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Osmium NHC Complexes from Alcohol-Functionalized Imidazoles and Imidazolium Salts†

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Supporting Information

ABSTRACT: The hexahydride complex $OsH_6(P^iPr_3)_2$ (**1**) reacts with 1-mesitylimidazole, 1-methylimidazole, 1-(2-hydroxy-2-phenylethyl)imidazole, and 1-(2-hydroxypropyl)imidazole to give the N-bound imidazole compounds $OsH_4(RIm)(P^iPr_3)_2$ (R = Mes (**2**), Me (**3**), $CH_2CH(OH)Ph$ (**4**), $CH_2CH(OH)CH_3$ (**5**)) and H_2. In toluene under reflux the alcohol derivatives **4** and **5** evolve into the C-bound imidazole complexes $OsH_3\{CNHCHCHNCH{=}C(R)O\}(P^iPr_3)_2$ (R = Ph (**6**), CH_3 (**7**)), bearing an NH wingtip. These NHC-enolate species result from the N-bound to C-bound transformation of the heterocycle and the deprotonation−dehydrogenation of the alcohol substituent. The addition of HBF_4 to **6** and **7** affords the NHC-keto derivatives $[OsH_3\{CNHCHCHNCH_2C(R){=}O\}(P^iPr_3)_2]BF_4$ (R = Ph (**8**), CH_3 (**9**)). Treatment of **1** with 3-benzyl-1-(2-hydroxy-2-phenylethyl)imidazolium tetrafluoroborate and 3-benzyl-1-(2-hydroxypropyl)imidazolium tetraphenylborate leads to the NHC-keto complexes $[OsH_3\{CN(CH_2Ph)CHCHNCH_2C(R){=}O\}(P^iPr_3)_2]A$ (A = BF_4, R = Ph (**10**); A = BPh_4, CH_3 (**11**)), as a consequence of the direct metalation of the heterocycle and the dehydrogenation of the alcohol substituent. The deprotonation of **10** and **11** with K^tBuO gives the NHC-enolate derivatives $OsH_3\{CN(CH_2Ph)CHCHNCH{=}C(R)O\}(P^iPr_3)_2$ (R = Ph (**12**), CH_3 (**13**)). The X-ray diffraction structures of **2**, **6**, and **10** are also reported.

INTRODUCTION

N-heterocyclic carbenes (NHCs) are cyclic "Fischer-type" ligands bearing at least one α-amino substituent.[1] During the past few years, their chemistry has experienced explosive development, due to the design of diverse homogeneous catalytic systems comprising such carbene ligands[2] and use of NHC complexes as antimicrobial and cytotoxic agents,[3] as photoactive sites in luminescent materials for self-assembly into liquid crystalline materials and metallosupramolecular structures, and as synthons for molecular switches and conducting polymeric materials.[4]

The vast majority of reported NHC ligands are substituted at nitrogen(s) by alkyl or aryl groups. Deprotonation of imidazolium salts and transmetalation from silver are the most used synthetic pathways for the preparation of complexes containing these ligands.[5] However, the cleanest synthetic strategy is undoubtedly direct metalation. This method requires the presence at the starting complex of strong Brønsted bases, which afford labile Brønsted acid ligands as a result of the deprotonation of the imidazolium salt. Unfortunately, the basic precursors are limited to $[M(\mu\text{-OMe})(\text{diolefin})]_2$ (M = Rh, Ir)[6] and $M(OAc)_2$ (M = Ni,[7] Pd,[8] Pt[9]). Recent reports have shown that these compounds can undergo transformations via a range of NHC reactions,[10] including migratory insertion,[11] N-substituent cleavage,[12] ring expansion involving heterocyclic N−C bond cleavage,[13] and C−H[14] and C−C[15] bond activation of the N-alkyl or N-aryl substituents.

Imidazolium salts with carbonyl,[16] pyridyl,[16a,17] pyrazolyl,[18] amine,[19] and phosphine[20] substituents are also known. They can be deprotonated and are thus suitable for the preparation of metal complexes. Alcohol-functionalized imidazolium salts are readily accessible by the nucleophilic opening of epoxides.[21] The alcohol function appears to be more acidic than the heterocycle. A single deprotonation leads to a zwitterionic alcoholate

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imidazolium derivative. However, the reaction with 2 equiv of base yields the alkali-metal carbene adducts, which have been shown to be carbene transfer agents for the preparation of transition-metal complexes with these functionalized NHC ligands.[22] Direct metalation has been not explored.

There are also some C-bound imidazole derivatives bearing an NH wingtip.[23] The limited number of examples of this type is chiefly because tautomerization to the N-bound imidazole,[12b,23e,24] a 1,3-ligand to metal hydrogen shift,[25] or deprotonation to form an anionic ligand[23g,h] may occur. Stable C-bound imidazole complexes have been prepared by tautomerization of N-bound imidazole precursors,[23a,c,d,f,h−j,l] coupling of isocyanides with propargylamines,[23b,g,k] and deprotection of N-acyl-substituted NHC complexes.[23e,m] The imidazole tautomer is more stable than the carbene form for free ligands.[26] However, theoretical calculations suggest that, once coordinated to a metal, either the N- or C-bound form can be thermodynamically favored, depending on the environment of the metal.[27] Some cases of NH-bearing carbenes derived from pyridines have been also reported.[28]

The saturated d^2 hexahydride complex $OsH_6(P^iPr_3)_2$ activates C−H bonds of different organic substrates[29] and, by protonation with weak Brønsted acids, releases molecular hydrogen, affording d^4 species, which contain the corresponding conjugated Brønsted base as a ligand.[30] In agreement with this, it also reacts with N-alkyl and N-aryl imidazolium salts to give osmium derivatives with normal and abnormal NHC ligands.[17f,31] In the search for direct metalation for alcohol-functionalized imidazole and imidazolium salts, we have now studied the reactivity of the hexahydride complex toward these types of NHC precursors.

This paper reports (i) the formation of d^4 osmium tetrahydride compounds containing N-bound imidazole ligands, (ii) their transformation to C-bound derivatives bearing an NH wingtip, and (iii) O-functionalized, N-disubstituted osmium NHC complexes formed by direct metalation of alcohol-functionalized imidazolium salts.

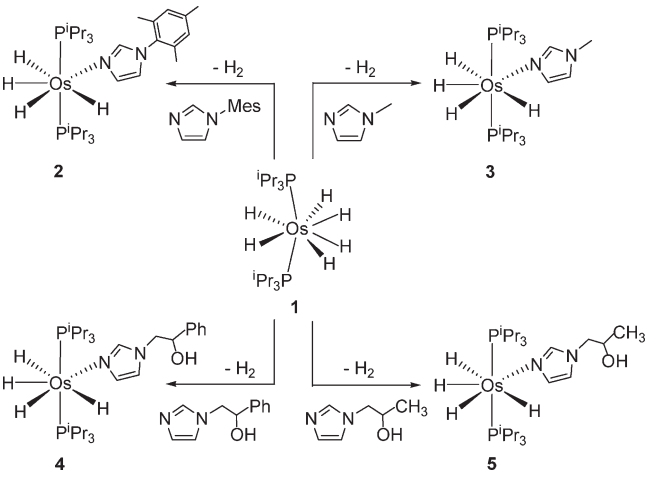
RESULTS AND DISCUSSION

1. N-Bound Imidazole Complexes. Treatment between 5 and 17 h of tetrahydrofuran solutions of the hexahydride $OsH_6(P^iPr_3)_2$ (**1**) with 1.2 equiv of 1-mesitylimidazole, 1-methylimidazole, 1-(2-hydroxy-2-phenylethyl)imidazole, and 1-(2-hydroxypropyl)imidazole under reflux leads to the tetrahydride derivatives $OsH_4(Rim)(P^iPr_3)_2$ (R = Mes (**2**), Me (**3**), $CH_2CH(OH)Ph$ (**4**), $CH_2CH(OH)CH_3$ (**5**)), containing a N-bound imidazole ligand. These compounds were isolated as white solids in 26−89% yields, according to Scheme 1.

Complex **2** has been characterized by X-ray diffraction analysis. Its structure (Figure 1) proves the N-bound coordination of the heterocycle in these species. The geometry around the osmium atom can be rationalized as a distorted pentagonal bipyramid with axial phosphines (P(1)−Os−P(2) = 174.55(5)°). The metal coordination sphere is completed by the hydride ligands (H−H > 1.61(4) Å), and the imidazole group, which lies between H(1A) and H(1D). The Os−N(1) bond length of 2.159(4) Å compares well with the osmium−pyridine separation in the related compound $OsH_4(py)(P^iPr_3)_2$ (2.162(6) Å).[29i]

The $^{31}P\{^1H\}$ and ^1H NMR spectra of **2**−**5** in toluene-d_8 are consistent with the structure shown in Figure 1. In agreement with equivalent phosphines, the $^{31}P\{^1H\}$ spectra contain a singlet at about 44 ppm, whereas, according to the presence of four inequivalent hydride ligands, the ^1H NMR spectra at 193 K show four hydride resonances between −4 and −16 ppm.

Scheme 1



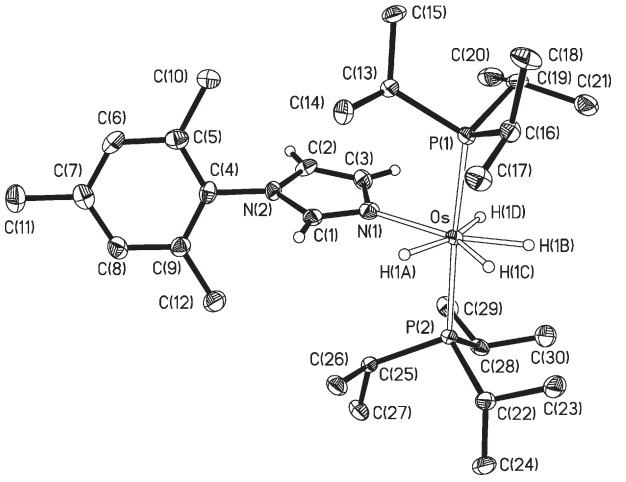


Figure 1. Molecular diagram of complex **2**. Selected bond lengths (Å) and angles (deg): Os−P(1) = 2.3223(13), Os−P(2) = 2.3185(13), Os−N(1) = 2.159(4), H(1A)···H(1C) = 1.61(4), H(1C)···H(1B) = 1.81(5), H(1B)···H(1D) = 1.68(5); P(1)−Os−P(2) = 174.55(5), P(1)−Os−N(1) = 90.99(10), P(2)−Os−N(1) = 94.11(10).

2. C-Bound Imidazole Complexes: Influence of the Alcohol Function on the Coordination Mode of the Heterocycle. The substituent of the imidazole group has a marked influence on the behavior of the heterocycle of these systems. In contrast to **2** and **3**, which remain unaltered after 17 h in toluene under reflux, the alcohol derivatives **4** and **5** evolve into the C-bound imidazole complexes $OsH_3\{CNHCHCHNCH{=}C(R)O\}(P^iPr_3)_2$ (R = Ph (**6**), CH_3 (**7**)) in quantitative yield, according to eq 1. In addition to the N-bound to C-bound transformation of the heterocycle, the formation of these compounds implies the release of two hydrogen molecules. One of them results from the protonation of the OsH_4 units of **4** and **5** with the alcohol function of the ligands, whereas the other is generated by dehydrogenation of the aliphatic chain. Complexes **6** and **7** are

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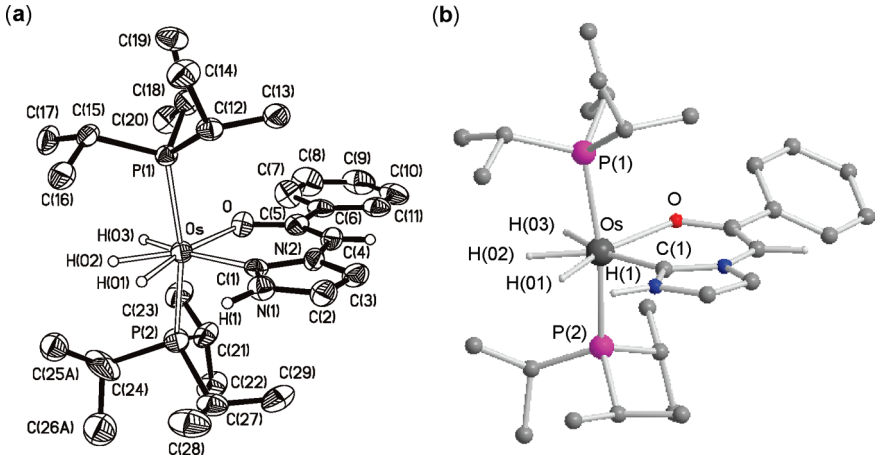
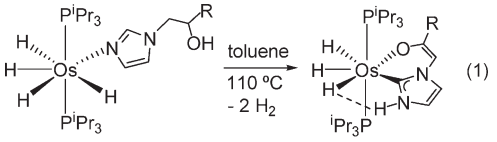


Figure 2. (a) Molecular diagram of complex **6**. Selected bond lengths (Å) and angles (deg): Os−P(1) = 2.3223(16), Os−P(2) = 2.3474(17), Os−O = 2.172(4), Os−C(1) = 2.102(6), N(2)−C(4) = 1.422(7), C(4)−C(5) = 1.334(8), C(5)−O = 1.306(6), H(01)−H(02) = 1.54(1), H(02)−H(03) = 1.57(5), H(01)−H(1) = 2.53; P(1)−Os−P(2) = 166.31(6), O−Os−C(1) = 85.21(19). (b) Optimized structure (B3PW91) of complex **6**. Selected bond lengths (Å) and angles (deg): H(01)···H(02) = 1.573, H(02)···H(03) = 1.689, H(01)···H(1) = 2.241; H(01)−Os−H(02) = 58.6, H(02)−Os−H(03) = 62.4.

isolated as green solids in moderate yields (30−60%) due to their high solubility in the usual precipitating agents.



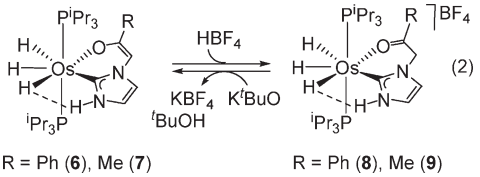
R = Ph (**4**), Me (**5**) R = Ph (**6**), Me (**7**)

Figure 2a shows a view of the structure of **6**. The coordination geometry around the osmium atom can be rationalized as a distorted pentagonal bipyramid with the phosphorus atoms of the phosphine ligands occupying axial positions (P(1)−Os−P(2) = 166.31(6)°). The osmium sphere is completed by the hydride ligands and the chelate group, which has a bite angle C(1)−Os−O of 85.21(19)°. The B3PW91 optimized structure (Figure 2b) confirms the trihydride character of the OsH_3 unit. The H(01)−H(02) and H(02)−H(03) separations are 1.573 and 1.689 Å, whereas the H(01)−Os−H(02) and H(02)−Os−H(03) angles are 58.6 and 62.4°. Furthermore, the calculations reveal that the distance between the NH hydrogen H(1) and the hydride H(01) is short (2.241 Å) and lies within the range reported for the H−H separations in rings of the type LH---HM with an electrostatic hydrogen−hydrogen interaction.[28d,32] The osmabicycle is planar (maximum deviation 0.0376(33) Å for O). The Os−C(1) bond length of 2.102(6) Å agrees well with those previously reported for Os−NHC compounds with normal coordination of the NHC unit.[15c,17f,31,33] The Os−O bond length of 2.172(4) Å compares well with those found in lower π-electron osmacyclic oxygen-containing compounds,[28i] whereas the C(4)−C(5) and C(5)−O distances of 1.334(8) and 1.306(6) Å, respectively, lie between those expected for single and double bonds. This indicates electron delocalization between C(4) and O, which appears to be the driving force for the dehydrogenation of the aliphatic chain of the substituent of the heterocycles.

Aliphatic dehydrogenation is a strongly endothermic process. The equilibrium can be shifted to the right, however, by adding a hydrogen acceptor. The presence of a transition-metal catalyst facilitates the hydrogen transfer.[34] Recently, we have shown that the aromatization by dehydrogenation is a method which can be applied to the synthesis of aromatic heterometallacyclic compounds. In this case, a hydrogen acceptor is not necessary, even under mild conditions.[35] The aliphatic dehydrogenation in **4** and **5** is consistent with the latter.

The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of **6** and **7** agree well with the structures shown in Figure 2. In the ^{1}H NMR spectra the most noticeable feature is the presence of the NH resonances, which appear at 7.68 (**6**) and 7.64 ppm (**7**) . The CH protons of the six-membered heterometallaring display singlets at 6.33 (**6**) and 5.47 ppm (**7**). In the high-field region, the spectrum of **6** at 139 K in $CDCl_2F$ contains two broad resonances at −5.0 and −14.5 ppm, whereas that of **7** shows three resonances at −5.51, −13.41, and −16.87 ppm, in agreement with the presence of three inequivalent hydride ligands in these compounds. In the ^{13}C{^{1}H} NMR spectra the OsC resonances are observed at 169.2 (**6**) and 167.4 ppm (**7**), as triplets with C−P coupling constants of about 8 Hz, whereas the OC and CH carbon atoms of the six-membered ring display singlets at 151.5 and 97.2 ppm (**6**) and 152.3 and 95.5 ppm (**7**). As expected for equivalent phosphine ligands, the ^{31}P{^{1}H} NMR spectra contain singlets at 31.5 (**6**) and 31.4 ppm (**7**).

Complexes **6** and **7** are Brønsted bases. Thus, the addition at room temperature of 1.0 equiv of HBF_4 to diethyl ether solutions of these compounds produces the precipitation of the C-bound imidazole-keto derivatives $[OsH_3\{CNHCHCHNCH_2C(R)=O\}(P^iPr_3)_2]BF_4$ (R = Ph (**8**), CH_3 (**9**)) as a result of the addition of the proton of the acid to the β-carbon atom of the enolate units of **6** and **7** (eq 2). The reaction is reversible; treatment of **8** and **9** with K^{t}BuO in tetrahydrofuran regenerates **6** and **7**.



R = Ph (**6**), Me (**7**) R = Ph (**8**), Me (**9**)

Complexes **8** and **9** are isolated as brown solids in 56 and 96% yields, respectively. The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR

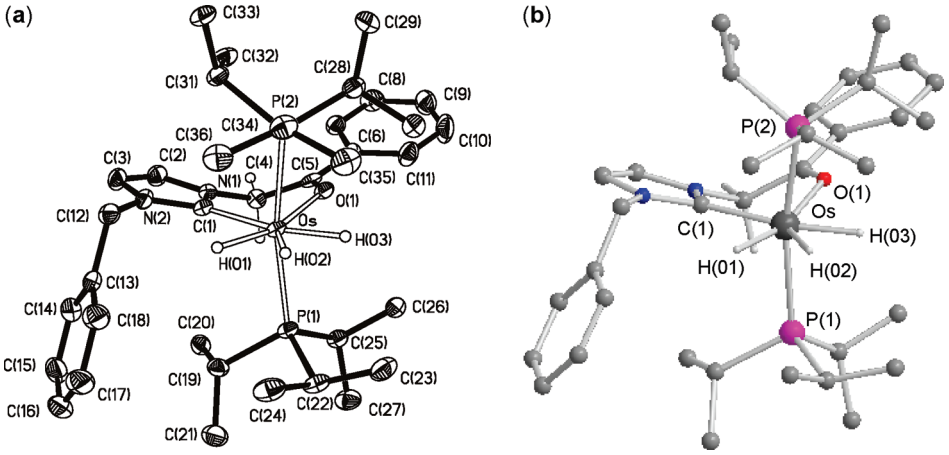


Figure 3. (a) Molecular diagram of the cation of **10**. Selected bond lengths (Å) and angles (deg): Os−P(1) = 2.3438(11), Os−P(2) = 2.3631(11), Os−O(1) = 2.157(2), Os−C(1) = 2.107(4), H(01)···H(02) = 1.58(3), H(02)···H(03) = 1.67(3); P(1)−Os−P(2) = 164.85(3), O−Os−C(1) = 82.65(11). (b) Optimized structure (B3PW91) of the cation of complex **10**. Selected bond lengths (Å) and angles (deg): H(01)···H(02) = 1.605, H(02)···H(03) = 1.611; H(01)−Os−H(02) = 60.2, H(02)−Os−H(03) = 59.5.

spectra of these compounds strongly support the structure proposed in eq 2. In agreement with the presence of three inequivalent hydride ligands, the ^{1}H NMR spectra at 189 K in CD_2Cl_2 contain three high-field resonances between −7 and −17 ppm. The NH resonances are observed at 9.50 (**8**) and 9.61 ppm (**9**), whereas the signals corresponding to the CH_2 groups of the six-membered rings appear at 6.15 (**8**) and 5.62 ppm (**9**). The $^{13}C\{^1H\}$ spectra reveal the presence of the keto function in the compounds, showing singlets at 192.0 (**8**) and 206.0 ppm (**9**). The OsC NHC resonances are observed at 176.1 (**8**) and 176.3 ppm (**9**), as triplets with C−P coupling constants of about 7 Hz. According to the presence of equivalent phosphines, the $^{31}P\{^1H\}$ NMR spectra show singlets at about 29 ppm.

3. Direct Metalation of Alcohol-Functionalized Imidazolium Salts. Treatment of tetrahydrofuran solutions of **1** with 1.2 equiv of 3-benzyl-1-(2-hydroxy-2-phenylethyl)imidazolium tetrafluoroborate and 3-benzyl-1-(2-hydroxypropyl)imidazolium tetraphenylborate for 29 h under reflux leads to the NHC-keto derivatives

$$[OsH_3\{CN(CH_2Ph)CHCHNCH_2C(R)=O\}(P^iPr_3)_2]A \ (A = BF_4,$$

R = Ph (**10**); A = BPh_4, CH_3 (**11**)) as a result of the direct metalation of the imidazolium moieties and the dehydrogenation of the alcohol functions. Complexes **10** and **11** are isolated as garnet and yellow solids in 61% and 90% yields, respectively, according to eq 3.

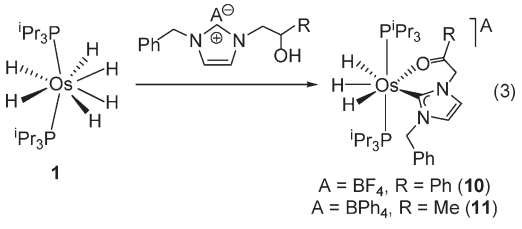


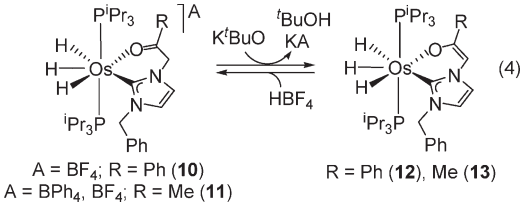
Figure 3a shows a view of the cation of **10**. The structure proves the metalation of the imidazolylidene group and the dehydrogenation of the alcohol function. The geometry around the osmium atom can be rationalized as a distorted pentagonal bipyramid with the phosphine ligands occupying axial positions (P(1)−Os−P(2) = 164.85(3)°). The metal coordination sphere is completed by the O and C(1) atoms of the chelate group and the H(01), H(02), and H(03) hydrogen atoms. The B3PW91 optimized structure (Figure 3b) supports the trihydride character of the OsH_3 unit. The H(01)−H(02) and H(02)−H(03) separations are 1.605 and 1.611 Å, respectively, whereas the H(01)−Os−H(02) and H(02)−Os−H(03) angles are 60.2 and 59.5°, respectively. The chelate group has an O−Os−C(1) bite angle of 82.65(11)° and forms a six-membered ring with the metal center with a boat conformation. The Os−C(1) and Os−O(1) bond lengths of 2.107(4) and 2.157(2) Å, respectively, are statistically identical with those of **6**.

The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **10** and **11** are consistent with the structures shown in Figure 3. As expected for three inequivalent hydride ligands, the ^{1}H NMR spectra in $CDCl_2F$ at 181 K contain three high-field signals between −6 and −18 ppm. In the $^{13}C\{^1H\}$ NMR spectra, the OsC NHC resonances are observed at 183.5 (**10**) and 181.9 ppm (**11**) as triplets with C−P coupling constants of about 6 Hz. In spite of the presence of inequivalent phosphine ligands in these compounds, the $^{31}P\{^1H\}$ NMR spectra show singlets at about 30 ppm, even at 143 K in $CDCl_2F$.

Complexes **10** and **11** are as easily deprotonated as **8** and **9**. Treatment of tetrahydrofuran solutions of **10** and **11** with 2.0 equiv of K^{t}BuO for 40 min at room temperature produces the extraction of one of the hydrogen atoms of the CH_2 groups of the six-membered rings, to afford the NHC-enolate

derivatives $OsH_3\{CN(CH_2Ph)CHCHNCH{=}C(R)O\}(P^iPr_3)_2$

(R = Ph (**12**), R = CH_3 (**13**)). The reaction is reversible; the addition of 1.0 equiv of HBF_4 to the diethyl ether solutions of **12** and **13** produces the precipitation of **10** and **11** as their BF_4 salts (eq 4).



Complexes **12** and **13** are isolated as yellow solids in moderate yields (40−50%). The ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra

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of these compounds agree well with those of **6** and **7**. At low temperature, 138 K for **12** and 172 K for **13**, the ^{1}H NMR spectra in $CDCl_2F$ shows three hydride resonances between −5 and −16 ppm. In this context we should mention the presence of an AB spin system, in the $^1H\{^{31}P\}$ NMR spectrum of **13** at 172 K, centered at −15 ppm and defined by J_{A-B} = 288 Hz and $\Delta\nu$ = 684, which can be explained in terms of quantum exchange coupling[36] between two of the hydride ligands. In the $^{13}C\{^1H\}$ NMR spectra the OC resonances appear at 151.4 (**12**) and 152.4 ppm (**13**), shifted by 45.3 and 54.3 ppm, respectively, toward higher field with regard to those of **10** (196.7 ppm) and **11** (206.7 ppm). The OsC NHC resonances are observed at 175.1 (**12**) and 173.8 ppm (**13**), as triplets with a C−P coupling constant of 7.5 Hz. The $^{31}P\{^1H\}$ NMR spectra between 290 and 193 K show singlets at about 32 ppm.

■ CONCLUDING REMARKS

This study has revealed that the hexahydride complex $OsH_6(P^iPr_3)_2$ promotes the N-bound to C-bound transformation and the alcohol deprotonation−dehydrogenation of alcohol-functionalized imidazoles and the imidazolium metalation and alcohol dehydrogenation of alcohol-functionalized imidazolium salts. In the first case NHC-enolate derivatives bearing an NH- wingtip are obtained, whereas in the second case NHC-keto compounds are formed. The conversion to the respective NHC-keto and NHC-enolate is easily achieved by protonation and deprotonation reactions.

The deprotonation−dehydrogenation process of the alcohol substituent is determinant for the N-bound to C-bound transformation of the imidazole moiety of these ligands. In contrast to 1-(2-hydroxy-2-phenylethyl)imidazole and 1-(2-hydroxypropyl)-imidazole, 1-mesitylimidazole and 1-methylimidazole do not undergo tautomerization. As in other related tautomerization processes,[28a,d,e,i,j,q] an intramolecular LM- - -HM hydrogen bond between a hydride ligand and the NH hydrogen atom of the C-bound heterocycle seems to contribute to the stabilization of the formed species.

In conclusion, polyhydride complexes promote the N-bound to C-bound transformation of alcohol-functionalized imidazole and the metalation of alcohol-functionalized imidazolium salts. The alcohol function is relevant for both processes. In addition to stabilizing by chelation the resulting species, it undergoes dehydrogenation.

■ EXPERIMENTAL SECTION

General Information. All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents (except acetonitrile and acetone, which were dried and distilled under argon) were obtained oxygen- and water-free from an MBraun solvent purification apparatus. ^{1}H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker ARX 300 MHz, Bruker Avance 300 MHz, and Bruker Avance 400 MHz instruments. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, $^{13}C\{^1H\}$) or to external 85% H_3PO_4 ($^{31}P\{^1H\}$). Coupling constants J and N are given in hertz. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 spectrometer as neat solids or oils. C, H, and N analyses were carried out with 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). 1-Mesitylimidazole,[37] 1-(2-hydroxy-2-phenylethyl) imidazole,[21] $OsH_6(P^iPr_3)_2$ (**1**),[38] and $CDCl_2F$[39] were prepared by published methods.

Preparation of 1-(2-Hydroxypropyl)imidazole. This molecule was synthesized analogously as described in the literature[21] starting from imidazole and propylene oxide. It was isolated as a yellow oil in 85% yield. HRMS: m/z calcd for $C_6H_{10}N_2O$ 126.0788, found 127.0869. IR (cm^{-1}): ν(O−H) 3112 (m). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 7.30 (s, 1H, NC*H*N), 6.90 (s, 1H, C*H* im), 6.82 (s, 1H, C*H* im), 5.20 (s, 1H, OH), 3.97 (m, 1H, C*H*OH), 3.86 (dd, J_{H-H} = 13.9, J_{H-H} = 3.5, 1H, CH_2CHOH), 3.75 (dd, J_{H-H} = 13.9, J_{H-H} = 3.5, 1H, CH_2CHOH), 1.14 (d, J_{H-H} = 6.3, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, 293 K): δ 138.0, 128.8, 120.4 (all s, *C*H im), 66.9 (s, *C*H(OH)), 55.2 (s, CH_2CH(OH)), 21.1 (s, CH_3).

Preparation of 3-Benzyl-1-(2-hydroxy-2-phenylethyl) imidazolium Chloride. Benzyl chloride (633 μL, 5.5 mmol) was added at room temperature to a solution of 1-(2-hydroxy-2-phenylethyl)imidazole (941 mg, 5.0 mmol) in acetonitrile (15 mL) placed in a round-bottom flask, and the resulting mixture was stirred at 80 °C for 16 h. The resulting solution was evaporated to dryness, and acetone was added to the residue to afford a white solid, which was washed with further portions of acetone and dried in vacuo. Yield: 944 mg (60%). Anal. Calcd for $C_{18}H_{19}ClN_2O$: C, 68.76; H, 6.10; N, 8.91. Found: C, 69.11; H, 6.48; N, 9.05. HRMS: m/z calcd for $C_{18}H_{19}N_2O$ 279.1492, found 279.1486. IR (cm^{-1}): ν(O−H) 3213 (m). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 10.00 (s, 1H, NC*H*N), 7.45−7.25 (m, 10H, Ph), 7.22 (s, 1H, C*H* im), 6.99 (s, 1H, C*H* im), 6.34 (s, 1H, OH), 5.33 (s, 2H, CH_2Ph), 5.26 (dd, J_{H-H} = 7.6, J_{H-H} = 3.2, 1H, C*H*(OH)), 4.73 (dd, J_{H-H} = 14.0, J_{H-H} = 3.2, 1H, CH_2CH(OH)), 4.39 (dd, J = 14.0, J_{H-H} = 7.6, 1H, CH_2CH(OH)). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, 293 K): δ 140.0 (s, C_{ipso} Ph), 137.4 (s, NCHN), 132.7 (s, C_{ipso} Ph), 129.4, 128.7, 128.5, 127.8, 126.0 (all s, *C*H Ph), 123.5, 120.6 (both s, *C*H im), 70.9 (s, *C*H(OH)), 56.9 (s, CH_2CH(OH)), 53.3 (s, CH_2Ph).

Preparation of 3-Benzyl-1-(2-hydroxypropyl)imidazolium Chloride. Benzyl chloride (633 μL, 5.5 mmol) was added at room temperature to a solution of 1-(2-hydroxypropyl)imidazole (631 mg, 5.0 mmol) in acetonitrile (15 mL) placed in a round-bottom flask, and the resulting mixture was stirred at 80 °C for 16 h. The resulting solution was evaporated to dryness, and diethyl ether was added to the residue to afford a yellow oil, which was washed with further portions of diethyl ether and dried in vacuo. Yield: 1.00 g (72%). HRMS: m/z calcd for $C_{13}H_{17}N_2O$ 217.1335, found 217.1322. IR (cm^{-1}): ν(O−H) 3247 (m). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ 10.01 (s, 1H, NC*H*N), 7.60 (s, 1H, C*H* im), 7.40 (m, 5H, Ph), 7.26 (s, 1H, C*H* im), 5.63 (d, J_{H-H} = 8, −OH), 5.48 (s, 2H, CH_2Ph), 4.42 (m, 1H, CH_2CH(OH)), 4.25 (m, 1H, CH_2CH(OH)), 4.16 (m, 1H, CH(OH)), 1.23 (d, J_{H-H} = 4.0, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, 293 K): δ 137.0 (s, NCHN), 133.7 (s, C_{ipso} Ph), 129.5, 129.9, 130.0 (all s, *C*H Ph), 124.3, 121.7 (both s, *C*H im), 66.4 (s, *C*H(OH)), 57.4 (s, CH_2CH(OH)), 53.9 (s, CH_2Ph), 20.9 (s, CH_3).

Anion Exchange of 3-Benzyl-1-(2-hydroxy-2-phenylethyl) imidazolium Chloride to Give 3-benzyl-1-(2-hydroxy-2-phenylethyl)imidazolium Tetrafluoroborate. A 1:1 mixture of the imidazolium chloride salt and $AgBF_4$ was stirred in acetone in the dark for 12 h. The reaction mixture was filtered through Celite and the solvent of the filtrate removed in vacuo. The salt that formed was used without further purification.

Preparation of 3-Benzyl-1-(2-hydroxypropyl)imidazolium Tetraphenylborate. 3-Benzyl-1-(2-hydroxypropyl)imidazolium chloride (77.3 mg, 0.31 mmol) and $NaBPh_4$ (105 mg, 0.31 mmol) were dissolved in acetone (6 mL) and MeOH (2 mL), and this mixture was stirred for 2 h. The resulting solution was taken to dryness. Dichloromethane (10 mL) was added, giving a precipitate of NaCl. After filtering, the resulting solution was evaporated to dryness. The addition of diethyl ether to the residue afforded a white solid that was washed with diethyl

ether (6 × 3 mL) and dried in vacuo. Yield: 94 mg (57%). Anal. Calcd for $C_{37}H_{37}BN_2O$: C, 82.83; H, 6.95; N, 5.22. Found: C, 83.15; H, 7.10; N, 5.37. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.42−6.83 (m, 26H, C*H* im, Ph and BPh_4), 6.62 (s, 1H, C*H* im), 5.95 (s, 1H, C*H* im), 4.62 (s, 2H, CH_2Ph), 4.59 (s, 1H, OH), 3.61 (m, 1H, C*H*(OH)), 3.30 (m, 2H, CH_2CH(OH)), 1.08 (d, J_{H-H} = 6.3, 3H, $-CH_3$). ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, 293K): δ 164.4 (q, J_{B-C} = 36.9, C_{ipso} BPh_4), 136.1 (s, *C*H BPh_4), 135.7 (s, NCHN), 132.3 (s, C_{ipso} Ph), 129.9, 129.8, 128.6 (all s, *C*H Ph), 126.4 (q, J_{B-C} = 2, *C*H BPh_4), 123.5 (s, *C*H im), 122.4 (s, *C*H BPh_4), 121.2 (s, *C*H im), 66.3 (s, −*C*H(OH)), 56.1 (s, $-CH_2$CH(OH)), 53.6 (s, CH_2Ph), 20.9 (s, $-CH_3$).

Preparation of $OsH_4(MesIm)(P^iPr_3)_2$ (2). A solution of **1** (150 mg, 0.291 mmol) in THF (20 mL) was treated with the stoichiometric amount of 1-mesitylimidazole (54.1 mg, 0.291 mmol). The resulting solution was stirred at 90 °C for 6 h. After it was cooled to room temperature, the solution was filtered through Celite and the solvent removed. Addition of methanol to the residue at 223 K afforded a white solid that was washed with methanol and dried in vacuo. Yield: 182 mg (89%). Anal. Calcd for $C_{30}H_{60}N_2OsP_2$: C, 51.40; H, 8.63; N, 4.00. Found: C, 51.57; H, 8.33; N, 4.20. IR (cm^{-1}): ν(Os−H) 2102 (w); ν(C═N) 1785 (s). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.72 (s, 1H, NC*H*N), 7.40 (s, 1H, C*H* im), 6.95 (s, 2H, C*H* mes), 6.49 (s, 1H, C*H* im), 2.30 (s, 3H, *p*-CH_3), 1.91 (s, 6H, *o*-CH_3), 1.68 (m, 6H, PC*H*-$(CH_3)_2$), 1.14 (dvt, J_{H-H} = 6, *N* = 12, 36H, PCH(CH_3)$_2$), −10.11 (br, 4H, OsH). ^{1}H{^{31}P} NMR (300 MHz, toluene-d_8, 183 K, high-field region): δ −5.4 (br, 1H, Os−H), −5.6 (br, 1H, Os−H), −15.1 (br, 1H, Os−H), −15.2 (br, 1H, Os−H). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 293 K): δ 44.6 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus apt): δ 145.5 (s, NCHN), 141.3 (s, *C*H im), 139.5 (s, mes), 135.5 (s, mes), 132.8 (s, mes), 129.3 (s, *C*H mes), 120.5 (s, *C*H im), 27.1 (vt, *N* = 22.2, PCH(CH_3)$_2$), 21.1 (s, *p*-CH_3 mes), 20.3 (s, PCH(CH_3)$_2$), 17.2 (s, *o*-CH_3 mes).

Preparation of $OsH_4(MeIm)(P^iPr_3)_2$ (3). A solution of **1** (100 mg, 0.19 mmol) in THF (15 mL) was treated with 1.2 equiv of 1-methylimidazole (18.5 μL, 0.23 mmol). The resulting solution was heated under reflux for 6 h. After it was cooled to room temperature, the resulting solution was filtered through Celite and the solvent removed. Pentane was added to afford a solution that was cooled overnight to afford a white solid, which was washed with further portions of pentane and dried in vacuo. Yield: 53 mg (46%). Anal. Calcd for $C_{22}H_{52}N_2OsP_2$: C, 44.27; H, 8.78; N, 4.69. Found: C, 44.33; H, 8.53; N, 4.86. IR (cm^{-1}): ν(Os−H) 2123 (w), ν(C═N) 1769 (s). ^{1}H NMR (300 MHz, toluene-d_8, 293 K): δ 7.43 (s, 1H, NC*H*N), 7.24 (s, 1H, OsNC*H*), 5.50 (s, 1H, C*H*NCH_3), 2.18 (s, 3H, CH_3), 1.73 (m, 6H, PC*H*(CH_3)$_2$), 1.32 (dvt, J_{H-H} = 5.7, *N* = 12, 36H, PCH(CH_3)$_2$), −9.70 (br t, 4H, OsH). ^{1}H{^{31}P} NMR (300 MHz, toluene-d_8, 203 K, high-field region): δ −4.7 (br, 1H, Os−H), −4.8 (br, 1H, Os−H), −14.3 (br, 1H, Os−H), −14.4 (br, 1H, Os−H). ^{31}P{^{1}H} NMR (121.5 MHz, toluene-d_8, 298 K): δ 44.0 (s). ^{13}C{^{1}H} APT NMR plus HSQC and HMBC (75.47 MHz, toluene-d_8, 253 K): δ 145.4 (s, NCHN), 140.5 (s, OsNCH), 119.4 (s, C*H*NCH_3), 31.4 (s, CH_3) 27.1 (vt, *N* = 22.1, PCH(CH_3)$_2$), 20.2 (s, PCH(CH_3)$_2$).

Preparation of $OsH_4[PhCH(OH)CH_2Im](P^iPr_3)_2$ (4). A colorless solution of **1** (100 mg, 0.19 mmol) in THF (10 mL) was treated with 1.2 equiv of 1-(2-hydroxy-2-phenylethyl)imidazole (45.7 mg, 0.23 mmol) and the mixture heated under reflux for 17 h. The resulting solution was cooled to room temperature, filtered through Celite, and taken to dryness. Addition of methanol to the residue at 223 K afforded a white solid that was washed with methanol and dried in vacuo. Yield: 101 mg (74%). Anal. Calcd for $C_{29}H_{58}N_2OOsP_2$: C, 49.54; H, 8.32; N, 3.98. Found: C, 49.32; H, 8.45; N, 4.10. IR (cm^{-1}): ν(OsH) 2108 (w), ν(C═N) 1775 (s). ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 7.73 (s, 1H, C*H* im), 7.25 (s, 1H, C*H* im), 7.14−6.96 (m, 5H, Ph), 5.79 (s, 1H, C*H* im), 4.71 (br, 1H, −OH), 4.16 (t, J_{H-H} = 5.2, 1H, C*H*(OH)Ph), 3.19 (m, 2H, N−CH_2), 1.84 (m, 6H, PC*H*(CH_3)$_2$), 1.35 (dvt, J_{H-H} = 6.4, *N* = 12, 36H, PCH(CH_3)$_2$), −9.63 (br, 4H, Os−H). ^{1}H{^{31}P} NMR (300 MHz, toluene-d_8, 183 K, high-field region): δ −4.8 (br, 1H, Os−H), −4.9 (br, 1H, Os−H), −14.3 (br, 1H, Os−H), −14.4 (br, 1H, Os−H). ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6, 298 K): δ 44.2 (s). ^{13}C{^{1}H} APT NMR plus HSQC (100.62 MHz, C_6D_6, 298 K): δ 150.2 (s, NCHN), 141.8 (s, C_{ipso} Ph), 140.3 (s, *C*H im), 128.3, 127.0, 126.1 (all s, *C*H Ph), 119.7 (s, *C*H im), 73.0 (s, *C*HOH), 53.9 (s, CH_2), 27.4 (vt, *N* = 21.9, PCH(CH_3)$_2$), 20.7 (s, PCH(CH_3)$_2$).

Preparation of $OsH_4[CH_3CH(OH)CH_2Im](P^iPr_3)_2$ (5). A colorless solution of **1** (132 mg, 0.26 mmol) in THF (10 mL) was treated with 1.2 equiv of 1-(2-hydroxypropyl)imidazole (38.7 mg, 0.31 mmol) and heated under reflux for 5 h. The resulting solution was filtered through Celite and was taken to dryness. Addition of methanol to the residue at 223 K afforded a white solid that was washed with methanol and dried in vacuo. ^{1}H and ^{31}P{^{1}H} NMR spectra show that the reaction is quantitative, but the obtained yield is very low due to the high solubility of the complex in methanol. Yield: 43 mg (26%). Anal. Calcd for $C_{24}H_{56}N_2OOsP_2$: C, 44.97; H, 8.08; N, 4.37. Found: C, 45.13; H, 8.17; N, 4.55. IR (cm^{-1}): ν(OsH) 2105 (w), ν(C═N) 1786 (s). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.76 (s, 1H, NC*H*N), 7.37 (s, 1H, C*H* im), 6.04 (s, 1H, C*H* im), 3.63 (br, 1H, −OH), 3.33 (m, H, −C*H*(OH)CH_3), 2.95 (m, 2H, $-CH_2-$), 1.86 (m, 6H, PC*H*-$(CH_3)_2$), 1.35 (dvt, J_{H-H} = 6.4, *N* = 11.7, 36H, PCH(CH_3)$_2$), 0.64 (d, J_{H-H} = 6.2, 3H, CH_3), −9.56 (br, 4H, Os−*H*). ^{1}H{^{31}P} NMR (C_7D_8, 400 MHz, 193 K, high-field region): δ −5.1 (br, 1H, Os−H), −5.3 (br, 1H, Os−H), −14.1 (br, 1H, Os−H), −14.5 (br, 1H, Os−H). ^{31}P{^{1}H} NMR (121.49 MHz, C_6D_6, 298 K): δ 43.7 (s). ^{13}C{^{1}H} APT NMR plus HSQC (75.47 MHz, C_6D_6, 298 K): δ 146.1 (s, NCHN), 140.7 (s, *C*H im), 119.6 (s, *C*H im), 66.4 (s, *C*HOH), 53.5 (s, $-CH_2-$), 27.54 (vt, *N* = 22, PCH(CH_3)$_2$), 20.6 (s, PCH(CH_3)$_2$), 20.1 (s, $-CH_3$).

Preparation of $OsH_3\{CNHCHCHNCH{=}C(Ph)O\}(P^iPr_3)_2$ (6). A solution of **4** (100 mg, 0.14 mmol) in toluene was heated under reflux for 17 h. During this time the solution changed from colorless to dark green. After it was cooled room temperature, the resulting solution was filtered through Celite and the solvent was removed. Pentane was added at 223 K to the residue to afford a green solid, which was washed with further portions of pentane and dried in vacuo. ^{1}H and ^{31}P{^{1}H} NMR spectra show that the reaction is quantitative, but the obtained yield is very low due to the high solubility of the complex in pentane. Yield: 45 mg (33%). Anal. Calcd for $C_{29}H_{54}N_2OOsP_2$: C, 49.83; H, 7.78; N, 4.01. Found: C, 49.71; H, 7.89; N, 4.23. IR (cm^{-1}): ν(NH) 3120 (w), ν(OsH) 2111 (w). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 8.04 (d, J_{H-H} = 7.5, *o*-Ph), 7.68 (br, 1H, NH), 7.29 (t, J_{H-H} = 7.5, 2H, *m*-Ph), 7.13 (m, 1H, *p*-Ph), 6.33 (s, 1H, ═C*H*), 6.22 (dd, J_{H-H} = J_{H-H} = 2, 1H, C*H* im), 6.01 (dd, J_{H-H} = J_{H-H} = 2, 1H, C*H* im), 2.00 (m, 6H, PC*H*(CH_3)$_2$), 1.22 (dvt, J_{H-H} = 6.8, *N* = 12.8, 18H, PCH(CH_3)$_2$), 1.06 (dvt, J_{H-H} = 6.8, *N* = 12, 18H, PCH(CH_3)$_2$), −11.3 (br, 3H, Os−H). ^{1}H{^{31}P} NMR (400 MHz, $CDCl_2F$, 139 K, high-field region): δ −5.0 (br t, J_{H-H} = 20, 1H, Os−H), −14.5 (br, 2H, Os−H). ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6, 298 K): δ 31.5 (s). ^{13}C{^{1}H} APT NMR plus HSQC (75 MHz, C_6D_6, 298 K): δ 169.2 (t, J_{P-C} = 7.8, NCN), 151.5 (s, *C*O), 142.5 (s, C_{ipso}), 126.6, 125.6, 125.3 (all s, Ph), 116.9, 115.8 (both s, *C*H im), 97.2 (s, ═*C*H), 26.9 (vt, *N* = 23, PCH(CH_3)$_2$), 20.5 and 19.7 (both s, PCH(CH_3)$_2$).

Preparation of $OsH_3\{CNHCHCHNCH{=}C(CH_3)O\}(P^iPr_3)_2$ (7). A solution of **5** (100 mg, 0.16 mmol) in toluene was heated under reflux for 15 h. During this time the solution changed from colorless to dark green. After it was cooled to room temperature, the resulting solution was filtered through Celite and the solvent was removed in

vacuo. Pentane was added to the residue to afford a green solid that was washed with pentane (2 × 2 mL) and dried in vacuo. Yield: 95 mg (52%). Anal. Calcd for $C_{24}H_{52}N_2OOsP_2$: C, 45.26; H, 8.23; N, 4.39. Found: C, 44.91; H, 7.98; N, 4.21. IR (cm^{-1}): ν(N−H) 3132, ν(Os−H) 2120. ^1H NMR (300 MHz, C_6D_6, 298 K): δ 7.64 (br, 1H, NH), 6.12 (dd, $J_{H-H} = J_{H-H} = 2$, 1H, C*H* im), 5.99 (dd, $J_{H-H} = J_{H-H} = 2$, 1H, C*H* im), 5.47 (s, 1H, =C*H*), 2.03 (m, 6H, PC*H*$(CH_3)_2$), 1.85 (s, 3H, $-CH_3$), 1.25 (dvt, $J_{H-H} = 6.9$, $N = 12.6$, 18H, PCH$(CH_3)_2$), 1.10 (dvt, $J_{H-H} = 6.9$, $N = 12$, 18H, PCH$(CH_3)_2$), −11.24 (br, 3H, OsH). $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_2F$, 143 K, high-field region): δ −5.5 (d, $J_{H-H} = 25$, 1H, Os−H), −14.4 (dd, $J_{H-H} = 25$, $J_{H-H} = 72$, 1H, Os−H), −16.9 (d, $J_{H-H} = 72$, 1H, Os−H). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 298 K): δ 31.4 (s). $^{13}C\{^1H\}$ APT NMR plus HSQC and HMBC (75.47 MHz, C_6D_6, 298 K): δ 167.4 (t, $J_{P-C} = 7.9$, NCN), 152.3 (s, CO), 116.1, 115.5 (both s, C*H* im), 95.5 (s, =C*H*), 27.1 (vt, $N = 22.6$, PCH$(CH_3)_2$), 23.7 (s, CH_3), 20.4 and 19.7 (both s, PCH$(CH_3)_2$).

Preparation of [OsH$_3${CNHCHCHNCH$_2$C(Ph)=O}(P^{i}Pr$_3$)$_2$]BF$_4$ (8). A solution of **6** (50 mg, 0.07 mmol) in diethyl ether (5 mL) was treated with 1 equiv of $HBF_4 \cdot OEt_2$ (9.8 μL, 0.07 mmol) and stirred for 15 min at room temperature. During the course of the reaction a brown solid formed. The solvent was removed, and the solid was washed with further portions of diethyl ether (2 × 2 mL) and dried in vacuo. Yield: 42 mg (56%). Anal. Calcd for $C_{29}H_{55}BF_4N_2OOsP_2$: C, 44.27; H, 7.04; N, 3.56. Found: C, 44.58; H, 7.32; N, 3.45. IR (cm^{-1}): ν(N−H) 3145 (w), ν(Os−H) 2151 (w), ν(C=O) 1593 (m), $\nu(BF_4)$ 1023 (s). ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 9.50 (br, 1H, NH), 8.09 (d, $J_{H-H} = 7.2$, 2H, *o*-Ph), 7.76 (t, $J_{H-H} = 7.5$, 1H, *p*-Ph), 7.59 (t, $J_{H-H} = 7.5$, 2H, *m*-Ph), 7.34 (dd, $J_{H-H} = J_{H-H} = 2.0$, 1H, C*H* im), 7.25 (dd, $J_{H-H} = J_{H-H} = 2.0$, 1H, C*H* im), 6.15 (t, $J_{H-P} = 2$, 2H, CH_2), 1.93 (m, 6H, PC*H*$(CH_3)_2$), 1.04 (dvt, $J_{H-H} = 6.9$, $N = 13$, 18H, PCH$(CH_3)_2$), 1.03 (dvt, $J_{H-H} = 6.9$, $N = 13$, 18H, PCH$(CH_3)_2$), −10.5 (very br, 3H, Os−H). $^1H\{^{31}P\}$ NMR (300 MHz, CD_2Cl_2, 189 K, high-field region): δ −7.6 (br, 1H, Os−H), −8.1 (br, 1H, Os−H), −16.5 (t, $J_{H-H} = 16$, 1H, Os−H). $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2, 298 K): δ 29.3 (s). $^{13}C\{^1H\}$ APT NMR plus HSQC and HMBC (125.75 MHz, CD_2Cl_2, 298 K): δ 192.0 (CO), 176.1 (t, $J_{P-C} = 6.8$, NCN), 135.0 (s, C*H* Ph), 133.2 (s, C_{ipso} Ph), 129.2, 127.8 (both s, C*H* Ph), 121.1 (s, C*H* im), 119.5 (s, C*H* im), 53.7 (s, CH_2), 26.7 (vt, $N = 25.5$, PCH$(CH_3)_2$), 19.1 and 18.6 (both s, PCH$(CH_3)_2$).

Preparation of [OsH$_3${CNHCHCHNCH$_2$C(CH$_3$)=O}(P^{i}Pr$_3$)$_2$]BF$_4$ (9). A solution of **7** (100 mg, 0.16 mmol) in THF (5 mL) was treated with 1 equiv of $HBF_4 \cdot OEt_2$ (21 μL, 0.16 mmol). The resulting solution was stirred at room temperature for 15 min. During this time the solution changed from green to dark brown. The solvent was removed, and diethyl ether was added to afford a brown solid, which was washed with further portions of diethyl ether and dried in vacuo. Yield: 96 mg (90%). Anal. Calcd for $C_{24}H_{53}BF_4N_2OOsP_2$: C, 39.78; H, 7.37; N, 3.86. Found: C, 40.07; H, 6.94; N, 3.93. IR (cm^{-1}): ν(NH) 3358, ν(OsH) 2158 (w), ν(C=O) 1584 (m), $\nu(BF_4)$ 1023 (s). ^1H NMR (300 MHz, CD_2Cl_2, 298 K): δ 9.61 (br s, 1H, N−H), 7.19 (s, 1H, C*H* im), 7.04 (s, 1H, C*H* im), 5.62 (s, 2H, CH_2), 1.85 (m, 6H, PC*H*$(CH_3)_2$), 1.02 (dvt, $J_{H-H} = 6.8$, $N = 16$, 18H, PCH$(CH_3)_2$)), 0.99 1.06 (dvt, $J_{H-H} = 6.8$, $N = 15$, 18H, PCH$(CH_3)_2$), −11.1 (very br, 3H, Os−H). $^1H\{^{31}P\}$ NMR (300 MHz, CD_2Cl_2, 189 K, high-field region): δ −7.8 (br, 1H, Os−H), −8.6 (br, 1H, Os−H), −17.0 (t, $J_{H-H} = 20$, 1H, Os−H). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 298 K): δ 29.2 (s). $^{13}C\{^1H\}$ APT NMR plus HSQC (75.47 MHz, CD_2Cl_2, 263 K): δ 206.0 (CO), 176.3 (t, $J_{P-C} = 7.1$, NCN), 120.6 (s, C*H* im), 120.1 (s, C*H* im), 57.6 (s, CH_2), 29.6 (s, CH_3), 27.2 (vt, $N = 25.7$, PCH$(CH_3)_2$), 19.5 and 19.0 (both s, PCH$(CH_3)_2$).

Reaction of 8 with K^{t}BuO. A brown solution of **8** (100 mg, 0.127 mmol) in THF was treated with 2 equiv of K^{t}BuO (28 mg, 0.253 mmol) and stirred for 30 min at room temperature. The resulting suspension was filtered through Celite and was taken to dryness. Addition of pentane afforded a green solid (73 mg, 80% yield) that was identified as **6** by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

Reaction of 9 with K^{t}BuO. A brown solution of **9** (100 mg, 0.138 mmol) in THF was treated with 2 equiv of K^{t}BuO (31 mg, 0.28 mmol) and stirred for 30 min at room temperature. The resulting suspension was filtered through Celite and was taken to dryness. Addition of pentane afforded a green solid (72 mg, 82% yield) that was identified as **7** by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.

Preparation of [OsH$_3${CN(CH$_2$Ph)CHCHNCH$_2$C(Ph)=O}(P^{i}Pr$_3$)$_2$]BF$_4$ (10). A colorless solution of **1** (100 mg, 0.19 mmol) in THF (10 mL) was treated with 1.2 equiv of 3-benzyl-1-(2-hydroxy-2-phenylethyl)imidazolium tetrafluoroborate and heated at reflux temperature for 29 h. During this time the solution changed from colorless to garnet. After the mixture was cooled to room temperature, it was filtered through Celite and the solvent removed in vacuo. Subsequent addition of diethyl ether to the residue afforded a garnet solid, which was washed with diethyl ether (2 × 3 mL) and dried in vacuo. Yield: 104 mg (61%). Anal. Calcd for $C_{36}H_{61}BF_4N_2OOsP_2$: C, 49.31; H, 7.01; N, 3.19. Found: C, 48.96; H, 6.85; N, 3.34. IR (cm^{-1}): ν(OsH) 2158 (w), ν(C=O) 1593 (m), $\nu(BF_4)$ 1038 (s). ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 8.15 (d, $J_{H-H} = 7.3$, 2H, *o*-Ph), 7.77 (t, $J_{H-H} = 7.3$, 1H, *p*-Ph), 7.60 (m, 3H, *m*-Ph and C*H* im), 7.35−7.23 (m, 5H, Ph), 7.16 (d, $J_{H-H} = 1.5$, 1H, C*H* im), 6.07 (s, 2H, CH_2COPh), 5.39 (s, 2H, CH_2Ph), 1.75 (m, 6H, PC*H*$(CH_3)_2$), 1.01 (dvt, $J_{H-H} = 6.9$, $N = 13.2$, 18H, PCH$(CH_3)_2$), 0.98 (dvt, $J_{H-H} = 6.6$, $N = 12.6$, 18H, PCH$(CH_3)_2$), −10.9 (br, 3H, OsH). $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_2F$, 189 K, high-field region): δ −6.7 (br, 1H, Os−H), −9.6 (br, 1H, Os−H), −16.5 (t, $J_{H-H} = 36$, 1H, Os−H). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 298 K): δ 30.2 (s). $^{13}C\{^1H\}$ APT NMR plus HSQC and HMBC (75.47 MHz, CD_2Cl_2, 298 K): δ 196.7 (t, $J_{P-C} = 1.5$, CO), 183.5 (t, $J_{P-C} = 6.3$, NCN), 136.1 (s, CH Ph), 135.8 and 133.9 (both s, C_{ipso} Ph), 130.1, 129.4, 129.3, 128.7, 128.2 (all s, CH Ph), 124.0 (s, C*H* im), 123.1 (s, C*H* im), 55.8 (s, CH_2Ph), 55.0 (s, CH_2COPh), 27.1 (vt, $N = 25.3$, PCH$(CH_3)_2$), 19.9 and 19.7 (both s, PCH$(CH_3)_2$).

Preparation of [OsH$_3${CN(CH$_2$Ph)CHCHNCH$_2$C(CH$_3$)=O}(P^{i}Pr$_3$)$_2$]BPh$_4$ (11). A colorless solution of **1** (125 mg, 0.24 mmol) in THF (10 mL) was treated with 1.2 equiv of 3-benzyl-1-(2-hydroxypropyl)imidazolium tetraphenylborate (131.0 mg, 0.29 mmol) and heated under reflux during 29 h. During this time the solution changed from colorless to yellow. After the mixture was cooled to room temperature, it was filtered through Celite and taken to dryness. Subsequent addition of diethyl ether to the residue afforded a yellow solid, which was washed with diethyl ether (2 × 3 mL) and dried in vacuo. Yield: 227 mg (90%). Anal. Calcd for $C_{55}H_{79}BN_2OOsP_2$: C, 63.08; H, 7.60; N, 2.67. Found: C, 63.41; H, 7.44; N, 2.80. IR (cm^{-1}): ν(OsH) 2157. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ 7.49 (br, 8H, *o*-BPh_4), 7.41−7.23 (m, 5H, Ph), 7.06 (t, $J_{H-H} = 7.4$, 8H, *m*-BPh_4), 6.93 (d, $J_{H-H} = 2$, 1H, C*H* im), 6.90 (t, $J_{H-H} = 7.2$, 4H, *p*-BPh_4), 6.41 (d, $J_{H-H} = 2$, 1H, C*H* im), 5.28 (s, 2H, CH_2Ph), 3.87 (s, 2H, CH_2COCH_3), 1.82 (s, 3H, CH_3), 1.73 (m, 6H, PC*H*$(CH_3)_2$), 0.99 (dvt, $J_{H-H} = 6.9$, $N = 13$, 18H, PCH$(CH_3)_2$), 0.98 (dvt, $J_{H-H} = 6.9$, $N = 13$, 18H, PCH$(CH_3)_2$), −11.4 (br, 3H, OsH). $^1H\{^{31}P\}$ NMR (300 MHz, $CDCl_2F$, 189 K, high-field region): δ −7.4 (br, 1H, Os−H), −9.9 (br, 1H, Os−H), −17.1 (t, $J_{H-H} = 39$, 1H, Os−H). $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2, 298 K): δ 29.4 (s). $^{13}C\{^1H\}$ APT NMR plus HSQC and HMBC (100.63 MHz, CD_2Cl_2, 298 K): δ 206.7 (s, CO), 181.9 (t, $J_{P-C} = 6$, NCN), 163.9 (q, $J_{B-C} = 49.2$, C_{ipso} BPh_4), 135.6 (q, $J_{B-C} = 1.2$, *o*-CH BPh_4), 125.2 (q, $J_{B-C} = 2.6$, *m*-CH BPh_4), 122.8 (s, C*H* im), 121.7 (s, *p*-CH BPh_4), 120.5 (s, C*H* im), 56.6 (s,

CH_2COCH_3), 55.2 (s, CH_2Ph), 29.0 (s, CH_3), 26.3 (vt, N = 25.2, $PCH(CH_3)_2$), 19.1 and 19.0 (both s, $PCH(CH_3)_2$).

Preparation of $OsH_3\{CN(CH_2Ph)CHCHNCH{=}C(Ph)O\}(P^iPr_3)_2$ (12). A solution of **10** (100 mg, 0.11 mmol) in THF (5 mL) was treated with 2 equiv of K^{t}BuO (25 mg, 0.22 mmol). After the mixture was stirred for 40 min at room temperature, it changed from orange to green. The resulting suspension was filtered through Celite, and the resulting solution was taken to dryness, affording a yellow solid that was washed with pentane and dried in vacuo. Yield: 41 mg (46%). Anal. Calcd for $C_{36}H_{60}N_2OOsP_2$: C, 54.79; H, 7.66; N, 3.44. Found: C, 54.42; H, 7.83; N, 3.21. IR (cm^{-1}): ν(Os−H) 2120 (w), ν(C=N) 1865. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 8.04 (d, J_{H-H} = 7.5, 2H, Ph), 7.29 (t, J_{H-H} = 7.5, 2H, Ph), 7.11 (m, 6H, Ph), 6.44 (d, J_{H-H} = 1.8, 1H, C*H* im), 6.41 (d, J_{H-H} = 1.8, 1H, C*H* im), 6.40 (s, =C*H*), 5.31 (s, 2H, CH_2), 1.96 (m, 6H, $PCH(CH_3)_2$), 1.23 (dvt, J_{H-H} = 6.7, N = 13, 18H, $PCH(CH_3)_2$), 1.00 (dvt, J_{H-H} = 6.5, N = 12, 18H, $PCH(CH_3)_2$), −11.3 (br, 3H, OsH). ^{1}H{^{31}P} NMR (400 MHz, $CDCl_2F$, 138 K, high-field region): δ −5.4 (br, 1H, Os−H), −14.6 (br, 1H, Os−H), −15.2 (br, 1H, Os−H). ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, 298 K): δ 32.7 (s). ^{13}C{^{1}H} APT NMR plus HSQC and HMBC (75.47 MHz, C_6D_6, 298 K): δ 175.1 (t, J_{P-C} = 7.5, NCN), 151.4 (s, CO), 142.2 and 137.3 (both s, C_{ipso} Ph), 128.8, 128.3, 127.9, 126.6, 125.2 (all s, CH Ph), 119.7 (s, CH im), 118.3 (s, CH im), 97.9 (s, =CH), 55.2 (s, $-CH_2-$), 26.12 (vt, N = 22.7, $PCH(CH_3)_2$), 20.3 and 19.9 (both s, $PCH(CH_3)_2$).

Preparation of $OsH_3\{CN(CH_2Ph)CHCHNCH{=}C(CH_3)O\}(P^iPr_3)_2$ (13). A yellow solution of **11** (120 mg, 0.12 mmol) in THF was treated with 2 equiv of K^{t}BuO (27 mg, 0.24 mmol) and stirred for 40 min at room temperature. The resulting suspension was filtered through Celite and was taken to dryness. Addition of pentane to the residue afforded a yellow solid that was washed with pentane and dried in vacuo. Yield: 34 mg (41%). Anal. Calcd for $C_{31}H_{58}N_2OOsP_2$: C, 51.22; H, 8.04; N, 3.85. Found: C, 50.85; H, 8.32; N, 3.64. IR (cm^{-1}): ν(OsH) 2115. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.09−6.98 (m, 5H, Ph), 6.37 (d, J_{H-H} = 1.8, 1H, C*H* im), 6.31 (d, J_{H-H} = 1.8, 1H, C*H* im), 5.52 (s, 1H, C*H*), 5.29 (s, 2H, CH_2), 1.98 (m, 6H, $PCH(CH_3)_2$), 1.90 (s, CH_3), 1.26 (dvt, J_{H-H} = 6.8, N = 12.9, 18H, $PCH(CH_3)_2$), 1.05 (dvt, J_{H-H} = 6.8, N = 12, 18H, $PCH(CH_3)_2$), −11.4 (br, 3H, OsH). ^{1}H{^{31}P} NMR (300 MHz, $CDCl_2F$, 172 K, high-field region): δ −5.7 (br, 1H, Os−H), −15.0 (AB spin system, J_{A-B} = 288, $\Delta\nu$ = 684, 2H, Os−H). ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6, 298 K): δ 32.3 (s). ^{13}C{^{1}H}- APT NMR plus HSQC and HMBC (75.47 MHz, C_6D_6, 298 K): δ 173.8 (t, J_{P-C} = 7.5, NCN), 152.4 (s, CO), 137.6 (s, C_{ipso} Ph), 128.7, 128.3 (both s, CH Ph), 119.3, 117.6 (both s, CH im), 96.1 (s, CH), 55.1 (s, CH_2), 26.5 (vt, N = 22, $PCH(CH_3)_2$), 23.4 (s, CH_3), 20.1 and 20.0 (both s, $PCH(CH_3)_2$).

Structural Analysis of Complexes 2, 6, and 10. Crystals suitable for X-ray diffraction were obtained by slow diffusion of methanol into a solution of complex **2** in dichloromethane, by cooling a solution of complex **6** to −20 °C, and by slow diffusion of diethyl ether into a solution of complex **10** in dichloromethane. X-ray data for all complexes were collected on a Bruker Smart APEX CCD diffractometer equipped with a normal-focus, 2.4 kW sealed-tube source (Mo radiation, λ = 0.710 73 Å) operating at 50 kV and 30 mA (**2**) or 40 mA (**6**, **10**). Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s (**2**, **10**) or 50 s (**6**) covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[40] The structures of all compounds were solved by the Patterson method. Refinement, by full-matrix least squares on F^2 with SHELXL97,[41] was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters. The hydrogen atoms were observed or calculated and refined freely or refined with a restricted riding model. Hydride ligands were observed in the difference Fourier maps and refined with restrained Os−H bond lengths (1.59(1) Å, CSD). Two methyl groups (C25 and C26) of one of the triisopropylphosphine ligands of complex **6** were refined in two positions (0.7/0.3). These methyl groups were refined with an isotropic model and restrained geometry. For **6** 0.25 molecule of pentane was observed in the asymmetric unit as crystallization solvent. For **10**, 0.25 (diethyl ether) and 0.5 (dichloromethane, disordered) molecules were observed in the asymmetric unit as crystallization solvents. They were refined with restrained geometry, with isotropic atoms, and without hydrogens. All the highest electronic residuals were observed in the close proximity of the Os centers and make no chemical sense.

Crystal Data for ***2****:*. $C_{30}H_{60}N_2OsP_2$, M_w = 700.94, colorless, prism (0.20 × 0.12 × 0.10), monoclinic, space group $P2_1/n$, a = 12.2220(16) Å, b = 15.4235(19) Å, c = 17.219(2) Å, α = 90.00°, β = 98.900(2)°, γ = 90.00 °, V = 3206.8(7) Å^3, Z = 4, D_{calcd} = 1.452 g cm^{-3}, $F(000)$ = 1440, T = 100(2) K, μ = 4.096 mm^{-1}, 39 565 measured reflections (2θ = 3−58°, ω scans 0.3°), 7856 unique reflections (R_{int} = 0.0785); minimum/maximum transmission factors 0.504/0.659, final agreement factors R1 = 0.0384 (5176 observed reflections, $I > 2\sigma(I)$) and wR2 = 0.0556, 7856/5/354 data/restraints/parameters, GOF = 0.740, largest peak and hole 1.114 and −1.241 e/Å^3.

Crystal Data for ***6****:*. $C_{29}H_{54}N_2OOsP_2\cdot 0.25C_5H_{12}$, M_w = 716.92, brown, prism (0.14 × 0.03 × 0.03), tetragonal, space group $I4_1/a$, a = 35.231(9) Å, b = 35.231(9) Å, c = 11.818(4) Å, α = 90.00°, β = 90.00°, γ = 90.00°, V = 14669(7) Å^3, Z = 16, D_{calcd} = 1.298 g cm^{-3}, $F(000)$ = 5864, T = 100(2) K, μ = 3.586 mm^{-1}. 47 362 measured reflections (2θ: = 3−58°, ω scans 0.3°), 9055 unique reflections (R_{int} = 0.1108), minimum/maximum transmission factors 0.694/0.801, final agreement factors R1 = 0.0398 (4622 observed reflections, $I > 2\sigma(I)$) and wR2 = 0.0810, 9055/23/368 data/restraints/parameters, GOF = 0.803, largest peak and hole 0.864 and −0.878 e/Å^3.

Crystal Data for ***10****:*. $C_{36}H_{61}BF_4N_2OOsP_2\cdot 0.25C_4H_{10}O\cdot 0.5CH_2Cl_2$, M_w = 937.81, orange, irregular block (0.10 × 0.10 × 0.08), triclinic, space group $P\bar{1}$, a = 11.352(3) Å, b = 13.480(4) Å, c = 15.209(4) Å, α = 75.175(5)°, β = 80.377(5)°, γ = 74.714(4)°, V = 2157.8(11) Å^3, Z = 2, D_{calcd} = 1.443 g cm^{-3}, $F(000)$ = 955, T = 100(2) K, μ = 3.139 mm^{-1}, 27 164 measured reflections (2θ = 4−58°, ω scans 0.3°), 10 376 unique reflections (R_{int} = 0.0447), minimum/maximum transmission factors 0.700/0.803, final agreement factors R1 = 0.0310 (8227 observed reflections, $I > 2\sigma(I)$) and wR2 = 0.0595, 10 376/25/512 data/restraints/parameters, GOF = 0.845, largest peak and hole 1.097 and −0.974 e/Å^3.

Computational Details. The calculations have been carried out using the Gaussian 03 computational package.[42] The structures have been optimized using DFT and the B3LYP functional. The 6-31G** basis set has been used for all atoms except for Os, where the LANL2DZ basis and pseudopotential have been used instead.

■ ASSOCIATED CONTENT

Supporting Information. Tables, text, and CIF files giving details of the X-ray analysis and crystal structure determination, including bond lengths and angles of compounds **2**, **6**, and **10**, orthogonal coordinates of the optimized theoretical structures, and the full ref 42. This material is available free of charge via the Internet at http://pubs.acs.org.

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DEDICATION

†Dedicated to Prof. Kenneth G. Caulton on the occasion of this 70th birthday.

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