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# A New Tris(diphenylstannylene)triosmium Carbonyl Cluster Complex and Its Reactions with $Pt(PBu^{t}_{3})_2$ and $Pt(PPh_3)_4$

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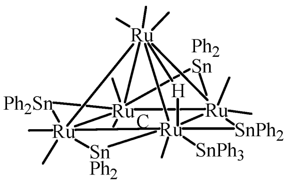
The reaction of $Os_3(CO)_{12}$ with $Ph_3SnH$ yielded the bimetallic Os−Sn cluster complexes $Os_3(CO)_{11}(SnPh_3)(\mu\text{-}H)$ (**16**) and $Os_3(CO)_9(\mu\text{-}SnPh_2)_3$ (**17**) in 20 and 21% yields, respectively. Compound **16** consists of an $Os_3$ triangle with a terminal $SnPh_3$ group on one of the Os atoms and a bridging hydrido ligand across one of the Os−Os bonds. Compound **17** consists of a central $Os_3$ triangle with $SnPh_2$ groups bridging each of the three Os−Os bonds. $Pt(PBu^{t}_{3})_2$ reacts with compound **17** to afford $Os_3(CO)_9[Pt(PBu^{t}_{3})](\mu\text{-}SnPh_2)_3$ (**18**)**,** a $Pt(PBu^{t}_{3})$ adduct of **17**, in 29% yield by adding a $Pt(PBu^{t}_{3})$ group across one of the Os−Sn bonds. The osmium and tin atoms lie in a plane, while the $Pt(PBu^{t}_{3})$ group is displaced slightly out of that plane. $Pt(PPh_3)_4$ reacts with **17** to give the cluster complex $Os_3(CO)_9[Pt(Ph)(PPh_3)_2](\mu\text{-}SnPh_2)_2(\mu_3\text{-}SnPh)$ (**19**) in 21% yield by insertion of a $Pt(PPh_3)_2$ into one of the Sn−C bonds to one of the phenyl groups. The osmium and tin atoms are coplanar, and there is a $Pt(Ph)(PPh_3)_2$ group terminally bonded to one of the tin atoms. The platinum atom of the $Pt(Ph)(PPh_3)_2$ group has a square-planar geometry with the two $PPh_3$ ligands in cis coordination sites. All new products were characterized crystallographically by single-crystal X-ray diffraction techniques.

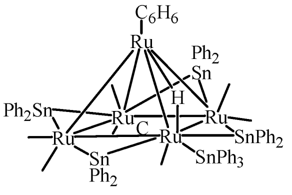
## Introduction

In recent years, bimetallic cluster complexes have been used as precursors to prepare bimetallic nanoparticles by gentle thermolysis on high-area mesoporous supports and have been shown to be superior catalysts for hydrogenation reactions.[1] Tin is often used as a modifier in bimetallic catalysts used for petroleum re-forming.[2] It is also used to enhance the activity of noble metal catalysts.[3] It has been reported that oxophilic elements such as tin can help individual nanoparticles distribute and anchor on the nanoporous supports in a firm and uniform manner.[4]

We have recently prepared some unusual new high-nuclearity ruthenium−tin cluster compounds, e.g. $Ru_5(CO)_{10}(SnPh_3)(\mu\text{-}SnPh_2)_4(\mu_5\text{-}C)(\mu\text{-}H)$ (**1**) and $Ru_5(CO)_7(SnPh_3)(\mu\text{-}SnPh_2)_4(\mu_5\text{-}C)(\mu\text{-}H)$ (**2**), from the reactions of $Ru_5(CO)_{15}(\mu_5\text{-}C)$ and $Ru_5(CO)_{15}(C_6H_6)(\mu_5\text{-}C)$ with $Ph_3SnH$, respectively.[5] Cleavage of phenyl groups from intermediates containing triphenyltin and hydrido ligands leads to the formation of $SnPh_2$ ligands by the facile formation and elimination of benzene.

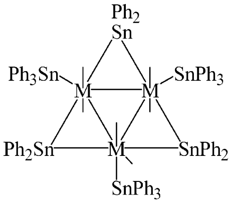


**1**

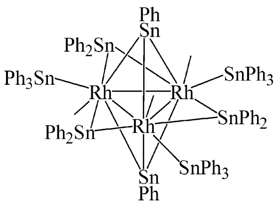


**2**

The rhodium and iridium bimetallic clusters $M_3(CO)_6(\mu\text{-}SnPh_2)_3(SnPh_3)_3$ (**3**, M = Rh; **4**, M = Ir), containing large numbers of tin ligands, were obtained from the reactions of $Ph_3SnH$ with $Rh_4(CO)_{12}$ and $Ir_4(CO)_{12}$, respectively.[6] Interestingly, compound **3** reacts further with $Ph_3SnH$ at 172 °C to give the complex $Rh_3(CO)_3(SnPh_3)_3(\mu\text{-}SnPh_2)_3(\mu_3\text{-}SnPh)_2$ (**5**), which contains two triply bridging SnPh groups.[6]



**3** M=Rh, **4** M=Ir



**5**

We have also synthesized the rhenium−tin cluster complex $Re_2(CO)_8(\mu\text{-}SnPh_2)_2$ (**6**) from the reaction of $Re_2(CO)_8[\mu\text{-}\eta^4\text{-}C(H){=}C(H)Bu^n](\mu\text{-}H)$ with $Ph_3SnH$ at 68 °C (eq 1).[7]

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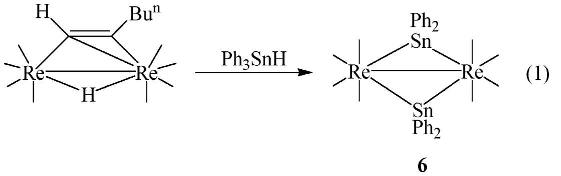
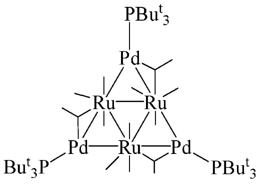
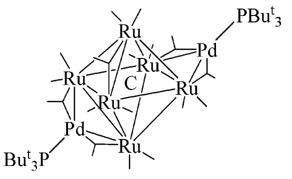


**6**

We have had much success in recent years preparing bimetallic cluster complexes of Pd and Pt by using the complexes $M(PBu^t_3)_2$ (M = Pd, Pt), which contain the bulky tri-*tert*-butylphosphine ligand, to add $M(PBu^t_3)$ groups across metal−metal bonds in polynuclear metal carbonyl cluster complexes.[8] For example, $Pd(PBu^t_3)_2$ reacts with the ruthenium carbonyl cluster complexes $Ru_3(CO)_{12}$ and $Ru_6(CO)_{17}(\mu_6\text{-}C)$ at room temperature to yield the Ru−Pd adducts $Ru_3(CO)_{12}[Pd(PBu^t_3)]_3$ (**7**) and $Ru_6(CO)_{17}(\mu_6\text{-}C)[Pd(PBu^t_3)]_2$ (**8**), respectively.[8e]

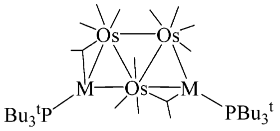


**7**

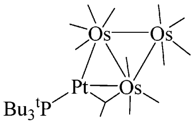


**8**

Similarly, $Pd(PBu^t_3)_2$ and $Pt(PBu^t_3)_2$ react with $Os_3(CO)_{12}$ at room temperature to yield the trimetalated triosmium complexes $Os_3(CO)_{12}[M(PBu^t_3)]_3$ (**9**, M = Pd;[9] **10**, M = Pt[10]), which are similar in structure to compound **7**. However, from the $Os_3(CO)_{12}$ reaction we were also able to isolate the dipalladium and diplatinum adducts $Os_3(CO)_{12}[M(PBu^t_3)]_2$ (**11**, M = Pd; **12**, M = Pt) as well as the monoplatinum adduct $Os_3(CO)_{12}[Pt(PBu^t_3)]$ (**13**).

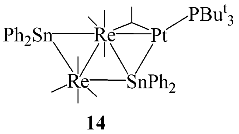


**11** M = Pd, **12** M = Pt

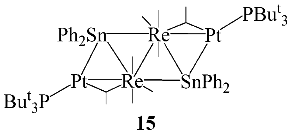


**13**

We have also shown that $M(PBu^t_3)$ groups (M = Pd, Pt) can add across heteronuclear metal−metal bonds.[11] For example, compound **6** reacts with $Pt(PBu^t_3)_2$ to yield the Re−Sn−Pt trimetallic clusters $Re_2(CO)_8(\mu\text{-}SnPh_2)[Pt(PBu^t_3)]_n$ (**14**, $n = 1$; **15**, $n = 2$).[11a]



**14**



**15**

To explore the interactions of phosphine-containing platinum groups with transition-metal−tin bonds further, we have now prepared and characterized the Os−Sn cluster complexes $Os_3(CO)_{11}(SnPh_3)(\mu\text{-}H)$ (**16**) and $Os_3(CO)_9(\mu\text{-}SnPh_2)_3$ (**17**) and investigated the reactions of **17** with $Pt(PBu^t_3)_2$ and $Pt(PPh_3)_4$. The results of this study are reported here.

## Experimental Section

**General Considerations.** All the reactions were performed under a nitrogen atmosphere using Schlenk techniques. Reagent-grade solvents were dried by standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on an AVATAR 360 FT-IR spectrophotometer. $^1H$ NMR and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Mercury 400 spectrometer operating at 400 and 162 MHz, respectively. $^{31}P\{^1H\}$ NMR spectra were externally referenced against 85% ortho-$H_3PO_4$. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Mass spectrometric measurements performed by direct exposure probe using electron impact ionization (EI) were made on a VG 70S instrument. $Ph_3SnH$ was purchased from Aldrich, and $Pt(PBu^t_3)_2$ and $Pt(PPh_3)_4$ were purchased from Strem, and they were used without further purification. $Os_3(CO)_{12}$ was prepared according to the previously reported procedure.[12] Product separations were performed by TLC in air on Analtech 0.25 and 0.5 mm silica gel 60 Å $F_{254}$ glass plates.

**Preparation of $Os_3(CO)_{11}(SnPh_3)(\mu\text{-}H)$ (16) and $Os_3(CO)_9(\mu\text{-}SnPh_2)_3$ (17).** A 26.0 mg amount of $Os_3(CO)_{12}$ (0.029 mmol) was dissolved in 12 mL of xylene in a 50 mL three-neck flask. A 39.5 mg amount of $Ph_3SnH$ (0.11 mmol) was then added, and the solution was heated to reflux for 60 min. The solvent was removed in vacuo, and the product was purified by TLC by using a 7:1 hexane−methylene chloride solvent mixture to yield, in order of elution, 9.9 mg (21% yield) of **17** and 7.1 mg (20% yield) of **16**. Spectral data for **16**: IR $\nu_{CO}$ (cm$^{-1}$ in $CH_2Cl_2$) 2136 (m), 2083 (vs), 2054 (vs), 2031 (w), 2019 (m), 2002 (s), 1967 (w); $^1H$ NMR (in $CDCl_3$) $\delta$ 7.29−7.58 (m, 15H, Ph), −18.59 (s, 1H, hydride, $^2J_{Sn-H} = 29$ Hz); EI-MS showed the parent ion at $m/z$ 1230, and the observed isotope pattern is exactly the same as theoretical isotope pattern, with ions corresponding to loss of one phenyl group followed by the loss of each of the 11 CO ligands also being prominently displayed. Spectral data for **17**: IR $\nu_{CO}$ (cm$^{-1}$ in $CH_2Cl_2$) 2050 (m), 2014 (s), 1985 (m). Anal. Calcd: C, 32.91; H, 1.83. Found: C, 32.97; H, 2.09.

**Preparation of $Os_3(CO)_9[Pt(PBu^t_3)](\mu\text{-}SnPh_2)_3$ (18).** A 10 mg amount of **17** (0.0074 mmol) was dissolved in 25 mL of hexane in a 50 mL three-neck flask. A 11 mg amount of $Pt(PBu^t_3)_2$ was added, and the solution was heated to reflux for 45 min. The solvent was removed in vacuo, and the product was purified by TLC using a 6:1 hexane−methylene chloride solvent mixture to yield 3.6 mg (29%) of **18**. Spectral data for **18**: IR $\nu_{CO}$ (cm$^{-1}$ in hexane) 2106 (vw), 2083 (w), 2046 (m), 2036 (w), 2009 (s), 1985 (w), 1978 (m), 1791 (vw, br); $^1H$ NMR (in $CDCl_3$) $\delta$ 1.27 (d, 27H, $CH_3$, $^3J_{P-H} = 13$ Hz); $^{31}P\{^1H\}$ NMR (in $CDCl_3$) $\delta$ 117.2 (s, 1P, $^1J_{Pt-P} = 5830$ Hz, $^2J_{Sn-P} = 97$ Hz). Anal. Calcd: C, 33.56; H, 2.80. Found: C, 33.70; H, 2.78.

**Preparation of $Os_3(CO)_9[Pt(Ph)(PPh_3)_2](\mu\text{-}SnPh_2)_2(\mu_3\text{-}SnPh)$ (19).** An 11 mg amount of **17** (0.0067 mmol) was dissolved in 15 mL of $CH_2Cl_2$ in a 50 mL three-neck flask to which 25 mg of $Pt(PPh_3)_4$ (0.020 mmol) was added. The solution was heated to reflux for 30 min, and the solvent was removed in vacuo. The product was purified by TLC by using a 6:1 hexane−methylene chloride solvent mixture to yield 3.4 mg (21%) of **19**. Spectral data for **19**: IR $\nu_{CO}$ (cm$^{-1}$ in hexane) 2051 (w), 2045 (m), 2036 (w), 2016 (m), 2007 (s), 1987 (w), 1979 (m), 1969 (w); $^{31}P\{^1H\}$ NMR

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**Table 1. Crystallographic Data for Compounds 16−19**

| | 16 | 17 | 18 | 19 |
|---|---|---|---|---|
| empirical formula | $Os_3SnO_{11}C_{29}H_{16}$ | $Os_3Sn_3O_9C_{45}H_{30}$ | $PtOs_3Sn_3PO_9C_{61}H_{66}$ | $PtOs_3Sn_3P_2O_9C_{81}H_{60}\cdot 2Et_2O$ |
| formula wt | 1229.71 | 1641.36 | 2095.87 | 2509.23 |
| cryst syst | triclinic | monoclinic | triclinic | monoclinic |
| lattice params | | | | |
| $a$ (Å) | 9.0694(2) | 24.8866(11) | 13.6850(6) | 13.5555(4) |
| $b$ (Å) | 16.4421(4) | 16.4500(7) | 13.7194(6) | 23.8225(6) |
| $c$ (Å) | 23.2581(6) | 25.8650(11) | 19.6270(8) | 28.7065(8) |
| $\alpha$ (deg) | 71.65 | 90 | 84.2250(10) | 90 |
| $\beta$ (deg) | 81.1030(10) | 117.6930(10) | 82.0030(10) | 112.2750(10) |
| $\gamma$ (deg) | 85.3170(10) | 90 | 62.7160(10) | 90 |
| $V$ (Å$^3$) | 3250.31(14) | 9375.8(7) | 3240.3(2) | 9058.1(4) |
| space group | $P\bar{1}$ | $P2_1/n$ | $P\bar{1}$ | $P2_1/n$ |
| $Z$ | 4 | 8 | 2 | 4 |
| $\rho_{calcd}$ (g/cm$^3$) | 2.513 | 2.326 | 2.148 | 1.840 |
| $\mu$(Mo K$\alpha$) (mm$^{-1}$) | 12.505 | 9.724 | 9.220 | 6.632 |
| temp (K) | 294(2) | 294(2) | 293(2) | 294(2) |
| $2\theta_{max}$ (deg) | 56.6 | 56.6 | 56.6 | 52.0 |
| no. of observns ($I > 2\sigma(I)$) | 11 954 | 15 662 | 12 108 | 11 459 |
| no. of params | 751 | 1081 | 712 | 932 |
| goodness of fit | 1.007 | 1.000 | 1.040 | 1.021 |
| max shift in cycle | 0.003 | 0.002 | 0.001 | 0.001 |
| residuals:[a] R1; wR2 | 0.0322; 0.0769 | 0.0408; 0.0906 | 0.0415; 0.1047 | 0.0456; 0.0898 |
| abs cor | SADABS | SADABS | SADABS | SADABS |
| max/min abs | 1.000/0.422 | 1.000/0.431 | 1.000/0.648 | 1.000/0.593 |
| largest peak in final diff map (e/Å$^3$) | 1.999 | 1.836 | 2.204 | 1.696 |

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

(in $CDCl_3$) $\delta$ 34.8 (d, 1P, $^1J_{Pt-P} = 2415$ Hz, $^2J_{P-P} = 15.8$ Hz), 15.5 (s, 1P, $^1J_{Pt-P} = 2125$ Hz, $^2J_{P-P} = 15.8$ Hz). Anal. Calcd: C, 41.49; H, 2.54. Found: C, 42.01; H, 2.50.

**Thermal Treatment of 19.** A 8.3 mg amount of **19** (0.0035 mmol) was dissolved in 20 mL of heptane in a 50 mL three-neck flask, and the solution was heated to reflux for 1 h. The solvent was removed in vacuo. The product was purified by TLC by using a 6:1 hexane−methylene chloride solvent mixture to yield 3.0 mg (52%) of **17**.

**Detection of Benzene in the Preparation of 17.** A 10.0 mg amount of $Os_3(CO)_{12}$ (0.011 mmol) and a 35.1 mg amount of $Ph_3SnH$ (0.098 mmol) were dissolved in 2 mL of toluene-$d_8$. $^1H$ NMR of this solution showed multiple resonances in the region $\delta$ 7.07−7.64, corresponding to the protons on the phenyl rings, and a resonance at $\delta$ 7.134. The solution was then sealed in a stainless steel Parr pressure reactor and placed in an oil bath at 140 °C for 1 h. The Parr reactor was then cooled to room temperature. $^1H$ NMR of the reaction mixture showed that the resonance at $\delta$ 7.134 had greatly increased in intensity, indicating the formation of benzene during the course of the reaction.

**Crystallographic Analysis.** Yellow single crystals of **16** suitable for diffraction analysis were grown by slow evaporation of solvent from a $CH_2Cl_2$/hexane solution at 8 °C. Orange single crystals of **17** and red single crystals of **18** suitable for diffraction analysis were grown by slow evaporation of solvent from a benzene/octane solution at 8 °C. Dark orange single crystals of **19** suitable for diffraction analysis were grown by slow evaporation of solvent from a diethyl ether solution at −25 °C. Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity data were measured using a Bruker SMART APEX CCD-based diffractometer using Mo K$\alpha$ radiation ($\lambda = 0.710\,73$ Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.[13] Corrections for the Lorentz and polarization effects were also applied by SAINT. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied by using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier synthesess and refined by full-matrix least squares on $F^2$, by using the SHELXTL software package.[14] Crystal data, data collection parameters, and results of the analyses for compounds are given in Table 1.

Compounds **17** and **19** crystallized in the monoclinic crystal system. For both compounds the systematic absences in the intensity data were consistent with the space group $P2_1/n$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Two molecules of diethyl ether from the crystallization solvent cocrystallized with compound **19**. The two diethyl ether molecules were modeled using three geometric restraints. The solvent molecules were included in the analysis and were refined with isotropic thermal parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms.

Compounds **16** and **18** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure in each case. For compound **16**, there are two independent formula equivalents of the complex present in the asymmetric unit. All non-hydrogen atoms except for C91−C146 were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms. The hydrido ligand was allocated and refined satisfactorily. The three phenyl rings (C91−C146) in one of the two molecules were each disordered over two orientations and were satisfactorily refined in the ratio 50:50. Atoms of these rings were refined with a common isotropic thermal parameter. For compound **18**, all non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms.

## Results and Discussion

The reaction of $Os_3(CO)_{12}$ with $Ph_3SnH$ at 140 °C provided the compounds $Os_3(CO)_{11}(SnPh_3)(\mu\text{-}H)$ (**16**) and $Os_3(CO)_9(\mu\text{-}SnPh_2)_3$ (**17**) in 20 and 21% yields, respectively (see eq 2). Compound **16** was obtained previously in a better yield from the reaction of $Os_3(CO)_{11}(NCMe)$ with $Ph_3SnH$ at room temperature.[15] We have performed a single crystal X-ray

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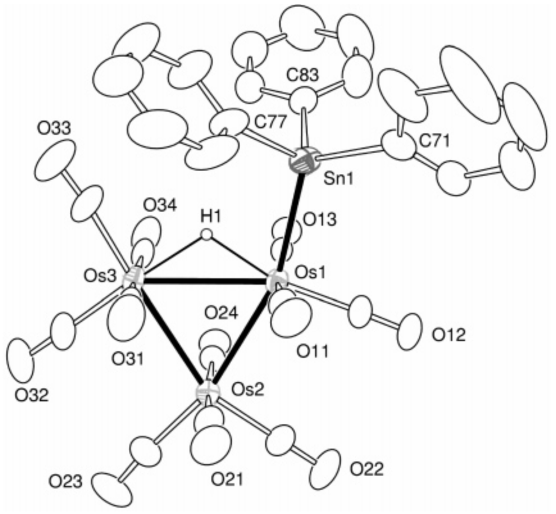
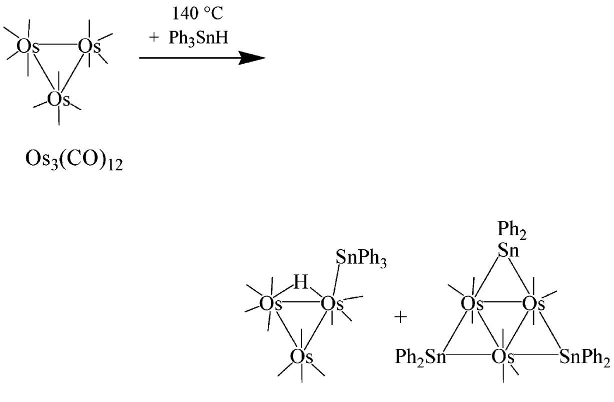


**Figure 1.** ORTEP diagram of $Os_3(CO)_{11}(SnPh_3)(\mu\text{-}H)$ (**16**) showing 30% probability thermal ellipsoids. Selected interatomic distances (Å): molecule 1, Os(1)−Os(2) = 2.8714(4), Os(2)−Os(3) = 2.9171(4), Os(1)−Os(3) = 3.0155(3), Os(1)−Sn(1) = 2.6949(6), Os(1)−H(1) = 1.79(6), Os(3)−H(2) = 1.86(6); molecule 2, Os(4)−Os(5) = 3.0080(3), Os(5)−Os(6) = 2.9055(3), Os(4)−Os(6) = 2.8804(3), Os(4)−Sn(2) = 2.7056(4), Os(4)−H(2) = 1.74(9), Os(5)−H(2) = 1.94(9).

diffraction analysis of **16**. An ORTEP diagram of the molecular structure of **16** is shown in Figure 1. Selected intramolecular distances are listed in the caption to Figure 1. There are two independent molecules in the asymmetric unit in this crystal of **16**, and both molecules are structurally similar. Compound **16** was formed by a loss of one CO ligand from the $Os_3(CO)_{12}$ group and the oxidative addition of 1 equiv of $Ph_3SnH$ at the Sn−H bond. The compound consists of an $Os_3$ triangle with one $SnPh_3$ group bonded terminally to one osmium atom, Os(1). It also contains one hydrido ligand (located and refined crystallographically) that bridges the osmium−osmium bond next to the $SnPh_3$ ligand. Further evidence for the hydrido ligand was obtained in its $^1$H NMR spectrum, which exhibits a high-field resonance at $\delta$ −18.59, showing appropriate coupling to tin: $^2J_{Sn-H}$ = 29 Hz. The hydride-bridged Os−Os bond (molecule 1, Os(1)−Os(3) = 3.0155(3) Å; molecule 2, Os(4)−Os(5) = 3.0080(3) Å) is significantly longer than the non-hydride-bridged Os−Os bonds (molecule 1, Os(1)−Os(2) = 2.8714(4) Å and Os(2)−Os(3) = 2.9171(4) Å; molecule 2, Os(5)−Os(6) = 2.9055(3) Å and Os(4)−Os(6) = 2.8804(3) Å). This is due to bond-lengthening effects caused by the presence of bridging hydride ligands.[16]



(2)

**16** **17**

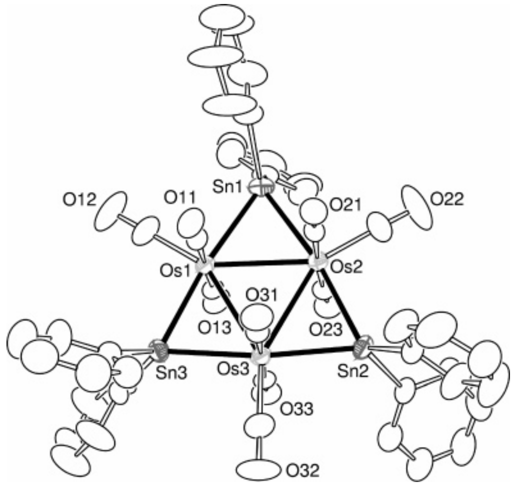


**Figure 2.** ORTEP diagram of $Os_3(CO)_9(\mu\text{-}SnPh_2)_3$ (**17**) showing 30% probability thermal ellipsoids. Selected interatomic distances (Å): Os(1)−Os(2) = 2.9629(4), Os(1)−Os(3) = 2.9572(4), Os(1)−Sn(1) = 2.6787(6), Os(1)−Sn(3) = 2.6645(6), Os(2)−Os(3) = 2.9906(4), Os(2)−Sn(1) = 2.6664(6), Os(2)−Sn(2) = 2.6740(6), Os(3)−Sn(2) = 2.6483(6), Os(3)−Sn(3) = 2.6665(6).

The Os−Sn bond distances, Os(1)−Sn(1) = 2.6949(6) Å and Os(4)−Sn(2) = 2.7056(4) Å, are similar to those found in the compound $Os_3(CO)_{10}(SnMe_3)_2(\mu\text{-}H)_2$, Os−Sn = 2.726(5) and 2.696(4) Å, which was obtained from the reaction of $Os_3(CO)_{10}(\mu\text{-}H)_2$ with $Me_3SnH$.[17] Compound **16** contains 48 cluster valence electrons; therefore, each osmium atom formally has an 18-electron configuration.[18]

Compound **17** was characterized by a combination of IR, NMR, single-crystal X-ray diffraction, and elemental analysis. An ORTEP diagram of the molecular structure of **17** is shown in Figure 2. Selected intramolecular distances are listed in the caption to Figure 2. The structure of **17** consists of a central triosmium triangle with a $SnPh_2$ ligand bridging each of the three Os−Os bonds. Each of the osmium atoms has three terminal carbonyl ligands. All of the Sn atoms lie in the plane defined by the $Os_3$ triangle. The arrangement of the six metal atoms can be described best as a planar “raft” structure. Compound **17** is structurally very similar to the compound $Os_3(CO)_9(\mu\text{-}SnMe_2)_3$ (**20**) reported by Pomeroy.[19] All three Os−Os bonds in **17** are significantly longer (Os(1)−Os(2) = 2.9629(4) Å, Os(1)−Os(3) = 2.9572(4) Å, and Os(2)−Os(3) = 2.9906(4) Å) than that found in $Os_3(CO)_{12}$ (2.877(3) Å), which has no bridging ligands, but are similar to that found in **20** (Os(1)−Os(2) = 2.974(1) Å).[20] We found recently that the Rh−Rh bonds in **3** are also unusually long.[6] This was attributed to the presence of strong Rh−Sn bonding. The Os−Sn bond distances in **17** lie in the range 2.6483(6)−2.6787(6) Å and are similar to those found to the bridging $SnMe_2$ groups in **20** (2.667(1)−2.673(11) Å).[19] Compound **17** also contains 48 cluster valence electrons, with each osmium atom having an 18-electron configuration.[18]

The mechanism for the formation of **17** is believed to be similar to that proposed for the formation of the high-nuclearity Ru−Sn cluster complexes **1** and **2**. That was shown to involve species containing triphenyltin and hydrido ligands (just as in

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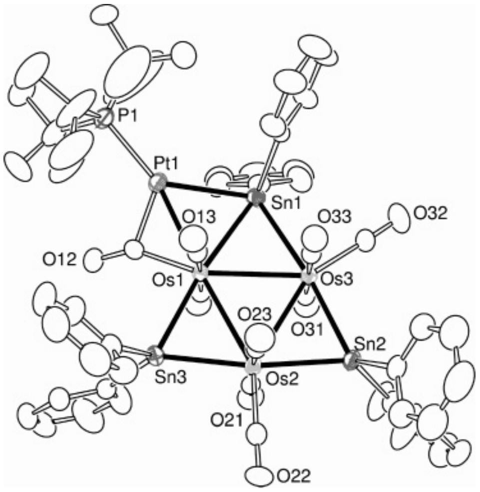
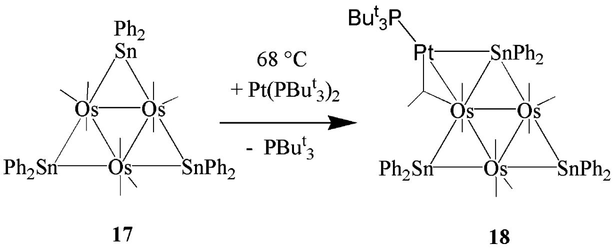


**Figure 3.** ORTEP diagram of $Os_3(CO)_9[Pt(PBu^t_3)](\mu\text{-}SnPh_2)_3$ (**18**) showing 30% probability thermal ellipsoids. Selected interatomic distances (Å): Pt(1)−Os(1) = 2.7474(4), Pt(1)−Sn(1) = 2.7757(6), Os(1)−Os(2) = 2.9829(4), Os(1)−Os(3) = 2.9538(4), Os(1)−Sn(1) = 2.6992(5), Os(1)−Sn(3) = 2.6631(5), Os(2)−Os(3) = 2.9829(4), Os(2)−Sn(2) = 2.6835(5), Os(2)−Sn(3) = 2.6504(5), Os(3)−Sn(1) = 2.7079(6), Os(3)−Sn(2) = 2.6407(6).

compound **16**) formed by oxidative addition of the Sn−H bond of $Ph_3SnH$ to the metal atoms of the cluster. This was followed by cleavage of a phenyl group from the $SnPh_3$ ligand, combination of the phenyl group with a hydrido ligand, and reductive elimination of benzene and formation of a bridging $SnPh_2$ ligand.[5] The formation of benzene was observed by $^1H$ NMR in the reaction of $Os_3(CO)_{12}$ with $Ph_3SnH$. Between the two compounds **16** and **17**, compound **17** is more interesting with respect to the fact that it has more Os−Sn bonds. Hence, to investigate the interactions of phosphine-containing platinum groups with transition-metal−tin bonds, we carried out the reactions of $Pt(PBu^t_3)_2$ and $Pt(PPh_3)_4$ with **17**.

Compound **18** was obtained in 29% yield from the reaction of **17** with $Pt(PBu^t_3)_2$ at 68 °C (see eq 3). Compound **18** was characterized by a combination of IR, $^1H$ and $^{31}P$ NMR, single-crystal X-ray diffraction, and elemental analyses. An ORTEP diagram of the molecular structure of **18** is shown in Figure 3. Selected intramolecular distances for **18** are listed in the caption to Figure 3.



(3)

**17** **18**

Compound **18** retains the structure of the $Os_3Sn_3$ core of the cluster found in **17** but includes a $Pt(PBu^t_3)$ group that bridges one of the Os−Sn bonds (Pt(1)−Os(1) = 2.7474(4) Å, Pt(1)−Sn(1) = 2.7757(6) Å). A carbonyl group from Os(1) has formed a bridging interaction across the Pt−Os bond. Compound **18** can be viewed as a monoplatinum adduct of compound **17**, as there was no loss of a carbonyl group from the starting cluster **17**. The $^{31}P\{^1H\}$ NMR spectrum for **18** appropriately shows one-bond coupling to platinum ($^1J_{Pt-P}$ = 5830 Hz) and two-bond coupling to Sn(1) ($^2J_{Sn-P}$ = 97 Hz). The Os and Sn atoms all lie in the same plane, while the platinum atom is displaced out of the plane by 0.5690(7) Å. The Os(1)−Pt(1) bond distance (2.7474(4) Å) is shorter than the similar carbonyl-bridged Os−Pt bonds in compounds **10**, **12**, and **13** (range 2.7929(9)−2.8527(6) Å). This could be because the $Pt(PBu^t_3)$ group is bonded to only one osmium atom instead of two, as found in **10**, **12**, and **13**, and the Pt−Sn interaction in **18** is weak. The Pt(1)−Sn(1) distance (2.7757(6) Å) in **18** is significantly longer than the Pt−Sn distance found in the compound $HPt(PPh_3)_2(SnPh_3)$ (2.564(1) Å)[21] but is still consistent with a significant Pt−Sn interaction. It is similar to the Pt−Sn bond distances found in **14** and **15** (2.7505(8) and 2.8166(4) Å).[7]

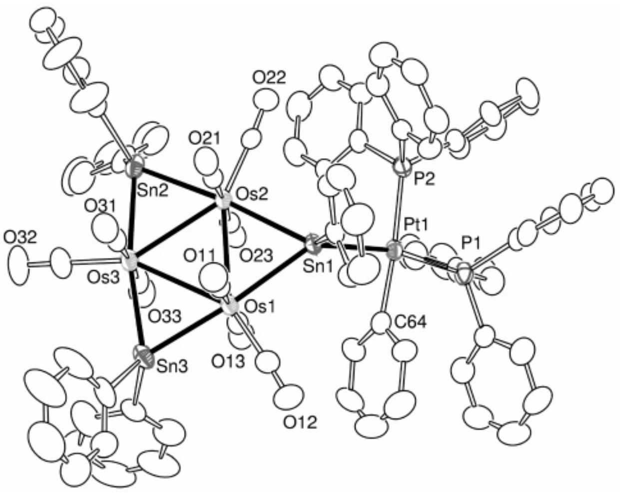
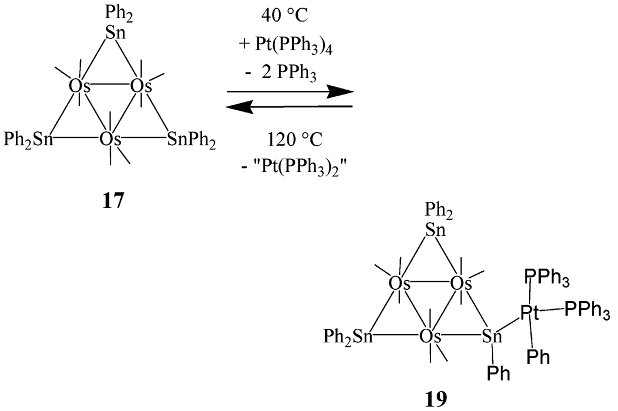


**Figure 4.** ORTEP diagram of $Os_3(CO)_9[Pt(Ph)(PPh_3)_2](\mu\text{-}SnPh_2)_2(\mu_3\text{-}SnPh)$ (**19**) showing 30% probability thermal ellipsoids. Selected interatomic distances (Å): Pt(1)−Sn(1) = 2.6298(6), Os(1)−Os(2) = 2.9247(5), Os(1)−Os(3) = 3.0033(5), Os(1)−Sn(1) = 2.7703(6), Os(1)−Sn(3) = 2.6501(7), Os(2)−Os(3) = 3.0036(5), Os(2)−Sn(1) = 2.7637(6), Os(2)−Sn(2) = 2.6537(7), Os(3)−Sn(2) = 2.6582(8), Os(3)−Sn(3) = 2.6680(8).

Compound **17** reacts with $Pt(PPh_3)_4$ at 40 °C to afford $Os_3(CO)_9[Pt(Ph)(PPh_3)_2](\mu\text{-}SnPh_2)_2(\mu_3\text{-}SnPh)$ (**19**) in 21% yield (see eq 4). Compound **19** was characterized by a combination of IR, $^1H$ and $^{31}P$ NMR, single-crystal X-ray diffraction, and elemental analyses. An ORTEP diagram of the molecular structure of **19** is shown in Figure 4. Selected intramolecular distances for **19** are listed in the caption to Figure 4.



**17**

(4)

**19**

Compound **19** contains a planar $Os_3Sn_3$ cluster with nine carbonyl ligands arranged just as in **17** and **18**. A $Pt(PPh_3)_2$ group was added to **17** to form **19**, but unlike the formation of **18**, the platinum atom was inserted into one of the Sn−C bonds

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to one of the phenyl groups of one of the bridging $SnPh_2$ ligands. That phenyl group is bonded only to the platinum atom, and the platinum atom is bonded directly to the tin atom Sn(1) (Pt(1)−Sn(1) = 2.6298(6) Å). Including the two phosphine ligands, the platinum atom has four substituents. Its coordination geometry is approximately square planar. Surprisingly, the two bulky $PPh_3$ ligands occupy cis coordination sites. Because of the large size, the angle between the $PPh_3$ ligands at the Pt atom is significantly greater than 90° (P(1)−Pt(1)−P(2) = 97.75(9)°). The two phosphorus ligands are inequivalent, and as expected, the $^{31}P\{^1H\}$ NMR spectrum shows two resonances at $\delta$ 34.8 ($^1J_{Pt-P}$ = 2415 Hz, $^2J_{P-P}$ = 15.8 Hz) and $\delta$ 15.5 ($^1J_{Pt-P}$ = 2125 Hz, $^2J_{P-P}$ = 15.8 Hz) with appropriate coupling to $^{195}Pt$ and $^{31}P$. The platinum atom lies out of the $Os_3Sn_3$ plane by 1.562(1) Å. Attempts to produce additional transformations of **19** were performed by heating a solution in heptane to reflux for 1 h, but surprisingly the principal product was simply its precursor **17** (52% yield), indicating that the insertion of $Pt(PPh_3)_2$ into the Sn−C bond is largely reversible. Pidcock and Schubert have shown that Pt(phosphine) groups can be readily inserted into Sn−C bonds, but they did not report on their reversibility.[22]

The main difference between the reactions of $Pt(PBu^t_3)_2$ and $Pt(PPh_3)_4$ with **17** is that $Pt(PBu^t_3)_2$ loses one $PBu^t_3$ ligand and adds a $Pt(PBu^t_3)$ group across one of the Os−Sn bonds, but while $Pt(PPh_3)_4$ loses two $PPh_3$ ligands, it still retains two $PPh_3$ ligands coordinated to the Pt atom and is thus more sterically crowded than a $Pt(PBu^t_3)$ group. The $Pt(PPh_3)_2$ group probably cannot fit comfortably into the area required to form a sufficiently strong bonding interaction across an Os−Sn bond in **17**, so instead it attacks the Sn−C bond to one of the phenyl rings and inserts into it (a known reaction pathway) to yield the less crowded planar $Pt(PPh_3)_2Ph$ grouping that remains bonded to the Sn atom.

## Summary

The mono(triphenylstannylane)triosmium hydrido carbonyl cluster **16** and tris(diphenylstannylene)triosmium carbonyl cluster complex **17** have been synthesized and structurally characterized. Compound **17** was shown to react with $Pt(PBu^t_3)_2$ by adding a $Pt(PBu^t_3)$ group across one of the Os−Sn bonds to a bridging $SnPh_2$ ligand in **17**, but a similar reaction of **17** with $Pt(PPh_3)_4$ leads instead to insertion of a $Pt(PPh_3)_2$ group into the Sn−C bonds of one of the phenyl rings of one of the bridging $SnPh_2$ groups. Interestingly, the insertion reaction is reversible.

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**Supporting Information Available:** CIF files are given 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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