Organometallics **1996,** *15,* 1589−1596

Osmium−Germanium Clusters. Structures of $[(OC)_4Os(GeMe_2)]_2$, $Os_2(GeMe_2)_3(CO)_6$, $Os_3(GeMe_2)_2(CO)_{11}$, $[(OC)_3Os(GeMe_2)]_3$, and $Os_4(GeMe_2)_4(CO)_{12}$

Weng Kee Leong, Frederick W. B. Einstein, and Roland K. Pomeroy*

Department of Chemistry, Simon Fraser University, Burnaby,
British Columbia, Canada V5A 1S6

Received August 30, 1995[⊗]

The complex $[(OC)_4Os(GeMe_2)]_2$ (**1**) has been prepared from $Na_2[Os(CO)_4]$ and Me_2GeCl_2 in THF. Photolysis of **1** in hexane affords the known $[(OC)_3Os(GeMe_2)]_3$ (**4**) as the major product, along with the new clusters $Os_3(GeMe_2)_2(CO)_{11}$ (**3**) and $Os_4(GeMe_2)_4(CO)_{12}$ (**5**). Pyrolysis of **1**, in hexane at 100 °C, gives the same compounds except that $Os_2(GeMe_2)_3(CO)_6$ (**2**) was also isolated, albeit in low yield. The structures of **1**−**5** have been determined; the configurations of **1**, **2**, and **4** are analogous to those previously found for group 8−group 14 congeners. The skeleton of **3** consists of two Os_2Ge triangles that share a common osmium atom, that is, a "bow-tie" arrangement; the Os−Os lengths in **3** are crystallographically equivalent at 2.981(1) Å, and the Os−Ge lengths are 2.520(1) and 2.522(1) Å. The framework of **5** consists of a central triangulated (raftlike) Os_3Ge_3 unit (similar to that in **4**) to one Os atom of which is bound an $(OC)_4Os(GeMe_2)$ fragment so as to give an Os_2Ge triangle that lies in the plane of the other metal atoms. The Os−Os bond length associated with this triangle is long (3.069(1) Å). The other Os−Os lengths in **4** range from 2.860(1) to 2.967(1) Å; the Os−Ge lengths are in the range 2.475(2)−2.584(2) Å. The ^1H NMR spectrum of **5** in toluene-d_8 is consistent with rotation of the $(OC)_4Os(GeMe_2)$ unit with respect to the rest of the molecule at temperatures above 60 °C.

Introduction

Numerous group 8−group 14 derivatives have been reported with a wide variety of structural motifs as established by X-ray crystallography.[1,2] Although there have been several Os−Ge compounds described in the literature,[3,4] the structure of only one of these compounds, namely $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$, has been determined.[5]

In a recent study we have described the UV photolysis of $[(OC)_4Os(SnMe_2)]_2$ to yield the sparingly soluble $Os_4(SnMe_2)_4(CO)_{14}$.[6] The structure of the product revealed a central Os_2Sn_2 rhomboid linked to two outer Os_2Sn triangles via the osmium atoms, a skeleton previously unknown for the group 8−group 14 class of complexes.

Herein, we report the structural characterization of the products isolated from the corresponding photolysis of $[(OC)_4Os(GeMe_2)]_2$ (**1**). Two products formed in low yields, $Os_3(GeMe_2)_2(CO)_{11}$ and $Os_4(GeMe_2)_4(CO)_{12}$, have structural types that similarly have not been previously observed in this class of compounds. Also described are the structures of the major product from the photolysis reaction, the previously known $[(OC)_3Os(GeMe_2)]_3$, and $Os_2(GeMe_2)_3(CO)_6$, isolated as a minor product from the pyrolysis of **1**.

Experimental Section

Standard Schlenk techniques were employed in the syntheses. Solvents were rigorously dried and stored under nitrogen before use. The precursor compounds $Os_3(CO)_{12}$ and Me_2GeCl_2 were obtained from commercial sources. The anion $[Os(CO)_4]^{2-}$ as the sodium salt was prepared as described previously.[7] An external, medium-pressure mercury discharge lamp (200 W, Hanovia Model 654 A36) contained in a water-cooled quartz jacket was employed in the UV irradiation experiment; there was ∼5 cm between the UV source and the edge of the reaction vessel. Infrared spectra were obtained with a Perkin-Elmer 983 spectrometer. NMR spectra were recorded on a Bruker SY-100 or WM400 spectrometer. Electron-impact (70 eV) mass spectra were recorded on a Hewlett-Packard 5985 GC−MS instrument. Microanalyses were performed by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

Preparation of $[(OC)_4Os(GeMe_2)]_2$ (1). To $Na_2[Os(CO)_4]$ (prepared from 250 mg (0.276 mmol) of $Os_3(CO)_{12}$) in THF (40.0 mL) at −40 °C was added Me_2GeCl_2 (150 mg, 0.867 mmol) in hexane. The reaction mixture was stirred under a partial vacuum in darkness and warmed to room temperature overnight to give a lemon yellow suspension. Solvent and volatiles were removed on the vacuum line and the cream-colored residue extracted with hexane (3 × 15 and 4 × 10 mL); the extracts were filtered through a short column of silica, combined, and concentrated. Storage of the solution at −25 °C afforded yellow, crystalline $[(OC)_4GeMe_2]_2$ (**1**; 156 mg,45%): IR (hexane) ν(CO) 2077 (m), 2019.5 (vs), 2007 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.247; MS (EI) m/z 782 ($[M - CO]^+$).

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1996.

(1) (a) Bonny, A. *Coord. Chem. Rev.* **1978**, *25*, 229. (b) Compton, N. A.; Errington, R. J.; Norman, N. C. *Adv. Organomet. Chem.* **1990**, *31*, 91.

(2) Holt, M. S.; Wilson, W. L.; Nelson, J. H. *Chem. Rev.* **1989**, *89*, 11.

(3) (a) Ash, M. J.; Brookes, A.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 458. (b) Burgess, K.; Guerin, C.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1985**, *295*, C3. (c) Lu, C.-Y.; Einstein, F. W. B.; Johnston, V. J.; Pomeroy, R. K. *Inorg. Chem.* **1989**, *28*, 4212.

(4) Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 2874.

(5) Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 854.

(6) Leong, W. K.; Einstein, F. W. B.; Pomeroy, R. K. *Organometallics* **1996**, *15*, 1582.

(7) (a) George, R. D.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 972. (b) Collman, J. P.; Murphy, D. W.; Fleischer, E. B.; Swift, D. *Inorg. Chem.* **1974**, *13*, 1.

0276-7333/96/2315-1589$12.00/0

Table 1. Summary of Crystal Data and Details of Intensity Collection for $[(OC)_4Os(GeMe_2)]_2$ (1), $Os_2(GeMe_2)_3(CO)_6$ (2), and $Os_3(GeMe_2)_2(CO)_{11}$ (3)

	1	2	3
formula	$C_{12}H_{12}Ge_2O_8Os_2$	$C_{12}H_{18}Ge_3O_6Os_2$	$C_{15}H_{12}Ge_2O_{11}Os_3$
fw	809.80	856.44	1084.03
cryst syst	monoclinic	hexagonal	monoclinic
space group	$P2_1/n$	$P6_3/m$	$C2/c$
a, Å	9.0673(6)	9.8931(19)	19.5964(15)
b, Å	11.8070(9)		9.3322(10)
c, Å	9.5914(9)	12.1864(14)	13.2785(8)
β, deg	97.182(7)		90.949(6)
V, Å^3	1018.78(14)	1032.9	2428.0(4)
2θ range of unit cell, deg	30.0−40.2	37.8−43.8	30.0−40.0
Z	2	2	4
D_{calc}, g cm^{-3}	2.640	2.754	2.966
μ(Mo Kα), cm^{-1}	153.62	165.52	181.26
cryst size, mm	0.18 × 0.21 × 0.30	0.19 × 0.20 × 0.25	0.07 × 0.12 × 0.15
transmissn coeff	0.0488−0.1204	0.1003−0.1339	0.1599−0.2973
scan range (2θ), deg	3.6−45.0	4.0−50.0	2.0−50.0
scan width (ω), deg	$0.70 + 0.35 \tan\theta$	$1.40 + 0.70 \tan\theta$	$0.75 + 0.35 \tan\theta$
scan rate (ω), deg min^{-1}	0.573−3.296	0.35	0.614−3.296
no. of unique rflns	1323	648	2121
no. of obs rflns[a]	1148	605 (590)[b]	1778
no. of params	90	44	144
R[c]	0.031	0.025	0.020
R_w[d]	0.041	0.033	0.025
instrument instability factor (k)	0.00005	0.0001	0.00007
extinction	0.230(17)		0.269(12)
largest shift/esd in final ls cycle	0.01	<0.01	<0.01
largest positive/negative residual electron density in final diff map, e Å^{-3}	1.52(16)/−0.94(16)	0.77(16)/−0.72(16)	0.53(14)/−0.69(14)
GOF[e]	2.9	2.4	1.4
F(000)	728	772	1928

[a] $I_o > 2.5\sigma(I_o)$. [b] See Experimental Section. [c] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1/(\sigma^2(F_o) + k|F_o|^2)$. [e] GOF $= [\sum w(|F_o| - |F_c|)^2/(\text{degrees of freedom})]$.

Anal. Calcd for $C_{12}H_{12}Ge_2O_8Os_3$: C, 17.80; H, 1.49. Found: C, 17.93; H, 1.44.

Preparation of $Os_3(GeMe_2)_2(CO)_{11}$ (3), $[(OC)_3Os(GeMe_2)]_3$ (4), and $Os_4(GeMe_2)_4(CO)_{14}$ (5). A solution of **1** (147 mg, 0.182 mmol) in hexane (40.0 mL) contained in a quartz Carius tube fitted with a Teflon valve was cooled to −196 °C; the vessel was evacuated and the solution degassed with three freeze−pump−thaw cycles. The solution was subjected to UV photolysis for 16.5 h, during which time the solution changed from pale yellow to orange. The solution was transferred via a cannula to a Schlenk flask and evaporated to dryness on the vacuum line. The residue was dissolved in a minimum amount of hexane and chromatographed on silica. Elution with hexane gave three bands. The first yellow band was collected; the solution was concentrated and stored at 0 °C to yield a mixture of $Os_3(GeMe_2)_2(CO)_{11}$ (**3**; 2 mg) and $[(OC)_3Os(GeMe_2)]_3$ (**4**; 11 mg) as pale yellow and orange crystals, respectively, which were separated by hand. The second orange band was rechromatographed on silica to give a major orange band, which yielded $Os_4(GeMe_2)_4(CO)_{14}$ (**5**; 6 mg). The constituent of the third band that provided only trace amounts of solids was not identified. Compound **3**: IR (hexane) ν(CO) 2112.5 (w), 2088.5 (m), 2028 (s), 2014 (w), 2002 (mw), 1997 (mw), 1985 (w) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.125. Anal. Calcd for $C_{15}H_{12}Ge_2O_{11}Os_3$: C, 16.62; H, 1.12. Found: C, 16.62; H, 1.03. Compound **4**: IR (hexane) ν(CO) 2052 (m), 2014 (s), 1984.5 (m) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.178; $^{13}C\{^1H\}$ NMR (C_7H_8) δ 186.3 (2C), 181.2 (1C), 17.6 (CH_3). Anal. Calcd for $C_{15}H_{30}Ge_3O_9Os_3$: C, 15.93; H, 1.60. Found: C, 16.19, H, 1.58. Compound **5**: IR (hexane) ν(CO) 2107.5 (w), 2078 (mw), 2046 (m), 2036 (s), 2016.5 (m), 2002 (s), 1983.5 (mw), 1972 (m) cm^{-1}; ^{1}H NMR (C_7D_8) δ 1.843, 1.257, 1.238, 1.160; $^{13}C\{^1H\}$ NMR (C_7D_8) δ 191.4 (1C), 187.4 (1C), 185.0 (2C), 184.9 (2C), 182.7 (2C), 180.3 (1C), 178.8 (1C), 170.4 (2C), 26.1 (CH_3), 17.8 (CH_3), 16.5 (CH_3), 9.5 (CH_3). Anal. Calcd for $C_{20}H_{24}Ge_4O_{12}Os_4$: C, 15.93; H, 1.60. Found: C, 16.16; H, 1.62.

Pyrolysis of 1. A Carius tube with **1** (163 mg, 0.201 mmol) and hexane (10 mL) was cooled to −196 °C and evacuated; the solution was degassed with three freeze−pump−thaw cycles. The vessel and contents were heated at 100 °C under exclusion of light for 4 days to give a red solution. The solution was cooled to room temperature, transferred to a Schlenk flask, and stored at −25 °C to afford orange-yellow crystals of **4** (113 mg, 50%) and bright yellow crystals of $Os_2(GeMe_2)_3(CO)_6$ (**2**; <1 mg) that were separated by hand: IR (hexane) ν(CO) 2024.5 (s), 1986.5 (m) cm^{-1} (insufficient material for elemental analysis). The supernatant solution was concentrated and chromatographed on silica (30 × 1.5 cm) with hexane as the eluant. The first light yellow band afforded further **4** (5 mg), the second yellow band provided **3** (7 mg after recrystallization), and the third red band gave **5** (6 mg).

X-ray Analysis of 1−5. Crystals suitable for X-ray crystallography were obtained by recrystallization from toluene (**1**) or hexane (**2**−**5**). In each case a crystal was mounted, in air, on an Enraf-Nonius diffractometer and intensity data were collected with the use of graphite-monochromated Mo Kα radiation. The final unit cell was determined from 25 well-centered high-angle reflections that were widely scattered in reciprocal space. Two intensity standards were measured at intervals of 60 min of X-ray exposure time. Absorption corrections were made with either a Gaussian numerical integration (checked against φ-scan measurements) (for **1**, **3**, and **4**) or the empirical method of North *et al.*[8] (for **2** and **5**). Data reduction included corrections for intensity scale variation and for Lorentz and polarization effects.

The positions of the Os atoms were determined by direct methods or from Patterson maps. Subsequent electron density difference syntheses revealed the remaining non-hydrogen atoms. Hydrogen atoms were generally not located and were placed in calculated positions (C−H distance 0.96 Å) and given isotropic temperature factors 10% larger than the thermal parameter of the carbon atom to which they were attached. The coordinates of carbon atoms with attached hydrogen atoms

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(8) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *24*, 351.

Table 2. Summary of Crystal Data and Details of Intensity Collection for $[(OC)_3Os(GeMe_2)]_3$ (4) and $Os_4(GeMe_2)_4(CO)_{12}$ (5)

	4	5
formula	$C_{15}H_{18}Ge_3O_9Os_3$	$C_{20}H_{24}Ge_4O_{12}Os_4$
fw	1130.67	1507.56
cryst syst	hexagonal	monoclinic
space group	$P6_3/m$	$P2_1/c$
a, Å	10.937(4)	10.9761(14)
b, Å		16.317(9)
c, Å	12.213(2)	19.377(5)
β, deg		91.473(15)
V, Å^3	1265.0(4)	3469(1)
2θ range of unit cell, deg	30.0−40.0	30.0−38.0
Z	2	4
D_{calc}, g cm^{-3}	2.968	2.886
μ(Mo Kα), cm^{-1}	185.36	180.26
cryst size, mm	0.10 × 0.12 × 0.12	0.12 × 0.19 × 0.19
transmissn coeff	0.2372−0.3064	0.0494−0.1630
scan range (2θ), deg	3.0−45.0	3.6−45.0
scan width (ω), deg	$0.60 + 0.35 \tan \theta$	$0.90 + 0.35 \tan \theta$
scan rate (ω), deg min^{-1}	0.491−2.747	0.405−3.296
no. of unique rflns	584	4491
no. of obs rflns[a]	483	3441
no. of params	54	175
R[b]	0.018	0.064
R_w[a]	0.021	0.074
instrument instability factor (k)	0.00006	
extinction	0.091(9)	
largest shift/esd in final ls cycle	0.00	0.05
largest positive/negative residual electron density in final diff map, e Å^{-3}	0.52(14)/−0.44(14)	2.5(5)/−4.0(5)
GOF[d]	1.3	1.1
$F(000)$	1008	2687

[a] $I_o > 2.5\sigma(I_o)$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum||F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1/(\sigma^2(F_o) + k|F_o|^2)$. [d] GOF $= [\sum w(|F_o| - |F_c|)^2/(\text{degrees of freedom})]^{1/2}$.

were linked so that the derived coordinates included contributions from derivatives from the appropriate atom sites. Unit weights were employed initially, but at the final stage of each refinement a weighting scheme based on counting statistics was adopted (except for **5**), for which $\langle w(|F_o| - |F_c|)^2\rangle$ was near constant as a function of both $|F_o|$ and $(\sin \theta)/\lambda$. Comments on individual structure determinations follow this section. Complex scattering factors for neutral atoms[9] were employed in the calculation of structure factors. The programs used for data reduction, structure solution, and initial refinement were from the NRCVAX[10] crystal structure system. The program suite CRYSTALS[11] was employed in the final refinement. All computations were carried out on an Intel 486DX2-based microcomputer running at a clock speed of 66 MHz. Crystallographic data are summarized in Tables 1 and 2. Final fractional coordinates for the non-hydrogen atoms of **1**−**5** are given in Tables 3, 5, 7, 9, and 11, respectively, and bond length and angle data are in Tables 4, 6, 8, 10, and 12, respectively.

Table 3. Fractional Atomic Coordinates and Isotropic or Equivalent Isotropic Temperature Factors (Å^2) for $[(OC)_4Os(GeMe_2)]_2$ (1)

atom	x/a	y/b	z/c	U(iso)	occ
Os(1)	0.58347(5)	0.04066(3)	0.20264(4)	0.0514	0.953(2)
Ge(1)	0.6624(1)	−0.02798(9)	−0.0334(1)	0.0510	0.953(2)
O(11)	0.608(1)	0.2780(7)	0.0761(9)	0.0883	1.0000
O(12)	0.908(1)	0.0376(8)	0.353(2)	0.1034	1.0000
O(13)	0.531(1)	−0.2133(6)	0.2463(9)	0.0828	1.0000
O(14)	0.402(1)	0.1178(9)	0.430(1)	0.1155	1.0000
C(11)	0.596(1)	0.194(1)	0.126(1)	0.071(3)	1.0000
C(12)	0.794(2)	0.038(1)	0.300(2)	0.090(4)	1.0000
C(13)	0.548(1)	−0.120(1)	0.230(1)	0.063(3)	1.0000
C(14)	0.468(2)	0.090(1)	0.343(2)	0.093(4)	1.0000
C(1)	0.799(2)	0.076(1)	−0.111(2)	0.105(5)	1.0000
C(2)	0.763(1)	−0.1755(9)	−0.016(1)	0.076(3)	1.0000
Os(10)	0.368(1)	−0.0018(8)	0.162(1)	0.058(4)	0.047(2)
Ge(10)	0.613(3)	0.081(2)	0.087(3)	0.061(7)	0.047(2)

Table 4. Bond Lengths (Å) and Selected Bond Angles (deg) for $[(OC)_4Os(GeMe_2)]_2$ (1)

Bond Lengths			
Os(1)−Ge(1)	2.588(1)	Ge(1)−C(1)	1.96(1)
Os(1)−Ge(1′)	2.593(1)	Ge(1)−C(2)	1.96(1)
Os(1)−C(11)	1.96(1)	Os(1)−C(12)	2.02(2)
Os(1)−C(13)	1.94(1)	C−O	1.09(2)−1.13(2)
Os(1)−C(14)	1.90(2)		
Bond Angles			
Ge(1)−Os(1)−Ge(1′)	75.20(4)	Ge(1′)−Os(1)−C(12)	168.1(4)
C(11)−Os(1)−C(13)	165.3(5)	C(12)−Os(1)−C(14)	104.4(6)
Os(1)−Ge(1)−Os(1′)	104.80(4)	Os(1)−Ge(1)−C(1)	113.1(4)
Os(1)−Ge(1′)−C(1′)	109.5(4)	Os(1)−Ge(1)−C(2)	112.3(3)
Os(1)−Ge(1′)−C(2′)	110.9(3)	C(1)−Ge(1)−C(2)	106.3(5)

Table 5. Fractional Atomic Coordinates and Isotropic or Equivalent Isotropic Temperature Factors (Å^2) for $Os_2(GeMe_2)_3(CO)_6$ (2)

atom	x/a	y/b	z/c	U(iso)
Os(1)	0.3333	0.6667	0.12921(4)	0.0334
Ge(1)	0.1092(1)	0.6343(1)	0.2500	0.0370
O(11)	0.2934(8)	0.9169(9)	0.0086(6)	0.0706
C(11)	0.306(1)	0.825(1)	0.0537(6)	0.0521
C(1)	0.046(2)	0.793(2)	0.2500	0.0544
C(2)	−0.087(1)	0.437(2)	0.2500	0.0565

Table 6. Bond Lengths (Å) and Selected Bond Angles (deg) for $Os_2(GeMe_2)_3(CO)_6$ (2)

Bond Lengths			
Os(1)−Os(1′)	2.944(1)	Ge(1)−C(1)	1.96(1)
Os(1)−Ge(1)	2.545(1)	Ge(1)−C(2)	1.95(1)
Os(1)−C(11)	1.943(8)	C(11)−O(11)	1.13(1)
Bond Angles			
Ge(1)−Os(1)−Ge(1′)	89.89(3)	Os(1)−Ge(1)−Os(1′)	70.68(4)
Ge(1)−Os(1)−C(11)	85.1(3)	Os(1)−Ge(1)−C(1)	120.4(3)
Ge(1)−Os(1)−C(11′)	85.2(3)	Os(1)−Ge(1)−C(2)	119.6(4)
Ge(1)−Os(1)−C(11″)	172.9(2)	C(1)−Ge(1)−C(2)	104.3(7)
C(11)−Os(1)−C(11′)	99.4(3)	Os(1)−C(11)−O(11)	178.5(9)

Compound 1. Two intensity standards were monitored over the period of data collection; one showed a steady decrease over time (long-term instability of ca. 1%), while the other showed a rapid *increase* with time (long-term instability of 8%). Closer inspection of the latter intensity standard revealed that the increase in intensity was a function of X-ray exposure time. The crystal was thus photolyzed under UV light for about 22 h, and a complete set of data were re-collected with the same parameters but with an additional intensity standard. This second data set showed a steady decrease in intensities for all three intensity standards (long-term instabilities of 3.2%, 3.0%, and 1.8%, respectively). Analysis of peak profiles suggested that the reflections were sharper in the second data set; the peak widths for five reflections that were examined were in the 0.2−0.3° range, as opposed to 0.5−0.6° in the initial set. The refined models for each of the two data sets, however, did not show any significant differences. The results reported here are from the second data set. The final model had the Os, Ge, and O atoms anisotropic. During the refinement extra peaks were found that were attributed to a disordered molecule such that the Ge and Os atom positions were systematically interchanged, with the plane of the disordered molecule tilted with respect to the main molecule.

Compound 2. A yellow, hexagonal needle was cut to about 0.3 mm in length. The two intensity standards showed random fluctuations corresponding to a ±2% variation in scale.

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[9] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, p 99 (present distributor Kluwer Academic: Dordrecht, The Netherlands).

[10] Gabe, E. J.; LePage, Y.; Charland, J.-P.; Lee, F. L. NRCVAX-An Interactive Program System for Structural Analysis. *J. Appl. Crystallogr.* **1989**, *22*, 384.

[11] Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS*; Chemical Crystallography Laboratory, University of Oxford: Oxford, England, 1985.

Table 7. Fractional Atomic Coordinates and Isotropic or Equivalent Isotropic Temperature Factors (Å^2)for $Os_3(GeMe_2)_2(CO)_{11}$ (3)

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(iso)
Os(1)	0.14286(1)	0.11717(3)	0.67859(2)	0.0393
Os(2)	0.0000	0.14402(3)	0.7500	0.0323
Ge(1)	0.08126(3)	0.34745(7)	0.71741(4)	0.0385
O(11)	0.1938(3)	0.1144(7)	0.8994(4)	0.0733
O(12)	0.1636(4)	−0.2095(6)	0.6557(5)	0.0855
O(13)	0.0896(3)	0.1535(6)	0.4604(4)	0.0616
O(14)	0.2731(3)	0.2636(8)	0.6173(4)	0.0807
O(21)	0.0506(3)	0.1764(6)	0.9688(3)	0.0556
O(22)	0.0000	−0.1866(8)	0.7500	0.0635
C(1)	0.1184(4)	0.4640(8)	0.8274(5)	0.0625
C(2)	0.0662(4)	0.4790(8)	0.6052(5)	0.0614
C(11)	0.1734(3)	0.1136(7)	0.8181(6)	0.0490
C(12)	0.1545(4)	−0.0904(8)	0.6640(6)	0.0593
C(13)	0.1084(3)	0.1390(7)	0.5411(6)	0.0467
C(14)	0.2240(4)	0.2053(9)	0.6405(5)	0.0560
C(21)	0.0316(3)	0.1619(7)	0.8880(5)	0.0416
C(22)	0.0000	−0.064(1)	0.7500	0.0462

Table 8. Bond Lengths (Å) and Selected Bond Angles (deg) for $Os_3(GeMe_2)_2(CO)_{11}$ (3)

Bond Lengths			
Os(1)−Os(2)	2.981(1)	Os(1)−C(14)	1.868(8)
Os(1)−Ge(1)	2.522(1)	Os(2)−C(21)	1.931(7)
Os(2)−Ge(1)	2.520(1)	Os(2)−C(22)	1.95(1)
Os(1)−C(11)	1.938(7)	Ge(1)−C(1)	1.952(6)
Os(1)−C(12)	1.960(8)	Ge(1)−C(2)	1.950(7)
Os(1)−C(13)	1.946(8)	C−O	1.132(9)−1.152(8)
Bond Angles			
Os(1)−Os(2)−Ge(1)	82.23(1)	Os(2)−Os(1)−Ge(1)	53.72(2)
Os(1)−Ge(1)−Os(2)	72.49(2)	Os(1)−Ge(1)−C(1)	117.0(2)
Ge(1)−Os(2)−Ge(1′)	82.23(3)	Os(1)−Ge(1)−C(2)	116.6(2)
C(11)−Os(1)−C(13)	174.4(3)	Os(2)−Ge(1)−C(1)	121.3(2)
C(12)−Os(1)−C(14)	107.9(3)	Os(2)−Ge(1)−C(2)	121.2(2)
C(21)−Os(2)−C(21′)	170.1(4)	C(1)−Ge(1)−C(2)	105.7(3)
C(21)−Os(2)−C(22)	95.0(2)		

Table 9. Fractional Atomic Coordinates and Isotropic or Equivalent Isotropic Temperature Factors (Å^2) for $[(OC)_3Os(GeMe_2)]_3$ (4)

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(iso)
Os(1)	0.15990(4)	0.54522(4)	0.2500	0.0340
Ge(1)	0.1240(1)	0.7550(1)	0.2500	0.0397
O(11)	0.1518(5)	0.5361(5)	−0.0026(5)	0.0605
O(12)	−0.1519(8)	0.3223(9)	0.2500	0.0821
C(1)	0.0407(8)	0.7930(8)	0.1215(7)	0.0568
C(11)	0.1584(6)	0.5426(6)	0.0914(8)	0.0408
C(12)	−0.035(1)	0.405(1)	0.2500	0.0629

Table 10. Selected Bond Lengths (Å) and Selected Bond Angles (deg) for $(OC)_3Os(GeMe_2)]_3$ (4)

Bond Lengths			
Os(1)−Os(1′)	2.920(1)	Os(1)−C(12)	1.90(1)
Os(1)−Ge(1)	2.514(1)	Ge(1)−C(1)	1.960(7)
Os(1)−Ge(1′)	2.525(1)	C(11)−O(11)	1.15(1)
Os(1)−C(11)	1.937(9)	C(12)−O(12)	1.14(1)
Bond Angles			
Ge(1)−Os(1)−Os(1′)	54.76(3)	C(11)−Os(1)−C(12)	89.5(2)
Ge(1′)−Os(1)−Os(1′)	54.41(3)	Os(1)−Ge(1)−Os(1′)	70.82(4)
Ge(1)−Os(1)−Ge(1′)	169.18(3)	Os(1)−Ge(1)−C(1)	119.6(2)
Ge(1)−Os(1)−C(12)	96.4(3)	Os(1′)−Ge(1)−C(1)	118.8(2)
C(11)−Os(1)−C(11′)	178.5(3)	C(1)−Ge(1)−C(1′)	106.4(5)

A 21% twinning was found and successfully modeled, with a 2-fold rotation about the ($x + y$) direction as the twin operator. An error analysis at this stage, with Os, Ge, and O atoms anisotropic, suggested the presence of extinction, but our present version of the software did not permit us to refine extinction on twinned structures. Removal of the 15 strongest reflections (based on observed F_o's) led to a dramatic improvement in R from ca. 5% to 2.5%. All non-hydrogen atoms were anisotropic in the final model.

Table 11. Fractional Atomic Coordinates and Isotropic or Equivalent Isotropic Temperature Factors for $Os_4(GeMe_2)_4(CO)_{12}$ (5)

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(iso)
Os(1)	1.00789(7)	−0.01798(5)	0.22674(4)	0.0483
Os(2)	0.76712(6)	0.07603(4)	0.23861(3)	0.0363
Os(3)	0.53655(6)	0.16708(5)	0.25818(4)	0.0403
Os(4)	0.66329(6)	0.10278(5)	0.37708(4)	0.0415
Ge(1)	0.8801(2)	0.0514(2)	0.1313(1)	0.0527
Ge(2)	0.6269(2)	0.1356(1)	0.1455(1)	0.0476
Ge(3)	0.4729(2)	0.1855(2)	0.3818(1)	0.0516
Ge(4)	0.8607(2)	0.0227(1)	0.3529(1)	0.0417
O(11)	1.136(2)	0.144(1)	0.2565(9)	0.082(2)
O(13)	0.855(2)	−0.172(1)	0.1956(9)	0.082(2)
O(21)	0.902(2)	0.240(1)	0.2483(9)	0.082(2)
O(23)	0.620(2)	−0.082(1)	0.2195(9)	0.082(2)
O(31)	0.667(2)	0.333(1)	0.2717(9)	0.082(2)
O(33)	0.371(2)	0.017(1)	0.2480(9)	0.082(2)
O(41)	0.815(2)	0.255(1)	0.4020(9)	0.082(2)
O(43)	0.521(2)	−0.059(1)	0.3700(9)	0.082(2)
O(12)	1.149(2)	−0.102(1)	0.344(1)	0.093(3)
O(14)	1.184(2)	−0.054(1)	0.110(1)	0.093(3)
O(32)	0.332(2)	0.257(1)	0.185(1)	0.093(3)
O(42)	0.705(2)	0.063(1)	0.528(1)	0.093(3)
C(11)	1.090(2)	0.083(1)	0.243(1)	0.058(2)
C(13)	0.912(2)	−0.113(1)	0.207(1)	0.058(2)
C(21)	0.853(2)	0.175(1)	0.246(1)	0.058(2)
C(23)	0.675(2)	−0.023(1)	0.227(1)	0.058(2)
C(31)	0.623(2)	0.270(1)	0.268(1)	0.058(2)
C(33)	0.442(2)	0.072(1)	0.253(1)	0.058(2)
C(41)	0.756(2)	0.199(1)	0.391(1)	0.058(2)
C(43)	0.571(2)	0.006(1)	0.370(1)	0.058(2)
C(12)	1.093(2)	−0.064(1)	0.303(1)	0.064(3)
C(14)	1.114(2)	−0.040(1)	0.155(1)	0.064(3)
C(32)	0.412(2)	0.224(1)	0.216(1)	0.064(3)
C(42)	0.690(2)	0.082(1)	0.470(1)	0.064(3)
C(1)	0.961(2)	0.142(2)	0.083(1)	0.074(2)
C(2)	0.817(2)	−0.025(2)	0.060(1)	0.074(2)
C(3)	0.676(2)	0.230(2)	0.088(1)	0.074(2)
C(4)	0.530(2)	0.063(2)	0.084(1)	0.074(2)
C(5)	0.467(2)	0.293(2)	0.421(1)	0.074(2)
C(6)	0.322(2)	0.144(2)	0.418(1)	0.074(2)
C(7)	0.992(2)	0.074(2)	0.408(1)	0.074(2)
C(8)	0.844(2)	−0.090(2)	0.390(1)	0.074(2)

Compound 3. The two intensity standards showed random variations in scale of ±3%. All non-hydrogen atoms were anisotropic in the final model.

Compound 4. The intensity standards showed random variations in the range ±1%. All non-hydrogen atoms were anisotropic in the final model.

Compound 5. The two intensity standards showed random variations in scale of ±2%. The Os and Ge atoms were given anisotropic thermal parameters in the final model, while a common isotropic temperature factor was given to all the axial O atoms and another to the equatorial O atoms; the carbonyl C atoms were treated likewise. All the methyl C atoms were also given a common isotropic temperature factor. A "robust-resistant" weighting scheme was used in the final refinement: $w = w'[1 - (\Delta/6\Delta_{est})^2]^2$, where Δ_{est} is estimated from a least-squares minimization of the coefficients a_i of a Chebyshev series for w given by $w = 1/[a_0t_0'(x) + a_1t_1'(x) + ... + a_{n-1}t_{n-1}'(x)]$ ($x = F_c/F_c^{max}$). In this structure, $n = 3$ was used.

Results and Discussion

$[(OC)_4Os(GeMe_2)]_2$ (1). Complex **1** was prepared by the reaction of $[Os(CO)_4]^{2-}$ with Me_2GeCl_2 (eq 1), methodology previously well established for the preparation of osmium−group 14 derivatives.[7] Given the

$$[Os(CO)_4]^{2-} + Me_2GeCl_2 \xrightarrow[40\%]{THF} [(OC)_4Os(GeMe_2)]_2 \quad (1)$$

1

Table 12. Selected Bond Lengths (Å) and Selected Bond Angles (deg) for $Os_4(GeMe_2)_4(CO)_{12}$ (5)

	Bond Lengths		
Os(1)−Os(2)	3.069(1)	Os(2)−Os(4)	2.974(1)
Os(2)−Os(3)	2.967(1)	Os(3)−Os(4)	2.860(1)
Os(1)−Ge(1)	2.557(2)	Os(3)−Ge(2)	2.475(2)
Os(2)−Ge(1)	2.481(2)	Os(3)−Ge(3)	2.531(2)
Os(2)−Ge(2)	2.535(2)	Os(4)−Ge(3)	2.492(2)
Os(2)−Ge(4)	2.569(2)	Os(4)−Ge(4)	2.584(2)
Os(1)−C(11)	1.90(2)	Os(1)−C(12)	1.89(2)
Os(1)−C(13)	1.91(2)	Os(1)−C(14)	1.87(2)
Os(2)−C(21)	1.88(2)	Os(2)−C(23)	1.91(2)
Os(3)−C(31)	1.93(2)	Os(4)−C(41)	1.88(2)
Os(3)−C(33)	1.88(2)	Os(4)−C(43)	1.88(2)
Os(3)−C(32)	1.82(2)	Os(4)−C(42)	1.84(2)
Ge(1)−C(1)	1.97(2)	Ge(3)−C(5)	1.92(2)
Ge(1)−C(2)	1.97(2)	Ge(3)−C(6)	1.93(2)
Ge(2)−C(3)	1.97(2)	Ge(4)−C(7)	1.96(2)
Ge(2)−C(4)	1.96(2)	Ge(4)−C(8)	1.98(2)
C−O	1.14(3)−1.20(3)		
	Bond Angles		
Os(2)−Os(1)−Ge(1)	51.35(5)	Ge(1)−Os(1)−C(14)	83.4(7)
Os(2)−Os(1)−C(12)	123.4(7)	C(12)−Os(1)−C(14)	101.7(10)
Ge(1)−Os(1)−C(12)	174.7(7)	C(11)−Os(1)−C(13)	174.2(9)
Os(2)−Os(1)−C(14)	134.7(7)	Os(4)−Os(2)−Ge(2)	110.25(6)
Os(1)−Os(2)−Os(3)	176.95(3)	Ge(1)−Os(2)−Ge(2)	76.87(8)
Os(1)−Os(2)−Os(4)	119.45(3)	Os(1)−Os(2)−Ge(4)	64.48(5)
Os(3)−Os(2)−Os(4)	57.55(3)	Os(3)−Os(2)−Ge(4)	112.52(5)
Os(1)−Os(2)−Ge(1)	53.59(6)	Os(4)−Os(2)−Ge(4)	54.98(5)
Os(3)−Os(2)−Ge(1)	129.38(6)	Ge(1)−Os(2)−Ge(4)	118.04(7)
Os(4)−Os(2)−Ge(1)	172.41(6)	Ge(2)−Os(2)−Ge(4)	164.90(7)
Os(1)−Os(2)−Ge(2)	130.27(6)	C(21)−Os(2)−C(23)	176.8(9)
Os(3)−Os(2)−Ge(2)	52.75(5)	Ge(2)−Os(3)−Ge(3)	170.55(7)
Os(2)−Os(3)−Os(4)	61.35(3)	Os(2)−Os(3)−C(32)	145.9(7)
Os(2)−Os(3)−Ge(2)	54.62(5)	Os(4)−Os(3)−C(32)	152.8(7)
Os(4)−Os(3)−Ge(2)	115.90(6)	Ge(2)−Os(3)−C(32)	91.3(7)
Os(2)−Os(3)−Ge(3)	115.96(6)	Ge(3)−Os(3)−C(32)	98.1(7)
Os(4)−Os(3)−Ge(3)	54.65(5)	C(31)−Os(3)−C(33)	174.9(9)
Os(2)−Os(4)−Os(3)	61.11(3)	Os(2)−Os(4)−C(42)	142.8(7)
Os(2)−Os(4)−Ge(3)	117.01(6)	Os(3)−Os(4)−C(42)	156.1(7)
Os(3)−Os(4)−Ge(3)	55.95(6)	Ge(3)−Os(4)−C(42)	100.2(7)
Os(2)−Os(4)−Ge(4)	54.51(5)	Ge(4)−Os(4)−C(42)	88.3(7)
Os(3)−Os(4)−Ge(4)	115.61(5)	C(41)−Os(4)−C(43)	176.2(9)
Ge(3)−Os(4)−Ge(4)	171.47(7)	Os(2)−Ge(2)−Os(3)	72.63(6)
Os(1)−Ge(1)−Os(2)	75.05(7)	Os(2)−Ge(2)−C(3)	122.0(7)
Os(1)−Ge(1)−C(1)	115.5(7)	Os(3)−Ge(2)−C(3)	117.1(8)
Os(2)−Ge(1)−C(1)	121.4(7)	Os(2)−Ge(2)−C(4)	120.5(8)
Os(1)−Ge(1)−C(2)	113.8(8)	Os(3)−Ge(2)−C(4)	115.8(8)
Os(2)−Ge(1)−C(2)	121.1(8)	C(3) −Ge(2)−C(4)	106.0(10)
C(1) −Ge(1)−C(2)	106.8(11)	Os(2)−Ge(4)−Os(4)	70.51(6)
Os(3)−Ge(3)−Os(4)	69.40(6)	Os(2)−Ge(4)−C(7)	126.7(8)
Os(3)−Ge(3)−C(5)	120.0(8)	Os(4)−Ge(4)−C(7)	107.1(8)
Os(4)−Ge(3)−C(5)	123.2(8)	Os(2)−Ge(4)−C(8)	126.0(7)
Os(3)−Ge(3)−C(6)	123.8(7)	Os(4)−Ge(4)−C(8)	108.4(8)
Os(4)−Ge(3)−C(6)	123.1(8)	C(7) −Ge(4)−C(8)	105.8(11)
C(5) −Ge(3)−C(6)	98.2(11)		

paucity of structural data on Os−Ge compounds mentioned in the Introduction, the structure of **1** was determined by X-ray crystallography. The structure is somewhat disordered, but nevertheless it shows (Figure 1) a crystallographically imposed, planar Os_2Ge_2 unit, similar to that found for $[(OC)_4M(SnMe_2)]_2$ (M = Fe,[12] Os[6]). As with the last two complexes, there is a significant leaning of the axial carbonyls toward the group 14 ligands (in **1** the C(11)−Os(1)−C(13) angle is 165.3(5)°). A possible reason for this has been discussed.[6]

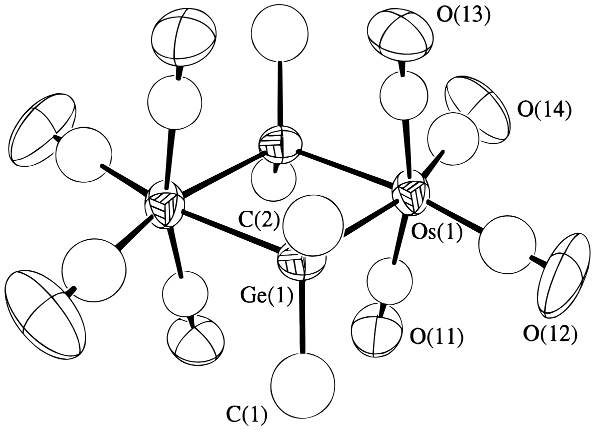

Figure 1. Molecular structure of $[(OC)_4Os(GeMe_2)]_2$ (**1**).

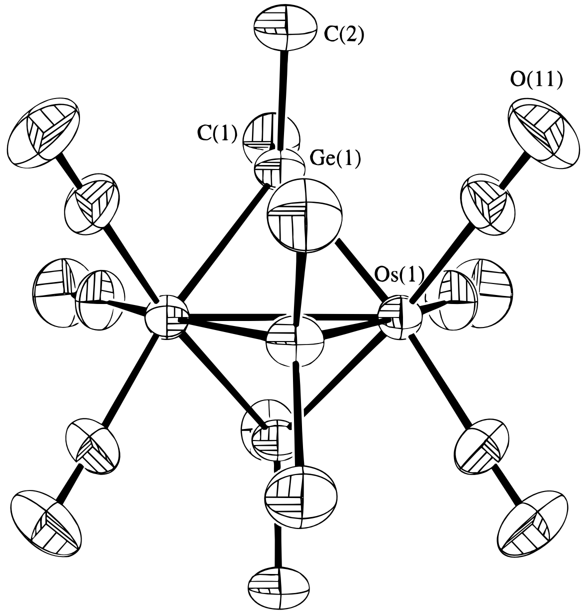

Figure 2. Molecular structure of $Os_2(GeMe_2)_3(CO)_6$ (**2**).

The Os−Ge lengths in **1** are 2.588(1) and 2.593(1) Å. As mentioned in the Introduction, apparently the only Os−Ge bond lengths reported in the literature are those for the three independent molecules in the unit cell of $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$.[5] The Os−Ge lengths in the latter compound are considerably shorter (range 2.418(3)−2.430(3) Å) than those in **1**. Although part of the difference in the lengths can be attributed to the different σ-donor, π-acceptor properties of a bridging $GeMe_2$ ligand versus a terminal $GeCl_3$ ligand, we have found that Os−Sn bonds of $Os_2(SnMe_2)_2$ units are significantly longer than other similar Os−Sn bonds such as those associated with $Os_2(SnMe_2)$ groupings.[6] This point is discussed further for the structures described below.

$Os_2(GeMe_2)_3(CO)_6$ (2). Pyrolysis of **1** in hexane, in an evacuated sealed tube, at 100 °C gave $[(OC)_3Os(GeMe_2)]_3$, described in the next section, plus a small amount of $Os_2(GeMe_2)_3(CO)_6$ (**2**) (eq 2). Pyrolysis of the

$$\mathbf{1} \xrightarrow{100\ °C} \underset{\mathbf{4}}{[(OC)_3Os(GeMe_2)]_3} + \underset{\mathbf{2}}{Os_2(GeMe_2)_3(CO)_6} \qquad (2)$$

tin analogue of **1**, $[(OC)_4Os(SnMe_2)]_2$, similarly yields $[(OC)_3Os(SnMe_2)]_3$, but the reaction was sluggish at 130 °C and was conveniently carried out at 170 °C.[6] In other words, **1** with its Os−Ge bonds is thermally less stable than the analogue with Os−Sn bonds.

Compound **2** was first prepared by Knox and Stone in 1970 by the pyrolysis of $Os(CO)_4(GeMe_3)_2$, but its

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(12) Gilmore, C. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1972**, 1387.

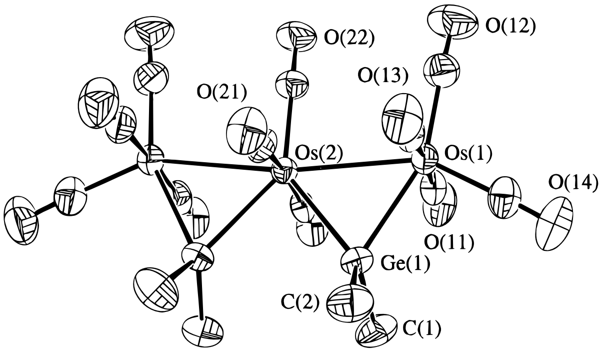

Figure 3. Molecular structure of $Os_3(GeMe_2)_2(CO)_{11}$ (**3**).

structure was not determined at that time.[4] The structure of **2** as determined here is shown in Figure 2. The configuration found is analogous to that of the iron analogue, $Fe_2(GeMe_2)_3(CO)_6$, reported by Graham and co-workers.[13] As has been mentioned previously, the structure resembles that of $Fe_2(CO)_9$, in which the bridging carbonyls have been replaced with bridging $GeMe_2$ ligands; $Os_2(CO)_9$ is, however, believed to have only one bridging carbonyl.[14] It is also interesting that the Si or Sn analogues of **2** (or of $Fe_2(GeMe_2)_3(CO)_6$) are apparently unknown.

The Os−Os distance in **2** of 2.944(1) Å is indicative of a bond and is required for **2** to satisfy the 18-electron rule. The Os−Ge distances in **2** are 2.545(1) Å (the molecule has crystallographic D_{3h} symmetry). This length is over 0.04 Å shorter than the corresponding lengths in **1**.

$Os_3(GeMe_2)_2(CO)_{11}$ (3). The UV photolysis of **1** in hexane produces a number of compounds (eq 3). Of

$$\mathbf{1} \xrightarrow{h\nu} \mathbf{4} + \underset{\mathbf{3}}{Os_3(GeMe_2)_2(CO)_{11}} + \underset{\mathbf{5}}{Os_4(GeMe_2)_4(CO)_{12}} \qquad (3)$$

these, $Os_3(GeMe_2)_2(CO)_{11}$ (**3**) was isolated in low yield as air-stable yellow crystals. The structure of **3** reveals (Figure 3) a metal skeleton not previously observed in group 8−group 14 compounds, namely, two Os_2Ge triangles sharing a common Os atom. This structural arrangement is observed in the homonuclear osmium clusters $Os_5(CO)_{18}(L)$ (L = CO,[15] PMe_3,[16] $CNBu^t$ [17]), where it is referred to as a bowtie arrangement. Since $GeMe_2$ is isolobal with $Os(CO)_4$, **3** is an isolobal analogue of $Os_5(CO)_{19}$. Cluster **3** has a crystallographic C_2 axis through the central Os atom and its axial carbonyl ligands. The two metal triangles are twisted somewhat with respect to each other: the dihedral angle between the two triangles is 5.6°. This twisting is not nearly as pronounced as in $Os_5(CO)_{19}$, where the corresponding angle is 21.2°.[15] The Os−Os bond length in **3** at 2.981(1) Å is long. Osmium−osmium bond lengths in open low-nuclearity osmium clusters are usually compared to 2.877(3) Å, the average Os−Os distance in $Os_3(CO)_{12}$.[18] In $Os_5(CO)_{19}$ the Os−Os lengths are in the range 2.848(2)−2.950(2) Å.[15] The Os−Ge lengths in **3** are 2.520(1) and 2.522(1) Å, significantly shorter than the corresponding lengths in **1**.

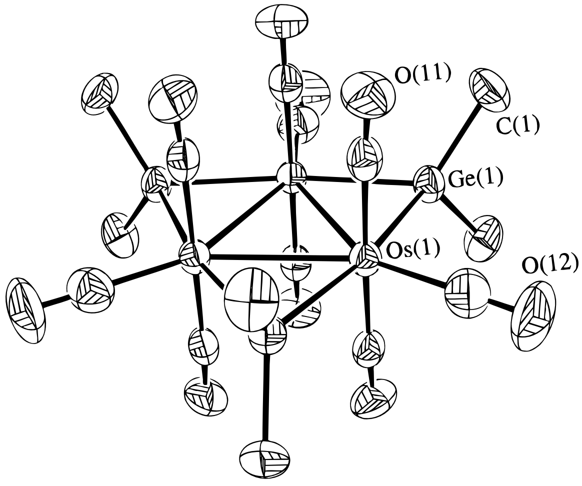

Figure 4. Molecular structure of $[(OC)_3Os(GeMe_2)]_3$ (**4**).

$[(OC)_3Os(GeMe_2)]_3$ (4). This cluster was isolated, as air-stable orange crystals, as the major product from either the pyrolysis (eq 2) or UV photolysis (eq 3) of **1**. Cluster **4** was first isolated as the major product from the pyrolysis of $Os(CO)_4(GeMe_3)_2$, mentioned earlier.[4] It is probable that **4** is thermodynamically the most stable OsGe cluster prepared in this study.

An X-ray investigation of **4** reveals it is isostructural with the Ru and Sn analogues $[(OC)_3Ru(GeMe_2)]_3$[19] and $[(OC)_3Os(SnMe_2)]_3$,[6] respectively. The central cores of these molecules are constrained by their crystallographic site symmetry ($\bar{6}$) to be planar. The transition-metal atoms have approximate pentagonal-bipyramidal coordination. In **4**, the Os−Os bond length is 2.920(1) Å, in the normal range for such lengths in open, low-nuclearity clusters of osmium. This distance is, however, significantly shorter than the corresponding length in $[(OC)_3Os(SnMe_2)]_3$ (2.974(1) Å),[6] no doubt reflecting the different steric requirements of the bridging group 14 ligands. (In $[(OC)_3Ru(GeMe_2)]_3$ the Ru−Ru length is 2.926(9) Å.[19]).

The Os−Ge lengths in **4** are 2.514(1) and 2.525(1) Å, while in the Ru analogue the Ru−Ge lengths are 2.482(11) and 2.500(12) Å.[19] The Os−Ge bond lengths in **4** are considerably shorter than the lengths in **1** (2.588(1), 2.593(1) Å); that is, the Os−Ge distances of triangular Os_2Ge units are shorter than those of rhomboidal Os_2Ge_2 groupings. We have observed a similar difference in the Os−Sn lengths of Os_2Sn and Os_2Sn_2 polygons.[6] This is somewhat unexpected since the OsGeOs angle in the Os_2Ge_2 unit of **1** (104.80(4)°) is much closer to the tetrahedral value than the corresponding angle of the Os_2Ge unit in **4** (70.82(4)°). It is interesting to speculate that the shorter Os−Ge bond lengths in **4** compared to the Os−Ge lengths in **1**, and the increased stability of **4** over **1**, is due to the presence of centrally located three-center, two-electron bonds in the Os_2Ge triangles of **4** that are not present in **1**. Such bonding is, of course, the basis of the polyhedral skeletal

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[13] Brooks, E. H.; Elder, M.; Graham, W. A. G.; Hall, D. *J. Am. Chem. Soc.* **1968**, *90*, 3587.

[14] Moss, J. R.; Graham, W. A. G. *J. Chem. Soc., Dalton Trans.* **1977**, 95.

[15] Farrar, D. H.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Rosales, M. J. *J. Chem. Soc., Dalton Trans.* **1982**, 2051.

[16] Wang, W.; Batchelor, R. J.; Einstein, F. W. B.; Lu, C.-Y.; Pomeroy, R. K. *Organometallics* **1993**, *12*, 3598.

[17] Wang, W.; Einstein, F. W. B.; Pomeroy, R. K. *Organometallics* **1994**, *13*, 1114.

[18] Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

[19] (a) Howard, J.; Woodward, P. *J. Chem. Soc. A* **1971**, 3648. (b) Howard, J.; Knox, S. A. R.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1970**, 1477.

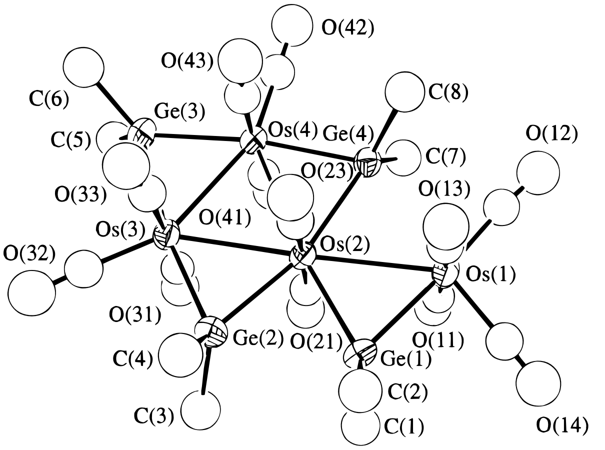


Figure 5. Molecular structure of $Os_4(GeMe_2)_4(CO)_{12}$ (**5**).

electron pair theory.[20] In other words, the Ge atoms are part of the cluster framework in **4**, whereas the Ge atoms in **1** are best considered as constituents of simple bridging ligands.

$Os_4(GeMe_3)_2(CO)_{12}$ (5). This cluster was obtained, in low to moderate yield, as air-stable, orange-red crystals from the photolysis of **1** in hexane (eq 3). It was also obtained from the pyrolysis of **1** in the same solvent at 100 °C. The structure of **5** (Figure 5) shows a triangulated planar Os_3Ge_3 core, similar to that in **4**, attached to which through a common Os atom is an Os_2-Ge triangle. The metal skeleton in **5** is essentially planar: the dihedral angle between the Os(2)Os(3)Os(4) and Os(1)Os(2)Ge(1) planes is 3.3°, and the displacement of any metal atom from the best plane of the central Os_3Ge_3 unit is 0.06 Å. Two of the Os atoms of the Os_3Ge_3 grouping have pentagonal-bipyramidal coordination as in **4**; however, the unique osmium atom in this grouping has the extremely rare hexagonal-bipyramidal geometry.[21] The Os(1)Ge(1)Ge(2)Os(3)Os(4)Ge(4) hexagon is close to planar with displacements of the atoms from the best-fit plane in the range 0.022–0.096 Å; the C(21)Os(2)C(23) angle is 176.8(9)°.

The Os–Os bond lengths of the Os_3Ge_3 unit are in the range 2.860(1)–2.974(1) Å; the Os–Ge lengths of this unit span 2.475(2)–2.584(2) Å. The external Os–Os bond is exceptionally long at 3.069(1) Å, whereas the corresponding Os–Ge bonds of the external Os_2Ge triangle, at 2.481(2) and 2.556(2) Å, are not of exceptional length.

Compound **5** may be regarded as derived from **4** by replacement of an equatorial carbonyl ligand with the germylene derivative $(OC)_4Os{=}GeMe_2$. Since this moiety is isolobal with C_2H_4, it might be expected to rotate about the osmium atom to which it is bound.[22] The ^1H NMR spectrum of **5** in toluene-d_8 at 21 °C showed four resonances (Figure 6) of equal intensity at δ 1.16, 1.24, 1.26, and 1.84. Such a spectrum is in agreement with the rigid solid-state structure for **5** persisting in solution. When the sample is warmed to 95 °C, however, the resonances at δ 1.16 and 1.84 broadened considerably (Figure 6), indicative of exchange. In the ambient-temperature 2D NOESY spectrum of **5** in the same solvent, the resonance at δ 1.16 showed a cross-peak with that at δ 1.26. There were no other cross-peaks except for weak peaks of opposite phase between the resonances at δ 1.16 and 1.84 due to exchange of the methyl groups. These NMR results are, indeed, consistent with the view that the $(OC)_4OsGeMe_2$ grouping rotates with respect to the rest of the molecule (Chart 1). (It also allows the unambiguous assignments of the methyl resonances as depicted in Chart 1 and Figure 6.) It is tempting to assume that the rotation of the $(OC)_4OsGeMe_2$ unit about the osmium atom occurs in much the same way as that of a coordinated alkene, but given the exceptionally long Os–Os bond associated with this unit, it cannot be ruled out that the rotation occurs via a transition state in which partial or complete breaking of this Os–Os bond takes place.

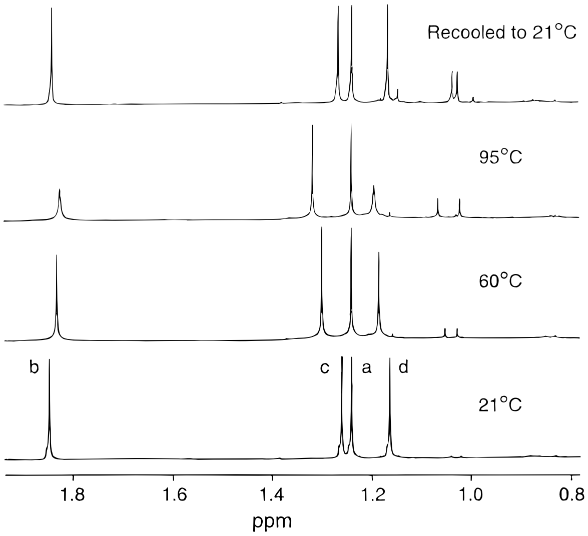
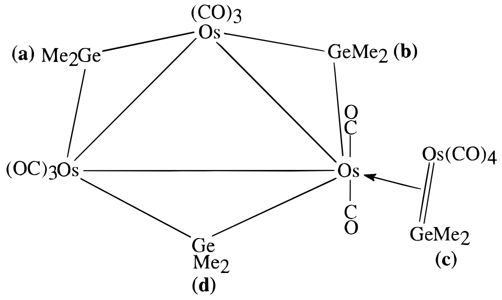


Figure 6. Variable-temperature ^1H NMR (400 MHz operating frequency) spectra of **5** in toluene-d_8. For the assignment see Chart 1. The identity of the species giving rise to the new resonances to high field of δ 1.1 has not been identified as yet.

Chart 1



Conclusions. Treatment of **5** in hexane with carbon monoxide (1 atm) at 100 °C does not produce **4**, from which it is concluded that the pyrolysis of **1** to yield **4** probably does not involve the intermediacy of **5**. A mechanism that accounts for the various products formed by photolysis of **1** is shown in Scheme 1. An intermediate similar to **1i** was proposed to account for the formation of $Os_4(SnMe_3)_2(CO)_{14}$ **(6)** from the photolysis of $[(OC)_4Os(SnMe_2)]_2$.[6] (A complex analogous to **6** was not observed in the photolysis or pyrolysis of **1**).

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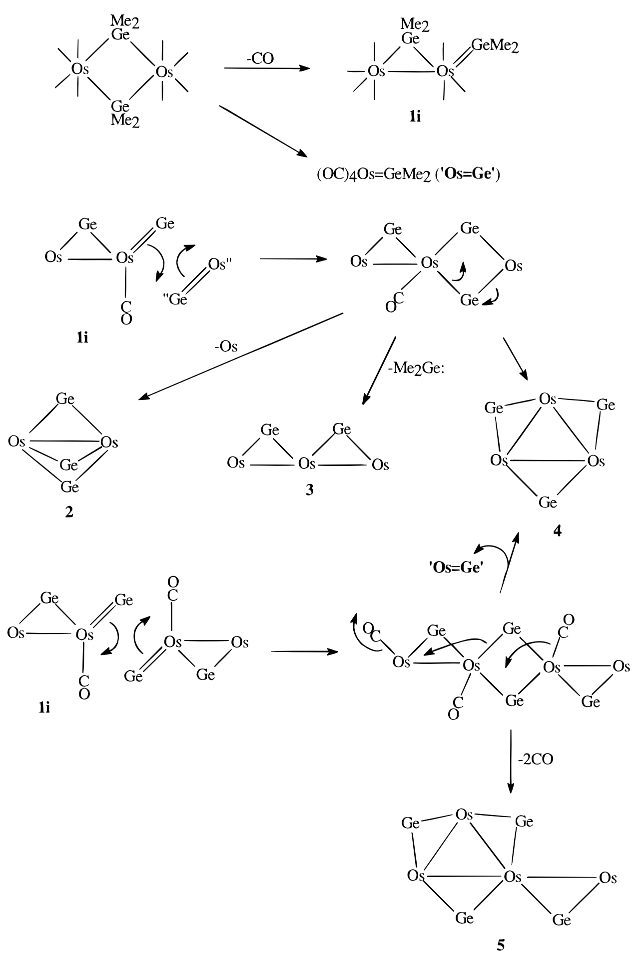
[20] (a) Wade, K. *Adv. Inorg. Radiochem.* **1976**, *18*, 1. (b) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311. (c) Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice Hall: Engelwood Cliffs, NJ, 1990.

[21] Kepert, D. L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, England, 1987; Vol. 1, p 83.

[22] (a) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711. (b) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.

Scheme 1



Given that $GeMe_2$ is isolobal with $Os(CO)_4$, it is not surprising that some of the clusters described here have analogues among the binary carbonyls of osmium; thus, the analogues of **1**, **3**, and **4** are $Os_4(CO)_{16}$,[23] $Os_5(CO)_{19}$,[15] and $Os_6(CO)_{21}$,[24] respectively. There is no binary carbonyl of osmium analogous to **5**. The binary carbonyl of Os closest in structure to **2** is $Os_5(CO)_{16}$,[25] but in the latter cluster there are bonds between the metal atoms in the equatorial plane of the trigonal-bipyramidal nucleus that are not present between the Ge atoms of **2**. An essential point is that osmium forms numerous condensed carbonyl clusters because of its ability to readily form $Os(CO)_4$ and $Os(CO)_3$ units which can exhibit different geometries and bonding modes. On the other hand, the $GeMe_2$ fragment is only isolobal with that $Os(CO)_4$ fragment that is based on octahedral coordination. For this reason, the Os−Ge clusters described here, and the Os−Sn clusters described earlier, have for the most part open, planar arrangements of metal atoms.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support. We also thank Professor D. Kepert (University of Western Australia) for useful discussion.

Supporting Information Available: Tables of hydrogen atom coordinates and anisotropic temperature factors for **1**−**5** (10 pages). Ordering information is given on any current masthead page.

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(23) Einstein, F. W. B.; Johnston, V. J.; Pomeroy, R. K. *Organometallics* **1990**, *9*, 2754.

(24) Goudsmit, R. J.; Jeffrey, J. G.; Johnson, B. F. G.; Lewis, J.; McQueen, R. C. S.; Sanders, A. J.; Liu, J.-C. *J. Chem. Soc., Chem. Commun.* **1986**, 24.

(25) Eady, C. R.; Johnson, B. F. G.; Lewis, J.; Reichert, B. E.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1976**, 271.