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Germanium-Rich Pentaruthenium Carbonyl Clusters Including $Ru_5(CO)_{11}(\mu\text{-}GePh_2)_4(\mu_5\text{-}C)$ and Its Reactions with Hydrogen

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The reaction of $Ru_5(CO)_{15}(\mu_5\text{-}C)$, **1**, with Ph_3GeH at 150 °C has yielded two new germanium-rich pentaruthenium cluster complexes: $Ru_5(CO)_{11}(\mu\text{-}CO)(\mu\text{-}GePh_2)_3(\mu_5\text{-}C)$, **2**; $Ru_5(CO)_{11}(\mu\text{-}GePh_2)_4(\mu_5\text{-}C)$, **3**. Both compounds contain square pyramidal Ru_5 clusters with $GePh_2$ groups bridging three and four of the edges of the Ru_5 square base, respectively. When treated with 1 equiv of Ph_3GeH at 150 °C compound **2** is converted to **3**. Reaction of **3** with H_2 at 150 °C yielded $Ru_5(CO)_{10}(\mu\text{-}GePh_2)_4(\mu_5\text{-}C)(\mu\text{-}H)_2$, **4**, containing two hydride ligands and one less CO ligand. Reaction of **4** with hydrogen at 150 °C yielded the compound $Ru_5(CO)_{10}(\mu\text{-}GePh_2)_2(\mu_3\text{-}GePh)_2(\mu_3\text{-}H)(\mu_4\text{-}CH)$, **5**, by loss of benzene and conversion of two of the bridging $GePh_2$ groups into triply bridging GePh groups. Compound **5** contains one triply bridging hydride ligand and a quadruply bridging methylidyne ligand formed by addition of one hydrogen atom to the carbido carbon atom.

Introduction

Preparation of bimetallic nanoparticles from bimetallic molecular clusters as precursors has received much attention in recent years.[1−8] Bimetallic nanoparticles have been shown to exhibit superior catalytic activity under heterogeneous conditions.[8,9] Ruthenium combined with the group 14 elements, germanium, tin, or lead, has also been of interest in catalysis.[10−12] There is extensive literature on transition metal complexes containing group 14 elements;[13−16] however, there are only a few examples of ruthenium−germanium complexes and these consist only of mono-, di-, and triruthenium species.[17−19]

In a previous study we reported that triethysilane reacts with $Ru_5(CO)_{15}(\mu_5\text{-}C)$ by oxidative addition to yield Ru−Si clusters.[20] Recently, we showed that multiple additions of triphenylstannane to pentaruthenium carbido carbonyl cluster complexes yields bimetallic clusters containing as many as five tin ligands.[21] Cleavage of phenyl groups from intermediates containing triphenyltin ligands facilitated the high incorporation of tin ligands into these clusters. Herein we report on the reaction of triphenylgermane, Ph_3GeH, with

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(1) Toshima, N.; Yonezawa, T. *New J. Chem.* **1998**, 1179.
(2) Johnson, B. F. G. *Coord. Chem. Rev.* **1999**, *192*, 1269.
(3) Midgley, P. A.; Weyland, M.; Thomas, J. M.; Johnson, B. F. G. *Chem. Commun.* **2001**, 907.
(4) Nashner, M. S.; Frenkel, A. I.; Somerville, D.; Hills, C. W.; Shapley, J. R.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 8093.
(5) Nashner, M. S.; Frenkel, A. I.; Adler, D. L.; Shapley, J. R.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 7760.
(6) Shephard, D. S.; Maschmeyer, T.; Johnson, B. F. G.; Thomas, J. M.; Sankar, G.; Ozkaya, D.; Zhou, W.; Oldroyd, R. D.; Bell, R. G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2242.
(7) Raja, R.; Sankar, G.; Hermans, S.; Shephard, D. S.; Bromley, S.; Thomas, J. M.; Johnson, B. F. G. *Chem. Commun.* **1999**, 1571.
(8) (a) Raja, R.; Khimyak, T.; Thomas, J. M.; Hermans, S.; Johnson, B. F. G.. *Angew. Chem., Int. Ed.* **2001**, *40*, 4639. (b) Shephard, D. S.; Maschmeyer, T.; Sankar, G.; Thomas, J. M.; Ozkaya, D.; Johnson, B. F. G.; Raja, R.; Oldroyd, R. D.; Bell, R. G. *Chem.*−*Eur. J.* **1998**, *4*, 1214.
(9) Sinfelt, J. H. *Bimetallic Catalysts. Discoveries, Concepts and Applications*; Wiley: New York, 1983.
(10) (a) Hermans, S.; Raja, R.; Thomas, J. M.; Johnson, B. F. G.; Sankar, G.; Gleeson, D. *Angew. Chem., Int. Ed.* **2001**, *40*, 1211. (b) Hermans, S.; Johnson, B. F. G. *Chem. Commun.* **2000**, 1955. (c) Raja, R.; Khimyak, T.; Thomas, J. M.; Hermans, S.; Johnson, B. F. G. *Angew. Chem., Int. Ed.* **2001**, *40*, 4638.
(11) Tijani, A.; Coq, B.; Figueras, F. *Appl. Catal.* **1991**, *76*, 255.
(12) Sanchez-Sierra, M. C.; García-Ruiz, J.; Proietti, M. G.; Blasco, J. *J. Mol. Catal., A* **1996**, *108*, 95.
(13) Hermann, W. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 56.
(14) Whitmire, K. H. *J. Coord. Chem.* **1988**, *17*, 95.
(15) Compton, N. A.; Errington, R. J.; Norman, N. C. *Adv. Organomet. Chem.* **1990**, *31*, 91.
(16) Leong W. K.; Fredrick, W. B.; Einstein, W. B.; Pomeroy, R. K. *Organometallics* **1996**, *15*, 1589.
(17) Howard, J.; Woodward, P. *J. Chem. Soc. A* **1971**, 3648.
(18) Ball, R.; Bennett, M. J. *Inorg. Chem.* **1972**, *11*, 1806.
(19) Zhang, Y.; Wang, B.; Xu, S.; Zhou, X. *Organometallics* **2001**, *20*, 3829.
(20) Adams, R. D.; Captain, B.; Fu, W. *Organometallics* **2000**, *19*, 3670.
(21) (a) Adams, R. D.; Captain, B.; Fu, W.; Smith, M. D. *Inorg. Chem.* **2002**, *41*, 5593. (b) Adams, R. D.; Captain, B.; Fu, W.; Smith, M. D. *Inorg. Chem.* **2002**, *41*, 2302.

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$Ru_5(CO)_{15}(\mu_5\text{-}C)$, **1**,[22] which also yields high-nuclearity ruthenium−germanium clusters in a similar manner. In addition, interesting reactions of one of these clusters, $Ru_5(CO)_{11}(\mu\text{-}GePh_2)_4(\mu_5\text{-}C)$, with hydrogen were also investigated.

Experimental Section

General Data. All reactions were performed under a nitrogen atmosphere. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Nicolet 5DXBO FTIR or a Nicolet Avatar 360 FTIR spectrophotometer. ^1H NMR were recorded on a Varian Inova 400 spectrometer operating at 400.15 MHz. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Ph_3GeH was purchased from Gelest and was used without further purification. $Ru_5(CO)_{15}(\mu_5\text{-}C)$, **1**,[22] was prepared according to the published procedure. Product separations were performed by TLC in air on Analtech 0.25 and 0.5 mm silica gel 60 Å F_{254} glass plates.

Reaction of $Ru_5(CO)_{15}(\mu_5\text{-}C)$ with Ph_3GeH. A 9.2 mg of amount of **1** (0.010 mmol) and 8.7 mg of Ph_3GeH (0.028 mmol) were dissolved in 15 mL of nonane. The solution was then heated to reflux for 20 min. After the solvent was removed, the products were separated by TLC on silica gel by using 3:1 hexane/methylene chloride solvent mixture to yield 5.3 mg (35%) of red $Ru_5(CO)_{11}(\mu\text{-}CO)(\mu\text{-}GePh_2)_3(\mu_5\text{-}C)$, **2**, and 4.0 mg (24%) of purple-pink product $Ru_5(CO)_{11}(\mu\text{-}GePh_2)_4(\mu_5\text{-}C)$, **3**. Spectral data for **2**: IR ν_{CO} (cm^{-1} in hexane) 2060 (m), 2030 (s), 2016 (vs), 1986 (w), 1967 (vw), 1961 (vw), 1877 (m); ^1H NMR (CD_2Cl_2 in ppm) $\delta = 7.21-7.86$ (m, Ph). Anal. Calcd: C, 38.33; H, 1.96. Found: C, 38.17; H, 1.94. Spectral data for **3**: IR ν_{CO} (cm^{-1} in hexane) 2020 (s), 2009 (sh), 1983 (w); ^1H NMR (CD_2Cl_2 in ppm) $\delta = 7.38-7.76$ (m, Ph). Anal. Calcd: C, 41.55; H, 2.31. Found: C, 41.63; H, 2.47.

Improved Synthesis of 3. A 68.0 mg amount of **1** (0.073 mmol) and 100.0 mg of Ph_3GeH (0.33 mmol) were dissolved in 30 mL of nonane, and then the mixture was heated to reflux for 45 min. The reaction mixture was cooled and separated on a silica gel column to yield trace amounts of a few uncharacterizable orange and yellow bands eluted by a hexane/CH_2Cl_2 (5:1) solvent mixture followed by 100.1 mg of **3** (80%) eluted by a hexane/CH_2Cl_2 (3:1) solvent mixture.

Conversion of 2 to 3. A 16.8 mg amount of **2** (0.011 mmol) and 3.3 mg of Ph_3GeH (0.011 mmol) were dissolved in 10 mL of nonane, and the mixture was heated to reflux for 30 min. The reaction mixture was then separated by TLC on silica gel by using 3:1 hexane/methylene chloride solvent mixture to yield 15.1 mg (80%) of **3**.

Synthesis of $Ru_5(CO)_{10}(\mu\text{-}GePh_2)_4(\mu_5\text{-}C)(\mu\text{-}H)_2$, 4. A 30.0 mg amount of **3** (0.017 mmol) dissolved in 15 mL of nonane was heated to reflux in the presence of a purge with hydrogen (1 atm) for 30 min. *Caution! Hydrogen is a highly flammable gas. The purge should be vented directly to the back of the hood to avoid contact with hot materials.* After the solvent was removed, the product was separated by TLC on silica gel by using a 5:2 hexane/CH_2Cl_2 solvent mixture to yield trace amounts of unreacted **3** and 9.0 mg (31%) of red $Ru_5(CO)_{10}(\mu\text{-}GePh_2)_4(\mu_5\text{-}C)(\mu\text{-}H)_2$, **4**. Spectral data for **4**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2055 (w), 2040 (m), 2004 (s), 1975 (w), 1964 (w); ^1H NMR (CD_2Cl_2 in ppm) $\delta = 7.35-7.95$ (m, 40H, Ph), −23.11 (s, 2H, hydride). Anal. Calcd: C, 41.60; H, 2.47. Found: C, 41.61; H, 2.76.

Synthesis of $Ru_5(CO)_{10}(\mu\text{-}GePh_2)_2(\mu_3\text{-}GePh)_2(\mu_3\text{-}H)(\mu_4\text{-}CH)$, 5. An 8.0 mg amount of **3** (0.011 mmol) dissolved in 15 mL of nonane was heated to reflux in the presence of a purge with hydrogen (1 atm) for 90 min. After the solvent was removed, the product was separated by TLC on silica gel by using a 5:2 hexane/CH_2Cl_2 solvent mixture to yield 5.5 mg (34%) of an orange product $Ru_5(CO)_{10}(\mu\text{-}GePh_2)_2(\mu_3\text{-}GePh)_2(\mu_3\text{-}H)(\mu_4\text{-}CH)$, **5**, minor amounts of **3,** and 2.2 mg (12%) of the red product **4**. Spectral data for **5**: IR ν_{CO} (cm^{-1} in hexane) 2027 (vs), 2009 (s), 1988 (w), 1980 (vw), 1961 (vw); ^1H NMR ($CDCl_3$ in ppm) $\delta = 11.21$ (d, 1H, μ_4-CH, $^3J_{H-H} = 1.52$ Hz), 6.86−8.16 (m, 30H, Ph), −21.88 (d, 1H, hydride,$^3J_{H-H} = 1.52$ Hz). Anal. Calcd: C, 36.4; H, 2.07. Found: C, 36.53; H, 1.95.

Table 1. Crystallographic Data for Compounds **2** and **3**

	2	**3**
empirical formula	$Ru_5Ge_3O_{12}C_{49}H_{30}$	$Ru_5Ge_4O_{11}C_{60}H_{40}\cdot 1/2CH_2Cl_2$
fw	1533.85	1774.08
cryst system	orthorhombic	monoclinic
lattice params		
a (Å)	20.5433(9)	15.8685(5)
b (Å)	13.8799(6)	19.8239(7)
c (Å)	18.5911(8)	39.44707(14)
α (deg)	90	90
β (deg)	90	96.343(1)
γ (deg)	90	90
V (Å^3)	5301.0(4)	12340.5(7)
space group	$Cmc2_1$	$C2/c$
Z value	4	8
ρ_{calc} (g/cm^3)	1.92	1.91
μ(Mo Kα) (mm^{-1})	3.12	3.21
temp (K)	296	296
$2\Theta_{max}$ (deg)	56.58	48.22
no. of observns ($I > 2\sigma(I)$)	5301	7543
no. of params	334	717
goodness of fit[a]	1.028	1.099
max shift in cycle	0.001	0.000
resids:[a] R1; wR2	0.0319; 0.0649	0.0556; 0.1181
abs corr, max/min	SADABS, 1.00/0.74	SADABS, 1.00/0.86
largest peak in final diff map (e/Å^3)	0.77	3.49

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/\sigma^2(F_o^2)$. $GOF = [\Sigma_{hkl}(w(|F_o^2| - |F_c^2|))^2/(n_{data} - n_{vari})]^{1/2}$.

Conversion of 4 to 5. A 9.0 mg amount of **5** (0.005 mmol) in 15 mL of nonane was heated to reflux in the presence of a purge with hydrogen (1 atm) for 45 min. After the solvent was removed, the product was separated by TLC on silica gel by using a 5:2 hexane/CH_2Cl_2 solvent mixture to yield 2.0 mg (24%) of **5**.

Crystallographic Analyses. Red crystals of **2**−**4** and orange crystals of **5** suitable for diffraction analysis were all grown by slow evaporation of solvent from solutions in hexane/methylene chloride solvent mixtures at 5 °C. Each data crystal was glued onto the end of thin glass fiber. X-ray intensity data were measured using a Bruker SMART APEX CCD-based diffractometer using Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The unit cells were initially determined on the basis of the reflections selected from a set of three scans measured in orthogonal wedges of reciprocal space. The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.[23] Correction for the Lorentz and polarization effects were also applied by SAINT. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied by using the program SADABS. All four structures were solved by a combination of direct methods and difference Fourier syntheses and refined by full-matrix least-

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[22] Nicholls, J. N.; Vargas, M. D.; Hriljac, J.; Sailor, M. *Inorg. Synth.* **1989**, *26*, 283.

[23] *SAINT+*, version 6.02a; Bruker Analytical X-ray System, Inc.: Madison, WI, 1998.

Table 2. Crystallographic Data for Compounds **4** and **5**

	4	**5**
empirical formula	$Ru_5Ge_4O_{10}C_{59}H_{42}$	$Ru_5Ge_4O_{10}C_{47}H_{32}$
fw	1706.64	1552.44
cryst system	tetragonal	triclinic
lattice params		
a (Å)	23.7015(10)	13.464(4)
b (Å)	23.7015(10)	13.616(2)
c (Å)	12.3989(11)	15.985(5)
α (deg)	90	82.001(6)
β (deg)	90	65.677(6)
γ (deg)	90	68.553(6)
V (Å^3)	6965.2 (7)	2485.0(13)
space group	$P4_1$	$P\bar{1}$
Z value	4	2
ρ_{calc} (g/cm^3)	1.63	2.08
μ(Mo Kα) (mm^{-1})	2.80	3.91
temp (K)	296	296
2Θ$_{max}$ (deg)	56.74	56.98
no. of observns ($I > 2\sigma(I)$)	13 734	9909
no. of params	711	603
goodness of fit[a]	1.041	1.000
max shift in cycle	0.001	0.002
resids:[a] R1; wR2	0.0467; 0.0946	0.0308; 0.0680
abs corr, max/min	SADABS, 1.00/0.81	SADABS, 1.00/0.73
largest peak in final diff map (e/Å^3)	0.91	0.74

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/\sigma^2(F_o^2)$. $GOF = [\Sigma_{hkl}(w(|F_o^2| - |F_c^2|))^2/(n_{data} - n_{vari})]^{1/2}$.

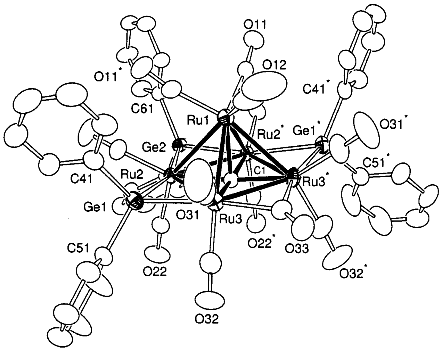


Figure 1. ORTEP diagram of the molecular structure of $Ru_5(CO)_{11}(\mu\text{-}CO)(\mu\text{-}GePh_2)_3(\mu_5\text{-}C)$, **2**, showing 30% probability thermal ellipsoids.

squares on F^2 by using the SHELXTL software package.[24] Crystal data, data collection parameters, and results of the analyses for compounds **2** and **3** are listed in Table 1 and for compounds **4** and **5** are listed in Table 2.

Results and Discussion

The reaction of $Ru_5(CO)_{15}(\mu_5\text{-}C)$, **1**,[22] with Ph_3GeH in a 1:3 ratio at 150 °C yielded two new pentaruthenium cluster complexes: $Ru_5(CO)_{11}(\mu\text{-}CO)(\mu\text{-}GePh_2)_3(\mu_5\text{-}C)$, **2,** in 35% yield; $Ru_5(CO)_{11}(\mu\text{-}GePh_2)_4(\mu_5\text{-}C)$, **3,** in 24% yield. Compounds **2** and **3** were characterized by a combination of IR, NMR, and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of **2** is shown in Figure 1. Selected bond distances and angles are listed in Table 3. Compound **2** consists of a square pyramidal cluster of five ruthenium atoms with three $GePh_2$ groups bridging three of the four edges of the base of the square pyramid. The fourth edge contains a bridging carbonyl ligand. The molecule contains mirror symmetry in the solid state with the mirror plane passing through the apical ruthenium atom, Ru1, the bridging CO ligand, and the germanium atom, Ge2. The Ru−Ge bond distances to the bridging $GePh_2$ groups lie in the range 2.4792(7)−2.5166(6) Å and are similar to those found for the bridging $GeMe_2$ groups in the compound $Ru_3(\mu\text{-}GeMe_2)_3(CO)_9$, 2.482(11)−2.500(12) Å.[17]

Table 3. Selected Intramolecular Distances and Angles for $Ru_5(CO)_{11}(\mu\text{-}Co)(\mu\text{-}GePh_2)_3(\mu_5\text{-}C)$, **2**[a]

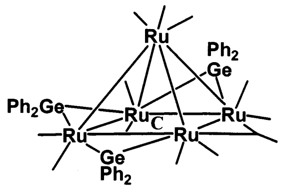
(a) Distances (Å)

Ru(1)−Ru(2)	2.8393(5)	Ru(3)−Ge(1)	2.4792(7)
Ru(1)−Ru(3)	2.8234(7)	Ru(1)−C(1)	2.112(7)
Ru(2)−Ru(3)	2.8620(5))	Ru(2)−C(1)	2.003(5)
Ru(2)−Ge(1)	2.5166(6)	Ru(3)−C(1)	2.043(5)
Ru(2)−Ge(2)	2.4858(6)	C−O(av)	1.14(1)

(b) Angles (deg)

Ru(2)−Ru(1)−Ru(3)*	90.95(2)	Ru(2)*−Ge(2)−Ru(2)	70.49(2)
Ru(3)−Ru(2)−Ru(2)*	89.56(1)	Ru(3)*−C(33)−O(33)	137.68(16)
Ru(2)−Ru(3)−Ru(3)*	90.44(1)	Ru−C−O(av)	176(1)
Ru(2)−Ge(1)−Ru(3)	69.90(1)		

[a] Estimated standard deviations in the least significant figure are given in parentheses.



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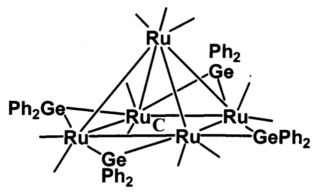

3

Compound **3** was obtained in 24% yield under the above reaction conditions; however, when **1** was allowed to react with Ph_3GeH in a 1:5 ratio at 150 °C, the yield of **3** is increased to 80% and no **2** was obtained. It appears that **2** is a precursor to **3,** and this was independently confirmed by the formation of **3** in 80% yield from **2** in reaction with Ph_3GeH at 150 °C. An ORTEP diagram of the molecular structure of **3** is shown in Figure 2. Selected bond distances and angles are listed in Table 4. Compound **3** consists of a square pyramidal cluster of five ruthenium atoms with four bridging $GePh_2$ groups, one on each edge of the base of the

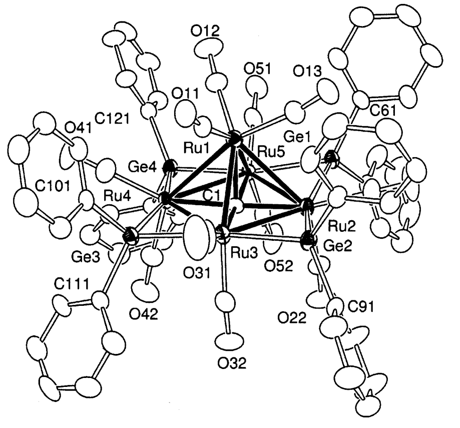

Figure 2. ORTEP diagram of the molecular structure of $Ru_5(CO)_{11}(\mu\text{-}GePh_2)_4(\mu_5\text{-}C)$, **3**, showing 30% probability thermal ellipsoids.

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(24) Sheldrick, G. M. *SHELXTL*, version 5.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

Table 4. Selected Intramolecular Distances and Angles for $Ru_5(CO)_{11}(\mu\text{-}GePh_2)_4(\mu_5\text{-}C)$, **3**[a]

(a) Distances (Å)

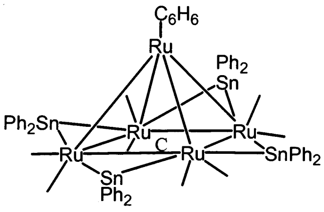
Ru(1)−Ru(2)	2.8398(10)	Ru(3)−Ge(3)	2.5062(11)
Ru(1)−Ru(3)	2.8190(11)	Ru(4)−Ge(3)	2.4839(11)
Ru(1)−Ru(4)	2.8870(10)	Ru(4)−Ge(4)	2.4874(11)
Ru(1)−Ru(5)	2.8299(10)	Ru(5)−Ge(1)	2.4732(11)
Ru(2)−Ru(3)	2.8682(10)	Ru(5)−Ge(4)	2.4957(11)
Ru(2)−Ru(5)	2.8550(10)	Ru(1)−C(1)	2.069(8)
Ru(3)−Ru(4)	2.8745(10)	Ru(2)−C(1)	2.024(8)
Ru(4)−Ru(5)	2.8972(9)	Ru(3)−C(1)	2.024(8)
Ru(2)−Ge(1)	2.5133(12)	Ru(4)−C(1)	2.046(8)
Ru(2)−Ge(2)	2.5083(12)	Ru(5)−C(1)	2.040(8)
Ru(3)−Ge(2)	2.4758(12)	C−O(av)	1.14(1)

(b) Angles (deg)

Ru(2)−Ru(1)−Ru(4)	90.53(3)	Ru(2)−Ge(1)−Ru(5)	69.85(3)
Ru(3)−Ru(1)−Ru(5)	91.86(3)	Ru(2)−Ge(2)−Ru(3)	70.26(3)
Ru(3)−Ru(2)−Ru(5)	90.33(3)	Ru(3)−Ge(3)−Ru(4)	70.34(3)
Ru(2)−Ru(3)−Ru(4)	90.21(3)	Ru(4)−Ge(4)−Ru(5)	71.10(3)
Ru(3)−Ru(4)−Ru(5)	89.37(3)	Ru−C−O(av)	175(1)
Ru(2)−Ru(5)−Ru(4)	90.02(3)		

[a] Estimated standard deviations in the least significant figure are given in parentheses.

square pyramid. Compound **3** is analogous to the compound $Ru_5(CO)_8(C_6H_6)(\mu\text{-}SnPh_2)_4(\mu_5\text{-}C)$ that we recently obtained from the reaction of $Ru_5(CO)_{15}(\mu_5\text{-}C)$ with Ph_3SnH.[21]



The Ru−Ge bond distances to the bridging $GePh_2$ groups in **3** are similar to those found in **2**, and all lie in the range 2.4732(11)−2.5133(12) Å.

The mechanism for the formation of compounds **2** and **3** is believed to be similar to that proposed for the high-nuclearity Ru−Sn clusters,[21] that is, oxidative addition of the Ge−H bond to the metal atoms of the cluster, followed by formation of $GePh_2$ groups by cleavage of a Ph group from intermediate $GePh_3$ ligands that then combines with a hydride ligand to eliminate as benzene. However, because of the limited number of hydrogen atoms (i.e. there is only one hydrogen/Ph_3GeH that can be used for benzene formation) only one benzene molecule is formed/germanium group. Thus, compounds **2** and **3** contain only $GePh_2$ ligands. An additional source of hydrogen is needed to form benzene by cleavage of additional phenyl groups. So we next investigated the reactions of **3** with hydrogen.

Reaction of **3** with H_2 (1 atm) at 150 °C for 30 min produced the compound $Ru_5(CO)_{10}(\mu\text{-}GePh_2)_4(\mu_5\text{-}C)(\mu\text{-}H)_2$, **4,** in 31% yield. Compound **4** was characterized by a combination of IR and ^{1}H NMR spectroscopy and single-crystal X-ray diffraction analysis. An ORTEP diagram of the molecular structure of **4** is shown in Figure 3. Selected bond distances and angles are listed in Table 5. Like **3**, compound **4** contains of a square pyramidal cluster of five ruthenium atoms with four bridging $GePh_2$ groups, one on each edge of the base of the square pyramid. The Ru−Ge distances to the bridging $GePh_2$ groups are similar to those in **3**, range 2.4704(10)−2.5172(9) Å. The compound contains two hydride ligands that bridge two oppositely positioned apical-basal edges of the Ru_5 square pyramid, Ru(1)−Ru(2) = 2.8411(8) Å and Ru(1)−Ru(4) = 2.8568(8) Å. These two hydride ligands (located and refined crystallographically) are equivalent and appear as one high-field resonance, $\delta = -23.11$ ppm, in the ^{1}H NMR spectrum of the compound. One CO ligand was eliminated from **3,** and two hydride ligands were added to the cluster to form **4**. Interestingly, when the above reaction with hydrogen was allowed to go for a longer period of time, the new compound $Ru_5(CO)_{10}(\mu\text{-}GePh_2)_2(\mu_3\text{-}GePh)_2(\mu_3\text{-}H)(\mu_4\text{-}CH)$, **5,** was obtained.

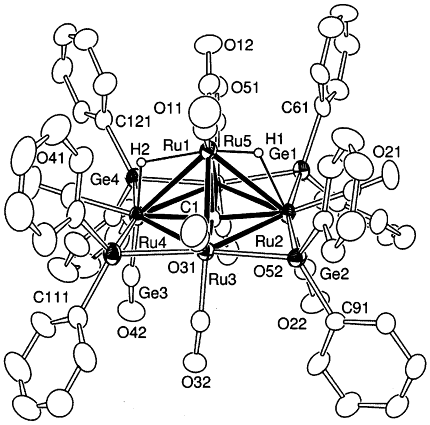


Figure 3. ORTEP diagram of the molecular structure of $Ru_5(CO)_{10}(\mu\text{-}GePh_2)_4(\mu_5\text{-}C)(\mu\text{-}H)_2$, **4**, showing 30% probability thermal ellipsoids.

Table 5. Selected Intramolecular Distances and Angles for $Ru_5(CO)_{10}(\mu\text{-}GePh_2)_4(\mu_5\text{-}C)(\mu\text{-}H)_2$, **4**[a]

(a) Distances (Å)

Ru(1)−Ru(2)	2.8411(8)	Ru(4)−Ge(4)	2.4986(1)
Ru(1)−Ru(3)	2.8229(8)	Ru(5)−Ge(1)	2.4806(9)
Ru(1)−Ru(4)	2.8568(8)	Ru(5)−Ge(4)	2.4822(9)
Ru(1)−Ru(5)	2.8257(8)	Ru(1)−C(1)	2.075(7)
Ru(2)−Ru(3)	2.9156(8)	Ru(2)−C(1)	2.083(7)
Ru(2)−Ru(5)	2.8854(7)	Ru(3)−C(1)	2.020(7)
Ru(3)−Ru(4)	2.8651(8)	Ru(4)−C(1)	2.093(7)
Ru(4)−Ru(5)	2.8811(8)	Ru(5)−C(1)	1.978(7)
Ru(2)−Ge(1)	2.5012(9)	Ru(1)−H(1)	1.37(8)
Ru(2)−Ge(2)	2.5172(9)	Ru(2)−H(1)	2.04(8)
Ru(3)−Ge(2)	2.4884(9)	Ru(1)−H(2)	1.86(6)
Ru(3)−Ge(3)	2.4981(10)	Ru(4)−H(2)	1.74(6)
Ru(4)−Ge(3)	2.4704(10)	C−O(av)	1.13(1)

(b) Angles (deg)

Ru(2)−Ru(1)−Ru(4)	94.00(2)	Ru(2)−Ge(1)−Ru(5)	70.79(3)
Ru(3)−Ru(1)−Ru(5)	90.02(2)	Ru(2)−Ge(2)−Ru(3)	71.25(3)
Ru(3)−Ru(2)−Ru(5)	87.04(2)	Ru(3)−Ge(3)−Ru(4)	70.43(3)
Ru(2)−Ru(3)−Ru(4)	92.25(2)	Ru(4)−Ge(4)−Ru(5)	70.68(3)
Ru(3)−Ru(4)−Ru(5)	88.08(2)	Ru− C−O(av)	177(1)
Ru(2)−Ru(5)−Ru(4)	92.55(2)		

[a] Estimated standard deviations in the least significant figure are given in parentheses.

The reaction of **3** with H_2 (1 atm) at 150 °C for 90 min provided the new compound $Ru_5(CO)_{10}(\mu\text{-}GePh_2)_2(\mu_3\text{-}GePh)_2(\mu_3\text{-}H)(\mu_4\text{-}CH)$, **5,** in 34% yield. Compound **5** was characterized by a combination of IR, ^{1}H NMR, and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of **5** is shown in Figure 4. Selected bond distances and angles are listed in Table 6. Compound **5** consists of a square pyramidal cluster of five ruthenium

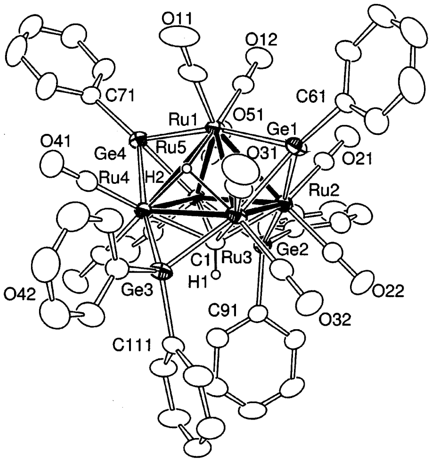


Figure 4. ORTEP diagram of the molecular structure of $Ru_5(CO)_{10}$-(μ-$GePh_2$)$_2$(μ-GePh)$_2$(μ_3-H)(μ_4-CH), **5**, showing 30% thermal ellipsoid probability.

atoms with two bridging $GePh_2$ groups occupying opposite two edges of the base of the square pyramid. Unlike the structures of compounds **2**−**4**, the two bridging $GePh_2$ groups (Ge2 and Ge3) in **5** are displaced below the Ru_4 square plane by 1.4507(6) and 1.3108(6) Å, respectively. The Ru−Ge bond distances to the bridging $GePh_2$ groups are slightly shorter, range 2.4517(7)−2.4903(8) Å, than those found in **2**−**4**. Interestingly, compound **5** contains two triply bridging GePh groups (Ge1 and Ge2) that occupy the Ru1−Ru2−Ru3 and Ru1−Ru4−Ru5 triangles on opposite sides of the square pyramid; see Figure 4. There is also one triply bridging hydride ligand (located and refined structurally) occupying the Ru1−Ru3−Ru4 triangle and a quadruply bridging methylidyne ligand (μ_4-CH) across the base of the Ru_5 square pyramid. The hydrogen atom of the CH group was also located and refined structurally. The Ru−C(1) distances to the methylidyne ligand range from 2.182(3) to 2.205(3) Å. The ^{1}H NMR spectrum of **5** exhibits a high-field resonance, $\delta = -21.88$ ppm, as a doublet, $^3J_{H-H} = 1.52$ Hz. A low-field signal at δ 11.21 ppm is attributed to the μ_4-CH[25] group, with proton−proton coupling to the hydride ligand, $^3J_{H-H} = 1.52$ Hz.

The formation of the μ_3-GePh groups must have involved the cleavage of one of the phenyl groups from each of two $GePh_2$ ligands followed by combination with a hydride ligand to eliminate benzene. Further reaction of hydrogen then yielded the triply bridging hydride ligand and the methylidyne group by hydrogen addition to the carbido carbon atom. The two triply bridging GePh groups donate three electrons to the cluster, the hydride ligand donates one electron, and the methylidyne group donates three electrons, and the total electron count of the cluster is 74, as expected for a square pyramidal pentanuclear cluster.

Table 6. Selected Intramolecular Distances and Angles for $Ru_5(CO)_{10}$(μ-$GePh_2$)$_2$(μ-GePh)$_2$(μ_3-H)(μ_4-CH), **5**[a]

(a) Distances (Å)

Ru(1)−Ru(2)	2.8538(7)	Ru(1)−Ge(4)	2.4456(7)
Ru(1)−Ru(3)	2.9128(10)	Ru(4)−Ge(4)	2.4778(9)
Ru(1)−Ru(4)	2.9431(7)	Ru(5)−Ge(4)	2.4111(7)
Ru(1)−Ru(5)	2.8505(9)	Ru(5)−Ge(2)	2.4517(7)
Ru(2)−Ru(3)	2.7972(7)	Ru(2)−C(1)	2.182(3)
Ru(2)−Ru(5)	2.7329(7)	Ru(3)−C(1)	2.205(3)
Ru(3)−Ru(4)	2.7939(7)	Ru(4)−C(1)	2.183(3)
Ru(4)−Ru(5)	2.8007(7)	Ru(5)−C(1)	2.201(3)
Ru(1)−Ge(1)	2.4501(7)	Ru(1)−H(2)	1.87(3)
Ru(2)−Ge(1)	2.4360(9)	Ru(3)−H(2)	1.82(3)
Ru(3)−Ge(1)	2.4629(6)	Ru(4)−H(2)	1.88(3)
Ru(2)−Ge(2)	2.4877(9)	C(1)−H(1)	0.89(2)
Ru(3)−Ge(3)	2.4802(8)	C−O(av)	1.13(1)
Ru(4)−Ge(3)	2.4903(8)		

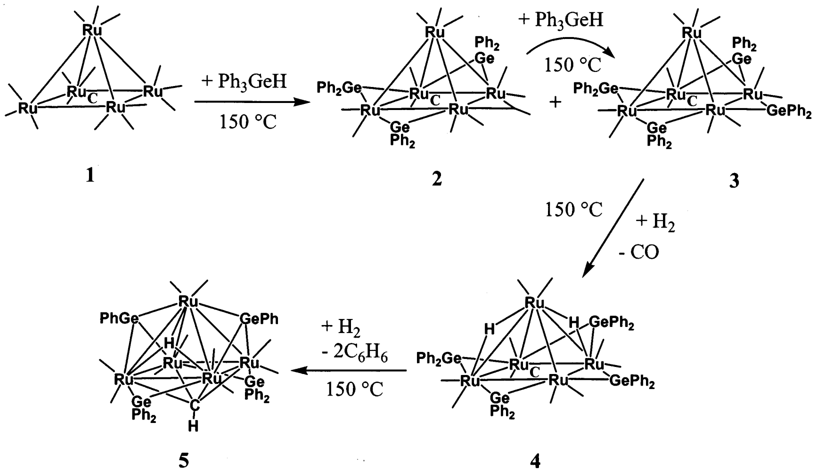
(b) Angles (deg)

Ru(2)−Ru(1)−Ru(4)	85.22(3)	Ru(2)−Ge(1)−Ru(3)	69.64(1)
Ru(3)−Ru(1)−Ru(5)	86.27(1)	Ru(2)−Ge(2)−Ru(5)	67.18(1)
Ru(3)−Ru(2)−Ru(5)	90.89(3)	Ru(3)−Ge(3)−Ru(4)	68.40(1)
Ru(2)−Ru(3)−Ru(4)	89.18(3)	Ru(1)−Ge(4)−Ru(4)	73.42(1)
Ru(3)−Ru(4)−Ru(5)	89.56(3)	Ru(1)−Ge(4)−Ru(5)	71.87(3)
Ru(2)−Ru(5)−Ru(4)	90.35(2)	Ru(4)−Ge(4)−Ru(5)	69.89(2)
Ru(1)−Ge(1)−Ru(2)	71.47(2)	Ru−C−O(av)	178(1)
Ru(1)−Ge(1)−Ru(3)	72.72(3)		

[a] Estimated standard deviations in the least significant figure are given in parentheses.

To our knowledge there are no previous reports of pentanuclear metal cluster complexes containing a μ_4-CH ligand. However, there are examples of methylidyne groups in the tetranuclear clusters: HFe_4(η^2-CH)$(CO)_{12}$;[26] {HC[Au-(PPh_3)]$_4$}$^+$;[27] Ru_2Pt_2(μ-H)(μ_4-CH)(μ-CO)$(CO)_2$(PPr^i3)$_2$(η-C_5H_5)$_2$.[25] The μ_4-CH ligand in Ru_2Pt_2(μ-H)(μ_4-CH)(μ-CO)-$(CO)_2$(PPr^i3)$_2$(η-C_5H_5)$_2$[25] is structurally the same as the one in **5**.

Scheme 1



A summary of the results of this study are shown in Scheme 1. The pentaruthenium carbonyl complex **1** reacts with Ph_3GeH to yield the two pentaruthenium carbonyl complexes **2** and **3** which contain three and four bridging diphenylgermyl groups, respectively, by cleavage of one phenyl group from each germanium grouping which is eliminated, presumably as benzene. Compound **2** is a precursor to **3**. Complex **3** reacts with hydrogen by loss of CO to yield the hydride containing complexes **4** and **5**. Compound **5** can be obtained directly from **4** by further treatment with hydrogen which leads to cleavage of phenyl groups from two of the four diphenylgermyl ligands to yield the two triply bridging GePh ligands. Interestingly, in this transformation a hydrogen atom was added to the carbido carbon atom of **4** to yield a quadruply bridging methylidyne ligand. Studies of the reactions of these hydride complexes with selected unsaturated organic compounds are in progress.

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Supporting Information Available: X-ray crystallographic data in CIF format for compounds **2**−**5** and details of their solution and refinement. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) Davies, D. L.; Jeffrey, J. C.; Miguel, D.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1987**, 254.

(26) Beno, M. A.; Williams, J. M.; Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 1485.

(27) Schmidbaur, H.; Gabbaï, F. P.; Schier, A.; Riede, J. *Organometallics* **1995**, *14*, 4969.