Osmium(II) Complexes Containing a Dianionic CCCC-Donor Tetradentate Ligand

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ABSTRACT: The preparation of osmium(II) complexes containing a $C_{C_6H_4}$,C_{BzIm},C_{BzIm},$C_{C_6H_4}$-tetradentate ligand with a $–CH_2CH_2–$ link between the benzimidazolidene (BzIm) groups is described and the influence of the link on their structures and emissive properties is analyzed. The hexahydride complex $OsH_6(P^iPr_3)_2$ (**1**) reacts with 1,1'-diphenyl-3,3'-ethylenedibenzimidazolium bromide in dimethylformamide to afford $OsBr\{\kappa^3\text{-}C,C,C\text{-}(C_6H_4\text{-BzIm-}CH_2CH_2\text{-BzIm-Ph})\}(CO)(P^iPr_3)_2$ (**2**), as a result of the direct metalation of both benzimidazolium moieties of the salt, the *ortho*-CH bond activation of a phenyl substituent, and the carbonylation of the metal center by action of the solvent. Treatment of **2** with $Na[BH_4]$ leads to the hydride derivative $OsH\{\kappa^3\text{-}C,C,C\text{-}(C_6H_4\text{-BzIm-}CH_2CH_2\text{-BzIm-Ph})\}(CO)(P^iPr_3)_2$ (**3**) which evolves into $Os\{\kappa^4\text{-}C,C,C,C\text{-}(C_6H_4\text{-BzIm-}CH_2CH_2\text{-BzIm-}C_6H_4)\}(CO)(P^iPr_3)_2$ (**4**) as a consequence of the assisted C-H bond activation of the second phenyl substituent. The use of dimethylsulfoxide instead of dimethylformamide allows the generation of the tetradentate ligand in one pot. Stirring of dimethylsulfoxide solutions of **1** leads to $Os\{\kappa^4\text{-}C,C,C,C\text{-}(C_6H_4\text{-BzIm-}CH_2CH_2\text{-BzIm-}C_6H_4)\}(DMSO)_2$ (**5**). The solvent molecules of **5** can be displaced by 1,2-bis(diphenylphosphino)ethylene (bdppe), 1,2-bis(diphenylphosphino)benzene (dppbz) and tetrafluorobenzobarrelene (TFB) to yield the [4+2]-derivatives $Os\{\kappa^4\text{-}C,C,C,C\text{-}(C_6H_4\text{-BzIm-}CH_2CH_2\text{-BzIm-}C_6H_4)\}L_2$ (L_2 = bdppe (**6**), dppbz (**7**), TFB (**8**)). The X-ray structures of **4**, **6** and **7** reveal that in these compounds, the tetradentate ligand adopts a *mer* three-planar disposition of a phenyl and two benzimidazolidene groups with the other phenyl group situated in a perpendicular direction *trans*-disposed to L. The reason of this preference is electronic. Thus, the stereochemistry of **7** is the same as that found in the related complexes $Os\{\kappa^2\text{-}C,C\text{-}(MeBzIm-C_6H_4)\}_2(dppbz)$ (**13**) and $Os\{\kappa^2\text{-}C,C\text{-}(MeBzIm^*\text{-}C_6H_4)\}_2(dppbz)$ (**14**) containing two free orthometalated N-phenylbenzimidazolidene ligands. Complexes **7**, **13** and **14** are phosphorescent. The first of them shows emissions narrower and bluer than those of **13** and **14**.

INTRODUCTION

Tetradentate ligands are less common than those with one, two, or three donor atoms. However, their marked abilities to enhance the stability of uncommon species make them a powerful tool for designing novel types of transition metal complexes with applications in catalysis,[1] material science,[2] biology,[3] or synthetic chemistry,[4] among other fields.

These ligands have been classified into three principal categories:[5] i) macrocyclic, ii) acyclic of linear chain, and iii) acyclic of branched chain. Macrocyclic tetradentate ligands mainly coordinate in a plane, being porphyrins a phthalocyanines classical examples.[6] Acyclic tetradentate ligands of linear chain afford complexes with stereochemistries which depend upon the rigidity of the ligand. More rigid ligands display planar[7] or tetrahedral[8] coordinations, whereas flexible molecules and anions orientate their donor atoms to stabilize six-coordinate geometrical isomers (**I**,[9] **II**,[10] and **III**[11] in Chart 1). The chain of the acyclic tetradentate ligands of branched chain can be bifurcated at a donor atom,[12] at an atom other than a donor atom,[13] or a bridging group links two bidentate moieties.[14] The first type is the most common and best known among the ligands of this category, being tetraphosphines and tetraarsines classical molecules of this class.[15]

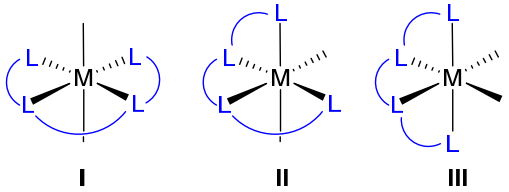
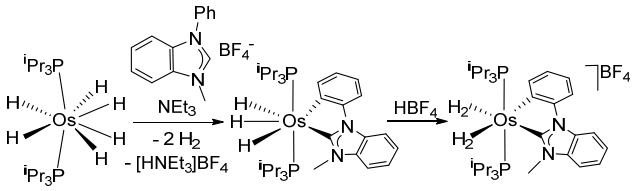


Chart 1.

Nitrogen, phosphorous, arsenic, oxygen and sulfur are typical donor atoms in tetradentate ligands.[5] Carbon is much less common from a classical point of view. The ability of the N-heterocyclic carbenes (NHCs) to tune the electron density of the metallic core of the complexes[16] has given rise to the design of an increasing number of ligands based on these moieties. Thus, in recent years, interesting families of complexes containing tetradentate ligands with one,[17] two,[18] three,[19] and four NHC groups have been reported. Those with four NHC moieties form a novel group of neutral C,C,C,C-donor ligands.

The large majority of them are macrocyclic systems, which coordinate to generate a plane[20] with some exceptions.[21] A few acyclic systems have been also described. They can be described as ligands of branched chain, with a rigid aromatic group linking two bidentate NHC units,[22] and flexible systems of linear chain displaying both geometries **I** and **II**.[23]

The chelate-assistance has been revealed as one of the most efficient ways to perform selective C-H bond activation reactions.[24] Among the used C-donor assistant groups, NHCs occupy a prominent place. As a consequence, NHC-assisted *ortho*-CH bond activation is a highly attractive synthetic method for creating anionic C_{NHC}-C_{aryl} chelate ligands. If one links two of these groups with a flexible chain, through a NHC-nitrogen atom, one could generate flexible dianionic tetradentate C_{aryl},C_{NHC},C_{NHC},C_{aryl}-donor ligands of linear chain. Previously, the union of two 1-phenyl-3-methylimidazolidene ligands, through one of the meta-phenyl atoms, with an oxygen link has allowed the formation of an square-planar C_{NHC},C_{aryl},C_{aryl},C_{NHC}-tetradentate platinum(II) complex, which has demonstrated high efficiency in both monomer and excimer emission.[25] In addition, it is well stablished that polyhydrides of platinum group metals, in particular $IrH_5(PPh_3)_2$[26] and $OsH_6(P^iPr_3)_2$,[27] promote the metalation of imidazolium and benzimidazolium cations, to afford normal and abnormal NHC-derivatives. These polyhydrides have also the ability of activating σ-bonds, including aromatic C-H bonds.[28] Thus, complex $OsH_6(P^iPr_3)_2$ has proven to facilitate the direct metalation of the benzimidazolium moiety of 1-phenyl-3-methyl-1-*H*-benzimidazolium and the *ortho*-CH bond activation of the phenyl substituent, to afford osmium(II)-bis(dihydrogen) complexes containing an anionic C_{aryl}-C_{NHC}-chelate ligand (Scheme 1).[27e] With these precedents in mind, we decided to link the free nitrogen atom of two 1-phenyl-benzimidazole moieties with a flexible ethylidene chain and to explore reactions of the d^2-osmium-hexahydride with the resulting 1,1'-diphenyl-3,3'-ethylenedibenzimidazolium dication, in order to prepare the first transition metal complexes containing a dianionic C_{aryl},C_{NHC},C_{NHC},C_{aryl}-tetradentate ligand. The bidentate character of the 1,1'-diphenyl-3,3'-ethylenedibenzimidazolidene moiety group has been previously demonstrated by Herrmann, Kühn, and co-workers.[29]



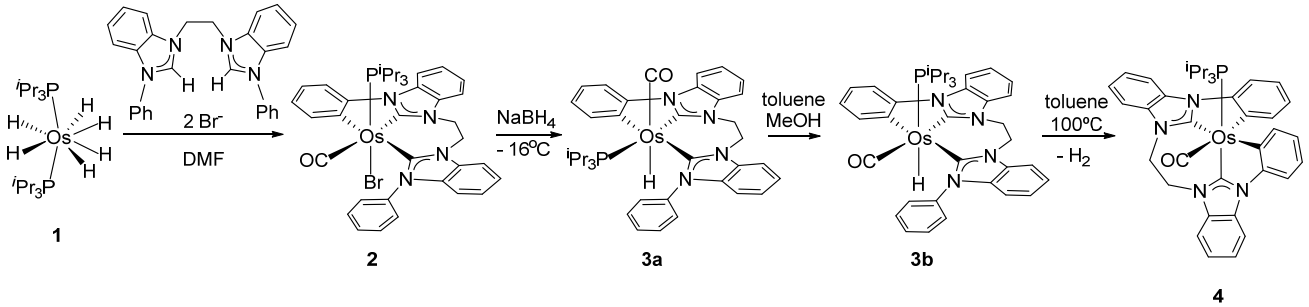
Scheme 1. Synthesis of Osmium(II)-bis(dihydrogen) Complexes Containing an Anionic Caryl-CNHC-chelate Ligand.

This paper reports the preparation of osmium complexes containing a dianionic C_{aryl},C_{NHC},C_{NHC},C_{aryl}-tetradentate ligand, *via* C_{NHC},C_{NHC},C_{aryl}-pincer intermediates and in one pot. Furthermore, it demonstrates that the link between the C_{NHC},C_{aryl} units does not determine the geometry of the resulting species, whereas seems to produce a narrowing of the emission band when the osmium complex is phosphorescent.

RESULTS AND DISCUSSION

Formation of an Osmium(II) Complex Containing a C_{aryl},C_{NHC},C_{NHC},C_{aryl}-tetradentate Ligand via C_{aryl},C_{NHC},C_{NHC}-pincer Intermediates. The process starts from the d^2-hexahydride $OsH_6(P^iPr_3)_2$ (**1**) and 1,1'-diphenyl-3,3'-ethylenedibenzimidazolium bromide and involves the direct metalation of both benzimidazolium units and the sequential *ortho*-CH bond activation of the phenyl substituents. The C-H cleavages are promoted by hydride ligands, in agreement with the ability of the osmium-hydride complexes, in particular **1**,[27,30] to activate C-H bonds. Scheme 2 summarizes the employed reactions.

Treatment of dimethylformamide solutions of **1** with 1.0 equiv of the dibenzimidazolium salt, under reflux, for 20 min affords the carbonyl derivative $OsBr\{\kappa^3\text{-}C,C,C\text{-}(C_6H_4\text{-BzIm-}CH_2CH_2\text{-BzIm-Ph})\}(CO)(P^iPr_3)$ (**2**), which was isolated as a green solid in 57% yield. In addition to the direct metalation of both benzimidazolium moieties of the salt and the *ortho*-CH bond activation of a phenyl substituent, the formation of **2** involves the carbonylation of the metal center by action of the solvent. In this context, it should be mentioned that the use of dimethylformamide as source of carbon monoxide is well-known.[31] Complex **2** was characterized by X-ray diffraction analysis. Figure 1 shows a view of the molecule. The structure proves the generation of a pincer ligand and the carbonylation of the metal center. The coordination around the osmium atom can be described as a distorted octahedron with the phosphine ligand and the bromide anion mutually *trans* disposed (P-Os-Br = 174.61(3)º). The perpendicular plane is formed by the pincer, which acts with C_{NHC}-Os-C_{aryl} angles of 167.47(14)º (C(16)-Os-C(1)) and 77.22(15)º (C(7)-Os-C(1)) and a C_{NHC}-Os-C_{NHC} angle of 94.31(15)º (C(7)-Os-C(16)), and the carbonyl group *trans* disposed to one of the benzimidazolidene units (C(7)-Os-C(29) = 162.67(16)º). The Os-C_{NHC} bond lengths of 2.092(4) Å (Os-C(16)) and 2.101(4) Å (Os-C(7)) compare well with those reported of Os-NHC compounds with normal coordination of the NHC ligand,[27,32] whereas the Os-C_{aryl} distance of 2.116(4) Å (Os-C(1)) is in accordance with those found in other five-membered osmacycles resulting from chelate-assisted C-H bond activation reactions.[33] As expected for the presence of the carbonyl ligand, the IR spectrum of the compound shows a ν(CO) band a 1911 cm^{-1}. In the $^{13}C\{^1H\}$ NMR spectrum in dichloromethane-d_2, at room temperature, the carbonyl ligand and the metalated carbon atoms of the pincer display at 192.2 (NHC), 191.7 (CO), 188.2 (NHC), and 152.6 (Ph) ppm doublets with typical *cis* C-P coupling constants, between 10 and 4 Hz. A singlet at 10.8 ppm in the $^{31}P\{^1H\}$ NMR spectrum is also a characteristic feature of this compound.



Scheme 2. Formation of an Osmium(II) Complex Containing a C_{aryl},C_{NHC},C_{NHC},C_{aryl}-tetradentate Ligand via C_{aryl},C_{NHC},C_{NHC}-pincer Intermediates.

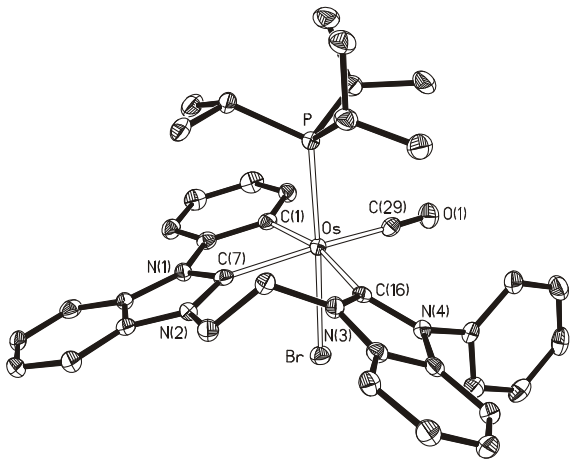
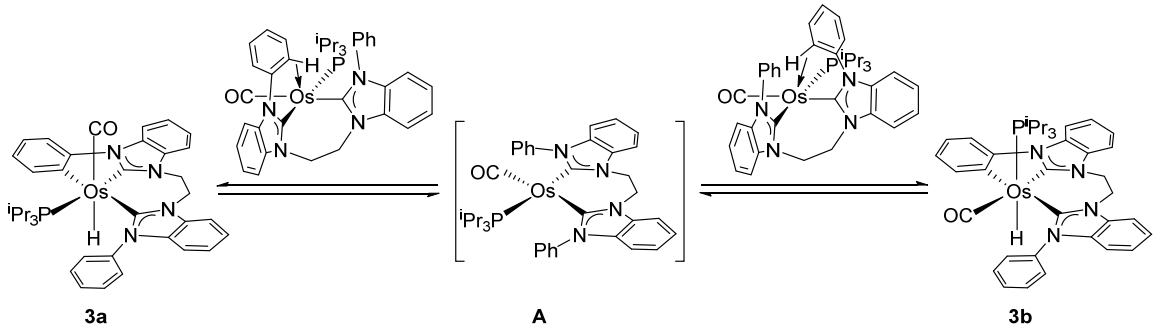


Figure 1. ORTEP diagram of complex **2** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os-Br = 2.6289(4), Os-P = 2.3447(10), Os-C(1) = 2.116(4), Os-C(7) = 2.101(4), Os-C(16) = 2.092(4), Os-C(29) = 1.880(4); Br-Os-P = 174.61(3), C(1)-Os-C(7) = 77.22(15), C(1)-Os-C(16) = 167.47(14), C(1)-Os-C(29) = 88.17(16), C(7)-Os-C(29) = 162.67(16), C(16)-Os-C(29) = 98.46(16), C(7)-Os-C(16) = 94.31(15).

Complex **2** reacts with Na[BH_4], at -16 ºC, to formally replace the bromide anion by a hydride ligand. At this temperature, in the presence of methanol, the addition of an excess of the tetrahydrideborate salt to toluene solutions of **2** selectively lead to the hydride **3a**, which was isolated as a yellow solid in 68% yield. The substitution is accompanied by a change in the disposition of the phosphine ligand, which moves from *cis* to both benzimidazolidene units to *trans* to one of them. The stereochemistry proposed for **3a** in Scheme 1 is strongly supported by the ^{1}H and ^{13}C{^{1}H} NMR spectra of this compound, in dichloromethane-d_2, at room temperature. In agreement with the mutually *cis* disposition of the hydride and phosphine ligands, the ^{1}H NMR spectrum contains at -8.31 ppm a doublet with a H-P coupling constant of 29.4 Hz. In the ^{13}C{^{1}H} NMR spectrum, the resonances corresponding to the carbonyl group and the phenyl metalated carbon atom appear at 198.2 and 159.7 ppm as doublets with typical *cis* C-P coupling constants of 8.5 and 7.7 Hz, respectively, whereas those due to the metalated carbon atoms of the benzimidazolidene units are observed at 192.7 and 191.2 ppm also as doublets but with very different C-P coupling constants of 63.6 and 8.1 Hz, respectively; being the first of them characteristic for a *trans* C-P disposition and the second one for a *cis* C-P arrangement. A singlet at 20.1 ppm in the ^{31}P{^{1}H} NMR spectrum and a ν(CO) band a 1874 cm^{-1} in the IR are also characteristic features of this compound.

Complex **3a** isomerizes in toluene:methanol (4:1), at room temperature, to afford **3b** in quantitative yield, after 4 days. The isomerization involves a change in the relative positions of the carbonyl and phosphine ligands. This is strongly supported by the ^{1}H and ^{13}C{^{1}H} NMR spectra of the white solid obtained from the isomerization reaction, in dichloromethane-d_2, at room temperature. According to the mutually *trans*-disposition of the hydride and phosphine ligands, the ^{1}H NMR spectrum shows the hydride resonance at -8.99 ppm as a doublet with a typical *trans* H-P coupling constant of 52.0 Hz. On the other, in agreement with the *cis*-disposition of phosphine, carbonyl and pincer ligands, the signals due to the carbonyl group and the metalated carbon atoms of the pincer are observed at 196.0 (CO), 195.9 (NHC), 190.8 (NHC), and 153.1 (Ph) ppm as doublets with typical *cis*-C-P coupling constants of 5.0, 6.3, 6.2 and 7.6 Hz, respectively, in the ^{13}C{^{1}H} NMR spectrum. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 9.9 ppm, whereas the IR contains a ν(CO) band a 1889 cm^{-1}.

The formation of **3a** and its isomerization into **3b** merit some additional comment. One should note that the direct replacement of the bromide anion of **2** by a hydride of the tetrahydrideborate salt should afford **3b** in one step, without the intermediation of **3a**. So, the direct substitution of bromide by hydride must be rejected as a reasonable proposal. On the other hand, it should be pointed out that **3a** and **3b** can be interconverted via the square-planar osmium(0) intermediate Os{κ^2-*C*,*C*-(Ph-BzIm-CH_2CH_2-BzIm-Ph)}(CO)(P^{i}Pr$_3$) (**A**). Although square-planar d^8-osmium complexes are rare, they are known.[32e,34] Thus, isomer **3a** could be generated by means of a concerted *cis*-oxidative addition of one of the *ortho*-CH bonds of the phenyl substituent of the benzimidazolidene group disposed cis to the carbonyl ligand of **A**, along the NHC-Os-CO axis, with the phenyl group on the carbonyl ligand. On the other hand the formation of **3b** should take place through an analogous process on the phenyl substituent of the benzymidazolidene group disposed *cis* to the phosphine ligand, along the NHC-Os-P^{i}Pr$_3$ axis (Scheme 3).[35] The smaller size of the carbonyl group with regard to the phosphine can explain why the formation of **3a** is kinetically favored. According to this, it appears to be reasonable to think that the first step of the reaction of **2** with Na[BH_4] is the generation of **A** as a consequence of the reduction of the starting complex by direct addition of one hydride of the tetrahydridoborate salt to the metalated phenyl group of **2** and subsequent release of bromide. In agreement with this, we have



Scheme 3. Interconversion between Complexes **3a** and **3b**.

observed that the reaction of **2** with $Na[BD_4]$ at -16 ºC leads to a partially deuterated **3a** containing 0.5 deuterium atoms at the hydride position.

The hydride ligand of **3b** promotes the cleavage of one of the *ortho*-CH bonds of the free phenyl substituent of the dibenzimidazolidene moiety with an activation barrier significantly higher than that corresponding to the first *ortho*-CH bond cleavage, which could be associated to the saturated character of **3a** and the need to dissociate a ligand, most probably P^iPr_3, to perform the C-H bond activation process.

Stirring of toluene solutions of **3b**, at 100 ºC, produces the release of a hydrogen molecule and the formation of complex Os{κ^4-*C*,*C*,*C*,*C*-(C_6H_4-BzIm-CH_2CH_2-BzImC_6H_4)}(CO)(P^iPr_3) (**4**, in Scheme 2), containing a C_{aryl},C_{NHC},C_{NHC},C_{aryl}-tetradentate ligand. This compound was isolated as a white solid in 89 % yield, after 4 days, and characterized by X-ray diffraction analysis. The structure (Figure 2) proves the formation of the tetradentate ligand, which coordinates in a type **II** mode (Chart 1) with the phosphine ligand *trans* to a benzimidazolidene unit and the carbonyl group *trans* to an aryl moiety. Thus, the coordination polyhedron around the osmium atom can be described as a distorted octahedron with NHC-Os-aryl, NHC-Os-P^iPr_3, and aryl-Os-CO angles of 155.3(3)º (C(16)-Os-C(1)), 172.0(2)º (C(7)-Os-P(1)) and 178.6(3)º (C(28)-Os-C(29)), respectively. The Os-NHC bond lengths of 2.029(8) (Os-C(7)) and 2.011(8) (Os-C(16)) Å and the Os-aryl distances of 2.144(8) (Os-C(1)) and 2.159(8) (Os-C(28)) Å compare well with the related parameters in **2** and complexes containing $C_{aryl}C_{MeBzIm}$-bidentate ligands.[27e,36] The asymmetry of the structure is also evident in the ^1H and $^{13}C\{^1H\}$ NMR spectra of this compound, in dichloromethane-d_2, at room temperature, which show resonances for inequivalent $C_{aryl}C_{BzIm}$ moieties. Thus, the $^{13}C\{^1H\}$ NMR spectrum contains four signals due to the metalated carbon atoms of the tetradentate ligand at 205.9 (NHC), 181.1 (NHC), 155.1 (Ph) and 154.0 (Ph) ppm. They appear as doublets with values for the C-P coupling constants of 6.3, 74.1, 11.9, and 6.4 Hz, respectively, which are consistent with the structure shown in Figure 2. The CO-resonance is observed at 190.3 ppm, as a doublet with a C-P coupling constant of 10.8 Hz, whereas the IR shows the ν(CO) band at 1907 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 6.9 ppm.

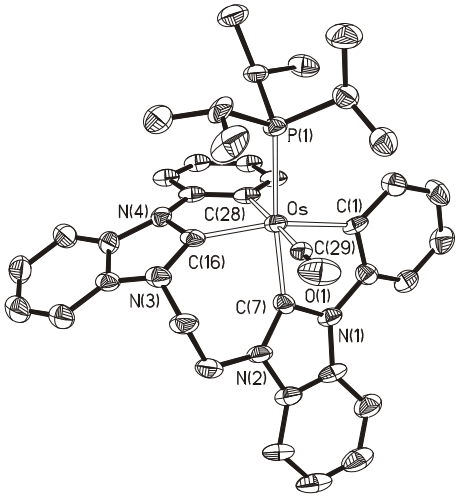
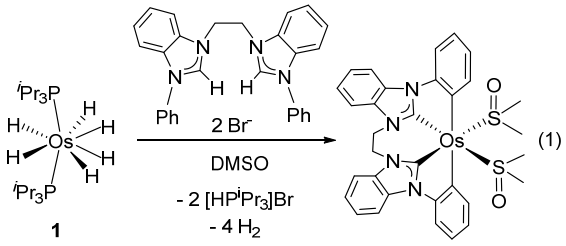


Figure 2. ORTEP diagram of complex **4** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os-P(1) = 2.424(2), Os-C(1) = 2.144(8), Os-C(7) = 2.029(8), Os-C(16) = 2.011(8), Os-C(28) = 2.159(8), Os-C(29) = 1.840(9); P(1)-Os-C(7) = 172.0(2), C(1)-Os-C(16) = 155.3(3), C(1)-Os-C(28) = 86.9(3), C(1)-Os-C(29) = 94.0(3), C(7)-Os-C(16) = 86.9(3), C(16)-Os-C(28) = 76.2(3), C(16)-Os-C(29) = 102.6(4), C(28)-Os-C(29) = 178.6(3).

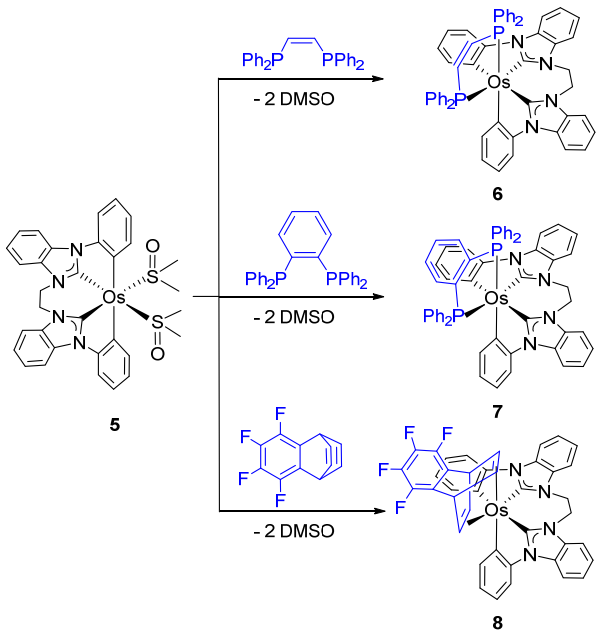
Generation of the C_{aryl},C_{NHC},C_{NHC},C_{aryl} Ligand in One Pot. The choice of the solvent in the planning of the chemical reactions of transition metal complexes is a crucial issue because of the physical and chemical properties of the employed medium can determine the nature of the final product.[37] This is now here better illustrated than in the case of the reactions involving imidazolium and benzimidazolium salts, which show a marked dependence of both solvents and anions.[26,27] In agreement with this, we have now observed that the use of dimethylsulfoxide instead of dimethylformamide allows the generation in one pot of the $C_{C6H4}C_{BzIm}(CH_2CH_2)C_{BzIm}C_{C6H4}$-tetradentate ligand without carbonylating the metal center. Stirring dimethylsulfoxide solutions of **1** and 1,1'-diphenyl-3,3'-ethylenedibenzimidazolium bromide at 140 ºC, for 5 hours leads to the bis(solvento) complex Os{κ^4-*C*,*C*,*C*,*C*-(C_6H_4-BzIm-CH_2CH_2-BzIm-C_6H_4)}$(DMSO)_2$ (**5**), containing the target ligand. This complex was isolated as a yellow solid in 73% yield, according to eq 1. Its ^1H and $^{13}C\{^1H\}$ NMR spectra, in dichloromethane-d_2, between 213 K and 298 K are consistent with a type **I** disposition of the tetradentate ligand

(Chart 1) with the mutually *cis*-disposed dimethylsulfoxide molecules lying *trans* to the benzimidazolidene moieties in a perpendicular plane to the aryl-Os-aryl direction. Thus, in contrast to **4**, the $^{13}C\{^{1}H\}$ NMR spectrum of **5** shows two resonances for the metalated carbon atoms of the tetradentate ligand, at 196.2 (NHC) and 156.4 (Ph) ppm.



1 **5**

The dimethylsulfoxide molecules of **5** can be displaced by bidentate ligands to afford [4+2]-osmium species. Treatment of tetrahydrofuran solutions of **5** with 1,2-bis(diphenylphosphine)ethylene (bdppe), 1,2-bis(diphenylphosphine)benzene (dppbz), and tetrafluorobenzobarrelene (TFB), for 60 h (bdppe and dppbz) or 24 h (TFB), at 100 ºC leads to Os{κ^4-*C*,*C*,*C*,*C*-(C_6H_4-BzIm-CH_2CH_2-BzIm-C_6H_4}(L_2) (L_2 = bdppe (**6**), dppbz (**7**), TFB (**8**)) containing a dianionic C,C',C',C-tetradentate ligand and a diphosphine (**6** and **7**) or diolefin (**8**) group. These compounds were isolated as yellow (**6** and **7**) or white (**8**) solids in 70-40% yield, according to Scheme 4.



5 **6** **7** **8**

Scheme 4. Synthesis of [4+2]-Osmium Species.

Complexes **6** and **7** were characterized by X-ray diffraction analysis. The structures have two molecules chemically equivalent but crystallographically independent in the asymmetric unit. Figure 3 shows a view of one of the molecules of **6**, whereas Figure 4 shows a view of one of the molecules of **7**. Both structures reveal that, in addition to the substitution, a change in the coordination mode of the tetradentate ligand, which goes from type **I** in **5** to type **II** in **6** and 7, has taken place. The change in the relative disposition of the donor atoms of the tetradentate ligand suggests a dissociative mechanism for the ligand substitution process, involving five-coordinate-osmium transitory species, which should result from the release of a dimethylsulfoxide molecule from **5**. The coordination polyhedron around the metal center of each complex can be described as a distorted octahedron with the phenyl group of a $C_{C6H4}C_{BzIm}$ moiety *trans* disposed to the benzimidazolidene group of the other one (C(1)-Os(1)-C(16) = 157.92(15)º) and 161.35(14)º for **6** and 158.3(3)º and 158.0(3)º for **7**) and the remaining metalated carbon atoms *trans*-disposed to the phosphorous atoms of the diphosphine (C(24)-Os(1)-P(2) = 169.84(10)º and 172.06(10)º for **6** and 167.9(2)º and 167.8(2)º for **7**, and C(7)-Os(1)-P(1) = 169.79(11)º and 169.48(10)º for **6** and 172.0(2)º and 171.7(2)º for **7**). The Os-aryl bond lengths of 2.138(4) and 2.132(4) Å (Os-C(1)) and 2.122(4) and 2.121(4) Å (Os-C(24)) for **6** and 2.144(7) and 2.155(7) Å (Os(1)-C(1)) and 2.121(7) and 2.123(7) Å (Os(1)-C(24)) for **7**, as well as the Os-NHC distances of 2.017(4) and 2.018(4) Å (Os(1)-C(16)) and 2.031(4) and 2.026(4) Å (Os(1)-C(7)) for **6** and 2.056(7) and 2.017(8) Å (Os(1)-C(16)) and 2.042(7) and 2.040(7) Å (Os(1)-C(7)) for **7**, compare well with those of **4**. The ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra of these compounds are consistent with the structures shown in Figures 3 and 4 and also support a change in the relative disposition of the donor atoms of the tetradentate ligand with regard to **5**. Thus, in contrast to the latter, the $^{13}C\{^{1}H\}$ NMR spectra, in dichloromethane-d_2, at room temperature contain four resonances for the metalated carbon atoms of the tetradentate ligand at 209.7 (NHC), 186.2 (NHC), 157.3 (Ph), and 152.5 (Ph) ppm for **6** and 210.9 (NHC), 187.4 (NHC), 158.1 (Ph), and 153.9 (Ph) ppm for **7**. In the $^{31}P\{^{1}H\}$ NMR spectra, the inequivalent phosphorous atoms of the diphosphines display two doublets at 35.4 and 22.2 ppm for **6** and at 32.1 and 18.7 ppm for **7** with P-P coupling constants of about 5 Hz.

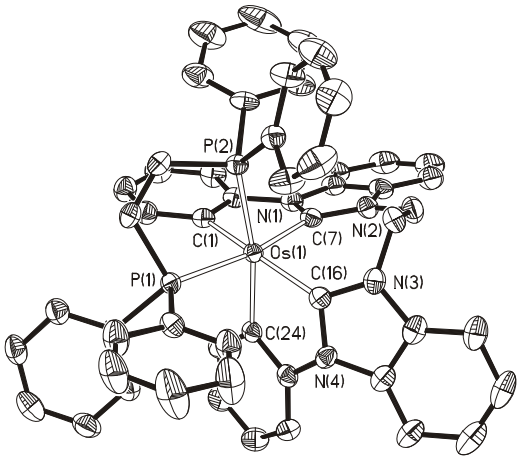
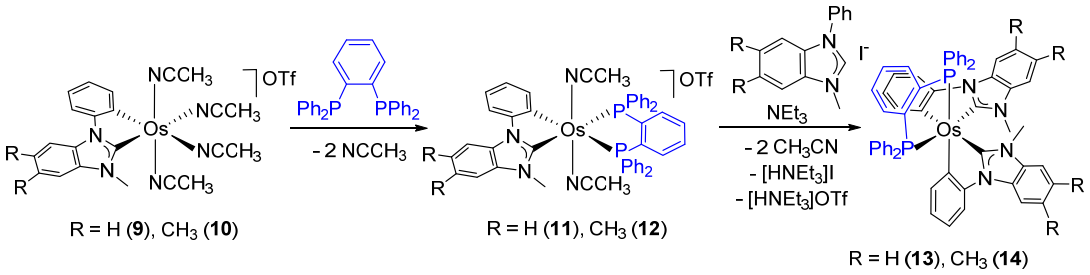


Figure 3. ORTEP diagram of complex **6** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os(1)-P(1) = 2.3599(14), 2.3446(14), Os(1)-P(2) = 2.3166(12), 2.3261(13), Os(1)-C(1) = 2.138(4), 2.132(4), Os(1)-C(7) = 2.031(4), 2.026(4), Os(1)-C(16) = 2.017(4), 2.018(4), Os(1)-C(24) = 2.122(4), 2.121(4); P(1)-Os(1)-P(2) = 82.19(4), 82.40(5), P(1)-Os(1)-C(1) = 93.17(11), 95.65(11), P(1)-Os(1)-C(7) = 169.79(11), 169.48(10), P(1)-Os(1)-C(16) = 103.06(11), 97.41(11), P(2)-Os(1)-C(24) = 169.84(10), 172.06(10), C(1)-Os(1)-C(7) = 77.49(15), 77.71(15), C(1)-Os(1)-C(16) = 157.92(15), 161.35(14), C(1)-Os(1)-C(24) = 89.96(15), 90.96(15), C(7)-Os(1)-C(16) = 87.04(15), 91.02(15), C(16)-Os(1)-C(24) = 75.77(15), 75.55(15).



Scheme 5. Synthesis of Osmium Complexes with two $C_{C6H4}C_{BzIm}$-bidentate Ligands.

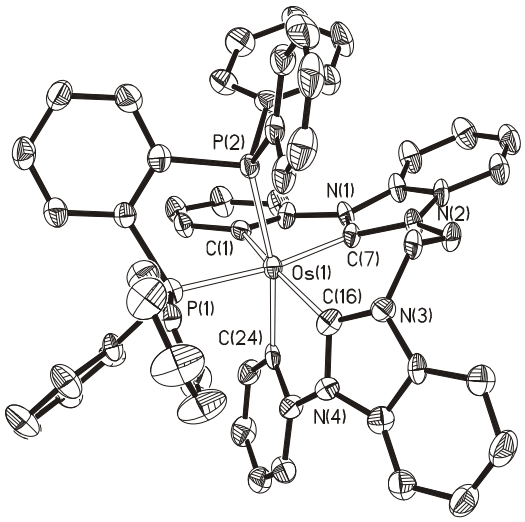


Figure 4. ORTEP diagram of complex **7** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os(1)-P(1) = 2.3407(19), 2.3374(19), Os(1)-P(2) = 2.3219(19), 2.3266(19), Os(1)-C(1) = 2.144(7), 2.155(7), Os(1)-C(7) = 2.042(7), 2.040(7), Os(1)-C(16) = 2.056(7), 2.017(8), Os(1)-C(24) = 2.121(7), 2.123(7); P(1)-Os(1)-P(2) = 81.32(7), 81.53(7), P(1)-Os(1)-C(1) = 98.1(2), 98.3(2), P(1)-Os(1)-C(7) = 172.0(2), 171.7(2), P(1)-Os(1)-C(16) = 97.7(2), 97.7(2), P(2)-Os(1)-C(24) = 167.9(2), 167.8(2), C(1)-Os(1)-C(7) = 76.9(3), 76.6(3), C(1)-Os(1)-C(16) = 158.3(3), 158.0(3), C(1)-Os(1)-C(24) = 89.5(3), 90.6(3), C(7)-Os(1)-C(16) = 88.8(3), 89.0(3), C(16)-Os(1)-C(24) = 76.1(3), 74.9(3).

The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of the tetrafluorobenzobarrelene complex **8**,[38] in dichloromethane-d_2, at room temperature also support a type **II** disposition of the donor atoms of the tetradentate ligand, showing inequivalent olefinic bonds and aryl and benzimidazolidene groups. In the ^{1}H NMR spectrum, the inequivalent olefinic hydrogen atoms display four resonances at 3.08, 2.82, 2.14, and 1.83 ppm, whereas the $^{13}C\{^{1}H\}$ NMR spectrum contains four signals for the coordinated atoms of the diolefin at 50.3, 49.8, 36.2, and 32.1 ppm, in addition to the resonances due to the metalated carbon atoms of the tetradentate ligand at 196.0 (NHC), 188.4 (NHC), 155.8 (Ph), and 152.0 (Ph) ppm.

Complexes with two $C_{C6H4}C_{BzIm}$-Bidentate Ligands: Influence of the Link. In order to know the influence of the $-CH_2CH_2-$ link between the benzimidazolidene groups on the disposition of the donor atoms of the tetradentate ligand around the metal center, we decided to prepare analogous compounds to **7** containing two free phenylbenzimidazolidene groups. Scheme 5 summarizes the procedure used.

Addition of one equivalent of dppbz to dichloromethane solutions of the tetra(solvento) complexes [Os{κ^2-*C*,*C*-(MeL-C_6H_4)}$(CH_3CN)_4$]OTf (L = BzIm (**9**), BzIm* (**10**)), recently reported by us,[36] produces the replacement of two acetonitrile molecules by a bidentate ligand to afford after 12 h the diphosphine derivatives [Os{κ^2-*C*,*C*-(MeL-C_6H_4)}(dppbz)$(CH_3CN)_2$]OTf (L = BzIm (**11**), BzIm* (**12**)), which were isolated as green solids in high yield (90-80%). The formation of these synthetic intermediates was confirmed by means of an X-ray diffraction structure of **11**. Figure 5 shows a view of the cation. The coordination polyhedron around the osmium atom can be rationalized as a distorted octahedron with the acetonitrile molecules mutually *trans*-disposed (N(3)-Os-N(4) = 176.12(14)º). The perpendicular plane is formed by the bidentate ligands, which act with C(1)-Os-C(10) and P(1)-Os-P(2) bite angles of 76.85(16)º and 82.03(4)º, respectively. The Os-NHC and Os-aryl bond lengths of 2.093(4) (Os-C(1)) and 2.124(4) (Os-C(10)) Å, respectively, compare well with those observed in **2**, **4**, **6**, and **7**. The ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra of **11** and **12**, in dichloromethane-d_2, at room temperature are consistent with the structure shown in Figure 5. In the ^{1}H NMR spectra, the most noticeable feature is the presence of only one acetonitrile resonance at 1.6 ppm, in accordance with the equivalence of these ligands. In the $^{13}C\{^{1}H\}$ NMR spectra, they display two singlets at 116 (CN) and 4 (CH_3) ppm, whereas the metalated carbon atoms of the orthometalated NHC ligand give rise at about 187 (NHC) and at 148 (aryl) ppm to double doublets with C-P coupling constants close to 90 and 4 Hz and of about 71 and 6 Hz, respectively. The $^{31}P\{^{1}H\}$ NMR spectra show at about 32 and 24 ppm doublets with a P-P coupling constant of 17 Hz.

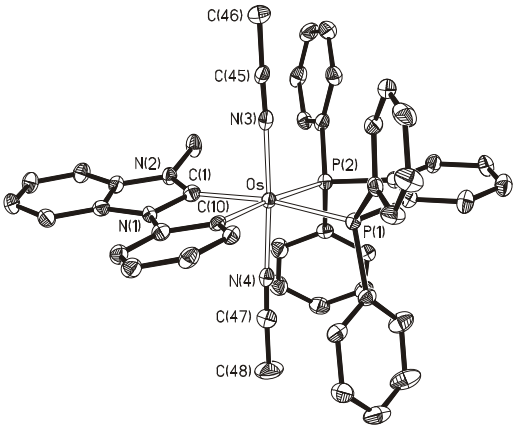


Figure 5. ORTEP diagram of the cation of complex **11** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os-P(1) = 2.3451(11), Os-P(2) = 2.3748(11), Os-N(3) = 2.032(4), Os-N(4) = 2.010(4), Os-C(1) = 2.093(4), Os-C(10) = 2.124(4); P(1)-Os-P(2) = 82.03(4), P(1)-Os-C(1) = 169.93(12), P(1)-Os-C(10) = 94.71(11), P(2)-Os-C(1) = 106.12(11), P(2)-Os-C(10) = 175.83(11), C(1)-Os-C(10) = 76.85(16), N(3)-Os-N(4) = 176.12(14).

Treatment of the dimethylformamide solutions of **11** and **12** with 1.0 equiv of 1-phenyl-3-methyl-1*H*-benzimidazolium iodide and 1.0 equiv of 1-phenyl-3-methyl-1*H*-5,6-dimethyl-benzimidazolium iodide, respectively, and 10 equiv of Et_3N, at 110 ºC, for 3 days gives rise to the replacement of the coordinated acetonitrile molecules by the respective orthometalated benzimidazolidene ligand, generating the target compounds Os{κ^2-*C*,*C*-(MeL-C_6H_4)}$_2$(dppbz) (L = BzIm (**13**), BzIm* (**14**)). These complexes were isolated as yellow solids with moderate yield from 60% (**13**) to 20% (**14**). Complex **13** was characterized by X-ray diffraction analysis. Its structure (Figure 6), which can be described as an octahedron similar to that of **7** with angles P-Os-NHC, P-Os-aryl, and NHC-Os-aryl of 172.85(12)º (P(1)-Os-C(7)), 172.18(12)º (P(2)-Os-C(24)), and 165.16(15)º (C(1)-Os-C(16)), respectively; demonstrates that the –CH_2CH_2– link between the benzimidazolidene groups of the tetradentate ligand does not determine the stereochemistry of **4** and **6-8**, since the disposition of the donor atoms around the metal centers of **13** and **7** is the same; i.e., the stereoisomers **4**, **6-8**, **13** and **14** are thermodynamically controlled and the reason of the observed disposition for the donor atoms is electronic in origin. However, the –CH_2CH_2– link appears to have a significant influence on some parameters of the octahedral structures of the complexes containing the tetradentate ligand. In this context, it should be noted that the link approaches the benzimidazolidene groups, reducing the NHC-Os-NHC angle. Thus, while this angle is 97.88(15)º (C(7)-Os-C(16)) for **13**, it decreases until 88.8(3)º and 89.0(3)º in **7**. The approach of the benzimidazolidene groups has also a marked influence on the dihedral angle containing these groups, which goes from 88.12 in **13** to 65.60º and 62.12º in **7**. In contrast to the NHC-Os-NHC angle, the aryl-Os-aryl angles are similar: 88.29(15) (C(1)-Os-C(24)) in **13** and 89.5(3)º and 90.6(3)º in **7**. The Os-NHC bond lengths 2.051(4) (Os-C(7)) and 2.059(4) (Os-C(16)) Å, and Os-aryl distances, 2.137(4) (Os-C(1)) and 2.127(4) (Os-C(24)) Å, in **13** are also similar to those in **7**. The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of **13** and **14** at room temperature, are in full agreement with those of **7**. The ^{13}C{^{1}H} NMR spectra, in dichloromethane-d_2, show two resonances for the metalated carbon atoms of the inequivalent benzimidazolidene groups, between 200 and 193 ppm, and two signals for the metalated carbon atoms of the inequivalent aryl groups between 159 and 152 ppm. The ^{31}P{^{1}H} NMR spectra, in dimethylformamide, contain two doublets ($^2J_{P\text{-}P} \approx 5$ Hz) at 30 ppm and at about 25 ppm.

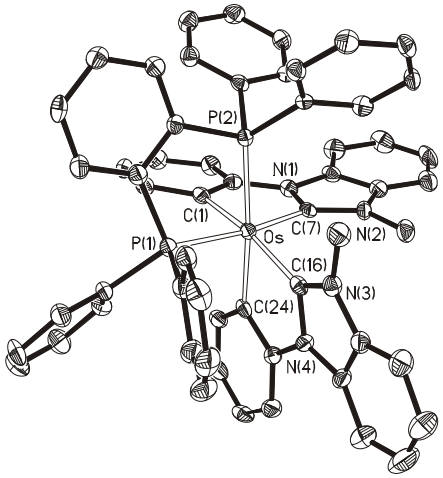


Figure 6. ORTEP diagram of complex **13** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os-P(1) = 2.3161(10), Os-P(2) = 2.3113(10), Os-C(1) = 2.137(4), Os-C(7) = 2.051(4), Os-C(16) = 2.059(4), Os-C(24) = 2.127(4); P(1)-Os-P(2) = 83.59(4), P(1)-Os-C(1) = 96.10(11), P(1)-Os-C(7) = 172.85(12), P(1)-Os-C(16) = 89.15(11), P(2)-Os-C(24) = 172.18(12), C(1)-Os-C(7) = 77.38(15), C(1)-Os-C(16) = 165.16(15), C(1)-Os-C(24) = 88.29(15), C(7)-Os-C(16) = 97.88(15), C(16)-Os-C(24) = 77.30(16).

Influence of the Link on the Emissive Properties of 7. Because several types of osmium(II) complexes with multidentate NHC ligands have shown to be emissive upon photoexcitation,[27d,39] the photophysical properties of **2-8** were investigated. However, only complex **7** proved to be emissive. Then, in order to analyze the influence of the –CH_2CH_2– link of the tetratentate ligand on its emission, the photophysical properties of **13** and **14**, with two free phenylbenzimidazolidene groups, were studied as well.

Absorption spectra of 2.0x10^{-4} M 2-methyltetrahydrofuran solutions of **7**, **13**, and **14** in the visible region are collected in Table 1. As expected, the spectra of the three compounds are very similar, showing an intense absorption centered at about 330 nm and a less intense band centered at 404 nm. On the basis of time-dependent calculations in tetrahydrofuran, they were assigned to metal-to-ligand charge transfer transitions with a remarkable π-π* character.

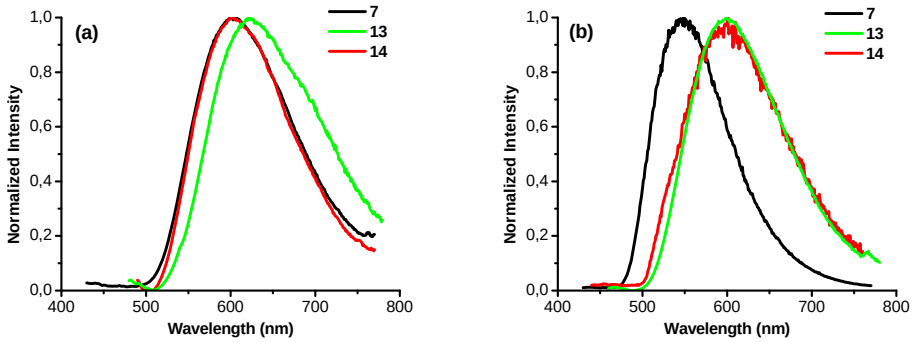


Figure 7. Emission spectra in the solid state at 298 K (a) and in 2-MeTHF at 77 K (b) for complexes **7**, **13** and **14**.

Table 1. UV/Vis Experimental Data[a] for Complexes **7**, **13** and **14** and Corresponding Computed TD-DFT Gas Phase Vertical Excitation Energies for Derivatives **7** and **13**.

Complex	Obsd λ (nm) (ε (10^4 M^{-1} cm^{-1}))	Calcd λ (nm)[b]
7	336 (5.0), 404 (0.6)	338 (*0.1163*), 341 (*0.0088*), 400 (*0.0119*)
13	328 (5.4), 404 (0.4)	321 (*0.1222*), 401 (*0.003*), 406 (*0.0063*)
14	330 (5.5), 404 (0.4)	

[a] UV/Vis data were recorded at room temperature in 2-MeTHF with a concentration $2.0 \cdot 10^{-4}$ M. [b] Values corresponding to the oscillator strength, *f*, are given in parentheses.

Complexes **7**, **13**, and **14** are emissive upon photoexcitation in the solid state at room temperature and in 2-methyltetrahydrofuran at 77 K,[40] displaying bands centered between 630 and 549 nm. Figure 7 depicts the emission spectra, whereas Table 2 collects lifetimes and quantum yields which lie in the range 0.24-4.85 μs and between 0.046 and 0.052, respectively. The emissions can be attributed to π-π* HOMO (65% Os + 38% NHC) to LUMO (94% diphosphine) S_o-T_1 metal-to-ligand (osmium-to-diphosphine) charge transfer transitions. In accordance with this, the computed emission wavelength for **7** and **13**, which has been estimated by means of the difference in energy between the optimized triplet excited state and the singlet state with the same geometry as the optimized triplet excited state, 662 nm for both compounds, is in reasonable agreement with the experimental values.

The comparison of the spectra of Figure 7 reveals that the emission of complex **7**, containing two orthometalated N-phenylbenzimidazolidene moieties linked by a $–CH_2CH_2–$ group, is narrower than those of **13** and **14**, containing two separated orthometalated N-phenylbenzimidazolidene ligands, and is slightly shifted towards the blue; i.e., the presence of the link between the benzimidazolidene moieties seems to give rise to a narrower and bluer emission.

Table 2. Photophysical Properties of Complexes **7**, **13** and **14** in Solid State at 298 K and Degassed 2-MeTHF at 77 K**.**

Complex	media (T/K)	λ_{em} (nm)	τ (μs)	Φ [a]
7	solid (298)	600 (λ_{exc} 435)	0.24	0.050
	2-MeTHF (77)	549 (λ_{exc} 337)	4.85	
13	solid (298)	630 (λ_{exc} 480)	0.17	0.046
	2-MeTHF (77)	599 (λ_{exc} 460)	1.66	
14	solid (298)	602 (λ_{exc} 460)	0.37	0.052
	2-MeTHF (77)	600 (λ_{exc} 400)	1.22	

[a] Measurements in solid state by doping 5% sample in PMMA film.

CONCLUDING REMARKS

This study has revealed that transition metal polyhydride complexes can promote the direct metalation of the benzimidazolium unit and the carbon direct C-H bond activation of the phenyl substituent of two N-phenylbenzimidazolium moieties linked through a flexible $–CH_2CH_2–$ chain, which is bonded to the remaining nitrogen atoms. The *multi* C-H bond activation process affords compounds containing a C_{aryl},C_{NHC},C_{NHC},C_{aryl}-tetradentate ligand. As a proof of concept, we show that the reactions of the d^2-hexahydride complex $OsH_6(P^iPr_3)_2$ with 1,1'-diphenyl-3,3'-ethylenedibenzimidazolium bromide give rise to Os{κ^4-*C*,*C*,*C*,*C*-(C_6H_4-BzIm-CH_2CH_2-BzIm-C_6H_4}L_2 derivatives via OsH{κ^3-*C*,*C*,*C*-(C_6H_4-BzIm-CH_2CH_2-BzIm-Ph}L_2 pincer-intermediates or in one pot, depending upon the reaction conditions.

The tetradentate ligand avoids a four-planar coordination, whereas it favors a *mer* three-planar disposition with the fourth donor atom situated in a perpendicular direction (**II** in Chart 1). The reason of this preference is electronic, since the observed disposition for the donor atoms is not determined by the presence of the link between the benzimidazolidene groups and is also the found one in complexes containing two free orthometalated N-phenylbenzimidazolidene ligands. The link has a modest influence on some parameters of the structures of the resulting complexes, such as the BzIm-M-BzIm bite angle and the dihedral angle between the planes containing the benzimidazoline groups. Although only one of the reported complexes containing the pincer ligand is emissive, the compari-

son of its emission spectra with those of compound containing two free phenylbenzimidazolidene groups seems to suggest that the link favors narrower and bluer emissions.

In conclusion, two procedures for the preparation of osmium(II) complexes containing novel C_{aryl},C_{NHC},C_{NHC},C_{aryl}-tetradentate ligands with a $–CH_2CH_2–$ link between the NHC groups have been discovered and the influence of the link on the structure of the complexes and their emissive properties has been analyzed.

EXPERIMENTAL SECTION

General Information. All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents (except DMF, THF and 2-MeTHF that were dried and distilled under argon) were obtained oxygen- and water-free from an MBraun solvent purification apparatus. ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra were recorded on Bruker 300 ARX, Bruker Avance 300 MHz, Bruker Avance 400 MHz, and Bruker Avance 500 MHz instruments. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}) or external 85% H_3PO_4 (^{31}P{^{1}H}), or external $CFCl_3$ (^{19}F). Coupling constants *J* are given in hertz. Attenuated total reflection infrared spectra (ATR-IR) of solid samples were run on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. High-resolution electrospray mass spectra were acquired using a MicroTOF-Q hybrid quadrupole time-of-flight spectrometer (Bruker Daltonics, Bremen, Germany). $OsH_6(P^iPr_3)_2$ (**1**),[41] 1,1'-diphenyl-3,3'-ethylenedibenzimidazolium dibromide,[29] [Os{κ^2-*C*,*C*-(MeL-C_6H_4)}$(CH_3CN)_4$]OTf (L = BzIm (**9**), BzIm* (**10**)),[36] [PhMeBzImH]I,[27e] and [PhMeBzIm*H]I[27e] were prepared by published methods.

Photophysical Studies. All the manipulations of the organometallic compounds were carried out in strict absence of oxygen and water. An Evolution 600 spectrophotometer was used to record UV-vis spectra. Steady-state photoluminescence spectra were obtained with a Jobin-Yvon Horiba Fluorolog FL-3-11 spectrofluorometer. An IBH 5000F coaxial nanosecond flash lamp was used to measure the lifetimes. Photoluminescent quantum yield data were measured on a Hamamatsu Quantaurus-QY Absolute PL quantum yield C11347-11 spectrometer.

Reaction of $OsH_6(P^iPr_3)_2$ (1) with 1,1'-diphenyl-3,3'-ethylenedibenzimidazolium dibromide in dimethylformamide: Preparation of OsBr{κ^3-*C*,*C*,*C*-(C_6H_4-BzIm-CH_2CH_2-BzIm-Ph)}(CO)(P^iPr_3) (2). A solution of **1** (250 mg, 0.484 mmol) in dimethylformamide (5 mL) was treated with 1,1'-diphenyl-3,3'-ethylenedibenzimidazolium dibromide (279 mg, 0.484 mmol). The resulting mixture was refluxed for 20 min, getting a dark brown solution. After cooling at room temperature the solvent was removed in vacuo, affording a brown residue. Dichloromethane (5 mL) was added and the resulting suspension was filtered, getting a brown solution that was evaporated to dryness. Addition of methanol (4 mL) afforded a green solid, which was washed with further portions of methanol (2 x 3 mL) and dried in vacuo. Yield: 240 mg (57 %). Anal. Calcd. for $C_{38}H_{42}BrN_4OOsP$: C, 52.35; H, 4.86; N, 6.43. Found: C, 52.05; H, 5.05; N, 6.12. HRMS (electrospray, *m*/*z*) calcd for $C_{38}H_{43}BrN_4OOsP$ $[M+H]^+$: 873.1949; found: 873.2000. IR (cm^{-1}): ν(CO) 1911 (s). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 8.48 (br, 1H, CH Ph), 8.24 (d, $^3J_{H-H}$ = 7.2, 1H, CH Ph), 7.88 (m, 2H, CH BzIm), 7.61 (m, 3H, Ph), 7.48 (m, 3H, CH Ph and BzIm), 7.39 (m, 2H, Ph), 7.27 (t, $^3J_{H-H}$ = 7.5, 1H, BzIm), 7.15 (t, $^3J_{H-H}$ = 7.5, 1H, BzIm), 6.98 (t, $^3J_{H-H}$ = 7.5, 1H, BzIm), 6.88 (t, $^3J_{H-H}$ = 7.5, 1H, BzIm), 6.75 (d, $^3J_{H-H}$ = 7.5, 1H, BzIm), 5.27, 5.00, 4.96, 4.59 (all m, 1H each, -CH_2-), 1.54 (m, 3H, PC*H*$(CH_3)_2$), 0.90 (dd, $^3J_{H-H}$ = 6.9, $^3J_{H-P}$ = 13.2, 9H, PCH(C*H*$_3)_2$), 0.71 (dd, $^3J_{H-H}$ = 7.2, $^3J_{H-P}$ = 12.9, 9H, PCH(C*H*$_3)_2$). ^{13}C{^{1}H} + HMBC+ HSQC NMR (75.42 MHz, CD_2Cl_2, 298 K): δ 192.2 (d, $^2J_{C-P}$ = 9.2, N*C*N), 191.7 (d, $^2J_{C-P}$ = 4.4, CO), 188.2 (d, $^2J_{C-P}$ = 6.2, N*C*N), 152.6 (d, $^2J_{C-P}$ = 7.4, Os-C Ph), 150.4 (s, C_q), 140.9 (s, CH Ph), 140.0, 138.9, 136.9, 134.7, 132.9 (all s, C_q Ph and BzIm), 132.6, 130.1, 129.8, 129.5, 129.0, 124.6, 124.1, 123.2, 123.1, 123.0, 121.6, 113.1, 112.6, 111.7, 109.9, 108.6 (all s, CH Ph and BzIm), 46.7, 45.2 (both s, -CH_2-), 29.0 (d, $^1J_{P-C}$ = 29, P*C*H$(CH_3)_2$), 19.7, 19.4 (both s, PCH$(CH_3)_2$). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2, 298 K): δ 10.8 (s).

Reaction of OsBr{κ^3-*C*,*C*,*C*-(C_6H_4-BzIm-CH_2CH_2-BzIm-Ph)}(CO)(P^iPr_3) (2) with Na[BH_4]: Preparation of *cis*-*H*,*P*-OsH{κ^3-*C*,*C*,*C*-(C_6H_4-BzIm-CH_2CH_2-BzIm-Ph)}(CO)(P^iPr_3) (3a). A solution of **2** (180 mg, 0.206 mmol) in toluene (5 mL) was cooled to -16 ºC and treated with an excess of Na[BH_4] (79 mg, 2.1 mmol). After addition of some drops of methanol, the resulting mixture was stirred for 10 min at -16ºC and dried in vacuo. Toluene (6 mL) was added and the resulting suspension was filtered, getting a yellow solution that was evaporated to dryness. After cooling at -78 ºC, addition of pentane (4 mL) afforded a light yellow solid that was washed with further portions of pentane (2 x 3 mL) and dried in vacuo. Yield: 111 mg (68 %). Anal. Calcd. for $C_{38}H_{43}N_4OOsP$: C, 57.56; H, 5.47; N, 7.07. Found: C, 57.32; H, 5.40; N, 7.09. HRMS (electrospray, *m*/*z*) calcd for $C_{38}H_{42}N_4OOsP$ $[M-H]^+$: 793.2708; found: 793.2718. IR (cm^{-1}): ν(Os-H) 1900 (m), ν(CO) 1874 (s). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 8.08 (m, 1H, CH), 7.70 (d, J_{H-H} = 7.6, 1H, CH), 7.63 (d, J_{H-H} = 7.1, 1H, CH), 7.49-7.28 (m, 6H, CH), 7.27 (m, 1H, -CH_2-), 7.19 (m, 2H, CH), 7.10 (t, J_{H-H} = 7.6, 1H, CH), 6.93 (m, 2H, CH), 6.78 (t, $^3J_{H-H}$ = 7.1, 1H, CH), 6.70 (d, $^3J_{H-H}$ = 7.6, 1H, CH), 6.43 (m, 1H, CH), 4.82 (m, 3H, -CH_2-), 1.80 (m, 3H, PC*H*$(CH_3)_2$), 0.99 (dd, $^3J_{H-H}$ = 7.1, $^3J_{H-P}$ = 12.5, 9H, PCH(C*H*$_3)_2$), 0.83 (dd, $^3J_{H-H}$ = 7.1, $^3J_{H-P}$ = 12.5, 9H, PCH(C*H*$_3)_2$), -8.31 (d, $^2J_{H-P}$ = 29.4, 1H, OsH). ^{13}C{^{1}H} + HMBC+ HSQC NMR (125.76 MHz, CD_2Cl_2, 298 K): δ 198.2 (d, $^2J_{C-P}$ = 8.5, CO), 192.7 (s, $^2J_{C-P}$ = 63.6, N*C*N), 191.2 (d, $^2J_{C-P}$ = 8.1, N*C*N), 159.7 (d, $^2J_{C-P}$ = 7.7, Os-C Ph), 149.1 (s, C_q), 144.8 (s, CH Ph), 138.8, 138.1, 137.8, 136.0, 133.0 (all s, C_q Ph and BzIm), 131.7, 129.6, 129.1, 128.6, 128.0, 123.5, 123.2 122.6, 122.5, 122.1, 119.2, 112.1, 111.7, 110.4 109.3, 108.6 (all s, CH Ph and BzIm), 47.3, 44.7 (both s, -CH_2-), 27.9 (d, $^1J_{P-C}$ = 23.1, P*C*H$(CH_3)_2$), 20.6, 19.6 (both s, PCH(*C*H$_3)_2$). ^{31}P{^{1}H} NMR (121.49 MHz, CD_2Cl_2, 298 K): δ 20.1 (s).

Isomerization of *cis*-*H*,*P*-OsH{κ^3-*C*,*C*,*C*-(C_6H_4-BzIm-CH_2CH_2-BzIm-Ph)}(CO)(P^iPr_3) (3a) to *trans*-*H*,*P*-OsH{κ^3-*C*,*C*,*C*-(C_6H_4-BzIm-CH_2CH_2-BzIm-Ph)}(CO)(P^iPr_3) (3b). 3a (50 mg, 0.063 mmol) was dissolved in toluene/methanol (4 mL/1 mL), and the solution was periodically checked by ^{31}P{^{1}H} NMR, showing that fter 3 days at room temperature the isomerization to **3b** is complete. The solution was evaporated to dryness, and pentane (4 mL) was added to afford a light yellow solid that was washed with further portions of pentane (2 x 3 mL) and dried in vacuo. Yield: 47 mg (94 %). Anal. Calcd. for $C_{38}H_{43}N_4OOsP$: C, 57.56; H, 5.47; N, 7.07. Found: C, 57.42; H, 5.23; N, 7.18. HRMS (electrospray, m/z) calcd for $C_{38}H_{42}N_4OOsP$ $[M-H]^+$: 793.2708; found: 793.2724. IR (cm^{-1}): ν(CO) 1889 (s). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 8.18 (d, $^3J_{H-H}$ = 7.2, 1H, CH), 7.91 (d, $^3J_{H-H}$ = 7.2, 1H, CH), 7.81 (d, $^3J_{H-H}$ = 7.2, 1H, CH), 7.59-7.47 (m, 5H, CH), 7.39-7.29 (m, 4H, CH), 7.18 (t, $^3J_{H-H}$ = 7.2, 1H, CH), 7.06 (t, $^3J_{H-H}$ = 7.5, 1H, CH), 6.94 (t, $^3J_{H-H}$ = 7.5, 1H, CH), 6.80 (t, $^3J_{H-H}$ = 7.0, 1H, CH), 6.70 (t, $^3J_{H-H}$ = 7.5, 1H, CH), 5.50, 4.84, 4.78, 4.59 (all m, 1H each, -CH_2-), 2.27 (m, 3H, PC*H*$(CH_3)_2$), 0.92 (dd, $^3J_{H-H}$ = 7.0, $^3J_{H-P}$ = 12.5, 9H, PCH(C*H*$_3)_2$), 0.70 (dd, $^3J_{H-H}$ = 7.0, $^3J_{H-P}$ = 12.0, 9H, PCH(C*H*$_3)_2$), -8.99 (d, $^2J_{H-P}$ = 52.0, 1H, OsH). ^{13}C{^{1}H} + HMBC+ HSQC NMR (125.76 MHz, CD_2Cl_2, 298 K): δ 196.0 (d, $^2J_{C-P}$ = 5.0, CO), 195.9 (d, $^2J_{C-P}$ = 6.3, N*C*N), 190.8 (d, $^2J_{C-P}$ = 6.2, N*C*N), 153.1 (d, $^2J_{C-P}$ = 7.6, Os-C Ph), 149.1 (s, C_q), 141.4 (s, CH Ph), 141.2, 138.9, 137.5, 135.1, 133.1 (all s, C_q Ph and BzIm), 132.1, 130.4, 130.0, 129.6, 129.1, 124.2, 123.5, 122.5, 122.4, 122.2, 119.7, 112.2, 111.9, 110.5, 109.2, 107.8 (all s, CH Ph and BzIm), 47.4, 44.7 (both s, -CH_2-), 29.0 (d, $^1J_{P-C}$ = 17.6, P*C*H$(CH_3)_2$), 20.3, 19.5 (both s, PCH(*C*H$_3)_2$). ^{31}P{^{1}H} NMR (121.49 MHz, CD_2Cl_2, 298 K): δ 9.9 (s).

Preparation of Os{κ^4-*C*,*C*,*C*,*C*-(C_6H_4-BzIm-CH_2CH_2-BzIm-C_6H_4)}(CO)(P^iPr_3) (4). A solution of **3b** (200 mg, 0.252 mmol) in toluene (10 mL) was heated at 100 ºC for 4 days in a schlenk provided with a Teflon closure. After cooling at room temperature the solution was filtered and dried in vacuo. Addition of diethyl ether (4 mL)

afforded an off white solid, which was washed with further portions of diethyl ether (4 x 3 mL) and dried in vacuo. Yield: 177.5 mg (89 %). Anal. Calcd. for $C_{38}H_{41}N_4OOsP$: C, 57.70; H, 5.22; N, 7.08. Found: C, 57.44; H, 5.17; N, 6.88. HRMS (electrospray, *m/z*) calcd for $C_{38}H_{42}N_4OOsP$ $[M+H]^+$: 793.2708; found: 793.2706. IR (cm^{-1}): ν(CO) 1907 (s). ^1H NMR (300 MHz, CD_2Cl_2, 298 K): δ 8.12 (dd, $^3J_{H-H}$ = 7.6, $^3J_{H-H}$ = 1.6, 1H, CH), 8.05 (d, $^3J_{H-H}$ = 1.6, 1H, CH), 7.90 (m, 2H, CH), 7.49 (m, 2H, CH), 7.28 (m, 4H, CH), 7.16 (m, 3H, CH), 6.85 (m, 1H, CH), 6.47 (m, 2H, CH), 6.30 (ddd, $^3J_{H-H}$ = 15.6, $^3J_{H-H}$ = 12.2, $^1J_{H-H}$ = 1.8, 1H, -CH_2-), 4.90 (ddd, $^3J_{H-H}$ = 15.6, $^3J_{H-H}$ = 3.4, $^1J_{H-H}$ = 1.8, 1H, -CH_2-), 4.57 (ddd, $^3J_{H-H}$ = 13.6, $^3J_{H-H}$ = 3.4, $^1J_{H-H}$ = 1.8, 1H, -CH_2-), 4.07 (ddd, $^3J_{H-H}$ = 13.6, $^3J_{H-H}$ = 12.2, $^1J_{H-H}$ = 1.8, 1H, -CH_2-), 2.08 (m, 3H, PC*H*(CH_3)$_2$), 1.21 (dd, $^3J_{H-H}$ = 6.8, $^3J_{H-P}$ = 14.0, 9H, PCH(CH_3)$_2$), 0.88 (dd, $^3J_{H-H}$ = 7.2, $^3J_{H-P}$ = 11.2, 9H, PCH(CH_3)$_2$). $^{13}C\{^1H\}$ + HMBC+ HSQC NMR (100.61 MHz, CD_2Cl_2, 298 K): δ 205.9 (d, $^2J_{C-P}$ = 6.3, N*C*N), 190.3 (d, $^2J_{C-P}$ = 10.8, CO), 181.1 (d, $^2J_{C-P}$ = 74.1, N*C*N), 155.1 (d, $^2J_{C-P}$ = 11.9, Os-*C* Ph), 154.0 (d, $^2J_{C-P}$ = 6.4, Os-C Ph), 150.7 (d, $^3J_{C-P}$ = 2.5, C_q Ph), 150.6 (d, $^3J_{C-P}$ = 4.5, C_q Ph), 145.2, 141.1 (both s, CH Ph), 138.2 (d, $^4J_{C-P}$ = 3.1, C_q BzIm), 136.6 (s, C_q BzIm), 135.8 (s, C_q BzIm), 132.4 (s, C_q BzIm), 125.0, 123.4, 123.1, 122.8, 122.6, 122.4, 122.3, 121.7, 112.9, 111.6, 111.5, 111.3, 110.1, 108.9 (all s, CH Ph and BzIm), 48.0, 44.9 (both s, -CH_2-), 24.6 (d, $^1J_{P-C}$ = 20.5, P*C*H(CH_3)$_2$), 22.2 (s, PCH(*C*H_3)$_2$), 18.8 (d, $^2J_{P-C}$ = 3.0, PCH(*C*H_3)$_2$). $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 298 K): δ 6.9 (s).

Reaction of $OsH_6(P^iPr_3)_2$ (1) with 1,1'-diphenyl-3,3'-ethylenedibenzimidazolium dibromide in dimethylsulfoxide: Preparation of Os{κ^4-*C*,*C*,*C*,*C*-(C_6H_4-BzIm-CH_2CH_2-BzIm-C_6H_4)}$(DMSO)_2$ (5). A solution of **1** (200 mg, 0.387 mmol) in dimethylsulfoxide (5 mL) was treated with 1,1'-diphenyl-3,3'-ethylenedibenzimidazolium dibromide (223 mg, 0.387 mmol). The resulting mixture was stirred at 140 ºC for 5 h, getting a yellow solution. After cooling at room temperature the solvent was removed in vacuo, affording a yellow residue. Acetonitrile (7 mL) was added and the resulting suspension was filtered. The yellow solution thus obtained was evaporated to dryness. Addition of diethyl ether (5 mL) caused the precipitation of a light yellow solid that was washed with further portions of diethyl ether (6 x 5 mL) and dried in vacuo. Yield: 215 mg (73 %). Anal. Calcd. for $C_{32}H_{32}N_4O_2OsS_2$: C, 50.64; H, 4.25; N, 7.38; S, 8.45. Found: C, 50.33; H, 4.45; N, 7.17; S, 8.21. HRMS (electrospray, *m/z*) calcd for $C_{32}H_{33}N_4O_2OsS_2$ $[M+H]^+$: 761.1651; found: 761.1737. IR (cm^{-1}): ν(C=C) 1570 (w), ν(S=O) 1047 (vs). ^1H NMR (300 MHz, CD_2Cl_2, 298 K): δ 8.46 (dd, $^3J_{H-H}$ = 6.3, $^4J_{H-H}$ = 2.1, 2H, Ph), 8.14 (m, 2H, BzIm), 7.94 (dd, $^3J_{H-H}$ = 7.5, $^4J_{H-H}$ = 1.5, 2H, Ph), 7.52 (m, 2H, BzIm), 7.34 (m, 4H, BzIm), 7.27-7.18 (m, 4H, Ph), 5.12-4.93 (m, 4H, -CH_2-), 2.33 (s, 6H, $(CH_3)_2$S=O), 2.26 (s, 6H, $(CH_3)_2$S=O). $^{13}C\{^1H\}$ + HMBC+ HSQC NMR (75.4 MHz, CD_2Cl_2, 298 K): δ 196.2 (s, N*C*N), 156.4 (s, Os-C Ph), 155.0 (s, C_q Ph), 141.8 (s, CH Ph), 138.3, 133.7 (both s, C_q BzIm), 124.7, 123.5, 123.1, 122.3, 113.0, 111.2, 109.4 (all s, CH Ph and BzIm), 46.9 (s, -CH_2-), 46.8, 46.6 (both s, $(CH_3)_2$S=O).

Reaction of Os{κ^4-*C*,*C*,*C*,*C*-(C_6H_4-BzIm-CH_2CH_2-BzIm-C_6H_4)}$(DMSO)_2$ (5) with *cis*-1,2-bis(diphenylphosphino)ethylene (bdppe): Preparation of Os{κ^4-*C*,*C*,*C*,*C*-(C_6H_4-BzIm-CH_2CH_2-BzIm-C_6H_4)}(bdppe) (6). In a schlenk flask provided with a teflon closure a solution of **5** (200 mg, 0.264 mmol) in THF (10 mL) was treated with bdppe (105 mg, 0.264 mmol). The resulting mixture was stirred at 100ºC for 60 h, getting a yellow solution. After cooling at room temperature the solvent was removed in vacuo. Dichloromethane (10 mL) was added and the resulting solution was filtered and evaporated to dryness. Addition of acetonitrile (5 mL) caused precipitation of a light yellow solid that was washed with further portions of acetonitrile (2 x 5 mL) and subsequently with diethyl ether (3 x 5 mL) and dried in vacuo. Yield: 108 mg (41 %). Anal. Calcd. for $C_{54}H_{42}N_4OsP_2$: C, 64.92; H, 4.24; N, 5.61. Found: C, 64.81; H, 4.08; N, 5.48. HRMS (electrospray, *m/z*) calcd for $C_{54}H_{43}N_4OsP_2$ $[M+H]^+$: 1001.2577; found: 1001.2537. IR (cm^{-1}): ν(C=C) 1570 (w). ^1H NMR (500 MHz, CD_2Cl_2, 298 K): δ 8.08-8.03 (m, 1H, CH), 7.75 (d, $^3J_{H-H}$ = 7.5, 1H, CH), 7.65 (ddd, $^2J_{H-P}$ = 50.2, $^3J_{H-H}$ = 9.0, $^3J_{H-P}$ = 7.5, 1H, PCH=), 7.59 (m, 1H, CH), 7.51 (d, $^3J_{H-H}$ = 7.5, 1H, CH), 7.37-7.35 (m, 1H, CH), 7.33-7.18 (m, 10H, CH and PCH=), 7.13 (dt, J_{H-H} = 2.0, $^3J_{H-H}$ = 8.0, 2H, CH), 7.09-6.90 (m, 11H, CH), 6.83 (dt, $^4J_{H-H}$ = 1.0, $^3J_{H-H}$ = 7.5, 1H, CH), 6.75-6.72 (m, 1H, CH), 6.70 (dt, $^4J_{H-H}$ = 1.0, $^3J_{H-H}$ = 7.0, 1H, CH), 6.50-6.44 (m, 1H, CH), 6.41 (dt, $^4J_{H-H}$ = 2.0, $^3J_{H-H}$ = 8.0, 2H, CH), 6.35 (t, J_{H-H} = 7.2, 1H, CH), 6.32-6.28 (m, 2H, CH), 5.85-5.78 (m, 1H, -CH_2-), 4.43-4.36 (m, 2H, -CH_2-), 3.93-3.87 (m, 1H, -CH_2-). $^{13}C\{^1H\}$ + HMBC+ HSQC NMR (125.68 MHz, CD_2Cl_2, 298 K): δ 209.7 (t, $^2J_{C-P}$ = 4.6, N*C*N), 186.2 (dd, $^2J_{C-P}$ = 8.4, $^2J_{C-P}$ = 80.9, N*C*N), 157.3 (t, $^2J_{C-P}$ = 6.1, Os-C Ph), 152.5 (dd, $^2J_{C-P}$ = 13.1, $^2J_{C-P}$ = 56.5, Os-C Ph), 152.2 (dd, $^2J_{C-P}$ = 30.3, $^1J_{C-P}$ = 41.5, P-CH=), 151.8 (d, J_{C-P} = 3.3, C_q), 148.9 (d, J_{C-P} = 3.8, C_q), 145.0 (dd, $^2J_{C-P}$ = 29.7, $^1J_{C-P}$ = 39.5, P-CH=), 142.7 (d, J_{C-P} = 38.8, C_q), 141.8 (d, J_{C-P} = 9.9, CH), 141.7 (s, CH), 138.6 (d, J_{C-P} = 3.5, C_q), 137.1 (d, J_{C-P} = 29.9, C_q), 137.0, 136.6 (both s, C_q), 135.0 (t, J_{C-P} = 2.1, CH), 134.6 (dd, J_{C-P} = 5.6, J_{C-P} = 34.9, C_q), 133.6 (d, J_{C-P} = 2.9, C_q), 133.2, 133.1 (both s, CH), 132.6 (d, J_{C-P} = 1.9, C_q), 131.9 (d, J_{C-P} = 10.4, CH), 129.5 (d, J_{C-P} = 1.6, CH), 129.3 (d, J_{C-P} = 9.3, CH), 128.6 (d, J_{C-P} = 1.6, CH), 128.4 (d, J_{C-P} = 8.5, CH), 127.9, 127.8 (both s, CH), 127.6 (d, J_{C-P} = 8.0, CH), 126.9 (d, J_{C-P} = 8.7, CH), 123.9, 123.6, 122.6, 122.1, 121.8, 121.2, 120.6, 119.2, 111.8, 111.4, 111.0, 110.5, 109.8, 107.4 (all s, CH), 47.6 (s, -CH_2-), 44.9 (d, $^4J_{C-P}$ = 3.5, -CH_2-). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 298 K): δ 35.4 (d, $^2J_{P-P}$ = 3.8), 22.2 (d, $^2J_{P-P}$ = 3.8).

Reaction of Os{κ^4-*C*,*C*,*C*,*C*-(C_6H_4-BzIm-CH_2CH_2-BzIm-C_6H_4)}$(DMSO)_2$ (5) with 1,2-bis(diphenylphosphino)benzene (dppbz): Preparation of Os{κ^4-*C*,*C*,*C*,*C*-(C_6H_4-BzIm-CH_2CH_2-BzIm-C_6H_4)}(dppbz) (7). In a schlenk flask provided with a teflon closure a solution of **5** (200 mg, 0.264 mmol) in THF (10 mL) was treated with dppbz (118 mg, 0.264 mmol). The resulting mixture was stirred at 100 ºC for 60 h, getting a yellow solution. After cooling at room temperature the solvent was removed in vacuo. Dichloromethane (10 mL) was added and the resulting solution was filtered and evaporated to dryness. Addition of acetonitrile (5 mL) caused precipitation of a yellow solid that was washed with further portions of acetonitrile (2 x 5 mL) and subsequently with diethyl ether (3 x 5 mL) and dried in vacuo. Yield: 215 mg (68%). Anal. Calcd. for $C_{58}H_{44}N_4OsP_2$: C, 66.40; H, 4.23; N, 5.34. Found: C, 66.01; H, 4.00; N, 5.07. HRMS (electrospray, *m/z*) calcd for $C_{58}H_{45}N_4OsP_2$ $[M+H]^+$: 1051.2734; found: 1051.2695. IR (cm^{-1}): ν(C=C) 1570 (w). ^1H NMR (500 MHz, CD_2Cl_2, 298K): δ 8.00 (dd, $^3J_{H-H}$ = 7.0, $^4J_{H-H}$ = 1.5, 1H, CH), 7.63 (t, $^3J_{H-H}$ = 8.0, 2H, CH), 7.58 (m, 1H, CH), 7.53-7.50 (m, 3H, CH), 7.38 (d, $^3J_{H-H}$ = 7.5, 1H, CH), 7.35 (d, $^3J_{H-H}$ = 7.5, 1H, CH), 7.29-7.25 (m, 8H, CH), 7.16-7.14 (m, 3H, CH), 7.08-7.00 (m, 3H, CH), 6.95-6.88 (m, 6H, CH), 6.79-6.76 (m, 3H, CH), 6.73 (t, $^3J_{H-H}$ = 7.5, 1H, CH), 6.63 (dt, $^4J_{H-H}$ = 1.0, $^3J_{H-H}$ = 7.2,1H, CH), 6.59 (dt, $^4J_{H-H}$ = 1.0, $^3J_{H-H}$ = 7.0,1H, CH), 6.39-6.35 (m, 3H, CH), 6.30 (t, $^3J_{H-H}$ = 8.5, 2H, CH), 5.80-5.74 (m, 1H, -CH_2-), 4.32-4.28 (m, 2H, -CH_2-), 3.86-3.80 (m, 1H, -CH_2-). $^{13}C\{^1H\}$ + HMBC+ HSQC NMR (125.68 MHz, CD_2Cl_2, 298K): δ 210.9 (t, $^2J_{C-P}$ = 4.3, N*C*N), 187.4 (dd, $^2J_{C-P}$ = 7.9, $^2J_{C-P}$ = 79.7, N*C*N), 158.1 (t, $^2J_{C-P}$ = 6.4, Os-C Ph), 153.9 (dd, $^2J_{C-P}$ = 12.5, $^2J_{C-P}$ = 55.5, Os-C Ph), 151.7 (d, J_{C-P} = 3.2, C_q), 149.4 (d, J_{C-P} = 3.8, C_q), 148.6 (dd, J_{C-P} = 47.2, J_{C-P} = 34.2, C_q), 144.9 (dd, J_{C-P} = 41.9, J_{C-P} = 36.3, C_q), 143.7 (d, J_{C-P} = 5.4, C_q), 143.5 (d, J_{C-P} = 5.4, CH), 142.3 (s, CH), 138.3 (d, J_{C-P} = 3.6, C_q), 137.2 (d, J_{C-P} = 28.8, C_q), 137.0, 136.7 (both s, C_q),136.2 (d, J_{C-P} = 9.7, CH), 133.8 (d, J_{C-P} = 11.9, CH), 133.5 (d, J_{C-P} = 3.3, C_q), 132.8 (d, J_{C-P} = 14.8, CH), 132.3 (d, J_{C-P} = 1.9, C_q), 132.2 (d, J_{C-P} = 10.3, CH), 131.9 (dd, J_{C-P} = 6.9, J_{C-P} = 31.8, C_q), 131.7 (d, J_{C-P} = 13.9, CH), 130.0 (d, J_{C-P} = 9.3, CH), 129.6 (d, J_{C-P} = 3.9, CH), 129.2, 129.0 (both s, CH), 128.9 (d, J_{C-P} = 3.6, CH), 128.3 (s, CH), 127.9 (d, J_{C-P} = 9.0, CH), 127.5, 127.4 (both s, CH), 127.2 (d, J_{C-P} = 8.7, CH), 126.4 (d, J_{C-P} = 8.4, CH), 123.3, 122.7, 122.5, 122.0, 121.7, 121.1, 120.4, 119.3, 112.3, 111.2, 111.1, 110.6, 109.7, 107.3 (all s, CH), 47.5 (s, -CH_2-), 45.0 (d, $^4J_{C-P}$ = 3.5, -CH_2-). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 298K): δ 32.1 (d, $^2J_{P-P}$ = 5.5), 18.7 (d, $^2J_{P-P}$ = 5.5).

Reaction of Os{κ^4-*C*,*C*,*C*,*C*-(C_6H_4-BzIm-CH_2CH_2-BzIm-C_6H_4)}$(DMSO)_2$ (5) with tetrafluorobenzobarrelene (TFB): Preparation of Os{κ^4-*C*,*C*,*C*,*C*-(C_6H_4-BzIm-CH_2CH_2-BzIm-C_6H_4)}(TFB) (8). In a Schlenk flask provided with a teflon closure a solution of complex **5** (200 mg, 0.264 mmol) in THF (10 mL) was treated with TFB (108 mg, 0.474 mmol). The resulting mixture was stirred at 100 ºC for 24 h, getting a light brown solution. After cooling at room temperature the solvent was removed in vacuo. The brown

residue thus obtained was dissolved in toluene (5 mL), and the resulting solution was filtered through Celite. Removal of toluene and addition of methanol (5 mL) afforded a white solid that was washed with further portions of methanol (2 x 3 mL) and dried in vacuo. Yield: 94 mg (43 %). Anal. Calcd. for $C_{40}H_{26}F_4N_4Os$: C, 57.96; H, 3.16; N, 6.76. Found: C, 58.23; H, 3.39; N, 6.51. HRMS (electrospray, *m/z*) calcd for $C_{40}H_{27}F_4N_4Os$ $[M+H]^+$: 831.1783; found: 831.1765. IR (cm^{-1}): ν(C=C) 1488 (s). ^1H NMR (500 MHz, CD_2Cl_2, 298 K): δ 8.85 (d, $^3J_{H-H}$ = 7.5, 1H, Ph), 8.19 (d, $^3J_{H-H}$ = 7.5, 1H, Ph), 8.08 (d, $^3J_{H-H}$ = 7.5, 1H, Ph), 8.04 (dd, $^3J_{H-H}$ = 7.5, $^4J_{H-H}$ = 1.0, 1H, Ph), 7.83 (dd, $^3J_{H-H}$ = 7.5, $^4J_{H-H}$ = 1.0, 1H, Ph), 7.77 (d, $^3J_{H-H}$ = 7.5, 1H, Ph), 7.76 (d, $^3J_{H-H}$ = 7.5, 1H, Ph), 7.59 (dt, $^4J_{H-H}$ = 1.0, $^3J_{H-H}$ = 7.5, 1H, Ph), 7.52 (dt, $^4J_{H-H}$ = 1.0, $^3J_{H-H}$ = 7.5, 1H, Ph), 7.48 (dt, $^4J_{H-H}$ = 1.0, $^3J_{H-H}$ = 7.5, 1H, Ph), 7.42 (dt, $^4J_{H-H}$ = 1.0, $^3J_{H-H}$ = 7.5, 1H, Ph), 7.21 (dt, $^4J_{H-H}$ = 1.0, $^3J_{H-H}$ = 7.5, 1H, Ph), 7.14 (t, $^3J_{H-H}$ = 7.5, 1H, Ph), 7.08 (d, $^3J_{H-H}$ = 7.5, 1H, Ph), 6.86 (dt, $^4J_{H-H}$ = 1.0, $^3J_{H-H}$ = 7.5, 1H, Ph), 6.68 (dt, $^4J_{H-H}$ = 1.0, $^3J_{H-H}$ = 7.5, 1H, Ph), 6.18 (dd, $^3J_{H-H}$ = 14.0, $^3J_{H-H}$ = 12.0, 1H, -CH_2-), 5.32 (dd, $^3J_{H-H}$ = 5.3, $^3J_{H-H}$ = 5.3, 1H, -CH TFB), 5.22 (ddd, $^3J_{H-H}$ = 14.0, $^3J_{H-H}$ = 3.0, $^2J_{H-H}$ = 1.5, 1H, -CH_2-), 4.85 (dd, $^3J_{H-H}$ = 5.3, $^3J_{H-H}$ = 5.3, 1H, -CH TFB), 4.79 (dd, $^3J_{H-H}$ = 14.0, $^3J_{H-H}$ = 3.0, 1H, -CH_2-), 4.02 (ddd, $^3J_{H-H}$ = 14.0, $^3J_{H-H}$ = 12.0, $^4J_{H-H}$ = 1.5, 1H, -CH_2-), 3.08 (dd, $^3J_{H-H}$ = 5.3, $^3J_{H-H}$ = 5.3, 1H, =CH TFB), 2.82 (dd, $^3J_{H-H}$ = 5.3, $^3J_{H-H}$ = 5.3, 1H, =CH TFB), 2.14 (dd, $^3J_{H-H}$ = 5.3, $^3J_{H-H}$ = 5.3, 1H, =CH TFB), 1.83 (dd, $^3J_{H-H}$ = 5.3, $^3J_{H-H}$ = 5.3, 1H, =CH TFB).$^{13}C\{^1H\}$+ HMBC+ HSQC NMR (125.68 MHz, CD_2Cl_2, 298 K): δ 196.0 (s, N*C*N), 188.4 (s, N*C*N), 155.8 (s, Os-C Ph), 152.0 (s, Os-C Ph), 148.1, 147.1 (both s, C Ph), 143.1 (s, CH Ph), 140.4 (m, C-F, TFB), 138.8 (s, C Ph), 138.5 (m, C-F, TFB), 137.9 (s, CH, Ph), 131.8, 134.4, 136.8 (all s, C Ph and BzIm), 134.1, 133.7 (both m, C TFB), 125.4, 124.2, 123.6, 123.5, 123.1, 122.4, 122.2, 121.9, 113.4, 112.4, 112.3, 111.3, 110.6, 108.6 (all s, CH Ph and BzIm), 50.3, 49.8 (both s, =CH TFB), 48.4, 44.1 (both s, -CH_2-), 39.4, 36.3 (both s, -CH TFB), 36.2, 32.1 (both s, =CH TFB). $^{19}F\{^1H\}$ NMR (282.34 MHz, CD_2Cl_2, 298 K): δ -149.2, -150.2, -163.3 (all m, C-F).

Reaction of [Os{κ²-*C*,*C*-(MeBzIm-C_6H_4)}(NCCH₃)₄]OTf (9) with 1,2-bis(diphenylphosphino)benzene (dppbz): Preparation of [Os{κ²-*C*,*C*-(MeBzIm-C_6H_4)}(dppbz)(NCCH₃)₂]OTf (11). dppbz (125.5 mg, 0.27 mmol) was added to a green solution of compound **9** (200.0 mg, 0.27 mmol) in dichloromethane (5 mL). The green solution was stirred overnight at room temperature and then concentrated to dryness. The addition of diethyl ether (3 mL) resulted in the precipitation of a pale green solid which was washed with further portions of diethyl ether (3 x 3 mL) and dried in vacuo. Yield: 290.0 mg (90 %). Anal. Calcd. for $C_{49}H_{41}F_3N_4O_3OsP_2S$: C, 54.74; H, 3.84; N, 5.21; S, 2.98. Found: C, 54.49; H, 4.12; N, 5.07; S, 2.88. HRMS (electrospray, *m/z*) calcd for $C_{48}H_{41}N_4OsP_2$ $[M]^+$: 927.2421; found: 927.2439. IR (cm^{-1}): ν(C≡N) 2259 (m), ν(CF) 1261 (vs), ν(SO) 1221 (m), ν(SO) 1147 (s), ν(SO) 1030 (vs). ^1H NMR (300 MHz, CD_2Cl_2, 298 K): δ 8.30-8.20 (m, 1H, CH), 8.00-7.90 (m, 1H, CH), 7.90-7.80 (s, 1H, CH), 7.60-7.20 (m, 27H, CH), 7.20-7.10 (m, 1H, CH), 6.80-6.70 (m, 1H, CH), 3.80 (s, 3H, NCH_3), 1.60 (s, 6H, 2 $NCCH_3$). $^{13}C\{^1H\}$ + HMBC+ HSQC NMR (75 MHz, CD_2Cl_2, 298 K): δ 187.8 (dd, $^2J_{C-P}$ = 90.2, $^2J_{C-P}$ = 4.4, NCN), 152.1 (d, $^3J_{C-P}$ = 2.5, C_q), 148.1 (dd, $^2J_{C-P}$ = 70.9, $^2J_{C-P}$ = 5.8, Os-C), 148.0 (d, $^1J_{C-P}$ = 46.0, $^2J_{C-P}$ = 33.3, C_q), 145.1 (d, $^1J_{C-P}$ = 47.5, $^2J_{C-P}$ = 33.3, C_q), 143.7 (d, $^3J_{C-P}$ = 6.8, CH), 137.0 (d, $^4J_{C-P}$ = 3.2, C_q), 135.3 (dd, J_{C-P} = 13.4, J_{C-P} = 1.8, CH), 135.5-134.9 (m, C_q), 134.6 (dd, J_{C-P} = 12.9, J_{C-P} = 2.0, CH), 133.8 (d, J_{C-P} = 9.7, CH), 133.2 (d, J_{C-P} = 10.3, CH), 132.3 (dd, $^1J_{C-P}$ = 43.9, $^2J_{C-P}$ = 2.3, C_q), 131.7 (dd, J_{C-P} = 4.9, J_{C-P} = 1.6, CH), 131.5 (dd, J_{C-P} = 5.4, J_{C-P} = 1.4, CH), 130.6 (d, J_{C-P} = 2.0, CH), 130.6 (d, J_{C-P} = 1.8, CH), 129.5 (d, J_{C-P} = 8.9, CH), 129.0 (d, J_{C-P} = 9.4, CH), 125.0 (dd, $^3J_{C-P}$ = 5.0, $^3J_{C-P}$ = 1.3, CH), 124.5 (s, CH), 123.7 (s, CH), 123.6 (s, CH), 116.4 (s, N*C*CH₃), 113.1 (d, J_{C-P} = 1.8, CH), 112.6 (s, CH), 111.6 (s, CH), 36.6 (d, $^4J_{C-P}$ = 3.6, NCH_3), 3.9 (s, NC*C*H₃). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 298 K): δ 32.3 (d, $^2J_{P-P}$ = 17), 23.8 (d, $^2J_{P-P}$ = 17). $^{19}F\{^1H\}$ NMR (282 MHz, CD_2Cl_2, 298 K): δ -80.7 (s).

Reaction of [Os{κ²-*C*,*C*-(MeBzIm*-C_6H_4)}(NCCH₃)₄]OTf (10) with 1,2-bis(diphenylphosphino)benzene (dppbz): Preparation of [Os{κ²-*C*,*C*-(MeBzIm-C_6H_4)} (bppbz)(NCCH₃)₂]OTf (12). dppbz (302.2 mg, 0.677 mmol) was added to a green solution of compound **10** (500.0 mg, 0.677 mmol) in dichloromethane (15 mL). The green solution was stirred overnight and then concentrated to dryness. The addition of diethyl ether (6 mL) resulted in the formation of a green oil which was stirred in a cold bath (195 K) and a pale green solid precipitated. The green solid was washed with further portions of diethyl ether (3x4 mL) and dried in *vacuo*. Yield: 568.5 mg (76 %). Anal. Calcd. for $C_{51}H_{45}F_3N_4O_3OsP_2S$: C, 55.53; H, 4.11; N, 5.08; S, 2.91. Found: C, 55.50; H, 4.44; N, 4.86; S, 2.88. HRMS (electrospray, *m/z*) calcd for $C_{50}H_{45}N_4OsP_2$ $[M]^+$: 955.2734; found: 955.2781. IR (cm^{-1}): ν(C≡N) 2258 (w), ν(CF) 1260 (s), ν(SO) 1221 (m), ν(SO) 1148 (s), ν(SO) 1029 (s). ^1H NMR (300 MHz, CD_2Cl_2, 298 K): δ 7.99 (s, 1H, CH), 8.00-7.90 (m, 1H, CH), 7.90-7.80 (m, 1H, CH), 7.50-7.20 (m, 24H, CH), 7.22 (s, 1H, CH), 7.20-7.00 (m, 1H, CH), 6.80-6.60 (m, 1H, CH), 3.70 (s, 3H, NCH_3), 2.51 and 2.44 (both s, 3H each, CH_3), 1.57 (s, 6H, 2 $NCCH_3$). $^{13}C\{^1H\}$ + HMBC+ HSQC NMR (75 MHz, CD_2Cl_2, 298 K): δ 186.3 (dd, $^2J_{C-P}$ = 90.2, $^2J_{C-P}$ = 4.5, NCN), 152.3 (d, $^3J_{C-P}$ = 2.4, C_q), 148.1 (d, $^1J_{C-P}$ = 45.9, $^2J_{C-P}$ = 33.5, C_q), 148.0 (dd, $^2J_{C-P}$ = 70.9, $^2J_{C-P}$ = 5.9, Os-C), 145.2 (d, $^1J_{C-P}$ = 47.4, $^1J_{C-P}$ = 33.4, C_q), 143.7 (d, $^3J_{C-P}$ = 6.8, CH), 135.6 (d, $^4J_{C-P}$ = 3.6, C_q), 135.3 (dd, J_{C-P} = 13.5, J_{C-P} = 1.6, CH), 135.2 (dd, $^1J_{C-P}$ = 36.4, $^2J_{C-P}$ = 2.4, C_q), 134.6 (dd, J_{C-P} = 12.9, J_{C-P} = 1.9, CH), 133.8 (d, J_{C-P} = 9.8, CH), 133.2 (d, J_{C-P} = 10.4, CH), 133.7 (s, C_q), 132.9 (s, C_q), 132.4 (dd, $^1J_{C-P}$ = 43.7, $^2J_{C-P}$ = 2.3, C_q), 131.7 (dd, J_{C-P} = 5.0, J_{C-P} = 1.6, CH), 131.6 (d, $^4J_{C-P}$ = 1.9, J_{C-P} = 1.6, C_q), 131.5 (dd, J_{C-P} = 5.6, J_{C-P} = 1.9, CH), 130.6 (d, J_{C-P} = 2.0, CH), 130.5 (d, J_{C-P}= 1.8, CH), 129.4 (d, J_{C-P} = 8.9, CH), 129.0 (d, J_{C-P} = 9.3, CH), 124.8 (dd, $^3J_{C-P}$ = 5.0, $^3J_{C-P}$ = 1.2, CH), 123.5 (s, CH), 116.3 (s, N*C*CH₃), 113.2 (s, CH), 113.0 (d, J_{C-P} = 2.2, CH), 111.9 (s, CH), 36.5 (d, $^4J_{C-P}$ = 3.7, NCH_3), 20.8 and 20.4 (both s, both CH_3), 3.9 (s, NC*C*H₃). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 298 K): δ 32.3 (d, $^2J_{P-P}$ = 17), 23.9 (d, $^2J_{P-P}$ = 17). $^{19}F\{^1H\}$ NMR (282 MHz, CD_2Cl_2, 298 K): δ -79.0 (s).

Reaction of [Os{κ²-*C*,*C*-(MeBzIm-C_6H_4)}(dppbz)(NCCH₃)₂]OTf (11) with 1-phenyl-3-methyl-1-*H*-benzimidazolium Iodide ([PhMeBzImH]I): Preparation of Os{κ²-*C*,*C*-(MeBzIm-C_6H_4)}₂(dppbz) (13). A solution of complex **11** (500 mg, 0.47 mmol), [PhMeBImH]I (157.7 mg, 0.47 mmol) and NEt_3 (630 µL, 4.5 mmol) in dimethylformamide (10 mL) was stirred for three days at 110 ºC. The resulting yellowish suspension was concentrated in *vacuo* to dryness. The addition of toluene (40 mL) resulted in a brownish-yellow suspension. The yellow solution was extracted and concentrated to ca~1 mL and cold methanol (8 mL) was added allowing to precipitate a yellow solid. The yellow solid was washed with further portions of methanol (2x3 mL) and dried in *vacuo*. Yield: 275.0 mg (56 %). Anal. Calcd. for $C_{58}H_{46}N_4P_2Os$: C, 66.27; H 4.41; N 5.33. Found: C 66.05; H 4.53; N 5.19. HRMS (electrospray, *m/z*) calcd for $C_{58}H_{46}N_4P_2Os$ $[M]^+$: 1052.2813; found: 1052.2818. ^1H NMR (500 MHz, CD_2Cl_2, 298 K): δ 8.01-8.00 (m, 1H, CH), 8.00-7.90 (m, 1H, CH), 7.90-7.80 (m, 1H, CH), 7.90-7.70 (m, 2H, CH), 7.80-7.50 (m, 6H, CH), 7.30-7.10 (m, 11H, CH), 7.10-7.00 (m, 1H, CH), 7.00-6.90 (m, 1H, CH), 6.90-6.80 (m, 1H, CH), 6.90-6.70 (m, 2H, CH), 6.80-6.70 (m, 2H, CH), 6.70-6.60 (m, 1H, CH), 6.60-6.50 (m, 1H, CH), 6.50-6.40 (m, 2H, CH), 6.40-6.20 (m, 5H, CH), 6.20-6.10 (m, 2H, CH), 3.35 (s, 3H, NCH_3), 2.16 (s, 3H, NCH_3). $^{13}C\{^1H\}$ + HMBC+ HSQC NMR (126 MHz, CD_2Cl_2, 298 K): δ 199.9 (br, NCN), 195.5 (br, NCN), 158.2 (br, Os-C Ph), 152.3 (br, C_q), 151.2 (br, C_q), 148.4 (br, C_q), 145.2 (br, C_q), 143.9 (br, C_q), 143.0 (s, CH), 142.5 (s, C_q), 140.6 (s, CH), 138.2 (s, C_q), 137.4 (s, CH), 136.5 (d, J_{C-P} = 8.6, CH), 134.4 (m, C_q), 133.7 (s, CH), 133.6 (s, C_q), 133.4 (s, CH), 133.2 (s, C_q), 130.8, 130.3, 130.2, 129.9, 129.3, 128.7, 128.3, 127.8, 127.5, 127.3, 126.4, 123.3 (all s, CH), 123.0 (br, C_q), 122.5, 121.9, 121.6, 121.2, 120.7 (all s, CH), 120.2 (br, C_q), 111.7 (br, C_q), 111.5, 111.2, 110.3, 109.5, 109.4 (all s, CH), 34.2 (s, CH_3), 34.2-34.0 (m, CH_3) (three CH aromatic signals are not observed, probably due to overlapping). $^{31}P\{^1H\}$ NMR (121.48 MHz, DMF, 298 K): δ 30.0 (d, $^2J_{P-P}$ = 5.0), 24.7 (d, $^2J_{P-P}$ = 5.0).

Reaction of [Os{κ²-*C*,*C*-(MeBzIm*-C_6H_4)}(dppbz)(NCCH₃)₂]OTf (12) with 1-phenyl-3-methyl-1-*H*-5,6-dimethylbenzimidazolium Iodide ([PhMeBzIm*H]I): Preparation of Os({κ²-*C*,*C*-(MeBzIm*-C_6H_4)}₂(dppbz) (14). A solution of complex **12** (400 mg, 0.36 mmol), [PhMeBIm*H]I (132.0 mg, 0.36 mmol) and NEt_3 (500 µL, 3.6 mmol) in DMF (8 mL) was stirred for three days at 110 ºC. The resulting yellowish suspension was concen-

trated in *vacuo* to dryness and purified by chromatography (silicagel 230-400 mesh and diethyl ether as eluent) yielding **14** as a yellow solid. Yield: 85 mg (21%). Anal. Calcd. for $C_{62}H_{54}N_4OsP_2$: C, 67.25; H, 4.91; N, 5.06. Found: C, 67.58; H, 4.54; N, 4.86. HRMS (electrospray, *m/z*) calcd for $C_{62}H_{54}N_4OsP_2$ $[M]^+$: 1108.3439; found: 1108.3424. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 8.10-8.00 (m, 1H, CH), 7.90-7.80 (m, 1H, CH), 7.80-7.70 (m, 4H, CH), 7.70-7.50 (m, 4H, CH), 7.50 (s, 1H, CH), 7.30-7.10 (m, 7H, CH), 7.00-6.90 (m, 1H, CH), 6.90 (s, 1H, CH), 6.80-6.70 (m, 4H, CH), 6.50-6.40 (m, 5H, CH), 6.40-6.30 (m, 4H, CH), 6.30-6.20 (m, 1H, CH), 6.20-6.10 (m, 2H, CH), 3.24 (s, 3H, NCH_3), 2.40, 2.37, 2.33 and 2.30 (all s, 3H each, -CH_3), 2.06 (s, 3H, NCH_3). $^{13}C\{^1H\}$ + HMBC+ HSQC NMR (126 MHz, CD_2Cl_2, 298 K): δ 197.2 (br, NCN), 193.6 (br, NCN), 157.4 (br, Os-C Ph), 152.0 (br, Os-C Ph), 148.4 (s, C_q), 145.2 (br, C_q), 143.2 (br, CH), 143.0 (br, C_q), 142.8 (C_q), 142.4 (br, C_q), 140.3 (s, CH), 137.3 (s, CH), 137.7 (br, C_q) 136.8 (s, C_q), 136.4 (br, CH), 135.9 (s, C_q), 133.6 (s, CH), 133.4 (s, CH), 132.1 (s, C_q), 131.7 (s, C_q), 130.9 (s, C_q), 130.8 (s, CH), 130.3, (s, CH), 130.2 (s, C_q), 130.0 (s, CH), 129.7 (s, CH), 129.7 (s, C_q), 129.2, 128.7, 128.2, 127.6, 127.5, 127.3, 126.3, 126.2, 122.9 (all s, CH), 122.5 (br, C_q), 120.5, 112.0, 111.3, 111.2 (all s, CH), 111.0 (br, C_q), 110.1 (s, CH), 110.1 (s, CH), 33. 9 (s, 2 CH_3), 20.6, 20.6, 20.3 and 20.3 (all s, CH_3) (some signals are not observed probably due to overlapping). $^{31}P\{^1H\}$ NMR (202 MHz, DMF, 298 K): δ 29.6 (br), 26.0 (br).

Structural Analysis of Complexes 2, 4, 6, 7, 11, and 13. X-ray data were collected for the complexes on a Bruker Smart APEX CCD (**2**, **4**, **11** and **13**) or APEX CCD DUO (**6** and **7**) diffractometers equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, λ = 0.71073 Å) operating at 50 kV and 40 mA (**4**, **6** and **7**) or 30 mA (**2**, **11**, and **13**). Data were collected over the complete sphere. Each frame exposure time was 10 s (**11** and **13**), 20 s (**2**, **6** and **7**) or 30 s (**4**) (covering 0.3º in ω). Data were corrected for absorption by using a multiscan method applied with the SADABS program.[42] The structures were solved by Patterson or direct methods and refined by full-matrix least squares on F2 with SHELXL97,[43] including isotropic and subsequently anisotropic displacement parameters. The hydrogen atoms were observed in the least Fourier Maps or calculated, and refined freely or using a restricted riding model. The solvent molecules of crystallization observed in the asymmetric unit in the different structures were mostly observed disordered and refined with different moieties with restrained geometry, complementary occupancy factors and isotropic displacement parameters.

Crystal data for **2**: $C_{38}H_{42}BrN_4OOsP$, 3.5(CH_2Cl_2), M_W 1169.08, yellow, irregular block (0.18 x 0.12 x 0.08 mm), triclinic, space group P-1, *a*: 11.8972(8) Å, *b*: 13.1287(8) Å, *c*: 16.5970(16) Å, *α*: 102.1450(10)°, *β*: 94.2660(10)°, *γ*: 114.7860(10)°, *V* = 2261.9(3) Å^3, *Z* = 2, *Z'* = 1, D_{calc}: 1.716 g cm^{-3}, F(000): 1158, T = 100(2) K, μ 4.189 mm^{-1}. 27672 measured reflections (2θ: 3-58º, ω scans 0.3º), 10562 unique (R_{int} = 0.0296); min./max. transm. factors 0.676/0.862. Final agreement factors were R^1 = 0.0337 (9198 observed reflections, I > 2θ(I)) and wR^2 = 0.0882; data/restraints/parameters 10562/8/514; GoF = 0.881. Largest peak and hole 2.200 (close to the osmium atom) and -2.313 e/Å^3.

Crystal data for **4**: $C_{38}H_{41}N_4OOsP$, M_W 790.92, yellow, irregular block (0.14 x 0.12 x 0.03), monoclinic, space group P21/n, *a*: 13.485(2) Å, *b*: 15.011(3) Å, *c*: 16.212(3) Å, *β*: 100.785(2)°, *V* = 3223.6(10) Å^3, *Z* = 4, *Z'* = 1, D_{calc}: 1.630 g cm^{-3}, F(000): 1584, T = 100(2) K, μ 4.043 mm^{-1}. 22489 measured reflections (2θ: 3-51o, ω scans 0.3º), 6061 unique (R_{int} = 0.0713); min./max. transm. factors 0.631/0.862. Final agreement factors were R^1 = 0.0509 (4295 observed reflections, I > 2θ(I)) and wR^2 = 0.1259; data/restraints/parameters 6061/50/413; GoF = 1.033. Largest peak and hole 3.495 (close to the osmium atom) and -1.786 e/Å^3.

Crystal data for **6**: $C_{54}H_{42}N_4OsP_2$, 0.875(CH_2Cl_2), M_W 1073.37, yellow, irregular block (0.14 x 0.05 x 0.04 mm), triclinic, space group P-1, *a*: 12.324(6) Å, *b*: 19.843(10) Å, *c*: 19.987(10) Å, *α*: 81.267(7)°, *β*: 75.348(6)°, *γ*: 88.797(7)°, *V* = 4673(4) Å^3, *Z* = 4, *Z'* = 2, D_{calc}: 1.526 g cm^{-3}, F(000): 2147, T = 150(2) K, μ 2.940 mm^{-1}. 71830 measured reflections (2θ: 3-57º, ω scans 0.3º), 24119 unique (R_{int} = 0.0357); min./max. transm. factors 0.682/0.862. Final agreement factors were R^1 = 0.0352 (19735 observed reflections, I > 2θ(I)) and wR^2 = 0.1011; data/restraints/parameters 24119/15/1146; GoF = 1.048. Largest peak and hole 2.170 (close to the osmium atoms) and -1.657 e/Å^3.

Crystal data for **7**: $C_{58}H_{44}N_4OsP_2$, 3/2(CH_2Cl_2), M_W 1176.50, yellow, irregular block (0.15 x 0.12 x 0.07 mm), monoclinic, space group C2, *a*: 20.470(3) Å, *b*: 19.715(3) Å, *c*: 24.976(3) Å, *β*: 104.265(2)°, *V* = 9768(2) Å^3, *Z* = 8, *Z'* = 2, D_{calc}: 1.600 g cm^{-3}, F(000): 4712, T = 100(2) K, μ 2.887 mm^{-1}. 66769 measured reflections (2θ: 3-58º, ω scans 0.3º), 19215 unique (R_{int} = 0.0572); min./max. transm. factors 0.634/0.862. Final agreement factors were R^1 = 0.0469 (17114 observed reflections, I > 2θ(I)) and wR^2 = 0.1196; Flack parameter 0.014(6); data/restraints/parameters 19215/7/1245; GoF = 1.041. Largest peak and hole 2.656 (close to the osmium atoms) and -1.646 e/Å^3.

Crystal data for **11**: $C_{48}H_{41}N_4OsP_2$, CF_3O_3S, 0.5(CH_2Cl_2), 0.5(C_2H_3N), M_W 1138.05, green, irregular block (0.14 x 0.08 x 0.04 mm), monoclinic, space group P21/c, *a*: 13.5713(14) Å, *b*: 19.295(2) Å, *c*: 18.4609(19) Å, *β*: 108.6970(10)°, *V* = 4579.1(8) Å^3, *Z* = 4, *Z'* = 1, D_{calc}: 1.651 g cm^{-3}, F(000): 2272, T = 100(2) K, μ 3.020 mm^{-1}. 55736 measured reflections (2θ: 3-51º, ω scans 0.3º), 11059 unique (R_{int} = 0.0690); min./max. transm. factors 0.720/0.862. Final agreement factors were R^1 = 0.0400 (8625 observed reflections, I > 2θ(I)) and wR^2 = 0.0793; data/restraints/parameters 11059/6/602; GoF = 1.03. Largest peak and hole 1.329 (close to the osmium atom) and -1.278 e/ Å^3.

Crystal data for **13**: $C_{58}H_{46}N_4OsP_2$, 4(C_6H_6), M_W 1363.56, yellow, irregular block (0.26 x 0.09 x 0.09 mm), triclinic, space group P-1, *a*: 12.5444(9) Å, *b*: 14.9861(11) Å, *c*: 18.2590(14) Å, *α*: 72.4820(10)°, *β*: 83.0130(10)°, *γ*: 78.5460(10)°, *V* = 3201.1(4) Å^3, *Z* = 2, *Z'* = 1, D_{calc}: 1.415 g cm^{-3}, F(000): 1392, T = 100(2) K, μ 2.092 mm^{-1}. 25024 measured reflections (2θ: 3-58º, ω scans 0.3o), 14260 unique (R_{int} = 0.0400); min./max. transm. factors 0.676/0.862. Final agreement factors were R^1 = 0.0440 (12115 observed reflections, I > 2θ(I)) and wR^2 = 0.0768; data/restraints/parameters 14260/0/804; GoF = 1.047. Largest peak and hole 0.887 (close to the osmium atom) and -1.710 e/ Å^3.

Computational details. All calculations were performed at the DFT level using the B3LYP functional[44] supplemented with the Grimme's dispersion correction D3[45] as implemented in Gaussian09.[46] The Os atom was described by means of an effective core potential SDD for the inner electron[47] and its associated double-ζ basis set for the outer ones, complemented with a set of f-polarization functions.[48] The 6-31G** basis set was used for the H, C, N and P atoms.[49] All minima were verified to have no negative frequencies. All geometries were fully optimized in THF (ε = 7.4257) solvent using the continuum SMD model.[50] For both **7** and **13** we performed TD-DFT calculations at the same level of theory calculating the lowest 50 singlet-singlet excitations at the ground state S_0 and the lowest 5 singlet-singlet and 5 singlet-triplet excitations at the lowest excited triplet T_1 optimized geometries. It has to be noticed that the singlet-triplet excitations are set to zero due to the neglect of spin-orbit coupling in the TDDFT calculations as implemented in G09. The UV/vis absorption spectra were obtained by using the GaussSum 3 software.[51]

Supporting Information

UV/Vis, normalized emission and excitation spectra for **7**, **13**, and **14**; molecular frontier orbitals for complexes **7** and **13**, calculated UV spectra of complexes **7** and **13** (50 highest transitions), ^{1}H NMR spectra of **3a** and of partially deuterated **3a**, and a CIF file giving positional and displacement parameters, crystallographic data, and bond lengths and angles of **2**, **4**, **6**, **7**, **11** and **13**. The supplemental file Cartesian_coord.xyz contains the computed Cartesian coordinates of computed **7** and **13**. The file may be opened as a text file to read the coordinates, or opened directly by a molecular modeling program such as Mercury for visualization. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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