Osmium- and Iridium-Promoted C-H Bond Activation of 2,2'-Bipyridines and Related Heterocycles: Kinetic and Thermodynamic Preferences

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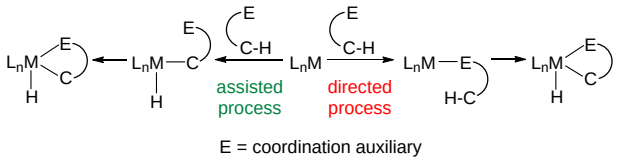
ABSTRACT: The d^2-hexahydride complex $OsH_6(P^iPr_3)_2$ (**1**) promotes the activation of C-H bonds of 2,2'-bipyridines and related heterocycles. The study of the same reactions with the deuteride counterpart $OsD_6(P^iPr_3)_2$ (**1-*d***) reveals that the activation of the C-H bonds situated in the sterically less hindered positions is kinetically preferred. However, the isolated products are the result of the thermodynamic control of the reactions. Thus, reactions of **1** with 2,2'-bipyridine, 6-phenyl-2,2'-bipyridine, and 6-methyl-2,2'-bipyridine give the "*rollover cyclometalation*" products $OsH_3\{\kappa^2\text{-}C,N\text{-}[C_5(R)H_2N\text{-}py]\}(P^iPr_3)_2$ (R = H (**2**), Ph (**3**), Me (**4**)), whereas 3,5-dimethyl-6-phenyl-2,2'-bipyridine affords $OsH_2\{\kappa^3\text{-}C,N,C\text{-}[C_5H_3N\text{-}(Me)_2py\text{-}C_5H_4]\}(P^iPr_3)_2$ (**5**), containing a dianionic C,N,C-pincer ligand. The behavior of substrates pyridyl-benzimidazolium and –imidazolium is similar. Reaction of **1** with 3-methyl-1-(6-phenylpyridin-2-yl)-1*H*-benzimidazolium tetrafluoroborate leads to $OsH_3\{\kappa^2\text{-}C,C\text{-}[MeBzim\text{-}C_5(Ph)H_2N]\}(P^iPr_3)_2$ (**6**), bearing an anionic C_{py},C_{NHC}-chelate. On the other hand 3-methyl-1-(6-phenylpyridin-2-yl)-1*H*-imidazolium tetrafluoroborate yields $[OsH_2\{\kappa^3\text{-}C,N,C\text{-}(MeIm\text{-}py\text{-}C_6H_4)\}(P^iPr_3)_2]BF_4$ (**7**), containing a monoanionic C,N,C-pincer with a NHC-unit coordinated in an abnormal fashion. The reactivity pattern of these substrates is also observed with the d^4-iridium-pentahydride $IrH_5(P^iPr_3)_2$ (**8**), which has generated $IrH_2\{\kappa^2\text{-}C,N\text{-}[C_5(R)H_2N\text{-}py]\}(P^iPr_3)_2$ (R = H, (**9**), Ph (**10**)) and $IrH\{\kappa^3\text{-}C,N,C\text{-}[C_5H_3N\text{-}(Me_2)py\text{-}C_5H_4]\}(P^iPr_3)_2$ (**11**). The osmium(IV)-carbon bonds display a higher degree of covalency than the iridium(III)-carbon bonds. In contrast to **2**, the metalated carbon atom of **9** undergoes the addition of a proton of methanol to give $[IrH_2\{\kappa^2\text{-}N,N\text{-}(bipy)\}(P^iPr_3)_2]BF_4$ (**12**).

INTRODUCTION

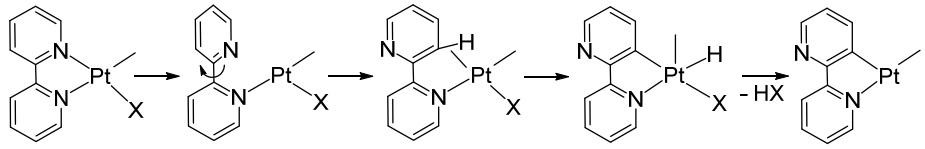
Metal-promoted C-H bond activation reactions are traditional organometallic processes of general interest,[1] by their connection with the selective functionalization of organic molecules.[2] However, many basic questions remain largely unanswered. It is generally assumed that the first step for the rupture of the C-H bond is its coordination to an unsaturated species, to form a $L_nM(\eta^2\text{-HC})$ intermediate, which evolves by C-H oxidative addition, heterolytic cleavage, or σ-bond metathesis, depending upon the electronic nature of the L_nM fragment. Basic metal centers favor C-H oxidative addition, while electrophilic centers promote the heterolysis of the bond. In contrast to oxidative addition, activations by heterolytic cleavage and σ-bond metathesis avoid the formal 2-electron oxidation of the metal.[3] The efficiency of the C-H coordination is increased by using an auxiliary. The procedure displays great thermodynamic selectivity when the activations of several bonds are kinetically competitive. Under these conditions, the activation can be directed or assisted (Scheme 1).[4] The directed process requires the previous coordination of the auxiliary,[5] while the coordination of the latter occurs after the C-H cleavage in the assisted reaction.[6]

Scheme 1. Directed or Assisted C-H Activation Processes



Nitrogen heterocycles are present in many compounds of enormous practical importance, ranging from pharmaceutical agents and biological probes to electroactive materials. For instance, 2,2'-bipyridine is the unique molecular scaffold of the bioactive natural products represented by caerulomycins and collismycins.[7] Although 2,2'-bipyridines are well known *N,N*-chelate ligands, which form extremely stable compounds with all transition metals,[8] some unsaturated d^8-complexes of iridium(I),[9] palladium(II),[10] platinum(II),[11] and gold(III)[12] and $IrCl_3.3H_2O$[13] have proved to promote their C-H bond activation in solution. This unusual reaction, so-called "*rollover cyclometalation*",[14] is viewed as originated from a chelated κ^2-*N,N*-adduct. The key of the process is the internal rotation of the ligand, which occurs before the C-H bond activation. On the basis on studies in the gas phase,[15] a mechanism involving C-H oxidative addition and subsequent H-X reductive elimination has been proposed for platinum(II) (Scheme 2).

Scheme 2. Accepted Mechanism for the "*Rollover Cyclometalation*"



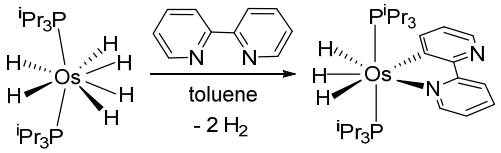
Polyhydrides of platinum group metals are certainly very different from d^8-square-planar complexes. In contrast to the latter, the strongly oxidized metal center is generally saturated, with high coordination index. However, they have demonstrated an extraordinary ability to activate a wide range of σ-bonds.[16] Furthermore, the presence of a high number of hydride ligands in the complexes facilitates the study of the reversibility of the activations, by means of isotopic labeling experiments, which are relevant from a mechanistic point of view and can allow to discern between the directed or assisted character of the activation.[6b]

The d^2-hexahydride $OsH_6(P^iPr_3)_2$ (**1**) promotes the C-H bond activation of a wide range of organic molecules,[17] in agreement with the ability shown by polyhydrides of platinum group metals to activate σ-bonds, being therefore an excellent candidate to study the C-H bond activation of 2,2'-bipyridine and related molecules. Furthermore its hexadeuteride counterpart can be easily prepared. This paper reveals that: i) polyhydrides of platinum group metals promote the C-H bond activation of this class of substrates, ii) in contrast to the classical "*rollover cyclometalation*", the activation is assisted by chelation and therefore the selectivity is only thermodynamic in origin, and iii) the stability of the resulting products is strongly dependent upon the central ion.

RESULTS AND DISCUSSION

C-H Bond Activation of 2,2'-Bipyridine. Treatment of toluene solutions of the hexahydride complex **1** with 1.3 equiv of the bicycle, under reflux, for 14 h affords the trihydride-osmium(IV) derivative $OsH_3\{\kappa^2\text{-}C,N\text{-}(C_5H_3N\text{-py})\}(P^iPr_3)_2$ (**2**), as a result of the C-H bond activation of a ring and the chelate N-coordination of the other one, and produces the release of two molecules of molecular hydrogen (Scheme 3). Complex **2** was isolated as an orange solid in 84% yield.

Scheme 3. Reaction of 1 with 2,2'-Bipyridine



The osmium-promoted C-H bond activation of 2,2'-bipyridine was confirmed by X-ray diffraction analysis. Figure 1 gives a view of the structure. The geometry around the osmium atom can be rationalized as a distorted pentagonal bipyramid with the phosphine ligands occupying axial positions (P-Os-P = 164.63(3)º). The metal coordination sphere is completed by the hydrides and the donor atoms, C(1) and N(1), of the generated chelate, which acts with a C(1)-Os-N(1) bite angle of 76.28(11)º, very close to the ideal value of 72º. The Os-C(1) and Os-N(1) bond lengths of 2.143(2) Å compare well with those found in related compounds bearing orthometalated 2-phenylpyridine groups.[18] The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra in toluene-d_8 of the obtained orange crystals are consistent with the structure shown in Figure 1. As expected for three inequivalent hydride ligands, the ^1H NMR spectrum at 193 K displays three hydride resonances at -5.94, -10.87, and -12.07 ppm. In the $^{13}C\{^1H\}$ NMR spectrum at room temperature, the most noticeable resonance is that due to the metalated carbon atom (C(1)), which is observed at 178.7 ppm, as a triplet with a C-P coupling constant of 6.7 Hz. In agreement with the presence of equivalent phosphines in the complex, the $^{31}P\{^1H\}$ NMR spectrum at room temperature shows a singlet at 20.0 ppm.

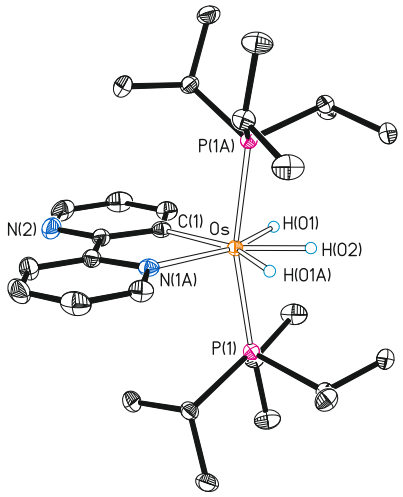
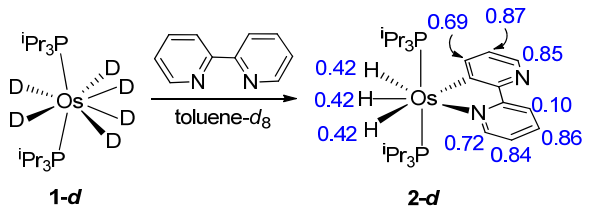


Figure 1. Molecular diagram of complex **2** (ellipsoids shown at 50% probability). All hydrogen atoms (except the hydrides) are omitted for clarity. Selected bond distances (Å) and angles (deg): Os-P(1) = 2.3399(5), Os-C(1) = 2.143(2), Os-N(1A) = 2.143(2); P(1)-Os-P(1A) = 164.63(3), C(1)-Os-N(1A) = 76.28(11).

To gain mechanistic insight about the formation of **2**, we carried out the reaction of 2,2'-bipyridine with the hexadeuteride complex $OsD_6(P^iPr_3)_2$ (**1-*d***). The latter was prepared as **1**,[19] starting from $OsH_2Cl_2(P^iPr_3)_2$, but by using $Na[BD_4]$ instead of $Na[BH_4]$ and deuterated solvents. Under the same conditions as those described for the formation of **2**, the treatment of **1-*d*** with 2,2'-bipyridine in toluene-d_8 led to a partially deuterated complex **2-*d*** (Scheme 4), as a result of the C-H bond activation of one of the rings and H/D isotopic exchanges between the osmium precursor, the organic molecule, and the solvent. The analysis of the deuterium distribution revealed a similar deuteration in both rings, which is between 70% and 90% for the positions *meta* and *para* with regard to the other ring and about 10% for the *ortho* position of the *N*-coordinated ring (the equivalent one to that metalated in the C-H activated ring). In contrast to the chelate ligand, the hydride positions are mainly protiated (58%). In addition, both positions of the isopropyl substituents of the phosphines also show deuterium incorporation.

Scheme 4. Reaction of *1-d* with 2,2'-Bipyridine. Values in Blue Denote the Extent of Deuteration



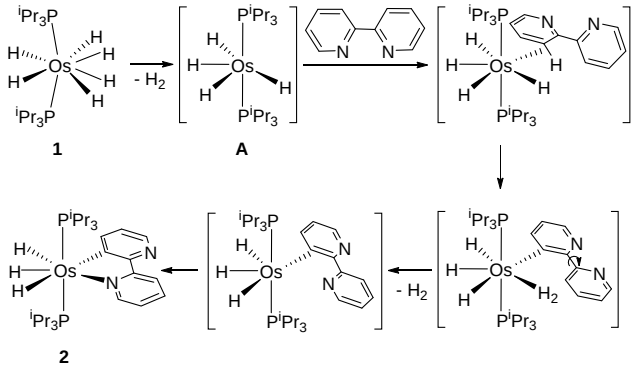
1-*d* **2-*d***

The deuteration of both rings demonstrates that the formation of **2** is not a *N*-directed C-H bond activation process but a chelating-assisted reaction. To the contrary a ring inhibits the *ortho*-CH bond activation of the other one (note that the less deuterated position of the N-coordinated ring is the *ortho* position to the activated ring). After the C-H rupture at the *ortho*-position with regard to the other ring, the nitrogen atom of the latter acts to trap the *ortho*-C-M product. The selectivity of the *ortho*-CH bond activation, which affords **2**, is thermodynamic in origin, while the C-H bond activation of the positions *meta* and *para* is kinetically preferred. The activation of primary and tertiary C(sp^3)-H bonds of the isopropyl substituents of the phosphines and the C-H bond activation of the reaction solvent are kinetically competitive with those of the *meta* and *para* positions of the rings. The presence of about 0.6 hydrogen atoms in each hydride position rules out a mechanism for the C-H rupture involving σ-bond metathesis. Complex **1** is a saturated species, which needs to release a hydrogen molecule to coordinate the C-H bond and to subsequently promoting its rupture. The resulting unsaturated $OsH_4(P^iPr_3)_2$ (**A**) species has been trapped with pyridines[20] and 2,6-dimethylbenzonitrile.[21] The interaction between the coordinated C-H bond and the metal center of **A** involves σ-donation from the σ-orbital of the C-H bond to empty orbitals of the metal and back bonding from the metal to the σ*(C-H) orbital.[22] The d^4-ion center is scarcely basic enough to provide back-donation. Therefore, the oxidative addition of the C-H bond is unlikely. Nevertheless, the electrophilicity of the +4 oxidation state should enhance the σ-donation to the metal, to promote the hydride-mediated heterolytic cleavage of the C-H bond. The generated H-D ligand, when **1-*d*** is the starting material, could distribute hydrogen atoms between the hydride positions, by means of hydride-dihydrogen position exchanges.[16] The dissociation of the coordinated hydrogen molecule and the subsequent coordination of the free ring should finally afford **2** (Scheme 5).

C-H Bond Activation of Substituted-2,2'-Bipyridines. Being aware of the lack of kinetic selectivity between the rings, we decided to introduce substitution in one of them in order to generate asymmetry and to study its influence on the kinetics and thermodynamics of the activation. We followed two protocols; firstly we placed a phenyl or methyl group at the position six and subsequently protected the positions three and five.

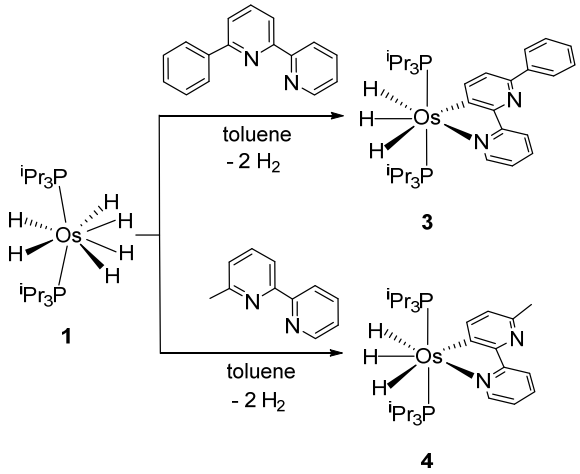
Treatment of toluene solutions of **1** with 1.3 equiv of 6-phenyl-2,2'-bipyridine, under reflux, for 14 h leads to $OsH_3\{\kappa^2\text{-}C,N\text{-}[C_5(Ph)H_2N\text{-}py]\}(P^iPr_3)_2$ (**3**), as a result of the selective C-H rupture at position 3 of the phenyl-substituted pyridine and the *N*-coordination of the peripheral one. In addition, two hydrogen molecules are released. Under the same conditions 6-methyl-2,2'-bipyridine gives the methyl-counterpart $OsH_3\{\kappa^2\text{-}C,N\text{-}[C_5(Me)H_2N\text{-}py]\}(P^iPr_3)_2$ (**4**). Complexes **3** and **4** were isolated as orange solids in 75% and 86% yield, respectively, according to Scheme 6.

Scheme 5. Proposed Mechanism for the Formation of 2



1 **A** **2**

Scheme 6. Reactions of 1 with 6-Phenyl-2,2'-bipyridine and 6-Methyl-2,2'-bipyridine



1 **3** **4**

The C-H bond activation of the doubly substituted ring was confirmed by means of the X-ray analysis of a single crystal of **3**. Figure 2 gives a view of the structure. The geometry around the metal center resembles that of **1** with P-Os-P and C(1)-Os-N(1) angles of 165.52(3)º and 76.18(11)º, respectively. The Os-C(1) and Os-N(1) bond lengths of 2.113(3) and 2.163(3) Å are also similar to those of **1**. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra in toluene-d_8 of **3** and **4** are consistent with the structure shown in Figure 2 and agree well with those of **1**. Thus, the ^1H NMR spectra at 183 K display three hydride resonances between -5.9 and -12.6 ppm, which are characteristic for $OsH_3(XY)(P^iPr_3)_2$ osmium(IV) complexes.[23] In the $^{13}C\{^1H\}$ NMR spectra at room temperature the resonance corresponding to the metalated carbon atom is observed as a triplet ($^2J_{C\text{-}P} \approx 6.7$ Hz) at about 176 ppm. The $^{31}P\{^1H\}$ NMR spectra at room temperature display a singlet at 20 ppm, as expected for equivalent phosphines.

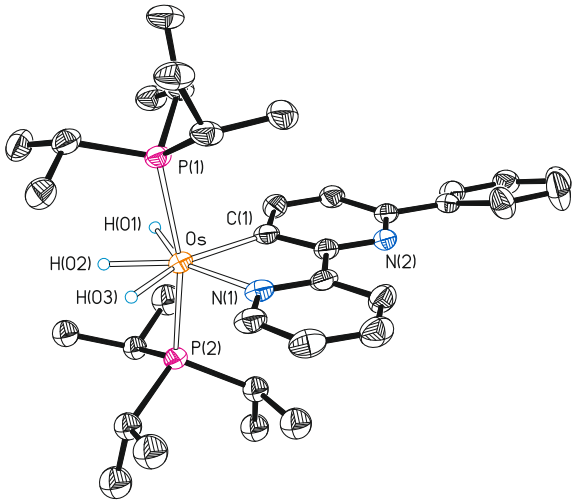
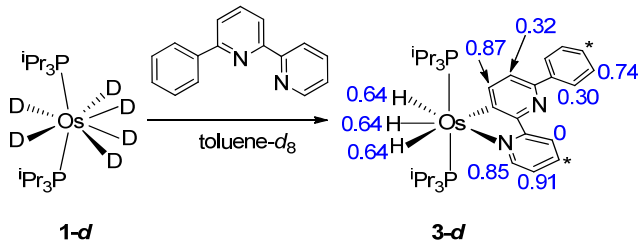


Figure 2. Molecular diagram of complex **3** (ellipsoids shown at 50% probability). All hydrogen atoms (except the hydrides) are omitted for clarity. Selected bond distances (Å) and angles (deg): Os-P(1) = 2.3491(8), Os-P(2) = 2.3412(9), Os-N(1) = 2.163(3), Os-C(1) = 2.113(3); P(1)-Os-P(2) = 165.52(3), C(1)-Os-N(1) = 76.18(11)

Neither of the C-H bond activations of 6-substituted 2,2'-bipyridines are *N*-directed processes. Like for the unsubstituted molecule, it is a chelating assisted reaction. Treatment of **1-*d*** with 6-phenyl-2,2'-bipyridine, in toluene-d_8, under the same conditions as those described for the formation of **3** afforded the partially deuterated compound **3-*d*** (Scheme 7). The deuterium distribution at the N-coordinated ring is fully consistent with that of **2-*d***; thus, positions disposed *meta* (4'and 6') and *para* (5') with regard to the C-H activated ring are mostly deuterated (80-90%), while the *ortho* one (position 3') does not contain any deuterium. The deuteration of the C-H activated ring shows the effect of the bulky substituent phenyl, which prevents the C-H rupture at its neighbor position (5). It is only 32% deuterated *versus* an 87% of deuterium at the contiguous position to the metalated one (4). The C-H bond activation of the phenyl substituent is kinetically competitive with the activation of the heterocycle and is also determined by steric factors. Thus, it displays 30% of deuterium at *ortho* positions and 74% of deuterium at *meta* positions. Isotopic osmium/polycycle exchanges also occur in this case; about a 40% of hydrogen atoms lie at the hydride positions.

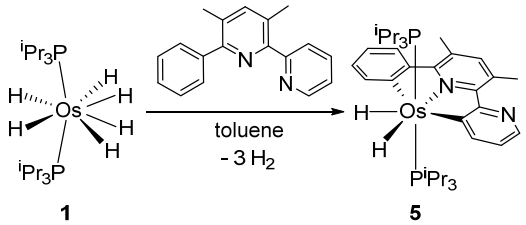
Scheme 7. Reaction of *1-d* with 6-Phenyl-2,2'-bipyridine. Values in Blue Denote the Extent of Deuteration (those of marked positions cannot be determined due to overlapping with benzene-d_6)



The activation energy for the rupture of a C-H bond depends upon two factors: the dissociation energy of the C-H bond and the stability of the M(η^2-C-H) intermediate. Within a molecule the strength of the different C-H bonds is generally similar, whereas the stability of the σ-intermediate strongly depends on the steric hindrance experienced by the coordinated C-H bond. As a consequence, the C-H bond activation is kinetically controlled by steric factors; i.e., the less sterically hindered C-H bonds are generally the first activated ones. On the other hand, from a thermodynamic point of view, the C-H bond activation is controlled by the difference between the strength of the activated bond and the strength of the formed bonds; i.e., the chelate effect is the driving force in the cyclometalations.[1,3,4] According to this, the isotopic distribution shown in Scheme 7 reveals that the inclusion of a substituent at α-position with regard to the N atom of one of the rings favors the C-H bond activation of this ring, from both kinetic and thermodynamic points of view, kinetically because of increases in the steric hindrance around the C-H bond at position 3' in the other ring and thermodynamically because of decreases in the coordination ability of the N atom of its ring. A similar phenomenon to the latter has been observed in α-substituted pyridines and quinolines, which undergo a metal-mediated C_α-to-N hydrogen shift during their reactions with some complexes of osmium[24] and iridium,[25] to afford N-H wingtip NHC ligands.

The protection of the position 3 of 6-phenyl-2,2'-bipyridine gives rise to a dramatic change in the behavior of the heterocycle; it is observed not only a change of the activated ring but the phenyl substituent also undergoes an *ortho*-CH bond activation. Thus, the treatment of toluene solutions of **1** with 1.0 equiv of 3,5-dimethyl-6-phenyl-2,2'-bipyridine, under reflux, for 14 h produces the release of three hydrogen molecules and the formation of the osmium(IV)-dihydride $OsH_2\{\kappa^3$-*C*,*N*,*C*-$[C_5H_3N$-$(Me)_2py$-$C_5H_4]\}(P^iPr_3)_2$ (**5**), bearing a dianionic C,N,C-pincer ligand, resulting of the C-H bond activation of the terminal heteroring, the coordination of the central pyridine, and the C-H bond activation of the phenyl group. Complex **5** was isolated as orange solid in 84% yield (Scheme 8).

Scheme 8. Reaction of 1 with 3,5-Dimethyl-6-phenyl-2,2'-bipyridine



Complex **5** was also characterized by X-ray diffraction analysis. The structure (Figure 3) proves the formation of the pincer ligand, with the activated rings situated pseudo *trans* (C(1)-Os-C(14) = 152.59(7)º). Thus, the coordination geometry around the osmium atom can be rationalized as a distorted pentagonal bipyramid with axial phosphines (P(1)-Os-P(2) = 159.848(16)º). As expected for a pincer, the Os-C bond lengths of 2.0994(19) (Os-C(1)) and 2.1069(19) Å (Os-C(14)) and the Os-N(1) distance, 2.1358(15) Å, are slightly shorter than those found in **2** and **3**. In agreement with the presence of two inequivalent hydrides in the complex, its ^{1}H NMR spec-

trum, in benzene-d_6, at room temperature shows two doublets of triplets ($^2J_{H\text{-}H} = {}^2J_{H\text{-}P}$ = 14.4 Hz) at -8.36 and -8.66 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances due to the metalated carbon atoms C(1) (Ph) and C(14) (py) are observed as triplets ($^2J_{C\text{-}P}$ = 7.1 and 6.8 Hz, respectively) at 178.7 and 171.8 ppm. The $^{31}P\{^1H\}$ displays a singlet at -0.8 ppm in accordance with the equivalence of the phosphine ligands.

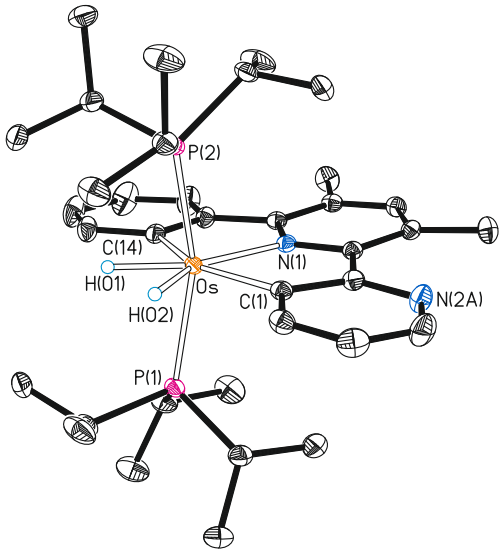
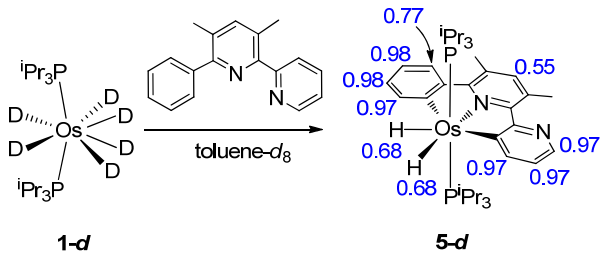


Figure 3. Molecular diagram of complex **5** (ellipsoids shown at 50% probability). All hydrogen atoms (except the hydrides) are omitted for clarity. Selected bond distances (Å) and angles (deg): Os-P(1) = 2.3715(5), Os-P(2) = 2.3658(5), Os-C(1) = 2.0994(19), Os-C(14) = 2.1069(19), Os-N(1) = 2.1358(15); P(1)-Os-P(2) = 159.848(16), C(1)-Os-N(1) = 76.46(6), C(14)-Os-N(1) = 76.15(6), C(1)-Os-C(14) = 152.59(7).

The formation of the pincer is also a thermodynamically controlled process. The deuterium distribution in **5-*d***, resulting of the reaction of **1-*d*** with 3,5-dimethyl-6-phenyl-2,2'-bipyridine under the same conditions as those described for the formation of **2-*d*** and **3-*d*** (Scheme 9), reveals that the C-H bond activation of the positions 4', 5', and 6' of the metalated pyridyl ring and the positions *meta* and *para* of the phenyl group, with 97% of deuterium, is kinetically favored. It should be also highlighted the presence of 77% of deuterium at position *ortho* of the phenyl group, which is much higher than the amount of deuterium at position 3' of the N-coordinated ring of **2-*d*** and **3-*d***, indicating a noticeable reversibility of this *ortho*-CH bond activation. Because the formation of the pincer should be obviously a stepwise process; this suggests that the last step is the activation of the phenyl group. After a chelating assisted activation of the pyridyl ring, the *N*-directed activation of the phenyl group seems to take place. In addition, it should be mentioned that activations of bonds C(sp^3)-H and C(sp^2)-H are kinetically competitive in these class of substrates. In agreement with a significant deuteration of the phosphines, deuteration of the methyl substituents of the central pyridine ring in a noticeable extent, 50-70%, is also observed.

Scheme 9. Reaction of 1-*d* with 3,5-Dimethyl-6-phenyl-2,2'-bipyridine. Values in Blue Denote the Extent of Deuteration

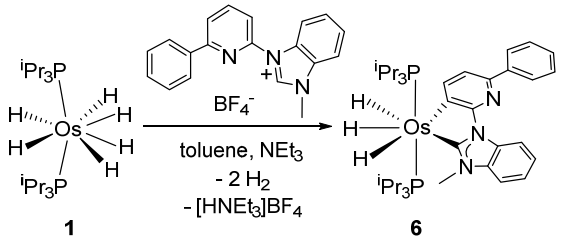


1-*d* **5-*d***

C-H Bond Activation of 6-Phenylpyridyl-Benzimidazolium and 6-Phenylpyridyl-Imidazolium Salts. Having observed the influence of the substitution in one of the rings on the C-H bond activation process and taking into account that the hexahydride complex **1** also promotes the direct metalation of benzimidazolium and imidazolium cations, to afford a wide range of NHC-complexes,[26] the behavior of substrates pyridyl-benzimidazolium and -imidazolium with two heterorings of different electronic nature was subsequently analyzed.

Complex **1** activates the C-H bond at position 3 of the pyridyl ring and metalates the benzimidazolium group of 3-methyl-1-(6-phenylpyridin-2-yl)-1*H*-benzimidazolium tetrafluoroborate, to afford the trihydride $OsH_3\{\kappa^2\text{-}C,C\text{-}[MeBzim\text{-}C_5(Ph)H_2N]\}(P^iPr_3)_2$ (**6**), an NHC-counterpart of **3**. Nevertheless, the benzimidazolium group also protonates a part of the polyhydride to afford the cation $[\{OsH_2(P^iPr_3)_2\}_2(\mu\text{-}H)_3]^+$, as a consequence of the release of 1.5 equiv of H_2 and a subsequent dimerization.[27] In agreement with this, the treatment of **1** with 1.1 equiv of the salt, in toluene, under reflux, for 4 h leads to a mixture of **6** and the dinuclear cation. The addition of triethylamine to the reaction mixture prevents the protonation of the polyhydride. As a consequence, in the presence of 10 equiv of the amine, the reaction selectively gives **6**, which was isolated as a white solid in 40% yield (Scheme 10).

Scheme 10. Reaction of 1 with 3-Methyl-1-(6-phenylpyridin-2-yl)-1*H*-benzimidazolium Tetrafluoroborate



1 **6**

Complex **6** was also characterized by X-ray diffraction analysis. The structure, which proves the double metalation of the salt to form an anionic C_{py},C_{NHC}-chelate ligand, has two chemically equivalent but crystallographically independent molecules in the asymmetric unit. Figure 4 shows one of them. The geometry around the metal center resembles that of **3** with a MeBzim group at the position of the N-coordinated ring and P(1)-Os(1)-P(2) and C(1)-Os(1)-C(10) angles of 162.24(3)º and 162.67(3)º and 75.76(13)º and 76.04(13)º, respectively.

The Os-pyridyl bond lengths (Os-C(10)) of 2.132(4) and 2.135(4) Å are similar to those of **1** and **3**, whereas the Os-MeBzim distances (Os-C(1)) of 2.071(3) and 2.060(3) Å compare well with those reported for Os-NHC complexes.[26] At 223 K, in toluene-d_8, two inequivalent hydride ligands undergo a position exchange process. According to this, the ^{1}H NMR spectrum at this temperature contains two hydride signals at -8.32 and -9.80 ppm, in a 1:2 intensity ratio. In the ^{13}C{^{1}H} NMR spectrum, at room temperature, the resonances due to metalated carbon atoms C(1) and C(10) appear at 201.8 and 150.3 ppm as triplets with C-P coupling constants of 5.5 and 6.7 Hz, respectively. The ^{31}P{^{1}H} NMR spectrum displays a singlet at 25.9 ppm.

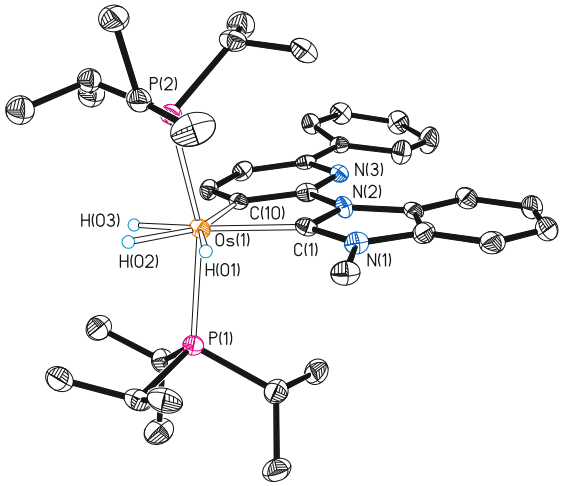
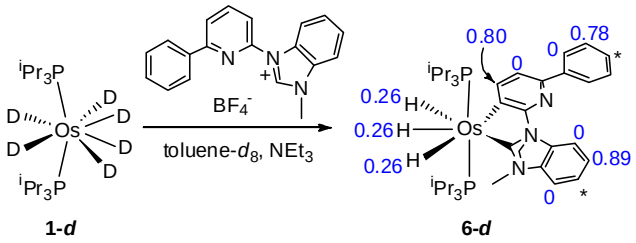


Figure 4. Molecular diagram of complex **6** (ellipsoids shown at 50% probability). All hydrogen atoms (except the hydrides) are omitted for clarity. Selected bond distances (Å) and angles (deg) for the two independent molecules in the asymmetric unit: Os(1)-P(1) = 2.3469(9), 2.3450(9), Os(1)-P(2) = 2.3416(9), 2.3338(9), Os(1)-C(1) = 2.071(3), 2.060(3), Os(1)-C(10) = 2.132(4), 2.135(4); P(1)-Os(1)-P(2) = 162.24(3), 162.67(3), C(1)-Os(1)-C(10) = 75.76(13), 76.04(13).

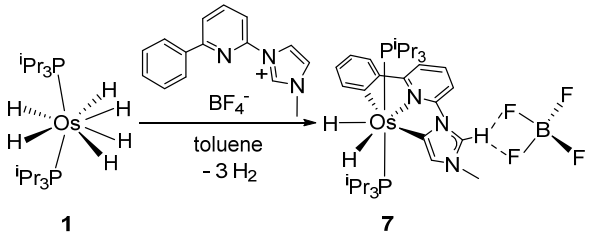
The formation of **6** can be rationalized as a NHC-assisted C-H bond activation of a 2-pyridyl substituent of a NHC ligand. The analysis of the deuterium distribution in the partially deuterated species **6-*d***, generated from **1-*d*** (Scheme 11), reveals that the C-H bond activation of the positions sterically less hindered of the chelate unit (4 of the pyridyl ring, meta of the phenyl substituent, and 6 of the benzimidazolylidene) are mostly deuterated (70-90%) and therefore their activation is kinetically preferred.

A completely different behavior of the salt is observed when the benzimidazolium group is replaced by imidazolium. The lack of protection in the cationic five-membered ring allows its C-H bond activation at an abnormal position. As in the case of 3,5-dimethyl-6-phenyl-2,2'-bipyridine, a C-H bond activation at a peripheral ring of the substrate provokes a C-H bond activation at the other one and the coordination of the central ring. Thus the treatment of toluene solutions of **1** with 1.0 equiv of 3-methyl-1-(6-phenylpyridin-2-yl)-1*H*-imidazolium tetrafluoroborate, under reflux, for 48 h leads to the osmium(IV)-dihydride derivative [OsH_2\{κ^3-*C*,*N*,*C*-(MeIm-py-C_6H_4)\}(P^iPr_3)$_2$]BF_4 (**7**), as a result of the double C-H bond activation of the starting salt (Scheme 12). Complex **7**, which bears a monoanionic C,N,C-pincer ligand with a NHC-unit coordinated in an abnormal fashion, was isolated as an orange-yellow solid in 60% yield.

Scheme 11. Reaction of 1-*d* with 3-Methyl-1-(6-phenylpyridin-2-yl)-1*H*-benzimidazolium Tetrafluoroborate. Values in Blue Denote the Extent of Deuteration (those of marked positions cannot be determined due to overlapping with benzene-d_6)



Scheme 12. Reaction of 1 with 3-Methyl-1-(6-phenylpyridin-2-yl)-1*H*-imidazolium Tetrafluoroborate



The formation of the **7** was confirmed by X-ray diffraction analysis. Figure 5 shows a view of the salt. As expected for the pincer coordination, the Os(C,N,C) skeleton is T-shaped with the metal center situated at the common vertex and C_{aryl}-Os-C_{NHC}, C_{aryl}-Os-N, and N-Os-C_{NHC} angles of 151.44(9)º (C(1)-Os-C(13)), 75.90(8)º (C(1)-Os-N(1)), and 75.58(8)º (N(1)-Os-C(13)), respectively. Thus, the coordination around the osmium atom can be described as a distorted pentagonal bipyramid with axial phosphines (P(1)-Os-P(2) = 161.50(2)º). The Os-C_{aryl} and Os-N(1) distances of 2.107(2) (Os-C(1)) and 2.101(19) Å are similar to those of **5**, whereas the Os-C_{NHC} bond length of 2.093(2) (Os-(13)) Å compares well with those reported for Os-NHC complexes with abnormal coordination.[26b] In addition, it should be mentioned the separation between the hydrogen atom H(12) of the imidazolium group and the fluorine atoms F(2A) and F(4A) of the tetrafluoroborate anion, 2.51(3) and 2.33(3) Å, which are shorter than the sum of the van der Waals radii of hydrogen and fluorine (r_{vdW}(H) = 1.20 Å, r_{vdW}(F) = 1.47 Å),[28] suggesting ion pairing. However, the interactions break apart in dichloromethane at room temperature. According to this, in the ^{1}H NMR spectrum of the compound, the resonance due to H(12) appears at 9.60 ppm as a singlet instead of the expected triplet resulting from the H-F spin coupling. The hydride resonances are observed in the higher field region of the spectrum, at -7.51 and -8.34 ppm. In the ^{13}C{^{1}H} NMR spectrum the signals corresponding to the metalated carbon atoms appear as triplets ($^2J_{C-P}$ = 7.5 Hz) at 174.0 (C(1)) and 155.1 (C(13)) ppm. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 0.4 ppm, as corresponds to equivalent phosphines.

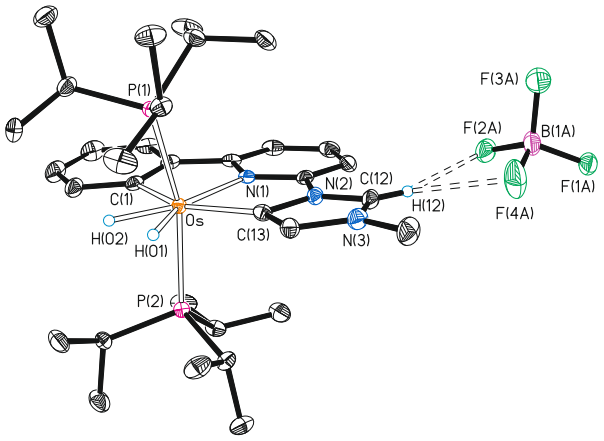
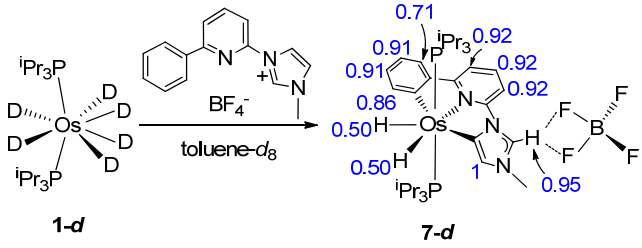


Figure 5. Molecular diagram of complex **7** (ellipsoids shown at 50% probability). All hydrogen atoms (except the hydrides and H(12)) are omitted for clarity. Selected bond distances (Å) and angles (deg): Os-P(1) = 2.3793(6), Os-P(2) = 2.3848(6), Os-C(1) = 2.107(2), Os-C(13) = 2.093(2), Os-N(1) = 2.1031(19), H(12)-F(2A) = 2.51(3), H(12)-F(4A) = 2.33(3); P(1)-Os-P(2) = 161.50(2), N(1)-Os-C(1) = 75.90(8), C(13)-Os-N(1) = 75.58(8), C(13)-Os-C(1) = 151.44(9).

The formation of this new pincer is also a thermodynamically controlled process, like in **5**. The deuterium distribution in the partially deuterated complex **7-*d***, resulting of the reaction of **1-*d*** with the salt (Scheme 13), again indicates that the C-H bond activation of the less sterically hindered positions of the substrate is kinetically favored with regard to the formation of the pincer. In addition, it reveals that the activation of the imidazolium group is faster than that of the phenyl substituent. Thus, in agreement with the formation of **5**, the pincer ligand of **7** appears to be the result of a pyridyl-assisted activation of an abnormal C-H position of the imidazolium group followed by the N-directed *ortho*-CH bond activation of the phenyl substituent.

Scheme 13. Reaction of 1-*d* with 3-Methyl-1-(6-phenylpyridin-2-yl)-1*H*-benzimidazolium Tetrafluoroborate. Values in Blue Denote the Extent of Deuteration

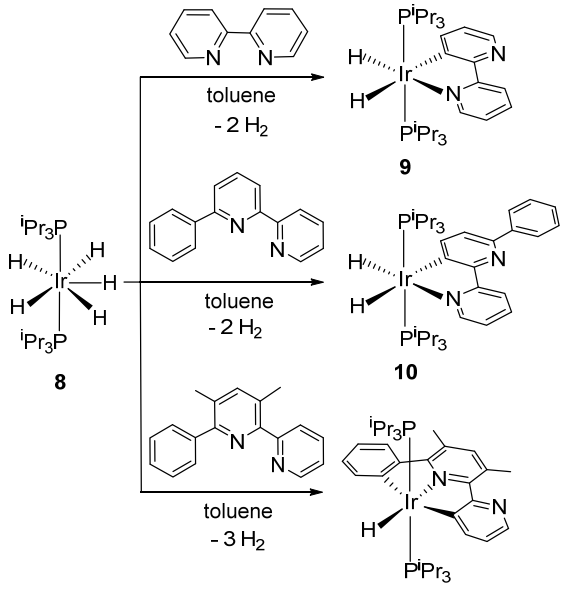


1-*d* **7-*d***

The Reactions Extension to the *d*^{4}-Pentahydride IrH$_5$(P^{i}Pr$_3$)$_2$ (8). Complex **8** has been much less studied than the hexahydride **1**, in particular from the point of view of the C-H bond activation reactions.[16] However, like **1**, it has shown a noticeable capacity to promote cyclometalations.[29] So, in order to know the generality of the observed trend in the reactions of C-H bond activation of two aromatic heterocycles connected by a C(sp^2)-C(sp^2) single bond the reactions shown in Schemes 3, 6 (R= Ph) and 8 were repeated with the pentahydride **8** which bears a different central ion and a different metal center from that of the hexahydride complex **1**.

Treatment of toluene solutions of **8** with 2,2'-bipyridine and 6-phenyl-2,2'-bipyridine, under reflux, for 12 h leads to the iridium(III)-dihydride counterparts of **2** and **3**, complexes IrH$_2${κ^2-*C*,*N*-[C$_5$(R)H$_2$N-py]}(P^{i}Pr$_3$)$_2$ (R = H, (**9**), Ph (**10**)), as a result of the C-H bond activation of one of the heterocycles at position 3 and the *N*-coordination of the other one. Similarly, under the same conditions, the reaction of **8** with 3,5-dimethyl-6-phenyl-2,2'-bipyridine affords the iridium(III)-monohydride counterpart of **5**, compound IrH{κ^3-*C*,*N*,*C*-[C$_5$H$_3$N-(Me)$_2$py-C$_6$H$_4$]}(P^{i}Pr$_3$)$_2$ (**11**), as a result of the *ortho* CH bond activation of the peripheral rings and the *N*-coordination of the central one (Scheme 14).

Scheme 14. Reactions of 8 with 2,2'-Bipyridine, 6-Phenyl-2,2'-bipyridine, and 3,5-Dimethyl-6-phenyl-2,2'-bipyridine

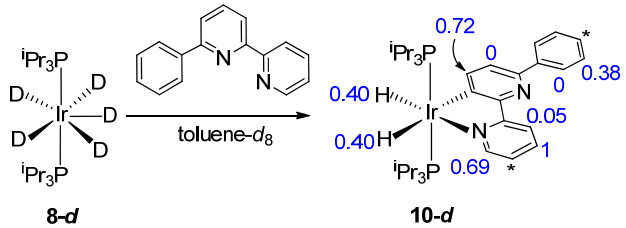


The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra, in benzene-d_6, at room temperature of **9-11** are consistent with the structures proposed in Scheme 14. In agreement with the presence of two inequivalent hydride ligands in **9** and **10**, their ^{1}H NMR spectra contains two doublets of triplets ($^2J_{H\text{-}H} \approx 4.9$ Hz, $^2J_{H\text{-}P} \approx 19$ Hz) about -12.5 and between -21 and -25 ppm, whereas the spectrum of **11** displays a triplet ($^2J_{H\text{-}P} = 20$ Hz) at -16.01 ppm. In the ^{13}C{^{1}H} NMR spectra, the resonances due to the metalated carbon atoms are observed as triplets ($^2J_{C\text{-}P} = 7$-9 Hz) at about 169 ppm for **9** and **10** and at 166.6 (Ph) and 160.3 (py) ppm for **11**. The ^{31}P{^{1}H} NMR spectra contain a singlet around 26 ppm for **9** and **10** and at 3.5 ppm for **11**, as expected for equivalent phosphines.

Complexes shown in Scheme 14 indicate that the iridium-promoted C-H bond activations follow the same thermodynamic pattern as those promoted by osmium. In order to confirm that these reactions are also kinetically similar, we carried out the reaction of 6-phenyl-2,2'-bipyridine with the pentadeuteride complex IrD$_5$(P^{i}Pr$_3$)$_2$ (**8-*d***), which was prepared as **8**[30] by using IrHCl$_2$(P^{i}Pr$_3$)$_2$, Na[BD$_4$], and deuterated solvents. The deuterium distribution in the formed, partially deuterated, derivative **10-*d*** (Scheme 15) reveals that also in this case the

C-H bond activation of the less sterically hindered positions of the rings is kinetically favored with regard to the formation of the chelate and, therefore, the generation of the iridaheterocycle can be rationalized as a pyridyl-assisted process.

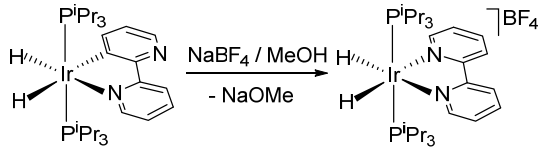
Scheme 15. Reaction of 8-*d* with 6-Phenyl-2,2'-bipyridine. Values in Blue Denote the Extent of Deuteration (those of marked positions cannot be determined due to overlapping with benzene-d_6)



8-*d* **10-*d***

A noticeable difference between the iridium and osmium complexes is the stability of the metalaheterocycle in alcohols, which is revealed by the behavior of complex **9** in methanol and suggests a higher degree of covalency for the osmium(IV)-carbon bonds than for the iridium(III)-carbon bonds. In contrast to the osmium counterpart **2**, the metalated carbon atom of **9** undergoes the addition of a proton of the solvent, at room temperature, to afford a usual N,N-coordinated 2,2'-bipyridine ligand. Thus the stirring of **9** in methanol solutions of Na[BF_4] leads to the salt [$IrH_2\{\kappa^2$-N,N-(bipy)$\}(P^iPr_3)_2$]BF_4 (**12**), which was isolated as a yellow solid in 74% yield (Scheme 16). In agreement with the presence of two equivalent hydride ligands in the cation, the ^{1}H NMR spectrum in dichloromethane shows a hydride resonance at -21.35 ppm, which appears as triplet with a H-P coupling constant of 17.2 Hz, whereas the $^{31}P\{^1H\}$ NMR spectrum displays a singlet at 24.0 ppm that is split into a triplet under off-resonance decoupling conditions.

Scheme 16. Formation of 12



9 **12**

CONCLUDING REMARKS

This study has revealed that polyhydrides of platinum group metals promote the activation of C-H bonds of the rings of 2,2'-bipyridines and related heterocycles, being kinetically preferred the activation of those situated in the sterically less hindered positions. However, the isolated products are the result of the thermodynamic control of the reactions. The observed selectivity is the result of the capture, by the heteroatom of a ring, of the intermediate resulting from the activation of an *ortho*-CH bond of the other ring. This position is sterically hindered and therefore kinetically slow. These results indicate that the cyclometalations, in particular those so-called "*rollover cyclometallations*", are C-H bond activation reactions directed to *ortho* position by means of the previously coordination of a heteroatom only when they are intramolecular processes. To the contrary, the intermolecular reactions are assisted through the chelation of a heteroatom; i.e., the C-H bond activation occurs before the heteroatom coordination.

Cyclometalations are proposed as the key step in a high number of cycles rationalizing catalytic *ortho*-CH functionalization. Because a catalytic cycle represents the reaction pathway with the lowest activation energy and the *ortho*-metalation reaction has higher activation energy than other C-H bond activations in the same ring, the role of the cyclometalation in the selectivity of this catalysis should be carefully reconsidered.

EXPERIMENTAL SECTION

General Information. All reactions were carried out with exclusion of air using Schlenk-tube techniques or in a drybox. Instrumental methods and X-ray details are given in the Supporting Information. In the NMR spectra the chemical shifts (in ppm) are referenced to residual solvent peaks (^{1}H, $^{13}C\{^1H\}$) or external 85% H_3PO_4 ($^{31}P\{^1H\}$), or $CFCl_3$ (^{19}F). Coupling constants J and N ($N = J_{P\text{-}H} + J_{P'\text{-}H}$ for ^{1}H and $N = J_{P\text{-}C} + J_{P'\text{-}C}$ for $^{13}C\{^1H\}$) are given in hertz.

Reaction of $OsH_6(P^iPr_3)_2$ (1) with 2,2'-bipyridine: Preparation of $OsH_3\{\kappa^2$-*C*,*N*-(C_5H_3N-py)$\}(P^iPr_3)_2$ (2). A mixture of **1** (200 mg, 0.387 mmol) and 2,2'-bipyridine (79 mg, 0.503 mmol) in toluene (8 mL) was refluxed for 14 h, giving a dark orange solution. After cooling the mixture to room temperature, the solvent was removed in vacuo, affording an orange residue. Methanol (4 mL) was added and the resulting solution was stored at -20 ºC for 4 h, affording dark orange crystals. Yield: 218 mg (84%). Anal. Calcd for $C_{28}H_{52}N_2OsP_2$: C, 50.28; H, 7.84; N, 4.19. Found: C, 50.79; H, 8.01; N, 4.10. HRMS (electrospray, *m/z*): calculated for $C_{28}H_{52}N_2OsP$ $[M]^+$ 671.3297; found 671.3293. IR (cm^{-1}): ν(Os-H) 2158 (w). ^{1}H NMR (300.13 MHz, toluene-d_8, 298 K): δ 9.43 (d, $^3J_{H\text{-}H}$ = 5.8, 1H, py), 8.70 (dd, $^3J_{H\text{-}H}$ = 7.6, $^4J_{H\text{-}H}$ = 1.8, 1H, activated py), 8.64 (dd, $^3J_{H\text{-}H}$ = 8.1, $^4J_{H\text{-}H}$ = 1.6, 1H, py), 8.40 (dd, $^3J_{H\text{-}H}$ = 4.4, $^4J_{H\text{-}H}$ = 1.8, 1H, activated py), 7.01 (m, 1H, py), 6.76 (dd, $^3J_{H\text{-}H}$ = 7.6, $^3J_{H\text{-}H}$ = 4.4, 1H, activated py), 6.30 (ddd, $^3J_{H\text{-}H}$ = 7.3, $^3J_{H\text{-}H}$ = 5.8, $^4J_{H\text{-}H}$ = 1.6, 1H, py), 1.77 (m, 6H, PC*H*$(CH_3)_2$), 0.91 (dvt, $^3J_{H\text{-}H}$ = 6.9, *N* = 12.6, 18H, PCH(C*H*$_3)_2$), 0.92 (dvt, $^3J_{H\text{-}H}$ = 6.6, *N* = 12.2, 18H, PCH(C*H*$_3)_2$), -8,53 (br, 2H, Os-H), -12.28 (br, 1H, Os-H). ^{1}H NMR (300.13 MHz, toluene-d_8, 193 K, high field region): δ -5.94 (m, 1H, Os-H), -10.87 (m, 1H, Os-H), -12.07 (m, 1H, Os-H). $^{13}C\{^1H\}$ NMR (75.48 MHz, toluene-d_8, 298 K): δ 178.7 (t, $^2J_{C\text{-}P}$ = 6.7, Os-C activated py), 167.2 (s, C py), 161.9 (s, C activated py), 158.5 (s, CH py), 152.5, 140.8 (both s, CH activated py), 133.5, 123.7 (both s, CH, py), 121.9 (s, CH activated py), 121.8 (s, CH, py), 27.5 (vt, *N* = 24.1, P*C*H$(CH_3)_2$), 20.0, 19.8 (both s, PCH(*C*H$_3)_2$). $^{31}P\{^1H\}$ NMR (121.50 MHz, toluene-d_8, 298 K): δ 20.0 (s). $T_{1(min)}$ (ms, OsH, 300 MHz, toluene-d_8, 213 K): 57 ± 6 (-6.01 ppm); 39 ± 4 (-10.82 ppm); 76 ± 6 (-12.12 ppm).

Preparation of $OsD_6(P^iPr_3)_2$ (1-*d*). Methanol-d_4 (1 mL) was slowly added to a mixture of $OsH_2Cl_2(P^iPr_3)_2$ (400 mg, 0.68 mmol) and Na[BD_4] (284.6 mg, 6.8 mmol) in benzene-d_6 (3 mL) until evolution of gas ceased, giving a white suspension. The solvents were removed in vacuo, affording a white residue. Benzene-d_6 was added and the resulting suspension was filtered through Celite. The solution obtained was concentrated to approx. 0.5 mL and methanol-d_4 was added to afford a white solid which was decanted and dried in vacuo. Yield: 309 mg (86%). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 1.78 (m, 6H, PC*H*$(CH_3)_2$), 1.13 (dvt, $^3J_{H\text{-}H}$ = 7.0, *N* = 13.7, 36H, PCH(C*H*$_3)_2$), -9.91 (t, $J_{H\text{-}P}$ = 8.8, 0.68H, corresponding to a 10% of non-deuterated product, OsH). $^{31}P\{^1H\}$ NMR (121.50 MHz, C_6D_6, 298 K): δ 57.7 (s). ^{2}H NMR (46.07 MHz, C_6H_6, 298 K): δ -9.86 (br).

Reaction of $OsD_6(P^iPr_3)_2$ (1-*d*) with 2,2'-bipyridine. The reaction of this substrate with **1-*d*** was performed under the same conditions as the reaction with **1**, starting from **1-*d*** (50 mg, 0.095 mmol), 2,2'-bipyridine (14.5 mg, 0.095 mmol), and toluene-d_8 (1 mL) and precipitation with pentane. The deuterium incorporation was measured in the ^{1}H NMR spectrum of the product in C_6D_6, adding 1,4-dioxane (0.25

equiv) as internal standard. ^{1}H NMR (300,13 MHz, C_6D_6, 298 K): δ 9.47 (s, 0.28H, py), 8.78 (s, 0.31H, activated py), 8.76 (s, 0.90H, py) 8.51 (s, 0.14H, activated py), 7.01 (s, 0.13H, py), 6.82 (s, 0.16H, activated py), 6.30 (s, 0.15H, py), 1.75 (s, 0.93H, PCH(CH_3)$_2$), 0.87 (m, 7.98H, PCH(CH_3)$_2$), -8.53 (br, 1.2H, Os-H), -12.27 (br, 0.55H, Os-H). ^{2}H NMR (61.42 MHz, C_6H_6, 298 K): δ 9.48, 8.78, 8.53, 7.20, 7.02, 6.83, 6.71, 6.34, 1.72, 0.85, -8.39, -12.14 (all br s).

Reaction of $OsH_6(P^iPr_3)_2$ (1) with 6-phenyl-2,2'-bipyridine: Preparation of $OsH_3\{\kappa^2$-*C,N*-[C_5(Ph)H_2N-py]$\}(P^iPr_3)_2$ (3). A mixture of **1** (250 mg, 0.484 mmol) and 6-phenyl-2,2'-bipyridine (112 mg, 0.484 mmol) in toluene (10 mL) was refluxed for 14 h. After cooling the mixture to room temperature, the resulting orange solution was filtered through Celite and the solvent removed under reduced pressure to ca. 0.5 mL. Addition of methanol (3 mL) caused the precipitation of an orange solid, which was washed with further portions of methanol (4 x 3 mL) and dried in vacuo. Yield: 270 mg (75%). Anal. Calcd for $C_{34}H_{56}N_2OsP_2$: C, 54.81; H, 7.58; N, 3.76. Found: C, 54.42; H, 7.59; N, 3.72. HRMS (electrospray, *m/z*) calcd for $C_{34}H_{57}N_2OsP_2$ $[M + H]^+$: 747.3608; found 747.3632. IR (cm^{-1}): ν(Os-H) 1962 (w). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 9.49 (d, $^3J_{H-H}$ = 5.8, 1H, CH py), 8.89 (d, $^3J_{H-H}$ = 7.8, 1H, CH activated py), 8.80 (dd, $^3J_{H-H}$ = 7.8, $^4J_{H-H}$ = 1.6, 1H, CH py), 8.44 (dd, $^3J_{H-H}$ = 8.0, $^4J_{H-H}$ = 1.3, 2H, CH Ph), 7.48 (d, $^3J_{H-H}$ = 7.8, 1H, CH activated py), 7.34 (t, $^3J_{H-H}$ = $^3J_{H-H}$ = 8.0, 2H, CH Ph), 7.23 (m, 1H, CH Ph), 7.08 (t, $^3J_{H-H}$ = 7.8, $^3J_{H-H}$ = 7.4, 1H, CH py), 6.34 (ddd, $^3J_{H-H}$ = 7.4, $^3J_{H-H}$ = 5.8, $^4J_{H-H}$ = 1.6, 1H, CH py), 1.82 (m, 6H, PC*H*(CH_3)$_2$), 0.97 (dvt, $^3J_{H-H}$ = 6.8, *N* = 12.4, 18H, PCH(C*H*$_3$)$_2$), 0.91 (dvt, $^3J_{H-H}$ = 6.8, *N* = 12.4, 18H, PCH(C*H*$_3$)$_2$), -8.41 (br, 2H, Os-H), -12.18 (br, 1H, Os-H). ^{1}H NMR (400 MHz, toluene-d_8, 183 K, high field region): δ -6.27 (dt, $^2J_{H-H}$ = 42.1, $^2J_{H-P}$ = 14.7, 1H, Os-H), -11.30 (ddt, $^2J_{H-H}$ = 42.1, $^2J_{H-H}$ = 12.3, $^2J_{H-P}$ = 12.7, 1H, Os-H), -12.53 (m, 1H, Os-H). $^{13}C\{^1H\}$-apt NMR (75.45 MHz, C_6D_6, 298 K): δ 178.7 (t, $^2J_{C-P}$ = 6.6, Os-C activated py), 166.8 (s, C py), 161.3 (s, C activated py), 158.4 (s, CH py), 153.1 (s, CH activated py), 147.2 (s, C py), 141.6 (s, C Ph), 133.3 (s, CH py), 128.5, 127.1, 125.9 (all s, CH Ph), 121.8, 121.8, (both s, CH py), 119.9 (s, CH, activated py), 27.3 (vt, *N* = 24.0, P*C*H(CH_3)$_2$), 19.8, 19.6 (both s, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6, 298 K): δ 20.6 (s). T_1(min) (ms, OsH, 400 MHz, toluene-d_8, 203 K): 45 ± 5 (-6.26 ppm); 44 ± 4 (-11.31 ppm); 124 ± 12 (-12.52).

Reaction of $OsD_6(P^iPr_3)_2$ (1-*d*) with 6-phenyl-2,2'-bipyridine. The reaction of this substrate with **1-*d*** was performed under the same conditions as the reaction with **1**, starting from **1-*d*** (50 mg, 0.095 mmol), 6-phenyl-2,2'-bipyridine (22.2 mg, 0.095 mmol), and toluene-d_8 (1 mL) and precipitation with pentane. The deuterium incorporation was measured in the ^{1}H NMR spectrum of the product in C_6D_6, adding 1,4-dioxane (0.25 equiv) as internal standard. ^{1}H NMR (300,13 MHz, C_6D_6, 298 K): δ 9.48 (s, 0.15H, CH py), 8.87 (s, 0.13H, CH activated-py), 8.69 (s, 1H, CH py), 8.43 (s, 1.40H, CH Ph), 7.48 (s, 0.68H, CH activated-py), 7.35 (s, 0.52H, CH Ph), 6.34 (s, 0.09H, CH py) 1.35 (s, 0.59H, PCH(CH_3)$_2$), 0.87 (m, 4.31H, PCH(CH_3)$_2$), -8.05 (br, 0.75H, Os-H), -12.27 (br, 0.33H, Os-H). ^{2}H NMR (61.42 MHz, C_6H_6, 298 K): δ 9.42, 8.98, 8.16, 6.53, 1.75, 0.97, -8.39, -12.05 (all br s).

Reaction of $OsH_6(P^iPr_3)_2$ (1) with 6-methyl-2,2'-bipyridine: Preparation of $OsH_3\{\kappa^2$-*C,N*-[C_5(Me)H_2N-py]$\}(P^iPr_3)_2$ (4). A mixture of **1** (200 mg, 0.387 mmol) and 6-methyl-2,2'-bipyridine (79 µL, 0.503 mmol) in toluene (8 mL) was refluxed for 14 h, giving a dark orange suspension. After cooling the mixture was cooled to room temperature, the solvent was removed in vacuo, affording an orange residue. Addition of cold methanol (3 mL) caused the precipitation of an orange solid that was washed with further portions of cold methanol (2 x 3 mL) and dried in vacuo. Yield: 226.8 mg (86%). Anal. Calcd. for $C_{29}H_{54}N_2OsP_2$: C, 51.00; H, 7.97; N, 4.10. Found: C, 51.18; H, 8.33; N, 4.04. HRMS (electrospray, *m/z*) calculated for $C_{29}H_{55}N_2OsP_2$ $[M^+ + H]$: 685.3451; found: 685.3433. IR (cm^{-1}): ν(Os-H) 2117 (w). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 9.49 (d, $^3J_{H-H}$ = 5.8, 1H, CH py), 8.76 (m, 2H, py + Mepy), 7.01 (t, $^3J_{H-H}$ = 7.31, 1H, CH py), 6.83 (d, $^3J_{H-H}$ = 7.6, 1H, CH Mepy), 6.30 (m, 1H, CH py), 2.61 (s, 3H, CH_3), 1.82 (m, 6H, PC*H*(CH_3)$_2$), 0.97 (dvt, $^3J_{H-H}$ = 6.6, *N* = 12.9, 18H, PCH(C*H*$_3$)$_2$), 0.92 (dvt, $^3J_{H-H}$ = 6.6, *N* = 12.7, 18H, PCH(C*H*$_3$)$_2$), -8.49 (br, 2H, OsH), -12.23 (br, 1H, OsH). ^{1}H NMR (300.13 MHz, toluene-d_8, 193 K, high field region): δ -5.92 (m, 1H, Os-H), -10.84 (m, 1H, Os-H), -12.12 (tt, $^2J_{H-H}$ = 7.1, $^2J_{H-P}$ = 15.2, 1H, Os-H). $^{13}C\{^1H\}$ NMR (75.48 MHz, toluene-d_8, 298 K): δ 173.8 (t, $^2J_{C-P}$ = 6.8, Os-C Mepy), 167.3 (s, C py), 161.0 (s, C Mepy), 158.6 (s, CH py), 153.1 (s, CH Mepy), 148.0 (s, C Mepy), 133.3 (s, CH, py), 123.7 (s, CH Mepy), 121.8, 121.7 (both s, CH py), 27.6 (vt, *N* = 24.0, P*C*H(CH_3)$_2$), 24.4 (s, CH_3), 20.1 and 19.8 (both s, PCH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (121.50 MHz, toluene-d_8, 298 K): δ 20.3 (s). T_1(min) (ms, OsH, 300 MHz, toluene-d_8, 213 K): 89 ± 9 (-12.16); the T_1(min) values of the resonances at -5.92 ppm and -10.84 ppm could not be calculated due to the broadness of them.

Reaction of $OsH_6(P^iPr_3)_2$ (1) with 3,5-dimethyl-6-phenyl-2,2'-bipyridine: Preparation of $OsH_2\{\kappa^3$-*C,N,C*-[C_5H_3N-(Me)$_2$py-C_6H_4]$\}(P^iPr_3)_2$ (5). A solution of **1** (100 mg, 0.193 mmol) and 3,5-dimethyl-6-phenyl-2,2'-bipyridine (50.4 mg, 0.193 mmol) in toluene (5 mL) was refluxed for 14 h. The resulting mixture was cooled to room temperature, filtered through Celite, and concentrated to approx. 0.5 mL. Methanol (4 mL) was added to afford an orange solid, which was washed with further portions of methanol (3 x 2 mL) and dried in vacuo. Yield: 126 mg (84%). Anal. Calcd for $C_{36}H_{58}N_2OsP_2$: C, 56.08; H, 7.58; N, 3.63. Found: C, 56.45; H, 7.49; N, 4.09. HRMS (electrospray, *m/z*) calcd for $C_{36}H_{58}N_2OsP_2$ $[M^+]$: 773.3765; found: 773.3759. IR (cm^{-1}): ν(Os-H) 2190 (w). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 8.52 (dd, $^3J_{H-H}$ = 4.2, $^4J_{H-H}$ = 1.5, 1H, py), 8.46 (dd, $^3J_{H-H}$ = 7.4, $^4J_{H-H}$ = 1.5, 1H, py), 8.41 (d, $^3J_{H-H}$ = 7.0, 1H, Ph), 8.07 (d, $^3J_{H-H}$ = 8.0, 1H, Ph), 7.07 (m, 2H, Ph), 6.89 (s, 1H, Me$_2$py), 6.70 (dd, $^3J_{H-H}$ = 7.4, $^3J_{H-H}$ = 4.2, 1H, py), 3.14 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 2.00 (m, 6H, PC*H*(CH_3)$_2$), 0.82 (dvt, $^3J_{H-H}$ = 6.9, *N* = 12.0, 36H, PCH(CH_3)$_2$), -8.36 (dt, $^2J_{H-H}$ = 14.4, $^2J_{H-P}$ = 14.4, 1H, Os-H), -8.66 (dt, $^2J_{H-H}$ = 14.4, $^2J_{H-P}$ = 14.4, 1H, Os-H). $^{13}C\{^1H\}$-apt NMR (75.48 MHz, C_6D_6, 298 K): δ 178.7 (t, $^2J_{C-P}$ = 7.1, Os-C Ph), 171.8 (t, $^2J_{C-P}$ = 6.8, Os-C py), 167.9 (s, C py), 164.2 (s, C Me$_2$py), 161.6 (s, C Me$_2$py), 151.0, (s, CH py), 148.9, (s, C Ph), 146.2 (s, CH Ph), 145.0 (s, CH Me$_2$py), 140.2 (s, CH py), 128.0 (s, CH py), 125.2 (s, C Me$_2$py), 122.9 (s, CH py), 119.4 (s, CH Ph), 26.8 (vt, *N* = 24.2 Hz, PCH(CH_3)$_2$), 23.3, 22.1 (both s, CH_3), 19.3, 19.2 (both s, PCH(*C*H$_3$)$_2$). Two resonances, one of a C Me$_2$py and a CH py, are masked by that of the solvent. $^{31}P\{^1H\}$ NMR (121.50 MHz, C_6D_6, 298 K): δ -0.8 (s).

Reaction of $OsD_6(P^iPr_3)_2$ (1-*d*) with 3,5-dimethyl-6-phenyl-2,2'-bipyridine. The reaction of this substrate with **1-*d*** was performed under the same conditions as the reaction with **1**, starting from **1-*d*** (40 mg, 0.076 mmol), 3,5-dimethyl-6-phenyl-2,2'-bipyridine (20 mg, 0.076mmol), and toluene-d_8 (1 mL) and precipitation with pentane. The deuterium incorporation was measured in the ^{1}H NMR spectrum of the product in C_6D_6, adding 1,4-dioxane (0.25 equiv) as internal standard. ^{1}H NMR (300,13 MHz, C_6D_6, 298 K): δ 8.51 (s, 0.03H, py), 8.45 (s, 0.03H, py), 8.40 (s, 0.03H, Ph), 8.07 (s, 0.23H, Ph), 7.07 (s, 0.04H, Ph), 6.88 (s, 0.45H, Me$_2$py), 6.69 (s, 0.03H, py), 3.15 (s, 0.95H, CH_3), 2.47 (s, 1.46H, CH_3), 1.94 (s, 0.19H, PCH(CH_3)$_2$), 0.75 (br, 1.08H, PCH(CH_3)$_2$), -8.43 (m, 0.31 H, Os-H), -8.72 (m, 0.34. H, Os-H). ^{2}H NMR (61.42 MHz, C_6H_6, 298 K): δ 8.73, 8.36, 7.42, 7.32, 6.98, 3.34, 2,17, 0.99, -8.07, -8.37 (all br s).

Reaction of $OsH_6(P^iPr_3)_2$ (1) with 3-Methyl-1-(6-Phenylpyridin-2-yl)-1*H*-benzimidazolium Tetrafluoroborate: Preparation of $OsH_3\{\kappa^2$-*C,C*-[MeBzim-C_5(Ph)H_2N]$\}(P^iPr_3)_2$ (6). A mixture of **1** (100 mg, 0.193 mmol) and 3-methyl-1-(6-phenylpyridin-2-yl)-1*H*-benzimidazolium tetrafluoroborate (79 mg, 0.212 mmol) in 5 mL of toluene was refluxed for 4 h in the presence of 10 equivalents of NEt_3 (270 µL, 1.93 mmol). The resulting mixture was cooled to room temperature, filtered through Celite, and the solution thus obtained concentrated to approx. 0.5 mL. Methanol was added to afford a white solid, which was washed with further portions of methanol (4 x 3 mL) and dried in vacuo. Yield: 62 mg (40%). Anal. Calcd for $C_{37}H_{59}N_3OsP_2$: C, 55.68; H, 7.45; N, 5.26. Found: C, 55.62; H, 6.88; N, 5.43. HRMS (electrospray, *m/z*): calcd for $C_{37}H_{59}N_3OsP_2$ $[M^+ + H]$ 798.3843; found 798.3865. IR (cm^{-1}): ν(Os-H) 2073 (w). ^{1}H NMR (400 MHz, toluene-d_8, 298 K): δ 9.50 (d, $^3J_{H-H}$ = 7.9, 1H, BzIm), 8.69 (d, $^3J_{H-H}$ = 7.5, 1H, py), 8.35 (m, 2H, Ph), 7.30 (m, 3H, py + Ph), 7.16 (m, 2H, BzIm + Ph), 7.08 (m, 1H, BzIm), 6.89 (d, $^3J_{H-H}$ = 7.8, 1H, BzIm), 3.90 (s, 3H, CH_3), 1.74 (m, 6H, PCH(CH_3)$_2$), 0.92 (dvt, $^3J_{H-H}$

= 6.5, *N* = 12.5, 18H, PCH(CH_3)$_2$), 0.80 (dvt, $^3J_{H-H}$ = 6.5, *N* = 12.5, 18H, PCH(CH_3)$_2$), -8.37 (br, 1H, Os-H), -9.89 (br, 2H, Os-H). ^{1}H NMR (400 MHz, toluene-d_8, high field region, 223 K): δ -8.32 (tt, $^2J_{H-H}$ = 7.1, $^2J_{H-P}$ = 16.7, 1H, Os-H), -9.81 (dt, $^2J_{H-H}$ = 7.1, $^2J_{H-P}$ = 13.7, 2H, Os-H). ^{13}C{^{1}H}-apt NMR (75.48 MHz, C_6D_6, 298 K): δ 201.8 (t, $^2J_{C-P}$ = 5.5, Os-C BzIm), 163.2 (s, C py), 154.2 (s, CH py), 150.3 (t, $^2J_{C-P}$ = 6.7, Os-C py), 147.2 (s, C py), 142.0 (s, C Ph), 137.2, 133.9 (both s, C BzIm), 128.9, 127.2, 126.2 (all s, CH Ph), 122.8 (s, CH BzIm), 122.2 (s, CH BzIm), 116.6 (s, CH py), 113.8, 108.7 (both s, CH BzIm), 35.7 (s, CH_3), 28.0 (vt, *N* = 25.2 Hz, PCH(CH_3)$_2$), 19.8, 19.7 (both s, PCH(CH_3)$_2$). ^{31}P{^{1}H} NMR (121.50 MHz, C_6D_6, 298 K): δ 25.9 (s). T_1(min) (ms, OsH, 400 MHz, toluene-d_8, 238 K): 141 ± 14 (-8.32 ppm); 118 ± 12 (-9.81 ppm).

Reaction of OsD$_6$(P^{i}Pr$_3$)$_2$ with 3-Methyl-1-(6-phenylpyridin-2-yl)-1*H*-benzimidazolium Tetrafluoroborate. The reaction of this salt with **1-*d*** was performed under the same conditions as the reaction with **1**, starting from **1-*d*** (50 mg, 0.095 mmol), 3-methyl-1-(6-phenylpyridin-2-yl)-1*H*-benzoimidazolium tetrafluroborate (35 mg, 0.095 mmol), and toluene-d_8 (1 mL) and precipitation with diethyl ether. The deuterium incorporation was measured in the ^{1}H NMR spectrum of the product in C_6D_6, adding 1,4-dioxane (0.25 equiv) as internal standard. ^{1}H NMR (300,13 MHz, C_6D_6, 298 K): δ 9.59 (s, 1H, BzIm), 8.76 (s, 0.20H, py), 8.43 (s, 1.98H, Ph), 7.41 (s, 1H, py), 7.31 (s, 0.43H, Ph), 7.05 (s, 0.11H, BzIm), 6.92 (s, 0.94H, BzIm), 3.89 (s, 2.94H, CH_3), 1.69 (br, 1.29H, PCH(CH_3)$_2$), 0.84 (br, 9.8H, PCH(CH_3)$_2$), -8.36 (br, 0.70H, Os-H), -9.91 (br, 1.52H, Os-H). ^{2}H NMR (61.42 MHz, C_6H_6, 298 K): δ 8.83, 7.46, 7.30, 7.17, 1.82, 0.94, -9.52 (all br s).

Reaction of OsH$_6$(P^{i}Pr$_3$)$_2$ with 3-Methyl-1-(6-phenylpyridin-2-yl)-1*H*-imidazolium Tetrafluoroborate: Preparation of [OsH$_2${κ^3-*C*,*N*,*C*-(MeIm-py-C$_6$H$_4$)}(P^{i}Pr$_3$)$_2$]BF$_4$ (7). A mixture of **1** (200 mg, 0.387 mmol) and 3-methyl-1-(6-phenylpyridin-2-yl)-1*H*-imidazolium tetrafluoroborate (125 mg, 0.387 mmol) in toluene (8 mL) was refluxed for 48 h. The resulting suspension was cooled to room temperature and an orange-yellow solid was decanted. This solid was washed with diethyl ether (4 x 3 mL) and dried in vacuo. Yield: 194 mg (60%). Anal. Calcd for $C_{33}H_{56}BF_4N_3OsP_2$: C, 47.53; H, 6.77; N, 5.04. Found: C, 47.21; H, 6.95; N, 4.93. HRMS (electrospray, *m*/*z*) calculated for $C_{33}H_{55}N_3OsP_2$ [M - H]$^+$: 748.3560; found: 748.3589. IR (cm^{-1}): ν(Os-H) 1905 (w), ν(BF_4) 1055 (vs). ^{1}H NMR (300.13 MHz, CD_2Cl_2, 298 K): δ 9.60 (s, 1H, im), 8.02 (m, 1H, Ph), 7.84 (m, 3H, py), 7.80 (dd, $^3J_{H-H}$ = 7.6, $^4J_{H-H}$ = 1.8, 1H, Ph), 7.07-6.95 (m, 2H, Ph), 6.55 (s, 1H, im), 4.00 (s, 3H, CH_3), 1.93 (m, 6H, PC*H*(CH$_3$)$_2$), 0.80 (dvt, $^3J_{H-H}$ = 6.8, *N* = 12.9, 18H, PCH(C*H*$_3$)$_2$), 0.75 (dvt, $^3J_{H-H}$ = 6.9, *N* = 12.6, 18H, PCH(C*H*$_3$)$_2$), -7.51 (dt, $^2J_{H-H}$ = 24.1, $^2J_{H-P}$ = 14.7, 1H, Os-H), -8.34 (dt, $^2J_{H-H}$ = 24.1, $^2J_{H-P}$ = 13.5, 1H, Os-H). ^{13}C{^{1}H}-apt NMR (75.48 MHz, CD_2Cl_2, 298 K): δ 174.0 (t, $^2J_{C-P}$ = 7.5, Os-C Ph), 166.8 (s, C py), 155.1 (t, $^2J_{C-P}$ =7.5, Os-C im), 151.0 (s, C py), 146.1 (s, CH Ph), 145.4 (s, C Ph), 138.2 (s, CH py), 134.2 (s, CH im, inferred from the HSQC spectrum), 131.1 (s, CH Ph), 127.6 (s, CH im), 126.0, 120.8 (both s, CH Ph), 115.0, 105.7 (both s, CH py), 36.2 (s, CH_3), 26.5 (vt, *N* = 25.5 Hz, P*C*H(CH$_3$)$_2$), 19.0, 18.9 (both s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.50 MHz, CD_2Cl_2, 298 K): δ 0.4 (s). ^{19}F{^{1}H} NMR (282.38 Hz, CD_2Cl_2, 298 K): δ -151.9 (s). The abnormal coordination of the NHC moiety has been confirmed by means of a NOE experiment.

Reaction of OsD$_6$(P^{i}Pr$_3$)$_2$ (1-*d*) with 3-Methyl-1-(6-phenylpyridin-2-yl)-1*H*-imidazolium tetrafluroborate. The reaction of this salt with **1-*d*** was performed under the same conditions as the reaction with **1**, starting from **1-*d*** (50 mg, 0.095 mmol), 3-methyl-1-(6-phenylpyridin-2-yl)-1*H*-imidazolium tetrafluroborate (30 mg, 0.095 mmol) and toluene-d_8 (1 mL) and precipitation with diethyl ether. The deuterium incorporation was measured in the ^{1}H NMR spectrum of the product in C_6D_6, adding 1,4-dioxane (0.25 equiv) as internal standard. ^{1}H NMR (300,13 MHz, CD_2Cl_2, 298 K): δ 9.67 (s, 0.05H, NHCN), 8.13 (s, 0.29H, CH Ph), 7.89 (s, 0.24H, CH py), 7.82 (s, 0.14H, CH Ph), 7.18 (s, 0.17H, CH Ph), 3.97 (s, 0.33H, CH_3), 0.87 (m, 1.67H, PCH(CH_3)$_2$), -7.55 (br, 0.5H, Os-H), -8.37 (br, 0.5H, Os-H). ^{2}H NMR (61.42 MHz, C_6H_6, 298 K): δ 8.04, 7.91, 7.13, 6.60, 1.92, 0.77 (all br s).

Preparation of IrD$_5$(P^{i}Pr$_3$)$_2$ (8-*d*). Methanol-d_4 (1 mL) was slowly added to a mixture of IrHCl$_2$(P^{i}Pr$_3$)$_2$ (400 mg, 0.68 mmol) and Na[BD_4] (284.6 mg, 6.8 mmol) in benzene-d_6 (3 mL), until evolution of gas ceased, giving a white suspension. The solvents were removed in vacuo, affording a white residue. Benzene-d_6 was added and the resulting suspension was filtered through Celite. The solution obtained concentrated to approx. 0.5 mL and methanol-d_4 was added to afford a white solid which was decanted and dried in vacuo. Yield: 298 mg (84%).^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 1.72 (m, 6H, PCH(CH_3)$_2$), 1.13 (dvt, $^3J_{H-H}$ = 6.8, *N* = 13.7, 36H, PCH(CH_3)$_2$), -10.85 (t, $^2J_{H-P}$ = 12.4, 0.27H, corresponding to a 5% of non-deuterated product, Ir-H). ^{31}P{^{1}H} NMR (121.50 MHz, C_6D_6, 298 K): δ 45.7 (s). ^{2}H NMR (46.07 MHz, C_6H_6, 298 K): δ -10.78 (br).

Reaction of IrH$_5$(P^{i}Pr$_3$)$_2$ (8) with 2,2'-bipyridine: Preparation of IrH$_2${κ^2-*C*,*N*-(C$_5$H$_3$N-py)}(P^{i}Pr$_3$)$_2$ (9). A mixture of **8** (200 mg, 0.386 mmol) and 2,2'-bipyridine (603 mg, 3.863 mmol) in toluene (8 mL) was refluxed for 14 h. After cooling the resulting dark yellow solution to room temperature, it was filtered through Celite and the solvent removed in vacuo, affording a yellowish residue with was extracted into pentane (4 x 10 mL). The yellow solution was concentrated to approximately 3 mL to afford a yellow solid, which was washed with further portions of pentane (6 x 3 mL) and dried in vacuo. Yield: 72 mg (28%). Although the reaction is quantitative, the isolated yield is low due to the solubility of the complex in pentane. Anal. Calcd for $C_{28}H_{51}IrN_2P_2$: C, 50.20; H, 7.67; N, 4.18. Found: C, 50.22; H, 7.63; N, 4.19. HRMS (electrospray, *m*/*z*) calcd for $C_{28}H_{52}IrN_2P_2$ [M + H]$^+$: 671.3231; found 671.3228. IR (cm^{-1}): ν(Ir-H) 2211 (m), 1997 (m). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 9.09 (d, $^3J_{H-H}$ = 5.5, 1H, CH py), 8.78 (d, $^3J_{H-H}$ = 8.1, 1H, CH py), 8.56 (m, 2H, CH activated py), 7.11 (m, 1H, CH py), 6.90 (m, 1H, CH activated py), 6.38 (m, 1H, CH py), 1.93 (m, 6H, PC*H*(CH$_3$)$_2$), 0.99 (dvt, $^3J_{H-H}$ = 6.6, *N* = 13.5, 18H, PCH(C*H*$_3$)$_2$), 0.92 (dvt, $^3J_{H-H}$ = 6.8, *N* = 13.6, 18H, PCH(C*H*$_3$)$_2$), -12.48 (dt, $^2J_{H-H}$ = 4.9, $^2J_{H-P}$ = 20.0, 1H, Ir-H), -21.13 (dt, $^2J_{H-H}$ = 4.9, $^2J_{H-P}$ = 18.5, 1H, Ir -H). ^{13}C{^{1}H}-apt NMR (75.45 MHz, C_6D_6, 298 K): δ 168.8 (s, C py), 168.6 (t, $^2J_{C-P}$ = 7.1, Ir-C activated py), 165.9 (s, C activated py), 157.6 (s, CH, py), 150.7, 141.6, (both s, CH, activated py), 134.6 (s, CH, py), 123.4 (s, CH, activated py), 122.15 (s, CH py), 26.8 (vt, *N* = 27.4, P*C*H(CH$_3$)$_2$), 20.1, 19.7 (both s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 298 K): δ 26.1 (s).

Reaction of IrH$_5$(P^{i}Pr$_3$)$_2$ (8) with 6-phenyl-2,2'-bipyridine: Preparation of IrH$_2${κ^2-*C*,*N*-[C$_5$(Ph)H$_2$N-py]}(P^{i}Pr$_3$)$_2$ (10). A mixture of **8** (200 mg, 0.386 mmol) and 6-phenyl-2,2'-bipyridine (90.0 mg, 0.386 mmol) in toluene (8 mL) was refluxed for 14 h. After this time, the resulting yellow dark solution was cooled to room temperature, filtered through Celite, and the solvent removed in vacuo obtaining a yellowish residue. Pentane (4 mL) caused the precipitation of a yellow solid, which was washed with further portions of pentane (6 x 3 mL) and dried in vacuo Yield: 216 mg (75%). Anal. Calcd. for $C_{34}H_{55}IrN_2P_2$: C, 54.74; H, 7.43; N, 3.75. Found: C, 54.76; H, 7.45; N, 3.76. HRMS (electrospray, *m*/*z*) calcd for $C_{34}H_{56}IrN_2P_2$ [M + H]$^+$: 747.3544; found 747.3549. IR (cm^{-1}): ν(Ir-H) 2192 (m), 1918 (m). ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 9.11 (d, $^3J_{H-H}$ = 5.5, 1H, CH py), 8.81 (d, $^3J_{H-H}$ = 8.0, 1H, CH py), 8.64 (d, $^3J_{H-H}$ = 7.4, 1H, CH activated py), 8.45 (d, $^3J_{H-H}$ = 7.6, 2H, CH Ph), 7.54 (d, $^3J_{H-H}$ = 7.4, 1H, CH activated py), 7.35 (t, $^3J_{H-H}$ = 7.6, 2H, CH Ph), 7.21 (m, 1H, CH py), 7.16 (m, 1H, CH Ph), 6.43 (t, $^3J_{H-H}$ = 6.4, 1H, CH py), 1.93 (m, 6H, PC*H*(CH$_3$)$_2$), 0.99 (dvt, $^3J_{H-H}$ = 6.6, *N* = 13.5, 18H, PCH(C*H*$_3$)$_2$), 0.95 (dvt, $^3J_{H-H}$ = 8.0, *N* = 13.0, 18H, PCH(C*H*$_3$)$_2$), -12.39 (dt, $^2J_{H-H}$ = 4.8, $^2J_{H-P}$ = 20.0, 1H, Ir-H), -21.11 (dt, $^2J_{H-H}$ = 4.8, $^2J_{H-P}$ = 18.5, 1H, Ir-H). ^{13}C{^{1}H}-apt NMR (75.45 MHz, C_6D_6, 298 K): δ 168.7 (t, $^2J_{C-P}$ = 7.2, C-Ir activated py), 168.6 (s, C activated py), 165.6 (s, C activated py), 157.7 (s, CH py), 151.7 (s, CH activated py), 148.3 (s, C py), 142.1 (s, C Ph), 134.6 (s, CH py), 128.8, 127.5, 126.3 (all s, CH Ph), 122.4 (s, CH py), 122.3 (s, CH py), 119.9 (s, CH activated py), 26.9 (vt, *N* = 27.4, P*C*H(CH$_3$)$_2$), 20.1, 19.7 (both s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 298 K): δ 26.5 (s).

Reaction of IrD$_5$(P^{i}Pr$_3$)$_2$ (8-*d*) with 6-phenyl-2,2'-bipyridine. The reaction of this substrate with **8-*d*** was performed under the same conditions as the reaction with **8**, but starting from **8-*d*** (50 mg, 0.095 mmol), 6-phenyl-2,2'-bipyridine (22 mg, 0.095 mmol) and toluene-d_8

(1 mL) and precipitation with pentane. The deuterium incorporation was measured in the ^{1}H NMR spectrum of the product in C_6D_6, adding 1,4-dioxane (0.25 equiv) as internal standard. ^{1}H NMR (300,13 MHz, C_6D_6, 298 K): δ 9.11 (m, 0.31H, CH py), 8.82 (m, 1H, CH py), 8.63 (m, 0.28H, CH activated-py), 8.46 (m, 2H, CH Ph), 7.55 (m, 1H, CH activated-py), 7.35 (m, 1.20H, CH Ph), 1.89 (m, 6H, PCH(CH_3)$_2$), 0.94 (m, 8.58H, PCH(CH_3)$_2$), -12.39 (m, 0.65H, Os-H), -21.11 (m, 0.56H, Os-H). ^{2}H NMR (61.42 MHz, C_6H_6, 298 K): δ 9.10, 8.63, 7.23, 6.43, 0.88, -12.37, -21.04 (all br s).

Reaction of IrH$_5$(P^{i}Pr$_3$)$_2$ (8) with 3,5-Dimethyl-6-phenyl-2,2'-bipyridine: Preparation of IrH{κ^3-*C*,*N*,*C*-[C$_5$H$_3$N-(Me)$_2$py-C$_6$H$_4$]}(P^{i}Pr$_3$)$_2$ (11). A solution of **8** (200 mg, 0.386 mmol) and 3,5-dimethyl-6-phenyl-2,2'-bipyridine (104 mg, 0.400 mmol) in toluene (8 mL) was refluxed for 14 h. The resulting mixture was cooled to room temperature, filtered through Celite, and concentrated to approx. 0.5 mL. Pentane (10 mL) was added to afford a yellow solid, which was washed with further portions of pentane (3 x 4 mL) and dried in vacuo. Yield: 262 mg (88%). Anal. Calcd for $C_{36}H_{57}N_2IrP_2$: C, 56.01; H, 7.44; N, 3.63. Found: C, 56.25; H, 7.43; N, 3.63. HRMS (electrospray, *m*/*z*) calcd for $C_{36}H_{58}N_2IrP_2$ [M + H]$^+$: 773.3701; found: 773.3679. IR (cm^{-1}): ν(Ir-H) 2188 (m). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 8.59 (m, 1H, py), 8.27 (d, $^3J_{H-H}$ = 7.4, 1H, py), 8.16 (m, 1H, Ph), 8.06 (m, 1H, Ph), 7.19 (m, 2H, Ph), 7.00 (s, 1H, Me$_2$py), 6.84 (dd, $^3J_{H-H}$ = 7.4, $^3J_{H-H}$ = 4.5, 1H, py), 3.18 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 2.09 (m, 6H, PC*H*(CH_3)$_2$), 0.88 (m, 36H, PCH(CH_3)$_2$), -16.01 (t, $^2J_{H-P}$ = 20.0, 1H, Ir-H). ^{13}C{^{1}H}-apt NMR (75.48 MHz, C_6D_6, 298 K): δ 172.2 (s, C py), 166.6 (t, $^2J_{C-P}$ = 9.1, Ir-C Ph), 164.5 (s, C Me$_2$py), 161.7 (s, C Me$_2$py), 160.3 (t, $^2J_{C-P}$ = 9.0, Ir-C py), 152.4 (s, C Ph), 147.9 (s, CH py), 145.1 (s, CH Me$_2$py), 142.3 (s, CH Ph), 172.2 (s, CH py), 129.2 (s, C Me$_2$py), 127.9 (s, CH Ph), 126.5 (s, C Me$_2$py), 122.3 (s, CH py), 120.3 (s, CH Ph), 26.2 (vt, *N* = 27.4, P*C*H(CH_3)$_2$), 22.9, 21.7 (both s, CH_3), 19.0, 18.9 (both s, PCH(*C*H_3)$_2$). ^{31}P{^{1}H} NMR (121.50 MHz, C_6D_6, 298 K): δ 3.5 (s).

Reaction of IrH$_2${κ^2-*C*,*N*-(C$_5$H$_3$N-py)}(P^{i}Pr$_3$)$_2$ (9) with MeOH: Formation of [IrH$_2${κ^2-*N*,*N*-(bipy)}(P^{i}Pr$_3$)$_2$]BF$_4$ (12). A mixture of **9** (50 mg, 0.075 mmol) and Na[BF_4] (10 mg, 0.09 mmol) in methanol (8 mL) was stirred at room temperature for 30 min. After that time, the solvent was removed to ca. 0.5 mL and diethyl ether was added to afford a pale-yellow solid, which was washed with further portions of ether (2 × 3 mL) and dried in vacuo. Yield: 42 mg (74%). Anal. Calcd for $C_{28}H_{52}BF_4IrN_2P_2$: C, 44.39; H, 6.92; N, 3.70. Found: C, 44.38; H, 6.92; N, 3.72. HRMS (electrospray, *m*/*z*) calcd for $C_{28}H_{52}IrN_2P_2$ [M]$^+$: 671.3231; found 671.3223. IR (cm^{-1}): ν(Ir-H) 2212 (m), 2158 (m), ν(BF_4) 1046 (s). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 9.09 (d, $^3J_{H-H}$ = 6.0, 2H, CH py), 8.43 (d, $^3J_{H-H}$ = 7.9, 2H, CH py), 8.09 (t, $^3J_{H-H}$ = 7.9, 2H, CH py), 7.47 (dd, $^3J_{H-H}$ = 6.0, $^3J_{H-H}$ = 7.9, 2H, CH py), 1.95 (m, 6H, PC*H*(CH_3)$_2$), 0.95 (dvt, $^3J_{H-H}$ = 6.8, *N* = 14.0, 36H, PCH(C*H*$_3$)$_2$), -21.35 (t, $^2J_{H-P}$ = 17.2, 2H, Ir-H). ^{13}C{^{1}H}-apt NMR (75.45 MHz, CD_2Cl_2, 298 K): δ 157.5 (s, C py), 155.9, 138.0, 127.5, 124.8 (all s, CH py), 26.2 (vt, *N* = 27.9, P*C*H(CH_3)$_2$), 19.7 (s, PCH(*C*H_3)$_2$). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 298 K): δ 24.0 (s). ^{19}F{^{1}H NMR (282.38 Hz, CD_2Cl_2, 298 K): δ -153.1 (s).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications web site.

Experimental details, crystallographic data, and NMR spectra (PDF)

Accession codes. CCDC 1987590-1987594 contain the crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing da-ta_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033

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Notes

The authors declare no competing financial interest.

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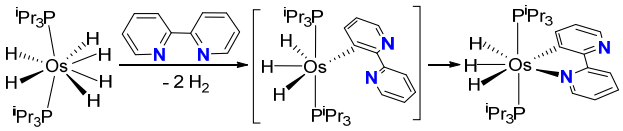

Assisted, no directed, "rollover cyclometalation"