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Article

Addition of $Pt(PBu^t_3)$ to Osmium–Tin Cluster Complexes

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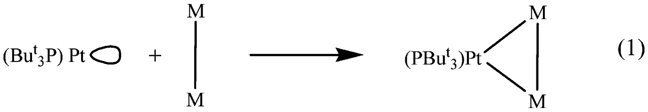
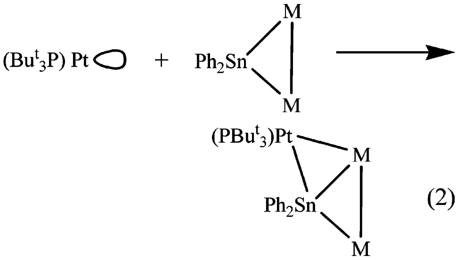
The reactions of the osmium–tin cluster complexes $Os_3(CO)_{12}(\mu_3\text{-}SnPh)Ph$, **9**, and $Os_4(CO)_{16}(\mu_4\text{-}Sn)$, **10**, with $Pt(PBu^t_3)_2$ have been investigated. Two products, $PtOs_3(CO)_{12}(Ph)(PBu^t_3)(\mu_3\text{-}SnPh)$, **11**, and $Pt_2Os_3(CO)_{12}(\mu_2\text{-}Ph)(PBu^t_3)_2(\mu_3\text{-}SnPh)$, **12**, were obtained from the reaction of **9** with $Pt(PBu^t_3)_2$. These are mono- and bis-$Pt(PBu^t_3)$ adducts of **9** formed by the addition of a $Pt(PBu^t_3)$ group to the Os–Os bond in **11** and the Os–Os bond and Os–C bond to the σ-bonded phenyl group in **12**. A PBu^t_3 derivative of **11**, $Os_2(CO)_8(\mu_3\text{-}SnPh)Os(CO)_3(PBu^t_3)Ph$, **13**, was obtained by treating **12** with PBu^t_3. The reaction of **10** with $Pt(PBu^t_3)_2$ provided the bis-$Pt(PBu^t_3)$ adduct $Os_4(CO)_{16}[Pt(PBu^t_3)]_2(\mu_4\text{-}Sn)$, **14**, that was formed by the addition of a $Pt(PBu^t_3)$ group across the Os–Os bond of both $Os_2(CO)_8$ groups in **10**. All four new compounds **11**–**14** were characterized by single-crystal X-ray diffraction analysis.

Introduction

In recent studies, we have shown that the $Pt(PBu^t_3)$ group is readily added to the bonds between transition metals in polynuclear metal carbonyl cluster complexes (eq 1).[1−6] An empty orbital on the platinum atom shares the pair of electrons between the two metal atoms (M) to form a delocalized three-center two-electron bond. Some examples of these $Pt(PBu^t_3)$ adducts are the compounds $Os_3(CO)_{12}[Pt(PBu^t_3)]_n$, **1**−**3**, $n = 1-3$.[1] Multiple additions of the $Pt(PBu^t_3)$ group are frequently observed, as found in the compounds **2** and **3** and the compounds $Ru_6(CO)_{17}(\mu_6\text{-}C)[Pt(PBu^t_3)]_2$, **4**,[2a] $Pt_2Ir_4(CO)_{12}(PBu^t_3)_2$, **5**,[4] and $Rh_6(CO)_{16}[Pt(PBu^t_3)]_4$, **6**[6] (see Chart 1).


(1)

We have also shown that the $Pt(PBu^t_3)$ group is readily added to the transition metal−tin and transition metal−germanium bonds in polynuclear metal carbonyl cluster complexes that contain phenyltin and phenylgermanium bonds (eq 2).[7] For example, $Re_2(CO)_8(\mu\text{-}SnPh_2)_2$ adds one and two $Pt(PBu^t_3)$ groups to form the compounds $Re_2(CO)_8(\mu\text{-}SnPh_2)_2[Pt(PBu^t_3)]_n$, **7**, and **8**, $n = 1,2$ (eq 3). Tin has recently been shown to be a useful modifier of heterogeneous nanoscale hydrogenation catalysts of the platinum group metals when placed on mesoporous supports.[8−9]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We have recently reported the synthesis of the osmium carbonyl cluster complexes $Os_3(CO)_{12}(\mu_3\text{-}SnPh)Ph$, **9**,

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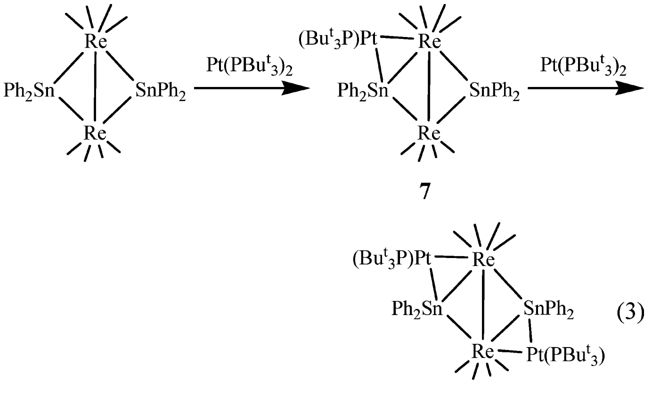

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(3)

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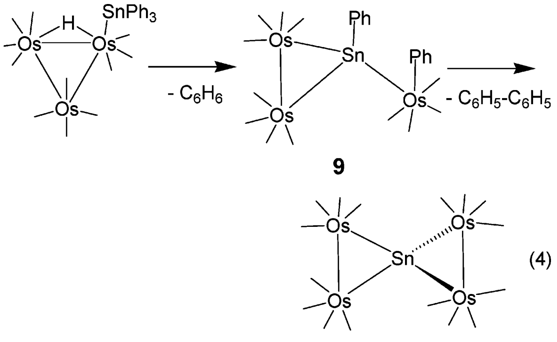
and $Os_4(CO)_{16}(\mu_4\text{-}Sn)$, **10**, that contain both Os−Os bonds and Os−Sn bonds from the thermal transformations of $HOs_3(CO)_{11}SnPh_3$ (eq 4).[10]



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(4)

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To try to establish the binding selectivity of the $Pt(PBu^t_3)$ group for Os−Os or Os−Sn bonds, we have now investigated the reactions of **9** and **10** with $Pt(PBu^t_3)_2$. The results of this study are reported here.

Experimental Section

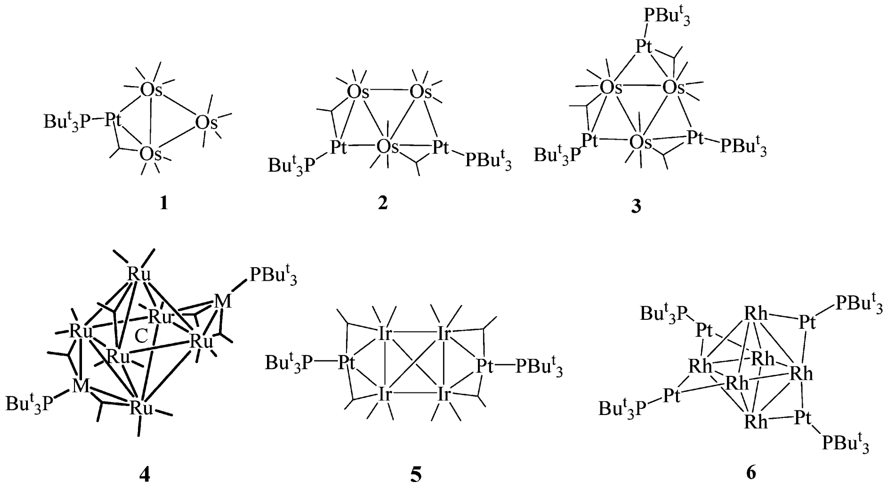
General Data. All the reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on an AVATAR 360 FTIR spectrophotometer. ^1H NMR and ^{31}P {^1H} NMR were recorded on a Varian Mercury 400 spectrometer operating at 400.1 and 161.9 MHz, respectively. ^{31}P {^1H} NMR spectra were externally referenced against 85% $o\text{-}H_3PO_4$. Electrospray mass spectrometric measurements were obtained on a MicroMass Q-TOF spectrometer. $Os_3(CO)_{12}(Ph)(\mu_3\text{-}SnPh)$, **9**, and $Os_4(CO)_{16}(\mu_4\text{-}Sn)$, **10**, were prepared as previously reported.[10] $Pt(PBu^t_3)_2$ was purchased from STREM and was used without further purification. Product separations were performed by TLC in air on Analtech 0.25 and 0.5 mm silica gel 60 Å F_{254} glass plates. Elemental analyses were performed by Desert Analytics, Tuscon, AZ.

Preparation of $PtOs_3(CO)_{12}(PBu^t_3)(Ph)(\mu_3\text{-}SnPh)$ (11) and $Pt_2Os_3(CO)_{12}(PBu^t_3)_2(\mu_2\text{-}Ph)(\mu_3\text{-}SnPh)$ (12). A 15 mg amount of **9** (0.013 mmol) was dissolved in 15 mL of CH_2Cl_2 solvent in a 50 mL three-neck flask. A 7.6 mg amount of $Pt(PBu^t_3)_2$ (0.013 mmol) was added, and the reaction continued at room temperature for 30 min. The solvent was removed in vacuo, and the products were isolated by TLC by using a 6:1 hexane−methylene chloride solvent mixture to yield (in order of elution) 8.8 mg of orange **11** (44% yield) and 2.3 mg of dark orange **12** (9% yield). Spectral data for **11**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2123 (m), 2084 (w), 2054 (s), 2007 (s), 1972 (m), 1838 (m), 1799 (m). ^1H NMR (in $CDCl_3$): δ = 1.49 (d, 27 H, CH_3, $^3J_{P-H}$ = 13 Hz). $^{31}P\{^1H\}$ NMR (in $CDCl_3$): δ = 124.7 (s, 1 P, $^1J_{Pt-P}$ = 5005 Hz). Anal. Calcd: C, 27.40; H, 2.35%. Found: C, 27.52; H, 1.73%. Spectral data for **12**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2094 (w), 2075 (w), 2050 (m), 2017 (s), 1997 (m), 1966 (m), 1829 (m), 1792 (m). ^1H NMR (in $CDCl_3$): δ = 1.37 (d, 27 H, CH_3, $^3J_{P-H}$ = 13 Hz), 1.09 (d, 27 H, CH_3, $^3J_{P-H}$ = 13 Hz). $^{31}P\{^1H\}$ NMR (in $CDCl_3$): δ = 125.9 (s, 1 P, $^1J_{Pt-P}$ = 4995 Hz), 102.7 (s, 1 P, $^1J_{Pt-P}$ = 6630 Hz). Anal. Calcd: C, 29.19; H, 3.24%. Found: C, 29.97; H, 3.90%.

Improved Yield of 12. A 11 mg amount of $Os_3(CO)_{12}(Ph)(\mu_3\text{-}SnPh)$ (0.0089 mmol) and 21.3 mg of $Pt(PBu^t_3)_2$ (0.356 mmol) were dissolved in 15 mL of CH_2Cl_2 solvent 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 2.1 mg of **11** (15% yield) and 7.0 mg of **12** (40% yield).

Conversion of 11 to 12. A 8.5 mg amount of **11** (0.0054 mmol) was dissolved in 15 mL of CH_2Cl_2 solvent in a 50 mL three-neck flask, and a 6.5 mg amount of $Pt(PBu^t_3)_2$ (0.011 mmol) was added. The solution was heated to reflux for 1 h, and the solvent was then removed in vacuo. The products were separated by TLC by using

Chart 1



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a 6:1 hexane−methylene chloride solvent mixture to yield 4.0 mg of **12** (38% yield).

Preparation of $PtOs_3(CO)_{11}(PBu^t_3)_2(Ph)(\mu_3\text{-}SnPh)$ (13). A 5.0 μL amount (0.0200 mmol) of PBu^t_3 was added to a solution of 7.6 mg of **12** (0.0038 mmol) in 15 mL of CH_2Cl_2 solvent. The solution was stirred at room temperature for 15 min, and the solvent was then removed in vacuo. The products were separated by TLC by using a 6:1 hexane−methylene chloride solvent mixture to yield (in order of elution) 1.8 mg of **11** (30% yield) and 1.0 mg of **13** (15% yield). Spectral data for **13**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2052 (m), 2011 (s), 1978 (m), 1830 (m), 1792 (m). ^{1}H NMR (in CD_2Cl_2): $\delta = 7.65-7.69$ and $6.78-7.08$ (m, 10 H, Ph), 1.50 (d, 27 H, CH_3, $^3J_{P-H} = 13$ Hz), 1.42 (d, broad, 27 H, CH_3, $^3J_{P-H} = 12$ Hz). $^{31}P\{^1H\}$ NMR (in CD_2Cl_2): $\delta = 123.2$ (s, 1 P, $^1J_{Pt-P} = 4957$ Hz), 64.2 (s, 1 P). Mass spectrometry: positive ion ESIMS *m/z* calcd for $[PtOs_3SnP_2O_{11}C_{47}H_{64} + H]^+$, 1753; found 1753. The isotope distribution pattern is consistent with the presence of one platinum atom and three osmium atoms.

Preparation of $Os_4(CO)_{16}[Pt(PBu^t_3)]_2(\mu_4\text{-}Sn)$ (14). An 8.0 mg amount of **10** (0.0060 mmol) was dissolved in 15 mL of CH_2Cl_2 solvent in a 50 mL three-neck flask. A 18 mg amount of $Pt(PBu^t_3)_2$ (0.030 mmol) was added, and the solution continued at reflux for 20 min. The solvent was removed in vacuo, and the products were isolated by TLC by using a 6:1 hexane−methylene chloride solvent mixture to yield 5.5 mg of an orange **14** (43% yield). Spectral data for **14**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2054 (m), 2013 (s), 1977 (w), 1841 (w), 1804 (w). ^{1}H NMR (in $CDCl_3$): $\delta = 1.52$ (d, 54H, CH_3, $^3J_{P-H} = 13$ Hz). $^{31}P\{^1H\}$ NMR (in $CDCl_3$): $\delta = 129.3$ (s, 1P, $^1J_{Pt-P} = 4999$ Hz). Mass spectrometry positive ion ESIMS *m/z* calcd for $[Pt_2Os_4SnP_2O_{16}C_{40}H_{54}]^+$, 2123; found 2123. The isotope distribution pattern is consistent with the presence of two platinum atoms and four osmium atoms.

Crystallographic Analysis. Orange single crystals of **11** and **13** were directly grown from solution in CH_2Cl_2−hexane solvent mixtures by cooling to −25 °C. Orange single crystals of **12** suitable for diffraction analysis were grown by slow evaporation of solvent from a benzene−octane solution at 8 °C. Orange single crystals of **14** suitable for diffraction analysis were grown by slow evaporation of solvent from a CH_2Cl_2−hexane solution at 8 °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 using Mo Kα radiation ($\lambda = 0.710\,73$ Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.[11] 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 syntheses and refined by full-matrix least-squares on F^2 by using the SHELXTL software package.[12] Crystal data, data collection parameters, and results of the analyses for the compounds are listed in Tables 1 and 2.

Compound **11** crystallized in the triclinic crystal system. Space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. There are two independent formula equivalents of the complex present in the asymmetric unit. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms.

Compound **12** crystallized in the monoclinic crystal system. There was one significant residual peak near the bridging carbon atom of the phenyl group. It was approximately 2.9 Å from the Sn atom and about 2.7 Å from the lone osmium atom. It is believed that this is an osmium atom from a minor disorder effect produced by rotating the entire molecule approximately 180° about the Sn−C(Ph) vector. This disorder would interchange the two $Pt(PBu^t_3)$ groups and one pair of $Os(CO)_3$ groups almost perfectly. The residual peak would correspond to the osmium atom of the unmatched $Os(CO)_3$. The disorder refined best at 8% Os at this site. At this very low value, the carbonyl ligands on the 8% osmium atom would not be observed. As a consequence of this disorder, the carbon atom of the bridging η^1-phenyl group which lies in the vicinity of this disordered osmium atom was refined with an isotropic thermal parameter only. All other non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms.

Compound **13** crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the space group $P2_1/c$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms. One molecule of hexane from the crystallization solvent cocrystallized with the complex and was refined with isotropic displacement parameters. Geometric restraints were used in modeling the hexane molecule which was disordered.

Compound **14** crystallized in the orthorhombic crystal system. Systematic absences in the intensity data were consistent with either of the space groups *Pnn*2 or *Pnnm*. The structure could only be solved in the former space group. The molecule sits on a crystallographic 2-fold symmetry axis. All non-hydrogen atoms were refined with anisotropic displacement parameters. It cocrystallized with a molecule of CH_2Cl_2 from the crystallization solvent. The solvent molecule exhibits a 2-fold disorder of the carbon atom. This solvent molecule was included in the analysis and satisfactorily refined with anisotropic thermal parameters with 50% occupancy of the chlorine atoms. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms.

Results and Discussion

Two products $PtOs_3(CO)_{12}(PBu^t_3)(Ph)(\mu_3\text{-}SnPh)$, **11**, and $Pt_2Os_3(CO)_{12}(PBu^t_3)_2(\mu_2\text{-}Ph)(\mu_3\text{-}SnPh)$, **12**, were obtained in the yields 44 and 9%, respectively, from the reaction of **9** with $Pt(PBu^t_3)_2$ when combined in a 1:1 ratio at room temperature. When the amount of $Pt(PBu^t_3)_2$ was increased to 4 times the amount of **9**, the yield of **12** was increased to 40% at the expense of **11**, yield of 15%.

Compounds **11** and **12** were both characterized by single-crystal X-ray diffraction analysis. Compound **11** crystallizes with two independent molecules in the asymmetric crystal unit. Both molecules are structurally similar. An ORTEP

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Table 1. Crystallographic Data for Compounds **11** and **12**

	11	**12**
empirical formula	$PtOs_3SnPO_{12}C_{36}H_{37}$	$Pt_2Os_3SnP_2O_{12}C_{54}H_{70}$
formula weight	1577.01	2067.73
crystal system	triclinic	monoclinic
lattice parameters		
a (Å)	17.3194(4)	9.2366(12)
b (Å)	17.4086(5)	14.6004(18)
c (Å)	17.6044(5)	46.617(6)
α (deg)	61.782(1)	90
β (deg)	70.331(1)	95.151(2)
γ (deg)	69.419(1)	90
V (Å^3)	4284.1(2)	6261.3(14)
space group	$P\bar{1}$	$P2_1/n$
Z value	4	4
ρ_{calc} (g/cm^3)	2.445	2.194
μ (Mo Kα) (mm^{-1})	12.786	11.174
temperature (K)	294(2)	294(2)
$2\Theta_{max}$ (deg)	55.76	47.58
no. observations > 2σ (I)	16299	9094
no. parameters	991	659
goodness of fit	1.002	1.053
max shift in cycle	0.00	0.02
residuals:[a] R1; wR2	0.0309; 0.0754	0.0579; 0.1226
absorption correction, max/min	multiscan 1.000/0.587	multiscan 1.000/0.344
largest peak in final difference map (e/Å^3)	1.937	3.543

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

Table 2. Crystallographic Data for Compounds **13** and **14**

	13	**14**
empirical formula	$PtOs_3SnP_2O_{11}C_{47}H_{64}\cdot 1.0C_6H_{14}$	$Pt_2Os_4SnP_2O_{16}C_{40}H_{54}\cdot {}^1/_2CH_2Cl_2$
formula weight	1837.47	2169.90
crystal system	monoclinic	orthorhombic
lattice parameters		
a (Å)	17.6264(5)	12.0546(3)
b (Å)	21.7527(7)	26.5750(7)
c (Å)	16.0451(5)	8.9479(2)
α (deg)	90	90
β (deg)	98.010(1)	90
γ (deg)	90	90
V (Å^3)	6092.0(3)	2866.40(12)
space group	$P2_1/c$	$Pnn2$
Z value	4	2
ρ_{calc} (g/cm^3)	2.003	2.514
μ (Mo Kα) (mm^{-1})	9.031	14.278
temperature (K)	294(2)	294(2)
$2\Theta_{max}$ (deg)	56.7	56.6
no. observations	11283	6733
no. parameters	610	311
goodness of fit	1.044	1.042
max shift in cycle	0.003	0.005
residuals:[a] R1; wR2	0.0382; 0.0989	0.0222; 0.0575
absorption correction, max/min	multiscan 1.000/0.595	multiscan 1.000/0.0.475
largest peak in final difference map (e/Å^3)	3.443	2.328

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

diagram of the molecular structure of one of the two molecules of **11** in the asymmetric crystal unit is shown in Figure 1. Selected bond distances and angles are listed in Table 3. The molecule is structurally similar to that of **9** except that it contains a Pt(PBu$^t_3$) group that has been added across the Os−Os bond that connects the two bonded Os(CO)$_4$ groups. The Os−Os bond distance in molecule 1 is slightly longer, Os(1)−Os(2) = 3.0139(3) Å, than the Os−Os bond in **9**, Os−Os = 3.0007(4) Å, but the distance in molecule 2 is Os(4)−Os(5) = 2.9910(3) Å, slightly shorter than that in **9**. Accordingly, we think the differences between the Os−Os bond lengths in **9** and **11** are chemically and structurally insignificant. The two Pt−Os bond distances in molecule 1 are significantly different, Pt(1)−Os(2) = 2.7264(3) Å and Pt(1)−Os(1) = 2.7897(3) Å, but in molecule 2 these two distances are almost the same: Pt(2)−Os(4) = 2.7527(3) Å and Pt(2)−Os(5) = 2.7644(3) Å. The reason for this is not clear. It may be due simply to effects of crystal packing, and thus it would probably not be chemically significant for the properties of the molecules in solutions. The long distances are similar to the CO bridged Pt−Os bond length in **1**, Pt(1)−Os(1) = 2.7929(9).[1] CO ligands on the two platinum bonded osmium atoms have adopted semibridging coordination to the platinum atom. As in **9**, there is a phenyl group σ-bonded to the third Os(CO)$_4$ group. The Os−C distance, Os(3)−C(46) = 2.163(7)Å and Os(6)−C(70)

Table 3. Selected Intramolecular Distances and Angles for Compounds **11**−**13**[a]

(a) Distances

compound **11**		compound **12**		compound **13**	
atoms	distance (Å)	atoms	distance (Å)	atoms	distance (Å)
Os(1)−Os(2)	3.0139(3)	Os(1)−Os(2)	2.9844(8)	Os(1)−Os(2)	2.9839(4)
Pt(1)−Os(1)	2.7897(3)	Pt(1)−Os(2)	2.7810(8)	Pt(1)−Os(1)	2.7736(3)
Pt(1)−Os(2)	2.7264(3)	Pt(1)−Os(1)	2.7505(8)	Pt(1)−Os(2)	2.7372(3)
Os(1)−Sn(1)	2.7021(5)	Pt(2)−Os(3)	2.7445(8)	Os(1)−Sn(1)	2.7219(4)
Os(2)−Sn(1)	2.7310(5)	Os(1)−Sn(1)	2.7360(11)	Os(2)−Sn(1)	2.7526(5)
Os(3)−Sn(1)	2.7638(5)	Os(2)−Sn(1)	2.7267(11)	Os(3)−Sn(1)	2.7354(5)
Os(3)−C(46)	2.163(7)	Os(3)−Sn(1)	2.7058(11)	Os(3)−C(46)	2.191(7)
Pt(1)−P(1)	2.3346(16)	Os(3)−C(46)	2.008(18)	Pt(1)−P(1)	2.3468(16)
Os(4)−Os(5)	2.9910(3)	Pt(2)−C(46)	2.16(2)	Os(3)−P(2)	2.5501(17)
Pt(2)−Os(4)	2.7527(3)	Pt(1)−P(1)	2.353(3)		
Pt(2)−Os(5)	2.7644(3)	Pt(2)−P(2)	2.268(4)		
Os(4)−Sn(2)	2.7220(4)				
Os(5)−Sn(2)	2.7209(5)				
Os(6)−Sn(2)	2.7592(5)				
Os(6)−C(70)	2.189(7)				
Pt(2)−P(2)	2.3548(14)				

(b) Angles

compound **11**		compound **12**		compound **13**	
atoms	angle (deg)	atoms	angle (deg)	atoms	angle (deg)
Os(1)−Sn(1)−Os(3)	130.592(17)	Os(1)−Sn(1)−Os(3)	125.02(4)	Os(1)−Sn(1)−Os(3)	131.906(17)
Os(2)−Sn(1)−Os(3)	124.941(18)	Os(2)−Sn(1)−Os(3)	134.95(4)	Os(2)−Sn(1)−Os(3)	123.213(17)
C(46)−Os(3)−Sn(1)	83.75(17)	C(46)−Os(3)−Sn(1)	84.2(6)	C(46)−Os(3)−Sn(1)	78.5(2)
Os(4)−Sn(2)−Os(6)	127.838(18)				
Os(5)−Sn(2)−Os(6)	127.569(17)				
C(70)−Os(6)−Sn(2)	82.63(17)				

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

= 2.189(7) Å, is similar to that in **9**, 2.172(9) Å.[10] The Os−Sn bond distances to Os(1) and Os(2) in molecule 1 are significantly different, Os(1)−Sn(1) = 2.7021(5) Å and Os(2)−Sn(1) = 2.7310(5) Å, but in molecule 2, they are virtually the same length, Os(4)−Sn(2) = 2.7220(4) and Os(5)−Sn(2) = 2.7209(5), so we think that the difference observed in molecule 1 is chemically and structurally insignificant. The Os−Sn distance to the phenyl substituted osmium atom is the longest of all, Os(3)−Sn(1) = 2.7638(5) Å and Os(6)−Sn(2) = 2.7592(5), but is similar to that in **9**.[10]

An ORTEP diagram of the molecular structure of **12** is shown in Figure 2. Selected bond distances and angles are listed in Table 3. The molecule is structurally similar to that of **11**, except that there is a second Pt(PBu$^t_3$) group that has been added across the Os−C bond to the σ-bonded phenyl group. As in **11**, two of the CO ligands on the osmium atoms have adopted semibridging coordination to the platinum atom Pt(1). The Os−Os bond distance in **12**, Os(1)−Os(2) = 2.9844(8) Å, is slightly shorter than that in **11** and also shorter than that in **9**. The Pt−Os bond distances are significantly different, but they are much closer together than they were in **11**, Pt(1)−Os(1) = 2.7505(8) Å and Pt(1)−Os(2) = 2.7810(8) Å. Interestingly, the second platinum atom Pt(2) bridges the Os−C bond to the σ-bonded phenyl group, Pt(2)−Os(3) = 2.7445(8) Å and Pt(2)−C(46) = 2.16(2) Å. The Os−C bond distance to the σ-bonded phenyl group is slightly shorter than that in **11**, Os(3)−C(46) = 2.008(18) Å. This may be due to the presence of the bridging platinum atom. The Os−Sn bond distances to Os(1) and Os(2) are also much closer together in length than those in **11**, Os(1)−Sn(1) = 2.7360(11) Å and Os(2)−Sn(1) = 2.7267(11) Å, but the Os(3)−Sn(1) = 2.7058(11) Å is significantly shorter than the others.[10]

When **12** was treated with PBu$^t_3$, the platinum phosphine group that bridges the Os−C (phenyl) bond was removed and the compounds **11** and **13** were formed in the yields 30% and 15%, respectively. An ORTEP diagram of the molecular structure of **13** is shown in Figure 3. Selected bond distances and angles are listed in Table 3. Compound **13** is structurally similar to **11** but has a PBu$^t_3$ ligand trans to the Os−Sn bond in place of one of the CO ligands on the osmium atom Os(3). The Os−Os bond length in the $Os_2(CO)_8$ group is similar in length to that in **11**, Os(1)−Os(2) = 2.9839(4) Å. The Pt−Os bonds are unequal, Pt(1)−Os(1) = 2.7736(3) Å and Pt(1)−Os(2) = 2.7372(3) Å, but as with **11**, we think this is of no chemical significance. The

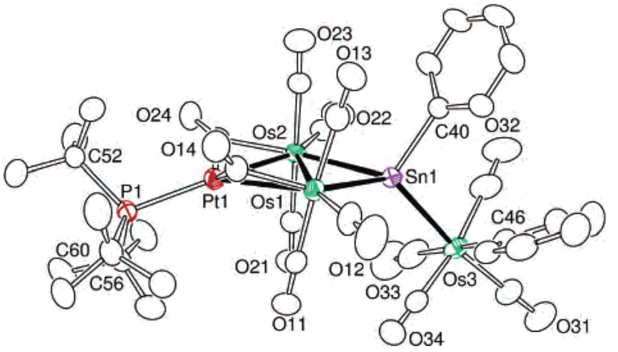


Figure 1. An ORTEP diagram of **11** showing 30% probability thermal ellipsoids.

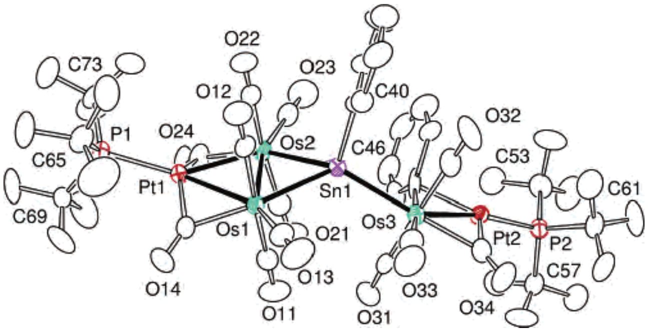


Figure 2. An ORTEP diagram of **12** showing 30% probability thermal ellipsoids.

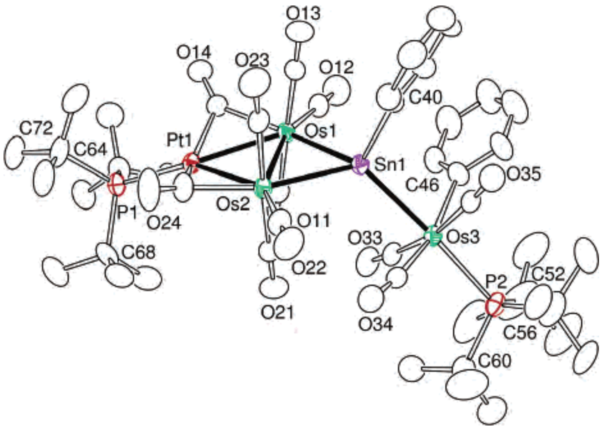


Figure 3. An ORTEP diagram of **13** showing 30% probability thermal ellipsoids.

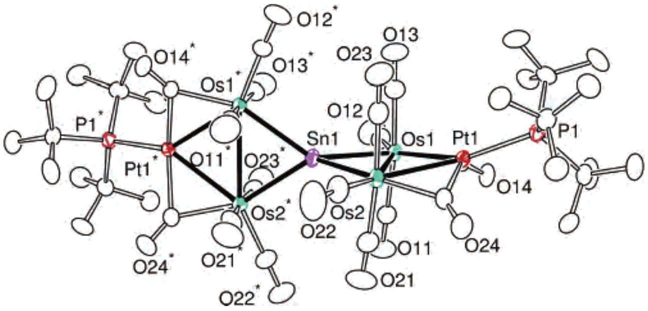


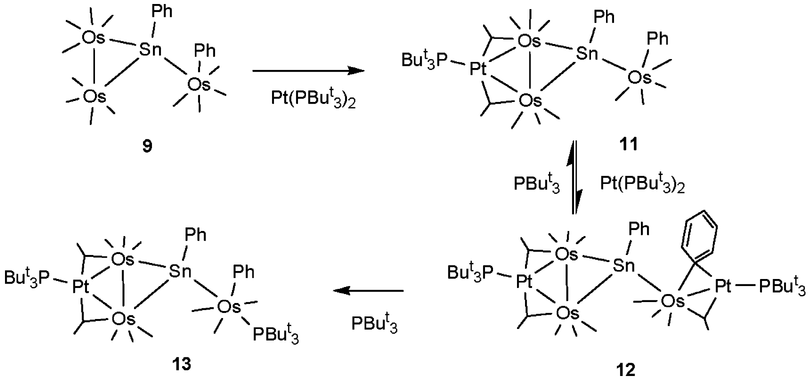
Figure 4. An ORTEP diagram of **14** showing 30% probability thermal ellipsoids. Selected interatomic distances (Å) are Os(1)−Os(2) = 3.0251(3), Pt(1)−Os(1) = 2.7609(3), Pt(1)−Os(2) = 2.7557(3), Os(1)−Sn(1) = 2.6824(3), Os(2)−Sn(1) = 2.6756(4), and Pt(1)−P(1) = 2.3602(16). Selected angles (deg) are Os(1)−Sn(1)−Os(2) = 68.749(7), Os(1)−Sn(1)−Os(1′) = 135.53(3), and Os(1)−Sn(1)−Os(2′) = 133.53(1).

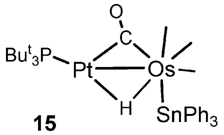
Os−C distance to the σ-bonded phenyl group, Os(3)−C(46) = 2.191(7) Å, is slightly longer than that in **11**, and the C−Os−Sn angle is significantly less than 90°, C(46)−Os(3)−Sn(1) = 78.5(2)°, and the P(2)−Os(3)−C(46) angle, 103.4(2)°, is much larger than 90°. This might be due to steric effects from the neighboring $\mathrm{PBu^{t}_{3}}$ ligand. The Os−Sn distances are similar to those in **11**, Os(1)−Sn(1) = 2.7219(4), Os(2)−Sn(1) = 2.7526(5), and Os(3)−Sn(1) = 2.7354(5).

Compound **10** reacts with $\mathrm{Pt(PBu^{t}_{3})_{2}}$ to form a bis-Pt($\mathrm{PBu^{t}_{3}}$) adduct, $\mathrm{Os_4(CO)_{16}[Pt(PBu^{t}_{3})]_2(\mu_4\text{-}Sn)}$, **14**, in a good yield (43%). An ORTEP drawing of the molecular structure of **14** is shown in Figure 4. Compound **14** lies on a crystallographic 2-fold axis, so only half of the molecule is structurally independent. The $\mathrm{Os_4Sn}$ core of **14** is similar to that of its precursor **10** and contains a spiro-structure with the Sn atom in the center. A $\mathrm{Pt(PBu^{t}_{3})}$ group was added across each Os−Os bond in **14**. The Os−Os bond distance in **14**, Os(1)−Os(2) = 3.0251(3) Å, is slightly longer than that in **10**, 3.0081(5) and 3.0038(5) Å. The Pt−Os bond distances, Pt(1)−Os(1) = 2.7609(3) Å and Pt(1)−Os(2) = 2.7557(3) Å, are nearly equal and similar in length to those in compounds **11**−**13**. As found in **11**−**13**, one CO ligand on each neighboring osmium atom has formed a bridging interaction to the platinum atom. The Os−Sn bond distances, Os(1)−Sn(1) = 2.6824(3) Å and Os(2)−Sn(1) = 2.6756(4) Å, are very similar to those in **10**, 2.6927(7), 2.6883(7), 2.6983(7), and 2.6797(7) Å.

A summary of the products obtained from the reactions of **9** with $\mathrm{Pt(PBu^{t}_{3})_{2}}$ is shown in Scheme 1. The work reaffirms the strong affinity of the $\mathrm{Pt(PBu^{t}_{3})}$ group for Os−Os bonds. We have not observed any products with Pt−Sn interactions. The first $\mathrm{Pt(PBu^{t}_{3})}$ addition occurs at the Os−Os bond of the $\mathrm{Os_2(CO)_8}$ group to yield **11**. Interestingly, we have observed the addition of a $\mathrm{Pt(PBu^{t}_{3})}$ group to an Os−C bond, in this case to the σ-bonded phenyl group in **12**. $\mathrm{Pt(PBu^{t}_{3})}$ additions to M−C bonds have not been seen before and could lead to new chemistry. For example, we have recently observed the addition of a $\mathrm{Pt(PBu^{t}_{3})}$ group to the Os−H bond of the compound $\mathrm{HOs(CO)_4(SnPh_3)}$ to yield the adduct $\mathrm{PtOs(CO)_4(SnPh_3)(PBu^{t}_{3})(\mu\text{-}H)}$, **15**.[13] It was found that the $\mathrm{Pt(PBu^{t}_{3})}$ group in **15** facilitates the insertion of phenylacetylene in the Os−H bond. It will be interesting to

Scheme 1





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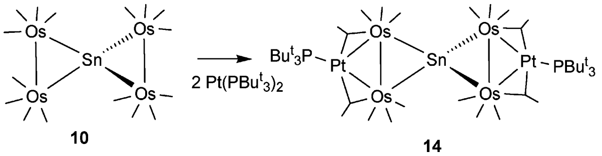
see if the addition of Pt(PBu$^t{}_3$) groups to M−C bonds will facilitate the insertion of unsaturated small molecules into these bonds.

We have also found that Pt(PBu$^t{}_3$) groups can facilitate the substitution of CO ligands by phosphine ligands.[1] This effect appears to be operative in the chemistry of **12** because compound **13**, which contains a PBu$^t{}_3$ ligand on the phenyl-substituted carbon atom, was obtained from the reaction of **12** with PBu$^t{}_3$ in the course of the removal of the Pt(PBu$^t{}_3$) group. Interestingly, the Pt(PBu$^t{}_3$) group that bridges the Os−Os bond in **12** was not removed in the treatment with PBu$^t{}_3$.

When **10** was treated with Pt(PBu$^t{}_3$)$_2$, Pt(PBu$^t{}_3$) groups were added to the Os−Os bond of each Os$_2$(CO)$_8$ group to yield **14**; see eq 5.



10 **14**

(5)

Tin containing cluster complexes are now proving to be useful precursors to new supported bi- and trimetallic heterogeneous catalysts.[8,9] We are also interested to see how the addition of Pt(PBu$^t{}_3$) groups to polynuclear metal complexes containing tin can activate them for homogeneous catalysis.[13,14]

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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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