# Osmium−Germanium and Osmium−Germanium−Gold Carbonyl Cluster Complexes: Syntheses, Structures, Bonding, and Reactivity

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Ⓢ *Supporting Information*

ABSTRACT: Reactions of $Os_3(CO)_{10}(NCMe)_2$ with $HGePh_3$ have yielded the compounds $Os_3(CO)_{10}(NCMe)(GePh_3)(\mu\text{-H})$ (**1**) and $Os_3(CO)_{10}(GePh_3)_2(\mu\text{-H})_2$ (**2**) by the sequential replacement of the NCMe ligands and the oxidative addition of the GeH bonds of one and two $HGePh_3$ molecules, respectively, to the osmium atoms of the cluster. Compound **2** exists as two isomers in solution at low temperatures which interconvert rapidly on the ^1H NMR time scale at room temperature. When it was heated, **1** was transformed into the pentaosmium complex $Os_5(CO)_{17}(\mu\text{-GePh}_2)$ (**3**), which exhibits a planar raft structure with one bridging $GePh_2$ ligand. Compound **1** reacts with the compound $PhAu(PPh_3)$ to yield the compound $Os_3(CO)_8(\mu\text{-CO})(\mu\text{-O}=CPh)(\mu\text{-GePh}_2)(\mu\text{-AuPPh}_3)$ (**4**), which contains a bridging $O=CPh$ ligand and a $Au(PPh_3)$ group that bridges an Os−Ge bond. A minor product, $Os(CO)_4(GePh_3)(AuPPh_3)$ (**5**), was also obtained in this reaction. Compound **4** was also obtained from the reaction of **1** with $CH_3Au(PPh_3)$. Compound **4** reacted with PhC_2Ph to yield the complex $Os_3(CO)_7(\mu\text{-GePh}_2)(\mu\text{-AuPPh}_3)[\mu\text{-(O)CPhCPhCPh}]$ (**6**), which contains a novel bridging oxametallacycle formed by the coupling of PhC_2Ph to the bridging $O=CPh$ ligand in **4** and is another example of a $Au(PPh_3)$ group that bridges an Os−Ge bond. The bonding of the bridging $Au(PPh_3)$ group to the Os−Ge bonds in **4** and **6** was investigated by DFT computational analyses.
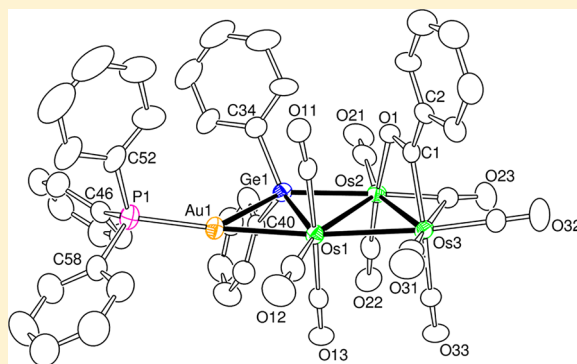
INTRODUCTION

Germanium[1] and tin[2] are well-known to be valuable modifiers for heterogeneous transition-metal catalysts. It has been shown that transition metal−tin complexes can serve as precursors to excellent bi- and multimetallic supported heterogeneous catalysts.[3]

The reactions of $Ir_3(CO)_9(\mu\text{-Bi})$ with $HGePh_3$ and $HSnPh_3$ have yielded the tris-EPh_3 (E = Ge, Sn) triiridium trihydrido carbonyl complexes $Ir_3(CO)_6(\mu\text{-Bi})(EPh_3)_3(\mu\text{-H})_3$, which were converted to the tris-germylene-bridged and tris-stannylene-bridged triiridiium complexes $Ir_3(CO)_6(\mu\text{-Bi})(\mu\text{-EPh}_2)_3$, upon mild heating (eq 1).[4]
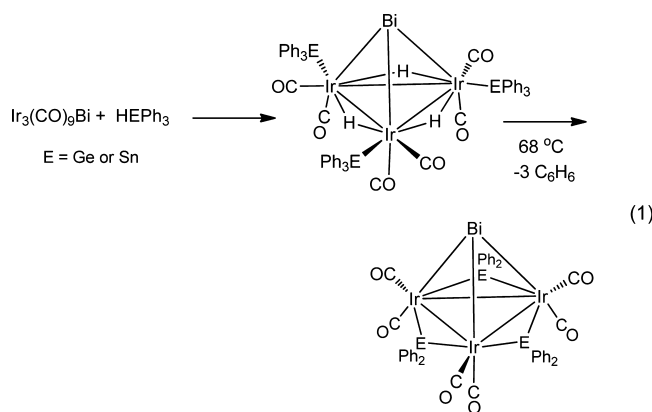
The complexes $Ru_3(CO)_9(EPh_3)(\mu\text{-H})_3$ also eliminate 3 equiv of benzene when heated to yield the tris-EPh_2 complexes $Ru_3(CO)_9(\mu\text{-EPh}_2)_3$ (E = Ge, Sn) (eq 2).[5,6]
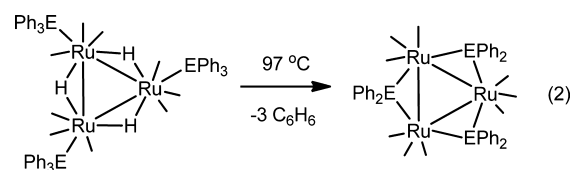
It has recently been shown by a computational analysis that the α-cleavage of a phenyl group from a $GePh_3$ ligand occurs at a single iridium atom in the transformation of the triiridium complex $Ir_3(CO)_6(\mu\text{-CO})(\mu\text{-GePh}_2)_2(GePh_3)_3$ to the complex $Ir_3(CO)_6(\eta^1\text{-Ph})(\mu\text{-GePh}_2)_3(GePh_3)_2$ (eq 3).[7]
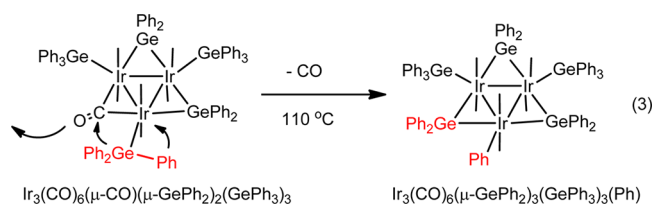
We have now investigated the reactions of $Os_3(CO)_{10}(NCMe)_2$ with $HGePh_3$ and have obtained the new compounds $Os_3(CO)_{10}$-$(NCMe)(GePh_3)(\mu\text{-}H)$ (**1**) and $Os_3(CO)_{10}(GePh_3)_2(\mu\text{-}H)_2$ (**2**). Compound **1** contains a labile NCMe ligand, and this complex was found to react readily with the organogold phosphine compounds $RAu(PPh_3)$ (R = CH_3, Ph) to yield the gold–osmium–germylene complex $Os_3(CO)_8(\mu\text{-}CO)(\mu\text{-}O{=}CPh)$-$(\mu\text{-}GePh_2)(\mu\text{-}AuPPh_3)$ (**4**), which also contains a bridging benzoyl ligand and an $AuPPh_3$ group that bridges an Os–Ge bond. Compound **4** reacts with PhC_2Ph to yield the complex $Os_3(CO)_7$-$(\mu\text{-}GePh_2)(\mu\text{-}AuPPh_3)[\mu\text{-}(O)CPhCPhCPh]$ (**6**), which contains a novel bridging oxametallacycle formed by the coupling of PhC_2Ph to the bridging benzoyl ligand. The results of these studies are reported herein.

■ EXPERIMENTAL SECTION

General Data. Reagent-grade solvents were dried by the standard procedures and were freshly distilled prior to use. Unless indicated otherwise, all reactions were performed under an atmosphere of nitrogen. Infrared spectra were recorded on a Thermo Nicolet Avatar 360 FT-IR spectrophotometer. ^1H NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1 MHz. Variable temperature H NMR spectra for **2** were recorded on a Varian Mercury 400 spectrometer operating at 399.9 MHz. $^{31}P\{^1H\}$ NMR were recorded on a Bruker Avance/DRX 400 NMR spectrometer operating at 162.0 MHz. Mass spectral (MS) measurements were performed by a direct-exposure probe using either electron impact ionization (EI) or electrospray techniques (ES) on a VG 70S instrument. $Os_3(CO)_{12}$ and CH_3AuPPh_3 were purchased from STREM. $HGePh_3$ was purchased from Aldrich and was used without further purification. $Os_3(CO)_{10}(NCMe)_2$[8] and $PhAuPPh_3$[9] were prepared according to previously reported procedures. Product separations were performed by TLC in open air on Analtech 0.25 or 0.5 mm silica gel 60 Å F_{254} glass plates.

Reactions of $Os_3(CO)_{10}(NCMe)_2$ with $HGePh_3$. *(a). Synthesis of $Os_3(CO)_{10}(NCMe)(GePh_3)(\mu\text{-}H)$ (1).* A 29.5 mg (0.0316 mmol) amount of $Os_3(CO)_{10}(NCMe)_2$ was dissolved in 30 mL of methylene chloride in a 100 mL three-neck flask. To this solution was added 9.60 mg (0.0315 mmol) of $HGePh_3$, and the mixture was stirred at room temperature until the IR spectra showed that no $Os_3(CO)_{10}(NCMe)_2$ was remaining in the solution (approximately 15 min). Since the reagent $Os_3(CO)_{10}(NCMe)_2$ and the osmium products are air stable, samples can be removed from the reaction solution in order to follow the reaction by IR spectroscopy. The solvent was then removed in vacuo, and the product was isolated by TLC by using a 6/1 hexane/methylene chloride elution solvent mixture to yield 31.2 mg of yellow $Os_3(CO)_{10}(NCMe)(GePh_3)(\mu\text{-}H)$ (**1**; 64% yield). Spectral data for **1** are as follows. IR ν_{CO} (cm^{-1} in methylene chloride): 2102 (m), 2065 (vs), 2040 (s), 2019 (s), 2002 (s), 1987 (m), 1962 (sh). ^1H NMR (CD_2Cl_2, δ in ppm) at 25 °C: δ 7.25–7.57 (m, 15H, Ph), 2.31 (s, 3H, CH_3), −16.10 (s, hydride). ES+/MS: m/z 1197 (M$^+$).

(b). Synthesis of $Os_3(CO)_{10}(GePh_3)_2(\mu\text{-}H)_2$ (2). A 10.2 mg (0.0109 mmol) amount of $Os_3(CO)_{10}(NCMe)_2$ was dissolved in 20 mL of methylene chloride in a 50 mL three-neck flask. To this solution was added 8.3 mg (0.0272 mmol) of $HGePh_3$, and the mixture was stirred at room temperature until the IR spectra showed no $Os_3(CO)_{10}$-$(NCMe)_2$ was remaining in the solution (approximately 2 h). Since the reagent $Os_3(CO)_{10}(NCMe)_2$ and the osmium product **2** are air stable, samples can be removed from the reaction solution in order to follow the reaction by the IR spectroscopy. The solvent was then removed in vacuo, and the product was isolated by TLC by using a 6/1 hexane/methylene chloride elution solvent mixture to yield 15.9 mg of yellow $Os_3(CO)_{10}(GePh_3)_2(\mu\text{-}H)_2$ (**2**; 71% yield). Spectral data for **2** are as follows. IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2127 (w), 2099 (m), 2056 (m), 2044 (vs), 2029 (m), 1977 (w). ^1H NMR (CD_2Cl_2, δ in ppm) at 25 °C: 7.58–7.26 (m, 30H, Ph), −17.05 (s, hydride); the hydride resonances reveal the presence of two isomers assigned as **2** and **2′** at −80 °C, for isomer **2** −17.121 (d, $^2J_{H-H}$ = 1.32 Hz),

−17.162 (d, $^2J_{H-H}$ = 1.32 Hz), for isomer **2′** −17.231 (s) and −17.704 (s); the ratio of **2/2′** is 2.3/1 at −80 °C. ES+/MS: m/z 1501 (M + K).

Synthesis of $Os_3(CO)_{10}(GePh_3)_2(\mu\text{-}H)_2$ (2) from 1. A 25.3 mg (0.0211 mmol) of **1** was added to a 100 mL three-neck flask with a solution of 6.4 mg (0.0210 mmol) of $HGePh_3$ in 30 mL of CH_2Cl_2. The mixture was then stirred at room temperature until the IR spectrum showed no **1** remaining in the solution (approximately 30 min). The solvent was then removed in vacuo, and the product was isolated by TLC by using a 6/1 hexane/methylene chloride elution solvent mixture to yield a yellow band of **2** (10.8 mg, 35% yield).

Synthesis of $Os_5(CO)_{17}(\mu\text{-}GePh_2)$ (3). A 10.7 mg (0.0089 mmol) amount of **1** was dissolved in 30 mL of hexane in a 100 mL three-neck flask. The solution was heated to reflux for 4 h. After cooling, the solvent was removed in vacuo, and the product was then isolated by TLC by using a 6/1 hexane/methylene chloride elution solvent mixture to yield a purple band of $Os_5(CO)_{17}(\mu\text{-}GePh_2)$ (**3**; 1.06 mg, 9.3% yield) plus traces of a few uncharacterizable products. Spectral data for **3** are as follows. IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2125 (w), 2095 (w), 2080 (m), 2063 (m), 2043 (vs), 2004 (m), 1991 (m). ^1H NMR (CD_2Cl_2, δ in ppm) at 25 °C: 7.24–7.46 (m, 10H, Ph). EI/MS: m/z 1654 (M).

Synthesis of $Os_3(CO)_8(\mu\text{-}CO)(\mu\text{-}O{=}CPh)(\mu\text{-}GePh_2)(\mu\text{-}AuPPh_3)$ (4). A 19.5 mg (0.0163 mmol) amount of **1** was dissolved in 30 mL of hexane in a 100 mL three-neck flask. To this solution was added 7.9 mg (0.0166 mmol) of $CH_3Au(PPh_3)$, and the mixture was heated to reflux for 2 h. The solution changed from pale yellow to dark yellow. After cooling, the solvent was removed in vacuo, and the product was isolated by TLC by using a 3/1 hexane/methylene chloride elution solvent mixture to yield a dark yellow band of $Os_3(CO)_8(\mu\text{-}CO)(\mu\text{-}O{=}CPh)(\mu\text{-}GePh_2)(\mu\text{-}AuPPh_3)$ (**4**; 18.4 mg, 70% yield). Spectral data for **4** are as follows. IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2098 (w), 2073 (s), 2033 (vs), 2027 (vs), 1995 (vs), 1975 (s), 1877 (vw). ^1H NMR (CD_2Cl_2, δ in ppm) at 25 °C: 7.87–7.06 (m, 30H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C, 85% ortho-H_3PO_4): δ 60.30 (s, 1P). ES+/MS: m/z 1614 (M$^+$).

Reaction of 1 with $PhAuPPh_3$. A 19.2 mg (0.0160 mmol) amount of **1** was dissolved in 30 mL of hexane in a 100 mL three-neck flask. To this solution was added 9.8 mg (0.0183 mmol) of $PhAu(PPh_3)$, and the mixture was heated to reflux for 1.5 h. The solution changed from pale yellow to orange. After cooling, the solvent was then removed in vacuo, and the products were separated by TLC by using a 3/1 hexane/methylene chloride solvent mixture to yield, in order of elution, 0.6 mg of pale yellow $Os(CO)_4(GePh_3)(AuPPh_3)$ (**5**; 1% yield) and 12.4 mg of dark yellow **4** (47% yield). Spectral data for **5** are as follows. IR ν_{CO} (cm^{-1} in CH_2Cl_2): 2075 (m), 1990 (vs). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C, 85% ortho-H_3PO_4): δ 53.77 (s, 1P, P−Au). ES+/MS: m/z 1105 (M$^+$).

Synthesis of $Os_3(CO)_7(\mu\text{-}GePh_2)(\mu\text{-}AuPPh_3)[\mu\text{-}(O)CPhCPhCPh]$ (6). An 18.5 mg (0.0115 mmol) amount of **4** was dissolved in 30 mL of heptane in a 100 mL three-neck flask. To this solution was added 3.1 mg (0.0174 mmol) of PhC_2Ph, and the mixture was heated to reflux for 10 h. The color changed from orange to deep red. After cooling, the solvent was then removed in vacuo, and the product was isolated by TLC by using a 4/1 hexane/methylene chloride elution solvent mixture to yield a yellow band of unreacted **4** (7.7 mg) followed by a red band of $Os_3(CO)_7(\mu\text{-}GePh_2)(\mu\text{-}AuPPh_3)[\mu\text{-}(O)CPhCPhCPh]$ (**6**; 3.2 mg, 28% yield). Spectral data for **6** are as follows. IR ν_{CO} (cm^{-1} in hexane): 2063 (w), 2031 (vw), 2006 (s), 1996 (vs), 1985 (s), 1965 (w), 1946 (m), 1935 (m). ^1H NMR (CD_2Cl_2, δ in ppm) at 25 °C: 7.80–6.81 (m, 40H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C, 85% ortho-H_3PO_4): δ 61.32 (s,1P, P−Au). ES+/MS: 1736 (M$^+$).

Crystallographic Analyses. Yellow crystals of **1** suitable for X-ray diffraction analyses were obtained by slow evaporation of solvent from solutions in pure benzene solvent at room temperature. Yellow crystals of **2** and orange crystals of **4−6** suitable for X-ray diffraction analyses were obtained by slow evaporation of solvent from solutions in hexane/methylene chloride solvent mixtures at room temperature. Green crystals of **3** suitable for X-ray diffraction analyses were obtained by slow evaporation of solvent from a hexane solution at room temperature. Each data crystal was glued onto the end of a thin glass fiber. X-ray diffraction intensity data were measured by using a Bruker SMART APEX CCD-based diffractometer by using Mo Kα radiation

(λ = 0.71073 Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.[10] Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS.[10] All structures were solved by a combination of direct methods and difference Fourier syntheses and refined by full-matrix least squares on F^2 by using the SHELXTL software package.[11] All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydride ligands in the complexes were refined with isotropic thermal parameters. Crystal data, data collection parameters, and results of these analyses are given in Table S1 (see the Supporting Information).

Computational Details. All density functional theory (DFT) calculations were performed with the Amsterdam Density Functional (ADF) suite of programs[12a] by using the hybrid (B3LYP[12b]) and meta-GGA (M06-L[12c]) functionals for compounds **4** and **6**, respectively, with valence quadruple-ζ + 4 polarization function, relativistically optimized (QZ4P) basis sets for gold, osmium, and germanium atoms, and double-ζ (DZ) basis sets for phosphorus, carbon, oxygen, and hydrogen atoms with no frozen cores. The molecular orbitals and their energies were determined by single-point calculations based on the molecular structures of the compounds as established by the crystal structure analyses.

■ RESULTS AND DISCUSSION

Reactions of $Os_3(CO)_{10}(NCMe)_2$ with $HGePh_3$ have yielded the compounds $Os_3(CO)_{10}(NCMe)(GePh_3)(\mu\text{-}H)$ (**1**) and $Os_3(CO)_{10}(GePh_3)_2(\mu\text{-}H)_2$ (**2**) by the sequential replacement of the NCMe ligands and the oxidative addition of the GeH bonds of one and two $HGePh_3$ molecules to the osmium atoms of the cluster. The yield of **2** was increased by using an excess of $HGePh_3$. Compound **1** was converted to **2** by reaction with an additional quantity of $HGePh_3$. Both products were characterized by IR, ^{1}H NMR, mass spectra, and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular structure of **1** is shown in Figure 1. The structure of compound
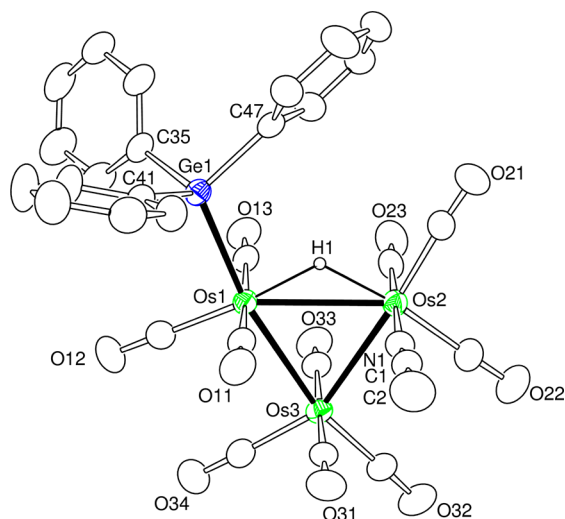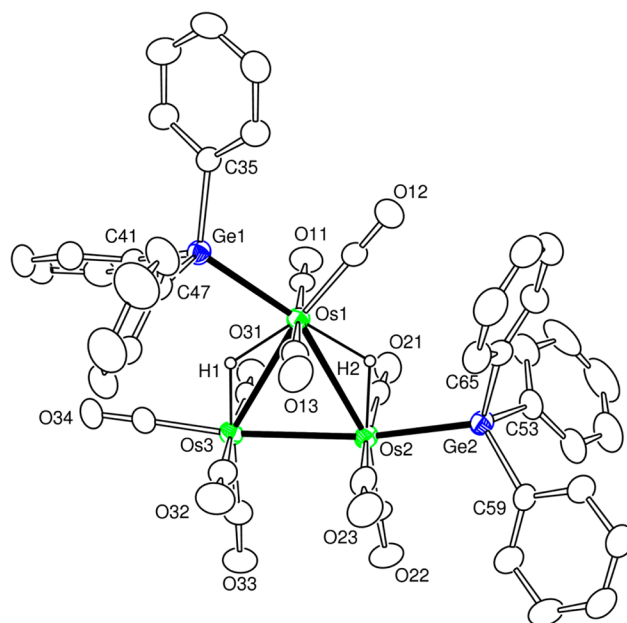

Figure 1. ORTEP diagram of the molecular structure of $Os_3(CO)_{10}(NCMe)(GePh_3)(\mu\text{-}H)$ (**1**) showing thermal ellipsoids at the 30% probability level. Selected interatomic bond distances (Å) are as follows: Os(1)−Os(2) = 3.0163(3), Os(1)−Os(3) = 2.8972(3), Os(2)−Os(3) = 2.8883(4), Os(1)−Ge(1) = 2.5301(6), Os(2)−N(1) = 2.107(5), Os(1)−H(1) = 1.74(6), Os(2)−H(1) = 1.76(6).

1 consists of a closed triangular cluster of three osmium atoms. There is one $GePh_3$ ligand coordinated to Os(1). The Os−Ge distance (Os(1)−Ge(1) = 2.5301(6) Å) is slightly longer than the Os−Ge distance (2.4933(9) Å) to the $GePh_3$ ligand in the

complex $PtOs_3(CO)_7(PBu^t_3)(\mu\text{-}PBu^t_2)(\mu_4\text{-}CHCMeCH)(GePh_3)(\mu\text{-}H)$.[13] The $GePh_3$ ligand lies in an equatorial position, in the plane of the Os_3 triangle. There is one hydride ligand that bridges the Os(1)−Os(2) bond and one NCMe ligand that occupies an axial coordination site on Os(2) (Os(2)−N(1) = 2.107(5) Å). As expected, the hydride-bridged Os−Os bond (Os(1)−Os(2) = 3.0163(3) Å) is significantly longer, than the other two Os−Os bonds (Os(1)−Os(3) = 2.8972(3) Å and Os(2)−Os(3) = 2.8883(4) Å).[14] The Os−Os bond distance found in $Os_3(CO)_{12}$ is 2.877(3) Å.[15] The position of the hydride ligand was located and refined in the analysis (Os(1)−H(1) = 1.74(6) Å and Os(2)−H(1) = 1.76(6) Å). The hydride ligand exhibits a high-field shift in the ^{1}H NMR spectrum (δ −16.10).

An ORTEP diagram of the molecular structure of **2** is shown in Figure 2. Like **1**, the structure of compound **2** consists of a


Figure 2. ORTEP diagram of the molecular structure of $Os_3(CO)_{10}(GePh_3)_2(\mu\text{-}H)_2$ (**2**) showing thermal ellipsoids at the 30% probability level. Selected interatomic bond distances (Å) are as follows: Os(1)−Os(2) = 3.0636(4), Os(1)−Os(3) = 3.0884(4), Os(2)−Os(3) = 2.9165(5), Os(1)−Ge(1) = 2.5634(8), Os(2)−Ge(2) = 2.5292(8), Os(1)−H(1) = 1.77(6), Os(3)−H(1) = 1.70(6), Os(1)−H(2) = 1.77(6), Os(2)−H(2) = 1.80(5).

closed triangular cluster of three osmium atoms, but it has two $GePh_3$ ligands on adjacent osmium atoms and two hydrido ligands that bridge neighboring Os−Os bonds. Both $GePh_3$ ligands occupy equatorial positions, in the plane of the Os_3 triangle, coordinated to Os(1) and Os(2) (Os(1)−Ge(1) = 2.5634(8) Å and Os(2)−Ge(2) = 2.5292(8) Å). The two hydride-bridged Os−Os bonds (Os(1)−Os(2) = 3.0636(4) Å and Os(1)−Os(3) = 3.0884(4) Å) are significantly longer than the Os−Os bond that does not have a bridging hydride ligand (Os(2)−Os(3) = 2.9165(5) Å).[14] Pomeroy reported a similar bis-$(SnMe_3)Os_3$ complex, $Os_3(CO)_{10}(SnMe_3)_2(\mu\text{-}H)_2$, that was obtained from the reaction of $Os_3(CO)_{10}(\mu\text{-}H)_2$ with $HSnMe_3$.[16]

The ^{1}H NMR spectrum of **2** exhibits a single high-field resonance for the two inequivalent hydride ligands at room temperature at δ −17.05, which is inconsistent with the solid-state structure. Suspecting dynamic activity, we performed a variable-temperature NMR study. ^{1}H NMR spectra of **2** at
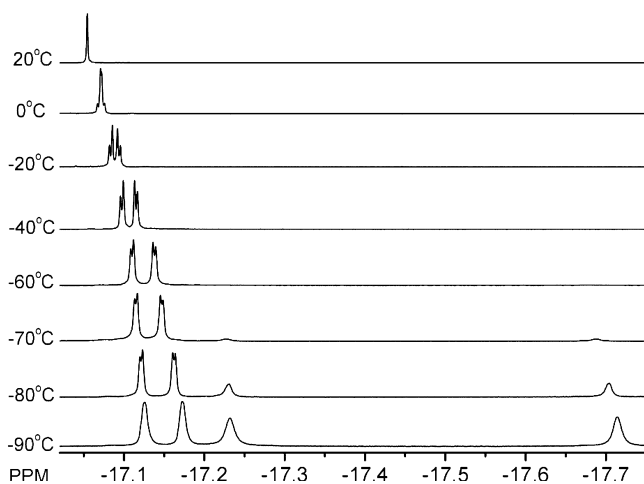
Figure 3. Variable-temperature ^{1}H NMR spectra for compound **2** in CD$_2$Cl$_2$ solvent recorded in the high-field region of the spectrum.

Scheme 1

Scheme 2

various temperatures in the high-field region are shown in Figure 3. These spectra reveal that not only are the two hydride resonances of the isomer found in the solid state averaged but also there is a second isomer present in solution at low temperatures which also exhibits two separate hydride resonances. The two isomers observed at −80 °C shall be called **2** (the major isomer) and **2′**, respectively. For isomer **2**, δ −17.121 (d) and −17.162 (d), and for isomer **2′**, δ −17.231 (s) and −17.704 (s); the ratio **2/2′** is 2.3/1 at −80 °C. The first two resonances are mutually coupled doublets ($^2J_{H-H}$ = 1.32 Hz); the latter two (**2′**) are broad singlets. In addition, it was found that the two isomers are interconverting rapidly on the NMR time scale at intermediate temperatures. This was confirmed by a 2D NOESY spectrum recorded at −80 °C, which showed magnetization transfer not only between the resonances of the two different isomers but also between the two resonances of the major isomer (at −40 °C) (see the Supporting Information). These spectral changes can be explained by either of two mechanisms, which differ depending on the identity and structure of the unknown minor isomer. Mechanism 1 involves hydride positional isomers. Without repositioning any of the non-hydride ligands, three isomers of **2** can be created by repositioning the hydride ligands about the three Os−Os bonds. These structures are represented by **2**, **2′**, and **2″**, as shown in Scheme 1. It is presumed that structure **2**, which is that found in the solid state, is the major isomer in solution. The spectra show the presence of only one other isomer in solution at low temperatures. The structure of **2′** is tentatively assigned as shown in Scheme 1. This isomer is probably more stable than **2″**, because **2′** retains one hydride on the Os−Os bond between the two electron-rich GePh$_3$ ligands. The isomerization between **2** and **2′** could occur by simply shifting the hydride ligand H2 back and forth between the two Os−Os bonds involving the Os(CO)$_4$ group (process A). Low-energy migration of hydride ligands between the metal−metal bonds in other trinuclear metal cluster complexes has been observed previously.[17] The barrier to the exchange of the hydrides H1 and H2 within isomer **2** itself is a higher energy process, because it is still not rapid on the NMR time scale at −20 °C. Without putting two hydride ligands onto the same Os−Os bond, a minimum of three hydride shifts must occur in order to complete the exchange of H1 and H2 in **2**. To do this, it is proposed to invoke the third isomer, presumably **2″**, which was not observed directly in the solutions. Isomer **2″** can
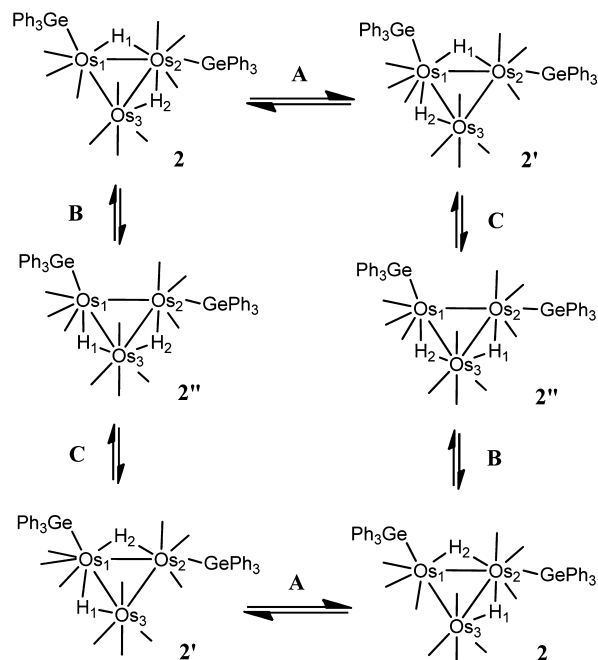
be accessed from isomer **2** by process B shown in Scheme 1 or by process C from isomer **2′**. The H1−H2 exchange is completed by shifting atom H2 to the bond between the two GePh$_3$-substituted Os atoms. This can be achieved in one step from **2′**, shown on the right of Scheme 1, and in two steps from **2″**, shown on the left of Scheme 1.

Mechanism 2 involves GePh$_3$ ligand positional isomers. Isomers of **2** could also be formed by repositioning the GePh$_3$ ligands and could be interconverted dynamically via polytopal rearrangements. We have recently observed examples of this in the compounds Ir$_3$(CO)$_6$(μ-Bi)(EPh$_3$)$_3$(μ-H)$_3$ (E = Ge, Sn), but the temperatures required for those rearrangements are higher than those observed for the isomerization and hydride ligand exchange processes observed in **2**.[6] Two plausible GePh$_3$ ligand positional isomers of **2** are shown in Scheme 2. One is
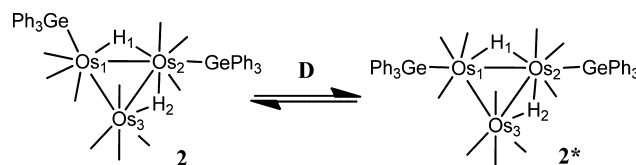
the observed solid-state structure of **2**; the other isomer, **2***, could be formed by repositioning the GePh$_3$ ligand on one of the Os atoms. There are other possible isomers, but isomers that have the bulky GePh$_3$ ligand in equatorial positions should be energetically more favorable for steric reasons. The two isomers **2** and **2*** can be interconverted by polytopal ligand rearrangements involving the GePh$_3$ ligands. Similar processes have been described for the bis-phosphine complex Os$_3$-(CO)$_{10}$(PMe$_2$Ph)$_2$.[18] However, the process shown in Scheme 2 does not allow for the observed exchange of the hydride ligands within a given isomer. To explain that observation, either additional hydride shift processes (e.g. Scheme 1) or perhaps a Ge−H "reductive elimination" coupled with a polytopal rearrangement

without dissociation of the HGePh$_3$ ligand would have to be invoked.[17f] These processes cannot be distinguished with the available data.

When a solution of **1** in hexane solvent was heated to reflux for 4 h, the higher nuclearity compound Os$_5$(CO)$_{17}$(μ-GePh$_2$) (**3**) was obtained in low yield (9.3%). Compound **3** was characterized by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of its molecular structure is shown in Figure 4. Compound **3** contains five osmium atoms arranged in
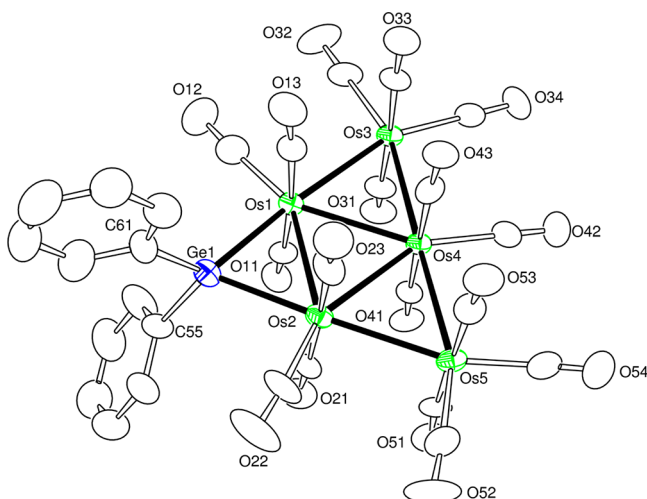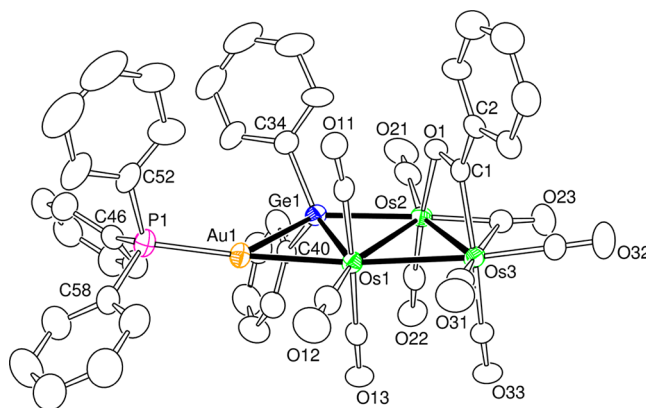

Figure 4. ORTEP diagram of the molecular structure of Os$_5$(CO)$_{17}$(μ-GePh$_2$) (**3**) showing thermal ellipsoids at the 30% probability level. Selected interatomic bond distances (Å) are as follows: Os(1)−Os(2) = 2.8691(7), Os(1)−Os(3) = 2.8713(8), Os(1)−Os(4) = 2.8536(7), Os(2)−Os(4) = 2.8376(8), Os(2)−Os(5) = 2.8531(8), Os(3)−Os(4) = 2.8631(7), Os(4)−Os(5) = 2.8804(7), Os(1)−Ge(1) = 2.5115(16), Os(2)−Ge(1) = 2.5286(16).

a planar raftlike structure with one GePh$_2$ ligand that bridges the Os(1)−Os(2) bond (Os(1)−Os(2) = 2.8691(7) Å). The six other Os−Os bonds are similar in length (Os(1)−Os(3) = 2.8713(8) Å, Os(1)−Os(4) = 2.8536(7) Å, Os(2)−Os(4) = 2.8376(8) Å, Os(2)−Os(5) = 2.8531(8) Å, Os(3)−Os(4) = 2.8631(7) Å, and Os(4)−Os(5) = 2.8804(7) Å). The metal cluster in **3** is structurally similar to that found in the two related Os$_5$ raft cluster complexes Os$_5$(CO)$_{17}$(μ-CO)[19] and Os$_5$(CO)$_{16}$(PMe$_3$)(μ-CO),[20] both of which have a bridging CO ligand at the site corresponding to the GePh$_2$ ligand in **3**. The Os−Ge bond distances (Os(1)−Ge(1) = 2.5115(16) Å and Os(2)−Ge(1) = 2.5286(16) Å) are similar to those found to the edge-bridging GePh$_2$ ligands in the complexes Os$_4$(CO)$_9$-(μ_4-GePh)$_2$(μ-GePh$_2$)$_3$ and Os$_4$(CO)$_8$(μ_4-GePh)$_2$(μ-GePh$_2$)$_4$.[21] Overall, compound **3** contains a total of 76 valence electrons on the metal atoms, which is in accord with the 18-electron rule for a cluster of 5 metal atoms having 7 metal−metal bonds.

We have recently shown that organogoldphosphines of the type PhAu(PPh$_3$) (R = Ph, naphthyl) react with Os$_3$(CO)$_{10}$-(NCMe)$_2$ by displacement of the NCMe ligand and oxidative addition of the Au−C bond of the gold complexes to yield the (organo)(goldphosphine)triosmium carbonyl complexes Os$_3$(CO)$_{10}$(μ-AuPPh$_3$)[μ-R].[22] Compound **1** was found to react with the compounds RAu(PPh$_3$) (R = CH$_3$, Ph) by loss of its NCMe ligand and oxidative addition of the Au−C bond of the gold complexes to yield the compound Os$_3$(CO)$_8$(μ-CO)(μ-O≡CPh)(μ-GePh$_2$)(μ-AuPPh$_3$) (**4**; 70% yield). One minor product, Os(CO)$_4$(GePh$_3$)(AuPPh$_3$) (**5**; 1% yield), was

obtained when PhAu(PPh$_3$) was used as the gold reagent. The molecular structures of both products were established by single-crystal X-ray diffraction analyses.

An ORTEP diagram of the molecular structure of **4** is shown in Figure 5. Compound **4** contains a triangular cluster of three
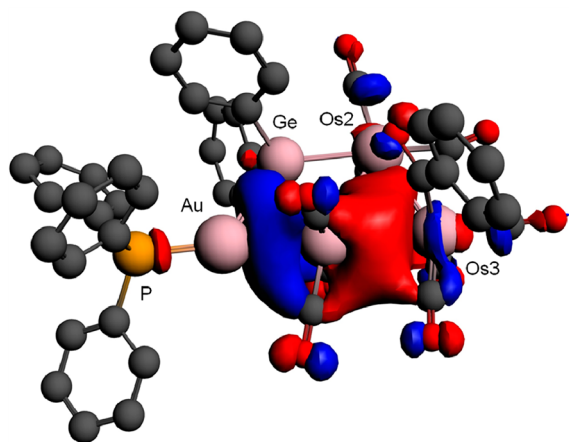

Figure 5. ORTEP diagram of the molecular structure of Os$_3$(CO)$_8$(μ-CO)(μ-OCPh)(μ-GePh$_2$)(μ-AuPPh$_3$) (**4**) showing thermal ellipsoids at the 30% probability level. Selected interatomic bond distances (Å) are as follows: Os(1)−Os(2) = 2.8671(5), Os(1)−Os(3) = 2.8822(5), Os(2)−Os(3) = 2.7643(5), Os(1)−Au(1) = 2.6757(5), Os(1)−Ge(1) = 2.5021(9), Os(2)−Ge(1) = 2.6107(9), Au(1)−Ge(1) = 2.7618(10), Au(1)−P(1) = 2.284(2), Os(2)−O(1) = 2.162(5), Os(3)−C(1) = 2.066(8), O(1)−C(1) = 1.293(9).

osmium atoms, one Au(PPh$_3$) group, one bridging GePh$_2$ ligand, and one bridging benzoyl ligand (O═CPh). There are two long Os−Os bonds (Os(1)−Os(2) = 2.8671(5) Å, Os(1)−Os(3) = 2.8822(5) Å) and one that is significantly shorter (Os(2)−Os(3) = 2.7643(5) Å); the latter contains the bridging benzoyl ligand (Os(2)−O(1) = 2.162(5) Å and Os(3)−C(1) = 2.066(8) Å) and also a bridging CO ligand, which could explain the shortness of that Os−Os bond. The GePh$_2$ ligand bridges the Os(1)−Os(2) bond, and the Os−Ge bond distances are significantly different (Os(1)−Ge(1) = 2.5021(9) Å, Os(2)−Ge(1) = 2.6107(9) Å); the latter is similar to the Os−Ge bond distances in **3**. The Au(PPh$_3$) group is primarily bonded to Os(1) (Os(1)−Au(1) = 2.6757(5) Å), but the Au atom does have a significant bridging/semibridging interaction to the germanium atom (Au(1)−Ge(1) = 2.7618(10) Å). There are only a few examples of Au−Ge bonds among the known complexes containing Au(PPh$_3$) groups. These are Au(GeCl$_3$)-(P-o-tolyl$_3$) (Au−Ge = 2.376(1) Å)[23] and Au(GeCl$_3$)(PPh$_3$)$_3$, (Au−Ge = 2.563(1) Å and [2.536(1)] Å),[24] and for both of these compounds, the Ge group has three strongly electron withdrawing Cl atoms. We are unaware of any previous examples of complexes having Au(PPh$_3$) groups bridging transition-metal−Ge bonds, but some years ago Ruiz did report the compound [Mn$_2$(CO)$_6$(dppm)(μ-SnCl$_2$){AuP(p-tol)$_3$}$_2$], which was shown to have AuP(p-tol)$_3$ groups bridging each of the Mn−Sn bonds to the bridging SnCl$_2$ ligand.[25] There are a few examples of hydrogen atoms bridging M−Ge bonds in polynuclear metal complexes.[26]

The phenyl group on the benzoyl ligand must have originated from the phenyl group that was cleaved from the GePh$_3$ ligand in the course of the formation of the GePh$_2$ ligand and not from the PhAu(PPh$_3$) reagent, because the same ligand (benzoyl not acetyl) was formed when the CH$_3$Au(PPh$_3$) was used as the reagent. Compound **4** contains nine carbonyl ligands and a total

of 48 valence electrons (the Au(PPh$_3$) group is a one electron donor); thus, each osmium atom achieves the conventional 18-electron configuration. To investigate the character of the Au−Ge interaction further, geometry-optimized DFT molecular orbital calculations were performed on the structures of compound **4** by using the B3LYP functional of the Amsterdam Density Functional program library. A significant Au−Ge interaction was confirmed by a significant orbital component found between the Au and Ge atoms in the highest occupied molecular orbital (HOMO) of **4** as shown in Figure 6. There is

Figure 6. Highest occupied molecular orbital of compound **4** (Iso = 0.03), showing that a significant component of the orbital is derived from a direct interaction between the Au and Ge atoms.

also a significant orbital component between the Au atom and the associated Os atom, Os(1).

An ORTEP diagram of the molecular structure of **5** is shown in Figure 7. Compound **5** contains only one osmium atom, in an
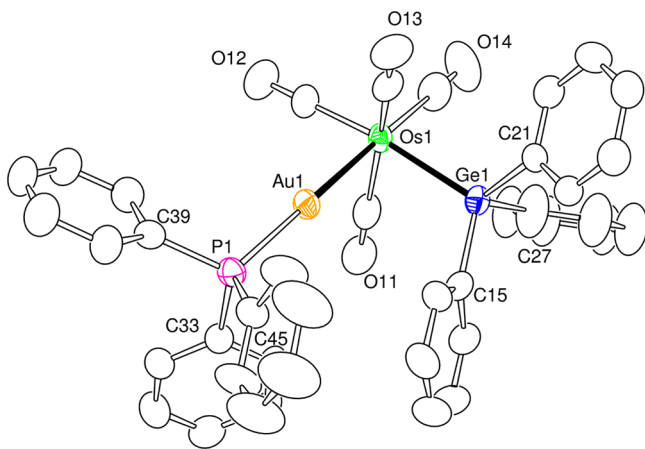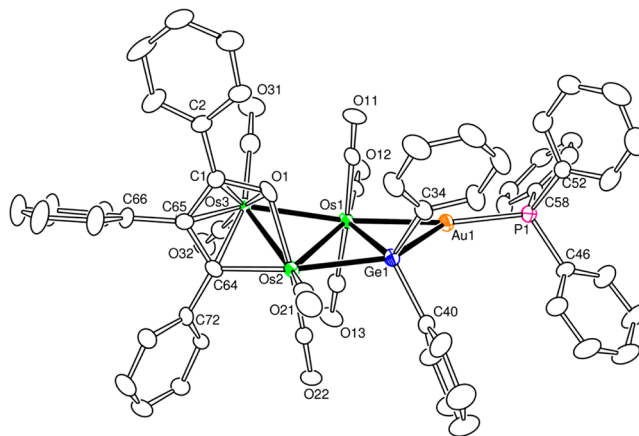

Figure 7. ORTEP diagram of the molecular structure of Os-(CO)$_4$(GePh$_3$)(AuPPh$_3$) (**5**) showing thermal ellipsoids at the 30% probability level. Selected interatomic bond distances (Å) and angles (deg) are as follows: Os(1)−Au(1) = 2.6574(5), Os(1)−Ge(1) = 2.5750(8), Au(1)−P(1) = 2.292(2), Ge(1)···Au(1) = 3.6833(8); Au(1)−Os(1)−Ge(1) = 89.47(2).

Os(CO)$_4$ group, and a Au(PPh$_3$) group and one GePh$_3$ ligand. Compound **5** is clearly the result of a cluster fragmentation process. The Os atom has an octahedral geometry, and the Au(PPh$_3$) and GePh$_3$ groups occupy cis coordination sites (Au(1)−Os(1)−Ge(1) = 89.47(2)°). However, unlike the case for **4**, there

does not appear to be any significant bonding interaction between the Au and Ge atoms (Ge(1)···Au(1) = 3.6833(8) Å). The Os−Au bonding distance (Os(1)−Au(1) = 2.6574(5) Å) is slightly shorter than that in **4**. The Os−Ge distance (Os(1)−Ge(1) = 2.5750(8) Å) is very slightly longer than those in **1** and **2**. The osmium atom in **5** has an 18-electron configuration.

To investigate the reactivity of compound **4** further, it was treated with PhC$_2$Ph in a heptane solution at reflux for 10 h. From this solution, the compound Os$_3$(CO)$_7$(μ-GePh$_2$)(μ-AuPPh$_3$)[μ-(O)CPhCPhCPh] (**6**) was obtained in 28% yield. An ORTEP diagram of the molecular structure of **6** is shown in Figure 8. Compound **6** contains a triangular cluster of three

Figure 8. ORTEP diagram of the molecular structure of Os$_3$(CO)$_7$(μ-GePh$_2$)(μ-AuPPh$_3$)[μ-OCPhCPhCPh] (**6**) showing thermal ellipsoids at the 20% probability level. Selected interatomic bond distances (Å) are as follows: Os(1)−Os(2) = 2.8170(6), Os(1)−Os(3) = 2.7731(6), Os(2)−Os(3) = 2.7025(7), Os(1)−Au(1) = 2.6803(6), Os(1)−Ge(1) = 2.5143(12), Os(2)−Ge(1) = 2.5992(11), Au(1)−Ge(1) = 2.7846(12), Au(1)−P(1) = 2.305(3), Os(2)−O(1) = 2.108(7), Os(2)−C(64) = 2.046(10), Os(3)−C(1) = 2.260(10), Os(3)−O(1) = 2.217(6), Os(3)−C(64) = 2.277(9), Os(3)−C(65) = 2.292(9), O(1)−C(1) = 1.374(12), C(1)−C(65) = 1.414(13), C(65)−C(64) = 1.451(13).

osmium atoms, one Au(PPh$_3$) group, one bridging GePh$_2$ ligand, and one bridging η^4-OCPhCPhCPh ligand. The last group was formed by the addition and coupling of one molecule of PhC$_2$Ph to the carbon atom of the bridging benzoyl ligand in **4**. As in **4**, the Au(PPh$_3$) group bridges one of the Os−Ge bonds to the GePh$_2$ ligand (Au(1)−Ge(1) = 2.7846(12) Å and Os(1)−Au(1) = 2.6803(6) Å). The Os−Ge bond distances (Os(1)−Ge(1) = 2.5143(12) Å and Os(2)−Ge(1) = 2.5992(11) Å) are similar to those in **4**. The η^4-OCPhCPhCPh ligand formed a metallacycle by coordination of its two terminal atoms O(1) and C(64) to the metal atom Os(2) (Os(2)−O(1) = 2.108(7) Å and Os(2)−C(64) = 2.046(10) Å). All four atoms of the OC$_3$ chain are π-bonded to Os(3) (Os(3)−C(1) = 2.260(10) Å, Os(3)−O(1) = 2.217(6) Å, Os(3)−C(64) = 2.277(9) Å, and Os(3)−C(65) = 2.292(9) Å). The formation of bridging metallacycles by the coupling of alkynes is well established,[27] but the formation of heteroatom metallacycles such as that found in **6** is very rare; in fact, we have not been able to find any other examples of the coupling of an alkyne to a bridging acyl ligand to form an oxametallacycle. However, there have been some examples of the insertion coupling of alkynes to terminally coordinated acyl ligands[28] and η^2-acyl ligands.[29] The nature of the Au−Ge bonding in **6** was also investigated by DFT MO calculations. The HOMO and HOMO-2 of **6** are shown in Figure 9. As seen in **4**, there is a significant orbital interaction
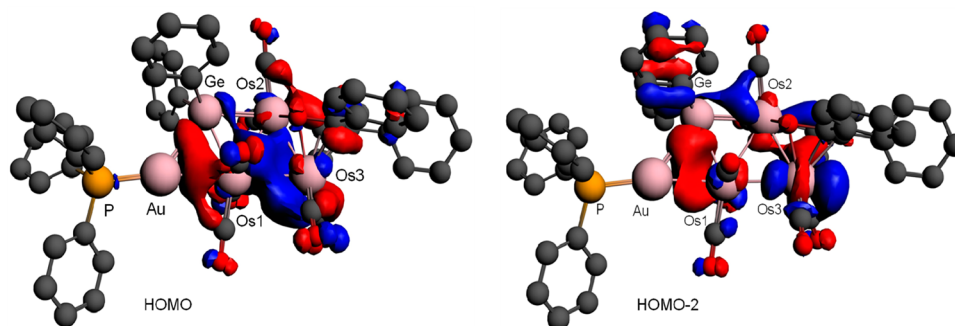
Figure 9. HOMO and HOMO-2 of compound **6** (Iso = 0.03), showing significant bonding interactions directly between the Au and Ge atoms.

Scheme 3
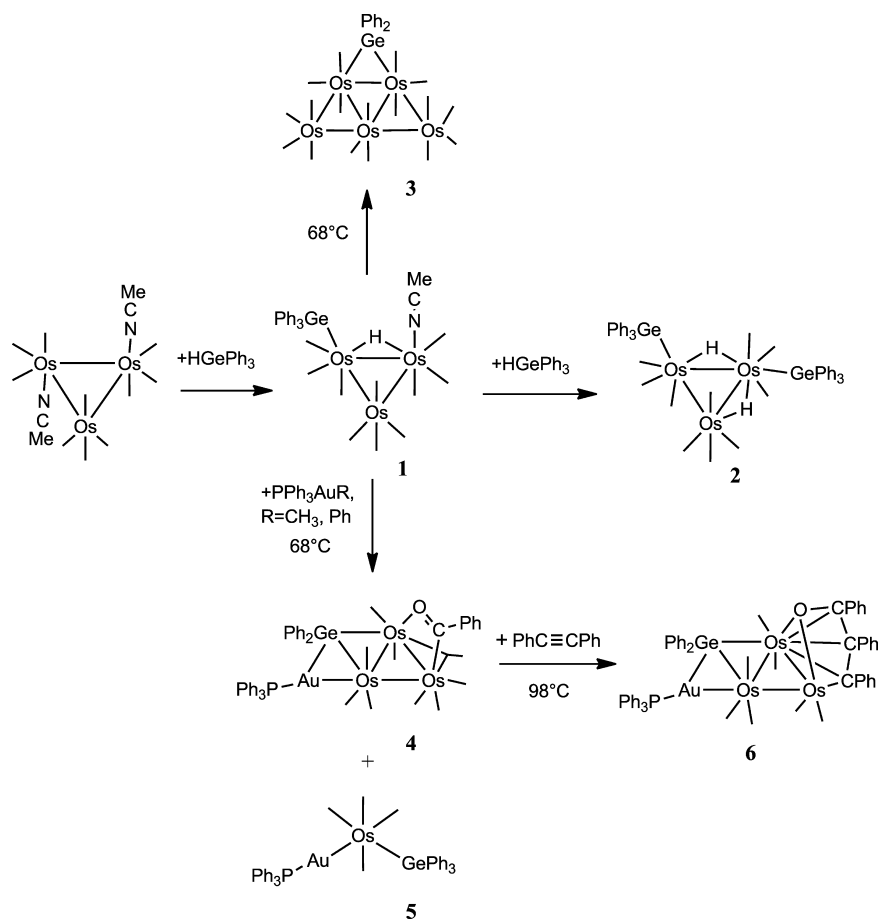
between the Au and Ge and the Au and Os(1) atoms in both of these orbitals.

■ SUMMARY

A summary of the results of our studies reported here is shown in Scheme 3. Compounds **1** and **2** were obtained by the sequential replacement of the two NCMe ligands from $Os_3(CO)_{10}^-(NCMe)_2$ and the oxidative addition of 1 and 2 equiv of $HGePh_3$ to the cluster. Compound **2** can be obtained from **1** by reaction with an additional quantity of $HGePh_3$. Compound **1**, which still contains one labile NCMe ligand, was transformed thermally into the Os_5 raft complex **3**, which contains a bridging $GePh_2$ ligand. Details of the process that led to the growth of the osmium cluster are not available at this time. Compound **1** was found to react with the organogold compounds $RAu(PPh_3)$ (R = CH_3, Ph) by loss of

its NCMe ligand and oxidative addition of the Au−C bond of the gold complexes to yield the compound **4** and one minor product **5**. The structural analyses of compounds **4** show that the $GePh_3$ ligand was transformed into a bridging $GePh_2$ ligand by cleavage of a phenyl group, and an $Au(PPh_3)$ group bridges one of the Os−Ge bonds. The phenyl ligand that was cleaved from the $GePh_3$ group was transferred to a CO ligand to form a bridging benzoyl ligand. Compound **4** was found to react with PhC_2Ph to yield compound **6** by coupling of the PhC_2Ph to the benzoyl ligand to form a bridging η^4-oxametallacycle.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

CIF files, text, a table, and figures giving crystallographic data for the structural analyses, mass spectra for compounds **1−6**,

and 2D NOESY spectra of compound **2** at low temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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