Azolium Control of the Osmium-Promoted Aromatic C–H Bond Activation in 1,3-Disubstituted Substrates

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ABSTRACT: The hexahydride complex OsH6(PiPr3)2 promotes the C–H bond activation of the 1,3-disubstituted phenyl group of the [BF4]− and [BPh4]− salts of the cations 1-(3-(isoquinolin-1-yl)phenyl)-3-methylimidazolium and 1-(3-(isoquinolin-1-yl)phenyl)-3-methylbenzimidazolium. The reactions selectively afford neutral and cationic trihydride-osmium(IV) derivatives bearing κ2-C,N- or κ2-C,C-chelating ligands, a cationic dihydride-osmium(IV) complex stabilized by a κ3-C,C,N-pincer group, and a bimetallic hexahydride formed by two trihydride-osmium(IV) fragments. The metal centers of the hexahydride are separated by a bridging ligand, composed of κ2-C,N- and κ2-C,C-chelating moieties, which allows electronic communication between the metal centers. The wide variety of obtained compounds and the high selectivity observed in their formation is a consequence of the main role of the azolium group during the activation and of the existence of significant differences in behavior between the azolium groups. The azolium role is governed by the anion of the salt, whereas the azolium behavior depends upon its imidazolium or benzimidazolium nature. While [BF4]− inhibits the azolium reactions, [BPh4]− favors the azolium participation in the activation process. In contrast to benzimidazolylidene, the imidazolylidene resulting from the deprotonation of the imidazolium substituent coordinates in an abnormal fashion to direct the phenyl C–H bond activation to the 2-position. The hydride ligands of the cationic dihydride-osmium(IV) pincer complex display intense quantum mechanical exchange splitting. In the last case, the abstractor of the C–H bond to the σ-intermediate, which is a function of the σ-intermediate and the C–H bond dissociation energy and the σ-intermediate and the C–H bond activation energy, is especially relevant to control the products. In such a case, in addition to the steric hindrance of the C–H bond, the selectivity of C(sp2)–H bond activation in substituted aromatic arenes is kinetically controlled by steric factors.

Introduction

The transition-metal-promoted activation of aromatic C–H bonds is one of the most relevant reactions in current chemistry, due to the wide range of fields with which it is connected, ranging from organic and organometallic synthesis to catalysis and materials science. The reaction is initiated by the coordination of the C–H bond to the unsaturated metal center of the promoter. The resulting σ-intermediate evolves by oxidative addition of the C–H bond or heterolytic C–H splitting. In the last case, the abstractor of the proton is a ligand of the metal coordination sphere or an external base. In accordance with this sequence of events, the activation energy for the C–H bond rupture depends upon two factors: the stability of the σ-intermediate and the C–H bond dissociation energy of the coordinated bond. Because in aromatic organic molecules the strengths of the different C(sp2)–H bonds are similar, the activation is mainly governed by the stability of the σ-intermediate, which is a function of the steric hindrance experienced by the coordinated C–H bond. As a consequence, the selectivity of C(sp2)–H bond activation in substituted aromatic arenes is kinetically controlled by steric factors.

The presence of a substituent with coordinating ability in the arene selectively ties the activation at the ortho position. Although the latter is sterically hindered and therefore the last position being activated, the substituent thermodynamically abducts the ortho-activation product by coordination. This is of central importance for the comprehension of catalytic organic reactions of ortho–CH functionalization. Since a catalytic cycle represents the reaction pathway with the lowest activation energy and the ortho-metalation reaction has an activation energy higher than those of other C–H bond activations in the same ring, the a-CH bond activation should form part of the fast stage of the functionalization, the ortho-metalated intermediate being the resting state of the catalyst. An additional issue of selectivity appears when the arene bears several substituents with coordinating ability. Then, understanding the drivers of the selectivity in the activation process is especially relevant to control the products. In such a case, in addition to the steric hindrance of the C–H bonds, the...
The study of C–H bond activation reactions of aryl substrates asymmetrically 1,3-disubstituted with coordinating groups is particularly challenging. Three different activations can have a thermodynamic preference in this case, which give rise to four distinct stable situations (Chart 1). Activation at the congested 2-position lead to pincer-type derivatives (A).16 whereas separate activations at positions 4 and 6 provoke $\kappa^2$-$\text{C}_\text{L}$ and $\kappa^2$-$\text{C}_\text{L'}$ coordinations of the activated substrate, which generate mononuclear derivatives bearing C–L and C–L’ chelating ligands (B and C, respectively).17 In contrast, the simultaneous or sequential C–H bond activations of both positions yield a bimetallic species (D).18 The S-position is the most accessible. This kinetically favors its activation. However, the absence of a neighboring group with coordinating ability causes such a C–H bond activation to be inhibited from a thermodynamic point of view.

The chemistry of the polyhydrides of platinum-group metals is an area of great potential. Such a prospect is the catalytic performance of the isolated complexes for hydrogen generation by dehydrogenation of 1,2,3,4-tetrahydrirosoquinoline and alcohols.

## RESULTS AND DISCUSSION

### Complexes Resulting from [BF$_4$]$^-$ and [BPh$_4$]$^-$ Salts of 1-(3-(isoquinolin-1-yl)phenyl)-3-methylimidazolium

The most clean, direct, and straightforward procedure to introduce an imidazolylidene ligand into the coordination sphere of a transition metal is generally direct metalation.15 The latter can take place by oxidative addition of an imidazolium C–H bond to an unsaturated metal fragment and by displacement of a coordinated Bronsted base, as a result of its protonation with the imidazolium salt. Complex 1 shows a marked tendency to undergo the reductive elimination of molecular hydrogen, at moderate temperatures (>50 °C), to afford the unsaturated tetrahydride OsH$_4$(P(1)Pr$_3$)$_2$ (E), which is the true species responsible for the proved ability of 1 to activate $\sigma$-bonds.11c,2b,24 On the other hand, the hydrides of 1 are basic enough to promote the deprotonation of imidazolium salts. The addition of the proton initially leads to the known trihydride-bis( dihydrogen) derivative [OsH$_3$(η$^2$-H$_2$)(P(1)Pr$_3$)$_2$]$,^+$, which loses molecular hydrogen and dimerizes to form the bimetallic cation [(OsH$_3$(P(1)Pr$_3$)$_2$]$_2$(μ-H)$_3]^+$ in equilibrium with the deprotonated polyhydride (P(1)Pr$_3$)$_2$H$_2$Os(μ-H)$_3$OsH(P(1)Pr$_3$)$_2$.25 To prevent side products resulting from the formation of the OsH$_2$ cation, the reactions of 1 with imidazolium salts are usually performed in the presence of triethylamine, including those where the imidazolylidene ligand acts as a chelating assistant.26

Treatment of toluene solutions of 1 with 1.0 equiv of the [BF$_4$]$^-$ salt of 1-(3-(isoquinolin-1-yl)phenyl)-3-methylimidazolium, in the presence of 15 equiv of triethylamine, under reflux leads to the cationic trihydride derivative 2 (Scheme 1) in 82% yield after 24 h, according to the $^1$H and $^{31}$P{1$^H$} NMR spectra of the crude reaction product in dichloromethane-d$_2$.23 The reaction can be rationalized as the isoquinolinyl-assisted activation of the C–H bond of the phenyl group at position 4 promoted by trihydride E. The imidazolium moiety of the salt does not interfere during the process. Consistently, in this case, the formation of the trihydride also takes place in the absence of the amine and in the same extension.

Complex 2 was isolated as a red solid in 73% yield and characterized by X-ray diffraction analysis. The structure has two cations and two anions chemically equivalent, but these are crystallographically independent in the asymmetric unit. Figure 1 gives a view of a cation. The metal center displays a typical coordination for a $d^4$ ion. Thus, the polyhedron can be idealized as a pentagonal bipyramid with axial phosphines (P(1)–Os(1)–P(2) = 164.64(4) and 166.91(4)$^3$). The $\kappa^2$-C$_N$-chelate group, which acts with bite angles of 75.51(14) and 75.06(14)$^a$ (C(1)–Os(1)–N(7)), and the hydride ligands, which are separated by more than 1.6 Å (X-ray and
Scheme 1. Formation of Complexes 2–4

![Diagram of complexes 2, 1, and 3](image)

**Figure 1.** Molecular diagram of one of the two independent cations of complex 2 (ellipsoids shown at 50% probability) in the asymmetric units. All hydrogen atoms (except the hydrides) are omitted for clarity. Selected bond distances (Å) and angles (deg): Os–P(1) = 2.3527(10), 2.3368(11), Os–P(2) = 2.3367(10), 2.3423(11), Os–C(1) = 2.102(4), 2.098(4), Os–N(7) = 2.151(3), 2.151(3); P(1)–Os–P(2) = 164.64(4), 166.91(4), C(1)–Os–N(7) = 75.51(14), 75.06(14).

DFT calculations (B3LYP-D3(SMD)/6-31G***(SDD))), lie at the base. The $^1$H, $^{13}$C($^1$H), and $^{31}$P($^1$H) NMR spectra in dichloromethane-$d_2$ are consistent with the solid-state structure. In agreement with the presence of three inequivalent hydride ligands, the $^1$H spectrum at 193 K shows three high-field resonances at $-6.19$, $-10.71$, and $-12.10$ ppm. The most noticeable signal in the $^{13}$C($^1$H) spectrum is a triplet ($^2$J$^{C-P} = 5.8$ Hz) at 199.1 ppm, corresponding to the metalated carbon atom. The $^{31}$P($^1$H) spectrum displays a singlet at 22.1 ppm, as expected for equivalent phosphines.

There are significant differences in behavior between the $[\text{BF}_4]^{-}$ and $[\text{BPh}_4]^{-}$ salts of the cation 1-(3-(isoquinolin-1-yl)phenyl)-3-methylimidazolium. Tentatively, these differences may be associate with the distinct sizes of the anions, which influence the cation–anion association and the respective solvations. In contrast to the $[\text{BF}_4]^{-}$ salt, the $[\text{BPh}_4]^{-}$ counterpart allows the disinhibition of the reactivity of the imidazolylidene moiety. This favors the activations of the C–H bonds of the phenyl group at the 2- and 6-positions (Scheme 1). Thus, the treatment of a toluene solution of 1 with the $[\text{BPh}_4]^{-}$ salt, in the presence of 15 equiv of triethylamine, under reflux affords a mixture of the cationic dihydride pincer complex 3 (73%) and the neutral trihydride 4 (27%).

The major product, complex 3, results from the activations of C–H bonds of the imidazolylidene moiety and of the phenyl group at 5- and 2-positions, respectively, whereas the neutral trihydride 4 arises from similar ruptures at 2- and 6-positions of the respective rings. The formation of a pincer isomer of 3 involving the coordination of the carbon atom at the 2-position of the imidazolylidene instead of that at the 5-position was not observed. This suggests that the C–H ruptures leading to 3 are connected and take place in a sequential manner. Because the 2-position of the phenyl group is sterically more hindered than the 5-position of the imidazolylidene moiety, it seems reasonable to think that the latter is kinetically favored and therefore it is previous to the former. As expected from the imidazolyl participation, the reaction is sensitive to triethylamine. In absence of the latter, in addition to the appearance of side products, the formation of 3 and 4 is slower.

Complex 3 was separated from the crude reaction mixture by silica column chromatography, isolated as a red solid in 57% yield, and subsequently fully characterized including an X-ray diffraction analysis. Figure 2 shows a view of the cation. The structure demonstrates the formation of the pincer, involving an abnormal coordination of the imidazolylidene moiety. The Os–imidazolylidene bond length of 2.077(2) Å (Os–C(1)) compares well with those reported for osmium compounds displaying abnormal-NHC coordination. The new monoanionic C$_2$C$_2$N-pincer ligand acts with C(1)–Os–N(1), C(1)–Os–C(10), and C(1)–Os–C(10) angles of 150.42(8), 76.18(8), and 74.24(8)$^\circ$, respectively, which are close to the ideal values corresponding to three consecutive positions at the base of a pentagonal bipyramid (144, 72, and 72$^\circ$), the observed coordination polyhedron in this case, and point out that this pincer should be particularly useful to...
through eq 1, according to a two-dimensional harmonic oscillator model. As shown in Figure 3a, the observed H–H coupling constant (J_{obs}) in the AB part of the ABX_{2} (X = 31P) spin system corresponding to the dihydride resonance (5.7 ppm) is temperature (T) dependent, increasing from 101 to 444 Hz as T increases from 183 to 243 K. For a given hydrogen–hydrogen separation (a), J_{obs} and T are related through eq 1, according to a two-dimensional harmonic oscillator model, where J_{mag} is the classical H–H coupling constant due to the Fermi contact interaction, λ represents the hard sphere radius of the hydrides, and ν describes the H–M–H vibrational wag mode that allows the movement along the H–H vector. As for a, these parameters are temperature independent. Using the hydrogen–hydrogen separation obtained by DFT calculations for the optimized structure, the fitting of the plot shown in Figure 3b yields values of J_{mag} = 9.5 Hz, λ = 1.0 Å, and ν = 497 cm^{-1}, which compare well with those obtained for other osmium(IV)-hydride compounds.29

In the 13C{1H} spectrum, the most noticeable resonances are two triplets at 192.4 (J_{C−P} = 5.9 Hz) and 140.2 (J_{C−P} = 7.3 Hz) ppm, due to the metalated C(1) and C(10) atoms, respectively. The 31P{1H} spectrum shows a singlet at 3.4 ppm, in agreement with the equivalence of the phosphines.

Table 1. Emission Properties of Complex 3

| HOMO^{calc} (eV) | LUMO^{calc} (eV) | HOMO^{exp} (eV) | LUMO^{exp} (eV) | calc λ_{em} (nm) | medium (T, K) | λ_{em} (nm) | Φ | k_{r} (s^{-1}) | k_{nr} (s^{-1}) | k_{r}/k_{nr} |
|-----------------|-----------------|-----------------|-----------------|-----------------|----------------|----------------|---|---------------|---------------|-------------|
| PMMA (298) | -5.23 | -2.07 | 3.16 | -5.09 | 2.95 | 637 |
| MeTHF (298) | 642 | 0.8 | 0.15 | 1.8 × 10^{3} | 1.0 × 10^{4} | 0.18 |
| MeTHF (77) | 601 | 5.2 |

Complex 3 is a new case of a red phosphorescent emitter (601–644 nm) upon photoexcitation, in a 5 wt % doped poly(methyl methacrylate) (PMMA) film at room temperature and in 2-methyltetrahydrofuran (2-MeTHF) at room temperature and at 77 K (Table 1). The observed wavelengths are in accordance with those obtained by estimating the dihydride resonance (5.7 ppm) is temperature (T) dependent, increasing from 101 to 444 Hz as T increases from 183 to 243 K. For a given hydrogen–hydrogen separation (a), J_{obs} and T are related through eq 1, according to a two-dimensional harmonic oscillator model, where J_{mag} is the classical H–H coupling constant due to the Fermi contact interaction, λ represents the hard sphere radius of the hydrides, and ν describes the H–M–H vibrational wag mode that allows the movement along the H–H vector. As for a, these parameters are temperature independent. Using the hydrogen–hydrogen separation obtained by DFT calculations for the optimized structure, the fitting of the plot shown in Figure 3b yields values of J_{mag} = 9.5 Hz, λ = 1.0 Å, and ν = 497 cm^{-1}, which compare well with those obtained for other osmium(IV)-hydride compounds.29

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\[
J_{obs} = J_{mag} + 2 \left( \frac{\nu a}{\pi \lambda \coth(\nu a/2kT)} \right) \exp \left( -2\pi \lambda a (\nu a + \lambda^2) \right) \frac{h}{c} \coth(\nu a/2kT) \right)
\]

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more than 1.6 Å, and the imidazolylidene moiety, which forms a κ²-C,C-chelate with the ortho-metalated phenyl (C(1)−Os−C(S) = 75.83(12)°), occupying the isoquinolinyl group place. This ligand disposition is consistent with the NMR spectra of the molecule in dichloromethane-d₂. In accordance with 2, the ¹H spectrum at 183 K shows three hydride resonances at −8.90, −10.38, and −10.78 ppm. In the ¹³C{¹H} spectrum, the signals due to the metalated carbon atoms appear at 190.1 (C(1)) and 162.8 (C(S)) ppm, as triplets with C−P coupling constants of 5.9 and 7.6 Hz, respectively. The ³¹P{¹H} spectrum contains a singlet at 24.7 ppm for the equivalent phosphines.

Complexes Resulting from [BF₄]⁻ and [BPh₄]⁻ Salts of 1-(3-(Isoquinolin-1-yl)phenyl)-3-methylbenzimidazolium. The use of a benzimidazolium fragment instead of an imidazolium moiety should prevent the formation of a pincer species related to 3, confirming the linkage between the activation of the C−H bonds at the 5-position of the five-membered ring and the activation of the C−H bond at the 2-position of the phenyl group, while it would allow a better study of the C−H bond activation at the 6-position of the aryl group. This reasoning prompted us to study the reactions of 1 with the [BF₄]⁻ and [BPh₄]⁻ salts of the cation 1-(3-(isoquinolin-1-yl)phenyl)-3-methylbenzimidazolium, under the same conditions as those employed for the reactions summarized in Scheme 1. The results are consistent with those obtained for the cation 1-(3-(isoquinolin-1-yl)phenyl)-3-methylimidazolium and confirm our previous conclusions (Scheme 2).

The [BF₄]⁻ anion inhibits the reactions of the benzimidazolium fragment, which favors the isoquinolinyl-assisted activation of the C−H bond of the phenyl group at the 4-position. Thus, the reaction of 1 with this salt leads to 5 (82%), the benzimidazolylidene counterpart of 2, while the reaction with the [BPh₄]⁻ salt selectively gives 6 (78%), the benzimidazolylidene counterpart of 4. Complex 6 results from the activation of the C−H bond at the 6-position of the phenyl group along with the activation of the C−H bond at the 2-position of the benzimidazolium fragment. No pincer complex resulting from C−H bond activation of the phenyl group at the 2-position was detected, which suggests that the rupture of the C−H bond of the phenyl group at the 6-position is a NHC-assisted reaction promoted by the tetrahydride E, the genesis of the Os−NHC bond being a heterolytic C−H activation mediated by the triethylamine external base. Complexes 5 and 6 were isolated as red and yellow solids in 73% and 43% yields, respectively, and fully characterized by NMR spectroscopy, in dichloromethane-d₂. In agreement with the imidazolylidene counterparts 2 and 4, the ¹H spectra at 203 K contain signals due to three inequivalent hydrides at −6.19, −10.54, and −11.99 ppm for 5 and at −8.43 and −10.02 (2H) ppm for 6. In the ¹³C{¹H} spectra, the resonances corresponding to the metalated carbon atoms appear as triplets at 199.7 (J_C−P = 5.5 Hz) ppm for 5 and at 206.1 (J_C−P = 5.8 Hz) and 161.9 (J_C−P = 5.6 Hz) ppm for 6. The ³¹P{¹H} spectra display a singlet at 21.9 ppm for 5 and at 26.1 ppm for 6.

Scheme 2. Formation of Complexes 5 and 6
C–H Bond Activation of 6. The hexahydride complex 1 also activates the C–H bond of the metalated phenyl group of 6 disposed in para position with regard to the benzimidazolylidene moiety and ortho to the isoquinolyl group, the 4-position in the starting cation, to give the bimetallic hexahydride 7 (Scheme 3). At first glance, one should expect that such a complex could be also prepared from 5, by activation of the C–H bond at 2-position of the benzimidazolium fragment along with the ortho metatation of the phenyl group: i.e., the activation of the C–H bond of the phenyl group disposed in a para position with respect to the isoquinolyl moiety, the 6-position of the original cation. However, the previously mentioned inhibition of the reactivity of the benzimidazolium moiety by the action of the [BF4]- anion prevents such a possibility, in the presence and in absence of triethylamine and in both toluene and tetrahydrofuran, as solvents, under reflux.

Complex 7 was isolated as a garnet solid in 80% yield and characterized by an X-ray diffraction analysis. Figure 6 shows its structure, which can be described as two OsH2(P2P3) and metal fragments linked by a bridging ligand resulting from activations at the 4- and 6-positions of a phenyl substrate asymmetrically 1,3-disubstituted with benzimidazolylidene and isoquinolyl groups. The polyhedron around Os(1) resembles that of 6 with P(1)–Os(1)–P(2) and C(1)–Os(1)–C(10) angles of 160.57(3) and 76.19(12)°, respectively, whereas the polyhedron around Os(2) resembles that of 5 with P(3)–Os(2)–P(4) and N(1)–Os(2)–C(12) angles of 164.30(3) and 76.20(12)°, respectively. The classical nature of the polyhydride is supported by both the X-ray structure and the optimized structure through DFT calculations, which display hydride–hydride separations longer than 1.6 Å. In agreement with the structure, the NMR spectra in dichloromethane-d6 are combinations of those of 5 and 6. The 1H spectrum at 203 K contains high-field signals for six inequivalent hydrides at −6.23, −8.05, −10.05 (2H), and −11.04 (2H) ppm. The 13C{1H} spectrum shows three triplets (δC–p– → 6.1–5.7 Hz) for the metalated carbon atoms at 204.9, 186.5, and 166.6 ppm. The two pairs of equivalent phosphines give rise to two singlets at 26.7 and 22.6 ppm in the 31P{1H} spectrum.

The molecular diagram of complex 7 (ellipsoids shown at 50% probability). All hydrogen atoms (except the hydrides) are omitted for clarity. Selected bond distances (Å) and angles (deg): Os(1)–P(1) = 2.3411(9), Os(1)–P(2) = 2.3462(8), Os(2)–P(3) = 2.3319(9), Os(2)–P(4) = 2.3383(9), Os(1)–C(1) = 2.064(3), Os(1)–C(10) = 2.134(3), Os(2)–C(12) = 2.125(3), Os(2)–N(1) = 2.129(3); P(1)–Os(1)–P(2) = 160.57(3), P(3)–Os(2)–P(4) = 164.30(3); C(1)–Os(1)–C(10) = 76.19(12), C(12)–Os(2)–N(1) = 76.20(12).

Scheme 3. Formation of Complex 7

**Figure 6.** Molecular diagram of complex 7 (ellipsoids shown at 50% probability). All hydrogen atoms (except the hydrides) are omitted for clarity. Selected bond distances (Å) and angles (deg): Os(1)–P(1) = 2.3411(9), Os(1)–P(2) = 2.3462(8), Os(2)–P(3) = 2.3319(9), Os(2)–P(4) = 2.3383(9), Os(1)–C(1) = 2.064(3), Os(1)–C(10) = 2.134(3), Os(2)–C(12) = 2.125(3), Os(2)–N(1) = 2.129(3); P(1)–Os(1)–P(2) = 160.57(3), P(3)–Os(2)–P(4) = 164.30(3); C(1)–Os(1)–C(10) = 76.19(12), C(12)–Os(2)–N(1) = 76.20(12).
Catalytic Dehydrogenation of 1,2,3,4-Tetrahydroisoquinoline and Alcohols. The mononuclear complexes 2, 3, 5, and 6 and the bimetallic derivative 7 promote the dehydrogenation of 1,2,3,4-tetrahydroisoquinoline (Scheme 4). The reactions were carried out under argon, in p-xylene, at 140 °C, using a heterocycle concentration of 0.12 M and an osmium/heterocycle molar ratio of 1/14.6. Under these conditions, between 58% and 87% of all H₂ capacity of the heterocycle, 1.50 × 10⁻² mol g⁻¹, is released after 48 h. The dehydrogenation is sequential, the release of the first hydrogen molecule being faster than the liberation of the second molecule. The behavior the bimetallic complex 7 should be pointed out, which reveals a nice example of catalytic synergism.38 This compound is significantly more active than complexes 5 and 6, the mononuclear units forming it. Although the metal centers are separated by the bridging ligand, the latter allows their electronic coupling, as was previously demonstrated. The catalysis can take place in an independent manner in each metal center, but the events in one metal center affect those in the other. The catalytic synergism is a consequence of the gain in the efficiency of each metal center by the action of its colleague. Complexes 2, 3, and 5–7 also catalyze the dehydrogenation of primary and secondary alcohols, such as benzylic alcohol, 1-phenylethanol, and 1,2-phenylenedimethanol (Scheme 5). The reactions were performed under argon, in toluene, at 100 °C, using an alcohol concentration of 0.12 M and an osmium/substrate molar ratio of 1/14.6. The addition of a base to the catalytic solutions was not necessary. This finding is particularly notable in the case of 2, 3, and 5, which, given their cationic character, appear to have enough basic character to deprotonate the OH group of the substrates. The abstraction should release H₂, promoting the C–H bond activation reaction. In contrast, the [BPh₄]⁻ anion inhibits the azolium reactions. Then, the imidazolium groups depending upon their imidazolium or benzimidazolium nature. The [BF₄]⁻ anion inhibits the azolium substituent establishes the position of the C–H bond activation. This is due to the main role of the azolium group during the activation, which can be governed through the election of the anion of the salt, and to the existence of significant differences in behavior between the azolium groups depending upon their imidazolium or benzimidazolium nature. The [BF₄]⁻ anion inhibits the azolium groups. Consistently, both [BF₄]⁻ salts undergo the rupture of the ary-C₇H bond at the 4-position, as a consequence of an isoquinolinyl-assisted C–H bond activation reaction. In contrast, the [BPh₄]⁻ anion dishibits the azolium reactions. Then, the imidazolium substituent affords an imidazolylidene group. This moiety preferentially coordinates to the metal center in an abnormal efficiency with regard to 5 and 6, its catalytic activity is still moderate. Thus, only 56% of the ketone is obtained with this catalyst, after 24 h. The dehydrogenation of 1,2-phenylenedimethanol (Scheme 5c) in the presence of 7 affords 1-isobenzofuranone and molecular hydrogen in a quantitative yield after 24 h, whereas 70% of the lactone is formed after 12 h. The reaction yield in the presence of the pincer complex 3 is also good, 86%.

**CONCLUDING REMARKS**

This study shows that the hexahydride complex OsH₆(PPr₃)₂ promotes the C–H bond activation of aryl compounds asymmetrically 1,3-disubstituted, with two coordinating groups. The rationalization of the products formed in the reactions with the [BF₄]⁻ and [BPh₄]⁻ salts of the cations 1-(3-isooquinolin-1-yl)phenyl)-3-methylimidazolium and 1-(3-isooquinolin-1-yl)phenyl)-3-methylbenzimidazolium reveals that the azolium substituent establishes the position of the C–H bond activation. This is due to the main role of the azolium group during the activation, which can be governed through the election of the anion of the salt, and to the existence of significant differences in behavior between the azolium groups depending upon their imidazolium or benzimidazolium nature. The [BF₄]⁻ anion inhibits the azolium groups. Consistently, both [BF₄]⁻ salts undergo the rupture of the ary-C₇H bond at the 4-position, as a consequence of an isoquinolinyl-assisted C–H bond activation reaction. In contrast, the [BPh₄]⁻ anion dishibits the azolium reactions. Then, the imidazolium substituent affords an imidazolylidene group. This moiety preferentially coordinates to the metal center in an abnormal
fashion, to direct the C–H bond activation of the aryl at the 2-
position and finally to yield a pincer ligand by the coordination of
the isoquinolyl substituent. In contrast, the benzimidazolyl-
diene, resulting from the deprotonation of the benzimidazol-
ium substituent, assists the C–H bond activation at the 6-
position.

The pincer complex resulting from the C–H activation of the central aryl group at the 2-position and the coordination of both substituents possesses interesting features. Its hydride ligands show an intense quantum mechanical exchange coupling, and it is a red phosphorescent emitter upon
photoexcitation and displays a noticeable catalytic activity for
the dehydrogenation of 1-phenylethanol to acetophenone and
1,2-phenylenedimethanolate to 1-isobenzofuranone.

The sequential C–H bond activation of the 6- and 4-
positions of the central aryl group of the 1-(3-(isoquinolin-1-
yl)phenyl)-3-methylbenzimidazolium tetrabenzeneborate affords a bimetallic compound, which displays catalytic synergism between the metals, for the dehydrogenation of 1,2,3,4-
tetrahydroisoquinoline and alcohols. The synergism seems to
result from the electronic coupling between the metal centers and
gives rise to a noticeable catalytic activity of this compound in the dehydrogenation of 1,2-phenylenedimethanolate
1 to 1-isobenzofuranone.

In summary, the introduction of an azolium substituent into
phynyl groups previously bearing a coordinating group, to
form an asymmetrically 1,3-disubstituted aryl salt, allows an
efficient governing of the C–H bond activation of the aromatic
ring. As a result, compounds with interesting physical
properties and new catalysts can be prepared.

## 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. The chemical shifts (in ppm) in the NMR spectra
(Figures S1–S36) are referenced to residual solvent peaks (1H,
13C(2H)) or external 85% H3PO4 (31P{1H}) or CFCl3 (19F{1H}),
while the coupling constants in Hz are given in Hz.

### Reaction of OsH6(PiPr3)2 (1) with 1-(3-(Isoquinolin-1-y1)
phenyl)-3-methylimidazolium Tetrafluoroborate: Preparation of
3 and 4. A mixture of 1 (200 mg, 0.387 mmol), 1-(3-
isoquinolin-1-yl)phenyl)-3-methylimidazolium tetrafluoroborate
(330 mg, 0.503 mmol), and triethylamine (809 µL, 5.085 mmol) in tol
ylene (8 mL) was refluxed for 24 h, giving a dark brown suspension.
After the mixture was cooled to room temperature, the solvent was removed
in vacuo, affording a burgundy residue. A small portion of the residue was
resinated in dichloromethane using a flash column chromatography
and its 1H and 31P{1H} NMR spectra showed the formation of 3 in 4 in a 73/27 molar ratio.

The brown residue was washed with pentane (2 × 4 mL) and dried in vacuo.

### Data for 3. Anal. Calcd for C61H78BN3OsP2: C, 65.63; H, 7.04; N,
3.76. Found: C, 65.22; H, 6.92; N, 4.01. HRMS (electrospray, m/z):
calculated for C61H78BN3OsP2 [M+]: 879.3781; found, 879.3717. IR
(cm−1): ν(C=O) (Os=O) 2233 (m), 1713 (s), 1513 (s), 932 (m), 878 (m), 850 (m), 750 (w), 671 (w).

### Data for 4. Anal. Calcd for C61H78BN3OsP2: C, 65.63; H, 7.04; N,
3.76. Found: C, 65.22; H, 6.92; N, 4.01. HRMS (electrospray, m/z):
calculated for C61H78BN3OsP2 [M+]: 879.3781; found, 879.3717. IR
(cm−1): ν(C=O) (Os=O) 2233 (m), 1713 (s), 1513 (s), 932 (m), 878 (m), 850 (m), 750 (w), 671 (w).

### Reaction of OsH6(PiPr3)2 (1) with 1-(3-(Isoquinolin-1-yl)
phenyl)-3-methylimidazolium Tetraphenylborate: Preparation
of 3 and 4. A mixture of 1 (200 mg, 0.387 mmol), 1-(3-
isoquinolin-1-yl)phenyl)-3-methylimidazolium tetraphenylborate
(330 mg, 0.503 mmol), and triethylamine (809 µL, 5.085 mmol) in tol
ylene (8 mL) was refluxed for 24 h, giving a dark brown suspension.
After the mixture was cooled to room temperature, the solvent was removed
in vacuo, affording a burgundy residue. A small portion of the residue was
resinated in dichloromethane using a flash column chromatography
and its 1H and 31P{1H} NMR spectra showed the formation of 3 in 4 in a 73/27 molar ratio.

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(cm−1): ν(C=O) (Os=O) 2233 (m), 1713 (s), 1513 (s), 932 (m), 878 (m), 850 (m), 750 (w), 671 (w).

### Data for 4. Anal. Calcd for C61H78BN3OsP2: C, 65.63; H, 7.04; N,
3.76. Found: C, 65.22; H, 6.92; N, 4.01. HRMS (electrospray, m/z):
calculated for C61H78BN3OsP2 [M+]: 879.3781; found, 879.3717. IR
(cm−1): ν(C=O) (Os=O) 2233 (m), 1713 (s), 1513 (s), 932 (m), 878 (m), 850 (m), 750 (w), 671 (w).
in vacuo. Yield: 265 mg (73%). Anal. Calcld for C_{41}H_{60}N_{3}O_{3}P_{2} \[M^+] \text{ for } C_{59}H_{105}N_{3}O_{3}P_{2} \[M^+] +, 1360.5830; \text{ found, 1360.5691. IR (cm}^{-1}: v(\text{Os}−\text{H}) = 1910 (vs).} 

1^1H NMR (300.13 MHz, CD_{3}Cl_{2}, 298 K): \delta 9.54−6.94 (14H, C_{3}H_{2}N_{3}H), 4.32 (s, 3H, CH_{3}), 1.83 (m, 6H, PCH(CH_{3})_{2}), 0.93 (dt, J_{H,H} = 6.8, N = 12.6, 36H, PCH(CH_{3})_{2}). \text{ HRMS (electrospray, m/z): calculated for C}_{41}\text{H}_{60}N_{3}O_{3}P_{2} \[M^+] +, 1360.5830; \text{ found, 1360.5691. IR (cm}^{-1}: v(\text{Os}−\text{H}) = 1910 (vs).}
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Notes
The authors declare no competing financial interest.

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