The thermal rearrangement was later extended to silicon−ruthenium and germanium−iron analogues.[6] The replacement of the silicon−silicon bond by a germanium−germanium bond greatly accelerated the rearrangement reaction, indicating that the energy barrier for the rearrangement of germanium−iron analogues should be much lower. We now decide to investigate whether the germanium−ruthenium analogues might undergo similar thermal rearrangements.



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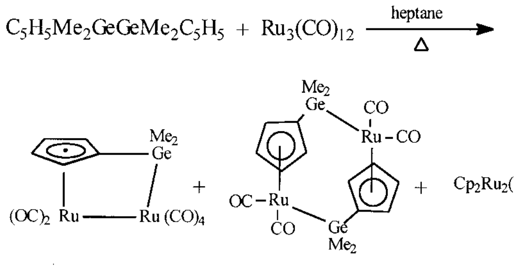
Results and Discussion

Thermal treatment of $Ru_3(CO)_{12}$ with $C_5H_5Me_2GeGeMe_2C_5H_5$ in refluxing heptane afforded three different bimetallic complexes, $[(Me_2Ge)(\eta^5\text{-}C_5H_4)Ru_2(CO)_6]$ (**1**) (11% yield), $[(Me_2Ge)(\eta^5\text{-}C_5H_4)Ru(CO)_2]_2$ (**2**) (1% yield), and ruthenium dimer $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$7 (4% yield) (eq 2). Complex **1** is yellow crystalline, but **2** is colorless. Thus, they could be separated mechanically. Both of them were fully characterized by ^1H and ^{13}C NMR, IR spectroscopy, and elemental analysis, and **2** has also been determined by X-ray diffraction analysis. The ^1H NMR and IR spectra of **2** are almost identical to those of its isomorphic silicon analogue $[(Me_2Si)(\eta^5\text{-}$



1 **2**

(2)

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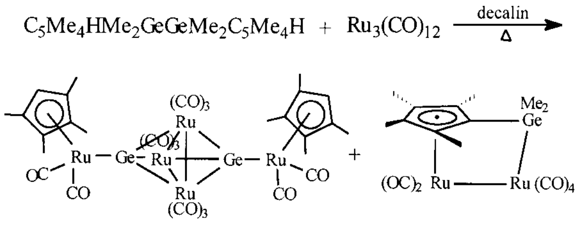
$C_5H_4)Ru(CO)_2]_2$[6a] and iron analogue $[(Me_2Ge)(\eta^5\text{-}C_5H_4)\text{-}Fe(CO)_2]_2$.[6b] Although the dinuclear ruthenium complex $(Me_2GeGeMe_2)[(\eta^5\text{-}C_5H_4)Ru(CO)]_2(\mu\text{-}CO)_2$ was not obtained, it could be reasonably assumed that the formation of **2** should be related to the thermal rearrangement illustrated in eq 1.

When the tetramethyl-substituted cyclopentadienyl ligand $C_5Me_4HMe_2GeGeMe_2C_5Me_4H$ and $Ru_3(CO)_{12}$ were refluxed similarly in boiling heptane, no reaction was observed except for a slight decomposition of $Ru_3(CO)_{12}$. The employment of the solvent decalin with a high boiling point resulted in the unexpected formation of the germanium−ruthenium cluster with a trigonal-bipyramidal Ge_2Ru_3 core, $[(\mu^3\text{-}Ge\{Ru(CO)_2(\eta^5\text{-}C_5Me_4H)\})_2\text{-}Ru_3(CO)_9$ (**3**) (14% yield), and the dinuclear ruthenium complex $[(Me_2Ge)(\eta^5\text{-}C_5Me_4)Ru_2(CO)_6]$ (**4**) (3% yield) (eq 3). When octane was utilized as a refluxing solvent instead of decalin, complex **4** was obtained as a major product and only a small amount of **3** was isolated (2% yield). This indicates that the high refluxing temperature will contribute to the formation of the cluster **3**. Both **3** and **4** are yellow crystals and could be separated by preparative TLC. They were fully characterized by ^1H and ^{13}C NMR, IR spectroscopy, and elemental analysis and have also been determined by X-ray diffraction analysis. The ^1H NMR spectrum of **3** exhibits only the resonances of the cyclopentadienyl rings; however, the $^{13}C\{^1H\}$ NMR spectrum shows the two different resonances for CO groups, indicating two different types of ruthenium atoms that exist in each molecule. Complex **4** shows the same carbonyl-region infrared absorptions as those of **1**, suggesting that they should be structurally isomophous.



(3)

3 **4**

The single-crystal structure of **2** is illustrated in Figure 1. The molecule consists of two $[(Me_2Ge)(\eta^5\text{-}C_5H_4)Ru(CO)_2]$ moieties linked by two Ru−Ge bonds. Like many related analogues,[4,6,8] **2** has C_i symmetry, and the six-membered ring Ru(1)−Ge(1)−C(11a)−Ru(1a)−Ge(1a)−C(11) constituting the molecular skeleton adopts a stable chair conformation. The Ru−Ge bond length (2.4623(7) Å) is longer than the shortest Ru−Ge bond reported so far, 2.408(2) Å in $[(\eta^6\text{-}C_6H_6)\text{-}Ru(CO)(GeCl_3)_2]$,[9] but slightly shorter than those in *trans*-$Ru(CO)_4(GeCl_3)_2$ (2.477(1) Å),[10] $C_8H_6[(CO)_2Ru\text{-}(GeMe_3)]_2$ (mean 2.487 Å),[11] and $[Ru(CO)_3]_3(\mu\text{-}GeMe_2)_3$ (2.49(1) Å).[12]

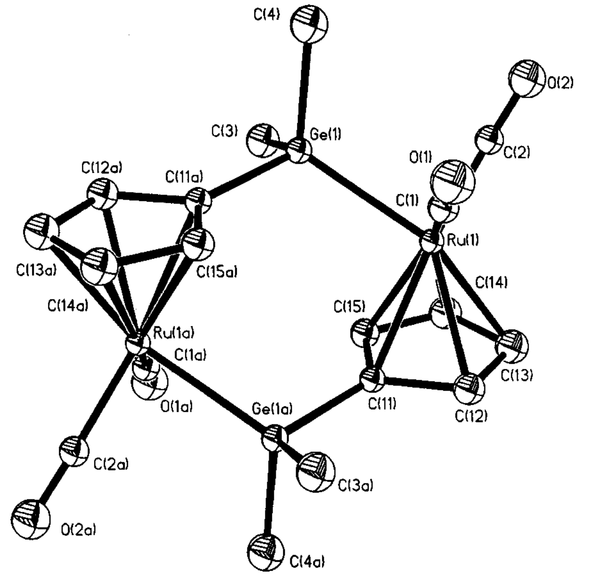


Figure 1. ORTEP drawing of **2**, 30% probability thermal ellipsoids.

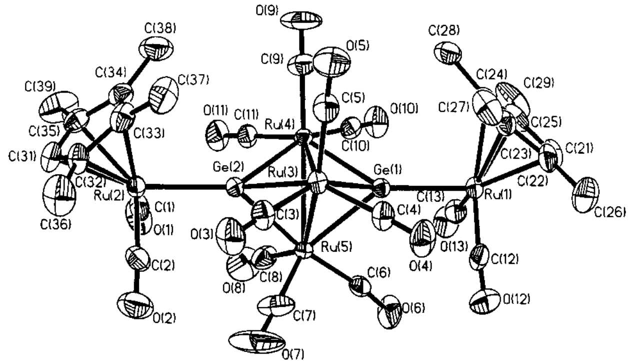


Figure 2. ORTEP drawing of **3**, 30% probability thermal ellipsoids.

The single-crystal structure of **3** is presented in Figure 2. The structure confirms the spectroscopic data analysis. The molecule of **3** consists of an equatorial triangular cluster $Ru_3(CO)_9$ capped on both sides by the apical fragment of $[(\mu^3\text{-}Ge\{Ru(CO)_2(\eta^5\text{-}C_5Me_4H)\}]$. Each of the ruthenium atoms in the triangular cluster $Ru_3(CO)_9$ 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 $^{13}C\{^1H\}$ NMR spectrum shows only one resonance for the nine CO groups, thereby indicating they 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 Ge−Ru bonds lie in the range of 2.435(1)−2.549(1) Å, and the Ru−Ge bond distances at the end of $[Ru\text{-}(CO)_2(\eta^5\text{-}C_5Me_4H)]$ (mean 2.439 Å) are much shorter than those at the end of $Ru_3(CO)_9$ (mean 2.516 Å), possibly due to the difference of electronic effects. The Ru−Ru bond distances (mean 2.904 Å) are close to those found in $Ru_3(CO)_{12}$ (2.854(1) Å)[13] and $[Ru(CO)_3]_3(\mu\text{-}GeMe_2)_3$ (2.926(9) Å),[12] but much longer than those in

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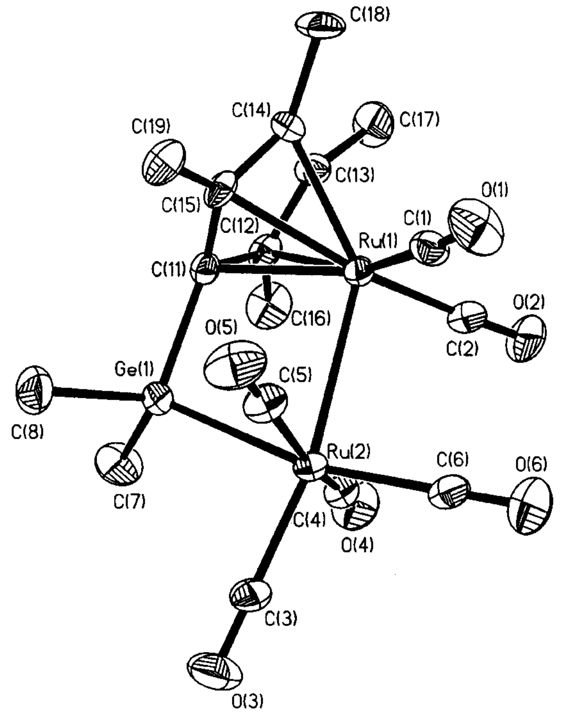

Figure 3. ORTEP drawing of **4**, 30% probability thermal ellipsoids.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 2

Bond Distances (Å)			
Ru(1)−Ge(1)	2.4623(7)	Ge(1)−C(11a)	1.966(6)
Ru(1)−C(11)	2.261(6)		
Bond Angles (deg)			
Ge(1)−Ru(1)−C(11)	100.9(1)	Ru(1)−Ge(1)−C(11a)	110.9(2)
Ru(1)−C(11)−Ge(1a)	130.1(3)		

Table 2. Selected Bond Distances (Å) and Angles (deg) for 3

Bond Distances (Å)			
Ru(1)−Ge(1)	2.435(1)	Ru(2)−Ge(2)	2.442(1)
Ru(3)−Ru(4)	2.938(1)	Ru(4)−Ru(5)	2.888(1)
Ru(3)−Ru(5)	2.886(1)	Ru(3)−Ge(1)	2.491(1)
Ru(3)−Ge(2)	2.517(1)	Ru(4)−Ge(1)	2.490(1)
Ru(4)−Ge(2)	2.509(1)	Ru(5)−Ge(1)	2.549(1)
Ru(5)−Ge(2)	2.539(1)		
Bond Angles (deg)			
Ru(4)−Ru(3)−Ru(5)	59.5(1)	Ge(1)−Ru(3)−Ge(2)	97.0(1)
Ru(3)−Ru(4)−Ru(5)	59.4(1)	Ge(1)−Ru(4)−Ge(2)	97.2(1)
Ru(3)−Ru(5)−Ru(4)	51.2(1)	Ge(1)−Ru(5)−Ge(2)	94.9(1)

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

Bond Distances (Å)			
Ru(1)−Ru(2)	2.861(1)	Ru(2)−Ge(1)	2.538(1)
Ge(1)−C(11)	1.985(7)	Ru(1)−C(11)	2.266(7)
Bond Angles (deg)			
Ru(2)−Ru(1)−C(11)	83.2(2)	Ru(1)−Ru(2)−Ge(1)	75.8(1)
Ru(2)−Ge(1)−C(11)	98.1(2)	Ru(1)−C(11)−Ge(1)	102.8(3)

dinuclear ruthenium complexes, e.g., 2.735(2) Å in *trans*-$[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$,[14] 2.821(1) Å in $[(\eta^5,\eta^{5'}\text{-}C_{10}H_8)Ru_2(CO)_4]$,[15] and 2.700−2.766 Å in bridged diruthenium complexes $E[(\eta^5\text{-}C_5H_4)Ru(CO)_2]_2$ (E = CH_2, Me_2Si, Me_2Ge, $Me_2SiSiMe_2$, $Me_2SiOSiMe_2OSiM_2$).[6a,16] The dihedral angle between two cyclopentadienyl rings is 72.8°.

The single-crystal structure of **4** is presented in Figure 3. The molecule of **4** has approximately mirror symmetry, and the molecular mirror plane passes through the four-membered ring plane, Ru(1)−Ru(2)−Ge(1)−C(11), which constitutes the molecular skeleton and is perpendicular to the Cp ring. The Ru(2) atom adopts the very common six-coordinate octahedral geometry with two apical CO groups slightly leaning to the Cp ligand. The Ru−Ru bond distance (2.861(1) Å) is comparatively close to that in $Ru_3(CO)_{12}$ (2.854(1) Å), but longer than the corresponding bond (2.8256(7) Å) in the related complex $[Ru_3(CO)_{10}(\eta^5,\eta^1\text{-}C_5H_4)]$.[17] The Ru−Ge bond distance (2.538(1) Å) is considerably close to the upper limit reported so far (2.549(1) Å in **3**).

Although there are several known clusters containing a closo-E_2M_3 core, where E is a group 14 element, almost all of them have only iron metal in their E_2M_3 core. Complex **3** is the first example of transition metal clusters with a closo-E_2Ru_3 core. The first trigonal-bipyramidal iron cluster, $[(\mu^3\text{-}Sn\{Fe(CO)_2Cp\}]_2Fe_3(CO)_9$, was accidentally synthesized by thermolysis of $[Cp_2SnFe(CO)_4]_2$ in boiling toluene.[3c] Recently the two analogues $[(\mu^3\text{-}E\{Fe(CO)_2Cp\}]_2Fe_3(CO)_9$ (E = Si, Ge) have been synthesized in good yields by thermal treatment of EH_4, $Fe(CO)_5$, and $[CpFe(CO)_2]_2$ in petroleum ether at 150 °C.[3g] Note that the formation of **3** is completely unrelated to the germanium hydrides since only the cyclopentadienyl ligand $C_5Me_4HMe_2GeGeMe_2C_5Me_4H$ was employed in the reaction. It is fairly apparent that the production of the bare germanium atom should be accompanied by the cleavage of all Ge−C bonds in the ligand. Although the cleavage of the Ge−C bond occurred in the formation of the cluster $[Ru(CO)_3]_3(\mu\text{-}GeMe_2)_3$ via thermal decomposition of $Me_3Ge_2Ru(CO)_4$[12] and in the reaction of $MeGeH_3$ with $Fe(CO)_5$ to generate a naked Ge atom in the cluster $Ge[Fe_2(CO)_8]_2$,[3g] the formation of naked germanium atoms via the cleavage of all Ge−C bonds is still relatively unusual. We have been unable to determine, up to date, the fate of these dissociated methyl groups. Complexes **1** and **4** possess a novel four-membered heterocyclic ring. Their formation is obviously involved in the cleavage of the Ge−Ge bond. However, a further detailed study on relatively stable intermediate transients is needed to explore the reaction mechanisms.

Experimental Section

General Considerations. 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. $Ru_3(CO)_{12}$ was purchased from Strem Co. $C_5H_5Me_2GeGeMe_2C_5H_5$ and $C_5Me_4HMe_2GeGeMe_2C_5Me_4H$ were prepared according to literature methods.[6b] ^1H and ^{13}C NMR spectra were obtained on a Bruker AC-P 200 spectrometer. Elemental analyses were performed by a Perkin-Elmer 240C instrument. Infrared

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Table 4. Summary of X-ray Diffraction Data

	2	**3**	**4**
formula	$C_{18}H_{20}Ge_2O_4Ru_2$	$C_{31}H_{26}Ge_2O_{13}Ru_5$	$C_{17}H_{18}GeO_6Ru_2$
fw	647.68	1257.08	593.06
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
cryst syst	monoclinic	monoclinic	monoclinic
Z	2	4	4
a (Å)	9.053(3)	9.171(3)	12.836(3)
b (Å)	10.749(2)	17.463(3)	9.540(2)
c (Å)	10.943(2)	24.452(5)	16.872(3)
α (deg)	90	90	90
β (deg)	96.52(2)	95.39(3)	94.40(3)
γ (deg)	90	90	90
volume (Å^3)	1058(1)	3899(3)	2060(1)
D_{calc} (g·cm^{-3})	2.33	2.141	1.912
cryst size (mm)	0.15 × 0.20 × 0.20	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.40
radiation (Å^3)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
μ (cm^{-1})	41.71	34.09	28.79
data collection method	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
max 2θ (deg)	46.0	46.0	46.0
total no. of observns	1486	5758	3189
no. of unique data, $I > 3\sigma(I)$	1278	5017	2790
final no. of variables	118	460	235
R	0.035	0.044	0.052
R_w	0.044	0.049	0.060
goodness of fit	2.413	1.75	1.45

spectra were obtained as KBr disks and recorded on a Nicolet 5DX FT-IR spectrometer.

Reaction of $C_5H_5Me_2GeGeMe_2C_5H_5$ with $Ru_3(CO)_{12}$. A solution of 1.0 g (1.56 mmol) of $Ru_3(CO)_{12}$ and 0.77 g (2.30 mmol) of $C_5H_5Me_2GeGeMe_2C_5H_5$ in 50 mL of heptane was refluxed for 20 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 preparative TLC yielded a yellow solid. Recrystallization of the product from a mixture of hexane and CH_2Cl_2 afforded two types of crystals with different colors, which were separated mechanically to afford 0.14 g (11%) of yellow crystals of **1** and 20 mg (1%) of colorless crystals of **2**. Elution with CH_2Cl_2 developed another yellow band, which was collected and after solvent removal afforded 40 mg (4%) of yellow product of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$.[7] **1**: mp 166−8 °C. Anal. Calcd for $C_{13}H_{10}GeO_6Ru_2$: C, 29.08; H, 1.88. Found: C, 29.42; H, 2.18. ^{1}H NMR ($CDCl_3$): δ 0.71 (s, 6H, GeMe), 4.41 (t, J = 1.96 Hz, 2H, Cp-H), 5.80 (d, J = 1.96 Hz, 2H, Cp-H). ^{13}C NMR ($CDCl_3$): δ 1.16 (GeMe), 78.3, 83.0, 92.8 (Cp), 196.7 (CpRu-*C*O), 197.4−201.1 (m, Ru−CO). IR (ν_{CO}, cm^{-1}): 2085(m), 2003(s), 1980(s), 1970(s), 1929(s), 1895(w). **2**: mp 156−8 °C. Anal. Calcd for $C_{18}H_{20}Ge_2O_4Ru_2$: C, 33.38; H, 3.11. Found: C, 33.66; H, 2.81. ^{1}H NMR ($CDCl_3$): δ 0.56 (s, 12H, $GeMe_2$), 5.33 (s, 8H, Cp-H). IR (ν_{CO}, cm^{-1}): 1989(s), 1946(s), 1933(s), 1906(w).

Reaction of $C_5Me_4HMe_2GeGeMe_2C_5Me_4H$ with $Ru_3(CO)_{12}$. A solution of 0.48 g (0.75 mmol) of $Ru_3(CO)_{12}$ and 0.50 g (1.12 mmol) of $C_5Me_4HMe_2GeGeMe_2C_5Me_4H$ in 30 mL of decalin was refluxed for 10 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 preparative TLC yielded 20 mg (3%) of yellow crystals of **4**. 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 80 mg (14%) of orange crystals of **3**. **3**: mp 218 °C (dec). Anal. Calcd for $C_{31}H_{26}Ge_2O_{13}Ru_5$: C, 29.62; H, 2.08. Found: C, 29.80; H, 2.08. ^{1}H NMR ($CDCl_3$): δ 2.07 (s, 12H, Cp-Me), 2.09 (s, 12H, Cp-Me), 5.10 (s, 2H, Cp-H). ^{13}C NMR ($CDCl_3$): δ 10.4, 11.9 (Cp-*Me*), 84.2 (*Cp*-H), 102.1, 102.5 (*Cp*-Me), 199.2 (CpRu-*C*O), 202.5 (m, Ru_3CO_9). IR (ν_{CO}, cm^{-1}): 2042(w), 2015(s), 1985(s), 1967(m), 1958(s), 1920(m). **4**: mp 126−8 °C. Anal. Calcd for $C_{17}H_{18}GeO_6Ru_2$: C, 34.24; H, 3.04. Found: C, 34.23; H, 3.30. ^{1}H NMR ($CDCl_3$): δ 0.83 (s, 6H, $GeMe_2$), 1.80 (s, 6H, Cp-Me), 2.16 (s, 6H, Cp-Me). IR (ν_{CO}, cm^{-1}): 2082(s), 2033(m), 2008(s), 1992(s), 1972(s), 1928(s).

Crystallographic Studies. Crystals suitable for X-ray diffraction were obtained from hexane/dichloromethane solutions. All data sets were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least squares. A summary of the crystallographic results is presented in Table 4.

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Supporting Information Available: Tables of final postional and thermal parameters of the non-hydrogen atoms, general temperature factors, and bond distances and angles for **2**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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