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Synthesis, Structure, and Reactivity of Organometallic Osmium(VI) Hydroxo Compounds

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The organometallic osmium(VI) hydroxo compounds $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_3(OH)]$, cis and trans isomers of $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2(OH)_2]$, result from the substitution of chloride for hydroxide ligands in precursor compounds. Depending on the molecular structure, these compounds behave as nucleophiles, Brønsted bases, or Lewis bases in their reactions. One of these, $[N(n\text{-}Bu)_4][\textit{cis}\text{-}Os(N)(CH_2SiMe_3)_2(OH)_2]$, reacts readily with CO_2 to produce the carbonate compound $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2(CO_3)]$. The other isomer, $[N(n\text{-}Bu)_4][\textit{trans}\text{-}Os(N)(CH_2SiMe_3)_2(OH)_2]$, reacts with CO_2 to slowly form the same carbonate compound. It is protonated by other acids to give the neutral hydroxo dimer $\{Os(N)(CH_2SiMe_3)_2(\mu\text{-}OH)\}_2$. The anti isomer of $\{Os(N)(CH_2SiMe_3)_2(\mu\text{-}OH)\}_2$ reacts with $Pd(bpy)(OSiMe_3)_2$ to produce the coordinatively unsaturated, heterometallic complex $\{Os(N)(CH_2SiMe_3)_2\}_2(\mu_3\text{-}O)_2Pd(bpy)$. The molecular structure of this complex shows two square-pyramidal osmium groups with an anti arrangement of the apical nitrido ligand and a square-planar palladium(II) center, all connected by the triply bridging oxo groups.

Introduction

Hydroxo complexes of the later transition metals[1] are often proposed as intermediates in catalytic oxidations of organic molecules,[2] Wacker oxidation,[3] and amide hydrolysis.[4] With the growing use of water as a nonpolluting solvent for metal-catalyzed reactions, the chemistry of organometallic hydroxo complexes will become more important.[5] Simple aquo and hydroxo complexes of the group VIII metals are basic to coordination chemistry, but very few organometallic complexes containing the hydroxo ligand have been prepared.[6]

Osmium and ruthenium hydroxo compounds include high-oxidation-state inorganic compounds such as $K_2[OsO_4(OH)_2]$ and $K_2[OsO_2(OH)_4]$[7] and a few M(II) organometallic compounds. Meyer and co-workers have explored the proton-coupled reduction of a ruthenium(VI) oxo complex to ruthenium(III) hydroxo species.[8] Organometallic hydroxo compounds include only $(PMe_3)_4Ru(Me)(OH)$,[9] $OsH(OH)(CO)(P(i\text{-}Pr)_3)_2$,[10] and the dimeric species $[\{(P(i\text{-}Pr)_3)(\eta^2\text{-}C_2H_4)_2Os\}_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)][BF_4]$[11] and $[(\eta^6\text{-arene})M(\mu\text{-}OH)_3M(\eta^6\text{-arene})]^+$.[12] Inorganic compounds containing σ-bonded alkyl or aryl ligands along with the hydroxo group include Ir(III)[13] and complexes of the nickel triad metals.[14]

Osmium compounds with bridging hydroxo ligands are not common. Gould and Stephenson in 1984 isolated an Os complex with four hydroxo ligands bridging two Os atoms each, as well as a μ_4-oxo ligand connecting all four osmium centers.[15] Esteruelas prepared $[\{(P(i\text{-}Pr)_3)_2(\eta^2\text{-}C_2H_4)_2Os\}_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)][BF_4]$, which has two hydroxo ligands bridging two Os^{II} centers.[16] In both cases, the hydroxo ligands are very reactive with either acids or bases.

Hydroxo ligands may exhibit multiple types of reactivity. Like water, a hydroxo complex could be amphoteric. Transfer of the hydroxy proton could produce an oxo complex, and protonation of the OH ligand could give an aquo complex.[17] The hydroxo group can also act as a nucleophile.[18] As a Lewis base, the

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(1) Roesky, H. W.; Singh, S.; Yusuff, K. K. M.; Maguire, J. A.; Hosmane, N. S. *Chem. Rev.* **2006**, *106*, 3813−3843.

(2) (a) Meunier, B.; de Visser, S. P.; Shaik, S. *Chem. Rev.* **2004**, *104*, 3947−3980. (b) Larsen, A. S.; Wang, K.; Lockwood, M. A.; Rice, G. L.; Won, T.-J.; Lovell, S.; Sadílek, M.; Tureek, F.; Mayer, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 10112−10123. (c) Shiota, Y.; Suzuki, K.; Yoshizawa, K. *Organometallics* **2005**, *24*, 3532−3538. (d) Korendovych, I. V.; Kryatov, S. V.; Reiff, W. M.; Rybak-Akimova, E. V. *Inorg. Chem.* **2005**, *44*, 8656−8658.

(3) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163−1188.

(4) Barrios, A. M.; Lippard, S. J. *J. Am. Chem. Soc*. **1999**, *121*, 11751−11757.

(5) (a) Balahura, R. J.; Sorokin, A.; Bernadou, J.; Meunier, B. *Inorg. Chem.* **1997**, *36*, 3488−3492. (b) Kervinen, K.; Korpi, H.; Mesu, J. G.; Soulimani, F.; Repo, T.; Rieger, B.; Leskela, M.; Weckhuysen, B. M. *Eur. J. Inorg. Chem.* **2005**, 2591−2599.

(6) Yi, C. S.; Zeczycki, T. N.; Guzei, I. A. *Organometallics* **2006**, *25*, 1047−1051.

(7) Griffith, W. P. *Chemistry of the Rarer Platinum Metals*; Interscience: New York, 1967; Chapter 3.

(8) Meyer, T. J.; Huynh, M. H. V. *Inorg. Chem.* **2003**, *42*, 8140−8160.

(9) Burn, M. J.; Fickes, M. G.; Hartwig, J. F.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 5875−5876.

(10) Edwards, A. J.; Elipe, S.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1997**, *16*, 3828−3836.

(11) Esteruelas, M. A.; Garcia-Yebra, C.; Olivan, M.; Onate, E. *Organometallics* **2000**, *19*, 3260−3262.

(12) (a) Cabeza, J. A.; Mulla, F.; Riera, V. *J. Organomet. Chem.* **1994**, *470*, 173−177. (b) Peacock, A. F. A.; Habtemariam, A.; Fernandez, R.; Walland, V.; Fabbiani, F. P. A.; Parsons, S.; Aird, R. E.; Jodrell, D. I.; Sadler, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 1739−1748.

(13) Bergman, R. G. *Polyhedron* **1995**, *14*, 3227−3237.

(14) (a) Campora, J.; Matas, I.; Palma, P.; Graiff, C.; Tiripicchio, A. *Organometallics* **2005**, *24*, 2827−2830. (b) Grushin, V. V.; Alper, H. *Organometallics* **1996**, *15*, 5242−5245. (c) Bennett, M. A.; Rokicki, A. *Inorg. Synth.* **1989**, *25*, 100−106. (d) Thorshaug, K.; Fjeldahl, I.; Romming, C.; Tilset, M. *Dalton Trans.* **2003**, 4051−4056. (e) Kuznetsov, V. F.; Bensimon, C.; Facey, G. A.; Grushin, V. V.; Alper, H. *Organometallics* **1997**, *16*, 97−106.

(15) Gould, R. O.; Jones, C. L.; Stephenson, T. A.; Tocher, D. A. *J. Organomet. Chem.* **1984**, *264*, 365−378.

(16) Esteruelas, M. A.; Garcia-Yebra, C.; Olivan, M.; Onate, E. *Organometallics* **2000**, *19*, 3260−3262.

(17) Ogo, S.; Makihara, N.; Kaneko, Y.; Watanabe, Y. *Organometallics* **2001**, *20*, 4903−4910.

(18) (a) Cuesta, L.; Hevia, E.; Morales, D.; Pérez, J.; Riera, L.; Miguel, D. *Organometallics* **2006**, *25*, 1717−1722. (b) Woerpel, K. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 7888. (c) Cámpora, J.; Palma, P.; del Río, D.; Álvarez, E. *Organometallics* **2004**, *23*, 1652−1655.

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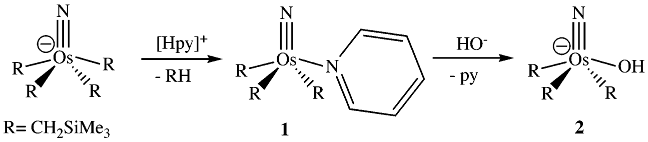
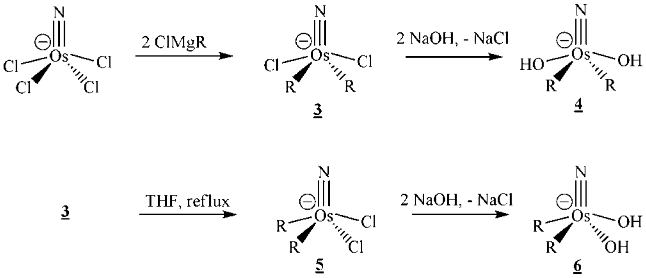
Scheme 1



Scheme 2



M−OH unit could interact with other metals to produce heterometallic compounds.

Mechanistic studies on the oxidation of alcohols by $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2(\mu\text{-}O)_2CrO_2]$ with isotopically labeled O_2 provided evidence for a reactive, hydroxo intermediate in the catalytic cycle, but this intermediate could not be isolated and characterized.[19] Here we report our work on the synthesis, properties, and reaction chemistry of organometallic hydroxo compounds related to this oxidation catalyst. We have prepared both terminal and bridging hydroxo compounds of osmium(VI) and have demonstrated that these can be useful precursors to the rational synthesis of heterometallic compounds.

Results

The osmium(VI) alkyl compound $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_4]$ is stable to water but reacts with 1 or 2 equiv of stronger acids. The reaction between $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_4]$ and 1 equiv of pyridinium tetrafluoroborate in dichloromethane cleanly produces the neutral pyridine complex $Os(N)(CH_2SiMe_3)_3(py)$ (**1**) (Scheme 1). The hydroxo compound $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_3(OH)]$ (**2**) results from the addition of $[N(n\text{-}Bu)_4][OH]$ to **1**.

The NMR spectra of **1** and **2** show that there two sets of alkyl groups in each compound: equivalent alkyl groups cis to the pyridine or hydroxo ligand and a unique alkyl trans to it. Compound **2** is soluble in most organic solvents. It is stable to air and water but is hygroscopic. Although **2** is quite stable at room temperature, it reacts slowly above 100 °C in wet toluene to form a carbonate compound (see below).

The trans and cis isomers of $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2(OH)_2]$ can be prepared by substitution reactions between osmium chloro compounds and sodium hydroxide. The reaction between $[N(n\text{-}Bu)_4][\textit{trans}\text{-}Os(N)(CH_2SiMe_3)_2Cl_2]$ (**3**) and an excess quantity of dry NaOH in diethyl ether produces a yellow solution of $[N(n\text{-}Bu)_4][\textit{trans}\text{-}Os(N)(CH_2SiMe_3)_2(OH)_2]$ (**4**) in 2−4 h at room temperature (Scheme 2). A ^1H NMR spectrum of an aliquot of the reaction mixture shows a nearly quantitative conversion of **3** to **4**. Compound **4** is recrystallized from ether/hexane to yield the analytically pure dihydroxo compound in good yield. A similar reaction between $[N(n\text{-}Bu)_4][\textit{cis}\text{-}Os(N)(CH_2SiMe_3)_2Cl_2]$ (**5**) and dry NaOH produces $[N(n\text{-}Bu)_4][\textit{cis}\text{-}Os(N)(CH_2SiMe_3)_2(OH)_2]$ (**6**).

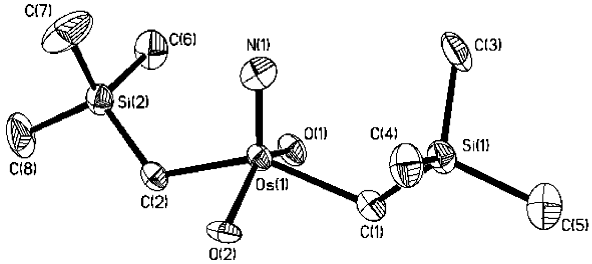


Figure 1. ORTEP diagram of the anion in **4**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 35% probability level.

Table 1. Selected Bond Angles (deg) and Distances (Å) of 4 and 12

	4	12
Os−N	1.583(9)	1.640(5), 1627(5)
Os−O	1.983(6), 1.969(6)	2.086(3), 2.095(4), 2.079(3), 2.085(4)
Os−C	2.146(9), 2.111(9)	2.092(6), 2.083(6), 2.094(6), 2.086(6)
N−Os−C	108.0(4), 107.3(4)	103.5(2), 102.2(3), 103.3(2), 103.4(2)
N−Os−O	108.3(3), 107.3(3)	119.3(2), 118.4(2), 116.3(2), 118.6(2)
Pd−O		2.009(3), 2.008(3)
Pd−N		2.000(4), 2.011(4)
Pd−Os		2.8388(5), 2.8628(4)
O−Pd−O		73.80(14)
N−Pd−N		80.09(17)

The trans isomer of $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ is the kinetic product of alkylation of $[N(n\text{-}Bu)_4][Os(N)Cl_4]$, but the cis isomer is more stable due to the greater trans influence of the alkyl ligand over chloride. Heating a solution of **3** in tetrahydrofuran causes reversible dissociation of chloride and results in conversion of **3** to **5**. Under similar conditions **4** does not isomerize to **6**.

Complex **4** is thermally stable, air stable, and soluble in water as well as in moderately polar organic solvents such as diethyl ether, toluene, dichloromethane, and chloroform. It is insoluble in hexane. The hydroxyl proton of **4**, a sharp singlet at 3.7 ppm in the ^1H NMR spectrum, exchanges with D_2O at room temperature. The IR spectrum of **4** displays a strong O−H stretching vibration at 3417 cm^{-1} and an Os−N stretching vibration at 1112 cm^{-1}.

Compound **6** is moderately stable in dilute THF solution under an N_2 atmosphere but, under air, it reacts rapidly with atmospheric carbon dioxide and water to form a complex mixture of products. The IR spectrum includes two broad O−H stretching vibrations at 3567 and 3505 cm^{-1}, and the ^1H NMR includes a resonance for the hydroxyl proton at 2.25 ppm. Unlike the stable trans isomer, **6** oligomerizes in solution.

A molecular structure determination of **4** by single-crystal X-ray diffraction shows that the molecule has a square-pyramidal geometry with trans hydroxo ligands and an apical nitrido group. Figure 1 shows the anion $\textit{trans}\text{-}[Os(N)(CH_2Si(CH_3)_3(OH)_2]^-$. The $[N(n\text{-}Bu_4)]^+$ cation and hydrogen atoms (calculated) are omitted for clarity. The Os−N bond length is relatively short at 1.583(9) Å. The O(1)−Os and O(2)−Os bond lengths are 1.983(6) Å and 1.969(6) Å, respectively (Table 1). The O(1)−Os−O(2) bond angle is 144.4(3)°.

Both **4** and **6** react with CO_2 to form the carbonate complex $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2(\eta^2\text{-}CO_3)]$ (**7**), but under different conditions and at different rates. The trans-hydroxo complex **4** reacts with wet CO_2 to form a complex mixture of products including **7**, but that reaction is slow. Under a dry CO_2 atmosphere, there is a 45% conversion of **4** to **7** after 24 h (Scheme 3) at 35 °C. The more reactive complex **6** forms **7** when stirred under 20 psi of CO_2. We can isolate **7** from **6** in

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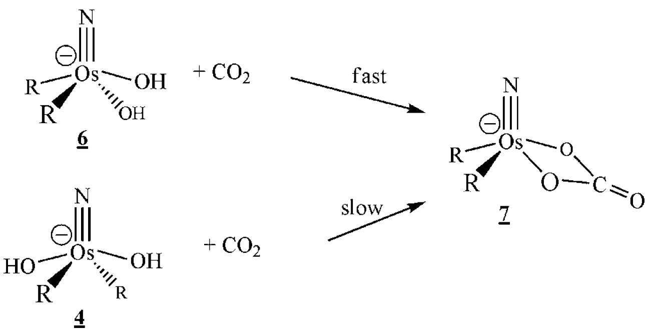
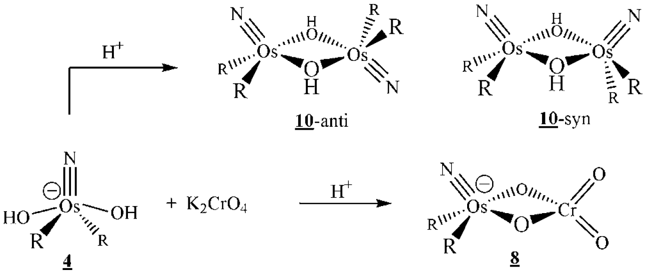
[19] Shapley, P. A.; Zhang, N.; Allen, J. L.; Pool. D. H.; Liang, H. C. *J. Am. Chem. Soc.* **2000**, *122,* 1079−1091.

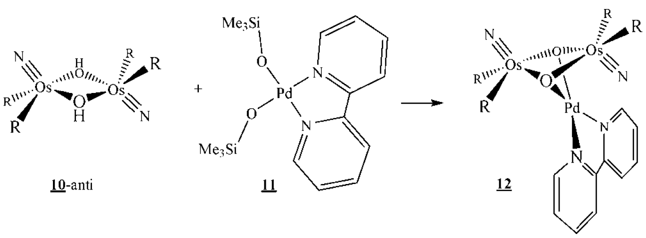
Scheme 3



Scheme 4



Scheme 5



90% yield under dry CO_2 after 2 h. Complex **7** also forms in the reaction between $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ and Ag_2CO_3.[20]

Aqueous solutions of CO_2 contain carbonic acid, and this weak acid facilitates substitution reactions of **4** (Scheme 4). Complex **4** does not react with K_2CrO_4 in CH_2Cl_2/H_2O, even after 48 h at room temperature. However, when CO_2 is added to the biphasic reaction mixture, **4** and K_2CrO_4 immediately react and form the purple heterometallic compound $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2(\mu\text{-}O)_2CrO_2]$ (**8**) and the blue protonation product $Os(N)(CH_2SiMe_3)_2(\mu\text{-}O)(\mu\text{-}OH)CrO_2$.[19] After chromatography on silica gel, we obtain **8** as a purple crystalline material in up to 40% yield, although the yield is variable. The same product is formed in 65% yield when $HOS(O)_2(p\text{-}C_6H_4\text{-}CH_3)$ is added to a mixture of **4** and K_2CrO_4 in CH_2Cl_2.

Osmium(VI) compounds form strong bonds to chloride, and the reaction between **2** and Me_3SiCl produces $[N(n\text{-}Bu)_4][\textit{trans}\text{-}Os(N)(CH_2SiMe_3)_3Cl]$ and Me_3SiOH. The early-transition-metal chloro complex $VOCl_3$ reacts with $[N(n\text{-}Bu)_4][\textit{trans}\text{-}Os(N)(CH_2SiMe_3)_2(OH)_2]$ to produce isomers of $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ in quantitative yield by ^1H NMR spectroscopy.

Treatment of **3** with 1 equiv of $AgBF_4(MeCN)_4$ produces the neutral dimer $\{Os(N)(CH_2SiMe_3)_2\}_2(\mu\text{-}Cl)_2$ (**9**). The reaction of $\{Os(N)(CH_2SiMe_3)_2\}_2(\mu\text{-}Cl)_2$ and Ag_2O produces the complex $\{Os(N)(CH_2SiMe_3)_2\}_2(\mu\text{-}OH)_2$ (**10**) in inconsistent yields. An alternative method uses strong acids to protonate **4**, which produce water and the neutral, bridging hydroxo complex. The reaction between **4** and 1 equiv of either *p*-toluenesulfonic acid at −78 °C or trifluoromethanesulfonic acid in diethyl ether at −30 °C produces **10** in a good and consistent yield (Scheme 4). Both the syn isomer and anti isomers are formed in the reaction, but the anti isomer (~70% by ^1H NMR) predominates. The mixture of the two isomers displays two strong O−H stretches at 3593 and 3579 cm^{-1} and two Os−N stretches at 1132 and 1124 cm^{-1}. The ^1H NMR spectrum shows 2 singlets at 0.064 and 0.047 ppm, for the protons of the trimethylsilyl moiety. Similarly, there are two distinct sets of resonances for the diastereotopic methylene protons of each isomer.

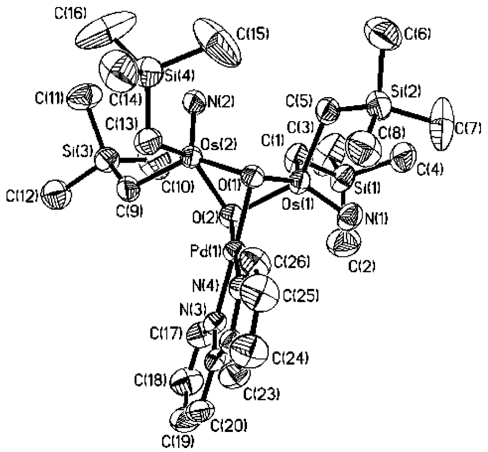


Figure 2. ORTEP diagram of **12**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 35% probability level.

Complex **10** is very soluble in nonpolar organic solvents, such as hexane, and is insoluble in water. We usually isolate **10** as a pure yellow oil, but it will crystallize from a concentrated solution of **10** in hexane at −20 °C. The complex is air stable and forms a complex mixture of products in the presence of NaH, $NaN(SiMe_3)_2$, and other strong Brønsted bases.

The neutral hydroxo dimer is a precursor to a new heterometallic complex. The reaction between **10** and $Pd(bpy)(OSiMe_3)_2$ (**11**) in diethyl ether at −30 °C produces $\{Os(N)(CH_2SiMe_3)_2\}_2(\mu_3\text{-}O)_2\{Pd(bpy)\}$ (**12**) (Scheme 5). The red trimetallic product crystallizes in analytically pure form from ether solution in 53% yield.

The air-stable heterometallic complex is soluble in THF and MeCN, sparingly soluble in CH_2Cl_2 and diethyl ether, and insoluble in hexane. The ^1H NMR spectrum in d_8-THF shows that the alkyl ligands on osmium are inequivalent, with two singlets at 0.073 and 0.097 ppm for the $SiMe_3$ groups and doublets at 1.602, 1.676, 2.735, and 3.016 ppm for the methylene protons. The IR spectrum shows a strong, sharp band at 1103 cm^{-1} for the Os−N stretching vibration, along with bands associated with the bipyridine ligand.

Single-crystal X-ray diffraction shows the molecular structure of **12** with two distorted-square-pyramidal osmium units and a square-planar palladium unit bridged by two oxo ligands as a monoclinic cell in the $P2_1/c$ space group with four molecules per unit cell. The sample used for structure determination included one molecule of THF in the crystal lattice per molecule of **12**: $\{Os(N)(CH_2SiMe_3)_2\}_2(\mu_3\text{-}O)_2\{Pd(bpy)\}\cdot C_4H_8O$. Figure 2 shows the crystal structure of **12** with the THF molecule omitted for clarity. The osmium−nitrogen and osmium−oxygen bond distances in **12** are longer than the analogous distances in **4**, while the osmium−carbon distances are shorter (Table 1). Although the osmium−palladium distances are less than 3 Å (Os(1)−Pd, 2.8388(5) Å; Os(2)−Pd, 2.8628(4) Å), there is no distortion in the geometries around either of the osmium atoms or the palladium atom that would indicate metal−metal bonding.

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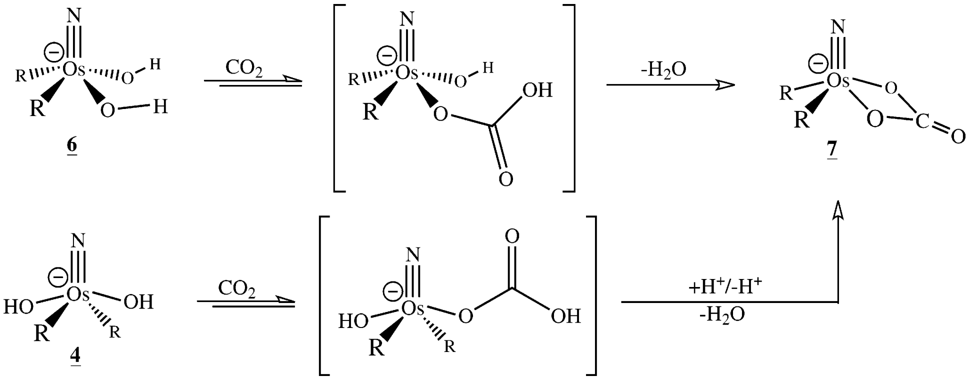
[20] Shapley, P. A.; Zhang, N. *Inorg. Chem.* **1988**, *27*, 976−977.

Scheme 6



The diosmium moiety in **12** has an anti configuration of the nitrido groups and must be derived from the isomer *anti*-**10**. The reaction mixture that produces **12** contains no unreacted *syn*-**10**. Instead, the ^{1}H NMR spectrum includes resonances for other (N)R_2Os/Pd(bpy) products. We have not yet successfully isolated the minor products.

Discussion

Hydroxo complexes of the later transition metals are key intermediates in the oxidation of organic molecules.[3] Because there are so few examples of stable, organometallic hydroxy complexes of the later transition metals it is important that we understand the structure, properties, and reactivity of these new osmium(VI) hydroxo compounds.

The structures of **4** and **12** include similar distorted-square-pyramidal osmium units with a trans orientation of the oxygen ligands in **4** and a cis orientation in **12**. Complex **12** is comparable to the μ-sulfido complex $\{Os(N)(CH_2SiMe_3)_2\}_2(\mu_3\text{-}S)_2\{Pt(dppe)\}$.[21] The overall geometries and bond distances and angles of the $Os(N)(CH_2SiMe_3)_2$ moieties are very similar. The O(1)−Pd(1)-O(2) angle in **12** is 73.80(14)°, significantly less than the S−Pt−S angle of 80.45(5)°, due to the shorter Pd−O the bond length. The N(3)−Pd(1)−N(4) angle of 80.09(17)° compares very well to those of other (bpy)Pd^{II} compounds.[22] Because there is no metal−metal bonding in **12**, the electron count around each metal center is 16. Each metal is coordinatively unsaturated and is potentially reactive with Lewis bases.

While compound **9** reacts with Ag_2O to form **10** in good yield, the reaction yield varies drastically on the basis of the concentration of water in the solvent and the purity of the Ag_2O. Direct protonation of **4** gives **10** in good yield and eliminates the need to prepare **9**.

Although **10** consists of isomers with both syn and anti arrangements of the nitrido ligands in the dimer, only the anti isomer can form a stable Os_2Pd heterometallic complex. Steric interactions with the alkyl ligands in *syn*-**10** likely prevent interaction of the complex with $Pd(bpy)(OSiMe_3)_2$. Because the hydroxyl groups in **10** are not acidic, the hydroxyl oxygen atoms probably coordinate to the palladium center prior to the elimination of $HOSiMe_3$.

Hydroxymetal compounds could act as acids (forming oxometal products), as bases (upon reaction with Brønsted or Lewis acids), or as nucleophiles. Other Lewis bases may substitute for the hydroxide ligand. In alkylmetal hydroxo compounds, concerted formation of alkane may also occur. We see examples of several of these reaction types with $[N(n\text{-}Bu)_4][Os(N)(CH_2SiMe_3)_3(OH)]$, $[N(n\text{-}Bu)_4][trans\text{-}Os(N)(CH_2Si(CH_3)_3)_2(OH)_2]$, $[N(n\text{-}Bu)_4][cis\text{-}Os(N)(CH_2Si(CH_3)_3)_2(OH)_2]$, and $\{Os(N)(CH_2SiMe_3)_2\}_2(\mu\text{-}OH)_2$.

The reactivity of osmium(VI) and ruthenium(VI) nitrido alkyl complexes toward strong mineral acids is $[M(N)R_4]^- > [M(N)R_3X]^- \gg [M(N)R_2X_2]^-$.[23] For example, the compounds $[N(n\text{-}Bu)_4][M(N)Me_4]$, with four electron-donating alkyl groups, react with excess aqueous HNO_3 at room temperature to give $[N(n\text{-}Bu)_4][M(N)Me_2(ONO_2)_2]$, with two electron-donating and two electron-withdrawing ligands in the basal plane. A coordinated hydroxyl group is more weakly acidic than HNO_3. Complex ***2*** loses 1 equiv of alkane through an internal proton transfer to the alkyl ligand but, because a coordinated hydroxyl group is a weak acid, the reaction is slow.

We propose that the isomerization of **3** to **5** occurs through reversible loss of chloride anion to yield the more thermodynamically favorable cis isomer. The isomerization occurs only in the presence of a coordinating solvent, such as THF. Pseudorotation is unlikely to occur, as the nitrido group is strongly trans-labilizing. The requisite trigonal-bipyramidal complex would be much less stable, in comparison to the square-pyramidal complex.

Because its structure facilitates proton transfer and the opening up of a coordination site, the *cis*-dihydroxo complex **6** is unstable in air and readily reacts with atmospheric carbon dioxide to form a complex mixture which includes **7**. The hydroxo ligand of **6** is nucleophilic. Attack by the hydroxo group on the carbon of CO_2 would form **7**, as shown in Scheme 6. The *trans*-dihydroxo complex similarly reacts with CO_2, but the steric bulk of the (trimethylsilyl)methyl ligands prevents intermolecular proton transfer. The formation of **7** from **4** probably requires bimolecular proton transfer.

The osmium(VI) hydroxo compounds are protonated by Brønsted acids. This dominates the reactivity of **4**. The hydroxo groups are not strongly nucleophilic, nor do they readily dissociate. Substitution reactions proceed when there is acid present to protonate one of the hydroxyl groups and form the reactive, four-coordinate species $Os(N)(CH_2SiMe_3)_2(OH)$. This can dimerize or react with Lewis bases such as $[HCO_3]^-$ and $[CrO_3(OH)]^-$.

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[21] Shapley, P. A.; Liang, H.-C.; Dopke, N. C. *Organometallics* **2001**, *20*, 4700−4704.

[22] (a) Canty, A. J.; Skleton, B. W.; Traill, P. R.; White, A. H. *Aust. J. Chem.* **1992**, *45*, 417−422. (b) Yamada, Y.; Uchida, M.; Fujita, M.; Miyashita, Y.; Okamoto, K.-I. *Polyhedron* **2003**, *22*, 1507−1513. (c) Stoccoro, S.; Alesso, G.; Cinellu, M. A.; Minghetti, G.; Zucca, A.; Bastero, A.; Claver, C.; Manassero, M. *J. Organometal. Chem.* **2002**, *664*, 77−84.

[23] Shapley, P. A.; Kim, H. S.; Wilson, S. R. *Organometallics* **1988**, *7*, 928−933.

Conclusion

The osmium(VI) hydroxo compounds **2**, **4**, **6**, and **10** are not strong acids. Only **2** eliminates alkane from proton transfer to an adjacent alkyl group, and this occurs only under forcing conditions. The chemistry of **6** is dominated by its ability to lose water and form a very reactive four-coordinate complex with a nucleophilic oxo group. The trans isomer **6** does not act as a nucleophile. Instead, it reacts with acids to form a neutral, four-coordinate hydroxo complex that can dimerize or react with oxy anions. The anti isomer of **10** has a conformation that allows the two bridging hydroxo groups to coordinate to another metal complex. The heterometallic complex **12** results from this initial interaction between $\{\mathrm{Os(N)(CH_2SiMe_3)_2}\}_2(\mu\text{-OH})_2$ and Pd(bpy)-$\mathrm{(OSiMe_3)_2}$ followed by loss of $\mathrm{HOSiMe_3}$. We are currently investigating the reactions between **10** and other metal compounds. This may provide a new, rational method for the synthesis of coordinatively unsaturated mixed-metal compounds.

Experimental Section

Toluene, diethyl ether, THF, and hexane were distilled from Na/$\mathrm{Ph_2CO}$ under $\mathrm{N_2}$. Dichloromethane was distilled from $\mathrm{CaH_2}$ under $\mathrm{N_2}$. Sodium trimethylsilanolate and pyridinium hydrochloride were sublimed under vacuum at 210 °C in a temperature-controlled oil bath. Sodium hydroxide was dried under vacuum at 210 °C for 4 days and stored under $\mathrm{N_2}$. *p*-Toluenesulfonic acid hydrate was recrystallized from acetone/toluene. Carbon dioxide ("bone dry grade", >99.8%) was purchased from MG Industries. All reactions were conducted under an $\mathrm{N_2}$ atmosphere using standard air-sensitive techniques in a Vacuum Atmospheres drybox unless otherwise stated. The compounds *trans*-$[\mathrm{N}(n\text{-Bu})_4][\mathrm{Os(N)(CH_2SiMe_3)_2Cl_2}]$,[24] *cis*-$[\mathrm{N}(n\text{-Bu})_4][\mathrm{Os(N)(CH_2SiMe_3)_2Cl_2}]$,[25] and $\mathrm{PdCl_2(bpy)}$[26] were prepared according to literature methods. Authentic samples of $[\mathrm{N}(n\text{-Bu})_4][\mathrm{Os(N)(CH_2SiMe_3)_2}(\mu\text{-O})_2\mathrm{CO}]$[20] and $[\mathrm{N}(n\text{-Bu})_4][\mathrm{Os(N)(CH_2SiMe_3)_2}(\mu\text{-O})_2\mathrm{CrO_2}]$[19] were prepared and compared with **7** and **8**, respectively.

NMR spectra were recorded on Varian Unity-500 and Varian Unity-400 FT NMR spectrometers at ambient temperature. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR. UV–visible spectra were recorded on a Hewlett-Packard 8452A spectrometer. Elemental analyses were performed by the University of Illinois Microanalytical service, and X-ray data were collected at the School of Chemical Sciences X-ray Diffraction Laboratory.

Preparation of $\mathbf{Os(N)(CH_2SiMe_3)(NC_5H_5)}$ (1). The yellow crystals of $[\mathrm{N}(n\text{-Bu})_4][\mathrm{Os(N)(CH_2SiMe_3)_4}]$ (0.100 g, 0.127 mmol) were dissolved in 10 mL of $\mathrm{CH_2Cl_2}$, and 1 equiv of pyridinium tetrafluoroborate (0.021 g, 0.127 mmol) was added all at once to the yellow stirring solution. After 15 min, the solution became yellow-gold and the $[\mathrm{Hpy}][\mathrm{BF_4}]$ was consumed. The reaction mixture was stirred for 1 h, after which the $\mathrm{CH_2Cl_2}$ was removed under vacuum. The yellow crystals which lined the flask were extracted with hexane, and the yellow extracts were filtered. The white insoluble solid $[\mathrm{N}(n\text{-Bu})_4][\mathrm{BF_4}]$ was discarded. The solvent was removed from the filtrate, during which time yellow microcrystals of **1** formed and were dried under vacuum. The product was recrystallized from hexane. Yield: 0.060 g (87%). IR (KBr pellet, $\mathrm{cm^{-1}}$): 3133–3022 (w, pyridine ν_{CH}), 2944–2856 (s, ν_{CH}), 1606 (w, pyridine δ_{NC}), 1450 (m, δ_{CH}), 1250 (s, δ_{SiC}), 1239 (s, δ_{SiC}), 1116 (s, ν_{OsN}). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 18 °C): δ 8.01 (d, J = 5.2 Hz, 2 H, py), 7.77 (t, J = 7.5 Hz, py), 7.43 (t, J = 7.2 Hz, 2 H, py), 2.45 (s, 2 H, $\mathrm{OsC}H_2$ trans to pyridine), 1.79 (d, J = 9.2 Hz, 2 H, $\mathrm{OsC}H^a\mathrm{H^b}$ cis to pyridine), 0.48 (d, J = 9.2 Hz, 2 H, $\mathrm{OsCH^a}H^b$ cis to pyridine), 0.00 (s, 18 H, $\mathrm{Si(C}H_3)_3$ cis to pyridine), −0.02 (s, 9 H, $\mathrm{Si(C}H_3)_3$ trans to pyridine). ^{13}C{^{1}H} NMR (100.6 Hz, $\mathrm{CDCl_3}$, 21.7 °C): δ 149.9 (py), 137.6 (py), 125.8 (py), 21.9 ($\mathrm{Os}C\mathrm{H_2}$ cis to pyridine), 2.94 ($\mathrm{Si}(C\mathrm{H_3})_3$ trans to pyridine), 1.58 ($\mathrm{Os}C\mathrm{H_2}$ trans to pyridine), 1.16 ($\mathrm{Si}(C\mathrm{H_3})_3$ cis to pyridine). MS (FD, *m*/*z*): 546 ($\mathrm{M^+}$), 467 ($\mathrm{M^+ - NC_5H_5}$); 934 (($\mathrm{M^+ - (NC_5H_5)_2}$). Anal. Calcd: C, 37.47; H, 7.03; N, 5.14. Found: C, 37.71; H, 7.04; N, 5.27.

Preparation of $[\mathbf{N}(\boldsymbol{n}\textbf{-Bu})_4][\mathbf{Os(N)(CH_2SiMe_3)_3(OH)}]$ (2). The yellow crystals of **1** (0.027 g, 0.050 mmol) were dissolved in 20 mL of $\mathrm{CH_2Cl_2}$, and 1 equiv of $[\mathrm{N}(n\text{-Bu})_4][\mathrm{OH}]$ (33 μL, 0.050 mmol) was added via syringe to the bright yellow-gold solution. The solution turned light yellow and was stirred for 2 h. The solvent was removed under vacuum. The oil was dissolved in toluene, and the solvent was distilled under reduced pressure to remove residual water. The yellow oil was then dissolved in diethyl ether, and the solution was filtered. The diethyl ether was removed to give a yellow oil of **2**. ^{1}H NMR ($\mathrm{CDCl_3}$, 300 MHz, 18 °C): δ 3.18 (t, J = 8 Hz, 8 H, $\mathrm{NC}H_2\mathrm{CH_2CH_2CH_3}$), 1.98 (s, 2 H, $\mathrm{OsC}H_2$ trans to OH ligand), 1.57 (m, 8 H, $\mathrm{NCH_2C}H_2\mathrm{CH_2CH_3}$), 1.43 (sextet, J = 7.2 Hz, 8 H, $\mathrm{NCH_2CH_2C}H_2\mathrm{CH_3}$), 1.42 (d, J = 10.3 Hz, 2 H, $\mathrm{OsC}H^a\mathrm{H^b}$ cis to OH ligand), 0.98 (t, J = 7.2 Hz, 12 H, $\mathrm{NCH_2CH_2CH_2C}H_3$), 0.75 (d, J = 10.3 Hz, 2 H, $\mathrm{OsCH^a}H^b$ cis to OH ligand), 0.010 (s, 18 H, $\mathrm{Si(C}H_3)_3$ cis to OH ligand), −0.083 (s, 9 H, $\mathrm{Si(C}H_3)_3$ trans to OH ligand). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 21.7 °C, 100.6 Hz): δ 58.80 ($\mathrm{N}C\mathrm{H_2CH_2CH_2CH_3}$), 24.08 ($\mathrm{NCH_2}C\mathrm{H_2CH_2CH_3}$), 19.75 ($\mathrm{NCH_2CH_2}C\mathrm{H_2CH_3}$), 15.77 ($\mathrm{Os}C\mathrm{H_2}$ cis to OH ligand), 13.70 ($\mathrm{NCH_2CH_2CH_2}C\mathrm{H_3}$), 2.24 ($\mathrm{Si}(C\mathrm{H_3})_3$ cis to OH ligand), 2.01 ($\mathrm{Si}C\mathrm{H_3})_3$ trans to OH ligand), 1.21 ($\mathrm{Os}C\mathrm{H_2}$ trans to OH ligand).

Synthesis of $[\mathbf{N}(\boldsymbol{n}\textbf{-Bu})_4][\boldsymbol{trans}\textbf{-}\mathbf{Os(N)(CH_2SiMe_3)_2(OH)_2}]$ (4). Under a dry $\mathrm{N_2}$ atmosphere, powdered NaOH (0.068 g, 1.69 mmol) was added to a stirred orange solution of *trans*-$[\mathrm{N}(n\text{-Bu})_4][\mathrm{Os(N)(CH_2SiMe_3)_2Cl_2}]$ (0.117 g, 0.169 mmol, 19:1 trans:cis) in 10 mL of $\mathrm{(C_2H_5)_2O}$ in a 15 mL vial. The reaction mixture was stirred vigorously for 4 h, at which time the solution was bright yellow. The solution was filtered to remove unreacted NaOH and NaCl. The yellow solution was concentrated under vacuum. Yellow crystals (0.096 g, 1.46 mmol, 87%) were collected, washed with hexane, and dried under vacuum. IR (KBr, pellet, $\mathrm{cm^{-1}}$): 3587 (m, ν_{OH}), 3579 (m, ν_{OH}), 3568 (m, ν_{OH}), 2955 (vs, ν_{CH}), 1112 (vs, ν_{OsN}). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 20 °C): δ 3.22–3.18 (t, 8 H, $\mathrm{NC}H_2\mathrm{CH_2CH_2CH_3}$), 1.64–1.57 (m, 8 H, $\mathrm{NCH_2C}H_2\mathrm{CH_2CH_3}$), 1.48–1.39 (m, 8 H, $\mathrm{NCH_2CH_2C}H_2\mathrm{CH_3}$), 1.03 (s, 2 H, $\mathrm{OsC}H_2$), 1.03–0.99 (t, 12 H, $\mathrm{NCH_2CH_2CH_2C}H_3$), 0.10 (s, 18 H, $\mathrm{Si(C}H_3)_3$). ^{13}C{^{1}H} NMR (101 MHz, $\mathrm{CDCl_3}$, 20 °C): δ 58.8 ($\mathrm{N}C\mathrm{H_2CH_2CH_2CH_3}$), 24.0 ($\mathrm{NCH_2}C\mathrm{H_2CH_2CH_3}$), 19.8 ($\mathrm{NCH_2CH_2}C\mathrm{H_2CH_3}$), 18.5 ($\mathrm{Os}C\mathrm{H_2}$), 13.7 ($\mathrm{NCH_2CH_2CH_2}C\mathrm{H_3}$), 1.47 ($\mathrm{Si}(C\mathrm{H_3})_3$). Anal. Calcd for $\mathrm{C_{24}H_{60}N_2O_2OsSi_2}$: C, 44.0; H, 9.23; N, 4.28. Found: C, 44.43; H, 9.61; N, 4.40.

Thermolysis of 2. Complex **2** (0.046 g, 0.064 mmol) in 10 mL of toluene was heated to 106 °C under $\mathrm{N_2}$ for 12 h, during which time the solution changed from yellow to red-orange. The solution was cooled to room temperature, after which the solution was filtered and the solvent was removed under vacuum. The orange oil was extracted with diethyl ether, and the solution was filtered. The solvent was removed under vacuum, giving 0.020 g (0.031 mmol, 48% crude yield) of **7** as an orange-red oil. The product was characterized by IR and ^{1}H NMR spectroscopy and was identified as $[\mathrm{N}(n\text{-Bu})_4][\mathrm{Os(N)(CH_2SiMe_3)_2}(\mu\text{-O})_2\mathrm{CO}]$.

Reaction of 4 with $\mathbf{ClSiMe_3}$. Complex **4** (0.006 g, 0.009 mmol) was dissolved in $\mathrm{CD_2Cl_2}$ in an NMR tube. Two equivalents of $\mathrm{ClSiMe_3}$ (2 μL, 0.016 mmol) was added to the yellow solution, and ^{1}H NMR spectra were obtained. Within 10 min, **4** was completely consumed and a mixture of cis and trans isomers of $[\mathrm{N}(n\text{-Bu})_4][\mathrm{Os(N)(CH_2SiMe_3)_2Cl_2)}]$ was formed along with $\mathrm{Me_3SiOH}$ (δ 0.12, s) and $\mathrm{Me_3SiOSiMe_3}$ (δ 0.062, s).

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[24] Belmonte, P. A.; Own, Z.-Y. *J. Am. Chem. Soc.* **1984**, *106*, 7493–7496.

[25] Zhang, N. Ph.D. Thesis, University of Illinois, **1991**.

[26] McCormick, B. J.; Jaynes, E. N., Jr.; Kaplan, R. I. *Inorg. Synth.* **1971**, *12*, 216–218.

Conversion of 3 to 5. A solution of $[\mathrm{N}(n\text{-Bu})_4][trans\text{-}\mathrm{Os(N)(CH_2SiMe_3)_2Cl_2)}]$ (0.500 g, 0.0723 mmol) in 25 mL of THF was heated to 64−65 °C for 32 h. Solvent was removed under vacuum. The residue was crystallized from $\mathrm{CH_2Cl_2}$/hexane at −20 °C to give red crystals (0.456 g, 91% yield) of $[\mathrm{N}(n\text{-Bu})_4][\mathrm{Os(N)(CH_2SiMe_3)_2Cl_2)}]$. By ^{1}H NMR spectroscopy,[22] this consisted of 97% trans and 3% cis.

Synthesis of $[\mathrm{N}(n\text{-Bu})_4][cis\text{-}\mathrm{Os(N)(CH_2SiMe_3)_2(OH)_2}]$ (6). To a solution of **5** (0.012 g, 0.017 mmol) in 1 mL of d_8-THF was added NaOH (0.004 g, 0.2 mmol), and the reaction mixture was stirred vigorously for 4 h. A ^{1}H NMR spectrum of the mixture showed conversion to one product. IR (THF solution, cm^{-1}): 3567 (m, ν_{OH}), 3505 (m, ν_{OH}), 2964 (vs, ν_{CH}), 2876 (vs, ν_{CH}), 1238 (m, ν_{OH}). ^{1}H NMR (400 MHz, d_8-THF, 20 °C): δ 3.49−3.45 (t, 8 H, $\mathrm{NC}H_2\mathrm{CH_2CH_2CH_3}$), 2.25 (s, 2 H, $\mathrm{O}H$), 2.08−2.06 (d, 2 H, $\mathrm{OsC}H_2$); 1.77−1.72 (m, 8 H, $\mathrm{NCH_2C}H_2\mathrm{CH_2CH_3}$), 1.48−1.42 (m, 8 H, $\mathrm{NCH_2CH_2C}H_2\mathrm{CH_3}$), 1.02−0.98 (t, 12 H, $\mathrm{NCH_2CH_2CH_2C}H_3$), 0.012 (s, 18 H, $\mathrm{Si(C}H_3)_3$).

Reaction of 6 with $\mathrm{CO_2}$. To a solution of **5** (0.072 g, 0.104 mmol, 97:3 cis:trans by ^{1}H NMR) in 6 mL of THF was added solid NaOH (0.021 g, 0.525 mmol), and the reaction mixture was stirred for 5 h. Additional NaOH (0.020 g, 0.500 mmol) was then added, and this mixture was stirred for another 1.5 h. It was filtered through Celite, and THF was added to increase the volume of the filtrate to 10 mL. The solution was stirred under 20 psi of $\mathrm{CO_2}$ for 4 h. The solvent was slowly removed under vacuum to give **7** as a microcrystalline yellow solid (0.064 g, 0.094 mmol). ^{1}H NMR ($\mathrm{CDCl_3}$, 500 MHz, 20 °C): δ 3.28−3.24 (m, 8 H, $\mathrm{NC}H_2\mathrm{CH_2CH_2CH_3}$), 3.03−3.00 (d, 2 H, $\mathrm{OsC}H_2$, J = 10.19 Hz), 1.79−1.76 (d, 2 H, $\mathrm{OsC}H_2$, J = 10.12 Hz), 1.68−1.60 (m, 8 H, $\mathrm{NCH_2C}H_2\mathrm{CH_2CH_3}$), 1.48−1.39 (m, 8 H, $\mathrm{NCH_2CH_2C}H_2\mathrm{CH_3}$), 1.02-.98 (t, 12 H, $\mathrm{NCH_2CH_2CH_2C}H_3$), 0.024 (s, 18 H, $\mathrm{Si(C}H_3)_3$). IR (KBr, pellet, cm^{-1}): 1703 (s, ν_{CO}), 1120 (s, ν_{OsN}).

Reaction of 4 with $\mathrm{CO_2}$. A solution of **4** (0.082 g, 0.25 mmol) in 10 mL of $\mathrm{CH_2Cl_2}$ in a thick-walled glass reaction vessel was stirred under 20 psi of $\mathrm{CO_2}$ at 35 °C for 24 h. The solvent was removed under vacuum, and the resulting red oil was crystallized from $\mathrm{CH_2Cl_2}$/hexane to yield yellow crystals of **7** (0.038 g, 0.056 mmol, 45%).

Synthesis of $[\mathrm{N}(n\text{-Bu})_4][\mathrm{Os(N)(CH_2SiMe_3)_2}(\mu\text{-O})_2\mathrm{CrO_2}]$ (8) using $\mathrm{CO_2}$. A solution of $[\mathrm{N}(n\text{-Bu})_4][\mathrm{Os(N)(CH_2SiMe_3)_2(OH)_2}]$ (0.096 g, 0.146 mmol) in 10 mL of $\mathrm{CH_2Cl_2}$ was combined with a solution of $\mathrm{K_2CrO_4}$ (0.285 g, 1.465 mmol) in 10 mL of $\mathrm{H_2O}$. The mixture was magnetically stirred, and a small piece of solid $\mathrm{CO_2}$ was added. The $\mathrm{CH_2Cl_2}$ layer turned purple and then deep blue within 30 s. After 2 min, the organic layer was separated and extracted three times with 10 mL portions of water. The solvent was removed under vacuum from the organic solution. The product was purified by chromatography on a short (1 in., eluted with $\mathrm{CH_3CN}$) silica gel column. The product, a purple solid (0.043 g, 0.0583 mmol, 40%), was identical by ^{1}H NMR with previously prepared samples of this complex. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 500 MHz, 20 °C): δ 3.18 (m, 8 H, $\mathrm{NC}H_2\mathrm{CH_2CH_2CH_3}$), 2.08 (s, 4 H, $\mathrm{OsC}H_2$), 1.63 (m, 8 H, $\mathrm{NCH_2C}H_2\mathrm{CH_2CH_3}$), 1.43 (m, 8 H, $\mathrm{NCH_2CH_2C}H_2\mathrm{CH_3}$), 1.02 (t, 12 H, $\mathrm{NCH_2CH_2CH_2C}H_3$), 0.09 (s, 18 H, $\mathrm{Si(C}H_3)_3$).

Synthesis of $[\mathrm{N}(n\text{-Bu})_4][\mathrm{Os(N)(CH_2SiMe_3)_2}(\mu\text{-O})_2\mathrm{CrO_2}]$ (8) using $\mathrm{HOSO_2}(p\text{-}\mathrm{C_6H_4Me})\cdot\mathrm{H_2O}$. A solution of $[\mathrm{N}(n\text{-Bu})_4][\mathrm{Os(N)(CH_2SiMe_3)_2(OH)_2}]$ (0.097 g, 0.148 mmol) in 10 mL of $\mathrm{CH_2Cl_2}$ was combined with a solution of $\mathrm{K_2CrO_4}$ (0.165 g, 0.850 mmol) in 10 mL of $\mathrm{H_2O}$. The mixture was magnetically stirred. A solution of $\mathrm{HOSO_2}(p\text{-}\mathrm{C_6H_4Me})\cdot\mathrm{H_2O}$ (0.056 g, 0.294 mmol) in 2 mL of $\mathrm{H_2O}$ was added dropwise. The $\mathrm{CH_2Cl_2}$ layer turned purple within 30 s. The reaction mixture was stirred for 10 min. The organic layer was separated and extracted three times with 10 mL portions of water. The solvent was removed under vacuum from the organic solution. The deep purple residue was recrystallized from $\mathrm{CH_2Cl_2}$/hexane. The product, a purple solid (0.071 g, 0.096 mmol, 65%), was identical by ^{1}H NMR with previously prepared samples of this complex. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 500 MHz, 20 °C): δ 3.18 (m, 8 H, $\mathrm{NC}H_2\mathrm{CH_2CH_2CH_3}$), 2.08 (s, 4 H, $\mathrm{OsC}H_2$), 1.63 (m, 8 H, $\mathrm{NCH_2C}H_2\mathrm{CH_2CH_3}$), 1.43 (m, 8 H, $\mathrm{NCH_2CH_2C}H_2\mathrm{CH_3}$), 1.02 (t, 12 H, $\mathrm{NCH_2CH_2CH_2C}H_3$), 0.09 (s, 18 H, $\mathrm{Si(C}H_3)_3$).

Synthesis of $\{\mathrm{Os(N)(CH_2SiMe_3)_2}\}_2(\mu\text{-Cl})_2$ (9). The crystals of **3** (0.100 mg, 0.144 mmol) were dissolved in 25 mL of $\mathrm{CH_2Cl_2}$. To the stirred orange-red solution of **3** was added 1 equiv of $\mathrm{AgBF_4(MeCN)_4}$ (0.052 mg, 0.144 mmol). Immediately a white solid precipitated from solution and the reaction mixture turned from orange-red to yellow-green and then yellow-orange. The solution was stirred for 1 h and then filtered through Celite. The filtrate was concentrated to approximately 1 mL, and hexane (∼30 mL) was added to precipitate the salts from solution. The cloudy solution was concentrated to remove most of the $\mathrm{CH_2Cl_2}$ and then filtered through Celite. The orange-yellow hexane solution was concentrated, and the solution was again filtered. The hexane was removed from the filtrate, and the yellow-orange oil was dried under vacuum, during which time microcrystals of **9** formed. The product was recrystallized from concentrated $\mathrm{CH_2Cl_2}$, giving red-orange crystals. Yield: 0.049 mg (82% based on **3**). IR (KBr pellet, cm^{-1}, *major*): 2956 (m, ν_{CH}), 2900 (m, ν_{CH}), 2856 (w, ν_{CH}), 1411 (w, δ_{CH}), 1367 (w, δ_{CH}), 1244 (s, δ_{SiC}), *1128* (m, ν_{OsN}), 1122 (m, ν_{OsN}), 1017 m, 968 w, 850 (s, ν_{SiC}), 834 (s, ν_{SiC}), 774 w, 750 w, 717 w, 683 w. ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$, 18 °C, *major*): δ *3.99* (d, J = 9.8 Hz, 2 H, $\mathrm{OsC}H^a\mathrm{H^bSiMe_3}$), 3.87 (d, J = 9.5 Hz, 2 H, $\mathrm{OsC}H^a\mathrm{H^bSiMe_3}$), *2.70* (d, J = 9.8 Hz, 2 H, $\mathrm{OsCH^a}H^b\mathrm{SiMe_3}$), 2.35 (d, J = 9.5 Hz, 2 H, $\mathrm{OsCH^a}H^b\mathrm{SiMe_3}$), *0.09* (s, 18 H, $\mathrm{Si(C}H_3)_3$), 0.06 (s, 18 H, $\mathrm{Si(C}H_3)_3$). ^{13}C{^{1}H} NMR (100.6 MHz, $\mathrm{CD_2Cl_2}$, 18 °C, *major*): δ *14.58* ($\mathrm{Os}C\mathrm{H_2SiMe_3}$), 13.96 ($\mathrm{Os}C\mathrm{H_2SiMe_3}$), *0.12* ($\mathrm{Si}(C\mathrm{H_3})_3$), 0.00 ($\mathrm{Si}(C\mathrm{H_3})_3$). Anal. Calcd for $\mathrm{C_8H_{22}ClOOsNSi_2}$: C, 23.20; H, 5.36; N, 3.38. Found: C, 23.17; H, 5.44; N, 3.25.

Synthesis of $[\mathrm{Os(N)(CH_2SiMe_3)_2(OH)}]_2$ using $\mathrm{Ag_2O}$. A sample of **9** (0.049 mg) was dissolved in 20 mL of $\mathrm{(C_2H_5)_2O}$. One equivalent of $\mathrm{Ag_2O}$ (0.027 g, 0.12 mmol) was added, and the vial was wrapped in foil. The reaction mixture was stirred for 2 days. The solution was then filtered through Celite. The solvents were removed under vacuum, and the oil was dissolved in pentane. The pentane solution was filtered and concentrated. The solution was cooled to −30 °C. Yellow-orange crystals of **10** were isolated. Yield: 0.027 g, 92%. IR (KBr pellet, cm^{-1}): 3593 (s, ν_{OH}), 3579 (s, ν_{OH}), 2951 (m, ν_{CH}), 2896 (w, ν_{CH}), 2829 (w, ν_{CH}), 1408 (w, δ_{CH}), 1367 (w, δ_{CH}), 1257 (s, δ_{SiC}), 1243 (s, δ_{SiC}), 1132 (s, ν_{OsN}), 1124 (w, ν_{OsN}), 1017 w, 955 m, 850 (s, ν_{SiC}), 830 (s, ν_{SiC}), 774 w, 747 w, 715 w, 683 w, 489 m. ^{1}H NMR (300 MHz, $\mathrm{CD_2Cl_2}$, 21.8 °C, *major*): δ 3.42 (d, J = 10.9 Hz, 2 H, $\mathrm{OsC}H^a\mathrm{H^bSiMe_3}$), *3.15* (d, J = 10.9 Hz, 2 H, $\mathrm{OsC}H^c\mathrm{H^dSiMe_3}$), 2.54 (s, 1 H, $\mathrm{Os(O}H)$), *2.51* (s, 1 H, $\mathrm{Os(O}H)$), 1.61 (d, J = 10.9 Hz, 2 H, $\mathrm{OsCH^a}H^b\mathrm{SiMe_3}$), *1.23* (d, J = 10.9 Hz, 2 H, $\mathrm{OsCH^c}H^d\mathrm{SiMe_3}$), 0.064 (s, 18 H, $\mathrm{Si(C}H_3)_3$), *0.047* (s, 18 H, $\mathrm{Si(C}H_3)_3$). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 125.6 MHz, 18 °C, *major*): δ 3.70 ($\mathrm{Os}C\mathrm{H_2SiMe_3}$), *3.23* ($\mathrm{Os}C\mathrm{H_2SiMe_3}$), 0.41 ($\mathrm{Si}(C\mathrm{H_3})_3$), *0.17* ($\mathrm{Si}(C\mathrm{H_3})_3$). MS (EI, 70 eV, m/z): 792 (M$^+$). Anal. Calcd for $\mathrm{C_8H_{23}OsONSi_2}$: C, 24.23; H, 5.86; N, 3.54. Found: C, 24.29; H, 5.75; N, 3.54.

Synthesis of $[\mathrm{Os(N)(CH_2SiMe_3)_2}(\mu\text{-OH})]_2$ (10). A cold (−20 °C) solution of $\mathrm{HOSO_2}(p\text{-}\mathrm{C_6H_4Me})\cdot\mathrm{H_2O}$ (0.030 g, 0.158 mmol) and **4** (0.105 g, 0.167 mmol) in 25 mL of $\mathrm{(C_2H_5)_2O}$ was warmed to 25 °C with stirring. After 75 min, the mixture was filtered, and solvent was removed from the filtrate under vacuum. The orange residue was purified by chromatography on silica gel (2 in. column, eluted with diethyl ether). The product, $[\mathrm{Os(N)(CH_2SiMe_3)_2}(\mu\text{-OH})]_2$, was isolated as a bright yellow oil. Yield: 0.039 g, 0.053 mmol, 63%.

Synthesis of $\mathrm{Pd(OSiMe_3)_2(bpy)}$ (11). Two equivalents of $\mathrm{NaOSiMe_3}$ (0.134 g, 1.20 mmol) was added to a suspension of $\mathrm{PdCl_2(bpy)}$ (0.200 g, 0.600 mmol) in 35 mL of $\mathrm{(C_2H_5)_2O}$, and the mixture was stirred for 24 h at 25 °C. The mixture was filtered through Celite. The bright yellow filtrate was concentrated to 20

Table 2. Summary of Crystal Data for 4 and 12

	4	**12**
empirical formula	$C_{24}H_{60}N_2O_2$-$OsSi_2$	$C_{30}H_{60}N_4O_3$-Os_2PdSi_4
formula wt	655.15	1123.98
temp, K	193(2)	297(2)
wavelength, Å	0.710 73	0.710 73
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/c$
a, Å	15.045(6)	12.3500(9)
b, Å	19.289(8)	18.3598(13)
c, Å	22.687(9)	19.9189(13)
α, deg	90.00	90.00
β, deg	90.00	101.883(3)
γ, deg	90.00	90.00
V, $Å^3$	6584(5)	4419.7(5)
Z	8	4
calcd density, Mg/m^3	1.322	1.689
abs coeff, mm^{-1}	3.966	6.277
F(000)	2704	2184
cryst size, mm	0.04 × 0.22 × 0.25	0.27 × 0.23 × 0.05
θ range for data collecn, deg	1.80−25.37	2.02−27.74
no. of rflns collected	48 249	46 288
no. of indep rflns (*R*(int) = 0.0314)	6030	10 317
no. of data/restraints/params	6030/0/290	10 317/166/455
largest diff peak and hole, e/$Å^3$	1.785 and −0.764	1.365 and −1.344
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0686 wR2 = 0.0955	R1 = 0.0327 wR2 = 0.0641
R indices (all data)	R1 = 0.1703 wR2 = 0.1165	R1 = 0.0624 wR2 = 0.0769
goodness of fit of F^2	0.971	1.020

mL, 3 mL of hexane was added, and the solution was cooled to −20 °C. Yellow crystals were collected by filtration and dried under vacuum (0.181 g, 0.370 mmol, 68.3%). ^{1}H NMR (400 MHz, C_6D_6, 21.7 °C): δ 9.11 (d, 2 H, bpy), 6.79 (t, 2 H, bpy), 6.53 (d, 2 H, bpy), 6.48 (t, 2 H, bpy), 0.77 (s, 18 H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 21.7 °C): δ 155.1, 149.4, 137.7, 125.1, 120.8 (*C* bpy), 5.4 (Si(*C*H$_3$)$_3$). IR (KBr pellet, cm^{-1}): 3056 (w, bpy ν_{CH}), 3033 (w, bpy ν_{CH}), 3003 (m, bpy ν_{CH}), 2944−2889 (s, ν_{CH}), 1606−1449 (m, ν_{CC}), 1249 (s, δ_{SiC}), 1237 (s, δ_{SiC}), 982 (vs, ν_{OSi}), 954 (vs, ν_{OSi}), 823 (vs, ν_{SiC}), 774. Anal. Calcd for $C_{16}H_{26}N_2O_2PdSi_2$: C, 43.58; H, 5.94; N, 6.35. Found: C, 43.33; H, 5.71; N, 6.30.

Synthesis of (bpy)Pd(μ_3-O)$_2${Os(N)(CH$_2$SiMe$_3$)$_2$}$_2$ (12). Solutions of [Os(N)(CH$_2$SiMe$_3$)$_2$(μ-OH)]$_2$ (0.024 g, 0.030 mmol) in 2 mL of $(C_2H_5)_2O$ and Pd(OSiMe$_3$)$_2$(bpy) (0.014 g, 0.032 mmol) in 2 mL of $(C_2H_5)_2O$ were cooled to −30 °C. The solution of **10** was slowly added to the solution of **11**. The color immediately changed from yellow to red and then to dark purple. After approximately 2 min, a red solid precipitated. The product was collected by filtration and dried under vacuum. It was recrystallized from THF/hexane at −20 °C (0.017 g, 0.016 mmol, 53%). ^{1}H NMR (500 MHz, d_8-THF, 21.7 °C): δ 8.54 (d, 2 H, bpy), 8.36 (d, 2 H, bpy), 8.23 (t, 2 H, bpy), 7.75 (t, 2 H, bpy), 3.02 (d, 2 H, OsCH^aH^b, J = 10.85 Hz), 2.73 (d, 2 H, OsCH^aH^b, J = 9.99 Hz), 1.67 (d, 2 H, OsCH^aH^b, J = 9.98 Hz), 1.60 (d, 2 H, OsCH^aH^b, J = 10.85 Hz), 0.096 (s, 18 H, SiC*H*$_3$), 0.072 (s, 18 H, SiC*H*$_3$). ^{13}C{^{1}H} NMR (126 MHz, d_8-THF, 21.7 °C): δ 156.1, 151.2, 141.6, 127.7, 124.0 (*C* bpy); 4.98 (OsC^aH$_2$), 0.96 (Si(C^aH$_3$)$_3$), 0.61 (Si(C^bH$_3$)$_3$), 0.015 (OsC^bH$_2$). IR (KBr pellet, cm^{-1}): 3108 (w, bpy ν_{CH}), 3047 (w, bpy ν_{CH}), 2947 (s, ν_{CH}), 1606−1452 (w, ν_{CC}), 1240 (vs, δ_{SiC}), 1103 (vs, ν_{OsN}), 856−834 (vs, ν_{SiC}). Anal. Calcd for $C_{26}H_{52}Os_2O_2PdSi_4N_4$: C, 29.69; H, 4.98; N, 5.33. Found: C, 29.51; H, 4.76; N, 5.24.

Structure Determination of 4. General crystallographic data are given in Table 2. Systematic absences for 0*kl* ($k \neq 2n$), *h*0*l* ($l \neq 2n$), and *hk*0 ($h \neq 2n$) were consistent with the space group *Pbca*. A face-indexed absorption correction was applied (absorption coefficient μ = 3.966 mm^{-1}), and the maximum and minimum transmission factors were 0.806 and 0.659. After the correction there were 3 systematic absence violations and 13 bad equivalents. Systematically absent reflections were deleted, and symmetry-equivalent reflections were averaged to yield the set of unique data. The remaining 6030 data were used in the least-squares refinement.

The structure was solved using direct methods by using the SHELXTL software package. The correct position for the osmium and silicon atoms were deduced from an *E* map. Subsequent least-squares refinement and difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and tied to those of the attached non-hydrogen atom. An anisotropic extinction parameter was not needed. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of least-squares refinement. The largest peak in the final Fourier difference map (1.79 e Å^{-3}) was located 1.07 Å from the osmium atom. Final analyses of variance between calculated and observed structure factors exhibited no perceptible errors.

Structure determination of 12. General crystallographic data are given in Table 2. Systematic absences for 0*k*0 ($k = 2n + 1$) and *h*0*l* ($l = 2n + 1$) were consistent with the space group $P2_1/c$. A face-indexed absorption correction was applied (absorption coefficient μ = 6.277 mm^{-1}), and the maximum and minimum transmission factors were 0.744 and 0.282. After the correction there were 6 systematic absence violations and 0 bad equivalents. Systematically absent reflections were deleted, and symmetry-equivalent reflections were averaged to yield the set of unique data. The reflection 011 was found to be a statistical outlier (ΔF^2/esd = 36.60). The remaining 10 317 data were used in the least-squares refinement.

The structure was solved using Patterson methods by using the SHELXTL software package. The correct positions for the osmium and palladium atoms were deduced from a sharpened Patterson map. Subsequent least-squares refinement and difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and tied to those of the attached non-hydrogen atom. An anisotropic extinction parameter was not needed. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of least-squares refinement. The largest peak in the final Fourier difference map (1.79 e Å^{-3}) was located 1.07 Å from the Os(1) atom. Final analyses of variance between calculated and observed structure factors exhibited no perceptible errors.

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Supporting Information Available: For **4** and **12**, CIF files giving details of the crystal data collection and refinement parameters, bond angles, bond distances, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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