Reactions of a Dihydrogen Complex with Terminal Alkynes: Formation of Osmium−Carbyne and −Carbene Derivatives with the Hydridotris(pyrazolyl)borate Ligand†

Ruth Castro-Rodrigo, Miguel A. Esteruelas,* Ana M. López,* and Enrique Oñate

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

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The dihydrogen complex $[OsTp(\eta^2\text{-}H_2)(\kappa^1\text{-}OCMe_2)(P^iPr_3)]BF_4$ (**1**; Tp = hydridotris(pyrazolyl)borate) reacts with *tert*-butylacetylene to give the hydride-carbyne derivative $[OsHTp(\equiv CCH_2{}^tBu)(P^iPr_3)]BF_4$ (**2**). Similarly, the treatment of **1** with (trimethylsilyl)acetylene in the presence of methanol leads to $[OsHTp(\equiv CCH_3)(P^iPr_3)]BF_4$ (**3**). In chloroform at 60 °C, complexes **2** and **3** evolve into the corresponding chloro derivatives $[OsClTp(\equiv CR)(P^iPr_3)]BF_4$ (R = $CH_2{}^tBu$ (**4**), CH_3 (**5**)), whereas in acetonitrile the carbenes $[OsTp(=CHR)(NCCH_3)(P^iPr_3)]BF_4$ (R = $CH_2{}^tBu$ (**6**), CH_3 (**7**)) are formed. Complex **1** also reacts with phenylacetylene. The reaction initially gives $[OsHTp(\equiv CCH_2Ph)(P^iPr_3)]BF_4$ (**8**). Subsequently, the insertion of a second molecule of alkyne into the Os−H bond of **8** and the migration of the resulting alkenyl group from the metal center to the carbyne carbon atom take place, to afford the carbene $[OsTp\{=C(CH_2Ph)C(Ph)=CH_2\}(P^iPr_3)]BF_4$ (**9**). The metal center of **9** is saturated by means of a strong agostic interaction (r_{bp} = 0.4(1)) between the osmium atom and one of the *ortho*-CH bonds of the phenyl substituent of the alkenyl unit of the alkenylcarbene ligand. Treatment of **1** with methylpropiolate leads to the carbene $[\overline{OsTp\{=CHCH_2C(O)}OMe\}(P^iPr_3)]BF_4$ (**10**) in a one-pot synthesis. Complexes **2**, **4**, **9**, and **10** have been characterized by X-ray diffraction analysis.

Introduction

Osmium compounds containing two hydrogen atoms bonded to the metal center have been shown to promote carbon−carbon coupling reactions. However, it is difficult to rationalize the processes, because the products from the reactions of these compounds with unsaturated organic molecules, in particular alkynes, depend on a variety of factors including the interactions within the OsH_2 unit.[1]

Complexes $OsH_2Cl_2(PR_3)_2$ react with terminal alkynes, R′C≡CH, to afford the hydride-carbyne derivatives $OsHCl_2(\equiv CCH_2R')(PR_3)_2$.[2] In contrast to these dihydrides, the reactions of the elongated dihydrogen $OsCl_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ (d_{H-H} = 1.1 Å) lead to the carbenes $OsCl_2(=CHCH_2R')(CO)(P^iPr_3)_2$.[3]

The character of the OsH_2 unit is not the sole factor determining the nature of the products. The substituent R′ of the alkyne also seems to have a significant influence. For instance, the dihydride cation $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]^+$ reacts with *tert*-butylacetylene and acetylene as $OsH_2Cl_2(P^iPr_3)_2$, to form the corresponding hydride-carbyne derivatives, while with phenylacetylene it gives a hydride-metallacyclopropene,[4] and mixtures of both types of compounds have been found in reactions with alkynols.[5]

Each elongated dihydrogen compound also appears to have a particular behavior. The reactions of the complex $[\overline{Os\{C_6H_4C(O)}\text{-}CH_3\}(\eta^2\text{-}H_2)\{N(OH)=CMe_2\}(P^iPr_3)_2]^+$ (d_{H-H} = 1.3 Å) with terminal alkynes lead to dihydride−carbynes[6] instead of carbenes, as is done by $OsCl_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$. On the other hand, the water compounds $[\overline{Os\{C_6X_4C(O)}CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^i\text{-}Pr_3)_2]BF_4$ (X = F, H; d_{H-H} = 1.3 Å) give in a competitive manner hydride-vinylidene-π-alkyne derivatives and/or hydride-osmacyclopropene species.[7] The treatment of the starting complex derived from acetophenone with 4.5 equiv of phenylacetylene and 2.0 equiv of HBF_4 leads to $[Os\{(E)\text{-}CH=CHPh\}(C\equiv CPh)(\equiv CCH_2Ph))(P^iPr_3)_2]BF_4$, which coordinates chloride to form the isometallabenzene with the structure of 1,2,4-cyclohexatriene $\overline{Os\{=C=C(Ph)CH(Ph)CH=C(CH_2Ph)\}}Cl(P^iPr_3)_2$.[8] In the presence of alkynols the hydride-hydroxyvinylidene-π-alkynol derivatives $[OsH\{=C=CHC(OH)R_2\}\{\eta^2\text{-}HC\equiv CC(OH)\text{-}R_2\}(P^iPR_3)]BF_4$(R = Ph, Me) are formed,[9] which are the entry to the dicationic hydride-alkenylcarbyne complexes [OsH-

† Dedicated to Professor José Gimeno on the occasion of his 60th birthday.

* Corresponding authors. E-mail: maester@unizar.es (M.A.E.); amlopez@unizar.es (A.M.L.).

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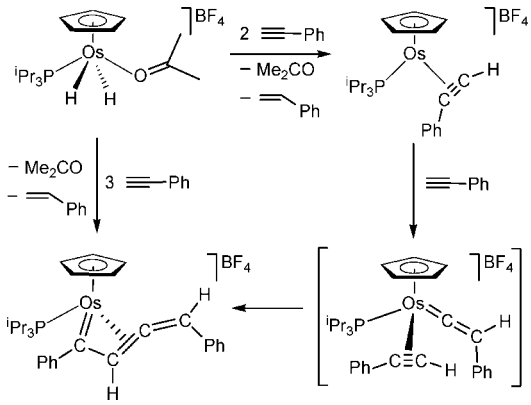
Scheme 1



(≡CCH═CR_2)S_2(P^iPr_3)$_2$][BF_4]$_2$ (S = H_2O, CH_3CN). In contrast to $OsHCl_2$(≡CCH_2R')(PR_3)$_2$, in acetonitrile, these dications undergo 1,2-hydrogen shift from the osmium to the carbyne carbon atom to afford the corresponding dicationic carbene derivatives [Os(═CHCH═CR_2)($NCCH_3$)$_3$(P^iPr_3)$_2$][BF_4]$_2$. The selective deprotonation of the alkenyl substituent of the alkenylcarbyne group of [OsH(≡CCH═CPh_2)($NCCH_3$)$_2$(P^iPr_3)$_2$][BF_4]$_2$ leads to the hydride-allenylidene [OsH(═C═C═CPh_2)($NCCH_3$)$_2$(P^iPr_3)$_2$]BF_4,[10] which is a strong nucleophile at the C_β atom of the C_3 chain.[11]

In the context of the studies on the chemistry of the Os(η^5-C_5H_5) unit,[12] we have reported that, in acetone, the dihydride-dihydrogen complex [OsH_2(η^5-C_5H_5)(η^2-H_2)(P^iPr_3)]BF_4 loses the dihydrogen ligand, and the resulting dihydride derivative [OsH_2(η^5-C_5H_5)(κ^1-$OCMe_2$)(P^iPr_3)]BF_4 reacts with 3 equiv of 1-phenyl-1-propyne and 2-butyne to give 2 equiv of olefin and [OsH(η^5-C_5H_5){κ^4-(P,C,C,C)-CH_2C[CH_2C(═CH_2)P^iPr_2]CHR}]BF_4 (R = Ph, Me), containing a γ-(η^3-allyl)-α-alkenylphosphine.[13] In contrast to these alkynes, the reaction with phenylacetylene yields the allenylcarbene [Os(η^5-C_5H_5){═CPh(η^2-CH═C═CHPh)}(P^iPr_3)]-BF_4 via a π-phenylacetylene intermediate (Scheme 1).[14]

The hydridotris(pyrazolyl)borate (Tp) ligand is frequently compared with the cyclopentadienyl (Cp) group due to the same number of electrons donated and the facial geometry adopted. However, there are marked differences between them.[15] For instance, Tp avoids the piano stool structures, typical for the Cp ligand, and enforces dispositions allowing N−Os−N angles close to 90°, which favor the nonclassical interactions between the hydrogen atoms bonded to the metal center.[16] Thus, within the OsTp chemistry,[17] the Tp counterpart of the dihydride [OsH_2(η^5-C_5H_5)(κ^1-$OCMe_2$)-(P^iPr_3)]BF_4 is the dihydrogen [OsTp(η^2-H_2)(κ^1-$OCMe_2$)(P^iPr_3)]-BF_4 with a H−H separation of 0.9 Å.[18]

Because the reactivity of osmium-dihydrogen complexes (d_{H-H} < 1.0 Å) with terminal alkynes has not been explored and we are interested in understanding the reactivity of the osmium compounds with two hydrogen atoms bonded to the metal center, we have carried out the reactions of [OsTp(η^2-H_2)(κ^1-$OCMe_2$)(P^iPr_3)]BF_4 with *tert*-butylacetylene, (trimethylsilyl)acetylene, phenylacetylene, and methylpropiolate. This paper reports the results of this study.

Results and Discussion

1. Reactions with *tert*-Butylacetylene and (Trimethylsilyl)acetylene. Treatment at room temperature of dichloromethane solutions of the dihydrogen-solvento complex [OsTp(η^2-H_2)(κ^1-$OCMe_2$)(P^iPr_3)]BF_4 (**1**) with 1.5 equiv of *tert*-butylacetylene leads after 2 h to the hydride-carbyne derivative [OsHTp-(≡$CCH_2{}^tBu$)(P^iPr_3)]BF_4 (**2**), which is isolated as a yellow solid in 57% yield according to Scheme 2.

Figure 1 shows a view of the cation of this compound. The geometry around the osmium atom can be described as a distorted octahedron with the coordinating nitrogen atoms of the Tp ligand in *fac* sites. The metal coordination sphere is completed by the phosphine ligand *trans* disposed to N(3) (P(1)−Os−N(3) = 170.95(11)°), the carbyne group *trans* disposed to N(5), (C(1)−Os−N(5) = 169.54(18)°), and the hydride *trans* disposed to N(1) (H(01)−Os−N(1) = 166.1(19)°). The Os−N bond lengths of 2.129(4) Å (Os−N(3)), <2.198(4) Å (Os−N(1)), and <2.243(4) Å (Os−N(5)) are consistent with a *trans* influence of the monodentate ligands increasing in the sequence P^iPr_3 < H < $CCH_2{}^tBu$. The Os−C(1) distance of 1.720(5) Å, which is statistically identical with that in the related

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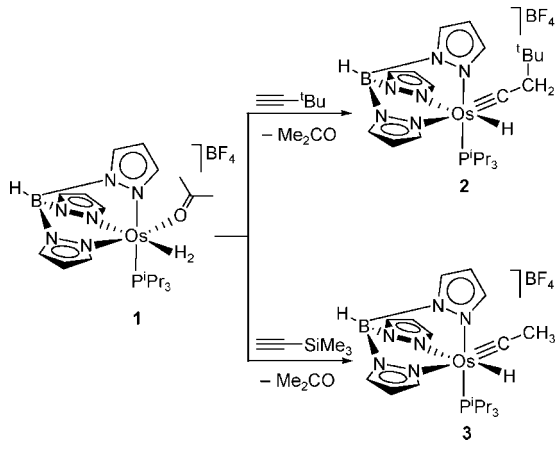
Scheme 2



Cp compound $[OsH(Cp)(\equiv CPh)(P^iPr_3)]PF_6$ (1.733(9) Å),[19] and the angle Os−C(1)−C(2) of 173.1(4)° support the Os−C triple bond formulation.[20] The ^1H and $^{13}C\{^1H\}$ NMR spectra in dichloromethane-d_2 at room temperature are consistent with the structure shown in Figure 1. Thus, they show nine pyrazolyl resonances. In agreement with the presence of a hydride ligand in the cation, the ^1H NMR spectrum contains at −6.73 ppm a doublet with a H−P coupling constant of 19.6 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance due to the C_α atom of the carbyne group appears at 300.7 ppm as a doublet with a C−P coupling constant of 13 Hz.

Complex **1** also reacts with (trimethylsilyl)acetylene. In the presence of traces of methanol, the addition of 1.5 equiv of this alkyne to the dichloromethane solutions of the dihydrogen-acetone starting compound leads to the hydride-carbyne $[OsHTp(\equiv CCH_3)(P^iPr_3)]BF_4$ (**3**), which is isolated as a yellow solid in 82% yield. A similar desilylation has been observed in the reactions of the dihydrides $OsH_2Cl_2(P^iPr_3)_2$ and $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]BF_4$ with (trimethylsilyl)acetylene, which also afford hydride-carbyne species: the complexes $OsHCl_2(\equiv CCH_3)(P^iPr_3)_2$[2a] and $[OsH(\kappa^2\text{-}O_2CCH_3)(\equiv CCH_3)(P^iPr_3)_2]BF_4$,[4a] respectively.

Complex **3** has a rigid structure in solution. This is strongly supported by the ^1H and $^{13}C\{^1H\}$ NMR spectra in dichloromethane-d_2, which contain nine pyrazolyl resonances like those of **2**. In the ^1H NMR spectrum the methyl substituent of the carbyne group gives rise to a doublet at 1.87 ppm, with a H−P coupling constant of 2.4 Hz, whereas the hydride ligand displays at −7.08 ppm a doublet with a H−P coupling constant of 19.2 Hz. In the ^1H NMR spectrum the C_α resonance of the carbyne group appears at 295.6 ppm, as a doublet with a C−P coupling constant of 14 Hz, while the methyl substituent of the carbyne gives rise to a singlet at 41.5 ppm.

The formation of **2** and **3** can be rationalized according to Scheme 3. The displacement of the acetone molecule by the alkynes in **1** should give π-alkyne intermediates, which would evolve into vinylidene species by 1,2-hydrogen shift. The electrophilic attack of the acidic hydrogen proton of the dihydrogen at the C_β atom of the vinylidenes should finally afford the hydride-carbynes. The cleavage of the Si−C bond promoted by methanol during the formation of **3** agrees well

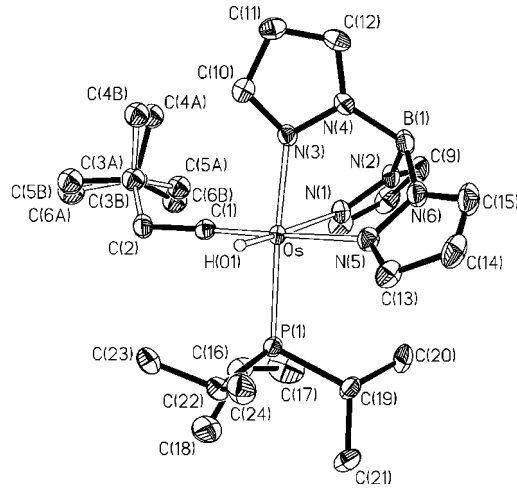
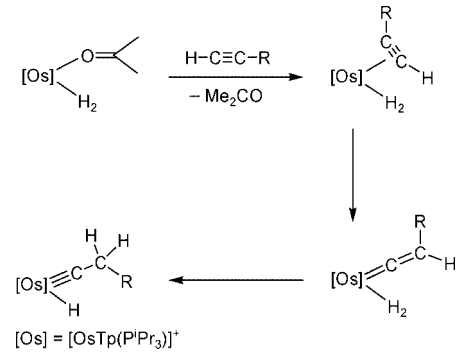


Figure 1. Molecular diagram of the cation of **2**. Selected bond lengths (Å) and angles (deg): Os−N(1) 2.198(4), Os−N(3) 2.129(4), Os−N(5) 2.243(4), Os−C(1) 1.720(5), Os−H(01) 1.60(5), Os−P(1) 2.3858(12); N(1)−Os−H(01) 166.1(19), N(3)−Os−P(1) 170.95(11), N(5)−Os−C(1) 169.54(18), Os−C(1)−C(2) 173.1(4).

Scheme 3



with the participation of vinylidene species as the key intermediates in the formation of these carbyne complexes.[2a,21]

It should be pointed out that the behavior of **1** toward *tert*-butylacetylene and (trimethylsilyl)acetylene is like the behavior of the dihydrides $OsH_2Cl_2(P^iPr_3)_2$ and $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]BF_4$, while it shows significant differences with regard to those of the elongated dihydrogens $[Os\{C_6X_4C(O)CH_3\}(\eta^2\text{-}H_2)L(P^iPr_3)_2]BF_4$ (X = H, F; L = N(OH)=CMe$_2$, H$_2$O).[6,7] In order to understand this, one should note that the co-ligands of **1** and those of the dihydride compounds do not have any direct participation in the formation reactions of the hydride-carbyne derivates. However, the elimination of the *ortho*-metalated ketone with a hydrogen atom of the elongated dihydrogen, to form highly unsaturated monohydride synthons, is the first step in the reactions starting from the elongated dihydrogen compounds. Furthermore, it should be mentioned that the coordination of the alkynes to the dihydrides produces a dihydride-dihydrogen transformation in the OsH_2 unit. Thus, the key intermediates for the formation of the hydride-carbyne products have the same nature starting from **1** as from the dihydrides.

Complexes **2** and **3** are unstable in chloroform at 60 °C. Under these conditions, they evolve into the chloro derivatives $[OsClTp(\equiv CR)(P^iPr_3)]BF_4$ (R = $CH_2{}^tBu$ (**4**), CH_3 (**5**)), which are

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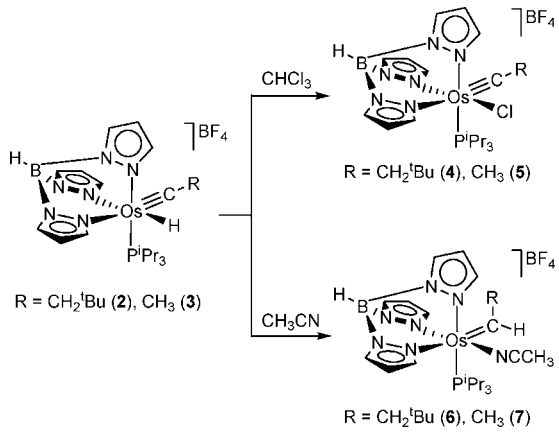
Scheme 4



isolated as yellow-orange (**4**) and brown (**5**) solids in 84% and 69% yield, respectively, according to Scheme 4. Figure 2 shows a view of the cation of **4**. Like for **2**, the geometry around the osmium atom can be described as a distorted octahedron, in this case, with the phosphine ligand *trans* to N(5) (P−Os−N(5) = 169.87(15)°), the carbyne group *trans* to N(3) (C(1)−Os−N(3) = 171.4(3)°), and the chloride *trans* to N(1) (Cl−Os−N(1) = 167.18(15)°). The Os−N bond lengths of 2.116(5) Å (Os−N(1)), 2.222(5) Å (Os−N(3)), and 2.120(6) Å (Os−N(5)) are consistent with those found in **2**. In this context, it should be noted that the separations between the metal center and the nitrogen atoms disposed *trans* to the phosphine and chloride ligands are statistically identical, indicating that the *trans* influence of both ligands is similar. The Os−C(1) distance of 1.734(7) Å agrees well with those found in **2** and in the related Cp compound [OsCl(η^5-C_5H_5)-{≡CCH=C(CH$_2$)$_4$CH$_2$}(P^iPr_3)]BF_4 (1.756(8) Å).[22]

Complexes **4** and **5** have also a rigid structure in solution at room temperature. As for **2** and **3**, the ^{1}H and ^{13}C{^{1}H} NMR spectra of these compounds show nine pyrazolyl resonances. In the ^{13}C{^{1}H} NMR, the most noticeable feature is the C_α resonances of the carbyne groups, which are observed at 312.2 (**4**) and 307.2 (**5**) ppm as doublets with a C−P coupling constant of 12 Hz in both cases.

Complexes **2** and **3** have a high tendency to evolve into carbene derivatives. Thus, in acetonitrile at 50 °C, they give rise to [OsTp(=CHR)($NCCH_3$)(P^iPr_3)]BF_4 (R = $CH_2{}^tBu$ (**6**), CH_3 (**7**)) as a result of the migration of the hydride ligand from the metal center to the carbyne carbon atom. Complexes **6** and **7** are isolated as green (**6**) and red (**7**) solids in 57% and 65% yield, respectively, according to Scheme 4.

These 1,2-hydrogen shifts are supported by the ^{1}H and ^{13}C{^{1}H} NMR spectra of **6** and **7**. The ^{1}H NMR spectrum of **6** in dichloromethane-d_2 at room temperature instead of a hydride resonance shows at 22.17 ppm a double triplet with H−P and H−H coupling constants of 5.2 and 4.2 Hz, corresponding to the C_αH proton of the formed carbene ligand. The methyl resonance of the coordinated acetonitrile molecule appears at 3.00 ppm as a singlet. In the ^{13}C{^{1}H} NMR spectrum the OsC resonance is observed at 308.1 ppm as a doublet with a C−P coupling constant of 7 Hz, whereas the acetonitrile resonances appear as singlets at 123.3 and 4.4 ppm. In the ^{1}H NMR spectrum of **7**, the C_αH proton of the carbene ligand gives rise to a double quartet at 21.49 ppm with H−P and H−H coupling constants of 7.2 and 5.1 Hz. In the ^{13}C{^{1}H} NMR spectrum, the OsC resonance appears at 307.1 ppm as a doublet with a C−P coupling constant of 9 Hz.

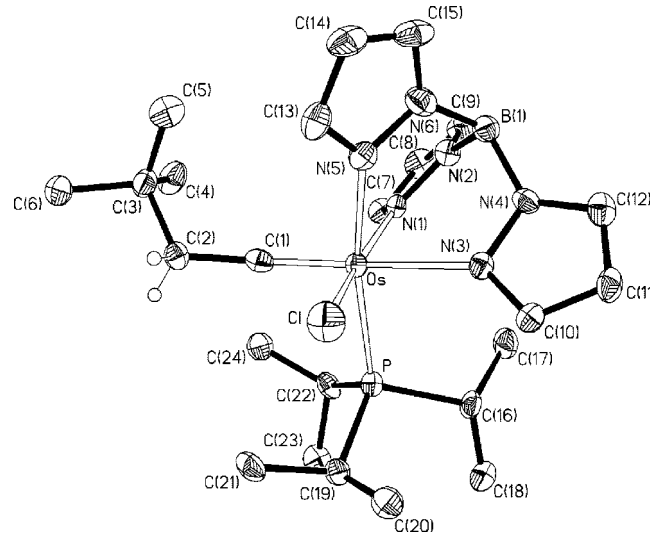


Figure 2. Molecular diagram of the cation of **4**. Selected bond lengths (Å) and angles (deg): Os−N(1) 2.116(5), Os−N(3) 2.222(5), Os−N(5) 2.120(6), Os−C(1) 1.734(7), Os−Cl 2.394(2), Os−P 2.4380(18); N(1)−Os−Cl 167.18(15), N(3)−Os−C(1) 171.4(3), N(5)−Os−P 169.87(15), Os−C(1)−C(2) 168.3(5).

The behavior of **2** and **3** agrees well with that observed for the dicationic [OsH(≡CCH=CR_2)($NCCH_3$)$_2$(P^iPr_3)$_2$][BF_4]$_2$ (R = Ph, Me) and monocationic [OsH{κ^1-OC(O)CH_3}(≡CCH=CPh_2)(NC-CH_3)(P^iPr_3)$_2$]BF_4 and [OsHCl(≡CCH=CPh_2)($NCCH_3$)(P^iPr_3)$_2$]BF_4 hydride-carbyne complexes, which in acetonitrile evolve into the corresponding carbene derivatives.[9,11a] However, it is in contrast with that reported for the neutral species $OsHCl_2$(≡CCH=CPh_2)-(P^iPr_3)$_2$, where the height of the activation barrier of the migration makes impossible the hydride-carbyne to carbene transformation, since the activation barrier for the substitution of one of the chloride ligands by an acetonitrile molecule is lower than that for the 1,2-hydrogen shift.[9]

Evidence for 1,2-hydrogen shift from the metal to the carbyne carbon atom has been also found in the tungsten complex WH(≡CMe_3)(CO){$P(OMe)_3$}$_3$, which affords W(=$CHMe_3$)-(CO)L{$P(OMe)_3$}$_3$ (L = CO, $P(OMe)_3$, PMe_3) via a five-coordinate carbene intermediate.[23] The 1,2-hydrogen shift has been mainly observed in the opposite sense. The extraction of the chloride ligand from the Cp-Os-carbene compounds Os(η^5-C_5H_5)Cl(=CHPh)(PR_3) gives rise to the hydride-carbyne derivatives [OsH(η^5-C_5H_5)(≡CPh)(PR_3)]PF_6 (PR_3 = P^iPr_3,[19] P^iPr_2[$C(CH_3)$=CH_2][24]). The related compounds [OsH(η^5-C_5H_5)(≡CCH_2Ph)(P^iPr_3)]BF_4,[25] [OsH(η^5-$C_5H_4SiPh_3$){≡CCH-(Ph)R}(P^iPr_3)]BF_4 (R = H, Me),[26] and [OsHX(≡CCH_2Ph)(Hpz)(P^iPr_3)$_2$]BF_4 (X = Cl, F)[27] are also known. Similarly, the rhenium-hydride-carbyne complexes ReH(≡CCH_3)(η^2-CH_2=CH_2)(PNP) (PNP = N($SiMe_2CH_2$-

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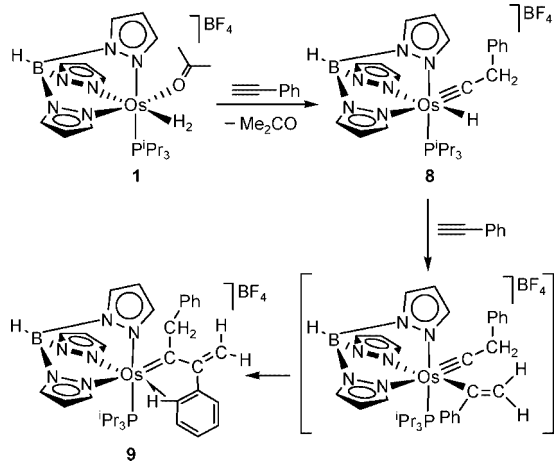
Scheme 5



$PCy_2)_2$),[28] $[ReH_2(\equiv CCH_2R)(mq)(PPh_3)_2]PF_6$, and $ReH(\equiv CCH_2R)(mq)(PPh_3)_2$ (mq = the anion of 2-mercaptoquinoline)[29] are stable, and the migratory insertion of the carbyne ligands into the Re−H bond is not observed.

2. Reaction with Phenylacetylene. There are marked differences in behavior between phenylacetylene and the alkynes shown in Scheme 2. In agreement with the latter alkynes, the addition at room temperature of 2.0 equiv of phenylacetylene to dichloromethane solutions of **1** initially gives rise to the hydride-carbyne $[OsHTp(\equiv CCH_2Ph)(P^iPr_3)]BF_4$ (**8**), related to **2** and **3**. Its formation is supported by the ^1H and $^{13}C\{^1H\}$ NMR spectra of the reaction mixture. The first of them shows at −6.69 ppm a doublet with a H−P coupling constant of 18.9 Hz, corresponding to the hydride ligand, whereas the second one contains at 293.0 ppm a doublet with a C−P coupling constant of 13 Hz due to the carbyne group. However, in contrast to *tert*-butylacetylene and (trimethylsilyl)acetylene, under reflux overnight, the insertion of a second alkyne molecule into the Os−H bond of **8** and the subsequent migration of the resulting alkenyl group from the metal center to the carbyne carbon atom bond take place. As a result of this sequence, the α,β-unsaturated alkenylcarbene derivative $[OsTp\{=C(CH_2Ph)C(Ph)=CH_2\}(P^iPr_3)]BF_4$ (**9**) is formed, which is isolated as a dark green solid in 88% yield, according to Scheme 5.

Complex **9** has also been characterized by X-ray diffraction analysis. Figure 3 shows a view of the cation. The most remarkable feature of this structure is the presence of an agostic interaction between the osmium atom and one of the *ortho*-CH bonds of the phenyl substituent of the alkenyl unit of the alkenylcarbene ligand, which saturates the metal center. Thus, also in this case, the geometry around the osmium atom can be described as a distorted octahedron with the terdentate ligand occupying *fac* positions. The metal coordination sphere is completed by the phosphine ligand *trans* disposed to N(5) (P−Os−N(5) = 170.50(14)°), the C(sp^2) atom of the carbene group *trans* disposed to N(3) (C(1)−Os−N(3) = 169.1(2)°), and the C−H bond *trans* disposed to N(1).

The coordination of the Tp ligand is asymmetric as a result of the chirality of the metal center. The Os−N bond lengths of 2.091(5) Å (Os−N(1)), 2.135(5) Å (Os−N(5)), and 2.195(5) Å (Os−N(3)) are consistent with a *trans* influence of the agostic

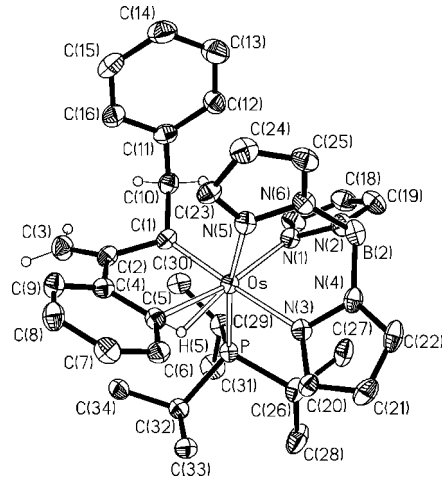


Figure 3. Molecular diagram of the cation of **9**. Selected bond lengths (Å) and angles (deg): Os−N(1) 2.091(5), Os−N(3) 2.195(5), Os−N(5) 2.135(5), Os−C(1) 1.932(6), Os−C(5) 2.307(6), Os−H(5) 1.54(7), C(5)−H(5) 1.35(7), Os−P 2.4300(16); N(1)−Os−C(5) 167.0(2), N(3)−Os−C(1) 169.1(2), N(5)−Os−P 170.50(14), C(1)−Os−C(5) 79.7(2), C(5)−Os−P 101.69(16).

interaction lower than those of the triisopropylphosphine and the chloride ligands, and a *trans* influence of the carbene group similar to that of the hydride ligand.

The Os−C(1) bond length of 1.932(6) Å supports the Os−C double bond formulation.[3,9,24,30] In agreement with the sp^2 hybridization at C(1), the angles around this atom are between 112.8(5)° and 128.3(4)°.

The Os−C(5) and Os−H(5) separations of 2.307(6) and 1.54(7) Å, respectively, as well as the C(5)−H(5) distance of 1.35(7) Å support the agostic interaction between the *ortho*-C(5)−H(5) bond of the phenyl substituent of the carbene and the metal center.[31] As a result of the interaction, the H(5) atom is removed from the aromatic plane by 20(3)°. The agostic interaction is certainly very strong; the calculated r_{bp} value of 0.4(1) lies below the lowest reported.[32] However, the aromaticity of the ring remains practically intact, with C−C distances in the range 1.387(9)−1.412(9) Å.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **9** are consistent with the structure shown in Figure 3 and, in agreement with its strength, reveal that the agostic interaction remains in dichloromethane and acetone solutions at room temperature. In the ^1H NMR spectrum, the most noticeable feature is the presence

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of the resonance due to H(5), which appears at unusually high field, −3.55 ppm, as a double doublet with H−P and H−H coupling constants of 15.3 and 4.8 Hz. The $^{13}C\{^1H\}$ NMR spectrum shows the C(1) resonance at 290.1 ppm, as a doublet with a C−P coupling constant of 9 Hz, whereas the resonance due to the agostic C(5) atom is observed as a singlet at 108.5 ppm, i.e., shifted more than 20 ppm toward higher field with regard to the other phenyl resonances of the complex. Furthermore, the INEPT ^{13}C spectrum shows a C−H coupling constant of 92 Hz for that resonance, which is about 70 Hz lower than the other phenyl $^1J_{C-H}$ coupling constants.

The key intermediate, the alkenyl-carbyne species, for the formation of **9** is the result of a Markovnikov type of insertion of phenylacetylene into the Os−H bond of **8**. This addition to a C−C triple bond is unusual in the osmium chemistry.[33] It has been proposed as the initial step in the formation of osmacyclopropene derivates.[34]

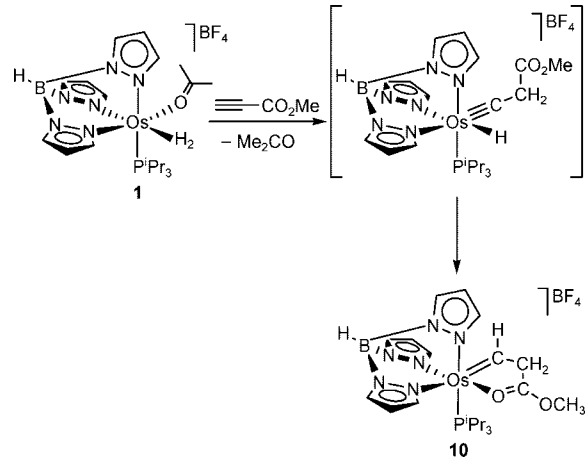
The behavior of **1** toward phenylacetylene is particular to this compound and has no precedent. Although the dihydride $OsH_2Cl_2(P^iPr_3)_2$ also reacts with 1.0 equiv of phenylacetylene to give a hydride-carbyne related to **8**, the insertion of a second alkyne molecule into the Os−H bond of this compound does not occur.[2a] On the other hand, as it has been previously mentioned, the reaction of the cationic dihydride complex $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]^+$ affords a hydride-osmacyclopropene derivative.[4a] The dihydride Cp counterpart $[OsH_2(\eta^5\text{-}C_5H_5)(\kappa^1\text{-}OCMe_2)(P^iPr_3)]BF_4$ also shows a very different behavior from **1**. In contrast to the Tp-Os-dihydrogen the Cp-Os-dihydride undergoes the initial insertion of the alkyne into one of the Os−H bonds and the subsequent reductive elimination of olefin to give a highly unsaturated metal fragment, which couples two phenylacetylene molecules to form the allenylcarbene shown in Scheme 1.[14] The elongated dihydrogen complexes $[\overline{Os\{C_6X_4C(O)}CH_3\}(\eta^2\text{-}H_2)L(P^iPr_3)_2]BF_4$[6,7] also have very different behavior from those above-mentioned. These results reveal that, although the behavior of the OsH_2 species toward aliphatic alkynes can be in some cases similar, each one reacts in a different manner toward phenylacetylene.

3. Reaction with Methylpropiolate. The addition at room temperature of 1.5 equiv of methylpropiolate to dichloromethane solutions of **1** leads to the carbene derivative $[\overline{OsTp\{=CHCH_2C(O)}OMe\}(P^iPr_3)]BF_4$ (**10**), which is isolated as a green solid in 85% yield according to Scheme 6.

Complex **10** has also been characterized by X-ray diffraction analysis. The structure has two chemically equivalent but crystallographically independent cations in the asymmetric unit. A drawing of one of them is shown in Figure 4. As for **2**, **4**, and **9**, the geometry around the metal center can be described as a distorted octahedron with the Tp ligand occupying *fac* positions. In this case, the metal coordination sphere is completed by the triisopropylphosphine ligand *trans* disposed to N(1) (P(1)−Os−N(1) = 171.1(3)° and 173.3(3)°) and the C,O-chelate group, which acts with bite angles C(1)−Os−O(1) of 80.9(5)° and 79.5(5)°, with C(1) *trans* disposed to N(5) (C(1)−Os−N(5) = 169.7(5)° and 167.3(5)°) and O(1) *trans* disposed to N(3) (O(1)−Os−N(3) = 171.6(4)° and 174.5(4)°).

The coordination of the terdentate ligand is asymmetric, as expected, with Os−N bond lengths of 2.113(10) and 2.119(10) Å (Os−N(1)), 2.039(11) and 2.056(11) Å (Os−N(3)), and 2.206(10) and 2.198(11) Å (Os−N(5)), which are consistent with a *trans* influence of the carbonyl group of the chelate carbene ligand lower than that of the agostic interaction in **9**. So, the comparison of the Os−N bond lengths in **2**, **4**, **9**, and **10** indicates the following *trans* influence sequence: RR′C═O < C−H < Cl ≈ P^iPr_3 < H ≈ ═CHR < ≡C−R.

Scheme 6



The Os−C(1) distances of 1.863(14) and 1.900(13) Å agree well with that of **9** and support the Os−C double bond formulation. In agreement with the sp^2 hybridization at C(1), the angles Os−C(1)−C(2) are 118.8(10)° and 120.4(10)°.

The ^1H and $^{13}C\{^1H\}$ NMR spectra are consistent with the structure shown in Figure 4. In the ^1H NMR spectrum the C(1)−H resonance appears at 21.10 ppm as a double doublet of doublets with H−H coupling constants of 3.6 and 2.8 Hz and a H−P coupling constant of 1.2 Hz. In the $^{13}C\{^1H\}$ NMR spectrum the C(1) resonance is observed at 264.6 ppm as a doublet with a C−P coupling constant of 10 Hz.

The one-pot synthesis of carbene derivatives using methylpropiolate as organic substrate has no precedent in osmium chemistry.[12,34,35] This unusual finding can be rationalized according to Scheme 6. Like *tert*-butylacetylene, (trimethylsilyl)acetylene, and phenylacetylene, methylpropiolate reacts with **1** to give initially a nondetectable hydride-carbyne species related to **2**, **3**, and **8**. As a consequence of the high tendency shown by the hydride ligand of these compounds to migrate from the metal center to the carbyne carbon atom, an unsaturated short-lived carbene derivative is formed. The latter undergoes rapid stabilization by coordination of the carbonyl group of the $CH_2C(O)OMe$ substituent, to afford **10**.

Concluding Remarks

The reactions of the osmium compounds containing two hydrogen atoms bonded to the metal center with terminal alkynes are not easily rationalized when the co-ligands of the complexes have some direct participation in the processes, as it has been observed for the elongated dihydrogen derivatives $[\overline{Os\{C_6X_4C(O)}CH_3\}(\eta^2\text{-}H_2)L(P^iPr_3)_2]^+$,[6,7] because depending upon the ligands each compound has a particular behavior. However, when the co-ligands contribute only to the electronic structure of the metal center, the difference in energy between the dihydride and dihydrogen tautomers seems to be the factor determining the formed product.

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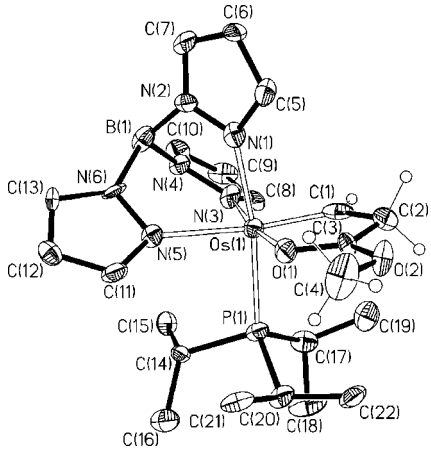

Figure 4. Molecular diagram of one of the two independent cations in the asymmetric unit of **10**. Selected bond lengths (Å) and angles (deg) for both cations: Os(1)−N(1) 2.133(10) (2.119(10)), Os(1)−N(3) 2.039(11) (2.056(11)), Os(1)−N(5) 2.206(10) (2.198(11)), Os(1)−C(1) 1.863(14) (1.900(13)), Os(1)−O(1) 2.125(9) (2.114(10)), Os(1)−P(1) 2.407(3) (2.409(3)), C(1)−C(2) 1.522(18) (1.473(18)), C(2)−C(3) 1.503(18) (1.495(19)), C(3)−O(1) 1.250(14) (1.267(16)); N(1)−Os(1)−P(1) 171.1(3) (173.3(3)), N(3)−Os(1)−O(1) 171.6(4) (174.5(4)), N(5)−Os(1)−C(1) 169.7(5) (167.3(5)), C(1)−Os(1)−O(1) 80.9(5) (79.5(5)).

The Cp ligand favors the dihydride form. Thus, phenylacetylene reacts with the dihydride $[OsH_2(\eta^5\text{-}C_5H_5)(\kappa^1\text{-}OCMe_2)(P^iPr_3)]BF_4$ by insertion of the C−C triple bond into one of the Os−H bonds. The subsequent reductive elimination in the resulting hydride-styryl intermediate affords styrene and the highly unsaturated metal fragment $[Os(\eta^5\text{-}C_5H_5)(P^iPr_3)]^+$, which couples two phenylacetylene molecules to give an allenylcarbene derivative.[14] In contrast to Cp, the Tp group favors the nonclassical interactions between the hydrogen atoms. Thus, the dihydrogen complex $[OsTp(\eta^2\text{-}H_2)(\kappa^1\text{-}OCMe_2)(P^iPr_3)]BF_4$ reacts with phenylacetylene to give initially a hydride-carbyne species, which undergoes the insertion of a second molecule into the Os−H bond. The subsequent migration of the resulting alkenyl group from the metal center to the carbyne carbon atom leads to an alkenylcarbene, which saturates the metal center by means of a strong agostic interaction between the osmium atom and one of the *ortho*-CH bonds of the phenyl substituent of the alkenyl unit of the carbene ligand.

The behavior of the dihydrogen complex $[OsTp(\eta^2\text{-}H_2)(\kappa^1\text{-}OCMe_2)(P^iPr_3)]BF_4$ toward *tert*-butylacetylene and (trimethylsilyl)acetylene is the same as that of the dihydrides $OsH_2Cl_2(P^iPr_3)_2$[2a] and $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]^+$.[4a] In this context, it should be noted that the coordination of electron-poor Lewis bases to the metal center of these dihydrides produces the dihydride-dihydrogen transformation.[36] Although with both types of OsH_2 species hydride-carbyne species are formed, there are significant differences in behavior between the resulting $[OsHTp(\equiv CCH_2R)(P^iPr_3)]BF_4$ and $OsHCl_2(\equiv CCH_2R)(P^iPr_3)_2$. The metal center of this cationic Tp complex is electron-poor in comparison with that of the bisphosphine derivatives. So, in agreement with the redox character of the hydride-carbyne to carbene transformation in osmium,[9,11a,34,37] the hydride ligand of $[OsHTp(\equiv CCH_2R)(P^iPr_3)]BF_4$ has a marked tendency to migrate from the metal center to the carbyne carbon atom, in contrast to $OsHCl_2(\equiv CCH_2R)(P^iPr_3)_2$.[9] Thus, in acetonitrile, the carbenes $[OsTp(=CHCH_2R)(NCCH_3)(P^iPr_3)]BF_4$ are formed. As a consequence of the high tendency of the hydride ligand to migrate, the reaction of the Os-Tp-dihydrogen complex with methylpropiolate allows us to prepare the carbene $[OsTp\{=CHCH_2C(O)OMe\}(P^iPr_3)]BF_4$ in a one-pot synthesis.

In conclusion, the reactions of dihydrogen- and dihydride-Os complexes, which afford dihydrogen species by coordination of electron-poor Lewis bases, with terminal alkynes lead to hydride-carbyne derivatives, which evolve into carbenes when the metal center is electron-poor and the substituent of the alkyne has a significant coordination power.

Experimental Section

General Methods and Instrumentation. All reactions were carried out under argon with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use or obtained oxygen- and water-free from an MBraun solvent purification apparatus. The starting material $[OsTp(\eta^2\text{-}H_2)(\kappa^1\text{-}OCMe_2)(P^iPr_3)]BF_4$ (**1**) was prepared according to the published method.[18] ^1H, $^{31}P\{^1H\}$, ^{13}C, and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Varian Gemini 2000, a Bruker ARX 300, a Bruker Avance 300 MHz, or a Bruker Avance 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^1H, $^{13}C\{^1H\}$) or external H_3PO_4 ($^{31}P\{^1H\}$). Coupling constants, *J*, are given in hertz. Spectral assignments were achieved by $^1H-^1H$ COSY, $^1H\{^{31}P\}$, ^{13}C APT, $^1H-^{13}C$ HSQC, and $^1H-^{13}C$ HMBC experiments. Infrared spectra were recorded on a Spectrum One spectrometer as neat solids. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer.

Preparation of $[OsHTp\{\equiv CCH_2C(CH_3)_3\}(P^iPr_3)]BF_4$ (2). *tert*-Butylacetylene (52 μL, 0.42 mmol) was added to a solution of **1** (200 mg, 0.28 mmol) in 5 mL of dichloromethane. The mixture was stirred at room temperature for 2 h. Then the solution was concentrated to ca. 1 mL. Diethyl ether (7 mL) was added, causing the precipitation of a sticky solid, which was washed with diethyl ether (5 × 5 mL) in a 2-propanol/dry ice bath and vacuum-dried. Yellow solid. Yield: 120 mg (57%). Anal. Calcd for $C_{24}H_{43}B_2F_4N_6OsP$: C, 39.25; H, 5.90; N, 11.44. Found: C, 39.18; H, 5.89; N, 11.36. IR (ATR, cm^{-1}): ν(BH) 2537 (w), ν(OsH) 2133 (w), ν(BF_4) 1047 (vs). ^1H NMR (400 MHz, CD_2Cl_2, 298 K): 8.05 (d, 1H, Tp), 7.99 (d, 1H, Tp), 7.90 (d, 1H, Tp), 7.72 (d, 1H, Tp), 7.70 (d, 1H, Tp), 7.64 (d, 1H, Tp), 6.57 (t, 1H, Tp), 6.30 (t, 1H, Tp), 6.23 (t, 1H, Tp), 2.53 (m, 3H, PCH), 2.07 (part AB of an ABX (X = ^{31}P) spin system, $\Delta\nu = 100.40$, $J_{A-B} = 18.0$, $J_{A-X} = 2.0$, $J_{B-X} = 3.2$, 2H, CH_2), 1.42 (dd, $J_{H-P} = 13.4$, $J_{H-H} = 7.0$, 9H, PCHC*H*$_3$), 1.04 (dd, $J_{H-P} = 16.0$, $J_{H-H} = 7.2$, 9H, PCHC*H*$_3$), 0.97 (s, 9H, C(C*H*$_3$)$_3$), −6.73 (d, $J_{H-P} = 19.6$, 1H, OsH), all coupling constants for the pyrazolyl proton resonances were about 2 Hz. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 298 K): 30.7 (s). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 298 K): 300.7 (d, $J_{C-P} = 13$, Os≡C), 148.3 (d, $J_{C-P} = 1$, Tp), 146.8, 146.3, 138.3, 138.1, 137.2, 108.4, 107.5 (all s, Tp), 107.3 (d, $J_{C-P} = 2$, Tp), 67.3 (s, CH_2), 34.5 (s, *C*(CH$_3$)$_3$), 30.9 (s, C(*C*H$_3$)$_3$), 25.5 (d, $J_{C-P} = 30$, PCH), 20.5 (s, PCH*C*H$_3$), 18.6 (d, $J_{C-P} = 4$, PCH*C*H$_3$).

Preparation of $[OsHTp(\equiv CCH_3)(P^iPr_3)]BF_4$ (3). (Trimethylsilyl)acetylene (69 μL, 0.49 mmol) and methanol (100 μL) were

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(37) (a) Caulton, K. G. *J. Organomet. Chem.* **2001**, *56*, 617–618. (b) Jacobsen, H. *J. Organomet. Chem.* **2003**, *674*, 50.

added to a yellow solution of **1** (230 mg, 0.32 mmol) in 5 mL of dichloromethane. The reaction mixture was stirred at room temperature. After 30 min the solution was concentrated to ca. 1 and diethyl ether (7 mL) was added, causing the precipitation of a sticky solid, which was isolated as described for **2**. Yellow solid. Yield: 178 mg (82%). Anal. Calcd for $C_{20}H_{35}B_2F_4N_6OsP$: C, 35.41; H, 5.20; N, 12.39. Found: C, 35.57; H, 4.85; N, 12.40. IR (ATR, cm^{-1}): ν(BH) 2512 (w), ν(OsH) 2101 (w), $\nu(BF_4)$ 1046 (vs). ^1H NMR (300 MHz, CD_2Cl_2, 298 K): 7.97 (m, 2H, Tp), 7.84 (d, 1H, Tp), 7.76 (d, 2H, Tp), 7.69 (d, 1H, Tp), 6.55 (t, 1H, Tp), 6.37 (t, 1H, Tp), 6.29 (t, 1H, Tp), 2.54 (m, 3H, PCH), 1.87 (d, $J_{H-P} = 2.4$, 3H, $\equiv CCH_3$), 1.44 (dd, $J_{H-P} = 13.2$, $J_{H-H} = 6.9$, 9H, PCHC*H*$_3$), 1.03 (dd, $J_{H-P} = 16.5$, $J_{H-H} = 7.2$, 9H, PCHC*H*$_3$), −7.08 (d, $J_{H-P} = 19.2$, 1H, OsH), all coupling constants for the pyrazolyl proton resonances were about 2 Hz. $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 298 K): 33.1 (s). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 298 K): 295.6 (d, $J_{C-P} = 14$, Os≡C), 146.3, 146.1, 145.7, 137.9, 137.8, 136.5, 108.1, 107.6 (all s, Tp), 41.5 (s, Os≡C−*C*H$_3$), 24.7 (d, $J_{C-P} = 30$, PCH), 20.7 (s, PCH*C*H$_3$), 18.7 (d, $J_{C-P} = 4$, PCH*C*H$_3$).

Preparation of [OsClTp{≡CCH$_2$C(CH$_3$)$_3$}(P^{i}Pr$_3$)]BF$_4$ (4). A solution of **2** (250 mg, 0.34 mmol) in 7 mL of chloroform was charged in a Schlenk flask equipped with a Teflon stopcock and stirred at 60 °C for 36 h. Then the solution was concentrated to ca. 0.5 mL and diethyl ether (10 mL) was added, causing the appearance of an orange oil, which was washed with diethyl ether (10 × 10 mL) in a 2-propanol/dry ice bath and dried *in vacuo*. Yellow-orange solid. Yield: 181 mg (69%). Anal. Calcd for $C_{24}H_{42}B_2ClF_4N_6OsP$: C, 37.49; H, 5.51; N, 10.93. Found: C, 37.62, H, 5.24; N, 10.45. IR (ATR, cm^{-1}): ν(BH) 2529 (w), $\nu(BF_4)$ 1049 (vs). ^1H NMR (300 MHz, CD_2Cl_2, 298 K): 8.06 (d, 1H, Tp), 7.99 (d, 1H, Tp), 7.96 (d, 1H, Tp), 7.86 (d, 1H, Tp), 7.81 (d, 1H, Tp), 7.75 (d, 1H, Tp), 6.63 (t, 1H, Tp), 6.37 (t, 1H, Tp), 6.33 (t, 1H, Tp), 2.91 (m, 3H, PCH), 2.59 (part AB of an ABX (X = ^{31}P) spin system, $\Delta\nu = 39.6$, $J_{A-B} = 19.2$, $J_{A-X} = J_{B-X} = 2.4$, 2H, CH_2), 1.42 (dd, $J_{H-P} = 14.0$, $J_{H-H} = 6.8$, 9H, PCHC*H*$_3$), 1.19 (dd, $J_{H-P} = 15.6$, $J_{H-H} = 7.2$, 9H, PCHC*H*$_3$), 1.09 (s, 9H, C(C*H*$_3$)$_3$), all coupling constants for the pyrazolyl proton resonances were about 2 Hz. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 298 K): 9.7 (s). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 298 K): 312.2 (d, $J_{C-P} = 12$, Os≡C), 148.9, 145.3, 144.2, 139.9, 138.3 (all s, Tp), 137.4 (d, $J_{C-P} = 2$, Tp), 109.8, 107.6 (all s, Tp), 107.3 (d, $J_{C-P} = 2$, Tp), 70.0 (s, CH_2), 36.5 (s, *C*(CH$_3$)$_3$), 31.3 (s, C(*C*H$_3$)$_3$), 27.1 (d, $J_{C-P} = 28$, PCH), 19.9 (d, $J_{C-P} = 1$, PCH*C*H$_3$), 19.6 (d, $J_{C-P} = 4$, PCH*C*H$_3$).

Preparation of [OsClTp(≡CCH$_3$)(P^{i}Pr$_3$)]BF$_4$ (5). This complex was prepared as described for **4** starting from 260 mg (0.38 mmol) of **3**, but the solution was allowed to react for 24 h at 60 °C. Brown solid. Yield: 229 mg (84%). Anal. Calcd for $C_{20}H_{34}B_2ClF_4N_6OsP$: C, 33.70; H, 4.81; N, 11.89. Found: C, 33.75, H, 4.92; N, 11.62. IR (ATR, cm^{-1}): ν(BH) 2500 (w), $\nu(BF_4)$ 1049 (vs). ^1H NMR (300 MHz, CD_2Cl_2, 298 K): 7.93 (m, 3H, Tp), 7.89 (d, 1H, Tp), 7.86 (d, 1H, Tp), 7.75 (d, 1H, Tp), 6.58 (t, 1H, Tp), 6.40 (t, 1H, Tp), 6.36 (t, 1H, Tp), 2.93 (m, 3H, PCH), 2.25 (d, $J_{H-P} = 2.1$, 3H, $\equiv CCH_3$), 1.33 (dd, $J_{H-P} = 14.0$, $J_{H-H} = 7.1$, 9H, PCHC*H*$_3$), 1.25 (dd, $J_{H-P} = 15.6$, $J_{H-H} = 7.2$, 9H, PCHC*H*$_3$), all coupling constants for the pyrazolyl proton resonances were about 2 Hz. $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 298 K): 13.5 (s). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 298 K): 307.2 (d, $J_{C-P} = 12$, Os≡C), 148.6, 145.5, 143.1, 139.4, 138.5 (all s, Tp), 136.8 (d, $J_{C-P} = 2$, Tp), 109.8 (s, Tp), 107.9 (d, $J_{C-P} = 2$, Tp), 107.5 (s, Tp), 44.0 (s, Os≡C*C*H$_3$), 25.7 (d, $J_{C-P} = 28$, PCH), 19.6 (d, $J_{C-P} = 1$, PCH*C*H$_3$), 19.5 (d, $J_{C-P} = 3$, PCH*C*H$_3$).

Preparation of [OsTp{=CHCH$_2$C(CH$_3$)$_3$}(NCCH$_3$)(P^{i}Pr$_3$)]BF$_4$ (6). 2 (140 mg, 0.19 mmol) was dissolved in 5 mL of acetonitrile and stirred at 50 °C for 24 h. After this time the solvent was removed *in vacuo* and the obtained dark green residue was dissolved in 1 mL of dichloromethane. Diethyl ether (10 mL) was added, causing the appearance of an oil, which was washed with diethyl ether (5 × 10 mL) in a 2-propanol/dry ice bath and vacuum-dried. Green solid. Yield: 77 mg (57%). Anal. Calcd for $C_{26}H_{46}B_2F_4N_7OsP$: C, 40.27; H, 5.98; N, 12.64. Found: C, 40.39; H, 5.60; N, 12.20. IR (ATR, cm^{-1}): ν(BH) 2487 (w), ν(CH$_3$CN) 2269 (w), $\nu(BF_4)$ 1046 (vs). ^1H NMR (300 MHz, CD_2Cl_2, 298 K): 22.17 (dt, $J_{H-P} = 5.2$, $J_{H-H} = 4.2$, 1H, =CH), 8.08 (d, 1H, Tp), 7.92 (d, 1H, Tp), 7.85 (d, 1H, Tp), 7.64 (d, 1H, Tp), 7.32 (d, 1H, Tp), 6.80 (d, 1H, Tp), 6.43 (t, 1H, Tp), 6.34 (t, 1H, Tp), 6.16 (t, 1H, Tp), 3.00 (s, 3H, CH$_3$CN), 2.37 (m, 3H, PCH), 1.27 (dd, $J_{H-P} = 12.2$, $J_{H-H} = 7.1$, 9H, PCHC*H*$_3$), 0.98 (s, 10H, 9H C(CH$_3$)$_3$ + 1H CH$_2$), 0.79 (dd, $J_{H-P} = 14.4$, $J_{H-H} = 7.2$, 10H, 9H PCHC*H*$_3$ + 1H CH$_2$), all coupling constants for the pyrazolyl proton resonances were about 2 Hz. $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 298 K): 4.8 (s). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 298 K): 308.1 (d, $J_{C-P} = 7$, Os≡C), 146.5, 145.5, 142.3, 137.9, 137.7, 135.6 (all s, Tp), 123.3 (s, CN), 108.3, 107.4, 107.0 (all s, Tp), 74.8 (s, CH_2), 31.9 (s, *C*(CH$_3$)$_3$), 29.8 (s, C(*C*H$_3$)$_3$), 24.9 (d, $J_{C-P} = 26$, PCH), 19.1 (d, $J_{C-P} = 3$, PCH*C*H$_3$), 18.7 (s, PCH*C*H$_3$), 4.4 (s, NC*C*H$_3$).

Preparation of [OsTp(=CHCH$_3$)(NCCH$_3$)(P^{i}Pr$_3$)]BF$_4$ (7). 3 (150 mg, 0.22 mmol) was dissolved in 5 mL of acetonitrile and stirred overnight at 50 °C. The resulting red solution was evaporated, and dichloromethane (0.5 mL) and diethyl ether (10 mL) were added. A red solid appeared, which was washed with diethyl ether (5 × 10 mL) and dried *in vacuo*. Yield: 106 mg (65%). Anal. Calcd for $C_{22}H_{38}B_2F_4N_7OsP$: C, 36.73; H, 5.32; N, 13.63. Found: C, 36.72; H, 5.27; N, 13.42. IR (ATR, cm^{-1}): ν(BH) 2518 (w), ν(CH$_3$CN) 2270 (w), $\nu(BF_4)$ 1044 (vs). ^1H NMR (300 MHz, CD_2Cl_2, 298 K): 21.49 (dq, $J_{H-P} = 7.2$, $J_{H-H} = 5.1$, 1H, Os=C), 8.07 (d, 1H, Tp), 7.94 (d, 1H, Tp), 7.84 (d, 1H, Tp), 7.63 (d, 1H, Tp), 7.34 (d, 1H, Tp), 6.95 (d, 1H, Tp), 6.49 (t, 1H, Tp), 6.33 (t, 1H, Tp), 6.17 (t, 1H, Tp), 2.95 (s, 3H, CH$_3$CN), 2.40 (m, 3H, PCH), 1.64 (dd, $J_{H-H} = 7.2$, $J_{H-P} = 2.4$, 3H, Os=CHC*H*$_3$), 1.27 (dd, $J_{H-P} = 12.3$, $J_{H-H} = 7.2$, 9H, PCHC*H*$_3$), 0.80 (dd, $J_{H-P} = 14.7$, $J_{H-H} = 7.2$, 9H, PCHC*H*$_3$) all coupling constants for the pyrazolyl proton resonances were about 2 Hz. $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 298 K): 6.1 (s). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 298 K): 307.1 (d, $J_{C-P} = 9$, Os=C), 146.7, 146.1, 142.7, 138.2, 138.0, 135.9 (all s, Tp), 123.6 (s, CN), 108.4, 107.7, 107.2 (all s, Tp), 51.1 (s, =CH*C*H$_3$), 24.5 (d, $J_{C-P} = 27$, PCH), 18.7 (d, $J_{C-P} = 3$, PCH*C*H$_3$), 18.2 (s, PCH*C*H$_3$), 4.1 (s, NC*C*H$_3$).

Reaction of [OsTp(η^2-H$_2$)(κ^1-OCMe$_2$)(P^{i}Pr$_3$)]BF$_4$ (1) with Phenylacetylene: Formation of [OsHTp(≡CCH$_2$Ph)(P^{i}Pr$_3$)]BF$_4$ (8). An NMR tube containing a yellow solution of **1** (30 mg, 0.04 mmol) in 0.5 mL of dichloromethane-d_2 was treated with phenylacetylene (9.3 μL, 0.08 mmol). The solution color changed immediately to dark green. After 7 h at room temperature, the NMR spectra showed the presence of **8** and **9** in a molar ratio of 3:2. Selected spectroscopic data for **8**: ^1H NMR (300 MHz, CD_2Cl_2, 298 K): −6.69 (d, $J_{H-P} = 18.9$, 1H, OsH). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 298 K): 32.7 (s). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 298 K): 293.0 (d, $J_{C-P} = 13$, Os≡C), 59.7 (s, CH_2).

Preparation of [OsTp{=C(CH$_2$Ph)C(=CH$_2$)Ph}(P^{i}Pr$_3$)]BF$_4$ (9). A solution of **1** (180 mg, 0.25 mmol) in 10 mL of dichloromethane was treated with phenylacetylene (70 μL, 0.63 mmol) and heated under reflux overnight. The resulting dark green solution was allowed to reach room temperature and concentrated to ca. 1 mL. The addition of diethyl ether resulted in the appearance of a green oil which was washed with diethyl ether (4 × 10 mL) and dried *in vacuo*. Green solid. Yield: 190 mg (88%). Anal. Calcd for $C_{34}H_{45}B_2F_4N_6OsP$: C, 47.67; H, 5.29; N, 9.81. Found: C, 47.29; H, 4.99; N, 10.05. IR (ATR, cm^{-1}): ν(BH) 2507 (w), ν(C=C) 1596 (w), $\nu(BF_4)$ 1047 (vs). ^1H NMR (300 MHz, CD_2Cl_2, 298 K): 8.07 (s, 2H, Tp), 8.03 (d, 1H, Tp), 7.87 (d, 1H, Tp), 7.65 (d, $J_{H-H} = 7.5$, 1H, Ph ag), 7.50 (t, $J_{H-H} = 7.8$, 1H, Ph ag), 7.36 (m 1H, Ph ag), 7.22 (s, 1H, Tp), 7.12 (t, $J_{H-H} = 7.5$, 1H, Ph ag), 6.91 (s, 1H, =CH$_2$), 6.84 (m, 1H, p-Ph), 6.74 (s, 1H, =CH$_2$), 6.69 (m, 3H, 1H Tp + 2H Ph), 6.54 (t, 1H, Tp), 6.07 (d, $J_{H-H} = 7.5$, 2H, o-Ph),

5.41 (d, J_{H-H} = 10.2, 1H, CH_2Ph), 5.09 (t, 1H, Tp), 4.26 (d, 1H, Tp), 3.96 (d, J_{H-H} = 10.2, 1H, CH_2Ph), 2.71 (m, 3H, PCH), 1.32 (dd, J_{H-P} = 12.8, J_{H-H} = 7.1, 9H, $PCHCH_3$), 0.78 (dd, J_{H-P} = 15.3, J_{H-H} = 7.2, 9H, $PCHCH_3$), −3.55 (dd, J_{H-P} = 15.3, J_{H-H} = 4.8, 1H, H ag), all coupling constants for the pyrazolyl proton resonances were about 2 Hz. $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2, 298 K): 4.4 (s). $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 298 K): 290.1 (d, J_{C-P} = 9, Os=C), 187.1 (s, C=CH_2), 156.8 (s, Cipso Ph ag), 148.6 (s, Tp), 147.2 (s, Tp), 143.4 (s, Ph ag), 141.1 (s, Tp), 138.3 (s, Tp), 137.9 (s, Tp), 134.7 (s, Tp), 132.3 (s, Ph ag), 131.8 (s, Ph ag), 128.7 (s, o-Ph), 128.5 (s, m-Ph), 127.5 (s, Cipso Ph), 126.5 (s, p-Ph), 126.1 (s, Ph ag), 108.7 (s, Tp), 108.5 (s, Tp), 108.5 (s, CH ag Ph ag), 106.4 (d, J_{C-P} = 2, Tp), 96.0 (s, =CH_2), 64.3 (s, CH_2Ph), 26.5 (d, J_{C-P} = 27, PCH), 19.3 (d, J_{C-P} = 4, $PCHCH_3$), 18.5 (s, $PCHCH_3$). ^{13}C NMR (100.63 MHz, CD_2Cl_2, 298 K): 290.1 (br, Os=C), 187.1 (br, C=CH_2), 156.8 (m, Cipso Ph ag), 148.6 (dt, J_{C-H} = 186, J_{C-H} = 7, Tp), 147.2 (dt, J_{C-H} = 184, J_{C-H} = 7, Tp), 143.4 (dd, J_{C-H} = 163, J_{C-H} = 9, Ph ag), 141.1 (dt, J_{C-H} = 189, J_{C-H} = 7, Tp), 138.3 (dt, J_{C-H} = 189, J_{C-H} = 7, Tp), 137.9 (br d, J_{C-H} = 190, Tp), 134.7 (br d, J_{C-H} = 190, Tp), 132.3 (dd, J_{C-H} = 163, J_{C-H} = 8, Ph ag), 131.8 (dm, J_{C-H} = 163, Ph ag), 128.7 (dd, J_{C-H} = 160, J_{C-H} = 8, o-Ph), 128.5 (dm, J_{C-H} = 157, m-Ph), 127.5 (m, Cipso Ph),126.5 (dt, J_{C-H} = 162, J_{C-H} = 8, p-Ph), 126.1 (dd, J_{C-H} = 162, J_{C-H} = 8, Ph ag), 108.7 (dt, J_{C-H} = 180, J_{C-H} = 8, Tp), 108.5 (dt, J_{C-H} = 182, J_{C-H} = 8, Tp), 108.5 (dm, J_{C-H} = 92, CH ag Ph ag), 106.4 (dtd, J_{C-H} = 181, J_{C-H} = 9, J_{C-P} = 2, Tp), 96.0 (t, J_{C-H} = 161, =CH_2), 64.3 (br t, J_{C-H} = 130, CH_2Ph), 26.5 (dd, J_{C-H} = 131, J_{C-P} = 27, PCH), 19.3 (qm, J_{C-H} = 128, $PCHCH_3$), 18.5 (qm, J_{C-H} = 129, $PCHCH_3$).

Preparation of [OsTp{=CHCH$_2$C(O)OMe}P^{i}Pr$_3$)]BF$_4$ (10). 1 (250 mg, 0.35 mmol) was dissolved in 5 mL of dichloromethane, and methyl propiolate (44 μL, 0.53 mmol) was added. The color of the solution changed from yellow to dark green. After stirring 1 h at room temperature the solution was concentrated to ca. 1 mL. Diethyl ether (7 mL) was added, and the oily residue was washed with diethyl ether and vacuum-dried. Green solid. Yield: 219 mg (85%). Anal. Calcd for $C_{22}H_{37}B_2F_4N_6O_2OsP$: C, 35.88; H, 5.06; N, 11.41. Found: C, 35.47; H, 4.87; N, 10.90. IR (ATR, cm^{-1}): ν(BH) 2527 (w), ν(C=O) 1603 (s), ν(C−O) 1277 (m), $\nu(BF_4)$ 1046 (vs). ^1H NMR (400 MHz, CD_2Cl_2, 298 K): 21.10 (ddd, J_{H-H} = 3.6, J_{H-H} = 2.8, J_{H-P} = 1.2, 1H, Os=CH) 8.16 (d, 1H, Tp), 7.98 (d, 1H, Tp), 7.89 (d, 1H, Tp), 7.77 (d, 1H, Tp), 7.51 (d, 1H, Tp), 6.69 (d, 1H, Tp), 6.58 (t, 1H, Tp), 6.38 (t, 1H, Tp), 6.12 (t, 1H, Tp), 4.25 (s, 3H, OMe), 2.30 (m, 3H, PCH), 1.08 (dd, J_{H-P} = 13.3, J_{H-H} = 7.2, 11H, 9H of $PCHCH_3$ and 2H corresponding to the overlapped signal of CH_2), 0.84 (dd, J_{H-P} = 14.0, J_{H-H} = 7.2, 9H, $PCHCH_3$), all coupling constants for the pyrazolyl proton resonances were about 2 Hz. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 298 K): 9.6 (s). $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_2Cl_2, 298 K): 264.6 (d, J_{C-P} = 10, Os=C), 194.9 (s, C=O), 147.1, 146.3, 138.5, 138.2, 137.5, 135.8, 108.2, 107.7, 106.5 (all s, Tp), 72.0 (s, CH_2), 57.3 (s, OCH_3), 24.7 (d, J_{C-P} = 7, PCH), 18.6 (s, $PCHCH_3$), 18.0 (s, $PCHCH_3$).

Structural Analysis of Complexes 2, 4, 9, and 10. Suitable crystals for the X-ray diffraction study were obtained by slow diffusion of diethyl ether into concentrated solutions of the complexes in dichloromethane (**2**, **9**, and **10**) or acetone (**4**) at −20 °C. X-ray data were collected for all complexes at low temperature on an Oxford Xcalibur Sapphire CCD (**2**) and Bruker Smart Apex CCD (**4**, **9**, and **10**) diffractometers with graphite-monochromated Mo radiation (λ = 0.71073 Å). Data were corrected for absorption by using a multiscan method applied with the Abspack[38] and Sadabs[39] programs. The structures for all compounds were solved by the direct methods. Refinement, by full-matrix least-squares on F^2 with SHELXL97,[40] was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters for all non-hydrogen nondisordered atoms. The hydrogen atoms were observed or calculated and refined freely or using a restricted riding mode respectively in the last cycles of refinement. Disordered solvates and counterions were treated with a split occupancy model, and in some cases intra-atomic distances were fixed and restrained. All the highest electronic residuals were observed in close proximity of the Os centers or disordered solvents and make no chemical sense.

Crystal data for **2**: $C_{24}H_{43}B_2F_4N_6OsP \cdot 0.5(CH_2Cl_2)$, M_w 767.83, yellow, irregular block (0.30 × 0.19 × 0.12 mm), monoclinic, space group $P2_1/c$, a: 8.5784(5) Å, b: 21.687(2) Å, c: 17.038(2) Å, β: 92.595(9)°, V = 3166.5(5) Å^3, Z = 4, D_{calc}: 1.611 g cm^{-3}, F(000): 1512, T = 150(2) K; μ 4.210 mm^{-1}); 63 671 measured reflections (2θ: 3−50°), 5896 unique (R_{int}= 0.0351); min./max. transm factors 0.7982/1.1231. Final agreement factors were R1 = 0.0337 (5614 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.0832; data/restraints/parameters 5896/62/373; GoF = 1.043. Largest peak and hole: 1.623 and −0.965 e/Å^3.

Crystal data for **4**: $C_{24}H_{42}B_2ClF_4N_6OsP \cdot (C_3H_6O)$, M_w 826.95, red, irregular block (0.14 × 0.06 × 0.06 mm), triclinic, space group $P\bar{1}$, a: 8.7865(14) Å, b: 12.962(2) Å, c: 15.089(3) Å, α: 91.752(3)°, β: 100.639(3)°, γ: 91.698(3)°, V = 1687.0(5) Å^3, Z = 2, D_{calc}: 1.628 g cm^{-3}, F(000): 828, T = 100.0(1) K; μ 3.959 mm^{-1}); 14 155 measured reflections (2θ: 3−51°), 6252 unique (R_{int}= 0.0485); min./max. transm factors 0.58/0.78. Final agreement factors were R1 = 0.0425 (5403 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.1024; data/restraints/parameters 6252/0/408; GoF = 1.075. Largest peak and hole: 1.391 and −1.637 e/Å^3.

Crystal data for **9**: $C_{34}H_{45}B_2F_4N_6OsP \cdot 0.625(CH_2Cl_2)$, M_w 909.63, red, irregular block (0.14 × 0.06 × 0.04 mm), monoclinic, space group $P2_1/c$, a: 10.1787(17) Å, b: 20.741(4) Å, c: 19.163(3) Å, β: 101.073(3)°, V = 3970.3(12) Å^3, Z = 4, D_{calc}: 1.522 g cm^{-3}, F(000): 1817, T = 100.0(1) K; μ 3.387 mm^{-1}); 48 619 measured reflections (2θ: 3−57°), 9741 unique (R_{int}= 0.0701); min./max. transm factors 0.683/0.876. Final agreement factors were R1 = 0.0548 (7957 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.1314; data/restraints/parameters 9741/18/481; GoF = 1.117. Largest peak and hole: 1.890 and −2.910 e/Å^3.

Crystal data for **10**: $C_{22}H_{37}B_2F_4N_6O_2OsP$, M_w 736.37, black, plate (0.16 × 0.07 × 0.01 mm), orthorhombic, space group $Pbca$, a: 17.3634(17) Å, b: 17.5365(16) Å, c: 36.970(4) Å, V = 11257.1(19) Å^3, Z = 16, D_{calc}: 1.738 g cm^{-3}, F(000): 5824, T = 100.0(1) K; μ 4.646 mm^{-1}); 63 928 measured reflections (2θ: 3−50°), 9921 unique (R_{int}= 0.1320); min./max. transm factors 0.498/ 0.955. Final agreement factors were R1 = 0.0790 (6882 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.1536; data/restraints/parameters 9921/53/686; GoF = 1.169. Largest peak and hole: 1.591 and −2.585 e/Å^3.

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Supporting Information Available: X-ray analysis and crystal structure determinations, including bond lengths and angles of compounds **2**, **4**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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