Synthesis and Properties of an Unusual New High-Symmetry Osmium−Palladium Carbonyl Cluster Complex

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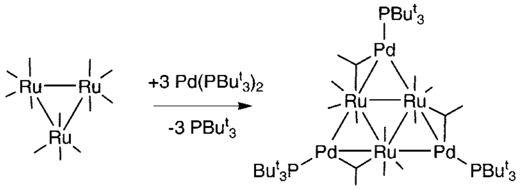
The new tetrahedral complex $Os_4(CO)_{12}[Pd(PBu^t_3)]_4$, **3**, was obtained from the reaction of $Os_3(CO)_{12}$ with $Pd(PBu^t_3)_2$ in octane solution at reflux. Compound **3** was characterized by IR, ^1H and ^{31}P NMR spectroscopy, mass spectroscopy, and single-crystal X-ray diffraction analysis. The electronic structure of **3** was evaluated by Fenske–Hall molecular orbital analysis. Compound **3** is electronically unsaturated and reacts with hydrogen at room temperature to yield the known compound $Os_4(CO)_{12}(\mu\text{-}H)_4$, **4**.

Introduction

Palladium has been shown to be of great value as a catalyst for the hydrogenation of unsaturated organic molecules.[1] When treated with additives, such as tin and lead, its catalytic activity is significantly modified.[2] Recent studies have shown that improved catalytic activity is also obtained when palladium is combined with certain transition metals.[3,4] It has also been shown that bimetallic complexes containing palladium can be good precursors to supported bimetallic catalysts. Dahl and coworkers have prepared and structurally characterized a series of remarkable high nuclearity heteronuclear palladium complexes.[5] Lee and Wong reviewed this field in 1998.[6]

In recent studies, we have shown that $Pd(PBu^t_3)_2$ readily loses one of its PBu^t_3 ligands in solutions and the remaining $Pd(PBu^t_3)$ group readily adds to the metal−metal bonds of polynuclear metal–carbonyl complexes to yield a variety of new mixed metal–carbonyl complexes containing palladium, e.g., $Ru_3(CO)_{12}[Pd(PBu^t_3]_3$, eq (1)[7] and $Re_2(CO)_8(\mu\text{-}SnPh_2)[Pd(PBu^t_3]_2$, eq (2).[8] $Rh_4(CO)_{12}$ reacts with $Pd(PBu^t_3)_2$ to yield the hexarhodium cluster complexes, $Rh_6(CO)_{12}[Pd(PBu^t_3]_3$ and $Rh_6(CO)_{12}[Pd(PBu^t_3]_4$ that contain three and four edge-bridging $Pd(PBu^t_3)$ groups, respectively, eq (3).[9]



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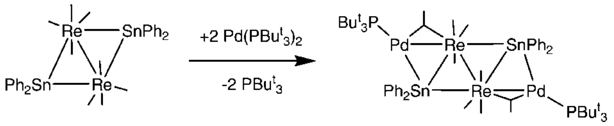

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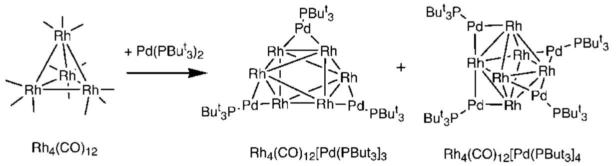
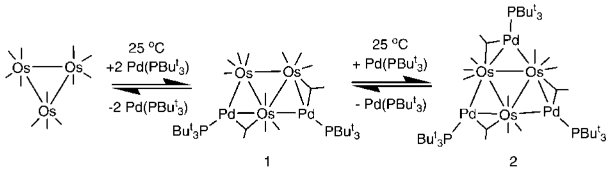


(3)

Palladium also adds across the Os−Os bonds of $Os_3(CO)_{12}$. The bis- and tris-$Pd(PBu^t_3)$ adducts, $Os_3(CO)_{12}[Pd(PBu^t_3]_2$ (**1**) and $Os_3(CO)_{12}[Pd(PBu^t_3]_3$ (**2**) were isolated and characterized, eq (4).[10] In this system the $Pd(PBu^t_3)$ groups are readily added and eliminated at room temperature and the three compounds exist in an equilibrium in solution.



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We have now obtained the unusual tetrahedral new octanuclear 4:4 Os:Pd cluster complex $Os_4(CO)_{12}[Pd(PBu^t_3)]_4$ (**3**) from the reaction of $Os_3(CO)_{12}$ with $Pd(PBu^t_3)_2$ in octane solution at reflux. The synthesis, structural characterization, and an analysis of the electronic structure of this complex by Fenske–Hall molecular orbital calculations are reported herein.

Experimental Section

General Data. The reaction was performed under nitrogen by using standard Schlenk techniques. Reagent grade solvents were dried by standard procedures and were freshly distilled prior to their use. Infrared spectra were recorded on a Nicolet Avatar 360 FTIR spectrophotometer. ^1H NMR and $^{31}P\{^1H\}$ NMR 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% $o\text{-}H_3PO_4$. Positive ion mass spectra were recorded on a Waters Micromass Q-T quadrupole time-of-flight instrument by using electrospray (ES) ionization. UV–vis spectra of **3** were recorded on a Jasco V-530 UV–vis spectrometer in methylene chloride solvent at a concentration of 3.90×10^{-5} M. $Pd(PBu^t_3)_2$ was purchased from STREM and was used without further purification. $Os_3(CO)_{12}$ was prepared by a previously reported procedure.[11] Product separations were performed by TLC in air by using Analtech 0.25, 0.5, and 1.0 mm silica gel 60 Å F_{254} glass plates.

Reaction of $Os_3(CO)_{12}$ with $Pd(PBu^t_3)_2$. A 20.0 mg (0.022 mmol) amount of $Os_3(CO)_{12}$ was dissolved in 15 mL of octane. $Pd(PBu^t_3)_2$ (60.0 mg, 0.117mmol) was added, and the solution was heated to reflux for 2 h. The solvent was then removed in vacuo, and the residue was extracted with methylene chloride and separated by thin layer chromatography by using a 4:1 (v/v) hexane/methylene chloride solvent mixture to yield in order of elution: 1.4 mg of red **1**[10] (4%), 5.0 mg of unreacted $Os_3(CO)_{12}$ (25%), 3.5 mg (4%) of blue $Os_4Pd_4[P(Bu^t_3)]_4(CO)_{12}$ (**3**), and 1.6 mg of purple **2**[10] (3%). Elution of the baseline with THF/methylene chloride (1:10 v/v) solvent mixture gave 2.4 mg (8%) of $Os_3(CO)_{10}(PBu^t_3)_2$.[12] Spectral data for **3**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 1980 (vs), 1938 (m, sh). ^1H NMR (CD_2Cl_2 in ppm) δ 1.43 (d, $^3J_{P-H} = 12$ Hz, 108H). ^{31}P NMR (CD_2Cl_2 in ppm) δ 88.24 (s, 4P). EI/MS *m/z* 2332.

Reaction of 1 with H_2. A 6.0 mg (0.003 mmol) amount of **3** was dissolved in 8 mL of hexane and purged with H_2 for 1 h at room temperature. The solvent was then removed in vacuo, and the residue was extracted with methylene chloride and separated by thin layer chromatography over silica gel with a 4:1 (v/v) hexane/methylene chloride solvent mixture to yield 1.5 mg (52%) of the known compound $Os_4(CO)_{12}(\mu\text{-}H)_4$, **4**.[13]

Molecular Orbital Calculations. Molecular orbital calculations reported here are from the Fenske–Hall method.[14] Fenske–Hall calculations were performed utilizing a graphical user interface developed[15] to build inputs and view outputs from stand-alone Fenske–Hall (Version 0.1.v117) and MOPLOT2[16] binary executables. Contracted double-ζ basis sets were used for the Os 5d, Pd 4d, P 3p, and C and O 2p atomic orbitals. PH_3 was used in place of PBu^t_3 in these calculations. The Fenske–Hall scheme is a nonempirical, approximate method that is capable of calculating molecular orbitals for very heavy transition metal systems and has built-in fragment analysis routines that allow one to assemble transition metal cluster structures from the ligand-containing fragments.

Table 1. Crystallographic Data for Compound 1

empirical formula	$Os_4Pd_4P_4C_{60}H_{108}$
formula weight	2331.74
crystal system	cubic
lattice parameters	
$a = b = c$ (Å)	16.4892(2)
$\alpha = \beta = \gamma$ (deg)	90
V (Å^3)	4483.39(9)
space group	$I\bar{4}3m$, no. 217
Z value	2
ρ_{calcd} (g/cm^3)	1.727
μ(Mo Kα) (mm^{-1})	6.541
temp (K)	293(2)
$2\Theta_{max}$ (deg)	56.6
no. obsd ($I > 2\sigma(I)$)	1037
no. of parameters	61
goodness of fit (GOF)[a]	1.49
max. shift in cycle	0.003
residuals:[a] R1; *w*R2	0.0224; 0.0883
abs cor, max/min	multiscan 1.000/0.673
largest peak in final diff map (e$^-$/Å^3)	1.975

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

Crystallographic Analysis. Dark blue single crystals of **3** suitable for X-ray diffraction analysis were obtained by slow evaporation of solvent from a solution of octane/methylene chloride at −25 °C. The 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 ($\lambda = 0.71073$ Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm.[17] 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 by using the program SADABS. The structure was 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.[18] Crystal data, data collection parameters, and results of the analysis are listed in Table 1. Compound **3** crystallized in the cubic crystal system. The space group $I\bar{4}3m$ was indicated on the basis of the systematic absences observed in the data and was confirmed by the successful solution and refinement of the structure. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms on the *tert*-butyl groups were calculated by assuming standard geometries and were included as fixed contributions on the final cycles of refinement. The molecule crystallized about a $\bar{4}3m$ crystallographic site. Only 1/12 of the molecule is occupied in the asymmetric crystal unit. The *tert*-butyl group exhibited a 2-fold rotational disorder about the 3-fold rotation axes that coincide with each Pd−P bond. The disordered carbon atoms were refined anisotropically at 50% occupancy.

Results and Discussion

The complex $Os_4(CO)_{12}[Pd(PBu^t_3)]_4$ (**3**) was obtained in 4% yield from the reaction of $Os_3(CO)_{12}$ with $Pd(PBu^t_3)_2$ in a

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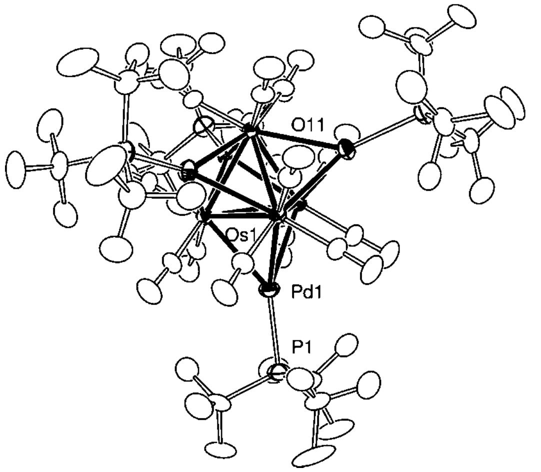


Figure 1. An ORTEP diagram of **3** showing 30% thermal ellipsoid probabilities. The hydrogen atoms and the 2-fold disorder in the *tert*-butyl groups are not shown for clarity. Interatomic bond distances (Å) and angles (deg) are as follows: Os(1)–Pd(1) = 2.8063(9), Os(1)–Os(1*) = 2.8635(7), Pd(1)–P(1) = 2.429(5), P(1)–C(1) = 1.948(16), C(11)–O(11) = 1.136(11); Os(1)–Pd(1)–Os(1*) = 61.35(2), Os(1*)–Os(1)–Pd(1) = 59.321(12), Pd(1)–Os(1)–Pd(1*) = 112.16(3), Os(1)–Pd(1)–P(1) = 143.905(15), Os(1)–C(11)–O(11) = 174.1(9).

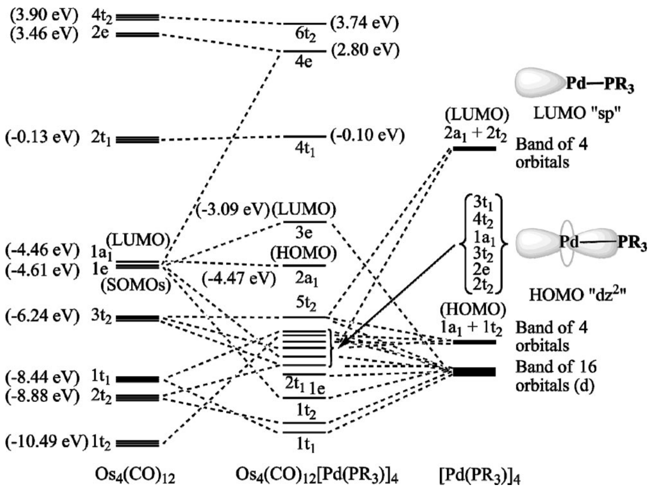
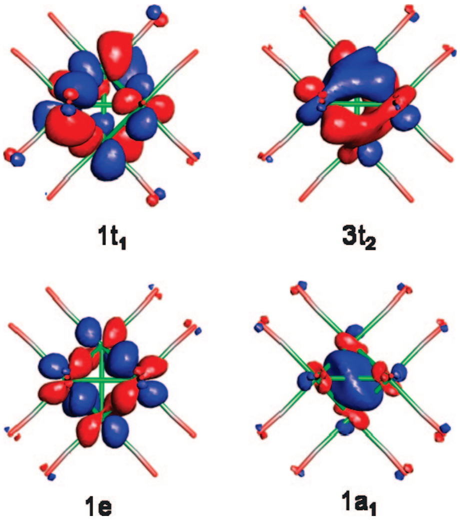


Figure 2. Fenske–Hall energy level diagram for the cluster Os$_4$(CO)$_{12}$[Pd(PR$_3$)]$_4$, R = H.



1t$_1$ **3t$_2$**

1e **1a$_1$**

Figure 3. Contour diagrams for the molecular orbitals 1t$_1$, 3t$_2$, HOMO 1e, and LUMO 1a$_1$ in the Os$_4$(CO)$_{12}$ fragment of **3**.

solution in octane solvent at reflux (127 °C) for 2 h. Compound **3** was characterized by a combination of IR, ^{1}H and ^{31}P{^{1}H} NMR, and single-crystal X-ray diffraction analyses. An ORTEP showing the molecular structure of compound **3** is shown in Figure 1. The molecule lies on a crystallographic $\bar{4}3m$ site in the solid state and ignoring *tert*-butyl groups has overall T_d symmetry. The *tert*-butyl groups exhibit a 50/50 reflection disorder that coincides with the C_3 axes that pass along each Pd–P bond in the molecule. This creates the overall T_d symmetry. This molecule consists of a central cluster of four osmium atoms. Each osmium atom contains three carbonyl ligands, only one is crystallographically independent. The other two are generated by the C_3 rotational symmetry. There is only one independent Os–Os bond distance, Os(1)–Os(1*) = 2.8635(7) Å, which is very similar to the Os–Os bond distance in Os$_3$(CO)$_{12}$, 2.877(3) Å.[19] The one independent osmium–palladium distance, Os(1)–Pd(1) = 2.8063(9) Å, is similar to those found for the edge-bridging Pd(PBu$^t_3$) groups in compounds **1** and **2**, 2.7935(9)–2.8846(9) Å.[10] Hui et al. characterized a triply bridging Pd(PPh$_3$) group in the compound Os$_5$Pd(CO)$_{14}$(PPh$_3$)$_2$(μ_5-C).[20] The Os–Pd distances in this compound were 2.809(3)–2.812(3) Å. The Pd–P distance in **3**, Pd(1)–P(1) = 2.429(5) Å, is also very similar to those in **1** and **2**, 2.369(2)–2.376(3) Å. The IR spectrum of **3** exhibits only two CO stretching absorptions: 1980 (vs) and 1938 (m), which is consistent with the overall symmetry of the molecule. As expected, the NMR spectra show a single resonance for the *tert*-butyl methyl groups δ 1.43 (d, $^3J_{P-H}$ = 12 Hz) and the four equivalent phosphorus atoms, δ 88.24.

A molecular orbital analysis of **3** was performed by using the Fenske–Hall molecular orbital fragment analysis. The electronic structure was analyzed as a combination of two fragments: (1) a central Os$_4$(CO)$_{12}$ core derived from a tetrahedral assembly of four Os(CO)$_3$ groups and (2) an arrangement of four Pd(PBu$^t_3$) fragments tetrahedrally disposed above the four Os$_3$ triangles of the Os$_4$ core. The Os$_4$(CO)$_{12}$ core was assembled from four Os(CO)$_3$ groups. Each Os(CO)$_3$ fragment contains eight d-electrons and three σ-type orbitals that can be visualized by removing three *fac*-related CO groups from an M(CO)$_6$ octahedron. These orbitals form 12 MOs having the following symmetries: A$_1$, E, T$_1$, and 2 T$_2$ when combined into the Os$_4$(CO)$_{12}$ core. A similar set of orbitals can be derived by combining the d$_{xy}$, d$_{xz}$, and d$_{yz}$ set of atomic orbitals on each of the four osmium atoms. An energy level diagram of the top 15 MOs in the Os$_4$(CO)$_{12}$ fragment is shown on the left side of Figure 2. The LUMO (−4.46 eV) is labeled 1a$_1$. A contour diagram of this fragment MO is shown in Figure 3. Just below this orbital is a doubly degenerate pair of orbitals at −4.61 eV that is labeled 1e. These two orbitals are singly occupied (SOMOs) and thus form a triplet ground state in the hypothetical Os$_4$(CO)$_{12}$ fragment. These orbitals are also shown in Figure 3. Below the 1e lies a triply degenerate set 3t$_2$ at −6.24 eV, also shown in Figure 3, and below that lies one more important triply degenerate set labeled 1t$_1$. There is very little direct Os–Os bonding in the 1t$_1$ set of orbitals, see Figure 3, but they play an important role in the bonding of the palladium phosphine groups to the Os$_4$(CO)$_{12}$ cluster.

Each Pd(PBu$^t_3$) fragment consists of an "sp" LUMO that projects away from the PBu$^t_3$ ligand. This orbital was originally

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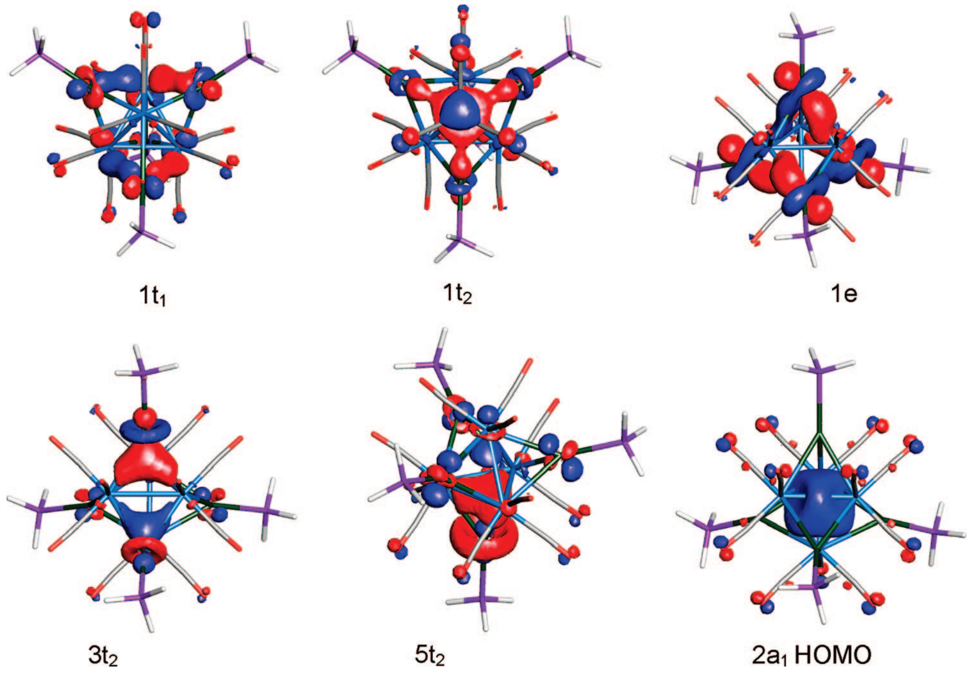


Figure 4. Contour diagrams for the molecular orbitals $1t_1$, $1t_2$, 1e, $3t_2$, $5t_2$, and the HOMO $2a_1$ that contain the metal–metal bonding in **3**.

occupied by the second PBu^t_3 ligand in the molecule $Pd(PBu^t_3)_2$. The HOMO is the "d_{z^2}" orbital that is coaxial to the "sp" orbital. Each of these orbitals forms a set of A_1 and T_2 orbitals when the four $Pd(PBu^t_3)$ fragments are tetrahedrally arranged. These are represented on the right-hand side of Figure 2. Below these orbitals is a band of 16 filled orbitals that is assembled from the 16 remaining d-orbitals, four from each Pd atom.

The Pd orbitals interact with the orbitals in the $Os_4(CO)_{12}$ fragment to form the series of orbitals shown in the center of Figure 2. The lowest energy orbital that is shown is labeled $1t_1$. It lies at −9.78 eV. The HOMO $2a_1$ lies at −4.47 eV and the LUMO 3e lies at −3.09 eV. The most important orbitals for the bonding of the $Pd(PBu^t_3)$ groups to the $Os_4(CO)_{12}$ cluster are the $1t_1$ (−9.78 eV), $1t_2$ (−9.66 eV), 1e (−8.82 eV), $3t_2$ (−7.38 eV), and $5t_2$ (−6.20 eV). Contours of a representative member from each of these degenerate sets are shown in Figure 4. The $1t_1$ orbital contains strong interactions between the Pd atoms and the Os atoms. Significant Pd–Os overlaps are also formed from the three sets of t_2 orbitals, $1t_2$, $3t_2$, and $5t_2$, via interactions between the t_2 sets derived from HOMO and LUMO of the $Pd(PBu^t_3)$ fragments which point toward the center of the Os_3 triangular faces of the $Os_4(CO)_{12}$ fragment. The 1e orbital in **3** also contains significant Pd–Os interactions, 78% Pd and 22% Os. This orbital is derived from interactions of "d_{xz}" and "d_{yz}" orbitals on the $Pd(PBu^t_3)$ fragments in the band of 16. As a result of this interaction, the 1e orbital in the $Os_4(CO)_{12}$ fragment is destabilized and becomes the LUMO 3e in **3** at −3.09 eV. The electrons that occupied this orbital in the $Os_4(CO)_{12}$ fragment go into the $2a_1$, which is the HOMO in **3**. There is very little Pd–Os bonding in the HOMO $2a_1$ formed by interactions of the $1a_1$ orbital of the $Os_4(CO)_{12}$ fragment and the a_1 orbitals formed form the $Pd(PBu^t_3)$ fragments. This is because the $1a_1$ orbital of the $Os_4(CO)_{12}$ fragment lies, for the most part, on the interior of the Os_4 tetrahedron. The energy of the HOMO $2a_1$ in **3**, −4.47 eV, is almost unchanged from that in the $Os_4(CO)_{12}$ fragment itself, −4.46 eV. This orbital actually contains a 0.0% contribution from the palladium atoms.

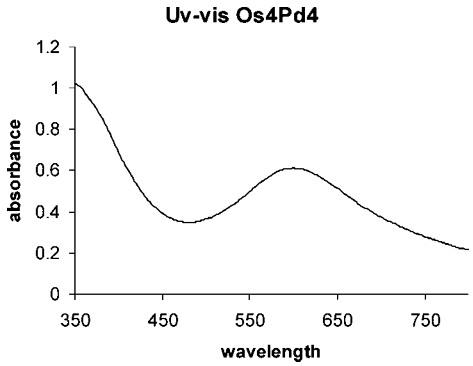


Figure 5. UV–vis spectrum of **3** in methylene chloride solvent.

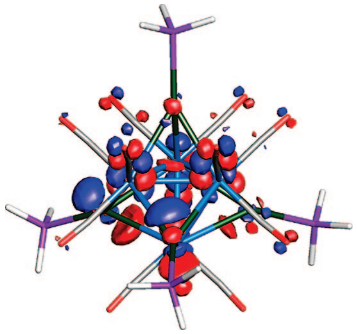


Figure 6. A contour diagram for the molecular orbital $6t_2$, the LUMO+3, in **3**.

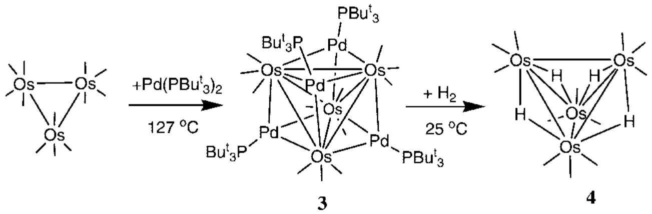
Compound **3** has a deep blue color. The UV–vis absorption spectrum of **3** shows only one strong absorption in the visible region of the spectrum, $\lambda_{max} = 600$ nm, $\epsilon = 1.569 \times 10^4$ cm^{-1} M^{-1}, see Figure 5. The dipole moment operator for T_d symmetry is t_2 so the only symmetry allowed transition from the $2a_1$ HOMO would have to be to an energy state of t_2 symmetry. The lowest lying empty t_2 orbitals that we have found by these calculations is the $6t_2$ set, LUMO+3, which lies at +3.74 eV. This orbital is shown in Figure 6. As expected, it has significant Pd–Os antibonding character. It seems to lie at too high an energy for the observed transition, but one must realize that these calculations are not calculating the energy of the excited state, which would have one electron in the $6t_2$ orbital set. More sophisticated calculations, such as time-dependent DFT, would be required to determine the energy of this electronic configuration accurately.[21]

A tetracapped tetrahedral metal cluster in which all the metal atoms have 18-electron configurations would contain 108 valence electrons.[22] This is consistent with the FH MO analysis above if the low-lying LUMO 3e is filled. Compound **3** contains a total of 104 valence electrons, so it is formally unsaturated by the amount of four electrons by these criteria. We and others have recently shown that electronically unsaturated mixed metal cluster complexes readily activate hydrogen under mild conditions.[12,23] Accordingly, compound **3** was examined for its reactivity toward hydrogen. Compound **3** was found to react with H_2 at 1 atm in hexane solvent to give the known compound $Os_4(CO)_{12}(\mu\text{-}H)_4$[13] (**4**) in 52% after 1 h at 25 °C. The fate of the palladium phosphine groups was not ascertained.

Summary

In previous studies we have shown that $Os_3(CO)_{12}$ reacts readily with $Pd(PBu^t_3)_2$ at room temperature to add $Pd(PBu^t_3)$ groups to the Os−Os bonds of the $Os_3(CO)_{12}$ molecule.[10] We have now shown that $Os_3(CO)_{12}$ reacts with $Pd(PBu^t_3)_2$ at 125 °C to form the new tetraosmiumtetrapalladium complex **3** that contains triply bridging $Pd(PBu^t_3)$ groups on all four triangular faces of a central tetrahedral $Os_4(CO)_{12}$ cluster. Compound **3** is electronically unsaturated and readily reacts with hydrogen to yield compound **4** in good yield under very mild conditions, see Scheme 1. We have observed the formation of triply bridging $Pt(PBu^t_3)$ groups in the formation of the compound $Os_3(CO)_{10}[Pt(PBu^t_3)]_2$ from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with $Pt(PBu^t_3)_2$,[12] but surprisingly, we have not yet been able to obtain the platinum homologue of **3** from the reaction of $Os_3(CO)_{12}$ with $Pt(PBu^t_3)_2$ at elevated temperatures.

Scheme 1



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

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