7170 *Inorg. Chem.* **2010**, *49*, 7170–7175
DOI: 10.1021/ic100994t

Inorganic Chemistry
Article

Osmium−Bismuth Complexes from the Reaction of $Os_3(CO)_{11}(NCMe)$ with $BiPh_3$

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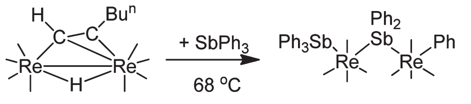
Received May 18, 2010

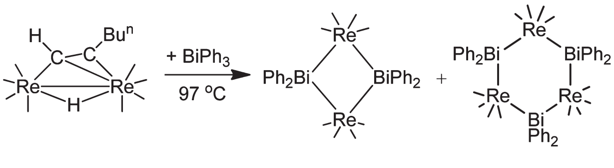
Five new compounds were obtained from the reaction of $Os_3(CO)_{11}(NCMe)$, **1**, with $BiPh_3$ in hexane solution at reflux. These have been identified as $Os_2(CO)_8(\mu\text{-BiPh})$, **2**, $Os(CO)_4Ph_2$, **3**, $Os_4(CO)_{14}(\mu\text{-}\eta^3\text{-O=CC}_6H_5)(\mu_4\text{-Bi})$, **4**, $Os_4(CO)_{15}Ph(\mu_4\text{-Bi})$, **5**, and $Os_5(CO)_{19}Ph(\mu_4\text{-Bi})$, **6**. Cleavage of the phenyl groups from the $BiPh_3$ was the dominant reaction pathway. Fragmentation of the original triosmium cluster was accompanied by reaggregation processes that were facilitated by the naked bismuth to yield the higher nuclearity osmium cluster complexes containing spiro-bridging bismuth ligands. Compound **6** was photo-decarbonylated to yield the compound $HOs_5(CO)_{18}(\mu\text{-}\eta^2\text{-C}_6H_4)(\mu_4\text{-Bi})$, **7**, formed by ortho-CH activation of the σ-bonded phenyl ring in **6** to form a bridging η^2-benzyne ligand. Compounds **2**− **7** were each characterized structurally by a single-crystal X-ray diffraction analysis.

Introduction

Whitmire et al. have prepared and characterized a number of interesting antimony and bismuth- transition metal cluster compounds over the years.[1−5] We have recently reported the synthesis and characterization of a number of new rhenium carbonyl complexes containing phenylantimony and phenylbismuth ligands from the reactions of $Re_2(CO)_8[\mu\text{-}\eta^2\text{-C(H)=C(H)Bu}^n](\mu\text{-H})$ with $SbPh_3$ and $BiPh_3$. The products of these reactions contain bridging $SbPh_2$ and $BiPh_2$ ligands formed by the facile cleavage of phenyl groups from the $SbPh_3$ and $BiPh_3$ reagents, eqs 1[6]−2[7].

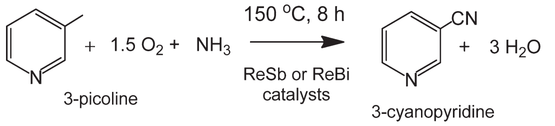


(1)



(2)

We have also shown that some of these new rhenium−antimony and rhenium−bismuth complexes are precursors to effective heterogeneous nanoscale catalysts for the ammoxidation of 3-picoline to 3-cyanopyridine, a precursor to niacin, also known as vitamin B_3, under unusually mild conditions, eq 3.[8]



(3)

We have now turned some of our attention to the chemistry of osmium carbonyl cluster complexes containing antimony and bismuth. Leong et al. have investigated the thermal transformations of the osmium−antimony compound $Os_3(CO)_{11}(SbPh_3)$.[9] The products of those thermal transformations were formed by cleavage of phenyl rings from the $SbPh_3$ ligand. A variety of osmium carbonyl cluster complexes containing $SbPh_2$, SbPh, and naked Sb ligands were obtained. Ang et al. obtained three osmium−bismuth cluster complexes: $H_3Os_3(CO)_9(\mu\text{-Bi})$, $Os_3(CO)_9Bi_2$, and $Os_4(CO)_{12}Bi_2$ in low yields from the reaction of $Os_3(CO)_{12}$ with $NaBiO_3$.[10] We have now investigated the reaction of $Os_3(CO)_{11}(NCMe)$, **1**, with $BiPh_3$. Several new osmium−bismuth complexes have been obtained including the first organobismuth−osmium carbonyl complex $Os_2(CO)_8(\mu\text{-BiPh})$, **2**. The results of these studies are reported herein.

Experimental Section

General Data. All the reactions were performed under a nitrogen atmosphere using the standard Schlenk techniques, unless otherwise stated. Reagent grade solvents were dried by

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(1) Whitmire, K. H. *J. Cluster Sci.* **1991**, *2*, 231–258.
(2) Luo, S. F.; Whitmire, K. H. *J. Organomet. Chem.* **1991**, *30*, 2788–2795.
(3) Cassidy, J. M.; Whitmire, K. H. *Inorg. Chem.* **2009**, *48*, 9519–9525.
(4) Bachman, R. E.; Whitmire, K. H. *Inorg. Chem.* **1995**, *34*, 1542–1551.
(5) Whitmire, K. H.; Evelan, J. R., Jr. *J. Chem. Soc., Chem. Commun.* **1994**, 1335–1336.
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(8) Raja, R.; Adams, R. D.; Blom, D. A.; Pearl, W. C., Jr.; Gianotti, E.; Thomas, J. M. *Langmuir* **2009**, *25*, 7200–7204.
(9) Leong, W. K.; Chen, G. *Organometallics* **2001**, *20*, 2280–2287.
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the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on an AVATAR 360 FT-IR spectrophotometer. ^{1}H NMR spectra were recorded on Varian Mercury 400 and 300 spectrometers operating at 399 and 300 MHz, respectively. Mass spectrometric measurements performed by direct exposure probe using electron impact ionization (EI) were made on a VG 70S instrument. Triphenylbismuth ($BiPh_3$) was purchased from STREM and was used without further purification. $Os_3(CO)_{11}NCMe$, **1**, was prepared according to a previously published procedure.[11] Product separations were performed by thin layer chromatography (TLC) in air on Analtech 0.50 mm silica gel 60 Å F254 glass plates.

Reaction of 1 with $BiPh_3$. A 100 mg portion (0.227 mmol) of $BiPh_3$ was added to a solution of 52.7 mg (0.0570 mmol) of **1** dissolved in 70 mL of hexane. The solution was then refluxed for 3 h. After cooling, the solvent was removed in vacuo, and the products were then separated by TLC using 4:1 hexane/methylene chloride (v/v) solvent mixture to give in order of elution: a yellow band of $Os_2(CO)_8(\mu\text{-BiPh})$, **2**, 3.5 mg (5% yield); a colorless band of $Os(CO)_4Ph_2$, **3**, 2.8 mg (5% yield); an orange band of $Os_4(CO)_{14}(\mu\text{-}\eta^2\text{-O=CPh})(\mu_4\text{-Bi})$, **4**, 2.0 mg (3% yield); a red band of $Os_4(CO)_{15}Ph(\mu_4\text{-Bi})$, **5**, 2.3 mg (4% yield); and an orange band of $Os_5(CO)_{19}Ph(\mu_4\text{-Bi})$, **6**, 1.6 mg (3% yield). Spectral data for **2** (ν_{CO} cm^{-1} in hexane): 2112(w), 2069(s), 2035(vs), 2028 (vs), 2016 (m), 2004(m), 1990(w). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C, TMS) δ = 7.1−7.7 (m, 5H, Ph). Mass Spec. EI/MS *m*/*z*. 892 (M^+), 864 (M^+-CO), 836 (M^+-2CO), 808 (M^+-3CO). The isotope distribution pattern is consistent with the presence of one bismuth and two osmium atoms. Spectral data for **3** (ν_{CO} cm^{-1} in hexane): 2140(w), 2059(vs), 2027(s). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) 7.1−7.5 (m, Ph, 10H), Mass Spec. EI/MS *m*/*z*. 458 (M^+), 402 (M^+-2CO), 374 (M^+-3CO). The isotope distribution pattern is consistent with the presence of only one osmium atom. Spectral data for **4** (ν_{CO} cm^{-1} in hexane): 2122(w), 2084(s), 2063(s), 2047(vs), 2031(m), 2021(w), 2005(w), 1992(m), 1984(w), 1971(vw), 1964(vw). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C, TMS) δ = 7.4−7.6 (m, 5H, Ph). Mass Spec. EI/MS *m*/*z*. 1468 (M^+). The isotope distribution pattern is consistent with the presence of one bismuth and four osmium atoms. Spectral data for **5** (ν_{CO} cm^{-1} in hexane): 2124(w), 2090(m), 2084(s), 2069(vw), 2057(vs), 2047(m), 2041(s), 2034(m), 2025(m), 2022(m), 2016(m), 2004(vw), 1997(w), 1980(w). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C, TMS) δ = 7.3−7.8 (m, 5H, Ph). Mass Spec. EI/MS *m*/*z*. 1468 (M^+), 1440 (M^+-CO). The isotope distribution pattern is consistent with the presence of one bismuth and four osmium atoms. Spectral data for **6** (ν_{CO} cm^{-1} in hexane): 2123(w), 2098(s), 2078(vs), 2074(vs), 2057(m), 2042(w), 2038(m), 2031(m), 2017(s), 2010(w), 2004(w), 1990(w), 1984(w), 1971(vw). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ = 6.9−7.7 (m, 5H, Ph). Mass Spec. EI/MS *m*/*z*. 1770 (M^+), 1742 (M^+-CO). The isotope distribution pattern is consistent with the presence of one bismuth and five osmium atoms.

Reaction of 1 with 2. A 5.2 mg portion (0.00582 mmol) of **2** was added to 5.5 mg (0.00595 mmol) of **1** dissolved in 5 mL of hexane and refluxed for 45 min. The solvent was then removed in vacuo, and the products were separated by TLC using 4:1 hexane/methylene chloride (v/v) solvent mixture to give products in order of elution, a yellow band of unreacted **2**, 1 mg, an orange band of $HOs_5(CO)_{18}(\mu\text{-}\eta^2\text{-}C_6H_4)(\mu_4\text{-Bi})$, **7**, 1 mg (10%) and a red band of **6**, 1.1 mg (11%). Spectral data for **7** (ν_{CO} cm^{-1} in hexane): 2121(w), 2092(s), 2082(vs), 2078(s), 2061(w), 2045(vw), 2040(s), 2028(m), 2021(m), 2016(w), 2012(w), 2006(m), 1990(w), 1987(w). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ = 7.6 (d, Ph, 1H), 7.4 (d, Ph, 1H), 7.1 (t, Ph, 1H), 6.9 (t, Ph, 1H), −18.8 (s, hydride, 1H). Mass Spec. EI/MS *m*/*z*. 1742 (M^+), 1712 (M^+-CO), 1686 (M^+-2CO). The isotope distribution pattern is consistent with the presence of one bismuth and five osmium atoms.

Conversion of 4 to 5. A 12.3 mg portion of **4** was dissolved in 10 mL of hexane and refluxed for 2 h. The solvent was removed in vacuo, and the products were separated by TLC by using a 4:1 hexane/methylene chloride mixture to yield in order of elution an orange band of unreacted **4**, 2.6 mg (21%), and a red band of **5**, 1.2 mg (10%).

Photoconversion of 6 to 7. A 6.0 mg portion of **6** was dissolved in 10 mL of hexane, and the flask was placed in an ice bath while photolyzing for 1 h using a 1000W UV lamp. The solvent was then removed in vacuo, and the products were separated by TLC using a 4:1 hexane/methylene chloride mixture to yield in order of elution a yellow band of $Os_3(CO)_{12}$, 3.5 mg (68% yield), an orange band of **7**, 0.7 mg (12% yield), and a red band of unreacted **6**, 0.6 mg (10%).

Carbonylation of 7. A 14.0 mg portion of **7** was dissolved in 5 mL of hexane and placed in a high pressure reactor under an atmosphere of CO (250 psi) and heated at 60 °C for 1.5 h. After cooling, the solvent was removed in vacuo, and the products were separated by TLC by using a 4:1 hexane/methylene chloride (v/v) solvent mixture to give 1.5 mg of $Os_4(CO)_{12}(\mu\text{-}Bi_2)$[10] and 1.0 mg of **6** (7% yield).

Crystallographic Structural Analyses. Yellow single crystals of **2**, colorless crystals of **3**, and red crystals of each of **4**−**7** suitable for X-ray diffraction analysis were obtained by slow evaporation of solvent from solutions in methylene chloride/hexane solvent at −25 °C. Each data crystal was glued onto the end of a thin glass fiber. X-ray 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.[12] 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 for each analysis by using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on F^2 using the SHELXTL software package.[13] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on the ligands were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. Crystal data, data collection parameters, and results of the refinements are listed in Table 1. Compounds **2** and **4** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed for each and was confirmed by the successful solution and refinement of the structures. In the crystal of **2**, there is one complete independent molecule of the complex in the asymmetric crystal unit. For **4**, there are two complete independent molecules in the asymmetric crystal unit. Compound **3** crystallized in the orthorhombic crystal system. The space group $P2_12_12_1$ was confirmed on the basis of the systematic absences observed in the data. Compound **3** contains one independent molecule in the asymmetric crystal unit. Compounds **5**−**7** all crystallized in the monoclinic crystal system. The space group $P2_1/n$ was confirmed for all three of these compounds on the basis of the systematic absences observed in the data. The crystal of **7** contains one formula equivalent of the complex in the asymmetric crystal unit. The crystal of compound **6** contains one independent molecule of the complex together with one molecule of methylene chloride from the crystallization solvent in the asymmetric crystal unit. The crystal of **7** contains one formula equivalent of the complex in the asymmetric crystal unit. The hydrido ligand in **7** was located and refined on its positional parameters and an isotropic thermal parameter.

Results

Five new compounds $Os_2(CO)_8(\mu\text{-BiPh})$, **2**, (5% yield), $Os(CO)_4Ph_2$, **3**, (5% yield), $Os_4(CO)_{14}(\mu\text{-}\eta^3\text{-O=CC}_6H_5)(\mu_4\text{-Bi})$, **4**,

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[11] Johnson, B. F. G.; Lewis, J.; Pippard, D. A. *J. Chem. Soc., Dalton Trans.* **1981**, 407–412.

[12] *SAINT+*, Version 6.2a; Bruker Analytical X-ray System, Inc.: Madison, WI, 2001.

[13] Sheldrick, G. M. *SHELXTL*, Version 6.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

Table 1. Crystallographic Data for the Structural Analyses of Compounds **2**−**7**

	2	**3**	**4**	**5**	**6**	**7**
empirical formula	$Os_2BiO_8C_{14}H_5$	$OsO_4C_{16}H_{10}$	$Os_4BiO_{15}C_{21}H_5$	$Os_4BiO_{15}C_{21}H_5$	$Os_5BiO_{19}C_{25}H_5 \cdot CH_2Cl_2$	$Os_5BiO_{18}C_{24}H_4$
formula weight	890.56	456.44	1467.03	1467.03	1854.20	1740.25
crystal system	triclinic	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic
lattice parameters						
a (Å)	9.5596(8)	7.7405(3)	12.953(3)	10.8919(4)	16.9824(6)	9.6781(4)
b (Å)	10.0335(8)	12.6633(5)	15.314(4)	17.0759(6)	9.7637(3)	21.3846(8)
c (Å)	10.7117(9)	15.6545(6)	15.976(4)	16.1745(6)	23.9049(8)	15.9979(6)
α (deg)	94.491(2)	90.00	71.752(4)	90.00	90.00	90.00
β (deg)	106.687(2)	90.00	80.406(4)	103.3050(10)	100.6750(10)	94.4480(10)
γ (deg)	104.987(2)	90.00	88.175(5)	90.00	90.00	90.00
V (Å^3)	937.67(13)	1534.46(10)	2966.8(12)	2927.53(18)	3895.1(2)	3301.0(2)
space group	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Z value	2	4	4	4	4	4
ρ_{calc} (g/cm^3)	3.154	1.976	3.284	3.328	3.162	3.502
μ (Mo Kα) (mm^{-1})	22.913	8.321	23.046	23.355	20.957	24.558
temperature (K)	294(2)	294(2)	294(2)	294(2)	294(2)	294(2)
$2\Theta_{max}$ (deg)	57.06	56.66	52.74	56.72	52.74	56.88
no. obs. ($I > 2\sigma(I)$)	3548	3396	6345	5599	6803	5585
no. parameters	226	190	739	370	478	433
goodness of fit	0.970	1.018	0.942	1.015	1.069	1.050
max. shift in cycle	0.001	0.001	0.001	0.001	0.002	0.001
residuals[a]: R1; wR2	0.0328; 0.0663	0.0265; 0.0513	0.0668; 0.1323	0.0299; 0.0613	0.0493; 0.1547	0.0497; 0.0727
absorption correction, max/min	1.000; 0.403	1.000/0.736	0.322/1.000	1.000/0.568	1.000/0.228	1.000/0.513
largest peak in final diff. map (e$^-$/Å^3)	1.371	0.870	2.381	1.961	3.341	1.775

[a] $R1 = \sum_{hkl}(||F_{obs}| - |F_{calc}||)/\sum_{hkl}|F_{obs}|$; $wR2 = [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\sum_{hkl}wF_{obs}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; $GOF = [\sum_{hkl}w(|F_{obs}| - |F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$.

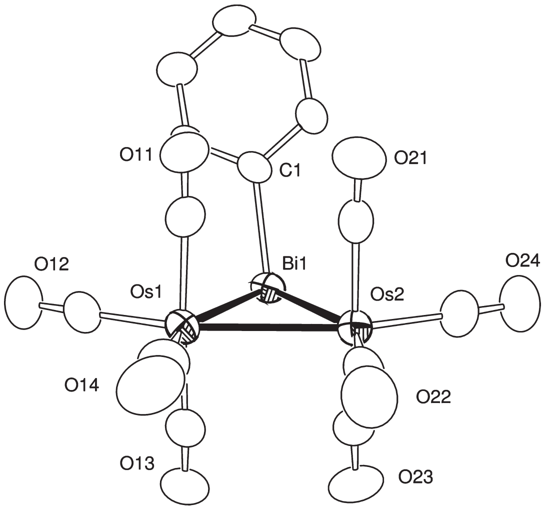

Figure 1. ORTEP diagram of the molecular structure of $Os_2(CO)_8(\mu\text{-}BiPh)$, **2**, showing 30% probability thermal ellipsoids. The hydrogen atoms on the ligands are omitted for clarity. Selected interatomic bond distances (Å) and angles (deg) are as follow: Os(1)−Os(2) = 2.9512(5), Os(1)−Bi(1) = 2.8305(4), Os(2)−Bi(1) = 2.8270(5), Bi(1)−C(1) = 2.269(7); Bi(1)−Os(1)−Os(2) = 58.500(12), Bi(1)−Os(2)−Os(1) = 58.614(11), C(1)−Bi(1)−Os(2) = 106.79(19), C(1)−Bi(1)−Os(1) = 99.83(18).

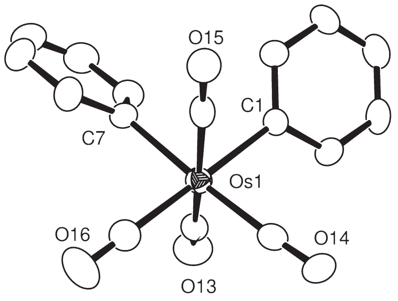

Figure 2. ORTEP diagram of the molecular structure of $Os(CO)_4Ph_2$, **3** showing 30% probability thermal ellipsoids. The hydrogen atoms on the ligands are omitted for clarity. Selected interatomic bond distances (Å) and angles (deg) are as follow: Os(1)−C(7) = 2.175(5), Os(1)−C(1) = 2.182(5), Os(1)−C(15) = 1.945(6), Os(1)−C(13) = 1.947(6), Os(1)−C(14) = 1.957(6), Os(1)−C(16) = 1.967(7); C(7)−Os(1)−C(1) = 90.6(2).

(3% yield), $Os_4(CO)_{15}Ph(\mu_4\text{-}Bi)$, **5**, (4% yield), and $Os_5(CO)_{19}Ph(\mu_4\text{-}Bi)$, **6**, (3% yield) were obtained all in low yields from the reaction of **1** with $BiPh_3$ in a hexane solution at reflux (68 °C) over a 3 h period. All five compounds were characterized by a combination of IR, NMR, mass spec and single crystal X-ray diffraction analyses. An Oak Ridge thermal ellipsoid plot (ORTEP) diagram of the molecular structure of **2** is shown in Figure 1. Compound **2** contains two osmium atoms, eight linear terminal carbonyl ligands, and a BiPh ligand that bridges the osmium−osmium bond. The osmium−osmium bond distance, Os(1)−Os(2) = 2.9512(5) Å, is slightly longer than that found in $Os_3(CO)_{12}$, 2.877(3) Å.[14] The Os−Bi distances, Os(1)−Bi(1) = 2.8305(4) Å, Os(2)−Bi(1) = 2.8270(5) Å, are slightly longer than Os−Bi distances to the triply bridging Bi ligand in $H_3Os_3(CO)_9(\mu\text{-}Bi)$, 2.800(2) Å; Bi(l)−Os(2), 2.807(l) Å; Bi(l)−Os(3), 2.799(2) Å.[10] The bridging monophenylbismuth ligand serves a two electron donor to the osmium atoms in **2** and with an Os−Os bond each of the osmium atoms achieves an 18 electron configuration. The BiPh ligand has been observed previously in the complexes $Re_2(CO)_8(\mu\text{-}BiPh)_2$[7] and $Fe_2(CO)_8(\mu\text{-}BiPh)_2$.[2] The former complex has a metal−metal bond while the latter complex does not.

An ORTEP diagram of the structure of the coproduct **3** is shown in Figure 2. The molecule contains one osmium atom, two σ-bonded phenyl rings and four linear terminal carbonyl groups. The six ligands exhibit an octahedral-type coordination geometry with the two phenyl rings in cis-related sites. The angle between the phenyl rings is very close to 90°, C(7)−Os(1)−C(1) = 90.6(2)°. As expected, the Os−C distances to the phenyl rings, Os(1)−C(7) = 2.175(5) Å and

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

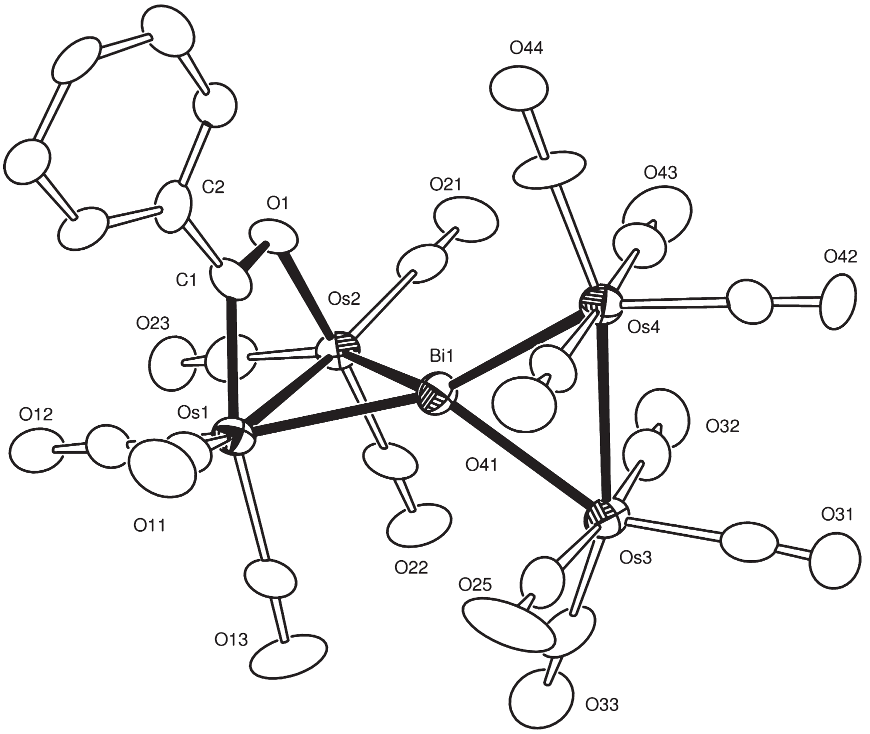
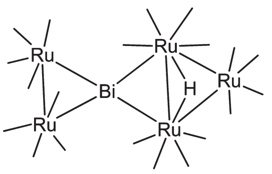


Figure 3. ORTEP diagram of the molecular structure of $Os_4(CO)_{14}(\mu\text{-}\eta^3\text{-}OCC_6H_5)(\mu_4\text{-}Bi)$, **4**, showing 30% probability thermal ellipsoids. The hydrogen atoms on the ligands are omitted for clarity. Selected interatomic bond distances (Å) and angles (deg) are as follow: Os(1)−Os(2) = 2.8238(14), Os(3)−Os(4) = 2.9691(14), Os(1)−Bi(1) = 2.7230(14), Os(2)−Bi(1) = 2.7065(13), Os(3)−Bi(1) = 2.7531(15), Os(4)−Bi(1) = 2.7514(13), Os(1)−C(1) = 2.06(2), Os(2)−O(1) = 2.133(15); C(1)−Os(1)−Bi(1) = 79.2(7), C(1)−Os(1)−Os(2) = 66.6(7), Bi(1)−Os(1)−Os(2) = 58.38(3), O(1)−Os(2)−Bi(1) = 82.0(4), O(1)−Os(2)−Os(1) = 69.4(4), Bi(1)−Os(2)−Os(1) = 58.95(3), Bi(1)−Os(3)−Os(4) = 57.33(3), Bi(1)−Os(4)−Os(3) = 57.39(3).

Os(1)−C(1) = 2.182(5) Å, are significantly longer than the Os−C distances to the CO ligands, Os(1)−C(15) = 1.945(6) Å, Os(1)−C(13) = 1.947(6) Å, Os(1)−C(14) = 1.957(6) Å, Os(1)−C(16) = 1.967(7) Å. There are no previous reports of structural characterizations of bis-arylosmium tetracarbonyl complexes, but there is a report of a bis-(pentafluorobenzyl)-osmium tetracarbonyl complex, $Os(CO)_4(CH_2C_6F_5)_2$, which has a similar structure.[15] There are number of related di-σ-alkylosmium tetracarbonyl complexes.[16]

An ORTEP diagram of the structure of **4** is shown in Figure 3. This compound contains four osmium atoms contained in two groups of two that are linked by a spiro-bridging bismuth atom, Bi(1). One of the pair of osmium atoms is an $Os_2(CO)_8$ group that contains an Os−Os bond, Os(3)−Os(4) = 2.9691(14) Å. The other group is an $Os_2(CO)_6$ group that has an Os−Os bond, Os(1)−Os(2) = 2.8238(14) Å, and a bridging benzoyl ligand that is C-coordinated to one osmium atom, Os(1)−C(1) = 2.06(2) Å, and O-coordinated to the other osmium atom, Os(2)−O(1) = 2.133(15) Å. The osmium−bismuth bonds are significantly shorter, Os(1)−Bi(1) = 2.7230(14) Å, Os(2)−Bi(1) = 2.7065(13) Å, Os(3)−Bi(1) = 2.7531(15) Å, Os(4)−Bi(1) = 2.7514(13) Å, than the osmium−bismuth bonds in **2**. The Os−Bi bonds to the $Os_2(CO)_6(\mu\text{-}O{=}CPh)$ group are significantly shorter than those to the $Os_2(CO)_8$ group. The spiro μ_4-Bi atom serves as a 5-electron donor to the metal atoms. With a proper distribution of those five electrons, each of the osmium atoms achieves an 18-electron configuration. There are very few examples of metal complexes containing bridging bismuth atoms in the spiro-coordination form. Johnson et al. reported the pentaruthenium complex $HRu_5(CO)_{18}(\mu_4\text{-}Bi)$, **8**, which contains a spiro-μ_4-Bi bridging a $Ru_2(CO)_8$ group and $HRu_3(CO)_{11}$ group.[17] Leong has reported some osmium carbonyl cluster complexes containing spiro-Sb atoms.[9]



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An ORTEP diagram of the structure of **5** is shown in Figure 4. This compound is similar to **4**. It contains four osmium atoms contained in two groups of two that are also linked by a spiro-bridging bismuth atom, Bi(1). One of the pair of the osmium atoms is a $Os_2(CO)_8$ group that contains an Os−Os bond that is very similar in length to that found in **4**, Os(3)−Os(4) = 2.9734(4) Å. The second Os_2 group is an $Os_2(CO)_7Ph$ group that contains a σ-bonded phenyl group in an axial site on one of the metal atoms. The Os−C distance, Os(1)−C(1) = 2.178(7) Å, is very similar to those in **3**. There is also an Os−Os bond in this Os_2 group that is very similar in length, Os(1)−Os(2) = 2.9759(4) Å, to that in the $Os_2(CO)_8$ group. The Os−Bi distances are similar to those in **4**, Os(1)−Bi(1) = 2.7159(3), Os(2)−Bi(1) = 2.7596(4), Os(3)−Bi(1) = 2.7635(4), Os(3)−Os(4) = 2.9734(4), Os(4)−Bi(1) = 2.7705(4). Each of the osmium atoms in **5** has a formal 18-electron configuration.

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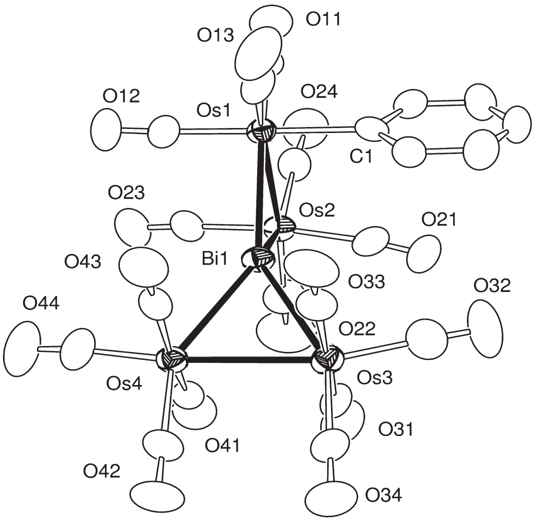


Figure 4. ORTEP diagram of the molecular structure of $Os_4(CO)_{15}Ph(\mu_4\text{-Bi})$, **5**, showing 30% probability thermal ellipsoids. The hydrogen atoms on the ligands are omitted for clarity. Selected interatomic bond distances (Å) and angles (deg) are as follow: Os(1)−C(1) = 2.178(7), Os(1)−Bi(1) = 2.7159(3), Os(1)−Os(2) = 2.9759(4), Os(2)−Bi(1) = 2.7596(4), Os(3)−Bi(1) = 2.7635(4), Os(3)−Os(4) = 2.9734(4), Os(4)−Bi(1) = 2.7705(4); C(1)−Os(1)−Bi(1) = 91.15(17), C(1)−Os(1)−Os(2) = 87.16(17), Bi(1)−Os(1)−Os(2) = 57.788(9), Bi(1)−Os(2)−Os(1) = 56.375(9), Bi(1)−Os(3)−Os(4) = 57.612(9), Bi(1)−Os(4)−Os(3) = 57.387(9), Os(1)−Bi(1)−Os(2) = 65.838(10), Os(1)−Bi(1)−Os(3) = 141.906(13), Os(2)−Bi(1)−Os(3) = 125.747(13), Os(1)−Bi(1)−Os(4) = 142.150(14), Os(2)−Bi(1)−Os(4) = 127.441(13), Os(3)−Bi(1)−Os(4) = 65.000(10).

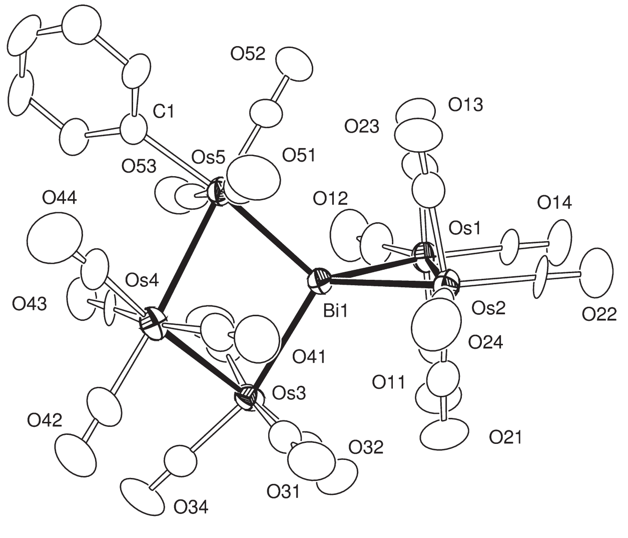


Figure 5. ORTEP diagram of the molecular structure of $Os_5(CO)_{19}Ph(\mu_4\text{-Bi})$, **6**, showing 30% probability thermal ellipsoids. The hydrogen atoms on the ligands are omitted for clarity. Selected interatomic bond distances (Å) and angles (deg) are as follow: Os(1)−Bi(1) = 2.8216(6), Os(1)−Os(2) = 2.9625(6), Os(2)−Bi(1) = 2.7850(6), Os(3)−Bi(1) = 2.8368(6), Os(3)−Os(4) = 2.9870(7), Os(4)−Os(5) = 3.0167(6), Os(5)−C(1) = 2.152(13), Os(5)−Bi(1) = 2.7922(6); Bi(1)−Os(1)−Os(2) = 57.505(15), Bi(1)−Os(2)−Os(1) = 58.705(15), Bi(1)−Os(3)−Os(4) = 77.855(16), Os(3)−Os(4)−Os(5) = 94.008(17), C(1)−Os(5)−Bi(1) = 174.0(3), C(1)−Os(5)−Os(4) = 96.6(3), Bi(1)−Os(5)−Os(4) = 78.035(17), Os(2)−Bi(1)−Os(5) = 123.113(19), Os(2)−Bi(1)−Os(1) = 63.789(16), Os(5)−Bi(1)−Os(1) = 126.943(18), Os(2)−Bi(1)−Os(3) = 119.465(19), Os(5)−Bi(1)−Os(3) = 102.537(18), Os(1)−Bi(1)−Os(3) = 118.663(19).

An ORTEP diagram of the structure of **6** is shown in Figure 5. Compound **6** contains five osmium atoms divided into two groups; one group contains two metal atoms in the form of an $Os_2(CO)_8$ group, and the other three in an $Os_3(CO)_{11}Ph$ group. The two groups are linked by a spiro-bridging bismuth atom, Bi(1). The Os−Os bond distance in the $Os_2(CO)_8$ group is similar in length to those found in **4** and **5**, Os(1)−Os(2) = 2.9625(6) Å. The $Os_3(CO)_{11}Ph$ group, Os(3)−Os(5), is an "open" cluster. The terminal osmium atoms Os(3) and Os(5) are bonded to the spiro-Bi atom. Os(3) and Os(4) have four linear terminal carbonyl ligands. Os(5) has three linear terminal carbonyl ligands and a σ-bonded phenyl group that is coordinated trans to the Bi atom. The Os−C distance to the σ-bonded phenyl group, Os(5)−C(1) = 2.152(13) Å, is similar in length to those in **3** and **5**. There are two Os−Os bonds in the $Os_3(CO)_{11}Ph$ group, Os(3)−Os(4) = 2.9870(7) Å, Os(4)−Os(5) = 3.0167(6) Å, which are significantly longer than those in the triangular cluster $Os_3(CO)_{12}$, 2.877(3) Å.[14] The Os−Bi distances, Os(1)−Bi(1) = 2.8216(6) Å, Os(2)−Bi(1) = 2.7850(6) Å, Os(3)−Bi(1) = 2.8368(6) Å, and Os(5)−Bi(1) = 2.7922(6) Å, are similar to those in compounds **3**− **5**. Each of the osmium atoms in **6** formally has an 18-electron configuration. Compounds **6** and **7** were both obtained in low yields from the reaction of **1** with **2**. Compound **6** was also converted to **7** upon exposure to UV−vis irradiation.

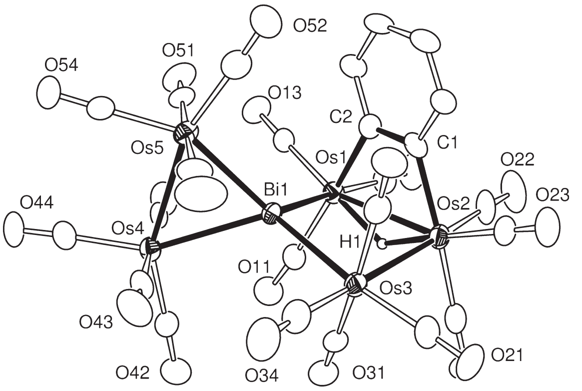
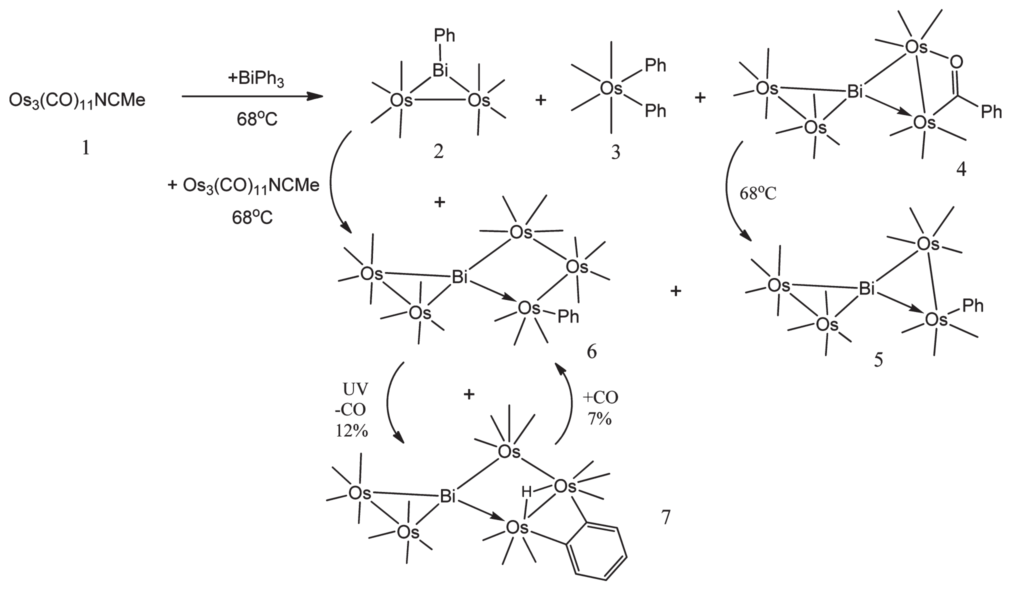


Figure 6. ORTEP diagram of the molecular structure of $HOs_5(\mu\text{-}C_6H_4)(\mu_4\text{-Bi})(CO)_{18}$, **7**, showing 30% probability thermal ellipsoids. The hydrogen atoms on the ligands are omitted for clarity. Selected interatomic bond distances (Å) and angles (deg) are as follow: Os(1)−C(2) = 2.110(11), Os(1)−Bi(1) = 2.7914(6), Os(1)−Os(2) = 3.1457(6), Os(1)−H(1) = 1.78(70), Os(2)−C(1) = 2.132(12), Os(2)−Os(3) = 2.9753(7), Os(2)−H(1) = 1.67(7), Os(3)−Bi(1) = 2.8130(6), Os(4)−Bi(1) = 2.8178(6), Os(4)−Os(5) = 2.9643(7), Os(5)−Bi(1) = 2.7682(6); C(2)−Os(1)−Bi(1) = 79.1(3), C(2)−Os(1)−Os(2) = 65.9(3), Bi(1)−Os(1)−Os(2) = 79.615(16), C(2)−Os(1)−H(1) = 89(2), Bi(1)−Os(1)−H(1) = 81(2), Os(2)−Os(1)−H(1) = 23(2), C(1)−Os(2)−Os(3) = 93.1(3), C(1)−Os(2)−Os(1) = 65.9(3), Os(3)−Os(2)−Os(1) = 91.646(17), Os(3)−Os(2)−H(1) = 87(2), Os(1)−Os(2)−H(1) = 25(2), Bi(1)−Os(3)−Os(2) = 82.298(17), Bi(1)−Os(4)−Os(5) = 57.140(15), Bi(1)−Os(5)−Os(4) = 58.765(15), Os(5)−Bi(1)−Os(1) = 124.76(2), Os(5)−Bi(1)−Os(3) = 123.01(2), Os(1)−Bi(1)−Os(3) = 103.176(19), Os(5)−Bi(1)−Os(4) = 64.095(17), Os(1)−Bi(1)−Os(4) = 119.302(19), Os(3)−Bi(1)−Os(4) = 119.41(2).

An ORTEP diagram of the structure of **7** is shown in Figure 6. Like **6**, compound **7** contains five osmium atoms divided into two groups; one group contains two metal atoms in an $Os_2(CO)_8$ group, Os(4)−Os(5) = 2.9643(7) Å, and the other three in an $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_6H_4)(\mu\text{-H})$ cluster. The Os_3 cluster is open as it was in **6** and it contains a rare example of a parallel coordinated $\mu\text{-}\eta^2\text{-}C_6H_4$ ligand across the Os(1)−Os(2) bond, Os(1)−C(2) = 2.110(11) Å, Os(2)−C(1) = 2.132(12) Å. The Os−Os bond is unusually long, Os(1)−Os(2) = 3.1457(6) Å, because of the presence of a bridging hydride ligand H(1) on the other side of this bond. Bridging hydride ligands are well-known to cause lengthening of their

Scheme 1



associated metal−metal bonds.[18] The hydride ligand in **7** was located and refined in the crystal structure analysis. As expected, it exhibits a high-field resonance shift, $\delta = -18.8$, in the ^{1}H NMR spectrum of **7**. The other Os−Os bond in the trisomium group has a normal length, Os(2)−Os(3) = 2.9753(7) Å, that is similar to that found in **6**. The Os−Bi distances to the spiro-bridging Bi ligand are similar to those in **4**−**6**, Os(1)−Bi(1) = 2.7914(6) Å, Os(3)−Bi(1) = 2.8130(6) Å, Os(4)−Bi(1) = 2.8178(6) Å and Os(5)−Bi(1) = 2.7682(6) Å. Each of the osmium atoms in **7** has an 18-electron configuration.

Discussion

A summary of the reactions and products obtained in this study are shown in the Scheme 1. The reaction of **1** with $BiPh_3$ results in the formation of five new compounds by fragmentation of the Os_3 cluster of **1** and the cleavage of phenyl rings from the $BiPh_3$. No triosmium and no $BiPh_3$ containing products were obtained. Compound **2** contains two osmium atoms and one bridging BiPh ligand while compound **3** contains only one osmium atom and two phenyl rings, presumably the same osmium atom and the two rings that were cleaved from the $BiPh_3$ in the formation of **2**, but this is not certain since the mechanism of the reaction was not confirmed in this study. It appears that **4** and **5** could be formed from **2** in some way, but we have not yet been able confirm this. We have been able to obtain **5** from **4** in a low yield by a shift of the phenyl group from the CO of the benzoyl ligand to one of the osmium atoms at the same temperature at which the original reaction was performed, so it seems likely that **4** is a precursor to **5** in the original reaction. Compound **6** appears to have been formed by a combination of **2** with an additional quantity of **1** in the original reaction mixture and that was supported by our independent synthesis of **6** and **7** from **2** and **1** under the same conditions as the original reaction of **1** with $BiPh_3$. The photodecarbonylation of **6** leads to an ortho-metalation of the σ-bonded phenyl ring to form the bridging η^2-C_6H_4 benzyne ligand and the bridging hydride ligand in **7**. Conversely, it is possible to obtain **6** in low yield (7%) together with a small amount of $Os_4(CO)_{12}(\mu\text{-}Bi_2)$[10] from **7** by heating a solution of **6** in hexane solvent to 60 °C under a slight pressure of CO (250 psi). It is anticipated that a range of new osmium−bismuth carbonyl complexes will be accessible from reactions of $BiPh_3$ with the known family of MeCN-labilized osmium carbonyl cluster complexes.[19] Further studies are in progress.

Acknowledgment. This research was supported by the USC NanoCenter and the National Science Foundation under Grant CHE-0743190 and the USC NanoCenter.

Supporting Information Available: CIF files for each of the structural analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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