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N−H and N−C Bond Activation of Pyrimidinic Nucleobases and Nucleosides Promoted by an Osmium Polyhydride

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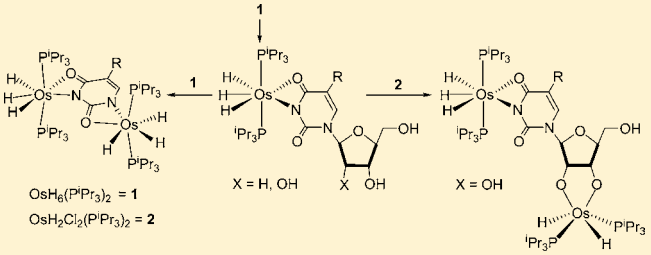
Supporting Information

ABSTRACT: Complex $OsH_6(P^iPr_3)_2$ (**1**) reacts with 1-methylthymine and 1-methyluracil to give $OsH_3(P^iPr_3)_2$(nucleobase') (**2**, **3**) containing the deprotonated nucleobases (nucleobase') κ^2-N,O coordinated by the nitrogen atom at position 3 and the oxygen bonded to the carbon atom of the ring at position 4. Similarly, the reactions of **1** with thymidine, 5-methyluridine, deoxyuridine, and uridine lead to $OsH_3(P^iPr_3)_2$(nucleoside') (**4**−**7**) with the deprotonated nucleoside (nucleoside') κ^2-N,O coordinated by the nitrogen atom at position 3 and the oxygen bonded to the carbon atom at position 4 of the nucleobases. Treatment of complexes **5** and **7**, containing nucleosides derived from ribose, with $OsH_2Cl_2(P^iPr_3)_2$ (**8**) in the presence of Et_3N affords dinuclear species $OsH_3(P^iPr_3)_2$(nucleobase')-(ribose)$(P^iPr_3)_2H_2Os$ (**9**, **10**) formed by two different metal fragments. Complex **1** also promotes the cleavage of the N−C bond of **2**−**7** to give the dinuclear species $\{OsH_3(P^iPr_3)_2\}_2$(nucleobase") (**11**, **12**) with the nucleobase skeleton (nucleobase") κ^2-N,O coordinated to both metal fragments. These compounds can be also prepared by reaction of **1** with 0.5 equiv of thymine and uracil. The use of 1:1 hexahydride:nucleobase molar ratios gives rise to the preferred formation of the mononuclear complexes $OsH_3(P^iPr_3)_2$(nucleobase"') (**13**, **14**; nucleobase"' = monodeprotonated thymine or uracil). The X-ray structures of complexes **6**, **11**, and **14** are also reported.



INTRODUCTION

Cisplatin, and the second generation alternatives carboplatin and oxaliplatin, are still the most widely used chemotherapeutic agents for cancer.[1] However, some toxicological side-effects of cisplatin and the drug resistance developed by some tumors have stimulated research toward the synthesis of complexes with another transition metals, in particular some group 8 compounds.[2] Thus, a few reports of anticancer active half-sandwich osmium d^6-complexes have recently appeared.[3]

DNA is an important potential biological target for many metal-based anticancer agents. Distortions of DNA structure often correlate with anticancer activity. Hence, it is of great important to understand DNA binding properties of transition-metal species.[4] It is generally accepted that the solvolytic activation of *cis*-$Pt^{II}(NH_3)_2X_2$-drugs involves the displacement of leaving groups X by water molecules, which are subsequently replaced by the DNA donor heteroatoms.[1] In contrast to square-planar platinum d^8-species, octahedral osmium d^6-complexes are relatively inert toward substitution reactions due to the dependence of the crystal field activation energy on Δ_0.[5] Thus, in order to develop new models of osmium anticancer drugs, we reasoned that osmium d^2-species containing some Brønsted base as a ligand could be a promising alternative, since the fair acidity of the hydrogen atoms bonded to the nucleobase heteroatoms. In this context, it should be noted that a nitride−osmium(VI) complex has recently shown anticancer activity *in vivo*.[6]

The saturated hexahydride d^2-complex $OsH_6(P^iPr_3)_2$ activates C−H bonds of a broad number of organic molecules[7] and, by protonation with weak Brønsted acids, releases molecular hydrogen to afford osmium-hydride d^4-species, which contain the corresponding conjugated Brønsted base as a ligand.[8] Thymine as a constituent of DNA and uracil as a constituent of RNA can both form transition-metal compounds resulting from deprotonation and subsequent coordination of the nitrogen atom at position 3 and the oxygen atoms bonded to the carbons at positions 2 and 4, depending on the coordination metal.[1b,9] Recently, deprotonated 1-methylthymine acting as a chelating ligand for the *cis*-$Pd(C_6F_3H_2)_2$ and *cis*-$Pd(C_6F_5)_2$ moieties through the nitrogen atom at position 3 and the oxygen atom bonded to the carbon at position 4 has been also reported.[10]

In the search for models of osmium anticancer drugs, we have studied the reactivity of the hexahydride d^2-complex $OsH_6(P^iPr_3)_2$[11] toward pyrimidinic N-methyl nucleobases and nucleosides. In this paper we report N−H and N−C bond activations of these compounds, in a sequential manner.

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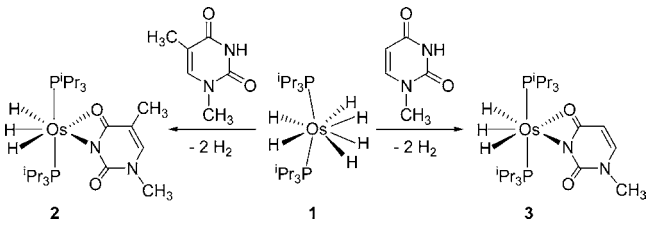
RESULTS AND DISCUSSION

N−H Bond Activation of Nucleobases. Treatment of toluene solutions of $OsH_6(P^iPr_3)_2$ (**1**) with 1.0 equiv of 1-methylthymine and 1-methyluracil for 3 h, under reflux, leads to complexes **2** and **3** according to Scheme 1. They result from the

Scheme 1



deprotonation of the nitrogen atom at position 3 and the chelate coordination of the generated anion, by the deprotonated nitrogen and the oxygen bonded to the carbon at position 4.

Complexes **2** and **3** were isolated as white solids in 70% and 61% yields, respectively. As expected, for three inequivalent hydride ligands, the ^1H NMR spectra in toluene-d_8 at 203 K show three hydride resonances at about −10.6 (H_A), −13.5 (H_B), and −14.9 (H_C). These resonances are temperature dependent (Figure 1). The coalescence between the H_B and H_C

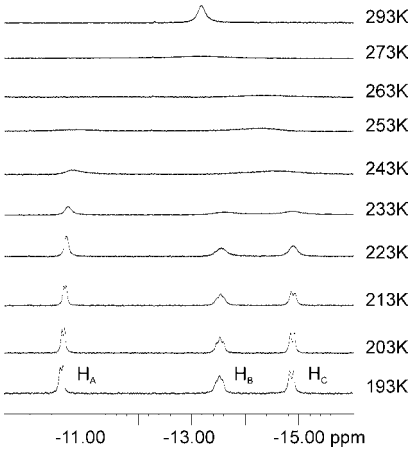
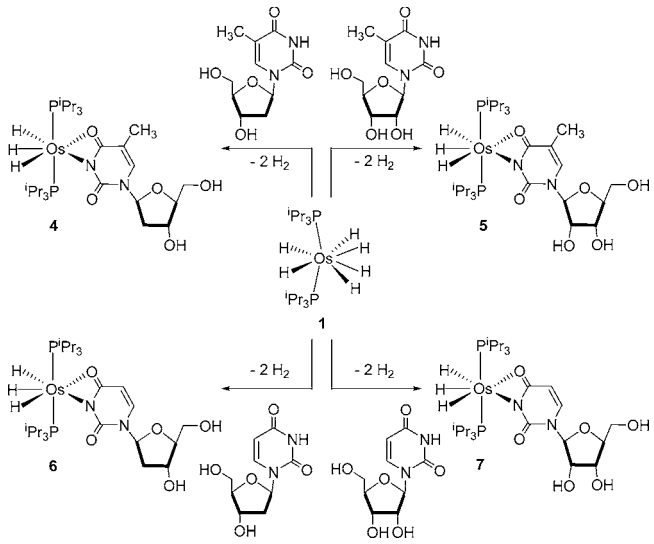


Figure 1. High field of the $^1H\{^{31}P\}$ NMR spectra (300 MHz, toluene-d_8) of complex **2** as a function of temperature.

resonances occurs between 233 and 243 K, whereas a single hydride signal is observed at temperatures higher than 273 K. This is consistent with the operation of two thermally activated site exchange processes, in agreement with the behavior of related OsH_3-derivatives.[8b,c] The exchange mechanism implies Os−H stretching, H−H shortening, and subsequent rotation of the resulting dihydrogen ligand. Since the activation barrier for both exchanges is similar, between 10 and 11 kcal·mol^{-1}, the transition states containing the dihydrogen ligand *trans* disposed to the nitrogen or oxygen atoms of the deprotonated nucleobase appear to be equally favored. The $^{31}P\{^1H\}$ NMR spectra at room temperature contain a singlet at about 34 ppm, according to the presence of equivalent phosphines in the complexes. In the $^{13}C\{^1H\}$ NMR spectra, the resonance corresponding to the coordinated carbonyl group appears at about 177 ppm whereas that due to the free one is observed at about 154 ppm, highfield shifted by about 23 ppm.

Thymidine, 5-methyluridine, deoxyuridine, and uridine show a behavior similar to 1-methylthymine and 1-methyluracil. Treatment of toluene solutions of **1** with 1.0 equiv of the nucleosides for 3 h, under reflux, affords the related derivatives **4**−**7** (Scheme 2), containing the corresponding deprotonated nucleoside that is chelated by the nitrogen atom at position 3 and the oxygen bonded to the carbon at position 4 of the nucleobase.

Scheme 2



Complexes **4**−**7** were isolated as white (**4** and **5**) and yellow (**6** and **7**) solids in 48−60% yield. Complex **6** was characterized by X-ray diffraction analysis.[12] The structure (Figure 2) proves

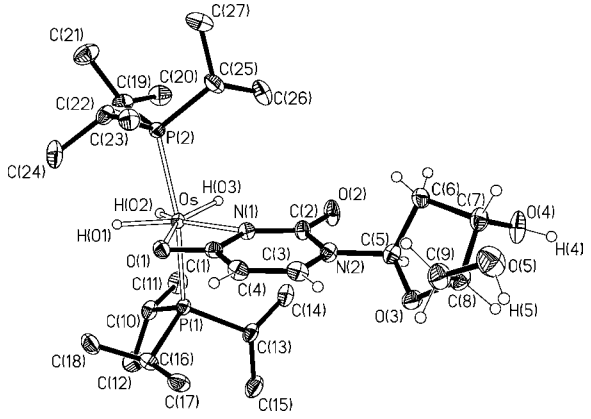


Figure 2. Molecular diagram of complex **6**. Selected bond lengths (Å) and angles (°): Os−P(1) = 2.3439(7), Os−P(2) = 2.3461(7), Os−O(1) = 2.2361(19), Os−N(1) = 2.210(2), O(1)−C(1) = 1.267(3), O(2)−C(2) = 1.229(3); P(1)−Os−P(2) = 167.87(2), N(1)−Os−O(1) = 59.01(7).

the deprotonation of the nitrogen atom at position 3 (N(1)) and the chelate coordination of the nucleobase by the latter and the oxygen atom bonded to the carbon atom at position 4 (O(1)). Thus, the geometry around the osmium atom can be rationalized as a distorted pentagonal bipyramidal with the phosphine ligands occupying axial positions (P(1)−Os−P(2) = 167.87(2)°). The metal coordination sphere is completed by the deprotonated nucleoside, which acts with a bite angle

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N(1)−Os−O(1) of 59.01(7)°, and the hydride ligands. The Os−N(1) and Os−O(1) bond lengths are 2.210(2) and 2.2361(19) Å, respectively. As expected the separation between the coordinated oxygen atom O(1) and C(1), 1.267(3) Å, is slightly longer than the separation between the free oxygen atom O(2) and C(2), 1.229(3) Å. An extended view of the structure (Figure 3) reveals that the molecules of the complex

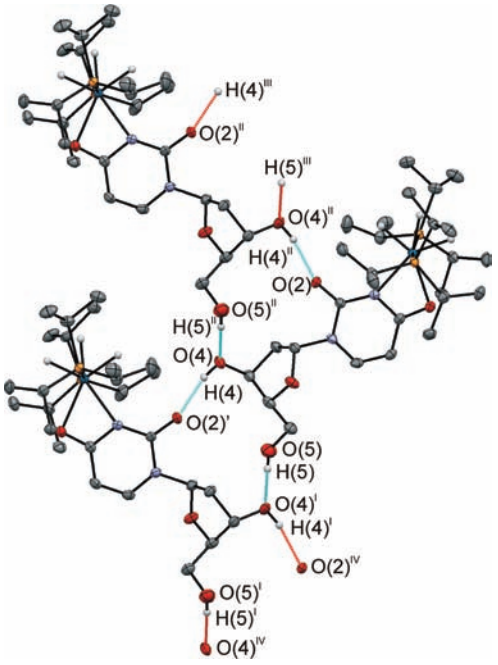


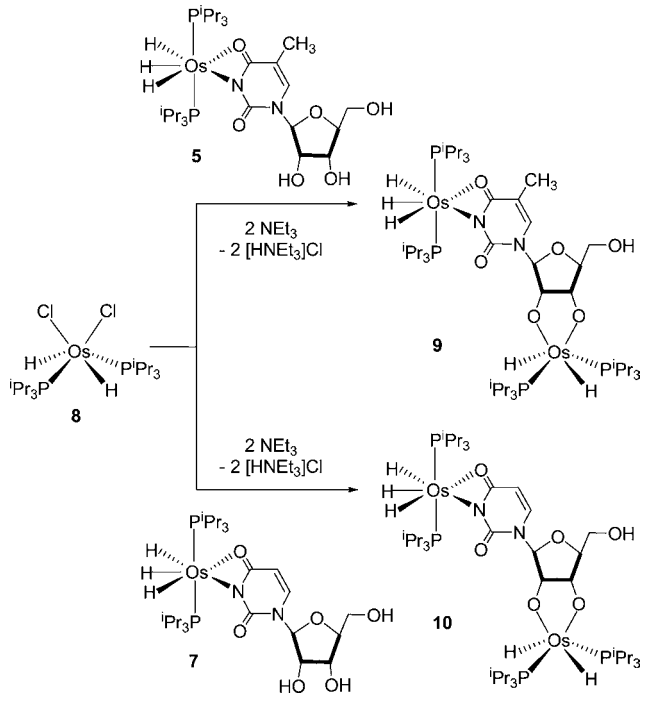
Figure 3. View of the interactions via hydrogen bonding in the structure of complex **6** [symmetry codes: (I) $x + 1/2, -y + 1/2, -z + 1$; (II) $x - 1/2, -y + 1/2, -z + 1$; (III) $x - 1, y, z$; (IV) $x + 1, y, z$].

form polymers in the *ab* plane by means of intermolecular O(5)−H(5)···O(4) hydrogen bonds between sugars of adjacent molecules, in addition to O(4)−H(4)···O(2) hydrogen bonds between the O(4)−H(4) substituent of the five-membered ring of the sugar of one molecule and the free O(2) oxygen atom of an neighboring molecule. In agreement with this, the separations H(5)···O(4) and H(4)···O(2) of 1.876(2) and 1.880(2) Å, respectively, are shorter than the sum of the van der Waals radii of hydrogen and oxygen (r_{vdw}(H) = 1.20 Å, r_{vdw}(O) = 1.52 Å).[13] Furthermore, the O(4)···O(5) and O(4)···O(2) separations are 2.729(3) and 2.705(3) Å, and the angles O(4)−H(4)−O(2) and O(5)−H(5)−O(4) are almost linear at 166.7(2)° and 179.4(2)°, respectively.

The ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra of **4**−**7** are consistent with the structure shown in Figure 2 and agree well with those of **2** and **3**. The ^{1}H NMR spectra in toluene-d_8 at 213 K show three hydride resonances at about −10.5, −13.6, and −15.5 ppm, whereas at room temperature only one hydride signal is observed. The activation barriers for the thermally activated site exchange processes are also, in the four cases, between 10 and 11 kcal·mol^{-1}. The ^{31}P{^{1}H} NMR spectra at 298 K show a singlet at about 34 ppm. In the ^{13}C{^{1}H} NMR spectra the resonance due to the coordinated carbonyl group is observed at about 177 ppm, whereas that corresponding to the free carbonyl group appears at about 154 ppm.

The protons of the OH functional groups of the ribose five-membered ring of **5** and **7** can be replaced by the $OsH_2(P^iPr_3)_2$ metal fragment. Thus, the treatment of toluene solutions of these compounds with 1.0 equiv of the known complex $OsH_2Cl_2(P^iPr_3)_2$ (**8**) in the presence of 4.0 equiv of Et_3N, at room temperature, for 20 min leads to the dinuclear derivatives **9** and **10** and $[Et_3NH]Cl$. These complexes were isolated as yellow solids in 59% and 64% yield, according to Scheme 3.

Scheme 3



Their dinuclear character is strongly supported by the high-resolution electrospray mass spectra, in acetonitrile, which show the molecular peaks at 1283.5936 (**9**) and 1269.5683 (**10**) with the isotope pattern as expected, as shown in Figure 4 for **9**.

The ^{1}H and ^{31}P{^{1}H} NMR spectra of **9** and **10** are consistent with the presence of two different metal fragments in these compounds. One of them is a seven-coordinate $OsH_3(P^iPr_3)_2$(nucleobase) moiety similar to those of **2**−**7**.

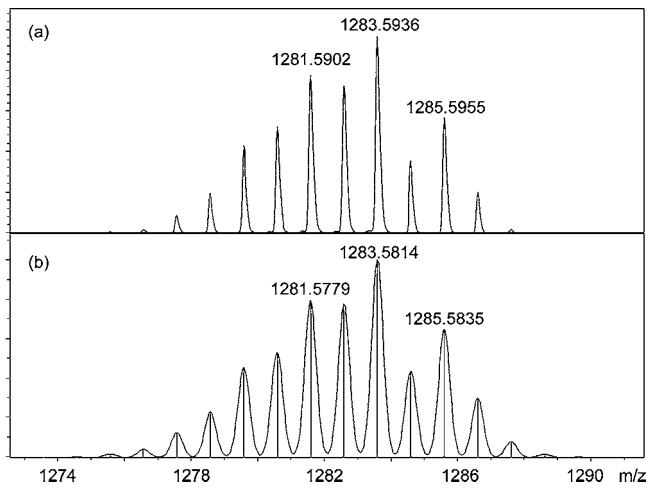


Figure 4. (a) Selected region of the ESI-HRMS spectrum of complex **9** showing the isotopic distribution of $[M + H]^+$ (highest peak at 1283.5936). (b) Simulated pattern for the molecular formula $C_{46}H_{101}N_2O_6Os_2P_4$ $[M + H]^+$.

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The other is a 16-valence electrons osmium(IV) $OsH_2(P^iPr_3)_2$(ribose) moiety with a structure in the solid state, characteristic for unsaturated $OsH_2P_2L_2$ d^4-species, which can be described as a C_2-square antiprism with two missing vertexes.[8a,14] Thus, as is shown in Figure 5 for **9**, the ^1H NMR

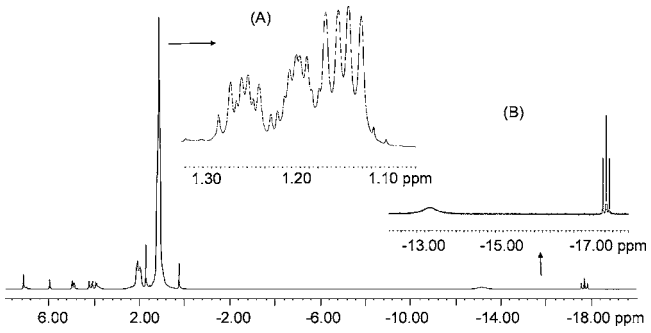


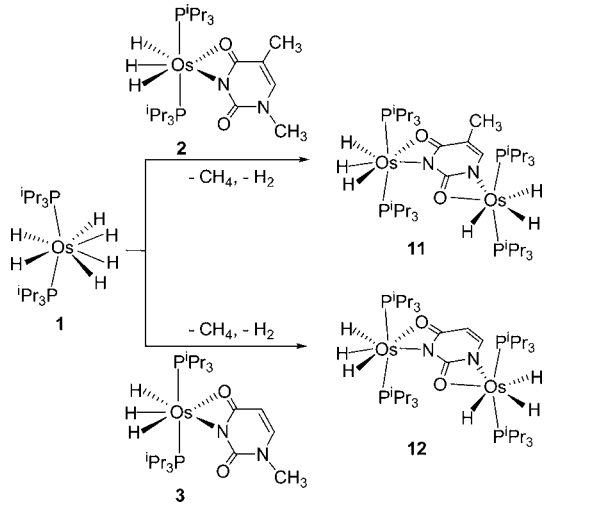
Figure 5. ^1H NMR spectrum (C_6D_6, 500 MHz) of complex **9**. (A) Methyl resonances of the P^iPr_3 ligands. (B) Hydride resonances.

spectra at room temperature contain doublets of virtual triplets corresponding to the P^iPr_3 methyl groups of the seven-coordinate metal fragment and a double doublet due to the P^iPr_3 methyl groups of the six-coordinate moiety. In the high field region of the spectra the OsH_3 unit of these compounds displays a broad resonance at about −13 ppm, whereas the OsH_2 unit gives rise to a triplet with a H−P coupling constant of 41 Hz at about −18 ppm. In agreement with **2**−**7**, the resonance at about −13 ppm is converted into three signals, at about −10.5, −13.6, and −14.9 ppm, at 233 K. However, at this temperature, the resonance at about −18 ppm generates a complex pattern as expected for the presence of two slowly interconverting dihydride−osmium(IV) isomers, one having C_2 symmetry and the other with no symmetry.[15] The $^{31}P\{^1H\}$ NMR spectra contain two singlets between 35 and 33 ppm. In addition, it should be mentioned that the replacement of the COH-protons of the ribose subtituents of **5** and **7** by the $OsH_2(P^iPr_3)_2$ metal fragment has a marked influence in the chemical shifts of the $^{13}C\{^1H\}$ NMR ribose-CO−Os resonances of **9** and **10** (92.6 and 90.9 (**9**); 93.2 and 90.9 (**10**) ppm), which appear downfield shifted by about 20 ppm with regard to the respective COH resonances of **5** and **7** (75.6 and 70.6 (**5**); 76.0 and 70.6 (**7**) ppm).

C−N Bond Activation of the Coordinated Nucleobase. The reactions providing straightforward examples of C−N single bond activation are rare in comparison with the known C−H bond activation processes.[16] In spite of this, the hexahydride complex **1** does not only promote the cleavage of the N−H bond of 1-methylthymine and 1-methyluracil but also the activation of the respective N−CH_3 bond. Thus, the treatment of toluene solutions of **2** and **3** with 1.0 equiv of **1** for 8.5 and 2 h, respectively, under reflux leads to the dinuclear complexes **11** and **12** (Scheme 4), as a result of the demethylation of the deprotonated nucleobases and the coordination of the demethylated nitrogen atom and the oxygen bonded to the carbon atom at position 2 to a new $OsH_3(P^iPr_3)_2$ metal fragment. These compounds were isolated as white solids in 65% (**11**) and 70% (**12**) yield.

The hexahydride complex **1** also promotes the rupture of the N-sugar bond of **4**−**7** to afford the dinuclear compounds **11** and **12**. However, the reactions are not clean and complex mixtures are generated. The formation of these mixtures is

Scheme 4



consistent with the versatile reactivity of the osmium polyhydrides,[17] in particular that of **1**,[7b−e,18] with alcohols, aldehydes, and ketones. As expected, the mixtures resulting from the reactions of the ribose derivatives **5** and **7** with **1** also contain the dinuclear complexes **9** and **10**.

Complex **11** was crystallized from the mixture generated from the reaction of **4** with **1** and characterized by X-ray diffraction analysis. Figure 6 shows a view of the molecule. The

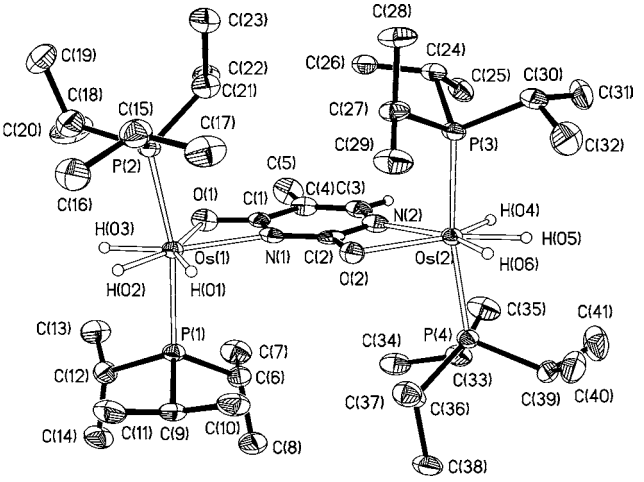


Figure 6. Molecular diagram of complex **11**. Selected bond lengths (Å) and angles (°): Os(1)−P(1) = 2.3366(8), Os(1)−P(2) = 2.3407(9), Os(2)−P(3) = 2.3356(9), Os(2)−P(4) = 2.3209(9), Os(1)−O(1) = 2.227(2), Os(1)−N(1) = 2.220(3), Os(2)−O(2) = 2.260(2), Os(2)−N(2) = 2.163(3), C(1)−O(1) = 1.283(4), C(2)−O(2) = 1.297(4); P(1)−Os(1)−P(2) = 167.46(3), P(3)−Os(2)−P(4) = 169.06(3), N(1)−Os(1)−O(1) = 59.77(10), N(2)−Os(2)−O(2) = 59.60(10).

structure proves the rupture of the N-sugar bond of **4** and the unprecedented coordination of the nucleobase skeleton, as a bridge ligand coordinated κ^2-N,O to both osmium atoms. Thus, the geometry around each metal center can be rationalized as a distorted pentagonal bipyramid with the phosphines occupying axial positions (P(1)−Os−(1)−P(2) = 167.46(3)°, P(3)−Os(2)−P(4) = 169.06(3)°). The metal coordination spheres are completed by the donor atoms of the nucleobase skeleton, which act with bite angles N(1)−Os(1)−O(1) and N(2)−

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Os(2)−O(2) of 59.77(10)° and 59.60(10)°, respectively, and the hydride ligands. The Os(1)−N(1) bond length of 2.220(3) Å is about 0.06 Å longer than the Os(2)−N(2) separation of 2.163(3) Å, while the Os(1)−O(1) distance of 2.227(2) Å is about 0.03 Å shorter than the Os(2)−O(2) bond length of 2.260(2) Å. The four distances compare well with the respective bond length of **6**. The C(1)−O(1) distance of 1.283(4) Å is statistically identical with the C(2)−O(2) bond length of 1.297(4) Å.

The ^{1}H NMR spectra of **11** and **12** in toluene-d_8 at 203 K are consistent with the structure shown in Figure 6. As shown in Figure 7 for **11**, they contain six high field resonances between

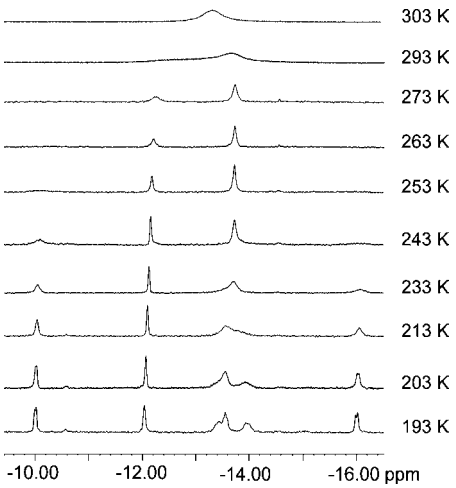


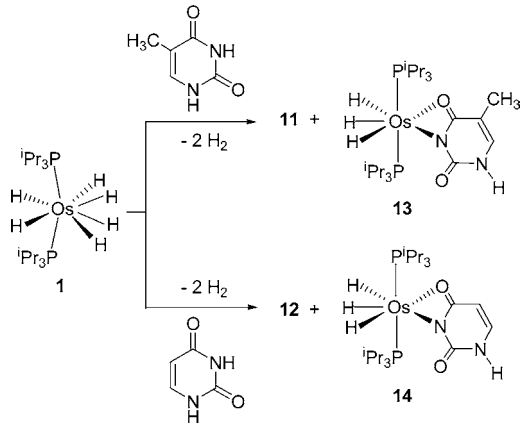
Figure 7. High field of the ^{1}H{^{31}P} NMR spectra (400 MHz, toluene-d_8) of complex **11** as a function of temperature.

−10 and −16 ppm, corresponding to the six inequivalent hydride ligands. At room temperature the different OsH_3 units share the same chemical shift. As a consequence of this and in agreement with the operation of four thermally activated site exchange processes, the spectra at 303 K show only one hydride signal at about −14 ppm. The activation barrier for all exchanges is similar to those of **2**−**10**. The ^{31}P{^{1}H} NMR spectra at room temperature contain two singlets at 36.9 and 30.9 (**11**) and 36.7 and 30.9 (**12**) ppm. In the ^{13}C{^{1}H} NMR spectra the resonances due to the coordinated carbonyl groups appear at 176.9 and 165.9 (**11**) and 178.8 and 167.4 (**12**) ppm.

Complexes **11** and **12** can be also prepared by treatment of toluene solutions of **1** with 0.5 equiv of thymine and uracil, respectively, for 3 h, under reflux. Their formation involves the double deprotonation of the nucleobase. The use of 1:1 hexahydride:nucleobase molar ratios leads to 0.2:1 mixtures of the dinuclear compounds **11** and **12** and the mononuclear derivatives **13** and **14** (Scheme 5), as a result of the preferred monodeprotonation of the nucleobases. Complexes **13** and **14**, which were isolated as white solids in 66% and 61% yield, contain a deprotonated nucleobase κ^2-N,O-coordinated by the ONO-nitrogen atom and the oxygen bonded to the carbon adjacent to the CR unit (R = CH_3, H).

The uracil derivate complex **14** was characterized by X-ray diffraction analysis. The structure has four chemically equivalent but crystallographically independent molecules in the asymmetric unit. Figure 8 shows a drawing of one of them. The geometry around the osmium atom is as the observed ones in **6** and **11**; i.e., a distorted pentagonal bipyramid with axial phosphines (P(1)−Os−P(2) = 171.42(6)°−167.64(9)°). The

Scheme 5



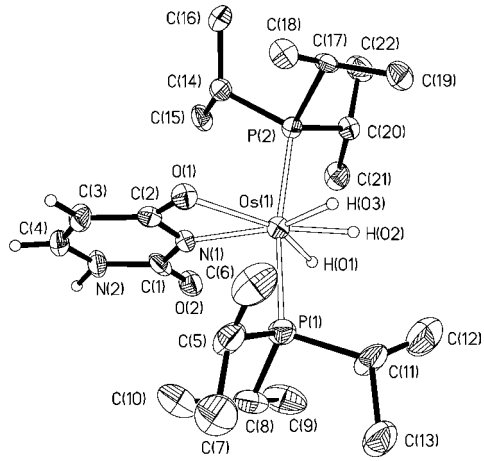


Figure 8. Molecular diagram of complex **14**. Selected bond lengths (Å) and angles (°): Os(1)−P(1) 2.3330(1), 2.3414(18), 2.329(2), 2.298(2); Os(1)−P(2) 2.3442(17), 2.3526(18), 2.326(2), 2.310(2); Os(1)−O(1) 2.266(4), 2.231(4), 2.212(4), 2.253(5); Os(1)−N(1) 2.175(5), 2.195(5), 2.180(6), 2.168(5); P(1)−Os(1)−P(2) 170.34(6), 171.42(6), 169.27(7), 167.64(9); O(1)−Os(1)−N(2) 58.85(17), 59.41(16), 59.60(18), 59.28(18).

metal coordination sphere is completed by the bidentate nucleobase (N(1)−Os(1)−O(1) = 59.60(18)°−58.85(17)°) and the hydrides. The Os(1)−O(1) (2.231(4)−2.212(4) Å) and Os(1)−N(1) = 2.195(5)−2.168(5) Å) bond lengths compare well with those of **6** and **11**.

An extended view of the structure (Figure 9) reveals that the molecules are associated, to form pairs, through intermolecular N−H···O hydrogen bonds between the free heteroatoms of the nucleobases. One of the pairs implies molecules of the same asymmetric unit. The other two molecules are associated with molecules of adjacent asymmetric units. The H···O separations are between 1.680(5) and 2.00(5) Å, whereas the N−H···O angles lie in the range 165.8(3)°−173.4(3)°. The separations N···O range from 2.759(8) to 2.805(7) Å.

The ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra of **13** and **14** are consistent with the structure shown in Figure 8 and agree well with those of **2**−**7** and **9**−**12**. In addition to three hydride resonances between −10 and −15.5 ppm, the ^{1}H NMR spectra in toluene-d_8 at 203 K contain the NH-resonances at 12.46 (**13**) and 12.14 (**14**). The ^{31}P{^{1}H} NMR spectra show singlets at 33.9 (**13**) and 34.1 (**14**). In agreement with **2**−**7**, the ^{13}C{^{1}H} NMR spectra show the resonances due to the

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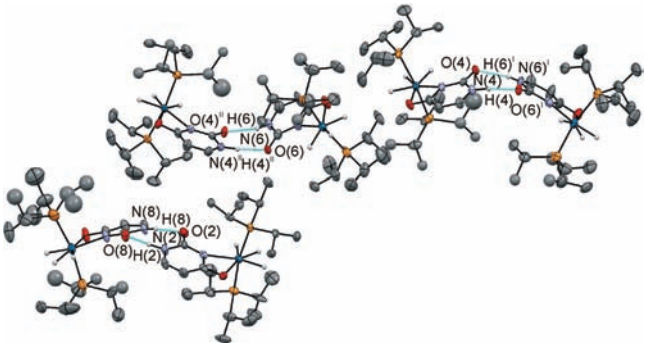

Figure 9. View of the interactions via hydrogen bonding in the structure of complex **14** [symmetry codes: (I) $x, -y + 3/2, z + 1/2$; (II) $x, -y + 1/2, z + 1/2$].

coordinated carbonyl group, 178.0 (**13**) and 178.1 (**14**) ppm, shifted by about 20 ppm toward lower field with regard to those corresponding to the free carbonyl group, 158.0 (**13**) and 157.8 (**14**) ppm.

■ CONCLUSION

This study has revealed that the hexahydride $OsH_6(P^iPr_3)_2$ promotes the N−H and N−C cleavages of pyrimidinic N-methyl nucleobases and nucleosides, in a sequential manner. The N−H rupture leads to trihydride−osmium(IV) complexes containing the deprotonated nucleobase or nucleoside κ^2-N,O coordinated by the nitrogen atom at position 3 and the oxygen bonded to the carbon atom of the ring at position 4. The N−C bond activation processes afford dinuclear derivatives showing an unprecedented coordination of the nucleobase skeletons, as bridge ligands κ^2-N,O to two $Os^{(IV)}H_3(P^iPr_3)_2$ metal fragments. Complexes containing nucleosides derived from ribose react with $OsH_2Cl_2(P^iPr_3)_2$ in the presence of a Brønsted base to give also unprecedented dinuclear species formed by two different metal fragments of osmium(IV): a seven-coordinate $OsH_3(P^iPr_3)_2$(nucleobase) moiety and a six-coordinate 16-valence electrons $OsH_2(P^iPr_3)_2$(ribose) unit.

■ EXPERIMENTAL SECTION

General Information. All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents (except methanol that was dried over magnesium and distilled under argon) were obtained oxygen- and water-free from an MBraun solvent purification apparatus. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on Bruker 300 ARX, Bruker Avance 300 MHz, Bruker Avance 400 MHz, and Bruker Avance 500 MHz instruments. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}) or to external 85% H_3PO_4 (^{31}P{^{1}H}). Coupling constants J and N are given in hertz. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 spectrometer as neat solids. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. High-resolution electrospray mass spectra were acquired using a MicroTOF-Q hybrid quadrupole time-of-flight spectrometer (Bruker Daltonics, Bremen, Germany). $OsH_6(P^iPr_3)_2$ (**1**) and $OsH_2Cl_2(P^iPr_3)_2$ (**8**) were prepared by published methods.[14a]

Reaction of $OsH_6(P^iPr_3)_2$ with 1-Methylthymine: Preparation of 2. A colorless solution of **1** (100 mg, 0.193 mmol) in toluene (10 mL) was treated with 1.0 equiv of 1-methylthymine (26.9 mg, 0.193 mmol) and heated under reflux during 3 h. During this time the solution changed from colorless to pale yellow. The resulting solution was filtered through Celite, and the solvent was removed in vacuo. The subsequent addition of cold pentane to the residue afforded a white solid. Yield: 88.4 mg (70%). Anal. Calcd for $C_{24}H_{52}N_2O_2OsP_2$: C, 44.15; H, 8.03; N, 4.29. Found: C, 44.56; H, 8.27; N, 4.06. ESI-HRMS (m/z): calcd for $C_{24}H_{51}N_2O_2OsP_2$ $[M - H]^+$ 653.0365; found 653.3036. IR (neat compound, cm^{-1}): ν(OsH) 2105 (w); ν(C═O) 1653 (s), 1629 (s); ν(C═C) 1518 (s). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 6.07 (s, 1H, =CH), 2.87 (s, 3H, N−CH_3), 2.01 (m, 6H, PCH(CH_3)$_2$), 1.69 (s, 3H, CH_3), 1.24 (dvt, J_{H-H} = 6.6, N = 13.5, 18H, PCH(CH_3)$_2$), 1.22 (dvt, J_{H-H} = 6.9, N = 13.5, 18H, PCH(CH_3)$_2$), −13.08 (br, 3H, Os−H). ^{1}H{^{31}P} NMR (300 MHz, toluene-d_8, 203 K, high-field region): δ −10.59 (d, J_{H-H} = 18.6, 1H, Os−H), −13.51 (dd, J_{H-H} = 18.6, J_{H-H} = 22.5, 1H, Os−H), −14.85 (d, J_{H-H} = 22.5, 1H, Os−H). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 298 K): δ 33.7 (s). ^{13}C{^{1}H} NMR plus HMBC (75 MHz, C_6D_6, 298 K): δ 176.8 (t, J_{C-P} = 1.5, OC−Os), 154.5 (s, CO), 142.1 (s, =CH), 105.1 (s, =CCH$_3$), 36.7 (s, N-CH_3), 27.3 (vt, N = 23.7, PCH(CH_3)$_2$), 20.5, 20.2 (both s, PCH(CH_3)$_2$), 10.6 (s, CH_3).

Reaction of $OsH_6(P^iPr_3)_2$ with 1-Methyluracil: Preparation of 3. A colorless solution of **1** (100 mg, 0.193 mmol) in toluene (10 mL) was treated with 1.0 equiv of 1-methyluracil (24.7 mg, 0.193 mmol) and heated under reflux during 3 h. During this time the solution changed from colorless to pale yellow. The resulting solution was filtered through Celite, and the solvent was removed in vacuo. The subsequent addition of cold pentane to the residue afforded a white solid. Yield: 75 mg (61%). Anal. Calcd for $C_{23}H_{50}N_2O_2OsP_2$: C, 43.24; H, 7.89; N, 4.38. Found: C, 43.55; H, 8.07; N, 4.14. ESI-HRMS (m/z): calcd for $C_{23}H_{49}N_2O_2OsP_2$ $[M - H]^+$ 639.2879; found 639.2900. IR (neat compound, cm^{-1}): ν(Os−H) 2127 (m); ν(C═O) 1654 (s), 1613 (s); ν(C═C) 1535 (s). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 6.12 (d, J_{H-H} = 7.2, 1H, =CH), 5.02 (d, J_{H-H} = 7.2, 1H, =CH), 2.79 (s, 3H, N−CH_3), 2.02 (m, 6H, PCH(CH_3)$_2$), 1.24 (dvt, J_{H-H} = 7.2, N = 13.5, 18H, PCH(CH_3)$_2$), 1.22 (dvt, J_{H-H} = 7.2, N = 13.5, 18H, PCH(CH_3)$_2$), −13.12 (br, 3H, Os−H). ^{1}H{^{31}P} NMR (400 MHz, toluene-d_8, 203 K, high-field region): δ −10.60 (d, J_{H-H} = 9.4, 1H, Os−H), −13.58 (dd, J_{H-H} = 9.4, J_{H-H} = 23.4, 1H, Os−H), −14.89 (d, J_{H-H} = 23.4, 1H, Os−H). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 298 K): δ 34.0 (s). ^{13}C{^{1}H} NMR plus HMBC (101 MHz, C_6D_6, 298 K): δ 177.1 (s, OC−Os), 154.2 (s, CO), 145.3 (s, =CH), 97.1 (s, =CHCO), 37.0 (s, N-CH$_3$), 27.2 (vt, N = 23.9, PCH(CH_3)$_2$), 20.4 (s, PCH(CH_3)$_2$).

Reaction of $OsH_6(P^iPr_3)_2$ with Thymidine: Preparation of 4. A colorless solution of **1** (100 mg, 0.193 mmol) in toluene (10 mL) was treated with 1.0 equiv of thymidine (46.9 mg, 0.193 mmol) and heated under reflux during 3 h. During this time the solution changed from colorless to pale yellow. The resulting solution was filtered through Celite, and the solvent was removed in vacuo. The subsequent addition of cold pentane to the residue afforded a white solid. Yield: 83 mg (60%). Anal. Calcd for $C_{28}H_{58}N_2O_5OsP_2$: C, 44.55; H, 7.74; N, 3.71. Found: C, 44.87; H, 8.03; N, 3.42. ESI-HRMS (m/z): calcd for $C_{28}H_{57}N_2O_5OsP_2$ $[M - H]^+$ 755.3353; found 755.3313. IR (neat compound, cm^{-1}): ν(OH) 3336 (br); ν(Os−H) 2118 (w); ν(C═O) 1649 (s), 1619 (s); ν(C═C) 1523 (s). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 7.30 (s, 1H, =CH), 6.24 (dd, J_{H-H} = 8.5, J_{H-H} = 6.8, 1H, NCH), 4.77 (br, 1H, CHOH), 4.18 (br, 3H, CHCH$_2$ and 2 OH), 3.90 (d, J_{H-H} = 11.2, 1H, CH_2OH), 3.82 (d, J_{H-H} = 11.2, 1H, CH_2OH), 2.59 (m, 1H, CH_2), 2.42 (m, 1H, CH_2), 1.99 (m, 6H, PCH(CH_3)$_2$), 1.79 (s, 3H, CH_3), 1.21 (dvt, J_{H-H} = 9.4, N = 14.5, 18H, PCH(CH_3)$_2$), 1.19 (dvt, J_{H-H} = 9.1, N = 13.8, 18H, PCH(CH_3)$_2$), −13.22 (br, 3H, OsH). ^{1}H{^{31}P} NMR (400 MHz, toluene-d_8, 203 K, high-field region): δ −10.50 (s, 1H, OsH), −13.58 (br, 1H, OsH), −15.36 (br, 1H, OsH). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 298 K): δ 33.7 (s). ^{13}C{^{1}H} NMR plus HMBC (101 MHz, C_6D_6, 298 K): δ 176.6 (s, CO−Os), 154.4 (s, CO), 139.4 (s, =CH), 106.8 (s, =CCH$_3$), 89.7 (s, N-CH), 88.5 (s, $CHCH_2$), 72.4 (s, $CHOH$), 63.1 (s, CH_2OH), 40.8 (s, CH_2), 27.3 (vt, N = 23.6, PCH(CH_3)$_2$), 27.2 (vt, N = 23.8, PCH(CH_3)$_2$), 20.4, 20.3, 20.2, 20.1 (all s, PCH(CH_3)$_2$), 10.8 (s, CH_3).

Reaction of $OsH_6(P^iPr_3)_2$ with 5-Methyluridine: Preparation of 5. A colorless solution of **1** (100 mg, 0.193 mmol) in toluene (10 mL) was treated with 1.0 equiv of 5-methyluridine (49.9 mg, 0.193 mmol) and heated under reflux during 3 h. During this time the solution changed from colorless to pale yellow. The resulting solution was filtered through Celite, and the solvent was removed in vacuo. The subsequent addition of cold pentane to the residue afforded a white

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solid. Yield: 87 mg (58%). Anal. Calcd for $C_{28}H_{58}N_2O_6OsP_2$: C, 43.62; H, 7.58; N, 3.63. Found: C, 43.27; H, 7.21; N, 3.35. ESI-HRMS (m/z): calcd for $C_{28}H_{57}N_2O_6OsP_2$ $[M - H]^+$ 771.3302; found 771.3265. IR (neat compound, cm^{-1}): ν(OH) 3371 (br); ν(OsH) 2142 (m); ν(C═O) 1648 (s), 1617 (s); ν(C═C) 1526 (s). ^1H NMR (400 MHz, C_6D_6, 298 K): δ 7.34 (s, 1H, =C*H*), 5.84 (d, J_{H-H} = 3.4, 1H, NC*H*), 5.35 (br, 1H, OH), 4.95 (br, 1H, OH), 4.85 (dd, J_{H-H} = 4.8, J_{H-H} = 4.8, 1H, C*H*OH), 4.71 (dd, J_{H-H} = 3.4, J_{H-H} = 4.8, 1H, C*H*OH), 4.33 (br s, 1H, CH_2CH), 4.08 (br, 1H, OH), 3.97 (d, J_{H-H} = 11.2, 1H, CH_2OH), 3.88 (d, J_{H-H} = 11.2, 1H, CH_2OH), 1.98 (m, 6H, PC*H*$(CH_3)_2$), 1.76 (s, 3H, CH_3), 1.20 (dvt, J_{H-H} = 6.8, N = 13.2, 18H, PCH$(CH_3)_2$), 1.19 (dvt, J_{H-H} = 6.8, N = 13.2, 18H, PCH$(CH_3)_2$), −13.22 (br, 3H, OsH). $^1H\{^{31}P\}$ NMR (400 MHz, toluene-d_8, 203 K, high-field region): δ −10.49 (br, 1H, OsH), −13.57 (br, 1H, OsH), −15.37 (br, 1H, OsH). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 298 K): δ 33.6 (s). $^{13}C\{^1H\}$ NMR plus HMBC (101 MHz, C_6D_6, 298 K): δ 176.8 (s, CO−Os), 155.2 (s, CO), 140.2 (s, =CH), 106.7 (s, =CCH_3), 95.5 (s, N-CH), 85.9 (s, $CHCH_2$), 75.6 (s, CHOH), 70.6 (s, CHOH), 62.2 (s, CH_2OH), 27.2 (vt, N = 23.9, PCH$(CH_3)_2$), 27.1 (vt, N = 23.9, PCH$(CH_3)_2$), 20.4, 20.3, 20.2, 20.1 (all s, PCH$(CH_3)_2$), 10.7 (s, CH_3).

Reaction of $OsH_6(P^iPr_3)_2$ with Deoxyuridine: Preparation of 6. A colorless solution of **1** (100 mg, 0.193 mmol) in toluene (10 mL) was treated with 1.0 equiv of deoxyuridine (44.1 mg, 0.193 mmol) and heated under reflux during 3 h. During this time the solution changed from colorless to pale yellow. The resulting solution was filtered through Celite, and the solvent was removed in vacuo. The subsequent addition of cold pentane to the residue afforded a yellow solid. Yield: 85 mg (59%). Anal. Calcd for $C_{27}H_{56}N_2O_5OsP_2$: C, 43.77; H, 7.62; N, 3.78. Found: C, 44.06; H, 8.01; N, 4.03. ESI-HRMS (m/z): calcd for $C_{27}H_{55}N_2O_5OsP_2$ $[M - H]^+$ 741.3197; found 741.3208. IR (neat compound, cm^{-1}): ν(OH) 3387 (br); ν(OsH) 2146 (w); ν(C═O) 1647 (s), 1632 (s); ν(C═C) 1536 (s). ^1H NMR (300 MHz, C_6D_6, 298 K): δ 7.26 (d, J_{H-H} = 7.5, 1H, =C*H*), 6.12 (dd, J_{H-H} = 8.5, J_{H-H} = 6.3, 1H, NC*H*), 5.24 (d, J_{H-H} = 7.5, 1H, =C*H*), 4.56 (br, 1H, C*H*OH), 4.01 (br s, 1H, $CHCH_2$), 3.80 (dd, J_{H-H} = 11.1, J_{H-H} = 3, 1H, CH_2OH), 3.68 (d, J_{H-H} = 11.1, 1H, CH_2OH), 3.17 (br, 2H, 2 OH), 2.50 (m, 1H, CH_2), 2.28 (m, 1H, CH_2), 2.00 (m, 6H, PC*H*$(CH_3)_2$), 1.24 (dvt, J_{H-H} = 6.9, N = 13.2, 18H, PCH$(CH_3)_2$), 1.19 (dvt, J_{H-H} = 6.9, N = 11.7, 18H, PCH$(CH_3)_2$), −13.21 (br, 3H, OsH). $^1H\{^{31}P\}$ NMR (300 MHz, toluene-d_8, 223 K, high-field region): δ −10.44 (br, 1H, OsH), −13.61 (br, 1H, OsH), −15.41 (br, 1H, OsH). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 298 K): δ 34.1 (s). $^{13}C\{^1H\}$ NMR plus HMBC (75 MHz, toluene-d_8, 353 K): δ 177.0 (br, CO−Os), 154.5 (s, CO), 142.3 (s, =CH), 98.9 (s, =CH), 89.6 (s, NCH), 88.5 (s, $CHCH_2$), 72.5 (s, CHOH), 63.3 (s, CH_2OH), 41.6 (s, CH_2), 27.8 (vt, N = 23.6, PCH$(CH_3)_2$), 20.8, 20.7 (both s, PCH$(CH_3)_2$).

Reaction of $OsH_6(P^iPr_3)_2$ with Uridine: Preparation of 7. A colorless solution of **1** (100 mg, 0.193 mmol) in toluene (10 mL) was treated with 1.0 equiv of uridine (47.2 mg, 0.193 mmol) and heated under reflux during 3 h. During this time the solution changed from colorless to pale yellow. The resulting solution was filtered through Celite, and the solvent was removed in vacuo. The subsequent addition of cold pentane to the residue afforded a yellow solid. Yield: 70 mg (48%). Anal. Calcd for $C_{27}H_{56}N_2O_6OsP_2$: C, 42.84; H, 7.46; N, 3.70. Found: C, 43.17; H, 7.79; N, 3.82. ESI-HRMS (m/z): calcd for $C_{27}H_{55}N_2O_6OsP_2$ $[M - H]^+$ 757.3146; found 757.3193. IR (neat compound, cm^{-1}): ν(OH) 3368 (br); ν(OsH) 2126 (w); ν(C═O) 1641 (s), 1608 (s); ν(C═C) 1534 (s). ^1H NMR (400 MHz, C_6D_6, 298 K): δ 7.75 (d, J_{H-H} = 7.6, 1H, =C*H*), 6.70 (br, 1H, OH), 5.98 (d, J_{H-H} = 5.1, 1H, NC*H*), 5.65 (br, 1H, OH), 5.30 (d, J_{H-H} = 7.6, 1H, =C*H*), 4.66 (dd, J_{H-H} = 6.1, J_{H-H}= 4.7, 1H, C*H*OH), 4.62 (dd, J_{H-H} = 5.1, J_{H-H} = 4.7, 1H, C*H*OH), 4.31 (m, 1H, CH_2CH), 3.88 (d, J_{H-H} = 11.2, 1H, CH_2OH), 3.77 (d, J_{H-H} = 11.2, 1H, CH_2OH), 3.46 (br, OH), 1.99 (m, 6H, PC*H*$(CH_3)_2$), 1.17 (dvt, J_{H-H} = 7.2, N = 13.2, 18H, PCH$(CH_3)_2$), 1.16 (dvt, J_{H-H} = 6.0, N = 12.0, 18H, PCH$(CH_3)_2$), −13.21 (br, 3H, OsH). $^1H\{^{31}P\}$ NMR (300 MHz, toluene-d_8, 213 K, high-field region): δ −10.56 (br, 1H, OsH), −13.59 (br, 1H, OsH), −15.28 (br, 1H, OsH). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K): δ 34.1 (s). $^{13}C\{^1H\}$ NMR plus HMBC (101 MHz, C_6D_6, 298 K): δ 176.9 (br, CO−Os), 155.1 (s, CO), 142.7 (s, =CH), 98.3 (s, =CH), 94.6 (s, NCH), 88.1 (s, $CHCH_2$), 76.0 (s, CHOH), 70.6 (s, CHOH), 61.9 (s, CH_2OH), 27.1 (vt, N = 23.6, PCH$(CH_3)_2$), 20.3, 20.2 (both s, PCH$(CH_3)_2$).

Reaction of Complex 5 with $OsH_2Cl_2(P^iPr_3)_2$ (8) in the Presence of NEt_3: Preparation of Complex 9. A solution of complex **5** (100.0 mg, 1.3×10^{-4} mmol) in toluene (6 mL) was treated with the stoichiometric amount of **8** (75.7 mg, 1.3×10^{-4} mmol) and 4.0 equiv of NEt_3 (75.0 μL, 5.6×10^{-4} mmol) during 20 min at room temperature. During this time the color changed from brown to orange. The resulting suspension was filtered through Celite to remove $[HNEt_3]Cl$ and the solution thus obtained concentrated in vacuo to afford a yellow solid. Yield: 98.0 mg (59%). Anal. Calcd for $C_{46}H_{100}N_2O_6Os_2P_4$: C, 43.11; H, 7.86; N, 2.18. Found: C, 42.70; H, 7.82; N, 2.07. ESI-HRMS (m/z): calcd for $C_{46}H_{101}N_2O_6Os_2P_4$ $[M + H]^+$ 1283.5814; found 1283.5936. IR (neat compound, cm^{-1}): ν(OH) 3358 (br), ν(OsH); 2155 (m), ν(C═O) 1663 (s), ν(C═C) 1523 (s). ^1H NMR (500 MHz, C_6D_6, 298 K): δ 7.15 (s, 1H, =C*H*), 6.00 (d, J_{H-H} = 3.0, 1H, NC*H*), 5.01 (m, 1H, C*H*O−Os), 4.92 (dd, J_{H-H} = 5.4, J_{H-H} = 5.4, 1H, C*H*CH_2OH), 4.25 (m, 1H, C*H*O−Os), 4.10 (d, J_{H-H} = 11.5, 1H, CH_2OH), 3.94 (m, 1H, CH_2OH), 3.38 (br, 1H, OH), 2.12 (m, 6H, PC*H*$(CH_3)_2$), 2.04 (m, 3H, PC*H*$(CH_3)_2$), 1.98 (m, 3H, PC*H*$(CH_3)_2$), 1.75 (s, 3H, CH_3), 1.26 (dvt, J_{H-H} = 6.5, N = 13, 9H, PCH$(CH_3)_2$), 1.24 (dvt, J_{H-H} = 6.5, N = 12.5, 9H, PCH$(CH_3)_2$), 1.19 (dvt, J_{H-H} = 7, N = 12.5, 9H, PCH$(CH_3)_2$), 1.18 (dvt, J_{H-H} = 7, N = 12.5, 9H, PCH$(CH_3)_2$), 1.14 (dd, J_{H-H} = 7, J_{H-P} = 12.5, 36H, PCH$(CH_3)_2$), −13.17 (br, 3H, OsH), −17.63 (t, J_{H-P} = 41, 2H, OsH). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K): δ 34.0 (s), 33.7 (s). $^{13}C\{^1H\}$ NMR plus HMBC (75.4 MHz, C_6D_6, 298 K): δ 176.5 (s, CO−Os), 153.9 (s, CO), 140.5 (s, =CH), 105.8 (s, =CCH_3), 100.1 (s, NCH), 92.6 (s, CHO−Os), 90.9 (s, CHO−Os), 87.7 (s, $CHCH_2$), 63.8 (s, CH_2OH), 27.4 (d, J_{C-P} = 31.4, PCH$(CH_3)_2$), 27.2 (vt, N = 23.4, PCH$(CH_3)_2$), 27.1 (vt, N = 23.4, PCH$(CH_3)_2$), 20.5, 20.4, 20.3, 20.2, 19.6, 19.5 (all s, PCH$(CH_3)_2$), 10.8 (s, CH_3).

Reaction of Complex 7 with $OsH_2Cl_2(P^iPr_3)_2$ (8) in the Presence of NEt_3: Preparation of Complex 10. A solution of complex **7** (100 mg, 1.3×10^{-4} mmol) in toluene (6 mL) was treated at room temperature with a stoichiometric amount of **8** (77.1 mg, 1.3×10^{-4} mmol) and 4.0 equiv of NEt_3 (73.0 μL, 5.6×10^{-4} mmol) during 20 min. During this time the solution changed from brown to orange. The resulting suspension was filtered through Celite to remove $[HNEt_3]Cl$ and the solution thus obtained concentrated in vacuo to afford a yellow solid. Yield: 106.6 mg (64%). Anal. Calcd for $C_{45}H_{98}N_2O_6Os_2P_4$: C, 42.64; H, 7.79; N, 2.21. Found: C, 42.40; H, 7.85; N, 2.09. ESI-HRMS (m/z): calcd for $C_{45}H_{99}N_2O_6Os_2P_4$ $[M + H]^+$: 1269.5657; found: 1269.5683. IR (neat compound, cm^{-1}): ν(OH) 3348 (br), ν(OsH); 2156 (m), 2134 (m), ν(C═O) 1649 (s), 1610 (s), ν(C═C) 1540 (s). ^1H NMR (500 MHz, C_6D_6, 298 K): δ 7.46 (d, J_{H-H} = 7.0, 1H, =C*H*), 6.00 (d, J_{H-H} = 3, 1H, NC*H*), 5.17 (d, J_{H-H} = 7.0, 1H, =C*H*), 4.93 (m, 1H, C*H*O−Os), 4.80 (dd, J_{H-H} = 5.5, J_{H-H} = 2.5, 1H, C*H*CH_2OH), 4.21 (m, 1H, C*H*O−Os), 4.04 (dd, J_{H-H} = 12, J_{H-H} = 2.5, 1H, CH_2OH), 3.87 (d, J_{H-H} = 12, 1H, CH_2OH), 3.07 (br, 1H, OH), 2.12 (m, 6H, PC*H*$(CH_3)_2$, 2.05 (m, 3H, PC*H*$(CH_3)_2$), 1.99 (m, 3H, PC*H*$(CH_3)_2$), 1.27 (dvt, J_{H-H} = 6.5, N = 12.5, 9H, PCH$(CH_3)_2$), 1.24 (dvt, J_{H-H} = 7, N = 13, 9H, PCH$(CH_3)_2$), 1.20 (dvt, J_{H-H} = 7, N = 13, 9H, PCH$(CH_3)_2$), 1.17 (dvt, J_{H-H} = 6.5, N = 13, 9H, PCH$(CH_3)_2$), 1.13 (dd, J_{H-H} = 7, J_{H-P} = 12.5, 36H, PCH$(CH_3)_2$), −13.16 (br, 3H, OsH), −17.68 (t, J_{H-P} = 41, 2H, OsH). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K): δ 34.4 (s), 33.6 (s). $^{13}C\{^1H\}$ NMR plus HMBC (101 MHz, C_6D_6, 298 K): δ 176.8 (s, CO−Os), 153.7 (s, CO), 143.3 (s, =CH), 98.9 (s, NCH), 97.7 (s, =CH), 93.2 (s, CHO−Os), 90.9 (s, CHO−Os), 87.2 (s, $CHCH_2$), 63.5 (s, CH_2OH), 27.4 (d, J_{C-P}= 33, PCH$(CH_3)_2$), 27.1 (vt, N = 20.2, PCH$(CH_3)_2$), 20.5, 20.4, 19.6, 19.5 (all s, PCH$(CH_3)_2$).

Reaction of 2 with $OsH_6(P^iPr_3)_2$: Preparation of 11. A yellow solution of **2** (63 mg, 0.096 mmol) in toluene (6 mL) was treated with 1.0 equiv of $OsH_6(P^iPr_3)_2$ (50 mg, 0.096 mmol) and heated under reflux. Periodically, aliquots were removed and checked by $^{31}P\{^1H\}$ NMR spectroscopy to follow the reaction. After 8.5 h the complete conversion of **2** in **11** is observed. The resulting solution was filtered through Celite, and the solvent was removed in vacuo. Addition of

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methanol to the residue afforded a white solid that was washed with methanol and dried in vacuo. Yield: 71.8 mg (65%). Anal. Calcd for $C_{41}H_{94}N_2O_2Os_2P_4$: C, 42.76; H, 8.23; N, 2.43; found: C, 42.43; H, 8.48; N, 2.71. ESI-HRMS (m/z): calcd for $C_{41}H_{93}N_2O_2Os_2P_4$ $[M - H]^+$ 1151.5390; found 1151.5437. IR (neat compound, cm^{-1}): ν(Os−H) 2149 (m), 2118 (m); ν(C═O) 1599 (s), 1542 (s); ν(C═C) 1505 (s). ^1H NMR (300 MHz, C_6D_6, 298 K): δ 7.57 (s, 1H, =C*H*), 2.01 (m, 12H, PC*H*$(CH_3)_2$), 1.96 (s, 3H, CH_3), 1.35 (dvt, J_{H-H} = 6.6, N = 13.2, 18H, PCH$(CH_3)_2$), 1.31 (dvt, J_{H-H} = 6.9, N = 13.5, 18H, PCH$(CH_3)_2$), 1.13 (dvt, J_{H-H} = 6.0, N = 11.7, 18H, PCH$(CH_3)_2$), 1.05 (dvt, J_{H-H} = 6.6, N = 12.3, 18H, PCH$(CH_3)_2$), −13.50 (very br, 6H, OsH). $^1H\{^{31}P\}$ NMR (400 MHz, toluene-d_8, 193 K, high-field region): δ −9.98 (d, 1H, J_{H-H} = 9.6, Os−H), −12.00 (br, 1H, Os−H), −13.38 (br, 1H, Os−H), −13.54 (t, J_{H-H} = 13.6, 1H, Os−H), −13.97 (br, 1H, Os−H), −15.97 (d, J_{H-H} = 13.6, 1H, Os−H). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 298 K): δ 36.9 (s), 30.9 (s). $^{13}C\{^1H\}$ NMR plus HSQC and HMBC (75 MHz, C_6D_6, 298 K): δ 176.9 (t, J_{C-P} = 1.5, CO), 165.9 (t, J_{C-P} = 1.5, CO), 152.5 (s, =CH), 105.7 (s, =CCH_3), 28.1 (vt, N = 23.2, P*C*H$(CH_3)_2$), 27.1 (vt, N = 23.2, P*C*H$(CH_3)_2$), 21.5, 21.1, 19.9, 19.6 (all s, PCH$(CH_3)_2$), 11.4 (s, CH_3).

Reaction of $OsH_6(P^iPr_3)_2$ with 0.5 Equiv of Thymine: Preparation of Complex 11. A colorless solution of **1** (100 mg, 0.193 mmol) in toluene (10 mL) was treated with 0.5 equiv of thymine (12.2 mg, 0.096 mmol) and heated under reflux during 3 h. During this time the solution changed from colorless to pale yellow. The resulting solution was filtered through Celite, and the solvent was removed in vacuo. ^1H and $^{31}P\{^1H\}$ NMR spectra show the presence of complexes **13** and **11** in a ratio 0.05:1. Addition of methanol to the residue afforded a white solid (complex **11**) that was washed with methanol and dried in vacuo. Yield: 74 mg (66%).

Reaction of 3 with $OsH_6(P^iPr_3)_2$: Preparation of 12. A yellow solution of **3** (61.3 mg, 0.096 mmol) in toluene (6 mL) was treated with 1.0 equiv of $OsH_6(P^iPr_3)_2$ (50 mg, 0.096 mmol) and heated under reflux. Periodically, aliquots were removed and checked by $^{31}P\{^1H\}$ NMR spectroscopy to follow the reaction. After 2 h the complete conversion of **3** in **12** is observed. The resulting solution was filtered through Celite, and the solvent was removed in vacuo. Addition of methanol to the residue afforded a white solid that was washed with methanol and dried in vacuo. Yield: 76.3 mg (70%). Anal. Calcd for $C_{40}H_{92}N_2O_2Os_2P_4$: C, 42.23; H, 8.15; N, 2.46. Found: C, 41.93; H, 8.04; N, 2.24. ESI-HRMS (m/z): calcd for $C_{40}H_{91}N_2O_2Os_2P_4$ $[M - H]^+$ 1137.5234; found 1137.5230. IR (neat compound, cm^{-1}): ν(Os−H) 2146 (w), 2123 (m); ν(C═O) 1564 (s), 1553 (s); ν(C═C) 1501 (s). ^1H NMR (300 MHz, C_6D_6, 298 K): δ 7.55 (d, J_{H-H} = 6.0, 1H, CH), 5.47 (d, J_{H-H} = 6.0, 1H, CH), 2.04 (m, 6H, PC*H*$(CH_3)_2$), 1.93 (m, 6H, PC*H*$(CH_3)_2$), 1.37 (dvt, J_{H-H} = 6.9, N = 13.2, 18H, PCH$(CH_3)_2$), 1.29 (dvt, J_{H-H} = 6.9, N = 13.2, 18H, PCH$(CH_3)_2$), 1.17 (dvt, J_{H-H} = 6.6, N = 12.0, 18H, PCH$(CH_3)_2$), 1.04 (dvt, J_{H-H} = 6.6, N = 11.7, 18H, PCH$(CH_3)_2$), −13.48 (br, 6H, OsH). $^1H\{^{31}P\}$ NMR (400 MHz, toluene-d_8, 193 K, high-field region): δ −9.96 (br, 1H, Os−H), −11.99 (br, 1H, Os−H), −13.36 (br, 1H, Os−H), −13.55 (br, 1H, Os−H), −14.00 (br, 1H, Os−H), −16.10 (br, 1H, Os−H). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 298 K): δ 36.7 (s), 30.9 (s). $^{13}C\{^1H\}$ NMR (101 MHz, tol-d_8, 298 K): δ 178.8 (s, CO), 167.4 (s, CO), 155.4 (s, =CH), 99.4 (s, =CH), 29.2 (vt, N = 23.9, PCH$(CH_3)_2$), 28.1 (vt, N = 23.4, PCH$(CH_3)_2$) 22.4, 22.1, 20.9, 20.7 (all s, PCH$(CH_3)_2$).

Reaction of $OsH_6(P^iPr_3)_2$ with 0.5 Equiv of Uracil: Preparation of Complex 12. A colorless solution of **1** (100 mg, 0.193 mmol) in toluene (10 mL) was treated with 0.5 equiv of uracil (10.8 mg, 0.096 mmol) and heated under reflux during 3 h. During this time the solution changed from colorless to pale yellow. The resulting solution was filtered through Celite, and the solvent was removed in vacuo. ^1H and $^{31}P\{^1H\}$ NMR spectra show the presence of complexes **14** and **12** in a ratio 0.21:1. Addition of methanol to the residue afforded a white solid (complex **12**) that was washed with methanol and dried in vacuo. Yield: 134 mg (61%).

Reaction of $OsH_6(P^iPr_3)_2$ with 1.0 Equiv of Thymine: Preparation of 13. A colorless solution of **1** (100 mg, 0.193 mmol) in toluene (10 mL) was treated with 1.0 equiv of thymine (24.4 mg, 0.193 mmol) and heated under reflux during 3 h. During this time the solution changed from colorless to pale yellow. The resulting solution was filtered through Celite, and the solvent was removed in vacuo. ^1H and $^{31}P\{^1H\}$ NMR spectra show the presence of **13** and **11** in a ratio 1: 0.2. Addition of methanol to the residue afforded a white solid (complex **11**) that was washed with methanol and dried in vacuo. The methanol solution was recollected and was taken to dryness. The subsequent addition of cold pentane to the residue afforded a white solid (complex **13**). Yield: 81 mg (66%). ***Complex 13:*** Anal. Calcd for $C_{23}H_{50}N_2O_2OsP_2$: C, 43.24; H, 7.89; N, 4.38. Found: C, 42.89; H, 8.03; N, 4.55. ESI-HRMS (m/z): calcd for $C_{23}H_{49}N_2O_2OsP_2$ $[M - H]^+$: 639.2879; found: 639.2912. IR (neat compound, cm^{-1}): ν(Os−H) 2133 (m); ν(C═O) 1661 (s), 1614 (s); ν(C═C) 1514 (s). ^1H NMR (400 MHz, C_6D_6, 298 K): δ 12.46 (s, 1H, NH), 6.51 (s, 1H, =C*H*), 1.98 (m, 6H, PC*H*$(CH_3)_2$), 1.64 (s, 3H, CH_3), 1.22 (dvt, J_{H-H} = 7.2, N = 14.0, 18H, PCH$(CH_3)_2$), 1.20 (dvt, J_{H-H} = 7.2, N = 13.6, 18H, PCH$(CH_3)_2$), −13.14 (br, 3H, OsH). $^1H\{^{31}P\}$ NMR (400 MHz, toluene-d_8, 203 K, high-field region): δ −10.53 (br, 1H, Os−H), −13.52 (br, 1H, Os−H), −15.05 (br, 1H, Os−H). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 298 K): δ 33.9 (s). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 298 K): δ 178.0 (t, J_{C-P} = 1.6, CO), 158.0 (s, CO), 138.9 (s, =CH), 105.2 (s, =CCH_3), 27.3 (vt, N = 23.7, PCH$(CH_3)_2$), 20.5, 20.2 (both s, PCH$(CH_3)_2$), 10.4 (s, CH_3).

Reaction of $OsH_6(P^iPr_3)_2$ with 1.0 Equiv of Uracil: Preparation of 14. A colorless solution of **1** (100 mg, 0.193 mmol) in toluene (10 mL) was treated with 1.0 equiv of uracil (21.7 mg, 0.193 mmol) and heated under reflux during 3 h, changing the color of the solution from colorless to pale yellow. After this time the mixture was cooled at room temperature and filtered through Celite, and the solvent was removed in vacuo. ^1H and $^{31}P\{^1H\}$ NMR spectra showed quantitative conversion to a 1:0.2 mixture of complexes **14** and **12**. Extraction of the resulting residue with methanol allows the isolation of both complexes in pure form: Complex **14** is extracted with methanol (10 mL), while complex **12** remains in the residue. Addition of methanol to the residue afforded a white solid (**12**) that was washed with methanol and dried in vacuo. The methanol solution containing complex **14** was taken to dryness. Subsequent addition of cold pentane to the resulting residue afforded a white solid (complex **14**). Yield: complex **14**: 73 mg (61%), complex **12**: 16 mg (15%). ***Complex 14:*** Anal. Calcd for $C_{22}H_{48}N_2O_2OsP_2$: C, 42.29; H, 7.74; N, 4.48; found: C, 42.56; H, 7.82; N, 4.29. ESI-HRMS (m/z): calcd for $C_{22}H_{47}N_2O_2OsP_2$ $[M - H]^+$ 625.2723; found 625.2728. IR (neat compound, cm^{-1}): ν(OsH) 2122 (w); ν(C═O) 1659 (m), 1613 (m); ν(C═C) 1527 (s). ^1H NMR (300 MHz, C_6D_6, 298 K): δ 12.14 (s, 1H, NH), 6.64 (d, J_{H-H} = 7.2, 1H, =C*H*), 5.02 (d, J_{H-H} = 7.2, 1H, =C*H*), 1.99 (m, 6H, PC*H*$(CH_3)_2$), 1.22 (dvt, J_{H-H} = 6.9, N = 12.9, 18H, PCH$(CH_3)_2$), 1.19 (dvt, J_{H-H} = 6.9, N = 12.6, 18 H, PCH$(CH_3)_2$, −13.13 (br, 3H, OsH). $^1H\{^{31}P\}$ NMR (400 MHz, toluene-d_8, 203 K, high-field region): δ −10.51 (br, 1H, Os−H), −13.56 (br, 1H, Os−H), −15.12 (br, 1H, Os−H). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 298 K): δ 34.1 (s). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K): δ 178.1 (t, J_{C-P} = 1.6, CO), 157.8 (s, CO), 141.9 (s, =CH), 97.2 (s, =CH), 27.2 (vt, N = 24.0, PCH$(CH_3)_2$), 20.3 (s, PCH$(CH_3)_2$).

Structural Analysis of Complexes 6, 11, and 14. Crystals suitable for the X-ray diffraction were obtained by slow diffusion of methanol into solutions of the complexes in toluene. X-ray data were collected on a Bruker Smart APEX (**11**, **14**) and Bruker Apex II CCD (**6**) difractometers equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, λ = 0.71073 Å) operating at 50 kV and 30 (**6**, **11**) or 40 (**14**) mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s (20 s for **6** and **14**) covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[19] The structures were solved by the Patterson (Os atoms of **6**, **11**, and **14**) method and conventional Fourier techniques and refined by full-matrix least-squares on F^2 with SHELXL97.[20] Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were observed or calculated and refined freely or using a restricted riding model. Hydride ligands were observed in the

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difference Fourier maps but refined with restrained Os−H bond length (1.59(1) Å, CSD). The disordered phosphine groups observed in the structure of complex **14** were refined with two moieties, complementary occupancy factors, and isotropic thermal parameters. For all structures the highest electronic residuals were observed in the close proximity of the Os centers and make no chemical sense.

Crystal data for **6**: $C_{27}H_{56}N_2O_5OsP_2$, M_W 740.88, colorless, irregular block (0.15 × 0.08 × 0.05), orthorhombic, space group $P2_12_12_1$, *a*: 11.0603(15) Å, *b*: 16.493(2) Å, *c*: 17.632(2) Å, V = 3216.3(8) Å^3, Z = 4, D_{calc}: 1.530 g cm^{-3}, F(000): 1512, T = 100(2) K, μ 4.100 mm^{-1}. 35436 measured reflections (2θ: 3−58°, ω scans 0.3°), 8389 unique (R_{int} = 0.0335); minimum/maximum transmission factors 0.645/0.862. Final agreement factors were R^1 = 0.0200 (8048 observed reflections, I > 2σ(I)) and wR^2 = 0.0447; data/restraints/parameters 8389/3/359; GoF = 1.009. Largest peak and hole 1.080 and −0.391 e/Å^3.

Crystal data for **11**: $C_{41}H_{94}N_2O_2Os_2P_4$, M_W 1151.46, colorless, prism (0.18 × 0.16 × 0.08), monoclinic, space group P2(1)/n, *a*: 14.6768(7) Å, *b*: 16.0063(7) Å, *c*: 21.5187(10) Å, α: 90.00°, β: 99.2180(10)°, γ: 90.00 °, V = 4989.9(4) Å^3, Z = 4, D_{calc}: 1.533 g cm^{-3}, F(000): 2328, T = 100(2) K, μ 5.249 mm^{-1}. 59788 measured reflections (2θ: 3−58°, ω scans 0.3°), 12026 unique (R_{int} = 0.0380); minimum/maximum transmission factors 0.445/0.589. Final agreement factors were R^1 = 0.0266 (9745 observed reflections, I > 2σ(I)) and wR^2 = 0.0566; data/restraints/parameters 12026/6/509; GoF = 0.984. Largest peak and hole 1.584 and −1.619 e/Å^3.

Crystal data for **14**: $C_{22}H_{48}N_2O_2OsP_2$, M_W 624.76, colorless, irregular block (0.10 × 0.06 × 0.03), monoclinic, space group P2(1)/c, *a*: 17.7824(17) Å, *b*: 20.108(2) Å, *c*: 30.682(3) Å, α: 90.00°, β: 96.9740(10)°, γ: 90.00 °, V = 10889.8(18) Å^3, Z = 16, D_{calc}: 1.524 g cm^{-3}, F(000): 5056, T = 100(2) K, μ 4.820 mm^{-1}. 131407 measured reflections (2θ: 3−58°, ω scans 0.3°), 26270 unique (R_{int} = 0.1160); minimum/maximum transmission factors 0.514/0.799. Final agreement factors were R^1 = 0.0420 (12537 observed reflections, I > 2σ(I)) and wR^2 = 0.0737; data/restraints/parameters 26270/64/1122; GoF = 0.774. Largest peak and hole 2.069 and −1.844 e/Å^3.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving positional and displacement parameters, crystallographic data, and bond lengths and angles of compounds **6**, **11**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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