Osmium-Promoted σ-Bond Activation Reactions on Nucleosides

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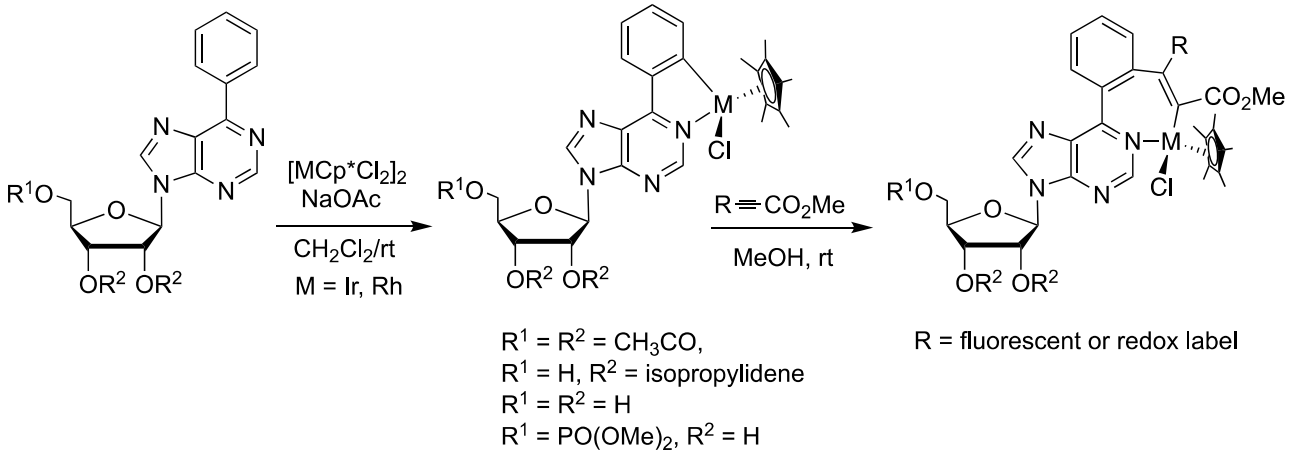
Abstract. $OsH_6(P^iPr_3)_2$ has been used to selectively activate C-H, H-O and C-C sigma bonds in nucleobases and nucleosides, including derivatives of 6-phenylpurine and 4-phenylpirimidine, leading to cyclometallated mononuclear Os-trihydride complexes, in excellent yields and as single products. Additionally, $OsH_6(P^iPr_3)_2$ promotes the efficient dehydrogenative decarbonylation of

primary alcohols in nucleosides having unprotected sugar moieties. The incorporation of $OsH_2Cl_2(P^iPr_3)_2$ in the structure of cyclometallated Ir(III) and Rh(III) half sandwich complexes derived from nucleosides, allows the preparation of a class of heterobimetallic bioorganometallic complexes having at least one M-C bond. These methodologies could be used in the future as a way for the orthogonal functionalization of oligonucleotides.

Introduction

The coordination chemistry of nucleobases has generated much interest in the last years,[1,2] specially due to the relevance of metal-DNA interactions in the antitumor activity of transition metal based drugs (in particular the clinically used *cis*-platinum and related compounds).[3] However, the synthesis of bio-organometallic derivatives of nucleosides and nucleotides bearing M-C bonds has been somewhat overlooked.[4] In this regard, we have used *N*-directed C-H bond activation reactions of 6-phenylpurine derivatives to prepare metallanucleosides, nucleotides and dinucleotides (M = Ir(III), Rh(III)).[5] The post-functionalization of these complexes using alkyne insertion reactions results in methodologies to selectively incorporate fluorescent or redox labels in their structures,[6] and to design novel tandem processes (Scheme 1).[7]



Scheme 1. Synthesis and post-functionalization of metallanucleosides.

The use of osmium polyhydrides[8] to study new ways of interaction and structural modification of biomolecules by transition metals is an emerging research field. Thus, the hexahydride complex $OsH_6(P^iPr_3)_2$ and the dihydride derivative $OsH_2Cl_2(P^iPr_3)_2$ selectively activate N−H, O−H and N−C bonds of pyrimidine nucleobases, leading to a new class of mono and dinuclear Os(IV) polyhydride nucleosides.[9] The reactions not only produce the metallation of the positions involved in the base-

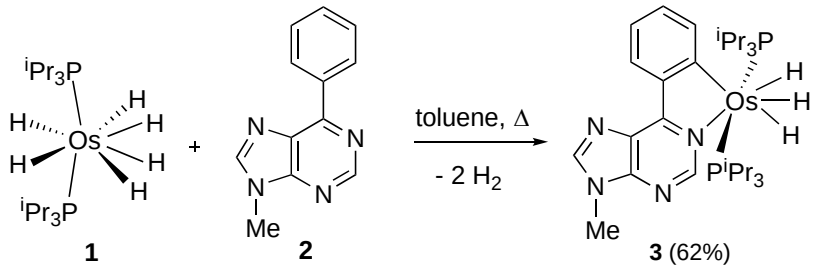
pairing, but also constitute a new way to incorporate metal hydrides in nucleobases. This is interesting, as nucleobases having metal-hydrides in their structures could be involved in the formation of non-conventional hydrogen bonds with other biomolecules. Additionally, metal-hydride complexes are susceptible of generating H_2,[8] which could be a novel strategy for DNA damage.[10,11]

The combination of the reactive metal polyhydrides with biomolecules could be also a source of novel and unexpected reactions. Thus, the reactivity of Os- and Ru-hydrides with β-lactams has been used by us to prepare a new class of osmium and ruthenium metallatrinems through N−H bond activation of 2-azetidinones.[12] Osmium hexahydride $OsH_6(P^iPr_3)_2$ was also able to promote new types of fragmentations in the 2-azetidinone ring.[13] Here we describe osmium polyhydride-promoted C-H, O-H and C-C bond activation reactions on phenyl-purine and phenyl-pyrimidine nucleosides, study the selectivity of the processes and combine the hydride reagents with metallanucleosides to prepare bimetallic Os-Ir, Os-Rh, complexes.

Results and Discussion

To determine the suitability of the reactions of modified nucleobases with $OsH_6(P^iPr_3)_2$ (**1**), 9-methyl-6-phenylpurine (**2**) was first tested. In agreement with the ability of **1** to activate C-H bonds,[8,14] the treatment of toluene solutions of this hydride with 1.2 equiv of **2**, under reflux, leads to the osmium trihydride **3**, as a result of the purine-supported *ortho*-CH bond activation of the phenyl group of the modified nucleobase. This compound was isolated as a dark red solid in 62% yield (Scheme 2) and characterized by X-ray diffraction analysis. The structure, which has two molecules chemically equivalent but crystallographically independent (Figure1 shows one of them), proves the C-H bond activation. The coordination geometry around the osmium atom can be described as a distorted pentagonal bipyramid with axial phosphines (P(1)-Os(1)-P(2) = 167.21(6)º

and 162.55(6)º). The metal coordination sphere is completed by the inequivalent hydrides and the orthometallated purine, which acts with N(1)-Os(1)-C(1) bite angles of 75.7(2)º and 76.0(2)º. According to the presence of three inequivalent hydride ligands in the complex, its ^{1}H NMR spectrum, in dichloromethane-d_2, at 193 K shows three high field resonances at -6.60, -11.32, and -12.15 ppm. In the $^{13}C\{^{1}H\}$ NMR spectrum in benzene-d_6, at room temperature, the signal corresponding to the metallated C(1) atom appears at 195.4 ppm. As expected for equivalent phosphines, the $^{31}P\{^{1}H\}$ NMR spectrum contains a singlet at 21.1 ppm.



Scheme 2. Synthesis of complex **3**

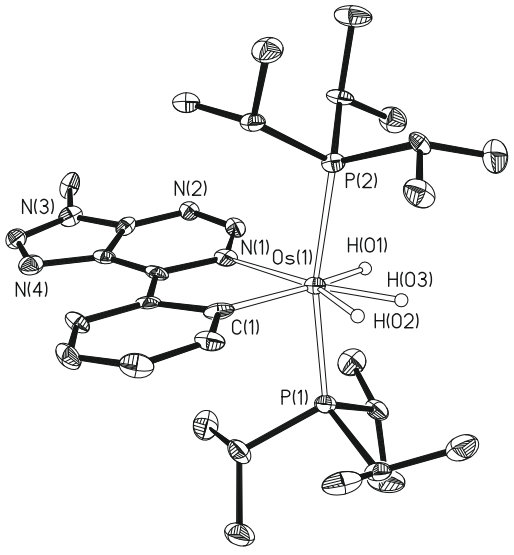
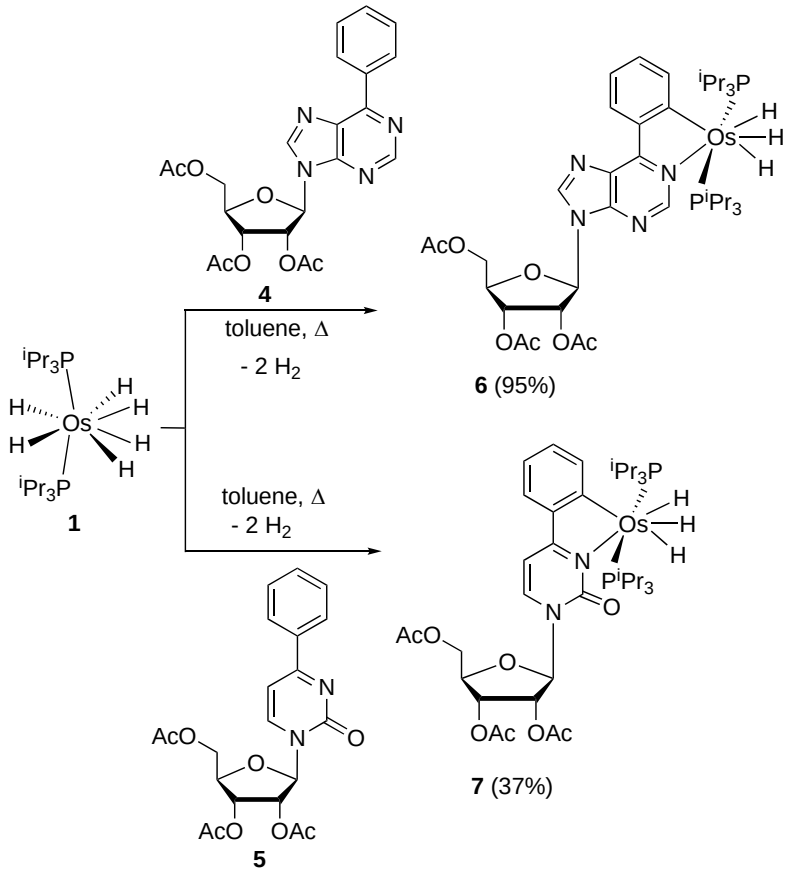


Figure 1. Molecular diagram of complex **3** (50% probability ellipsoids). Hydrogen atoms (except the hydrides) have been omitted for clarity. Selected bond lengths (Å) and angles (desg): Os(1)-P(1) = 2.3507(18), 2.3363(18), Os(1)-P(2) = 2.3434(18), 2.3373(18), Os(1)-N(1) = 2.152(5), 2.168(5),

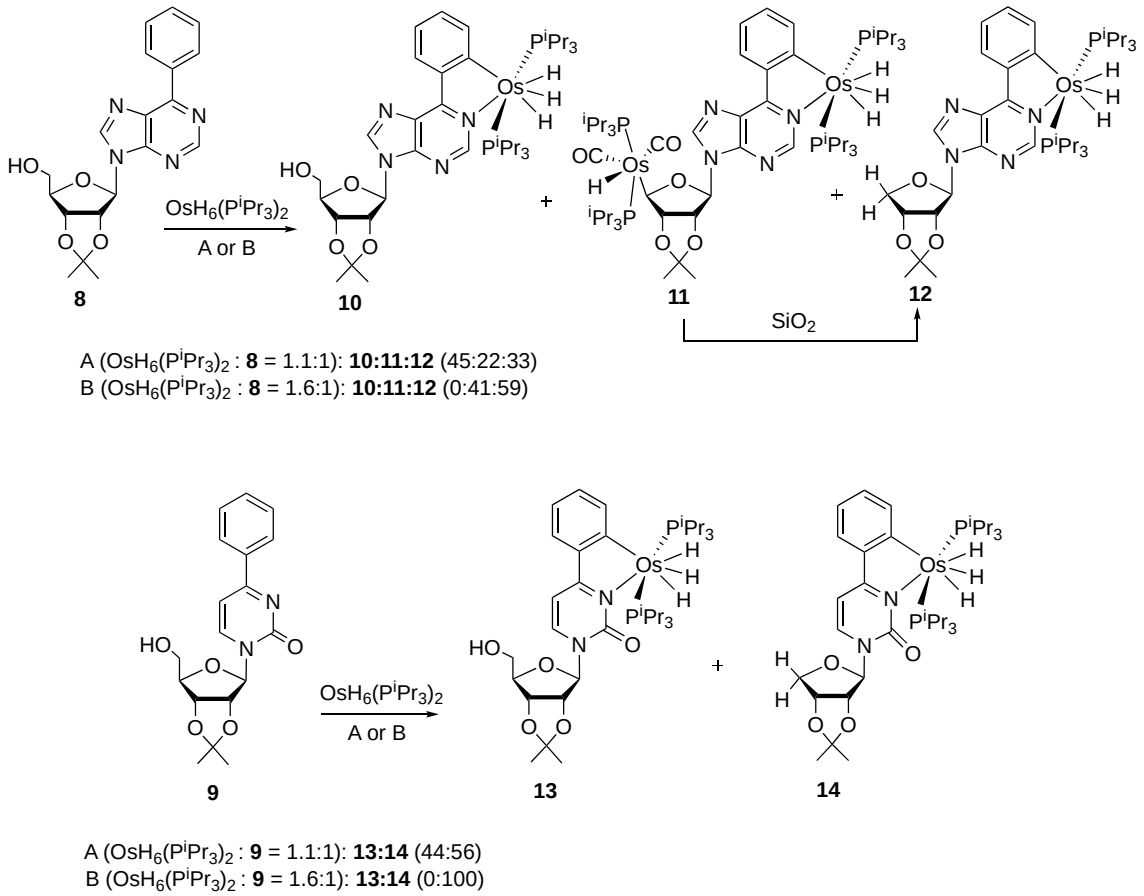
Os(1)-C(1) = 2.104(7), 2.115(7); P(1)-Os(1)-P(2) = 167.21(6), 162.55(6), N(1)-Os(1)-C(1) = 75.7(2), 76.0(2).

Having observed the behavior of **1** with a simple purine derivative, the reactions of this compound with nucleosides 9-(2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl)-6-phenylpurine (**4**) and (2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl)-4-phenylpyrimidine (**5**),[15] having more functionalized scaffolds, were studied under the conditions used for **2**. Cyclometallated Os(IV) trihydride derivatives **6** and **7** were isolated in 95% and 37% yields, respectively, after column chromatography on silicagel (Scheme 3). Their structures were established by spectroscopic and analytical methods. The ^{1}H NMR spectra, in dichloromethane-d_2, at 193K contain the expected hydride resonances between -6.5 and -12.2 ppm. In the $^{13}C\{^{1}H\}$ NMR spectra in benzene-d_6, at room temperature, the signal due to the metallated phenyl carbon atom appears at 196.8 ppm for **6** and at 207.1 ppm for **7**, whereas in the $^{31}P\{^{1}H\}$ NMR spectra, the equivalent phosphines give rise to a singlet at 23.9 ppm for **6** and 27.7 ppm for **7**.



Scheme 3. Synthesis of complexes **6** and **7**.

Being aware of the reactivity of osmium hydrides with alcohols [9,16] and in order to determine the ability of **1** for the selective cyclometallation of modified nucleobases, the competition between C-H and O-H activation was tested next with purine and pyrimidine nucleosides **8** and **9**,[15]having the primary OH group of the ribose moiety unprotected. Under the cyclometallation conditions tested above, the reaction of **1** with **8**, led to the expected C-H bond activation product **10**, together with a mixture of two new compounds **11** and **12** in a **10**:**11**:**12** molar ratio of 45:22:33, determined by ^{1}H NMR (Scheme 4). The products were separated by chromatography on silicagel and their structures were established by spectroscopic data and mass spectrometry.



8 **10** **11** **12**

9 **13** **14**

Scheme 4 . Synthesis of complexes **10-12** and **13-14**.

Complex **10** is the result of the selective purine-supported *ortho*-CH bond activation of the phenyl group in the presence of the ribose function, which remains intact. According to this, the ^{1}H NMR spectrum of **10**, in dichloromethane-d_2, at 193 K shows the characteristic three high field resonances of a trihydride-osmium(IV) $OsH_3(XY)(P^iPr_3)_2$ species,[17] at -6.55, -11.19, and -12.04 ppm, whereas in the lower region, it contains the ribose CH_2 signals at 3.76 and 3.47 ppm along with the OH-resonance at 4.68 ppm. In agreement with complexes **3**, **6**, and **7** (see above), the $^{13}C\{^{1}H\}$ NMR spectrum displays the resonance corresponding to the phenyl metallated carbon atom at 197.5 ppm and the $^{31}P\{^{1}H\}$ NMR spectrum shows a singlet at 21.2 ppm.

The binuclear complex **11** keeps the cyclometallated $OsH_3(XY)(P^iPr_3)_2$ structure. However, it

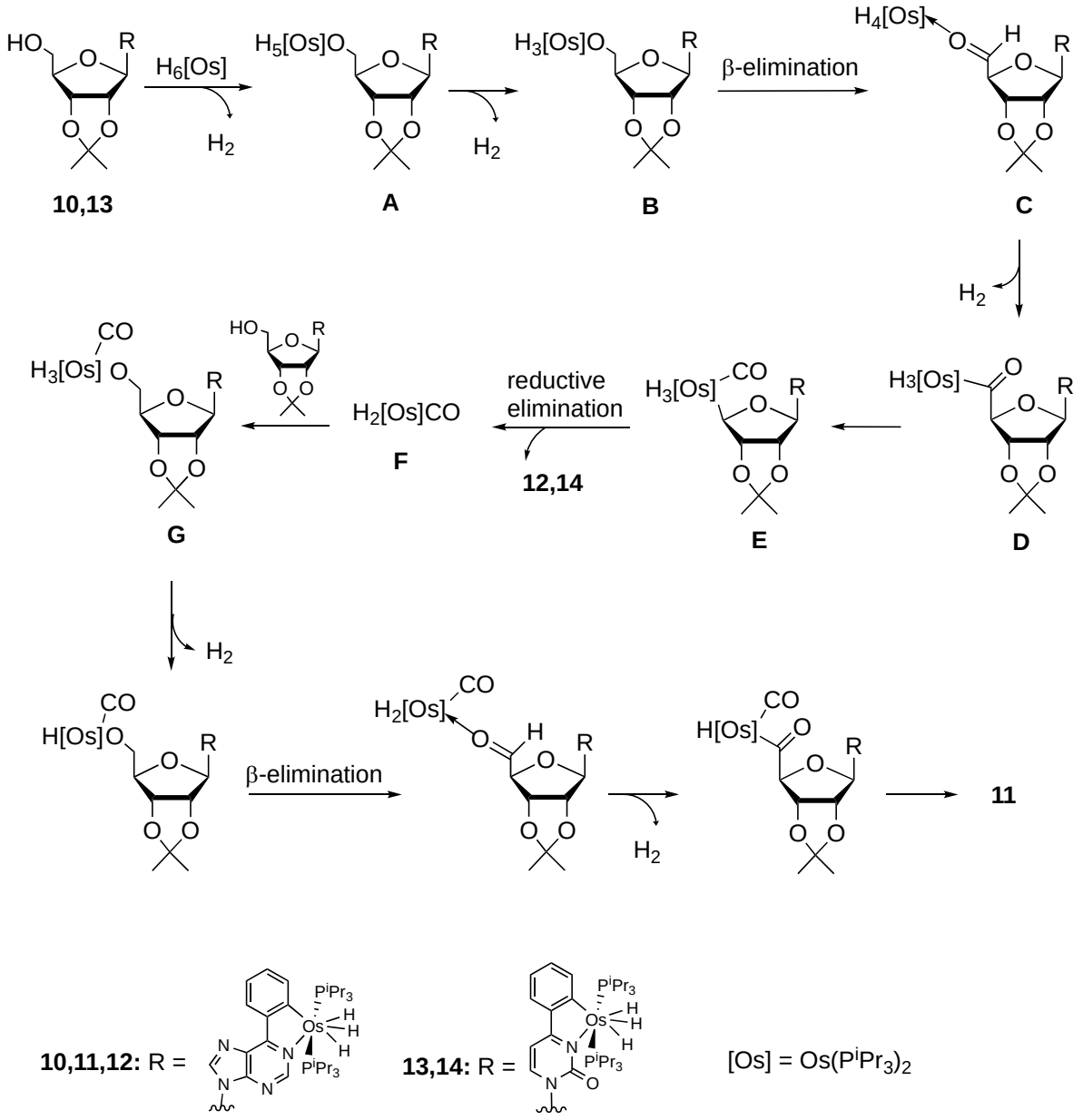
losses the ribose CH_2OH moiety, while incorporates an $Os(CO)_2H(P^iPr_3)_2$ fragment at the C4 position of the sugar ring. Thus, its ^1H NMR spectrum, in dichloromethane-d_2, at 298 K contains a triplet ($^2J_{H-P}$ = 21 Hz) at -7.20 ppm, in addition to the hydride resonances characteristic of the cyclometallated unit (-8.50, -11.74), while resonances corresponding to the CH_2OH moiety of the ribose are not observed in the lower field region of the spectrum. The presence of two different metallated carbon atoms in the molecule is supported by the $^{13}C\{^1H\}$ NMR spectrum, which shows the expected resonance for the metallated phenyl group at 195.6 ppm, together with that of the C4 atom of the sugar ring at 63.1 ppm. The $^{13}C\{^1H\}$ NMR spectrum also shows the signals corresponding to the inequivalent CO ligands of the $Os(CO)_2H(P^iPr_3)_2$ fragment, at 190.6 and 184.6 ppm. As expected for a *cis* disposition of the carbonyl groups, the IR contains the two characteristic ν(CO) bands typical to a C_{2v} point group at 1963 and 1896 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum is consistent with the binuclear character of the complex and displays two AB systems centered at 22.7 ppm and 21.3 ppm for the inequivalent OsP_2 units.

The third isolated complex **12** is, from a formal point of view, the result of the replacement of the CH_2OH moiety of the ribose in **10**, or the $Os(CO)_2H(P^iPr_3)_2$ fragment in **11**, by a hydrogen atom. In concordance, the ^1H NMR spectrum, in dichloromethane-d_2, at 193 K contains the expected three resonances for the characteristic inequivalent hydrides of a cyclometallated $OsH_3(XY)(P^iPr_3)_2$ fragment, at -6.60, -11.29, and -12.10 ppm, along with a doublet ($^2J_{H-H}$ = 12 Hz) at 4.03 ppm and a doublet of doublets ($^2J_{H-H}$ = 12 Hz and $^3J_{H-H}$ = 3 Hz) at 3.86 ppm, assigned to the diastereotopic protons attached to the C4 atom of the ribose unit. This carbon appears as a singlet at 75.6 ppm in the $^{13}C\{^1H\}$ NMR spectrum, which also shows the resonance due the metallated phenyl carbon atom at 196.3 ppm. Furthermore, as expected, in agreement with **10**, the $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 21.0 ppm.

Complex **10** is an intermediate species in the formation pathway of **11** and **12**. In agreement with this, it was not observed when a larger excess (1.6 equiv) of **1** was used. Under these conditions the reaction gives a mixture of **11** and **12** in a 41:59 molar ratio, according to the ^{1}H NMR spectrum of the crude.

Scheme 5 accounts for these findings, showing a sequence of processes involving osmium-promoted O-H, C-H, and C4-CO bond activations on the C4CH_2OH moiety of the ribose in **10**. In accordance with the ability of osmium-polyhydrides to activate O-H bonds,[8,16b,c,18] the reaction of **1** with the ribose OH-group of **10** should afford molecular hydrogen and an alkoxide species **A**, which by dissociation of a hydrogen molecule and subsequent β-hydrogen elimination on the alkoxide group of the resulting unsaturated intermediate **B**, would lead to the aldehyde derivative **C**. The heterolytic C-H bond activation of the aldehyde should give a new hydrogen molecule and the acyl species **D**, which could undergo CO deinsertion to generate the (OC)Os-C4 bond of intermediate **E**.[19] The reductive elimination of **12** from **E** would afford the previously described unsaturated osmium(II) complex $OsH_2(CO)(P^iPr_3)_2$ (**F** in Scheme 5),[20] which could undergo the oxidative addition of the ribose OH-group of a new molecule of **10** to give **G**. The evolution of **G** to dinuclear complex **11** should follow a sequence of steps analogous to that of **A** to **E**. Overall, the process agrees well with those previously reported with ethanol and 2-methoxyethanol, which behave similarly to afford $OsH(CH_3)(CO)_2(P^iPr_3)_2$ and $OsH(CH_2OMe)(CO)_2(P^iPr_3)_2$, respectively.[16b]

Experimental evidence for the proposed mechanism was gained by reaction of $OsH_2(\eta^2$-CH_2=CHEt)$(CO)(P^iPr_3)_2$ (intermediate **F**, generated by treatment of $OsHCl(CO)(P^iPr_3)_2$ with ^{n}BuLi, in pentane, at room temperature), with complex **10** in refluxing toluene. As expected, the reaction smoothly led to the formation of complex **11** as single reaction product (see Supporting Information for details).



Scheme 5. Proposed mechanistic pathway for the formation of complexes **11**, **12** and **14**.

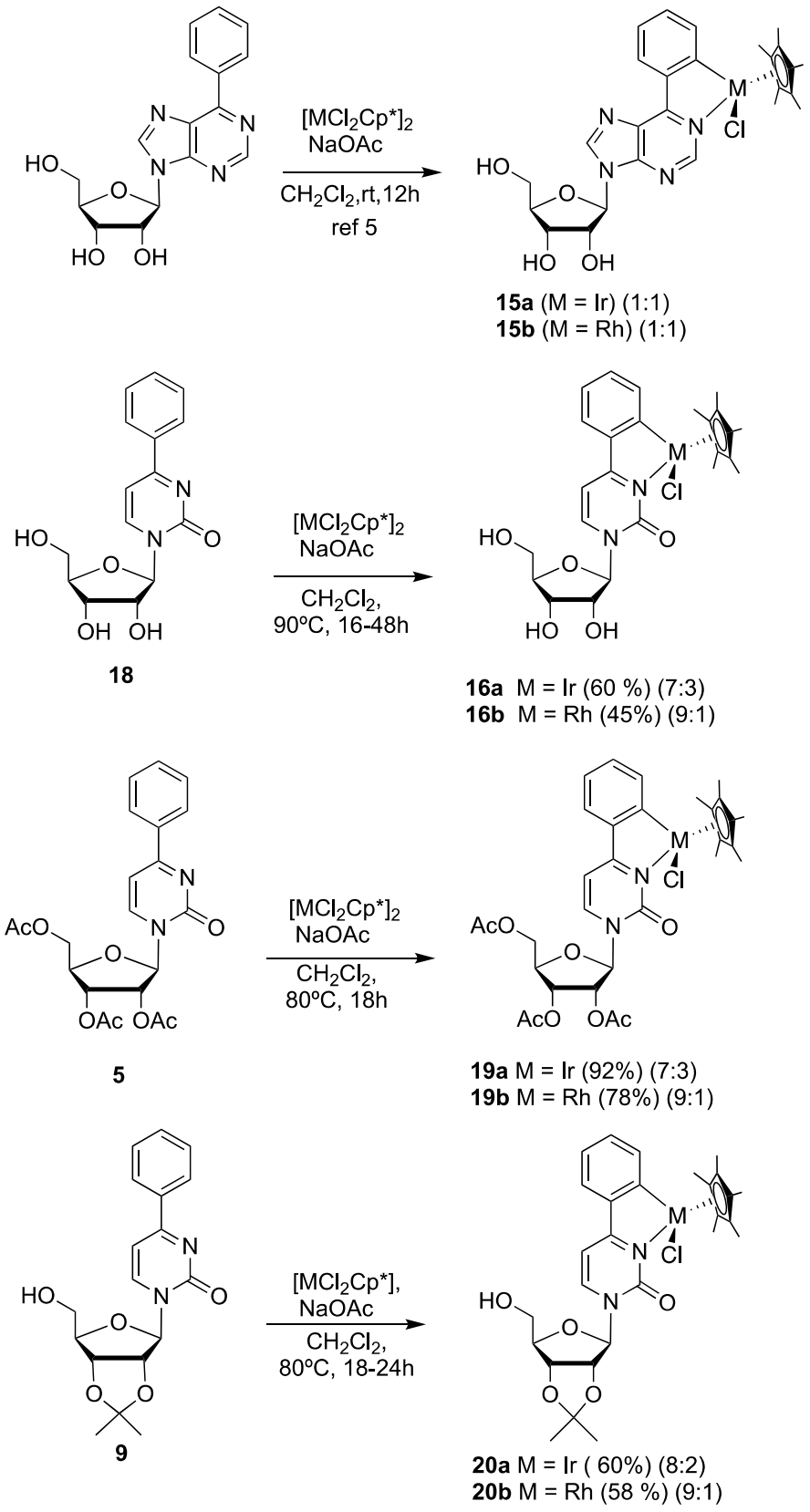
The stability of **11** towards the reductive elimination to **12** is noticeable and must be related to the concerted nature of the process, which would lead to a disfavored *trans*-dicarbonyl-osmium(0) species.[21] However, degradation of **11** to **12** occurs in acid medium, very likely by electrophilic attack to the basic C4 atom of the metallated ribose ring. In fact, when the components of the 41:59 mixture of **11** and **12**, obtained from the reaction of **8** with 1.6 equiv of **1** (Scheme 4), were

separated by column chromatography on silicagel, the yield of **11** decreased to 20% while that of **12** increased up to 70%, as a consequence of the action of the acidic support.

The reaction of **1** with (2,3-di-*O*-isopropylidene-β-D-ribofuranosyl)-4-phenylpyrimidine (**9**) had a similar outcome, although the ribose Os-C4 bond appears to be much less stable in this case. Thus, a mixture of the mononuclear complexes **13** and **14** was formed in a 44:56 molar ratio (Scheme 4). Complexes **13** and **14** were separated by chromatography on silicagel and fully characterized (see experimental section and supporting information for details). It is worth to mention that the dehydrogenative decarbonylation of alcohols is a synthetically valuable transformation, efficiently performed with complexes of platinum group metals.[17,22] Although different types of alcohols have been tested in these reactions (more frequently primary aliphatic and benzylic), sugars have been rarely employed as substrates[23] and, to the best of our knowledge, these processes have never been reported for nucleosides.

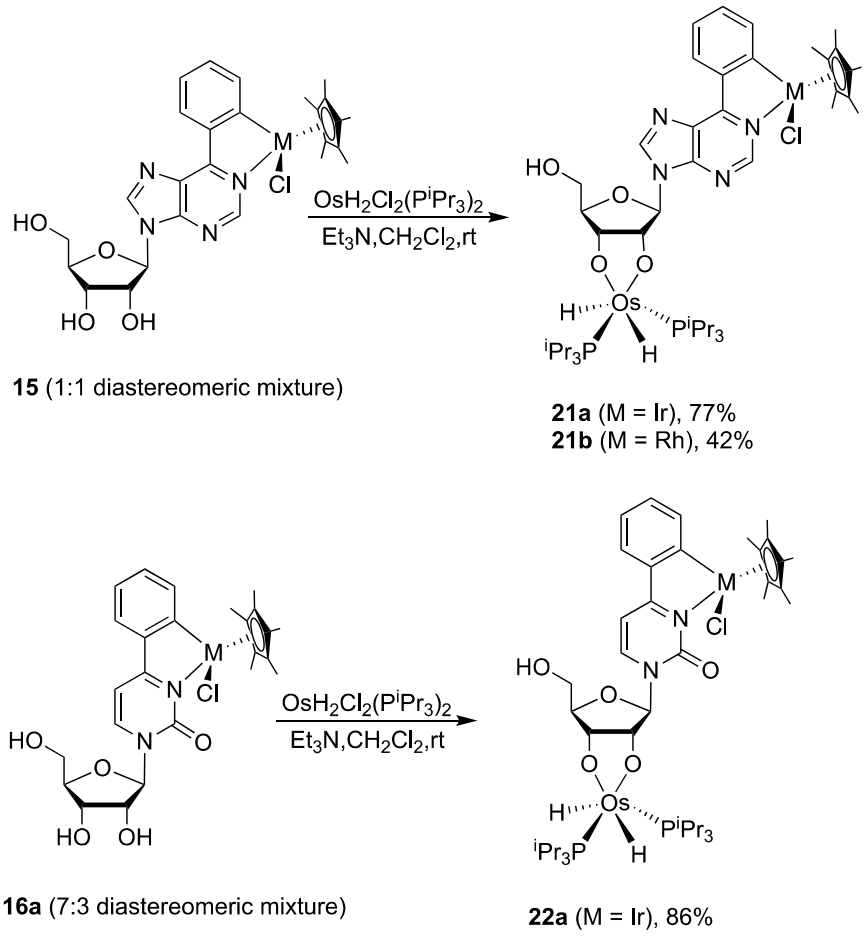
The opportunity of preparing heterobimetallic complexes by combining two different types of metal fragments in the structure of a nucleoside was next studied. In this case, we decided to combine half-sandwich cyclometallated Ir(III) and Rh(III) nucleosides **15** and **16** with $OsH_2Cl_2(P^iPr_3)_2$ (**17**), a reagent that has demonstrated ability for the formation of metallacycles by activation of OH bonds in sugars.[9a] Purine metallanucleosides **15a-b** were obtained as (1:1) diastereomeric mixtures by reaction of 9-β-D-ribofuranosyl-6-phenylpurine with $[MCl_2Cp^*]_2$ (M = Ir, Rh) in the presence of sodium acetate, in dichloromethane, at room temperature, following our own methodology (Scheme 6).[5] The preparation of the analogous pyrimidine nucleosides **16a-b** from β-D-ribofuranosyl-4-phenylpyrimidine (**18**),[15] required harder conditions and was carried out in a sealed tube, at 90 ˚C for 16-48 h (Scheme 6). The cyclometallations of pyrimidine nucleoside **18** were diastereoselective, leading to isomeric ratios of (70:30) for the Ir(III) derivative **16a** and (90:10) for the Rh(III) compound **16b**. This trend is general for the structurally related pyrimidine

nucleosides **5** and **9**, whose cyclometallations also occurred with good diastereomeric ratios, especially in the case of rhodium derivatives **19b** and **20b**. (Scheme 6). These results contrast to the lack of stereoselectivity observed for purine-cyclometallated complexes **15** and also with the data reported for other Ir(III) and Rh(III) half-sandwich purine-metallanucleosides and metallanucleotides, which were obtained in all cases with no selectivity.[5,6]



Scheme 6. Synthesis of Ir(III) and Rh (III) pyrimidine and purine metallanucleosides.

Heterobimetallic complexes **21** were prepared by reaction of cyclometallated purines **15a-b** (1:1 diastereomeric mixtures) with 1.0 equiv of the complex $OsH_2Cl_2(P^iPr_3)_2$ (**17**), in the presence of 4.0 equiv of Et_3N, in dichloromethane, at room temperature. The dinuclear complexes were obtained as dark red (**21a**, 77%) and orange (**21b**, 42%) solids by precipitation with pentane as 7:3 and 8:2 diastereomeric mixtures respectively (Scheme 7). Their structures were established by spectroscopic data. Relevant are the signals at -15.76 ppm (t, $J_{H\text{-}P}$ = 40 Hz, minor isomer) and -16.35 ppm (t, $J_{H\text{-}P}$ = 40 Hz, major isomer) assignable to the H-Os for both isomers in complex **21a** and at -15.75 ppm (t, $J_{H\text{-}P}$ = 38 Hz, major isomer), and -17.87 ppm (t, $J_{H\text{-}P}$ = 38 Hz, minor isomer) in complex **21b**.



Scheme 7. Synthesis of dinuclear complexes **21a-b** and **22a**

In a similar manner, reaction of Ir(III) pyrimidine nucleoside **16a** (7:3 isomeric mixture) led to the formation of dinuclear derivative **22a**, which was obtained by precipitation in pentane in 86% yield, as a brown-reddish solid (8:2 diastereomeric mixture). This compound decomposed in solution. The lower stability of pyrimidine derivatives compared to their purine counterparts was also shown in the preparation of the analogous dinuclear rhodium derivative. The formation of the complex could be confirmed by ^{1}H NMR and mass spectroscopy of the reaction crude, although it decomposed in solution and could not be isolated.

CONCLUSIONS

This study has revealed that the hexahydride $OsH_6(P^iPr_3)_2$ is able to activate C-H, H-O and C-C sigma bonds in nucleobases and nucleosides. This complex selectively cyclometallates derivatives of 6-phenylpurine and 4-phenylpirimidine in processes compatible with peracetylated ribose moieties, leading to mononuclear Os-trihydride complexes, in excellent yields and as single products. The osmium hydride also promotes the efficient dehydrogenative decarbonylation of primary alcohols in nucleosides having unprotected sugar moieties. Based on the reaction of key intermediates of the proposed reaction pathway, experimental support for this mechanism has been obtained. The study of the competition between C-H and O-H activation by $OsH_6(P^iPr_3)_2$ indicates that the *N*-supported *ortho*-cyclometallation of phenyl purine and phenylpyrimidine nucleosides is kinetically favored over the activation of the primary alcohol in the ribose fragment and that the processes occur sequentially. Additionally, we were able to incorporate two different metal fragments in the structure of a nucleoside by combining cyclometallated Ir(III) and Rh(III) half sandwich complexes with $OsH_2Cl_2(P^iPr_3)_2$. These are the first examples of heterobimetallic complexes of nucleosides having at least one M-C bond in their structures.

In summary, the development of methodologies to selectively introduce different metal

fragments in nucleosides has been achieved. These methodologies could be used in the future as a way for the orthogonal functionalization of oligonucleotides, taking advantage of the particular reactivity and properties of the each metal complex for metal-specific transformations.

EXPERIMENTAL SECTION

General Methods

Toluene was distilled over Na and benzophenone. Silica gel (Merck: 230-400 mesh) was used as stationary phase for purification of crude reaction mixtures by flash column chromatography. NMR spectra were recorded at 25ºC in C_6D_6, CD_2Cl_2 or $CDCl_3$ on a 300 MHz (300 MHz for ^{1}H, 75 MHz for ^{13}C, 121 MHz for ^{31}P), 400 MHz (400 MHz for ^{1}H, 100 MHz for ^{13}C, 162 MHz for ^{31}P) and 500 MHz (500 MHz for ^{1}H, 126 MHz for ^{13}C, 202 MHz for ^{31}P) spectrometers. Chemical shifts are given in ppm relative to the residual signals of C_6D_6 (C_6HD_5, ^{1}H, 7.16 ppm and ^{13}C, 128.0 ppm), CD_2Cl_2 ($CHDCl_2$, ^{1}H, 5.32 ppm and ^{13}C, 53.84 ppm) and $CDCl_3$ ($CHCl_3$, ^{1}H, 7.27 ppm and ^{13}C, 77.00 ppm). Coupling constants (*J* and *N*) are given in hertz. IR spectra were taken on a MIR (8000-400 cm^{-1}) spectrometer as solid films by slow evaporation of the solvent using the attenuated total reflectance (ATR) technique. HRMS experiments were conducted on an Accurate Mass Q-TOF system. Specific rotation $[\alpha]_D$ is given in deg, the concentration (c) is expressed in g per 100 mL. $OsH_6(P^iPr_3)_2$ (**1**),[24] 9-methyl-6-phenylpurine (**2**),[25] 9-(2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl)-6-phenylpurine (**4**),[26] **8**,[5] **15a**,[5] **15b**,[5] $OsHCl(CO)(P^iPr_3)_2$,[27] and $OsH_2Cl_2(P^iPr_3)_2$ (**17**)[24] were prepared according to literature procedures. Through the experimental part, in the NMR spectra of compounds derived from purine, numbering of the purine ring system has been used to denote the positions C2 and C8.

*Synthesis of **3**.*

To a solution of $OsH_6(P^iPr_3)_2$ (**1**) (300 mg, 0.58 mmol) in 20 mL of dry toluene was added 9-methyl-6-phenylpurine (**2**) (146 mg, 0.69 mmol). The resulting solution was heated at 120 ºC for 7 hours. During this time the color changed from pale yellow to dark red. The solution was cooled to room temperature and the solvent was evaporated in vacuo. Addition of pentane (2 mL) caused the precipitation of **3** as a dark red solid, which was washed with pentane (2 x 4 mL) and dried in vacuo. Yield: (260 mg 62%). ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 10.36 (s, 1H, C*H2*), 10.16 (d, J_{H-H} = 7 Hz, 1H, CH_{arom}), 8.83 (d, J_{H-H} = 7 Hz, 1H, CH_{arom}), 7.26 (t, J_{H-H} = 7 Hz, 1H, CH_{arom}), 7.10 (t, J_{H-H} = 6 Hz, 1H, CH_{arom}), 6.95 (s, 1H, C*H8*), 2.77 (s, 3H, N-CH_3), 1.85 (m, 6H, PC*H*$(CH_3)_2$), 0.98 (dvt, J_{H-H} = 6 Hz, *N* = 12, 18 H, PCH(C$H_3)_2$), 0.94 (dvt, J_{H-H} = 6 Hz, *N* = 15, 18 H, PCH(C$H_3)_2$), -8.43 (br, 2H, OsH), -11.72 (br, 1H, OsH). ^{1}H{^{31}P} NMR (CD_2Cl_2, 400 MHz, 193 K, high-field region): δ -6.60 (br d, J_{H-H} = 47 Hz, 1H, OsH), -11.32 (br d, J_{HH} = 47 Hz, 1H, OsH), -12.15 (t, J_{H-H} = 7 Hz, 1H, OsH). ^{13}C{^{1}H} NMR (C_6D_6, 75.48 MHz, 298 K): δ 195.4 (t, $^2J_{C-P}$ = 7 Hz, *C*-Os), 166.0 (s, C_{ipso}), 161.8 (s, *C*H*2*), 150.1 (s, C_{ipso}), 146.7 (s, *C*H$_{arom}$), 144.4 (s, C_{ipso}), 143.4 (s, *C*H*8*), 134.0 (s, *C*H$_{arom}$), 130.4 (s, C_{ipso}), 130.0, 119.4 (both s, *C*H$_{arom}$), 28.6 (s, N-*C*H$_3$), 27.7 (s, C(*C*H$_3)_2$), 27.6 (dvt, *N* = 24, Hz, P*C*H$(CH_3)_2$), 20.2 (s, PCH(*C*H$_3)_2$), 19.9 (s, PCH(*C*H$_3)_2$). ^{31}P{^{1}H} NMR (C_6D_6, 121.49 MHz, 298 K): δ 21.1 (s). $T_{1(min)}$ (ms, OsH, 300 MHz, CD_2Cl_2, 203 K): 88 ± 4 (-6.60 ppm), 95 ± 4 (-11.32 ppm), 101 ± 2 (-12,15 ppm). IR (Film): 2125 ν(Os-H), 1965, 1817, 1583 cm^{-1}. ESI-HRMS *m*/*z*: Calcd for: $C_{30}H_{50}N_4OsP_2$ $[M-4H]^+$ 720.3121; Found: 720.3156.

Synthesis of ***6***.

To a solution of $OsH_6(P^iPr_3)_2$ (**1**) (50 mg, 0.09 mmol) in 5 mL of dry toluene was added 9-(2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl)-6-phenylpurine (**4**) (37 mg, 0.09 mmol). The reaction was stirred under reflux for 7 hours under argon. The solvent was evaporated under reduced pressure. The crude was purified by flash SiO_2 chromatography (hexane/diethyl ether 1:1). Compound **6** was

eluted as a dark red band, that after further evaporation afforded a dark red solid (80 mg, 95%)**.** $[\alpha]_D^{25}$ = -106.8 (c = 0.10 g/100 mL, CH_2Cl_2)**.** ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ 10.31 (s, 1H, C*H2*), 10.10 (d, $J_{H\text{-}H}$ = 8 Hz, 1H, CH_{arom}), 8.81 (d, $J_{H\text{-}H}$ = 8 Hz, 1H, CH_{arom}), 7.90 (s, 1H, C*H8*), 7.25 (t, $J_{H\text{-}H}$ = 8 Hz, 1H, CH_{arom}), 7.07 (t, $J_{H\text{-}H}$ = 8, Hz 1H, CH_{arom}), 6.18-6.15 (m, 2H, C$H_{anomeric}$ and C*H*-O), 5.61 (m, 1H, C*H*-O), 4.17-4.12 (m, 2H, CH_2OAc), 4.13-4.07 (m, 1H, C*H*CH_2), 1.81 (m, 6H, PC*H*$(CH_3)_2$), 1.64 (s, 6H, COCH_3), 1.53 (s, 3H, COCH_3), 0.97-087 (m, 36H, PCH(C$H_3)_2$), -8.32 (br, 2H, OsH), -11.58 (br, 1H, OsH). ^{1}H{^{31}P} NMR (CD_2Cl_2, 400 MHz, 183K, high-field region): δ -6.59 (br d, $J_{H\text{-}H}$ = 42 Hz, 1H, OsH), -11.20 (br d, $J_{H\text{-}H}$ = 42 Hz, 1H, OsH), -12.08 (br, 1H, OsH). ^{13}C{^{1}H} NMR (C_6D_6, 75.48 MHz, 298 K): δ 196.8 (t, $^2J_{C\text{-}P}$ = 6 Hz, *C*-Os), 169.6, 169.0, 168.7 (s, *C*OCH_3), 166.4 (s, C_{ipso}), 162.0 (s, *CH2*), 149.4 (s, C_{ipso}), 146.8 (s, *C*H$_{arom}$), 143.9 (s, C_{ipso}), 141.3 (s, *CH8*), 134.1 (s, *C*H$_{arom}$), 131.1 (s, C_{ipso}), 130.2, 119.4 (both s, *C*H$_{arom}$), 86.5 (s, C$H_{anomeric}$), 80.9 (s, *C*HCH_2), 73.3 (s, *C*H-O), 71.5 (s, *C*H-O), 63.1 (s, CH*C*H_2), 27.6 (vt, *N* = 24, P*C*H$(CH_3)_2$), 20.1 (s, PCH(*C*$H_3)_2$ and CO*C*H_3), 19.8 (s, PCH(*C*$H_3)_2$ and CO*C*H_3). ^{31}P{^{1}H} NMR (C_6D_6, 121.49 MHz, 298 K): δ 23.9 (s). $T_{1(min)}$ (ms, OsH, 300 MHz, CD_2Cl_2, 183 K): 106 ± 4 (-6.59 ppm), 109 ± 4 (-11.26 ppm), 101 ± 2 (-12.08 ppm). IR (Film): 1949 ν(Os-H), 1901, 1752 ν(C=O), 1584, 1222 cm^{-1}. ESI-HRMS *m/z*: Calcd for: $C_{40}H_{65}N_4O_7OsP_2$ $[M\text{-}H]^+$ 967.3940; Found: 967.3934.

Synthesis of ***7****.*

To a solution of $OsH_6(P^iPr_3)_2$ (**1**) (67 mg, 0.13 mmol) in 5 mL of dry toluene was added (2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl)-4-phenylpyrimidine (**5**) (50 mg, 0.12 mmol). The reaction was stirred under reflux for 3 hours under argon. The solvent was evaporated under reduced pressure. The crude was purified by flash SiO_2 chromatography (hexane/ethyl acetate 1:1). Compound **7** was eluted as a dark purple band, that after further evaporation afforded a dark purple solid (40 mg,

37%). $[\alpha]_D^{25}$ = -48.1 (c = 0.10 g/100 mL, CH_2Cl_2)**.** ^{1}H NMR (C_6D_6, 500MHz, 298K): δ 8.95 (m, 1H, C*H*$_{arom}$), 7.81 (m, 1H, C*H*$_{arom}$), 7.24 (d, J_{H-H} = 7 Hz, 1H, C*H*=CH), 7.00 (m, 2H, C*H*$_{arom}$), 6.64 (d, J_{H-H} = 7 Hz, 1H, C*H*=CH), 6.31 (d, J_{H-H} = 4 Hz, 1H, C*H*$_{anomeric}$), 5.75 (dd, J_{H-H} = 6 Hz, 4 Hz, 1H, C*H*-O), 5.48 (dd, J_{H-H} = 6 Hz, ,5.5 Hz, 1H, C*H*-O), 4.30 (m, 1H, C*H*$_2$OAc), 4.22-4.17 (m, 2H, C*H*$_2$OAc and C*H*CH$_2$), 1.92 (m, 6H, PC*H*$(CH_3)_2$), 1.70 (s, 3H, COC*H*$_3$), 1.68 (s, 3H, COC*H*$_3$), 1.62 (s, 3H, COC*H*$_3$), 1.07-0.96 (m, 36H, PCH(C*H*$_3)_2$), -7.03 (br, 2H, OsH), -11.70 (br s, 1H, OsH). ^{1}H{^{31}P} NMR (CD_2Cl_2, 400 MHz, 193 K, high-field region): δ -7.81 (br s, 1H, OsH), -12.16 (br s, 2H, OsH). ^{13}C{^{1}H} NMR (C_6D_6, 125.77 MHz, 298 K): δ 207.1 (t, J_{C-P} = 6 Hz, *C*-Os), 177.0 (t, J_{C-P} = 2 Hz, C_{ipso}), 169.7, 169.1, 169.0 (all s, *C*OCH$_3$), 155.2 (s, N(*C*O)N), 147.4 (s, *C*H$_{arom}$), 143.2 (s, *C*-Ph), 136.1 (s, *C*H=CH), 130.6, 129.4, 118.4 (all s, *C*H$_{arom}$), 99.6 (s, *C*H=CH), 91.8 (s, *C*H$_{anomeric}$), 80.2 (s, *C*HCH$_2$), 74.3 (s, *C*H-O), 70.6 (s, *C*H-O), 63.2 (s, CH*C*H$_2$), 28.3 (vt, *N* = 24, P*C*H$(CH_3)_2$), 25.1, 24.6, 20.3 (all s, COCH$_3$), 20.2, 20.1 (both s, PCH(*C*H$_3)_2$). ^{31}P{^{1}H} NMR (C_6D_6, 121.49 MHz, 298 K): δ 27.7 (s). $T_{1(min)}$ (ms, OsH, 300 MHz, CD_2Cl_2, 243 K): 74 ± 4 (-7.65 ppm), 129 ± 4 (-12.10 ppm). IR (Film): 1749 ν(C=O), 1234 cm^{-1}. ESI-HRMS *m*/*z*: Calcd for: $C_{39}H_{65}N_2O_8OsP_2$ $[M-H]^+$ 943.3828; Found: 943.3836.

*Synthesis of **10**, **11** and **12**.*

Method A (ratio $OsH_6(P^iPr_3)_2$: **8** = 1.1:1)

To a solution of $OsH_6(P^iPr_3)_2$ (**1**) (228 mg, 0.44 mmol) in 5 mL of dry toluene was added **8** (146 mg, 0.39 mmol). The reaction was stirred under reflux for 6 hours under argon. The solvent was evaporated under reduced pressure. The analysis of the products ratio in the reaction crude by ^{1}H NMR (C_6D_6) was **10**:**11**:**12** (45:22:33). The crude was purified by flash SiO_2 chromatography. The silicagel was previously treated by stirring overnight with a mixture of triethylamine in hexane (20:80) and subsequent washings with hexane. The products were eluted in hexane to hexane/ethyl

acetate 1:1 mixture. In the first fraction was eluted mainly the minor complex **11** as a dark red solid (22 mg, 7.3%). In the second fraction was eluted mainly complex **12** as a dark red solid (30 mg, 8%) and in the last fraction was eluted **10** as a dark red solid (90 mg, 26%).

Method B (ratio $OsH_6(P^iPr_3)_2$: **8** = 1.6:1)

To a solution of $OsH_6(P^iPr_3)_2$ (**1**) (145 mg, 0.28 mmol) in 5 mL of dry toluene was added **8** (64 mg, 0.18 mmol). The reaction was stirred under reflux for 7 hours under argon. The solvent was evaporated under reduced pressure. The analysis of the products ratio in the reaction crude by ^1H NMR (C_6D_6) was **11:12** (41:59). The crude was purified by flash SiO_2 chromatography (hexane/diethyl ether 19:1 to 4:1). In the first fraction was eluted mainly complex **11** as a dark red solid (49 mg, 20%). In the second fraction was eluted complex **12** as a dark red solid (103 mg, 70%)**.**

*Complex **10**.*

Dark red solid. $[\alpha]_D^{25}$ = -69.4 (c = 0.11 g/100 mL, CH_2Cl_2)**.** ^1H NMR (C_6D_6, 500 MHz, 298 K): δ 10.26 (s, 1H, C*H2*), 10.06 (d, $J_{H\text{-}H}$ = 8 Hz, 1H, CH_{arom}), 8.78 (d, $J_{H\text{-}H}$ = 8, Hz 1H, CH_{arom}), 7.56 (br s, 1H, C*H8*), 7.21 (t, $J_{H\text{-}H}$ = 8 Hz, 1H, CH_{arom}), 7.05 (t, $J_{H\text{-}H}$ = 8 Hz, 1H, CH_{arom}), 5.88 (m, 1H, C$H_{anomeric}$), 5.22 (dd, $J_{H\text{-}H}$ = 5.9, 4.1 Hz, 1H, C*H*-O), 4.98 (m, 1H, C*H*-O), 4.68 (m, 1H, OH), 4.31 (m, 1H, C*H*CH_2), 3.76 (dd, $J_{H\text{-}H}$ = 9, 3 Hz, 1H, CH_2OH), 3.47 (m, 1H, CH_2OH), 1.79 (m, 6H, PC*H*$(CH_3)_2$), 1.46 (s, 3H, C(CH_3)$_2$), 1.07 (s, 3H, C(CH_3)$_2$), 0.90 (dvt, $J_{H\text{-}H}$ = 5 Hz, *N* = 10, 18 H, PCH(CH_3)$_2$), 0.87 (dvt, $J_{H\text{-}H}$ = 5 Hz, *N* = 10, 18 H, PCH(CH_3)$_2$), -8.40 (br, 2H, OsH), -11.70 (br, 1H, OsH). $^1H\{^{31}P\}$ NMR (CD_2Cl_2, 400 MHz, 193 K, high-field region): δ -6.55 (br d, $J_{H\text{-}H}$ = 67 Hz, 1H, OsH), -11.19 (br d, $J_{H\text{-}H}$ = 67 Hz, 1H, OsH), -12.04 (t, $J_{H\text{-}H}$ = 7 Hz, 1H, OsH). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.77 MHz, 298 K): δ 197.5 (t, $^2J_{C\text{-}P}$ = 5 Hz, *C*-Os), 166.7 (s, C_{ipso}), 161.3 (s, *C*H*2*), 148.5

(s, C_{ipso}), 146.8 (s, CH_{arom}), 143.8 (s, C_{ipso}), 142.7 (s, *C*H*8*), 134.3 (s, CH_{arom}), 131.8 (s, C_{ipso}), 130.2, 119.4 (both s, CH_{arom}), 114.0 (s, $C(CH_3)_2$), 93.4 (s, $CH_{anomeric}$), 86.9 (s, *C*HCH$_2$), 84.1 (s, *C*H-O), 81.9 (s, *C*H-O), 63.3 (s, CH*C*H$_2$), 27.7 (s, C(*C*H$_3$)$_2$), 27.6 (vt, *N* = 24, P*C*H(CH$_3$)$_2$), 27.5 (vt, *N* = 25 Hz, P*C*H(CH$_3$)$_2$), 25.2 (s, C(*C*H$_3$)$_2$), 20.0 (d, $J_{C\text{-}P}$ = 4 Hz, PCH(*C*H$_3$)$_2$), 19.8 (d, $J_{C\text{-}P}$ = 1 Hz, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.49 MHz, 298 K): δ 21.2 (s). $T_{1(min)}$ (ms, OsH, 300 MHz, CD_2Cl_2, 253 K): 101 ± 4 (-8.64 ppm), 108 ± 4 (-11.46 ppm). IR (Film): 2128 ν(Os-H), 1962, 1582 cm^{-1}. ESI-HRMS *m*/*z*: Calcd for: $C_{37}H_{62}O_4N_4OsP_2$ $[M\text{-}2H]^+$ 880.3873; Found: 880.3858.

*Complex **11**.*

Dark red solid. $[\alpha]_D^{25}$ = -40.0 (c = 0.14 g/100 mL, CH_2Cl_2)**.** ^1H NMR (C_6D_6, 300 MHz, 298 K): δ 10.20 (s, 1H, C*H2*), 10.10 (d, $J_{H\text{-}H}$ = 6 Hz, 1H, CH_{arom}), 8.79 (d, $J_{H\text{-}H}$ = 6 Hz, 1H, CH_{arom}), 7.54 (s, 1H, C*H8*), 7.22 (t, $J_{H\text{-}H}$ = 6 Hz, 1H, CH_{arom}), 7.08 (t, $J_{H\text{-}H}$ = 6 Hz, 1H, CH_{arom}), 5.70-5.63 (m, 2H, C$H_{anomeric}$ and C*H*-O), 5.21 (t, $J_{H\text{-}H}$ = 6 Hz, 1H, C*H*-O), 4.52 (dd, $J_{H\text{-}P}$ = 15 Hz, $J_{H\text{-}H}$ = 9 Hz, 1H, C*H*-Os), 2.43 (m, 6H, PC*H*(CH$_3$)$_2$), 1.82 (m, 6H, PC*H*(CH$_3$)$_2$), 1.46 (s, 3H, C(C*H*$_3$)$_2$), 1.27-1.16 (m, 36H, PCH(C*H*$_3$)$_2$), 1.22 (s, 3H, C(C*H*$_3$)$_2$), 1.00-0.84 (m, 36H, PCH(C*H*$_3$)$_2$), -7.20 (t, $J_{H\text{-}P}$ = 21 Hz, 1H, OsH), -8.50 (br, 2H, OsH), -11.74 (br, 1H, OsH). $^1H\{^{31}P\}$ NMR (CD_2Cl_2, 400 MHz, 193 K, high-field region): δ -6.65 (br d, $J_{H\text{-}H}$ = 44 Hz, 1H, OsH), -7.57 (br s, 1H, OsH), -11.39 (br d, $J_{H\text{-}H}$ = 44 Hz, 1H, OsH), -12.14 (t, $J_{H\text{-}H}$ = 7 Hz, 1H, OsH). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.48 MHz, 298 K): δ 195.6 (t, $^2J_{C\text{-}P}$ = 7 Hz, *C*-Os), 190.6 (t, $^2J_{C\text{-}P}$ = 6 Hz, Os-*C*O), 184.6 (t, $^2J_{C\text{-}P}$ = 9 Hz, Os-*C*O), 166.1 (s, C_{ipso}), 161.5 (s, *C*H*2*), 150.0 (s, C_{ipso}), 146.7 (s, CH_{arom}), 144.4 (s, C_{ipso}), 143.2 (s, *C*H*8*), 134.1 (s, CH_{arom}), 131.2 (s, C_{ipso}), 130.0, 119.4 (both s, CH_{arom}), 115.1 (s, $C(CH_3)_2$), 91.6 (s, *C*H-O), 91.2 (s, $CH_{anomeric}$), 83.8 (s, *C*H-O), 63.1 (t, $J_{C\text{-}P}$ = 8 Hz, *C*H-Os), 27.7 (s, C(*C*H$_3$)$_2$), 27.35 (dvt, *N* = 33, 7.5 Hz, P*C*H(CH$_3$)$_2$), 26.3 (dvt, *N* = 42, 5, P*C*H(CH$_3$)$_2$), 25.2 (s, C(*C*H$_3$)$_2$), 20.2 (d, J_{CP} = 9 Hz,

PCH(CH_3)$_2$), 19.9 (d, J_{CP} = 6 Hz, PCH(CH_3)$_2$), 19.4 (d, J_{CP} = 6 Hz, PCH(CH_3)$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.49 MHz, 298K): δ 22.7 (AB spin system, Δν = 207 Hz, $J_{A\text{-}B}$ = 202 Hz), 21.3 (AB spin system, Δν = 141 Hz, $J_{A\text{-}B}$ = 242 Hz). $T_{1(min)}$ (ms, OsH, 300 MHz, CD_2Cl_2, 253 K): 135±4 (-7.39 ppm), 67±4 (-12,04 ppm). IR (Film): 2016 ν(Os-H), 1963 ν(CO) , 1896 ν(CO), 1583 cm^{-1}. ESI-HRMS *m*/*z*: Calcd for: $C_{56}H_{102}O_5N_4Os_2P_4$ $[M\text{-}2H]^+$ 1416.6007; Found: 1416.5964.

*Complex **12**.*

Dark red solid. $[\alpha]_D^{25}$ = -81.2 (c = 0.1 g/100 mL, CH_2Cl_2)**.** ^1H NMR (C_6D_6, 300 MHz, 298K): δ 10.20 (s, 1H, C*H2*), 10.09 (d, J_{HH} = 8 Hz, 1H, CH_{arom}), 8.79 (d, J_{HH} = 8 Hz, 1H, CH_{arom}), 7.24 (s, 1H, C*H8*), 7.24 (t, J_{HH} = 8 Hz, 1H, CH_{arom}), 7.08 (t, J_{HH} = 8 Hz, 1H, CH_{arom}), 5.74 (s, 1H, C$H_{anomeric}$), 5.31 (d, J_{HH} = 6 Hz, 1H, C*H*-O), 4.83 (m, 1H, C*H*-O), 4.03 (d, *J* = 12 Hz ,1H, CH_2), 3.86 (dd, *J* = 12, 3 Hz, 1H, CH_2), 1.83 (m, 6H, PC*H*(CH_3)$_2$), 1.50 (s, 3H, C(CH_3)$_2$), 1.13 (s, 3H, C(CH_3)$_2$), 1.27-1.16 (m, 16H, PCH(CH_3)$_2$), 0.95 (dvt, J_{HH} = 9 Hz, *N* = 15, 18H, PCH(CH_3)$_2$), 0.88 (dvt, *J* = 9, Hz *N* = 12, 18H, PCH(CH_3)$_2$), -8.42 (br, 2H, OsH), -11.71 (br, 1H, OsH). $^1H\{^{31}P\}$ NMR (CD_2Cl_2, 400 MHz, 183K, high-field region): δ -6.60 (br d, $J_{H\text{-}H}$ = 45 Hz, 1H, OsH), -11.29 (br d, $J_{H\text{-}H}$ = 45 Hz, 1H, OsH), -12.10 (t, $J_{H\text{-}H}$ = 7 Hz, 1H, OsH). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.48MHz, 298K): δ 196.3 (t, $J_{C\text{-}P}$ = 7 Hz, *C*-Os), 166.2 (s, C_{ipso}), 161.5 (s, *CH2*), 149.0 (s, C_{ipso}), 146.7 (s, *C*H$_{arom}$), 144.0 (s, C_{ipso}), 142.8 (s, *CH8*), 134.2 (s, *C*H$_{arom}$), 131.1 (s, C_{ipso}), 130.2, 119.5 (both s, *C*H$_{arom}$), 113.0 (s, *C*(CH_3)$_2$), 91.6 (s, *C*H$_{anomeric}$), 84.7 (s, *C*H-O), 81.6 (s, *C*H-O), 75.6 (s, *C*H_2), 27.6 (m, J_{CP} = 17.3, 10.3, 7.8 Hz, P*C*H(CH_3)$_2$), 26.6 (s, C(*C*H_3)$_2$), 24.8 (s, C(*C*H_3)$_2$), 20.1 (d, J_{CP} = 3 Hz, PCH(*C*H_3)$_2$), 19.9 (d, J_{CP} = 3 Hz, PCH(*C*H_3)$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.49MHz, 298K): δ 21.0 (s, *P*CH(CH_3)$_2$). $T_{1(min)}$ (ms, OsH, 300 MHz, CD_2Cl_2, 243 K): 116 (-12.02 ppm). IR (Film): 2027 ν(Os-H), 1961, 1898, 1582 cm^{-1}. ESI-HRMS *m*/*z*: Calcd for: $C_{36}H_{60}N_4O_3OsP_2$ $[M\text{-}2H]^+$ 850.3752; Found: 850.3772.

*Synthesis of **13** and **14**.*

Method A (ratio $OsH_6(P^iPr_3)_2$: **9** = 1.1:1)

To a solution of $OsH_6(P^iPr_3)_2$ (**1**) (83 mg, 0.16 mmol) in 5 mL of dry toluene was added **9** (50 mg, 0.14 mmol). The reaction was stirred under reflux for 4 hours under argon. The solvent was evaporated under reduced pressure. The analysis of the products ratio in the reaction crude by ^{1}H NMR (C_6D_6) was **13**:**14** (44:56). The crude was purified by flash SiO_2 chromatography (hexane/ethyl acetate 3:1 to 1:1). In the first fraction was eluted mainly complex **14** as a dark purple solid (76 mg, 63%). In the second fraction was eluted complex **13** as a dark purple solid (40 mg, 32%)**.**

Method B (ratio $OsH_6(P^iPr_3)_2$: **9** = 1.1:1)

Under these conditions complex **14** was obtained as the only product in almost quantitative yield.

*Complex **13**.*

Dark red solid. $[\alpha]_D^{25}$ = -74.1 (c = 0.11 g/100 mL, CH_2Cl_2). ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ 8.92 (m, 1H, C*H*$_{arom}$), 7.72 (m, 1H, C*H*$_{arom}$), 6.98 (m, 2H, C*H*$_{arom}$), 6.66 (d, $J_{H\text{-}H}$ = 7 Hz, 1H, C*H*=CH), 6.64 (d, $J_{H\text{-}H}$ = 7 Hz, 1H, C*H*=CH), 5.57 (m, 1H, C*H*$_{anomeric}$), 5.44 (dd, *J* = 6 Hz, 3 Hz, 1H, C*H*-O), 5.32 (dd, *J* = 6 Hz, 3 Hz, 1H, C*H*-O), 4.38 (q, *J* = 3 Hz, 1H, C*H*CH_2), 4.20 (br s, 1H, CH_2O*H*), 3.96 (dd, *J* = 12 Hz, 2 Hz, 1H, C*H*$_2$OH), 3.75 (m, 1H, C*H*$_2$OH), 1.93 (m, 3H, PC*H*$(CH_3)_2$), 1.85 (m, 3H, PC*H*$(CH_3)_2$), 1.52 (s, 3H, C(C*H*$_3)_2$), 1.21 (s, 3H, C(C*H*$_3)_2$), 1.04-0.92 (m, 36H, PCH(C*H*$_3)_2$), -7.04 (br, 2H, OsH), -11.80 (br, 1H,OsH). ^{1}H{^{31}P} NMR (CD_2Cl_2, 400 MHz, 193K, high-field region): δ -7.77 (br, 1H, OsH), -12.21 (br, 2H, OsH). ^{13}C{^{1}H} NMR (C_6D_6, 125.77 MHz, 298 K): δ 207.3 (t, $J_{C\text{-}P}$ = 6 Hz, *C*-Os), 177.4 (s, *C*$_{ipso}$), 155.7 (s, N(*C*O)N), 147.2 (s, *C*H$_{arom}$), 143.1 (s, *C*-Ph), 140.2 (s, *C*H=CH), 130.6, 129.5, 118.4 (all s, *C*H$_{arom}$), 113.8 (s, *C*$(CH_3)_2$), 100.3 (s, *C*H$_{anomeric}$), 99.4 (s, *C*H=CH), 88.7 (s, *C*HCH_2), 84.3 (s, *C*H-O), 81.2 (s, *C*H-O), 63.2 (s, CH*C*H_2),

28.4 (d, $J_{C\text{-}P}$ = 7.6 Hz, P*C*H(CH$_3$)$_2$), 28.3 (d, $J_{C\text{-}P}$ = 7.6 Hz, P*C*H(CH$_3$)$_2$), 27.6 (s, C(*C*H$_3$)$_2$), 25.0 (s, C(*C*H$_3$)$_2$), 20.2 (d, $J_{C\text{-}P}$ = 9 Hz, PCH(*C*H$_3$)$_2$), 20.0 (d, $J_{C\text{-}P}$ = 13 Hz, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.49 MHz, 298 K): δ 23.9 (AB spin system, Δν = 99 Hz J_{AB} = 222 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.49 MHz, 183 K): δ 22.0 (AB spin system, Δν = 567 Hz, J_{AB} = 206 Hz). $T_{1(min)}$ (ms, OsH, 300 MHz, CD_2Cl_2, 253 K): 72±4 (-7.48 ppm), 113±4 (-12.08 ppm). IR (Film): ν(Os-H) 1894, ν(C=O) 1662, 1611, ν(C-O) 1262 cm^{-1}. ESI-HRMS *m/z*: Calcd for: $C_{36}H_{63}N_2O_5OsP_2$ $[M\text{-}H]^+$ 857.3824; Found: 857.3839.

*Complex **14**.*

Dark red solid. $[\alpha]_D^{25}$ = -80.7 (c = 0.10 g/100 mL, CH_2Cl_2)**.** ^1H NMR (C_6D_6, 500 MHz, 298K): δ 8.89 (m, 1H, C*H*$_{arom}$), 7.70 (m, 1H, C*H*$_{arom}$), 6.97 (m, 2H, C*H*$_{arom}$), 7.34 (d, *J* = 7 Hz, 1H, C*H*=CH), 6.31 (d, *J* = 7 Hz, 1H, C*H*=CH), 5.48 (s, 1H, C*H*$_{anomeric}$), 5.46 (d, *J* = 6 Hz, 1H, C*H*-O), 5.21 (dd, *J* = 6 Hz, 4 Hz, 1H, C*H*-O), 4.65 (dd, *J* = 9 Hz, 4 Hz, 1H, C*H*$_2$), 4.29 (d, *J* = 9 Hz, 1H, C*H*$_2$), 1.88 (m, 6H, PC*H*(CH$_3$)$_2$), 1.56, 1.27 (both s, 3H, C(C*H*$_3$)$_2$), 1.03-0.99 (m, 18H, PCH(C*H*$_3$)$_2$), 0.98-0.91 (m, 18H, PCH(C*H*$_3$)$_2$), -7.15 (br s, 2H, *H*-Os), -11.83 (br s, 1H, *H*-Os). $^1H\{^{31}P\}$ NMR (CD_2Cl_2, 400 MHz, 203 K, high-field region): δ -7.79 (br, 1H, OsH), -12.18 (br, 2H, OsH). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.77 MHz, 298K): δ 206.1 (t, $J_{C\text{-}P}$ = 6 Hz, Os-*C*), 177.9 (t, *J* = 2 Hz, *C*$_{ipso}$), 155.9 (s, N(*C*O)N), 147.2 (s, *C*H$_{arom}$), 143.4 (s, *C*-Ph), 140.1 (s, *C*H=CH), 130.6, 129.5, 118.4 (all s, *C*H$_{arom}$), 112.5 (s, *C*(CH$_3$)$_2$), 101.4 (s, *C*H$_{anomeric}$), 98.9 (s, *C*H=CH), 85.9 (s, *C*H-O), 83.0 (s, *C*H-O), 79.4 (s, *C*H$_2$), 28.3 (m, P*C*H(CH$_3$)$_2$), 28.2 (vt, *N* = 17 Hz, P*C*H(CH$_3$)$_2$), 26.8, 24.8 (s, C(*C*H$_3$)$_2$), 20.1 (d, *J* = 5 Hz, PCH(*C*H$_3$)$_2$), 19.9 (d, *J* = 8 Hz, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.49 MHz, 298K): δ 23.9 (AB spin system Δν = 63 Hz J_{AB} = 226 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.49 MHz, 193K): δ 21.2 (AB spin system, Δν = 228 Hz J_{AB} = 220 Hz). $T_{1(min)}$ (ms, OsH, 300 MHz, CD_2Cl_2, 233K): 76 (-

7.69 ppm), 131 (-12.13 ppm). IR (Film): ν(Os-H) 2022, 1899, ν(C=O) 1667, 1611 ν(C-O) 1263 cm^{-1}. ESI-HRMS *m/z*: Calcd for: $C_{35}H_{61}N_2O_4OsP_2$ $[M-H]^+$ 827.3718; Found: 827.3727.

*Synthesis of complex **11** from **10** and $OsH_2(\eta^2\text{-}CH_2\text{=}CHEt)(CO)(P^iPr_3)_2$*

Complex $OsH_2(\eta^2\text{-}CH\text{=}CHEt)(CO)(P^iPr_3)_2$ (0.10 mmol) was generated *in situ* by reacting $OsHCl(CO)(P^iPr_3)_2$ (58.7 mg, 0.10 mmol) with ^{n}BuLi (0.10 mmol, 1.6 M in hexane) following the previously reported procedure.[20a] To the colorless oil thus obtained was added a solution of complex **10** (90 mg, 0.10 mmol) in toluene (5 mL) and the mixture was refluxed for 6 h. The progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy, showing the exclusive formation of **11**.

*Complex **16a**.*

To a solution of $[IrCl_2Cp^*]_2$ (50 mg, 0.06 mmol) in 10 mL of dichloromethane was added NaOAc (12 mg, 0.15 mmol) and **18** (32 mg, 0.10 mmol). The mixture was heated at 90 ºC for 16 hours and filtered through celite. The solvent was removed under reduced pressure. The crude was purified by flash SiO_2 chromatography (ethyl acetate:methanol 9:1) to yield **16a** (red solid) (40 mg, 60%) as a 70:30 mixture of isomers. ^{1}H NMR ($CDCl_3$, 300 MHz, 298K): δ 8.31 (d, *J* = 7.1 Hz, 0.7H, C*H*-CPh major isomer), 7.96-7.92 (m, 1.4H, CH_{arom} major isomer and 0.3H, C*H*-CPh minor isomer), 7.87 (d, *J* = 7.1 Hz, 0.3H, CH_{arom} minor isomer), 7.57 (d, *J* = 7.9 Hz, 0.7H, CH_{arom} major isomer), 7.45 (d, *J* = 7.9 Hz, 0.3H, CH_{arom} minor isomer), 7.30-7.26 (m, 0.7H, CH_{arom} major isomer), 7.10 (t, *J* = 7.4 Hz, 0.7H, CH_{arom} major isomer), 6.97 (t, *J* = 7.4 Hz, 0.3H, CH_{arom} minor isomer), 6.57 (d, *J* = 7.2 Hz, 2H, , C*H*=CH both isomers), 5.88 (d, *J* = 3.0 Hz, 0.7H, C$H_{anomeric}$ major isomer), 5.82 (d, *J* = 3.0 Hz, 0.3H, C$H_{anomeric}$ minor isomer), 4.64, 4.24 (all broad s, 2H, O*H*), 4.17-4.03 (m, 4H, CH_2 both isomers), 3.95-3.90 (m, 1.4H, C*H* major isomer), 3.81-3.74 (m, 2H, C*H* both isomers), 3.72–

3.70 (m, 0.3H, C*H*, minor isomer), 3.64–3.60 (m, 0.3H, CH, minor isomer), 3.46-3.40 (m, 0.6H, CH_2, minor isomer), 2.53 (bs, 0.6H, OH, minor isomer), 1.66 (s, 15H, CH_3 Cp*, both isomers). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 298K): δ 179.5, 178.7 (*C*-Ir), 171.9, 171.5 (*C*O-N), 154.3, 154.2 (*C*-Ph), 144.8, 144.3 (*C*H-CPh), 144.0, 143.9, (C_{ipso}), 136.6, 136.2, 133.7 (CH), 129.3, 128.7, 122.4, 122.2 (CH_{arom}), 99.7, 98.9 (*C*H-N), 94.2, 92.7 ($CH_{anomeric}$), 89.90 (C_{cp*}), 86.2 (*C*HCH$_2$), 76.6, 75.2 (*C*H-CH), 70.6, 69.7 (*C*H-CH), 62.1, 60.7 (CH_2), 9.76, 9.67 (CH_3Cp*). IR (film): ν 3369, 3052, 2912, 1675, 1023 cm^{-1}. ESI-HRMS *m/z:* Calcd for: $C_{25}H_{30}N_2O_5Ir$ $[M-Cl]^+$: 631.1779; Found: 631.1758.

*Complex **16b**.*

To a solution of $[RhCl_2Cp^*]_2$ (50 mg, 0.08 mmol) in 10 mL of dichloromethane was added NaOAc (13 mg, 0.16 mmol) and **18** (41 mg, 0.13 mmol). The mixture was heated at 90 ºC for 48 hours and filtered through celite. The solvent was removed under reduced pressure. The crude was purified by flash SiO_2 chromatography (ethyl acetate/methanol, 9:1) to yield **20b** (orange solid) (34 mg, 45%) as a 90:10 mixture of isomers ^1H NMR ($CDCl_3$, 300 MHz, 298K): δ 8.45 (d, *J* = 7.0 Hz, 0.9H, C*H*-CPh, major isomer), 8.40 (d, *J* = 7.0 Hz, 0.1H, C*H*-CPh, minor isomer) 7.93-7.90 (m, 0.9H, CH_{arom} major isomer and 0.1H, C*H*-CPh minor isomer), 7.49 (d, *J* = 8.0, 0.9H, CH_{arom} major isomer), 7.43 (d, *J* = 8.0, 0.1H, CH_{arom} minor isomer), 7.35-7.31 (m, 1H, CH_{arom} both isomers), 7.13-7.10 (m, 0.9H, CH_{arom} major isomer), 7.03-6.98 (m, 0.1H, CH_{arom} minor isomer), 6.57 (d, *J* = 8.0, 0.1H, C*H*=CH minor isomer), 6.48 (d, *J* = 7.2 Hz, 0.9H, C*H*=CH, major isomer), 5.86 (d, *J* = 3.1 Hz, 0.9H, C$H_{anomeric}$ major isomer), 5.74 (d, *J* = 3.1 Hz, 0.1H, C$H_{anomeric}$ minor isomer), 4.56 (bs, 1H, OH, both isomers), 4.20-4.12 (m, 1H, C*H,* both isomers), 4.09-4.03 (m, 2H, CH_2, both isomers), 3.93-3.87 (m, 1H, C*H,* both isomers), 3.83-3.89 (m, 1H, C*H,* both isomers), 3.57 (bs, 1H, OH, both isomers), 2.53 (bs, 1H, OH, both isomers), 1.58 (s, 15H, CH_3Cp* both isomers). $^{13}C\{^1H\}$ NMR

($CDCl_3$, 75 MHz, 298K): δ 187.3 (d, *J* = 32.4 Hz, *C*-Rh), 177.3, 176.7 (s, O=*C*-N), 154.2, 154.1 (s, *C*-Ph), 144.5 (s, *C*H-CPh), 143.3, 143.2 (s, C_{ipso}), 137.6, 137.2, 132.7, 129.0, 128.6, 128.0, 123.2, 123.0 (all s, CH_{arom}), 99.5 (s, *C*H-N), 97.2 (d, *J* = 6.5 Hz, *C*-CH_3), 92.4 (s, $CH_{anomeric}$), 86.4, 86.2 (s, *C*H-CH_2), 76.6, 69.4 (s, *C*H-CH), 60.5 (s, CH_2-CH), 9.9, 9.8 (s, CH_3). IR (film): ν 3398, 2921, 2855, 2050, 1675, 1549, 1266, 1029 cm^{-1}. ESI-HRMS *m/z*: Calcd for: $C_{25}H_{30}N_2O_5Rh$ $[M-Cl]^+$: 541.1204; Found: 541.1229.

*Complex **19a**.*

In a Schlenck tube, to a solution of $[IrCl_2Cp^*]_2$ (55 mg, 0.07 mmol) in 10 mL of dichloromethane was added NaOAc (11.4 mg, 0.14 mmol) and **5** (50 mg, 0.12 mmol). The mixture was stirred at 80 ^oC for 18 hours. The solvent was removed under reduced pressure. The crude was purified by flash SiO_2 chromatography (Hexane:AcOEt, 1:1) to yield **19a** (orange solid) (83 mg, 90%) as a 70:30 mixture of isomers. ^1H NMR ($CDCl_3$, 300 MHz, 298K): δ 7.96 (d, *J* = 7.7 Hz, 1H, CH_{arom} both isomers), 7.80 (d, *J* = 7.0 Hz, 0.7 H, CH_{arom}, major isomer), 7.64 (d, *J* = 7.9 Hz, 0.3H, CH_{arom} minor isomer), 7.58 (d, *J* = 7.8 Hz, 0.7H, CH_{arom}, major isomer), 7.47 (d, *J* = 6.9 Hz, 0.3H, CH_{arom}, minor isomer), 7.31–7.20 (m, 1 H, CH_{arom}, both isomers), 6.99 (dd, *J* = 7.2, 7.1 Hz, 1H, CH_{arom}, both isomers), 6.80 (d, *J* = 7.2 Hz, 0.3H, C*H*=CH, minor isomer), 6.76 (d, *J* = 7.1 Hz, 0.7H, , C*H*=CH, major isomer), 6.16 (d, *J* = 3.2 Hz, 0.7H, C$H_{anomeric}$, major isomer), 6.05 (d, *J* = 3.8 Hz, 0.3H, C$H_{anomeric}$, minor isomer), 5.54-5.44 (m, 1.3H, C*H*, both isomers), 5.29-5.26 (m, 0.7H, C*H*, major isomer), 4.49-4.6 (m, 1H) and 4.43-4.41 (m,1.3H) (C*H* minor isomer and CH_2 both isomers), 2.16 (s, 3H, CH_3-CO), 2.14 (s, 3H, CH_3-CO), 2.11 (s, 3H, CH_3-CO), 1.70 (s, 15H, CH_3Cp*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 298K): δ 179.9, 179.6 (*C*-Ir), 173.5, 172.7 (*C*ON), 170.6, 170.3, 169.8, 169.7, 169.6, 169.2 (all CH_3CO), 153.3, 153.0 (*C*-Ph), 143.8, 143.7 (C_{ipso}), 142,6, 141.3 (*C*H-CPh),

136.2, 133.8, 129.3, 129.2, 122.1, 122.0 (CH$_{arom}$), 99.7, 99.4 (CH-N), 91.6, 90.1 (CH$_{anomeric}$), 90.0 (CCp$_*$), 80.1, 79.8 (CHCH$_2$), 74.2, 73.5 (CH-CH), 70.3, 69.5 (CH-CH), 62.8, 62.6 (CH$_2$), 21.0, 20.6, 20.5 (CH$_3$-CO), 9.7, 9.6 (CH$_3$Cp*). IR (film): ν 2913, 1749, 1687, 1612, 1228, 1100, 731 cm^{-1}. ESI-HRMS *m/z*: Calcd for: $C_{31}H_{36}N_2O_8Ir$ $[M-Cl]^+$: 757.2105; Found: 757.2117.

*Complex **19b**.*

In a Schlenck tube, to a solution of $[RhCl_2Cp^*]_2$ (43 mg, 0.07 mmol) in 10 mL of dichloromethane was added NaOAc (11.4 mg, 0.14 mmol) and **5** (50 mg, 0.12 mmol). The mixture was stirred at 80 ^oC for 18 hours. The solvent was removed under reduced pressure. The crude was purified by flash SiO_2 chromatography (Hexane:AcOEt, 1:1) to yield **19b** (orange solid) (38 mg, 78%) as a 95:5 mixture of isomers ^{1}H NMR ($CDCl_3$, 300 MHz, 298K): ◘ 7.97-7.91 (m, 2H, CH$_{arom}$), 7.65-7.59 (m, 1H, CH$_{arom}$), 7.34-7.26 (m, 1H, CH_{arom}), 7.07-7.02 (m, 1H, CH_{arom}), 6.81-6.77 (m, 1H, CH=CH), 6.13 (d, J = 3.3 Hz, 1H, C$H_{anomeric}$), 5.52-5.43 (m, 1H, CH), 5.30-5.26 (m, 1H, CH), 4.50-4.45 (m, 1H, CH), 4.43-4.37 (m, 2H, CH_2), 2.16 (s, 6H, CH_3-CO), 2.11 (s, 3H, CH_3-CO), 1.64 (s, 15H, CH_3Cp*). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 298K): ◘ 188.4 (d, J = 33 Hz, C-Rh), 177.7 (d, J = 1.3 Hz, CON), 170.6, 170.3, 169.9, 169.8, 169.7, 169.3 (all s, CH$_3C$O), 153.1, 153.0 (s, C-Ph), 143.0, 142.9 (s, C_{ipso}), 142.3, 141.2 (s, CH-CPh), 137.5, 132.9, 128.6, 128.4, 123.0 (all s, CH$_{arom}$), 99.8 (s, CH-N), 97.2 (d, J = 6 Hz, C_{cp^*}), 90.8, 90.1 (s, CH$_{anomeric}$), 80.3, 79.7 (s, CHCH$_2$), 74.2, 73.5 (s, CH-CH), 70.4, 69.4 (s, CH-CH), 62.5 (s, CH$_2$), 21.1, 21.0, 20.6 (s, CH$_3$-CO), 9.9 (s, CH$_3$Cp*). IR (film): ◘ 2923, 2854, 1749, 1683, 1456, 1230 1098, 759 cm^{-1}. ESI-HRMS *m/z*: Calcd for: $C_{31}H_{36}N_2O_8Rh$ $[M-Cl]^+$: 667.1521; Found: 667.1526.

*Complex **20a**.*

In a Schlenck tube, to a solution of $[IrCl_2Cp^*]_2$ (40 mg, 0.05 mmol) in 10 mL of dichloromethane was added NaOAc (8 mg, 0.11 mmol) and **9** (33 mg, 0.09 mmol). The mixture was stirred at 80 °C for 18 hours. The solvent was removed under reduced pressure. The crude was purified by flash SiO_2 chromatography (AcOEt) to yield **20a** (orange solid) (38 mg, 60%) as a 80:20 mixture of isomers ^{1}H NMR ($CDCl_3$, 300 MHz, 298K): □ 7.96 (d, *J* = 7.2 Hz, 1H, C*H*arom, both isomers), 7.79 (d, *J* = 7.1 Hz, 0.8H, C*H*arom, major isomer), 7.69–7.41 (m, 0.6H, C*H*arom, minor isomer), 7.29 (dd, *J* = 14.9, 1.2 Hz, 0.8H, C*H*arom, major isomer), 7.19 (d, *J* = 7.3 Hz, 0.8H, C*H*arom, major isomer), 7.02 (t, *J* = 7.5 Hz, 0.2H, C*H*arom, minor isomer), 6.99–6.92 (m, 0.8H, C*H*arom, major isomer), 6.70 (d, *J* = 7.2 Hz, 0.2H, C*H*=CH minor isomer), 6.30 (d, *J* = 7.2 Hz, 0.8H, C*H*=CH, major isomer), 6.18 (d, *J* = 3.8 Hz, 0.8H, C*H*anomeric, major isomer), 5.70 (d, *J* = 2.2 Hz, 0.2H, C*H*anomeric, minor isomer), 5.03-4.97 (m, 0.2H, C*H*, minor isomer), 4.87 (dd, *J* = 6.5, 4.0 Hz, 0.8H, C*H*, major isomer), 4.57 (dd, *J* = 6.5, 3.8 Hz, 0.8H, C*H*, major isomer), 4.36-4.34 (m, 0.2H, C*H*, minor isomer), 4.24–4.12 (m, 2H, CH_2, both isomers), 3.91–3.74 (m, 1H, C*H*, both isomers), 3.63 (bs, 0.2H, OH minor isomer), 1.70 (s, 15H, CH_3Cp*, both isomers), 1.61 (s, 3H, CH_3, both isomers), 1.32 (s, 3H, CH_3, both isomers). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 298K): □ 179.8, 179.4, (*C*-Ir), 172.3, 171.5 (O=*C*-N), 153.7, 153.5 (*C*-Ph), 145.3 (*C*H), 144.5 (*C*H), 144.1, 144.1 (C_{ipso}), 136.2, 135.9, 133.8, 133.6, 132.1, 129.6, 129.0, 122.1, 114.7 (all *C*H), 113.9 (*C*-(CH_3)$_2$), 100.1 (*C*H), 98.3 (*C*H), 92.4 (*C*H), 90.1 (*C*Cp*), 86.6 (*C*H), 86.3 (*C*H), 85.2 (*C*H), 79.9 (*C*H), 62.5 (*C*H_2), 61.7 (*C*H_2), 27.5 (*C*H_3), 25.7 (*C*H_3), 25.6 (*C*H_3), 9.8 (*C*H_3Cp*), 9.7 (*C*H_3Cp*). IR (film): □máx 3400, 3055, 2983, 2921, 1683, 1549, 1268, 1109, 757 cm^{-1}. ESI-HRMS *m/z*: Calcd for: $C_{28}H_{34}N_2O_5Ir$ $[M-Cl]^+$: 671.2093; Found: 671.2099.

*Complex **20b**.*

In a Schlenck tube, to a solution of $[RhCl_2Cp^*]_2$ (40 mg, 0.06 mmol) in 10 mL of dichloromethane was added NaOAc (12 mg, 0.14 mmol) and **9** (43 mg, 0.18 mmol). The mixture was stirred at 90 °C for 24 hours. The solvent was removed under reduced pressure. The crude was purified by flash

SiO_2 chromatography (AcOEt) to yield **20b** (42 mg, 58%) (orange solid) as a 90:10 mixture of isomers. ^{1}H NMR ($CDCl_3$, 300 MHz, 298K): ◘ 7.94 (d, *J* = 9 Hz, 0.9H, C*H*arom, major isomer), 7.92 (d, *J* = 7 Hz, 0.9H, C*H*arom, major isomer), 7.82 (d, *J* = 6 Hz, 0.1H, C*H*=CH, minor isomer), 7.70–7.63 (m, 0.1H, C*H*arom, minor isomer), 7.49 – 7.43 (m, 0.2H, C*H*arom, minor isomer), 7.37-7.32 (m, 0.9H, C*H*arom, major isomer), 7.11-7.07 (m, 1H, C*H*arom, both isomers), 6.97-6.95 (m, 0.9H, CHarom, major isomer), 6.62 (d, *J* = 6 Hz, 0.1H, C*H*=CH, minor isomer), 6.20 (d, *J* = 7 Hz, 0.9H, C*H*arom, major isomer), 6.17 (d, *J* = 3.9 Hz, 0.9H, C*H*anomeric, major isomer), 5.74 (d, *J* = 2.9 Hz, 0.1H, C*H*anomeric, minor isomer), 5.02-4.99 (m, 0.1H, C*H*, minor isomer), 4.95-4.93 (m, 0.1H, C*H*, minor isomer), 4.91-4.88 (m, 0.9H, C*H* major isomer), 4.60-4.56 (m, 0.9H, C*H,* major isomer), 4.41-4.34 (m, 1H, C*H*, major and minor isomers) , 4.24-4.18 (m, 2H, CH_2, major and minor isomers, OH major isomer), 3.86–3.78 (m, 1H, CH_2, major and minor isomers), 3.55 (brs, 0.10H, OH minor isomer), 1.64 (s, 15H, CH_3Cp*, both isomers), 1.62 (s, 2.7H, CH_3, major isomer), 1.59 (s, 0.3H, CH_3, minor isomer), 1.37 (s, 0.3H, CH_3, minor isomer), 1.33 (s, 2.7H, CH_3, major isomer). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 298K): ◘ 187.5 (d, *J* = 32.0 Hz, C-Rh), 186.5 (d, *J* = 32.6 Hz, C-Rh), 177.5, 177.1 (s, O=C-N), 153.7, 153.4 (s, *C*-Ph), 144.5 (*C*H), 143.3, 143.2 (*C*ipso), 137.0, 132.9, 132.3, 132.1, 129.0, 128.9, 122.9 (all s, *C*H), 114.7 (s, *C*-(CH_3)$_2$), 113.8, 100.6 (s, *C*H), 97.3 (d, *J* = 6.5 Hz, *C*Cp*), 97.1 (d, *J* = 6.5 Hz, *C*Cp*), 91.9 (s, *C*H), 86.3 (s, *C*H), 85.3 (s, *C*H), 79.9 (s, *C*H), 62.5 (s, *C*H_2), 61.8 (s, *C*H_2), 27.5 (s, *C*H_3), 25.7 (s, *C*H_3), 9.93 (s, *C*H_3Cp*). IR (film): ◘ 3439, 3053, 2985, 2852, 1675, 1550, 1455, 1269, 1027, 727 cm^{-1}. ESI-HRMS *m/z*: Calcd for: $C_{28}H_{34}N_2O_5Rh$ [M-Cl]$^+$: 581.1517; Found: 581.1526.

*Synthesis of dinuclear complex **21a**.*

To a solution of iridium complex **15a** (1:1 diastereomeric mixture) (45 mg, 0.065 mmol) in 5 mL of dry toluene was added $OsH_2Cl_2(P^iPr_3)_2$ (**17**) (38 mg, 0.065 mmol) and triethylamine (39.1 μL,

0.28mmol). The solution changed from orange to brown. After stirring for 30 minutes at room temperature, the solvent was evaporated under reduced pressure. Addition of pentane (2 mL) caused the precipitation of a dark red solid, which was washed with pentane (2 x 2 mL) and dried in vacuo. Complex **21a** (60 mg 77%, 7:3 diastereomeric mixture). ^{1}H NMR (CD_2Cl_2, 300 MHz, 298 K): δ 7.97-7.88 (m, 2H 1H, C*H*$_{arom,}$ both isomers, C*H2* both isomers), 7.71-7.66 (m, 0.7H, C*H*$_{arom,}$ major isomer), 7.51 (d, 0.7H, C*H*$_{arom}$ *,* J = 8 Hz, major isomer) 7.31-7.20 (m, 1H, C*H8*, both isomers), 7.08-7.00 (m, 1H, C*H*$_{arom,}$ both isomers), 6.75 (d, 0.3H, C*H*$_{arom}$ *,* J = 7 Hz, minor isomer), 6.57 (d, 0.3H, J = 7 Hz, C*H*$_{arom}$ minor isomer), 5.93 (br, 0.7H, C*H*$_{anomeric}$, major isomer), 5.83 (br, 0.3H, C*H*$_{anomeric}$, minor isomer), 4.41-4.31 (m, 0.7H, C*H* major isomer), 4.23-4.08 (m, 1.3H, C*H* both isomers), 3.95-3.86 (m, 1.7H, C*H*$_2$ major isomer and C*H* minor isomer), 3.84-3.71 (m, 1.3H, C*H* major isomer and C*H*$_2$ minor isomer), 2.37-2.22 (m, 6H, PC*H*$(CH_3)_2$), 1.68 (s, 15H, C*H*$_3$Cp*), 1.42-1.17 (m, 36 H, PCH(C*H*$_3)_2$), -15.76 (t, $^{2}J_{H\text{-}P}$ = 40, 1H, *H*-Os, minor isomer), -16.35 (t, $^{2}J_{H\text{-}P}$ = 40, 1H, *H*-Os, major isomer). ^{13}C{^{1}H} NMR (C_6D_6, 125.77 MHz, 298K): δ 169.6 (s, *C*-Ir), 166.4 (s, *C*$_{ipso}$), 154.0 (s, *C*H$_{arom}$), 151.2, 150.9 (s, *C*$_{ipso}$), 144.7 (s, *C*H$_{arom}$), 144.4 (s, *C*$_{ipso}$), 136.5, 136.4, 132.7, 132.6, 132.0 (all s, *C*H$_{arom}$), 131.4, 131.3 (s, *C*$_{ipso}$), 122.7, 122.6 (s, *C*H$_{arom}$), 97.6, 97.1 (s, both s, C*H*$_{anomeric}$), 92.6, 92.4 (s, *C*HCH$_2$), 92.0 (s, *C*Cp*), 89.2, 88.9 (s, *C*H-O), 88.6, 88.4, 88.1 (s, *C*CH$_3$), 65.9, 64.2 (s, CH*C*H$_2$), 27.4 (d, J = 30 Hz, P*C*H$(CH_3)_2$), 27.3 (d, J = 31 Hz, P*C*H$(CH_3)_2$), 19.6, 19.5, 19.4, 19.1 (s, PCH(*C*H$_3)_2$), 8.8 (s, *C*H$_3$Cp*). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.49 MHz, 298 K): δ 34.5 (s, minor isomer), 33.4 (s, major isomer). IR (Film): ν(Os-H) 2164, 1921, ν(C-O) 1600, ν(C=N) 1459 cm^{-1}.

*Synthesis of dinuclear complex **21b**.*

To a solution of rhodium complex **15b** (1:1 diastereomeric mixture) (50 mg, 0.08 mmol) in 5 mL of dry CH_2Cl_2 was added $OsH_2Cl_2(P^iPr_3)_2$ (48.5 mg, 0.08 mmol) and triethylamine (44.5 μL, 0.32mmol). The solution changed from orange to brown. After stirring for 30 minutes at room

temperature, the mixture was filtered through Celite and the solvent was evaporated under reduced pressure. Addition of pentane (2 mL) caused the selective precipitation of complex **21b** as a dark orange solid, which was washed with pentane (2 x 2 mL) and dried in vacuo (38 mg 42%, 8:2 diastereomeric mixture).^{1}H NMR (CD_2Cl_2, 300 MHz, 298K): δ 9.03-8.94 (m, 2H, C*H*2, CH_{arom} both isomers), 8.35 (s, 0.8H, C*H8*, major isomer), 8.14 (s, 0.2H, C*H8*, minor isomer), 7.87 (d, 0.8H, *J* = 7.8 Hz, CH_{arom}, major isomer), 7.36-7.30 (m, 1H, CH_{arom}, both isomers), 7.25-7.16 (m, 1.2H, CH_{arom}, both isomers), 5.00-5.90 (m, 0.8H, C$H_{anomeric}$, major isomer), 5.79-5.72 (m, 0.2H, C$H_{anomeric}$, minor isomer), 4.71-4.56 (m, 0.8H, C*H*, major isomer), 4.54-4.48 (m, 0.2H, C*H*, minor isomer), 4.34-4.11 (m, 2H, C*H* both isomers), 3.95-3.64 (m, 2H, CH_2OH, both isomers), 2.36-2.23 (m, 6H, PC*H*$(CH_3)_2$, both isomers), 1.64 (s, 15H, CH_3Cp*), 1.30-1.23 (m, 36H, PCH(CH_3)$_2$, both isomers), -15.75 (t, *J* = 38 Hz, 1.6H, *H*-Os, mayor isomer), -17.87 (t, *J* = 37 Hz, 0.4H, *H*-Os, minor isomer). ^{13}C{^{1}H} NMR (APT, CD_2Cl_2, 75 MHz, 298K): δ 184.0 (d, *J* = 22.0 Hz, C-Rh), 161.6 (s, C_{ipso}), 149.4 (s, C_{ipso}), 143.7 (s, C_{ipso}), 136.8, 136.7, 131.8, 131.7, 130.8, (all s, *C*H$_{arom}$), 125.2 (s, C_{ipso}), 123.2 (s, *C*H$_{arom}$), 96.9 (*C*Cp*), 94.4 (*C*Cp*), 91.7, 91.4, 88.0 (all s, *C*H), 87.5, 75.4, 74.3 (all s, *C*H), 72.2, 72.0 (s, *C*H), 63.3 (s, *C*H$_2$), 62.9 (s, *C*H$_2$), 28.6 (d, *J* = 32 Hz, P*C*H$(CH_3)_2$ major isomer), 27.8 (d, *J* = 33 Hz, P*C*H$(CH_3)_2$, minor isomer), 19.4 (s, PCH(*C*H$_3$)$_2$), 9.6 (s, *C*H$_3$Cp*). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.49 MHz, 298 K): δ 34.0 (s, minor isomer), 31.3 (s, major isomer).

ESI-HRMS *m*/*z*: Calcd for: $C_{44}H_{72}N_4O_4P_2OsRh$ $[M-Cl]^+$ 1077.3689; Found: 1077.3630.

*Synthesis of dinuclear complex **22a**.*

To a solution of iridium complex **16a** (7:3 diastereomeric mixture) (70.8 mg, 0.106 mmol) in 8 mL of dry toluene was added $OsH_2Cl_2(P^iPr_3)_2$ (**17**) (62 mg, 0.106 mmol) and triethylamine (60 μL, 0.42 mmol). The resulting mixture was stirred at room temperature for 1 h, and after this time it was filtered through Celite and the solvent was evaporated under reduced pressure to dryness. Addition

of pentane (2 mL) caused the precipitation of a brown reddish solid, which was washed with pentane (2 x 2 mL) and dried in vacuo. Compound **22a** was obtained as a 8:2 diastereomeric mixture (80 mg, 86%). ^{1}H NMR (CD_2Cl_2, 300 MHz, 298 K): δ 7.93-7.91 (m, 1.6H, 2CH_{arom} major isomer), 7.72-7.66 (m, 0.4H, 2CH_{arom} minor isomer), 7.54 (d, J = 8.1 Hz, 1H, CH_{arom} both isomers), 7.27-7.22 (m, 1H, CH_{arom} both isomers), 7.04-699 (m, 1H, CH_{arom} both isomers), 6.75 (d, J = 7.2 Hz, 0.2H, CH=CH minor isomer), 6.59 (d, J = 7.2 Hz, 0.8H, CH=CH major isomer), 5.93 (d, J = 2 Hz, 0.8H, C$H_{anomeric}$ major isomer), 5.83 (d, J = 2 Hz, 0.2H, C$H_{anomeric}$ minor isomer), 4.40-4.33 (m, 0.2H, CH minor isomer), 4.20-4.12 (m, 1H, CH both isomers), 3.90-3.70 (m, 3H, CH_2 both isomers), 2.90 (br s, OH), 2.30 (m, 6H, PCH(CH_3)$_2$ both isomers), 1.68 (s, 15H, CH_3Cp*, both isomers), 1.35-1.28 (m, 36H, PCH(CH_3)$_2$ both isomers), -17.71 (t, 0.2H, $^{2}J_{H\text{-}P}$ = 40.5 Hz, Os-H minor isomer), -18.30 (t, 0.8H, $^{2}J_{H\text{-}P}$ = 40.5 Hz, Os-H, major isomer). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.49 MHz, 298 K): δ 34.5 (s, minor isomer), 33.4 (s, major isomer). ESI-HRMS m/z: Calcd for: $C_{43}H_{72}IrN_2O_5OsP_2$ $[M\text{-}Cl]^+$ 1143.4160; found: 1143.4163.

ASSOCIATED CONTENT

Supporting Information.

Full experimental details for the preparation of compounds **5**, **9** and **18**, spectroscopic data for the compounds reported as well as crystallographic data for this paper.

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Notes

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15. (2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl)-4-phenylpyrimidine **5** was prepared by reaction of (2,3,5-tri-*O*-acetyl)uridine with $SOCl_2$ in DMF and subsequent Stille coupling ($PhSnBu_3$, 5% $Pd(PPh_3)_4$, sealed tube at 100 ˚C for 16 hours) (56% isolated yield, two steps). Deacetylation of **5** with NaOMe/MeOH affords **18** (73% yield). Isopropylidene derivative **9** was obtained by reaction of **18** with dimethoxypropane and *p*-TsOH in 62% yield. See the supporting information for details.

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