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Alkenylation of 2-Methylpyridine via Pyridylidene-Osmium Complexes

Sonia Bajo, Miguel A. Esteruelas, Ana M. López, and Enrique Oñate*

Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

Complex $[OsTp(\kappa^1\text{-}OCMe_2)_2(P^iPr_3)]BF_4$ (**1**; Tp = hydridotris(pyrazolyl)borate) reacts with 2-methylpyridine and pyridine, in acetone, at room temperature to give the N-coordinated heterocyclic derivatives $[OsTp\{\kappa^1\text{-}N[NC_5H_4Me]\}(\kappa^1\text{-}OCMe_2)(P^iPr_3)]BF_4$ (**2**) and $[OsTp\{\kappa^1\text{-}N[NC_5H_5]\}(\kappa^1\text{-}OCMe_2)(P^iPr_3)]BF_4$ (**3**). However, in fluorobenzene, at 100 ºC, the reaction of **1** with 2-methylpyridine leads to the pyridylidene compound $[OsTp\{\kappa^1\text{-}C[HNC_5H_3Me]\}(\kappa^1\text{-}OCMe_2)(P^iPr_3)]BF_4$ (**4**). The addition of phenylacetylene and cyclohexylacetylene to the fluorobenzene solutions of the latter affords the pyridylidene-vinylidene complexes $[OsTp\{\kappa^1\text{-}C[HNC_5H_3Me]\}(=C=CHR)(P^iPr_3)]BF_4$ (R = Ph (**5**), Cy (**6**)), which undergo selective deprotonation at the Cβ atom of the vinylidene ligand to generate the alkynyl-pyridylidene derivatives $OsTp(C{\equiv}CR)\{\kappa^1\text{-}C[HNC_5H_3Me]\}(P^iPr_3)$ (R = Ph (**7**), Cy (**8**)). Heating of toluene

solutions of **7** and **8** at temperatures higher than 50 ºC produces the hydrogen transfer from the nitrogen atom to the C$_\beta$ atom of the alkynyl ligands to afford the pyridyl-vinylidene intermediates [OsTp{κ^1-*C*[NC$_5$H$_3$Me]}(=C=CHR)(P^{i}Pr$_3$)]BF$_4$ (R = Ph (**7a**), Cy (**8a**)), which evolve by 1,2-migratory insertion of the vinylidene ligands into the Os-pyridyl bond to give the alkenylation products OsTp{κ^2-*C,N*[C(=CHR)C$_5$(Me)H$_3$N]}(P^{i}Pr$_3$) (R = Ph (**9**), Cy (**10**)). Protonation of **9** and **10** with HBF$_4$·EtO$_2$ yields [OsTp{κ^2-*C,N*[=C(CH$_2$R)C$_5$(Me)H$_3$N]}(P^{i}Pr$_3$)]BF$_4$ (R = Ph (**11**), Cy (**12**)). Complexes **7-9** have been characterized by X-ray diffraction analysis.

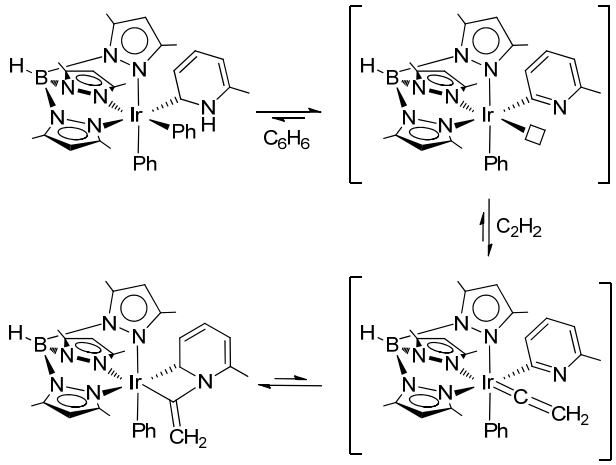
Introduction

The metal-promoted direct functionalization of nitrogen heterocycles through C–H bond activation constitutes a powerful mean of regioselectively introducing a variety of substituents with diverse functional groups onto the heterocycle scaffold.[1] In this respect, the intermolecular alkylations of pyridines and quinolines with functionalized olefins are notable for their high level of functional-group compatibility.[2] From a mechanistic point of view,[3] it has been proposed that the metal center of the catalyst precursor N-coordinates the heterocycle to subsequently afford six-membered[4] NHC carbene derivatives bearing an NH wingtip,[5] which have been isolated for Ru, Os,[6] and Ir.[7] The tautomerization takes place via hydride intermediates, which are formed by oxidative addition of a C–H bond adjacent to the nitrogen atom.[8]

Analogous reactions with alkynes are rare.[9] The propensity for terminal alkynes to undergo metal-promoted dimerization, trimerization, or polymerization reactions has made their use problematic,[10] whereas internal alkynes are often unreactive in C–H bond functionalization.[1b] As a consequence of this, the development of procedures to achieve the direct C-2 alkenylation of pyridines has become a hard challenge, which has been scarcely faced. Reaction of a previous α-methylpyridylidene-iridium(III) complex with acetylene leads to a metallacycle pyridylidene,

resulting from the nucleophilic attack of a pyridyl nitrogen atom to the α-carbon atom of a vinylidene intermediate,[11] instead of the insertion product into the metal-carbon bond (Scheme 1).

Scheme 1

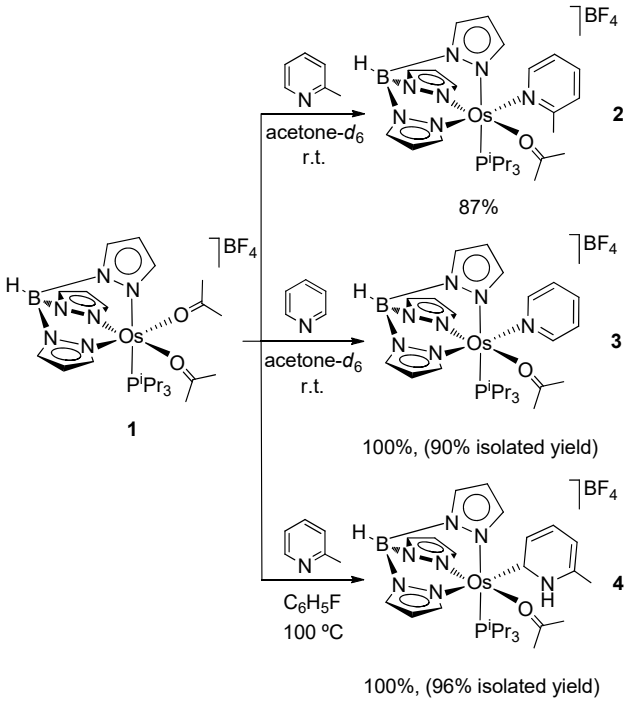


We have previously reported the preparation of the bis-solvento complex [OsTp(κ^1-$OCMe_2$)$_2$(P^iPr_3)]BF_4 (**1**; Tp = hydridotris(pyrazolyl)borate), which has been the starting point for the development of an interesting novel OsTp organometallic chemistry.[12] Now, we have observed that the metal center of this compound promotes the tautomerization of 2-methylpyridine to afford an α-methylpyridylidene ligand bearing an NH wingtip. In the search for the alkenylation of this ligand, we have investigated the reactivity of the new complex towards phenylacetylene and cyclohexylacetylene. This paper shows that, in fact, the [OsTp(P^iPr_3)]$^+$ metal fragment promotes the alkenylation of the heterocycle, in contrast to the iridium(III) system shown in Scheme 1.

Results and Discussion

1. Tautomerization of 2-Methylpyridine. The addition of 1.0 equiv of 2-methylpyridine, to an NMR tube containing an acetone-d_6 solution of **1**, at room temperature produces the partial selective substitution of an acetone molecule of the solvento complex by the heterocycle and the formation of [OsTp{κ^1-*N*[NC_5H_4Me]}(κ^1-$OCMe_2$)(P^iPr_3)]BF_4 (**2**) in 87% yield (Scheme 2). The N-coordination of 2-methylpyridine in this compound is strongly supported by the NCH-resonances of the heterocycle in the ^1H (δ, 9.89) and $^{13}C\{^1H\}$ (δ, 160.7) NMR spectra, which are observed shifted to lower field with regard to those of the free ligand (δ ^1H, 8.49; δ ^{13}C, 150.4). As a consequence of the substitution reaction, the P^iPr_3- resonance of **2** (δ, – 12.7) in the $^{31}P\{^1H\}$ NMR spectrum appears shifted by about 8 ppm to higher field than that of **1** (δ, – 4.3).

Scheme 2

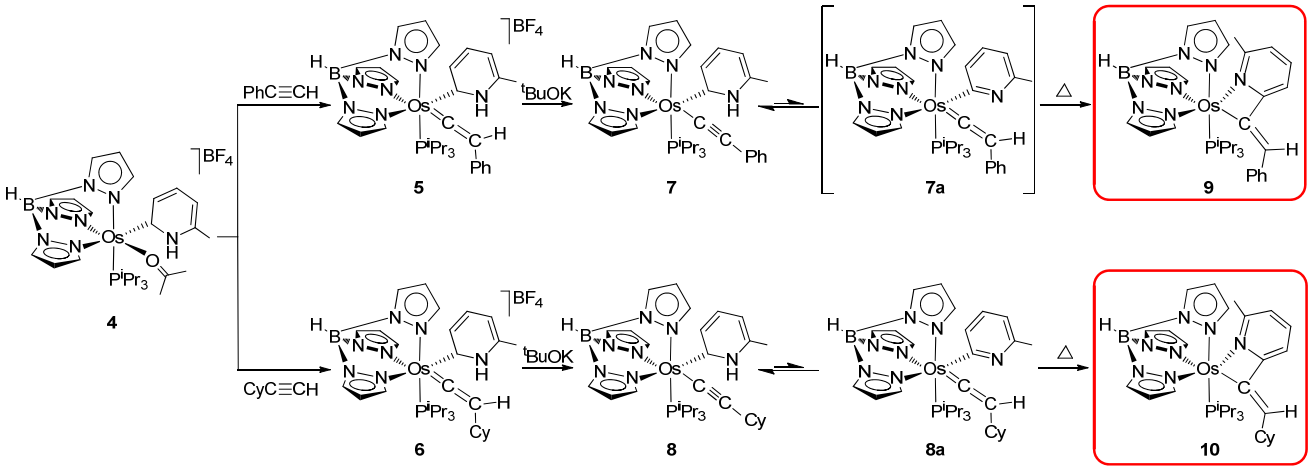


The methyl substituent of the heterocycle hampers the coordination of the nitrogen atom. Thus, in contrast to 2-methylpyridine, the addition of 1.0 equiv of pyridine to acetone solutions of **1**, at room temperature, produces the complete selective substitution of a solvento molecule by the heterocycle to quantitatively give [OsTp{κ^1-*N*[NC_5H_5]}(κ^1-$OCMe_2$)(P^iPr_3)]BF_4 (**3**), which was isolated as a yellow solid in 90% yield (Scheme 2). At – 40 ºC, pyridine does not rotate around the Os–N axis. As a consequence of this, the ^{1}H NMR spectrum of **3**, at this temperature, in acetone-d_6 shows five resonances due to the inequivalent pyridinic hydrogen atoms, between 9.61 and 7.17 ppm, whereas the $^{13}C\{^1H\}$ NMR spectrum contains five signals, corresponding to the inequivalent pyridinic carbon atoms, between 157.0 and 125.2 ppm.

The methyl substituent of 2-methylpyridine not only hampers the coordination of the nitrogen atom but is also determinant for the tautomerization of the heterocycle, in agreement with previous findings.[6,7] Thus, in contrast to pyridine, the treatment of fluorobenzene solutions of **1** with 1.4 equiv of 2-methylpyridine, for 12 h, at 100 ºC leads to the pyridylidene derivative [OsTp{κ^1-*C*[HNC_5H_3Me]}(κ^1-$OCMe_2$)(P^iPr_3)]BF_4 (**4**) in quantitative yield (Scheme 2). According to previous DFT calculations on related bis-phosphine systems, the N-coordination of the heterocycle to afford **2** should be the first step of the tautomerization process.[8] Complex **4** was isolated as an orange solid in 96% yield. In accordance with the presence of an N–H bond, the IR spectrum of this compound contains a ν(NH) band at 3381 cm^{-1} whereas its ^{1}H NMR spectrum, in acetone-d_6, at – 30 ºC shows a broad NH-resonance centered at 11.4 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the most noticeable resonance is a doublet ($J_{C\text{-}P}$ = 8 Hz) at 197.8ppm, assigned to the metalated carbon atom of the heterocycle, which strongly supports the tautomerization.[6-8,13] A singlet at – 2.8 ppm in the $^{31}P\{^1H\}$ NMR spectrum is also characteristic of **4**.

2. Alkenylation of the Coordinated Heterocycle of 4. The acetone ligand of **4** can be displaced by terminal alkynes, which tautomerize to the corresponding vinylidenes. Thus, the treatment of fluorobenzene solutions of this complex with 1.2 equiv of phenylacetylene and cyclohexylacetylene, for 6 h, at room temperature leads to the pyridylidene-vinylidene derivatives [OsTp{κ^1-*C*[HNC_5H_3Me]}(=C=CHR)(P^iPr_3)]BF_4 (R = Ph (**5**), Cy (**6**)), which were isolated as yellow (**5**) and orange (**6**) solids in 93% and 78% yield, respectively, according to Scheme 3.

Scheme 3



The pyridylidene-vinylidene formulation is strongly supported by the IR and ^1H and $^{13}C\{^1H\}$ NMR spectra of these compounds in dichloromethane-d_2. As expected for the pyridylidene NH wingtips, the IR spectra show ν(NH) bands at 2962 (**5**) and 3133 (**6**) cm^{-1} whereas the ^1H NMR spectra contain, in addition to the vinylidene C(sp^2)H-signals at 2.90 (**5**) and 1.86 (**6**) ppm, NH-resonances at 11.27 (**5**) and 11.89 (**6**) ppm. In the $^{13}C\{^1H\}$ NMR spectra the C_α atom of the vinylidene ligands display the characteristic low field resonances[14] at 316.2 (**5**) and 312.6 (**6**)

ppm, while the signals corresponding to the metalated carbon atom of the heterocycles are observed at 182.8 (**5**) and 184.1 (**6**) ppm. The $^{31}P\{^{1}H\}$ NMR spectra show singlets at about 4 ppm.

N-Heterocyclic carbenes bearing an NH wingtip undergo NH-deprotonation to afford anionic ligands[15] whereas monosubstituted vinylidenes are fairly acidic.[16] Thus, at first glance, one should expected a selectivity problem for the deprotonation reactions of **5** and **6**, due to the presence of both types of ligands. However, the deprotonation of the vinylidene ligands is favored with regard to the abstraction of the NH-hydrogen in both cases.

Treatment of tetrahydrofuran solutions of **5** with 1.1 equiv of potassium tert-butoxide, for 1 h, at room temperature produces the selective deprotonation of the vinylidene ligand to afford the alkynyl-pyridylidene derivative OsTp(C≡CPh){κ^1-*C*[HNC_5H_3Me]}(P^iPr_3) (**7**). Amounts of a pyridyl-vinylidene isomer **7a** (Scheme 3), resulting from the deprotonation of the coordinated heterocycle, were not detected by NMR spectroscopy. Complex **7** was isolated as a red solid in 88% yield and characterized by X-ray diffraction analysis. The structure (Figure 1) proves the deprotonation of the vinylidene ligand of **5**. The distribution of ligands around the metal center 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 disposed *trans* to N(2) (P–Os–N(2) 175.16(7)º), the heterocycle *trans* disposed to N(4) (C(1)–Os–N(4) 168.95(11)º) and the alkynyl group *trans* disposed to N(6) (C(7)–Os–N(6) 172.90(11)º). The Os–C(1) bond length of 1.994(3) Å agrees well with those previously reported for Os–NHC compounds with normal coordination of the NHC unit,[6,17] whereas the Os–C(7) distance of 1.998(3) Å supports an Os–C(sp) single bond[18] and indicates a low degree of metal to alkynyl

back-bonding.[19] The C(7)–C(8) distance and the Os–C(7)–C(8) and C(7)–C(8)–C(9) angles are 1.216(4) Å and 173.4(3)º and 174.9(4)º, respectively.

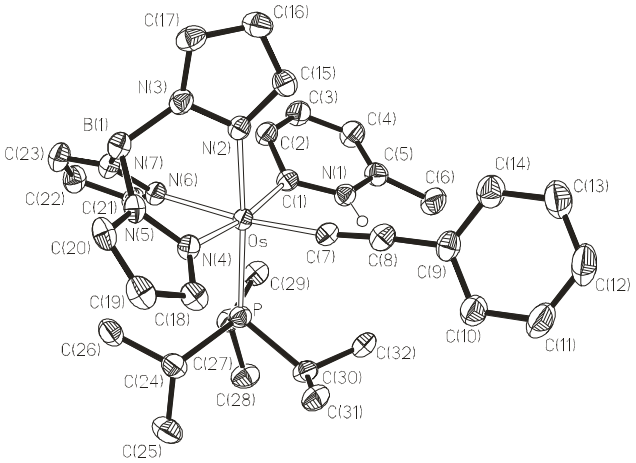


Figure 1. Molecular diagram of **7**. Selected bond lengths (Å) and angles (deg): Os–P 2.3404(8), Os–N(2) 2.122(3), Os–N(4) 2.165(3), Os–N(6) 2.160(3), Os–C(1) 1.994(3), Os–C(7) 1.998(3), C(7)–C(8) 1.216(4), C(8)–C(9) 1.443(5); N(2)–Os–P 175.16(7), N(4)–Os–C(1) 168.95(11), N(6)–Os–C(7) 172.90(11), C(1)–Os–C(7) 88.25(12), Os–C(7)–C(8) 173.4(3), C(7)–C(8)–C(9) 174.9(4). Displacement ellipsoids are given at the 50% probability level.

In agreement with the presence of the alkynyl ligand the IR spectrum shows a ν(C≡C) band at 2041 cm^{-1} along with the NH-absorption at 3276 cm^{-1}. The NH-resonance is observed at 12.58 ppm in the ^{1}H NMR spectrum in dichloromethane-d_2. The $^{13}C\{^{1}H\}$ NMR is also consistent with the alkynyl-pyridylidene formulation. The OsC(sp) and OsC(sp^2)-resonances appear at 145.2 and 200.0 ppm as doublets with C-P coupling constants of 12 and 7 Hz, respectively. A singlet at 0.4 ppm in the $^{31}P\{^{1}H\}$ NMR spectrum is also characteristic of this compound.

The cyclohexyl substituent increases the stability of the pyridyl-vinylidene isomer with regard to the phenyl one, although the alkynyl-pyridylidene species is still the most stable. Thus, in contrast to **5**, the treatment of tetrahydrofuran solutions of **6** with 1.1 equiv of potassium tert-

butoxide, for 1 h, at room temperature leads to a 1.3:1 equilibrium mixture of the alkynyl-pyridylidene derivative OsTp(C≡CCy){κ^1-*C*[HNC_5H_3Me]}(P^iPr_3) (**8**) and its pyridyl-vinylidene isomer [OsTp{κ^1-*C*[NC_5H_3Me]}(=C=CHCy)(P^iPr_3)]BF_4 (**8a**).

Crystals of **8** suitable for an X-ray diffraction analysis were obtained from the equilibrium mixture. Figure 2 shows the structure of this species. The geometry around the osmium center is as that of **7**. The Os-alkynyl and Os-pyridylidene separations of 2.013(3) Å (Os–C(1)) and 1.987(3) Å (Os–C(9)) are statistically identical with the respective parameters of the Ph-counterpart.

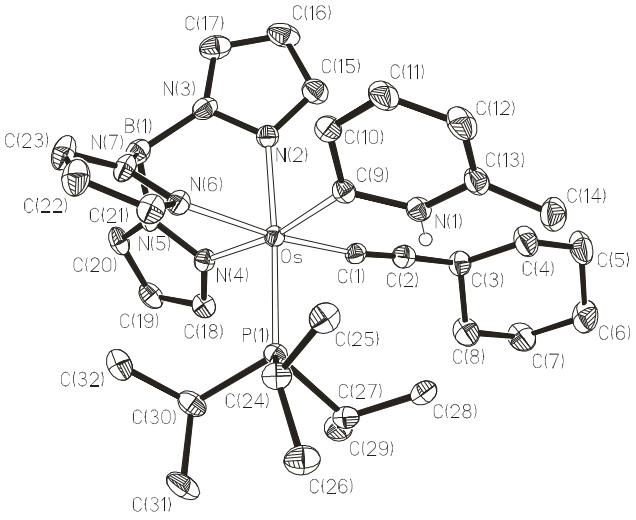


Figure 2. Molecular diagram of **8**. Selected bond lengths (Å) and angles (deg): Os–P(1) 2.3309(7), Os–N(2) 2.121(2), Os–N(4) 2.162(2), Os–N(6) 2.161(2), Os–C(1) 2.013(3), Os–C(9) 1.987(3), C(1)–C(2) 1.210(4), C(2)–C(3) 1.482(4); N(2)–Os–P(1) 175.76(6), N(4)–Os–C(9) 168.38(10), N(6)–Os–C(1) 172.44(10), C(1)–Os–C(9) 88.66(11), Os–C(1)–C(2) 173.2(2), C(1)–C(2)–C(3) 177.3(3). Displacement ellipsoids are given at the 50% probability level.

In the IR spectrum, the ν(C≡C) and ν(NH) bands are observed at 2066 and 3097 cm^{-1}, respectively. The NH-resonance appears at 12.70 ppm in the ^1H NMR spectrum in

tetrahydrofuran-d_8. Like for **7**, the OsC(sp) and OsC(sp^2)-carbon atoms of the alkynyl and pyridylidene ligands display doublets with C-P coupling constants of 9 and 6 Hz, at 97.9 and 201.4 ppm, respectively. The $^{31}P\{^1H\}$ spectrum contains a singlet at –1.3 ppm.

The most noticeable spectroscopic feature of **8a** is the OsC-vinylidene low field resonance at 305.0 ppm, in the $^{13}C\{^1H\}$ NMR spectrum at – 40 ºC, which is observed as a doublet with a C-P coupling constant of 9 Hz. The OsC-pyridyl signal appears at 182.7 ppm, shifted by about 20 ppm towards higher field with regard to the OsC(sp^2)-resonance of **8**. This suggests a slight decrease of the Os to C(sp^2) back-bonding in **8a** with regard to **8**. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at –7.0 ppm.

The equilibrium between **8** and **8a** was studied as a function of the temperature between 30 and – 70 ºC, in tetrahydrofuran, by integration of the $^{31}P\{^1H\}$ NMR resonances. Table 1 collects the values of the equilibrium constant (K = [**8a**]/[**8**]) at each temperature. Linear least-square analysis of ln$K$ versus 1/T (Figure 3) provides values for ΔH^o and ΔS^o of 2.14 ± 0.18 kcal·mol^{-1} and 6.7 ± 0.7 cal·K^{-1}·mol^{-1}, respectively.

Table 1. **Equilibrium constants, *K* = [8a]/[8]**)

Temp (ºC)	*K*	Temp (ºC)	*K*
-70	0.15	-10	0.46
-60	0.18	0	0.52
-50	0.23	10	0.68
-40	0.28	25	0.78
-30	0.34	30	0.87
-20	0.39		

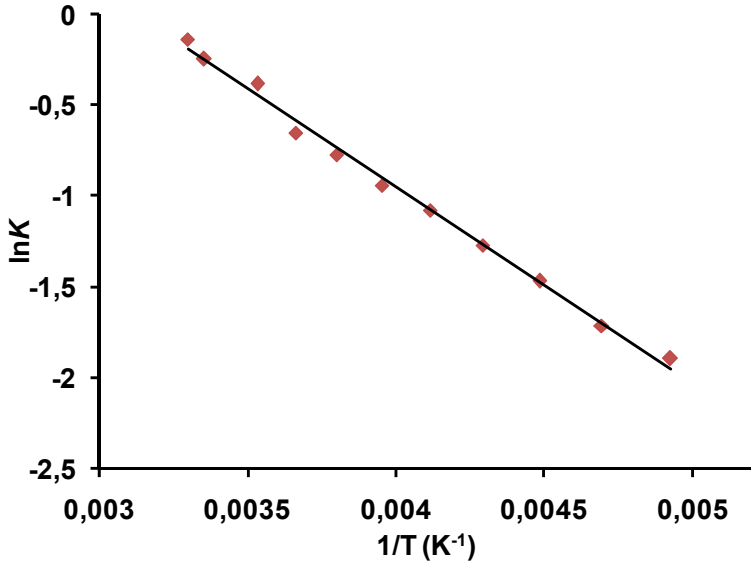


Figure 3. Van´t Hoff plot of the equilibrium constants K = [**8a**]/[**8**].

Table 1 shows that the pyridyl-vinylidene isomer is favored by temperature increasing. However, complexes **7a** and **8a** can not be obtained as pure species, since new compounds are formed at temperatures higher than 50 ºC. Heating of toluene solutions of **7** and the **8**:**8a** equilibrium mixture gives rise to the formation of OsTp{κ^2-*C,N*[C(=CHR)C_5(Me)H_3N]}(P^iPr_3) (R = Ph (**9**), Cy (**10**)), as a result of the 1,2-migratory insertion of the vinylidene ligands of **7a** and **8a** into the corresponding Os-pyridyl bonds and the subsequent N-coordination of the heterocycle. These 2-methylpyridine alkenylation products were isolated as black solids in 82% (**9**) and 54% (**10**) yield (Scheme 3).

Complex **9** was characterized by X-ray diffraction analysis. Figure 4 shows a view of the molecular geometry. The structure proves the coupling between the vinylidene and pyridyl moieties of **7a**. The coordination geometry around the osmium atom can be rationalized as a distorted octahedron with the coordinating nitrogen atoms of the Tp ligand in *fac* sites. The distortion is mainly due to the bite angle C(7)–Os–N(1) of the resulting alkenylpyridyne ligand,

64.8(2)º. Similar values have been found in other four-membered heteroosma rings.[20] The alkenyl unit shows *trans* disposition for the phenyl and pyridyl substituents. The Os–C(7) bond length of 2.073(5) Å compares well with those reported for other Os-alkenyl complexes and supports an Os–C(sp^2) single bond.[21] The C(7)–C(8) distance of 1.356(8) Å is consistent with a C–C double bond.

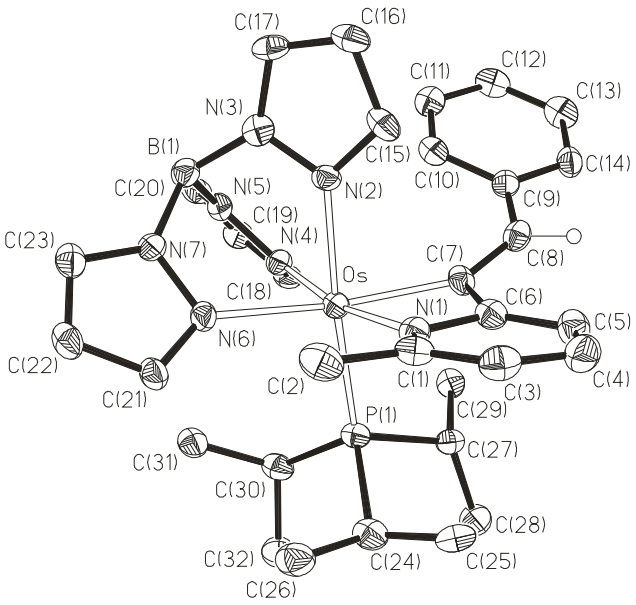
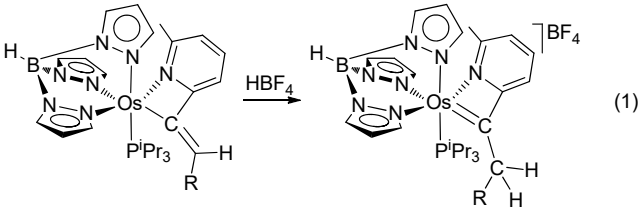


Figure 4. Molecular diagram of **9**. Selected bond lengths (Å) and angles (deg): Os–P(1) 2.3371(14), Os–N(2) 2.131(4), Os–N(4) 2.101(5), Os–N(6) 2.205(4), Os–C(7) 2.073(5), Os–N(1) 2.099(5), N(1)–C(6) 1.371(7), C(6)–C(7) 1.471(8), C(7)–C(8) 1.356(8); N(2)–Os–P(1) 175.68(12), N(4)–Os–N(1) 169.04(18), N(6)–Os–C(7) 165.15(19), C(7)–Os–N(1) 64.8(2), Os–C(7)–C(8) 147.4(5). Displacement ellipsoids are given at the 50% probability level.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **9** and **10** in benzene-d_6 are in agreement with the structure shown in Figure 4. The most noticeable features of these spectra are the C(sp^2)H-resonances of the alkenyl units, at 8.67 (**9**) and 7.35 (**10**) ppm, in the ^{1}H NMR spectra and the

OsC(sp^2)-signals, at 136.1 (**9**) and 129.2 (**10**) ppm, in the $^{13}C\{^1H\}$ NMR spectra. Singlets at –3.9 (**9**) and –0.4 (**10**) ppm in the $^{31}P\{^1H\}$ NMR spectra are also characteristic of these compounds.

Electronic structures and reactivities of organic fragments change, often dramatically, when they coordinate to transition metals to form organometallic species. Coordination of an alkenyl group transfers the nucleophilicity from the α- to β-carbon atom. Thus, X-ray and reactivity studies indicate that alkenyl complexes are nucleophilic at C$_\beta$ and their reactions, in particular those with H^+, afford carbene derivatives.[16d,22] In agreement with this, the addition of 1.1 equiv of $HBF_4{\cdot}Et_2O$ to diethyl ether solutions of **9** and **10** produces the instantaneous precipitation of [OsTp{κ^2-*C,N*[=C(CH_2R)C_5(Me)H_3N]}(P^iPr_3)]BF_4 (R = Ph (**11**), Cy (**12**)), as a result of the addition of the proton of the acid to the C$_\beta$ atoms of the alkenyl units. Complexes **11** and **12** were isolated as greenish yellow solids in 89% and 84% yield, respectively, according to eq 1. The $^{13}C\{^1H\}$ NMR spectra of the solids in dichloromethane-d_2 strongly support the protonations. Thus, they contain, at 227.4 (**11**) and 235.7 (**12**) ppm, doublets with C-P coupling constants of 12 (**11**) and 11 (**12**) Hz. The $^{31}P\{^1H\}$NMR spectra show singlets at – 2.2 (**11**) and – 3.0 (**12**) ppm.



(1)

Complexes **11** and **12** are isomers of **5** and **6**. Eq 1 suggests that the coupled fragments are more stable than the single vinylidene and pyridylidene moieties. However, the formation of **11** and **12** from the respective **5** and **6**, by hydrogen migration from the nitrogen atom to the C$_\beta$ atom

of the vinylidenes and the subsequent 1,2-migratory insertion of the resulting carbynes into an Os-pyridyl bond, appears to have a very high activation energy. Thus, the coupling does not take place even in fluorobenzene at 100 ºC.

Concluding Remarks

This study has revealed that the $[OsTp(P^iPr_3)]^+$ metal fragment promotes the alkenylation of 2-methylpyridine with monosubstituted alkynes, via pyridylidene and vinylidene intermediates.

The methyl substituent of the heterocycle hampers the coordination of the nitrogen atom while favors its tautomerization into α-methyl-pyridylidene, which is stabilized by coordination to osmium. The subsequent reaction of the resulting species with monosubstituted alkynes generates vinylidene-pyridylidene derivatives. These compounds are kinetically inert and do not evolve by 1,2-migratory insertion of vinylidenes into the Os-pyridylidene bond. However, the selective deprotonation of the C_β atom of the vinylidene ligands gives rise to alkynyl-pyridylidene complexes, which give the alkenylation products in contrast to their precursors. The alkenylation takes place in two steps. The first of them implies the hydrogen transfer from the nitrogen atom of the heterocycle to the C_β atom of the alkynyl ligands, to afford pyridyl-vinylidene intermediates. During the second one, the vinylidene undergoes 1,2-migratory insertion into the Os-pyridyl bond.

In conclusion, the pyridine-pyridylidene tautomerization is a key step not only for the alkylation of this type of heterocycles but also for the alkenylation.

Experimental Section

General Methods and Instrumentation. All manipulations were performed with rigorous exclusion of air using Schlenk-tube or glovebox 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(κ^1-OCMe$_2$)$_2$(P^{i}Pr$_3$)]BF$_4$ (**1**) was prepared according with the published method.[12a] ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on 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 (^{1}H, ^{13}C) or external H_3PO_4 (^{31}P). Coupling constants, *J*, are given in hertz. All coupling constants for the pyrazolyl proton resonances were about 2 Hz. Spectral assignments were achieved by ^{1}H-^{1}H COSY, NOESY, ^{1}H{^{31}P}, ^{13}C APT, ^{1}H-^{13}C HSQC, and ^{1}H-^{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. High-resolution electrospray mass spectra were acquired using a MicroTOF-Q hybrid quadrupole time-of-flight spectrometer (Bruker Daltonics, Bremen, Germany).

Formation and Characterization of [OsTp{κ^1-*N*[NC$_5$H$_4$Me]}(κ^1-OCMe$_2$)(P^{i}Pr$_3$)]BF$_4$ (2). An NMR tube containing a solution of **1** (42.8 mg, 0.056 mmol) in CD_3COCD_3 (0.5 mL) was treated with 2-methylpyridine (5.5 μL, 0.056 mmol). After 24 h at room temperature, the NMR spectra showed an 87:13 equilibrium mixture of **2** and **1**. Spectroscopic data for **2** are as follows: ^{1}H NMR (300 MHz, CD_3COCD_3, 298 K): δ 9.89 (d, $J_{H\text{-}H}$ = 6.0, 1H, Py), 8.02 (d, 1H, Tp), 7.95 (overlapping signals, 2H, Tp), 7.82 (overlapping signals, 2H, Tp), 7.72 (t, $J_{H\text{-}H}$ = 6.0, 1H, Py), 7.33 – 7.14 (overlapping signals, 2H, Py), 6.60 (d, 1H, Tp), 6.31 (overlapping signals, 3H, Tp), 2.69 (m, 3H, PC*H*CH$_3$), 2.09 (s, 6H, CH$_3$COCH$_3$), 1.19 (m, 18H, PCHC*H*$_3$), 0.99 (s, 3H, CH$_3$-Py), all coupling constants for the pyrazolyl proton resonances were about 2 Hz. ^{31}P{^{1}H} NMR (121.48 MHz, CD_3COCD_3, 298 K): δ – 12.7 (s). ^{13}C{^{1}H} NMR (75.45 MHz, CD_3COCD_3, 298 K): δ 226.4 (s, CH$_3$*C*OCH$_3$), 166.2 (C$_{ipso}$ Py), 160.7 (s, Py), 152.8, 148.9, 141.3, 138.5, 137.6 (all s, Tp), 137.2 (s, Py), 136.4 (s, Tp), 129.3, 122.0 (both s, Py), 107.8, 107.6, 107.3 (all s, Tp), 30.6

(s, *C*H$_3$CO*C*H$_3$), 25.0 (d, $J_{C\text{-}P}$ = 25, P*C*HCH$_3$), 22.6 (s, CH3-Py), 20.2 (s, PCH*C*H$_3$), 19.6 (s, PCH*C*H$_3$).

Preparation of [OsTp{κ^1-*N*[NC$_5$H$_5$]}(κ^1-OCMe$_2$)(P^{i}Pr$_3$)]BF$_4$ (3). A solution of **1** (100 mg, 0.13 mmol) in 3 mL of acetone was treated with pyridine (10.5 μL, 0.13 mmol) and stirred at room temperature for 1 hour. After this time, the solvent was removed in vacuo. Addition of 2 mL of diethyl ether caused the precipitation of a yellow solid, which was washed with diethyl ether (3 x 3 mL) and dried in vacuo. Yield: 92 mg (90%). Anal. Calcd for C$_{26}$H$_{42}$B$_2$F$_4$N$_7$OOsP: C, 39.66; H, 5.38; N, 12.45. Found: C, 39.79; H, 5.49; N, 11.96. HRMS (electrospray, *m/z*): calcd for C$_{23}$H$_{36}$BN$_7$OsP [M – (CH$_3$)$_2$CO]$^+$ 644.2482, found 644.2477. IR (ATR, cm^{-1}): ν(BF$_4$) 1053 (s). ^{1}H NMR (300 MHz, CD$_3$COCD$_3$, 233 K): δ 9.61 (d, $J_{H\text{-}H}$ = 5.9, 1H, Py), 8.07 (d, 1H, Tp), 8.06 (d, 1H, Tp), 8.00 (d, 1H, Tp), 7.87 (tt, $J_{H\text{-}H}$ = 5.9, $J_{H\text{-}H}$ = 1.3, 1H, Py), 7.86 (d, 1H, Tp), 7.58 (d, 1H, Tp), 7.51 (td, $J_{H\text{-}H}$ = 5.9, $J_{H\text{-}H}$ = 1.3, 1H, Py), 7.31 (d, $J_{H\text{-}H}$ = 5.9, 1H, Py), 7.17 (td, $J_{H\text{-}H}$ = 5.9, $J_{H\text{-}H}$ = 1.3, 1H, Py), 6.41 (m, overlapping signals, 2H, Tp), 6.36 (t, 1H, Tp), 6.21 (t, 1H, Tp), 2.49 (m, 3H, PC*H*CH$_3$), 2.09 (s, 6H, CH$_3$COCH$_3$), 1.20 (m, 18H, PCHC*H*$_3$), all coupling constants for the pyrazolyl proton resonances were about 2 Hz. ^{31}P{^{1}H} NMR (121.48 MHz, CD$_3$COCD$_3$, 233 K): δ – 11.0 (s). ^{13}C{^{1}H} NMR (75.45 MHz, CD$_3$COCD$_3$, 233 K): δ 226.4 (s, CH$_3$*C*OCH$_3$), 157.0, 155.6 (both s, Py), 148.8, 148.1, 140.6, 138.2, 137.6, 136.0 (all s, Tp), 135.9, 126.6, 125.2 (all s, Py), 108.5, 107.2 (both s, Tp), 30.3 (s, *C*H$_3$CO*C*H$_3$), 28.2 (br, P*C*HCH$_3$), 19.7 (br, PCH*C*H$_3$).

Preparation of [OsTp{κ^1-*C*[HNC$_5$H$_3$Me]}(κ^1-OCMe$_2$)(P^{i}Pr$_3$)]BF$_4$ (4). A solution of **1** (300 mg, 0.39 mmol) in 5 mL of fluorobenzene was treated with 2-methylpyridine (54.5 μL, 0.55 mmol) and heated at 100 ºC overnight in a Schlenk flask equipped with a Teflon stopcock. After this time, the orange solution was allowed to reach room temperature and the solvent was removed in vacuo. Addition of 2 mL of diethyl ether caused the precipitation of an orange solid,

which was washed with diethyl ether (3 x 3 mL) and dried in vacuo. Yield: 300 mg (96%). Anal. Calcd for $C_{27}H_{44}B_2F_4N_7OOsP$: C, 40.46; H, 5.53; N, 12.23. Found: C, 40.14; H, 5.40; N, 12.22. HRMS (electrospray, *m/z*): calcd for $C_{24}H_{38}BN_7OsP$ [M – $(CH_3)_2CO$]$^+$ 658.2634, found 658.2661. IR (ATR, cm^{-1}): ν(NH) 3381 (br), ν(BF_4) 1042 (s). ^{1}H NMR (300 MHz, CD_3COCD_3, 243 K): δ 11.39 (br, 1H, NH), 8.10 (d, 1H, Tp), 7.95 (m, 2H, Tp), 7.90 (d, 1H, Tp), 7.34 (d, 1H, Tp), 7.04 (t, $J_{H\text{-}H}$ = 7.2, 1H, Py), 6.80 (d, 1H, Tp), 6.73 (d, $J_{H\text{-}H}$ = 7.2, 1H, Py), 6.41 (m, 2H, Tp + Py), 6.29 (t, 1H, Tp), 6.13 (t, 1H, Tp), 2.58 (m, 6H, CH_3–Py + PC*H*CH_3), 2.09 (s, 6H, CH_3COCH_3), 1.21 (m, 9H, PCHC*H*$_3$), 0.75 (m, 9H, PCHC*H*$_3$), all coupling constants for the pyrazolyl proton resonances were about 2 Hz. ^{31}P{^{1}H} NMR (121.48 MHz, CD_3COCD_3, 243 K): δ – 2.8 (s). ^{13}C{^{1}H} NMR (75.45 MHz, CD_3COCD_3, 243 K): δ 227.7 (s, CH_3*C*OCH_3), 197.8 (d, $J_{C\text{-}P}$ = 8, OsC), 150.0 (s, Tp), 149.7 (s, C*ipso* Py), 147.7, 143.5 (both s, Tp), 140.2 (s, Py), 138.4, 137.8, 136.3 (all s, Tp), 135.5 (s, Py), 114.8 (s, Py), 108.7, 107.9, 107.5 (all s,Tp), 26.2 (s, *C*H_3CO*C*H_3), 20.6 (br, P*C*HCH_3), 20.5 (s, CH_3–Py), 20.4 (s, PCH*C*H_3), 20.2 (s, PCH*C*H_3).

Preparation of [OsTp{κ^1-*C*[HNC_5H_3Me]}(=C=CHPh)(P^iPr_3)]BF_4 (5). A solution of **4** (400 mg, 0.50 mmol) in 4 mL of fluorobenzene was treated with phenylacetylene (66.3 μL, 0.60 mmol) and stirred at room temperature for 6 h. During this time a yellow solution was formed. The solvent was removed in vacuo and the addition of 2 mL of diethyl ether caused the precipitation of a yellow solid, which was washed with diethyl ether (3 x 3 mL) and dried in vacuo. Yield: 397.1 mg (93%). Anal. Calcd for $C_{32}H_{44}B_2F_4N_7OsP$: C, 45.45; H, 5.24; N, 11.60. Found: C, 45.46; H, 5.32; N, 11.73. HRMS (electrospray, *m/z*): calcd for $C_{32}H_{44}BN_7OsP$ [M]$^+$ 760.3105, found 760.3179. IR (ATR, cm^{-1}): ν(NH) 2962 (br), ν(C=C) 1618 (s), ν(BF_4) 1010 (s). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 11.27 (s, 1H, NH), 8.10 (d, 1H, Tp), 8.05 (d, 1H, Tp), 7.89 (d, 1H, Tp), 7.74 (d, 1H, Tp), 7.69 (d, 1H, Tp), 7.35 (m, overlapping signals, 2H, Py), 6.98 (t, $J_{H\text{-}H}$ = 7.6, 2H, Ph), 6.89 (d, $J_{H\text{-}H}$ = 6.9, 1H, Py), 6.80 (t, $J_{H\text{-}H}$ = 7.6, 1H, Ph), 6.78 (d, 1H, Tp),

6.58 (t, 1H, Tp), 6.43 (d, $J_{H\text{-}H}$ =7.6, 2H, Ph), 6.37 (t, 1H, Tp), 6.02 (t, 1H, Tp), 2.90 (d, $J_{H\text{-}P}$ = 3.3, 1H, =C*H*Ph), 2.48 (m, 3H, PC*H*CH_3), 2.44 (s, 3H, CH_3–Py), 1.23 (dd, $J_{H–P}$ = 12.6, $J_{H–H}$ = 7.1, 9H, PCHC*H*$_3$), 0.78 (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 (161.98 MHz, CD_2Cl_2, 298 K): δ 4.1 (s). $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_2Cl_2, 298 K): δ 316.2 (d, $J_{C–P}$ = 10, Os=C=), 182.8 (d, $J_{C\text{-}P}$ = 9, OsCNH), 150.8 (s, C*ipso* Py), 146.6, 144.8, 138.9 (all s, Tp), 138.2 (s, Py), 137.7, 136.3 (both s, Tp), 128.8, 126.7, 126.1 (all s, Ph), 124.3 (s, C*ipso* Ph), 118.8 (s, Py), 114.4 (s, =*C*HPh), 108.9, 107.7, 107.1 (all s, Tp), 26.0 (d, $J_{C\text{-}P}$ = 27, P*C*HCH_3), 20.3 (s, CH_3–Py), 19.7 (s, PCH*C*H_3), 19.6 (d, $J_{C\text{-}P}$ = 3, PCH*C*H_3).

Preparation of [OsTp{κ^1-*C*[HNC_5H_3Me]}(=C=CHCy)(P^iPr_3)]BF_4 (6). A solution of **4** (150 mg, 0.19 mmol) in 4 mL of fluorobenzene was treated with cyclohexylacetylene (28.9 μL, 0.23 mmol) and stirred at room temperature for 6 h. During this time an orange solution was formed. The solvent was removed in vacuo and the addition of 2 mL of diethyl ether caused the precipitation of an orange solid, which was washed with diethyl ether (3 x 3 mL) and dried in vacuo. Yield: 124.1 mg (78%). Anal. Calcd for $C_{32}H_{50}B_2F_4N_7OsP$: C, 45.13; H, 5.92; N, 11.51. Found: C, 45.09; H, 6.14; N, 11.53. HRMS (electrospray, *m/z*): calcd for $C_{32}H_{50}BN_7OsP$: $[M]^+$ 766.3574, found 766.3632. IR (ATR, cm^{-1}): ν(NH) 3133 (br), ν(C=C) 1641 (s), ν(BF_4) 1046 (s). ^1H NMR (400 MHz, CD_2Cl_2, 233 K): δ 11.89 (br, 1H, NH), 7.94 (d, 1H, Tp), 7.88 (d, 1H, Tp), 7.82 (d, 1H, Tp), 7.62 (d, 2H, Tp), 7.21 (t, $J_{H\text{-}H}$ = 7.7, 1H, Py), 6.83 (d, $J_{H\text{-}H}$ = 7.7, 1H, Py), 6.77 (d, $J_{H\text{-}H}$ = 7.7, 1H, Py), 6.56 (d, 1H, Tp), 6.43 (t, 1H, Tp), 6.32 (t, 1H, Tp), 6.05 (t, 1H, Tp), 2.54 (s, 3H, CH_3–Py), 2.25 (m, overlapping signals, 4H, PC*H*CH_3 (3H) + C*H*–Cy (1H)), 1.86 (br, 1H, =C*H*Cy), 1.50 (m, 8H, Cy), 1.13 (m, overlapping signals, 20H, PCHC*H*$_3$ (18H) + Cy (2H)), all coupling constants for the pyrazolyl proton resonances were about 2 Hz. $^{31}P\{^1H\}$ NMR (161.98

MHz, CD_2Cl_2, 233 K): δ 4.4 (s). $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_2Cl_2, 233 K): δ 312.6 (d, J_{C-P} = 9, Os=C=), 184.1 (d, J_{C-P} = 7, OsCNH), 148.6 (s, C_{ipso} Py), 145.2, 144.7, 143.6 (both s, Tp), 138.3 (s, Py), 137.6 (s, Tp), 137.0 (s, Py), 136.6, 135.6 (both s, Tp), 117.4 (s, Py), 116.0 (br, =*C*HCy), 107.8, 106.9, 106.4 (all s, Tp), 38.9, 37.8, 26.7, 26.4, 25.3 (all s, Cy), 24.8 (br, Cy + P*C*HCH$_3$), 19.4 (s, CH$_3$–Py), 17.4 (s, PCH*C*H$_3$), 17.3 (s, PCH*C*H$_3$).

Preparation of OsTp(C≡CPh){κ^1-*C*[HNC$_5$H$_3$Me]}(P^{i}Pr$_3$) (7). A solution of **5** (200 mg, 0.24 mmol) in 4 mL of tetrahydrofuran was treated with potassium tert-butoxide (29.2 mg, 0.26 mmol) and stirred at room temperature for 1 h. During this time a red solution was formed. The solvent was evaporated to dryness to give a red solid that was extracted with toluene (20 mL). The solvent was removed in vacuo and a red solid precipitated, which was washed with cold *n*-pentane and dried in vacuo. Yield: 160 mg (88%). Anal. Calcd for $C_{32}H_{43}BN_7OsP$: C, 50.72 ; H, 5.72; N, 12.94 Found: C, 50.91; H, 5.83; N, 13.06. HRMS (electrospray, *m/z*): calcd for $C_{32}H_{44}BN_7OsP$ $[M + H]^+$ 760.3105, found 760.3109. IR (ATR, cm^{-1}): ν(NH) 3276 (br); ν(C≡C) 2041 (s). ^1H NMR (300 MHz, CD_2Cl_2, 298 K): δ 12.58 (br, 1H, NH), 8.12 (d, 1H, Tp), 7.80 (d, 1H, Tp), 7.71 (d, 1H, Tp), 7.54 (d, 2H, Tp), 7.18 – 7.08 (overlapping signals, 5H, Ph(4H) + Tp(1H)), 6.89 (t, J_{H-H} = 6.9, 1H, Ph), 6.76 (d, J_{H-H} = 8.0, 1H, Py), 6.65 (t, J_{H-H} = 8.0, 1H, Py), 6.25 – 6.20 (m, overlapping signals, 3H, Tp (2H) + Py (1H)), 5.97(t, 1H, Tp), 2.41 (m, 3H, PC*H*CH$_3$), 2.34 (s, 3H, CH$_3$–Py), 1.31 (dd, J_{H-P} = 11.3, J_{H-H} = 5.2, 9H, PCHC*H*$_3$), 0.81 (dd, J_{H-P} = 13.2, J_{H-H} = 6.0, 9H, PCHC*H*$_3$), all coupling constants for the pyrazolyl proton resonances were about 2 Hz. $^{31}P\{^1H\}$ NMR (121.48 MHz, CD_2Cl_2, 298 K): δ 0.4 (s). $^{13}C\{^1H\}$ NMR (75.45 MHz, CD_2Cl_2, 298 K): δ 200.0 (d, J_{C-P} = 7, Os*C*NH), 147.1 (s, C_{ipso} Py), 146.7 (s, Tp), 145.2 (d, J_{C-P} = 12, Os*C*≡C), 144.6, 141.2 (both s, Tp), 139.1 (s, Py), 135.3, 135.2, 133.6 (all s, Tp), 131.6 (s, Ph), 131.4 (s, Py), 128.0 (s, Ph), 122.6 (d, J_{C-P} = 8, OsC≡*C*), 122.4 (s, Ph), 111.1 (s, Py),

108.5 (s, C_{ipso} Ph), 106.1, 106.0, 105.5 (all s, Tp), 26.3 (d, $J_{C\text{-}P}$ = 24, P*C*HCH$_3$), 19.7 (s, CH$_3$–Py), 19.7 (s, PCH*C*H$_3$), 19.6 (d, $J_{C\text{-}P}$ = 3, PCH*C*H$_3$).

Formation and Characterization of OsTp(C≡CCy){κ^1-*C*[HNC$_5$H$_3$Me]}(P^{i}Pr$_3$) (8) and [OsTp{κ^1-*C*[NC$_5$H$_3$Me]}(=C=CHCy)(P^{i}Pr$_3$)]BF$_4$ (8a). A solution of **6** (100 mg, 0.12 mmol) in 4 mL of tetrahydrofuran was treated with potassium tert-butoxide (14.5 mg, 0.13 mmol) and stirred at room temperature for 1 h. The solvent was evaporated to dryness to give a red solid that was extracted with toluene (20 mL). The solvent was removed in vacuo and a red solid precipitated which was washed with cold *n*-pentane and dried in vacuo. Yield: 80 mg (87%). Anal. Calcd for C$_{32}$H$_{49}$BN$_7$OsP·0.2 C$_5$H$_{12}$: C, 50.93; H, 6.66; N, 12.59. Found: C, 50.53; H, 7.16; N, 12.24. HRMS (electrospray, *m/z*): calcd for C$_{32}$H$_{50}$BN$_7$OsP: [M + H]$^+$ 766.3574, found 766.3592. IR (ATR, cm^{-1}): ν(NH) 3097 (br); ν(C≡C) 2066 (s). The NMR spectra of the obtained solid showed the presence of **8** and **8a** in variable molar ratios depending on the temperature. Spectroscopy data for **8** are as follows: ^{1}H NMR (400 MHz, thf-d_8, 233 K): δ 12.70 (br, 1H, NH), 8.00 (d, 1H, Tp), 7.82 (d, 1H, Tp), 7.71 (d, 1H, Tp), 7.52 (d, 1H, Tp), 7.42 (d, 1H, Tp), 7.00 (d, 1H, Tp), 6.68 (d, $J_{H\text{-}H}$ = 8.6, 1H, Py), 6.55 (t, $J_{H\text{-}H}$ = 8.6, 1H, Py), 6.22 (d, $J_{H\text{-}H}$ = 8.6, 1H, Py), 6.20 (t, 1H, Tp), 6.10 (t, 1H, Tp), 5.87 (t, 1H, Tp), 2.39 (m, overlapping signals, 6H, PC*H*CH$_3$ (3H) + CH$_3$–Py (3H)), 2.00 (m, 3H, Cy), 1.61 (m, 5H, Cy), 1.27 (m, overlapping signals, 21H, PCHC*H*$_3$ (18H) + Cy (3H)), all coupling constants for the pyrazolyl proton resonances were about 2 Hz. ^{31}P{^{1}H} NMR (161.98 MHz, thf-d_8, 233 K): δ –1.3 (s). ^{13}C{^{1}H} NMR (100.63 MHz, thf-d_8, 233 K): δ 201.4 (d, $J_{C\text{-}P}$ = 6, OsCNH), 146.8 (s, C$_{ipso}$ Py), 146.6, 144.4 (both s, Tp), 141.0 (s, Py), 139.6, 135.9, 135.4, 133.2 (all s, Tp), 131.1 (s, Py), 110.6 (s, Py), 108.9 (s, OsC≡*C*), 106.2, 105.9, 105.3 (all s, Tp), 97.9 (d, $J_{C\text{-}P}$ = 9, Os*C*≡C), 38.8, 38.2, 27.4, 27.1, 26.9 (all s, Cy), 26.0 (d, $J_{C\text{-}P}$ = 27, P*C*HCH$_3$), 20.4 (s, CH$_3$–Py), 20.0 (s, PCH*C*H$_3$),

18.6(s, PCH*C*H$_3$). Spectroscopy data for **8a** are as follows: ^{1}H NMR (400 MHz, thf-d_8, 233 K): δ 8.24 (d, 1H, Tp), 7.93 (d, 1H, Tp), 7.80 (d, 1H, Tp), 7.67 (d, 2H, Tp), 7.33 (d, 1H, Tp), 6.59 (overlapping signals, 1H, Py), 6.29 (m, overlapping signals, 2H, Tp (1H) + Py (1H)), 6.20 (overlapping signals, 1H, Py), 6.14 (t, 1H, Tp), 6.02 (t, 1H, Tp), 2.68 (m, 3H, PC*H*CH$_3$), 2.48 (br, 1H, =C*H*Cy), 2.30 (s, 3H, CH$_3$–Py), 1.89 (m, 3H, Cy), 1.60 (m, 5H, Cy), 1.28 (m, overlapping signals, 21H, PCHC*H*$_3$ (18H) + Cy (3H)), all coupling constants for the pyrazolyl proton resonances were about 2 Hz. ^{31}P{^{1}H} NMR (161.98 MHz, thf-d_8, 233 K): δ –7.0 (s). ^{13}C{^{1}H} NMR (100.63 MHz, thf-d_8, 233 K): δ 305.0 (d, $J_{C–P}$ = 9, Os=C=), 182.7 (d, J_{C-P} = 8, OsCN), 153.7 (s, C$_{ipso}$ Py), 146.3, 145.6 (both s, Tp), 142.5 (s, Py), 136.4, 136.0, 134.1, 133.9 (all s, Tp), 131.4 (s, Py), 114.2 (s, Py), 112.0 (br, =*C*HCy), 106.3, 105.9, 105.3 (all s, Tp), 38.8, 38.2, 34.3, 26.9, 26.2 (all s, Cy), 25.3 (br, P*C*HCH$_3$), 19.9 (s, CH$_3$–Py), 18.6 (s, PCH*C*H$_3$), 17.0 (s, PCH*C*H$_3$).

Determination of Thermodynamic Parameters for the Equilibrium between 8 and 8a. The equilibrium constants K = [**8a**]/[**8**] were determined, between -70 and 30 ºC, by integration of the the ^{31}P{^{1}H} NMR resonances. Thermodynamic parameters ΔH° and ΔS° were obtained by least-squares fit of the Van´t Hoff plot. Errors were computed by published methods.[23]

Preparation of OsTp{κ^2-*C,N*[C(=CHPh)C$_5$(Me)H$_3$N]}(P^{i}Pr$_3$) (9). A red solution of **7** (100 mg, 0.13 mmol) in 5 mL of toluene was heated at 80 ºC in a Schlenk flask equipped with a Teflon stopcock overnight and a dark yellow solution was formed. After this time, it was allowed to reach room temperature and the solvent was removed in vacuo. The residue was chromatographed on neutral aluminum oxide (activity V) with CH$_3$CN as eluent. The resulting dark yellow solution was evaporated to dryness and the residue was washed with cold *n*-pentane and dried in vacuo to afford a black solid. Yield: 82 mg (82 %). Anal. Calcd for C$_{32}$H$_{43}$BN$_7$OsP: C, 50.72 ; H, 5.72; N, 12.94. Found: C, 50.68; H, 5.92; N, 13.06. HRMS (electrospray, *m/z*):

calcd for $C_{32}H_{44}BN_7OsP$ $[M + H]^+$ 760.3105, found 760.3202. ^1H NMR (300 MHz, C_6D_6, 298 K): δ 8.67 (s, 1H, =C*H*Ph), 8.08 (d, 1H, Tp), 7.63 (d, 2H, Tp), 7.58 (d, 1H, Tp), 7.53 (d, 2H, Tp), 7.06 (m, 4H, Ph), 6.98 (m, 1H, Ph), 6.86 (t, $J_{H\text{-}H}$ = 7.8, 1H, Py), 6.66 (d, $J_{H\text{-}H}$ = 7.8, 1H, Py), 6.08 (d, $J_{H\text{-}H}$ = 7.8, 1H, Py), 6.06 (t, 1H, Tp), 5.84 (t, 1H, Tp), 5.79 (t, 1H, Tp), 2.45 (m, 3H, PC*H*CH_3), 1.84 (s, 3H, CH_3–Py), 0.93 (dd, $J_{H–P}$ = 12.0, $J_{H–H}$ = 7.2, 9H, PCHC*H*$_3$), 0.89 (dd, $J_{H–P}$ = 11.1, $J_{H–H}$ = 7.2, 9H, PCHC*H*$_3$), all coupling constants for the pyrazolyl proton resonances were about 2 Hz. $^{31}P\{^1H\}$ NMR (121.48 MHz, C_6D_6, 298 K): δ –3.9 (s). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6, 298 K): δ 190.1 (s, N*C*(C=CHPh)), 159.0 (s, N*C*(Me)), 151.5, 147.9 (both s, Tp), 145.3 (s, *C*$_{ipso}$ Ph), 136.1 (d, $J_{C\text{-}P}$ = 7, Os*C*=CHPh), 134.7, 134.6, 134.4, 134.3 (all s, Tp), 132.2 (s, Py), 129.0 (s, Ph), 128.8 (s, Ph), 128.2 (s, OsC=*C*HPh), 127.5, 127.3, 123.6 (all s, Ph), 120.6 (s, Py), 107.0 (s, Py), 105.4, 105.3, 105.0 (all s, Tp), 26.4 (d, $J_{C\text{-}P}$ = 23, P*C*HCH_3), 23.8 (s, CH_3–Py), 20.5 (s, PCH*C*H$_3$), 20.2 (s, PCH*C*H$_3$).

Preparation of OsTp{κ^2-*C,N*[C(=CHCy)C$_5$(Me)H$_3$N]}(P^{i}Pr$_3$) (10). An equilibrium mixture of **8** and **8a** (100 mg, 0.13 mmol) in 5 mL of toluene was heated at 80 ºC for two days in a Schlenk flask equipped with a Teflon stopcock and a dark orange solution was formed. After this time, it was allowed to reach room temperature and the solvent was removed in vacuo. The residue was chromatographed on neutral aluminum oxide (activity V) with diethylether as eluent. The resulting dark orange solution was evaporated to dryness and the residue was washed with cold *n*-pentane and dried in vacuo to afford a black solid. Yield: 53.6 mg (54%). Anal. Calcd for $C_{32}H_{49}N_7OsBP$: C, 50.32 ; H, 6.47; N, 12.84. Found: C, 50.54; H, 6.75; N, 12.56. HRMS (electrospray, *m/z*): calcd for $C_{32}H_{49}BN_7OsP$ [M] 765.3496, found 765.3510. ^1H NMR (300 MHz, C_6D_6, 298 K): δ 8.23 (d, 2H, Tp), 8.07 (d, 2H, Tp), 7.62 (d, 1H, Tp), 7.58 (d, 1H, Tp), 7.50 (t, 1H, Tp), 7.35 (d, $J_{H\text{-}H}$ = 7.6, 1H, =C*H*Cy), 6.80 (t, 2H, Tp), 6.60 (1H, Py), 6.66 (2H, Py), 2.58

(m, 3H, PC*H*CH_3), 2.21 (m, 3H, Cy), 1.85 (s, 3H, CH_3–Py), 1.62 (m, 2H, Cy), 1.38 (m, 6H, Cy), 1.05 (overlapping signals, 18H, PCHC*H*$_3$), all coupling constants for the pyrazolyl proton resonances were about 2 Hz. The NOESY spectrum shows a cross-peak between the signals at 7.35 and 6.60 ppm, among others. $^{31}P\{^1H\}$ NMR (121.48 MHz, C_6D_6, 298 K): δ –0.39 (s). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_6D_6, 298 K): δ 190.7 (s, N*C*(C=CHCy)), 159.0 (s, N*C*(Me)), 149.9, 147.6, 136.7 (all s, Tp), 135.8 (s, OsC=*C*HCy), 134.7, 134.5, 133.9 (all s, Tp), 129.2 (br, Os*C*=CHPh), 119.7 (s, Py), 107.3 (s, Py), 41.9 (s, CH Cy), 33.6, 32.2, 30.2, 27.2 (all s, Cy), 26.4 (d, $J_{C\text{-}P}$ = 23, P*C*HCH$_3$), 26.7 (s, Cy), 23.8 (s, CH_3–Py), 20.3 (s, PCH*C*H$_3$), 20.2 (s, PCH*C*H$_3$).

Preparation of [OsTp{κ^2-*C*,*N*[=C(CH$_2$Ph)C$_5$(Me)H$_3$N]}(P^{i}Pr$_3$)]BF$_4$ (11). A dark yellow solution of **9** (100 mg, 0.13 mmol) in 5 mL of diethyl ether was treated with $HBF_4 \cdot Et_2O$ (20 μL, 0.14 mmol). Immediately a greenish yellow solid appeared. The solid was separated by decantation, washed with diethyl ether (3 x 3 mL), and dried in vacuo. Yield: 98 mg (89 %). Anal. Calcd for $C_{32}H_{44}B_2F_4N_7OsP$: C, 45.45 ; H, 5.24; N, 11.60. Found: C, 45.05; H, 5.24; N, 11.29. HRMS (electrospray, *m/z*): calcd for $C_{32}H_{44}BN_7OsP$ $[M]^+$ 760.3105, found 760.3132. ^1H NMR (300 MHz, CD_2Cl_2, 298 K): δ 7.89 – 7.86 (overlapping signals, 2H, Tp + Py), 7.78 – 7.70 (overlapping signals, 3H, Tp (2H) + Py (1H)), 7.62 (d, 1H, Tp), 7.53 (d, 1H, Tp), 6.98 – 6.91 (overlapping signals, 2H, Ph + Py), 6.73 (t, $J_{H\text{-}H}$ = 7.7, 2H, Ph), 6.45 (d, 1H, Tp), 6.42 (t, 1H, Tp), 6.27 (d, $J_{H\text{-}H}$ = 7.7, 2H, Ph), 5.69 (t, 1H, Tp), 5.58 (t, 1H, Tp), 4.47 (d, $J_{H\text{-}H}$ = 12.1, 1H, =CC*H*HPh), 2.62 – 2.48 (overlapping signals, 4H, =CCH*H*Ph (1H) + PC*H*CH$_3$ (3H)), 1.89 (s, 3H, CH_3–Py), 1.11 (dd, $J_{H\text{–}P}$ = 13.3, $J_{H\text{–}H}$ = 7.2, 9H, PCHC*H*$_3$), 0.96 (dd, $J_{H\text{–}P}$ = 13.8, $J_{H\text{–}H}$ = 7.2, 9H, PCHC*H*$_3$), all coupling constants for the pyrazolyl proton resonances were about 2 Hz. $^{31}P\{^1H\}$ NMR (121.48 MHz, CD_2Cl_2, 298 K): δ –2.2 (s). $^{13}C\{^1H\}$ NMR (75.45 MHz, CD_2Cl_2, 298 K): δ 227.4 (d, $J_{C\text{-}P}$ = 12, Os=*C*), 201.6 (d, $J_{C\text{-}P}$ = 3, OsNC), 168.8 (s, N*C*(Me)), 147.7, 145.4

(both s, Tp), 140.9 (s, Py), 137.1, 136.0, 135.9, 135.5 (all s, Tp), 129.1, 129.0, 128.5, 126.3 (all s, Ph), 121.8 (s, Py), 121.3 (d, $J_{C\text{-}P}$ = 2, C_{ipso} Ph), 107.1, 106.8, 106.1 (all s, Tp), 102.7 (s, Py), 61.2 (s, =C*C*H$_2$Ph), 25.8 (d, $J_{C\text{-}P}$ = 26, P*C*HCH$_3$), 22.3 (s, CH$_3$–Py), 18.9 (d, $J_{C\text{-}P}$ = 2, PCH*C*H$_3$), 18.3 (s, PCH*C*H$_3$).

Preparation of [OsTp{κ^2-*C*,*N*[=C(CH$_2$Cy)C$_5$(Me)H$_3$N]}(P^{i}Pr$_3$)]BF$_4$ (12). A dark orange solution of **10** (80 mg, 0.10 mmol) in 5 mL of diethyl ether was treated with HBF$_4$·Et$_2$O (14.4 μL, 0.10 mmol). Immediately a greenish yellow solid appeared. The solid was separated by decantation, washed with diethyl ether (3 x 3 mL), and dried in vacuo. Yield: 71 mg (84 %). Anal. Calcd for C$_{32}$H$_{50}$B$_2$F$_4$N$_7$OsP: C, 45.13 ; H, 5.92; N, 11.51. Found: C, 45.52; H, 5.69; N, 11.66. HRMS (electrospray, *m/z*): calcd for C$_{32}$H$_{50}$BN$_7$OsP [M]$^+$ 766.3574, found 766.3606. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 298 K): δ 7.96 (d, $J_{H\text{-}H}$ = 7.8, 1H, Py), 7.88 (d, 1H, Tp), 7.80 (d, $J_{H\text{-}H}$ = 7.8, 1H, Py), 7.73 (d, 1H, Tp), 7.66 (d, 1H, Tp), 7.62 (d, 1H, Tp), 7.56 (d, 1H, Tp), 6.71 (t, $J_{H\text{-}H}$ = 7.8, 1H, Py), 6.54 (d, 1H, Tp), 6.46 (t, 1H, Tp), 6.33 (t, 1H, Tp), 6.17 (t, 1H, Tp), 3.00 (dd, $J_{H\text{-}H}$ = 11.8, $J_{H\text{-}H}$ = 6.9, 1H, =CC*H*HCy), 2.53 (m, 3H, PC*H*CH$_3$), 1.98 (s, 3H, CH$_3$–Py), 1.47 (m, 5H, Cy), 1.30 – 1.12 (overlapping signals, 3H, Cy (2H) + =CCH*H*Cy), 1.02 (dd, $J_{H–P}$ = 13.5, $J_{H–H}$ = 7.2, 9H, PCHC*H*$_3$), 0.94 (dd, $J_{H–P}$ = 13.5, $J_{H–H}$ = 7.2, 9H, PCHC*H*$_3$), 0.46 (t, $J_{H–H}$ = 8.3, 2H, Cy), 0.22 (m, 2H, Cy), all coupling constants for the pyrazolyl proton resonances were about 2 Hz. ^{31}P{^{1}H} NMR (121.48 MHz, CD$_2$Cl$_2$, 298 K): δ –3.0 (s). ^{13}C{^{1}H} NMR (75.45 MHz, CD$_2$Cl$_2$, 298 K): δ 235.7 (d, $J_{C\text{-}P}$ = 11, Os=*C*), 203.2 (s, OsNC), 167.0 (s, N*C*(Me)), 148.5, 145.5 (both s, Tp), 141.3 (s, Py), 137.5, 136.7, 136.5, 136.3 (all s, Tp), 122.6 (s, Py), 107.4, 106.7, 106.6 (all s, Tp), 101.5 (s, Py), 64.4 (s, =C*C*H$_2$Cy), 35.3, 34.1, 26.6, 26.5 (all s, Cy), 26.4 (d, $J_{C\text{-}P}$ = 26, P*C*HCH$_3$), 26.0 (s, Cy), 22.8 (s, CH$_3$–Py), 19.2 (s, PCH*C*H$_3$), 18.7 (s, PCH*C*H$_3$).

Structural Analysis of Complexes 7, 8, and 9. X-ray data were collected for all complexes on a Bruker Smart APEX CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, λ = 0.71073 Å) operating at 50 kV and 30 (**7**)/40 (**8** and **9**) mA. Data were collected over the complete sphere. Each frame exposure time was 10s (**7** and **8**) or 30s (**9**) covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[24] The structures of all compounds was solved by direct methods. Refinement, by full-matrix least squares on F^2 with SHELXL97,[25] was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters. The hydrogen atoms were calculated or observed in the last cycles in the difference Fourier maps and refined freely or using a restricted riding model.

Crystal data for **7**: $C_{32}H_{43}BN_7OsP$ x 0.7 C_5H_{12}, M_W 808.22, red, irregular block (0.22 x 0.20 x 0.14), monoclinic, space group $P2_1/c$, *a*: 16.5362(8) Å, *b*: 15.2844(8) Å, *c*: 15.7550(8) Å, *β*: 107.3400(10)°, *V* = 3801.0(3) Å^3, *Z* = 4, D_{calc}: 1.412 g cm^{-3}, F(000): 1638, T = 100(2) K, μ: 3.430 mm^{-1}. 44965 measured reflections (2θ: 3-58°, ω scans 0.3°), 9064 unique (R_{int} = 0.0357); min./max. transm. Factors 0.692/0.862. Final agreement factors were R^1 = 0.0249 (7409 observed reflections, I > 2σ(I)) and wR^2 = 0.0697; data/restraints/parameters 9064/14/ 436; GoF = 1.041. Largest peak and hole 1.276 (close to osmium atom) and -0.616 e/ Å^3.

Crystal data for **8**: $C_{32}H_{49}BN_7OsP$ x C_5H_{12}, M_W 835.91, red, irregular block (0.16 x 0.15 x 0.14), monoclinic, space group $P2_1/c$, *a*: 16.9932(10) Å, *b*: 15.2993(9) Å, *c*: 15.7064(10) Å, *β*: 107.7380(10)°, *V* = 3889.3(4) Å^3, *Z* = 4, D_{calc}: 1.428 g cm^{-3}, F(000): 1712, T = 100(2) K, μ 3.355 mm^{-1}). 46616 measured reflections (2θ: 3-58°, ω scans 0.3°), 9316 unique (R_{int} = 0.0398); min./max. transm. Factors 0.767/0.862. Final agreement factors were R^1 = 0.0262 (7697

observed reflections, I > 2σ(I)) and wR^2 = 0.0675; data/restraints/parameters 9316/14/424; GoF = 0.973. Largest peak and hole 1.423 and -0.662 e/ Å^3

Crystal data for **9**: $C_{32}H_{43}BN_7OsP$, M_W 757.71, black, irregular block (0.12 x 0.10 x 0.06), monoclinic, space group $P2_1/n$, *a*: 10.5349(10) Å, *b*: 20.4383(18) Å, *c*: 14.8765(14) Å, *β*: 93.2380(10)º, *V* = 3198.0(5) Å^3, *Z* = 4, D_{calc}: 1.574 g cm^{-3}, F(000): 1520, T = 100(2) K, μ: 4.071 mm^{-1}. 29092 measured reflections (2θ: 3-58º, ω scans 0.3º), 7590 unique (R_{int} = 0.0599); min./max. transm. Factors 0.646/0.862. Final agreement factors were R^1 = 0.0437 (5984 observed reflections, I > 2σ(I)) and wR^2 = 0.0977; data/restraints/parameters 7590/0/392; GoF = 1.031. Largest peak and hole 1.892 and -0.985 e/ Å^3.

ASSOCIATED CONTENT

Supporting Information.

A CIF file giving positional and displacement parameters, crystallographic data, and bond lengths and angles of compounds **7** – **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

* E-mail: maester@unizar.es.

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REFERENCES

(1) (a) Lewis, J. C.; Bergman, R. G.; Ellman, J. A. *Acc. Chem. Res.* **2008**, *41*, 1013. (b) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624.

(2) Lewis, J. C.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc*. **2007**, *129*, 5332.

(3) Wiedemann, S. H.; Lewis, J. C.; Ellman, J. A.; Bergman, R. G. *J. Am. Chem. Soc*. **2006**, *128*, 2452.

(4) For a review of one-N six-membered heterocyclic carbene complexes, see: Raubenheimer, H. G.; Cronje, S. *Dalton. Trans.* **2008**, 1265.

(5) The limited number of examples of this type is chiefly because tautomerization to the N-bound imidazole, a 1,3-ligand to metal hydrogen shift, or deprotonation to form an anionic ligand may occur. For representative examples, see: (a) Burling, S.; Mahon, M. F.; Powell, R. E.; Whittlesey, M. K.; Williams, J. M. J. *J. Am. Chem. Soc*. **2006**, *128*, 13702. (b) Ruiz, J.; Perandones, B. F. *J. Am. Chem. Soc*. **2007**, *129*, 9298. (c) Wang, X.; Chen, H; Li, X. *Organometallics* **2007**, *26*, 4684. (d) Gribble Jr., M. W.; Ellman, J. A.; Bergman, R. G. *Organometallics* **2008**, *27*, 2152. (e) Huertos, M. A.; Pérez, J.; Riera, L.; Menéndez-Velázquez, A. *J. Am. Chem. Soc*. **2008**, *130*, 13530. (f) Huertos, M. A.; Pérez, J.; Riera, L.; Díaz, J.; López, R. *Chem. Eur. J.* **2010**, *16*, 8495. (g) Ruiz, J.; Perandones, B. F.; Van der Maelen, J. F.; García-Granda, S. *Organometallics* **2010**, *29*, 4639. (h) Song, G.; Su, Y.; Periana, R. A.; Crabtree, R. H.; Han, K.; Zhang, H.; Li, X. *Angew. Chem. Int. Ed.* **2010**, *49*, 912. (i) Miranda-Soto, V.; Grotjahn, D. B.; Cooksy, A. L.; Golen, J. A.; Moore, C. E.; Rheingold, A. L. *Angew. Chem. Int. Ed.* **2011**, *50*, 631. (j) Eguillor, B.; Esteruelas, M. A.; García-Raboso, J.; Oliván, M.; Oñate, E.; Pastor, I. M.; Peñafiel, I.; Yus, M. *Organometallics* **2011**, *30*, 1658.

(6) (a) Esteruelas, M. A.; Fernández-Alvarez, F. J.; Oñate, E. *J. Am. Chem. Soc*. **2006**, *128*, 13044. (b) Buil, M. L.; Esteruelas, M. A.; Garcés, K.; Oliván, M.; Oñate, E. *J. Am. Chem. Soc*. **2007**, *129*, 10998. (c) Esteruelas, M. A.; Fernández-Alvarez, F. J.; Oñate, E. *Organometallics* **2007**, *26*, 5239. (d) Buil, M. L.; Esteruelas, M. A.; Garcés, K.; Oliván, M.; Oñate, E. *Organometallics* **2008**, *27*, 4680.

(7) (a) Álvarez, E.; Conejero, S.; Paneque, M.; Petronilho, A.; Poveda, M. L.; Serrano, O.; Carmona, E. *J. Am. Chem. Soc*. **2006**, *128*, 13060. (b) Álvarez, E.; Conejero, S.; Lara, P.; López, J. A.; Paneque, M.; Petronilho, A.; Poveda, M. L.; del Río, D.; Serrano, O.; Carmona, E. *J. Am. Chem. Soc*. **2007**, *129*, 14130. (c) Esteruelas, M. A.; Fernández-Alvarez, F. J.; Oliván, M.; Oñate, E. *Organometallics* **2009**, *28*, 2276. (d) Conejero, S.; López-Serrano, J.; Paneque, M.; Petronilho, A.; Poveda, M. L.; Vattier, F.; Álvarez, E.; Carmona, E. *Chem. Eur. J.* **2012**, *18*, 4644.

(8) Esteruelas, M. A.; Fernández-Alvarez, F. J.; Oñate, E. *Organometallics* **2008**, *27*, 6236.

(9) Nakao, Y.; Kanyiva, K. S.; Hiyama, T. *J. Am. Chem. Soc.* **2008**, *130*, 2448.

(10) See for example: (a) Esteruelas, M. A.; Herrero, J.; López, A. M.; Oliván, M. *Organometallics* **2001**, *20*, 3202. (b) Chen, X.; Xue, P.; Sung, H. H. Y.; Williams, I. D.; Peruzzini, M.; Bianchini, C.; Jia, G. *Organometallics* **2005**, *24*, 4330. (c) Ito, J.; Kitase, M.; Nishiyama, H. *Organometallics* **2007**, *26*, 6412. (d) Katagiri, T.; Tsurugi, H.; Satoh, T.; Miura, M. *Chem. Commun*. **2008**, 3405.

(11) Álvarez, E.; Hernández, Y. A.; López-Serrano, J.; Maya, C.; Paneque, M.; Petronilho, A.; Poveda, M. L.; Salazar, V.; Vattier, F.; Carmona, E. *Angew. Chem. Int. Ed.* **2010**, *49*, 3496.

(12) (a) Castro-Rodrigo, R.; Esteruelas, M. A.; López, A. M.; Oliván, M.; Oñate, E. *Organometallics* **2007**, *26*, 4498. (b) Castro-Rodrigo, R.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **2008**, *27*, 3547. (c) Castro-Rodrigo, R.; Esteruelas, M. A.; Fuertes, S.; López, A. M.; Mozo, S.; Oñate, E. *Organometallics* **2009**, *28*, 5941. (d) Castro-Rodrigo, R.; Esteruelas, M. A.; Fuertes, S.; López, A. M.; López, F.; Mascareñas, J. L.; Mozo, S.; Oñate, E.; Saya, L.; Villarino, L. *J. Am. Chem. Soc.* **2009**, *131*, 15572. (e) Castro-Rodrigo, R.; Esteruelas, M. A.; López, A. M.; López, F.; Mascareñas, J. L.; Oliván, M.; Oñate, E.; Saya, L.; Villarino, L. *J. Am. Chem. Soc.* **2010**, *132*, 454. (f) Castro-Rodrigo, R.; Esteruelas, M. A.; López, A. M.; López, F.; Mascareñas, J. L.; Mozo, S.; Oñate, E.; Saya, L. *Organometallics* **2010**, *29*, 2372. (g) Castro-Rodrigo, R.; Esteruelas, M. A.; López, A. M.; Mozo, S.; Oñate, E. *Organometallics* **2010**, *29*, 4071. (h) Bajo, S.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **2011**, *30*, 5710. (i) Castro-Rodrigo, R.; Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **2012**, *31*, 1991.

(13) (a) Song, G.; Li, Y.; Chen, S.; Li, X. *Chem. Commun.* **2008**, 3558. (b) Paneque, M.; Poveda, M. L.; Vattier, F.; Alvarez, E.; Carmona, E. *Chem. Commun.* **2009**, 5561. (c) Cabeza, J. A.; del Río, I.; Pérez-Carreño, E.; Sánchez-Vega, M. G.; Vázquez-García, D. *Organometallics* **2010**, *29*, 4464. (d) Cabeza, J. A.; del Río, I.; Pérez-Carreño, E.; Pruneda, V. *Organometallics* **2011**, *30*, 1148.

(14) See for example: (a) Collado, A.; Esteruelas, M. A.; López, F.; Mascareñas, J. L.; Oñate, E.; Trillo, B. *Organometallics* **2010**, *29*, 4966. (b) Batuecas, M.; Escalante, L.; Esteruelas, M. A.; García-Yebra, C.; Oñate, E.; Saá, C. *Angew. Chem. Int. Ed*. **2011**, *50*, 9712.

(15) See for example: (a) Ruiz, J.; Perandones, B. F.; García, G.; Mosquera, M. E. G. *Organometallics* **2007**, *26*, 5687. (b) Miranda-Soto, V.; Grotjahn, D. B.; DiPasquale, A. G., Rheingold, A. L. *J. Am. Chem. Soc*. **2008**, *130*, 13200.

(16) (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev*. **1997**, *193-195*, 977. (c) Esteruelas, M. A.; López, A. M. *Organometallics* **2005,** *24*, 3584. (d) Esteruelas, M. A.; López, A. M.; Oliván, M. *Coord. Chem. Rev*. **2007**, *251*, 795. (e) Lynam, J. M. *Chem. Eur. J.* **2010**, *16*, 8238.

(17) See for example: (a) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2005**, *24*, 4343. (b) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2007**, *26*, 2129. (c) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2007**, *26*, 3082. (d) Baya, M.; Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Oñate, E. *Organometallics* **2007**, *26*, 6556. (e) Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Puerta, M. *Organometallics* **2008**, *27*, 445. (f) Castarlenas, R.; Esteruelas, M. A.; Lalrempuia, R.; Oliván, M.; Oñate, E. *Organometallics* **2008**, *27*, 795. (g) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2008**, *27*, 3240. (h) Buil, M. L.; Castarlenas, R.; Esteruelas, M. A.; Izquierdo, S.; Lalrempuia, R.; Oñate, E. *Organometallics* **2010**, *29*, 876. (i) Bolaño, T.; Buil, M. L.; Esteruelas, M. A.; Izquierdo, S.; Lalrempuia, R.; Oliván, M.; Oñate, E. *Organometallics* **2010**, *29*, 4517. (j) Buil, M. L.; Cadierno, V.; Esteruelas, M. A.; Gimeno, J.; Herrero, J.; Izquierdo, S.; Oñate, E. *Organometallics* **2012**, *31*, 6861.

(18) See for example: (a) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1993**, *12*, 663. (b) Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1995**, *14*, 2496. (c) Baya, M.; Crochet, P.; Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A. M.; Modrego, J.; Oñate, E.; Vela, N. *Organometallics* **2000**, *19*,

2585. (d) Baya, M.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 4875. (e) Buil, M. L.; Esteruelas, M. A.; Garcés, K.; Oñate, E. *J. Am. Chem. Soc.* **2011**, *133*, 2250. (f) Esteruelas, M. A.; López, A. M.; Mora, M.; Oñate, E. *Organometallics* **2012**, *31*, 2965.

(19) Nast, R. *Coord. Chem. Rev.* **1982**, *47*, 89.

(20) See for example: (a) Buil, M. L.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M. *Organometallics* **2000**, *19*, 2184. (b) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. . *Organometallics* **2001**, *20*, 2294.

(21) (a) Wen, T. B.; Yang, S.-Y.; Zhou, Z. Y.; Lin, Z.; Lau, C, -P.; Jia, G. *Organometallics* **2000**, *19*, 3757. (b) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E.; Tajada, M. A. *Organometallics* **2000**, *19*, 5098. (c) Yandulov, D. V.; Bollinger, J. C.; Streib, W. E.; Caulton, K. G. *Organometallics* **2001**, *20*, 2040. (d) Barrio, P.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 3627. (e) Xue, P.; Zhu, J.; Hung, H. S. Y.; Williams, I. D.; Lin, Z.; Jia, G. *Organometallics* **2005**, *24*, 4896. (f) Eguillor, B.; Esteruelas, M. A.; Oliván, M.; Oñate, E. *Organometallics* **2005**, *24,* 1428. (g) Hung, W. Y.; Zhu, J.; Wen, T. B.; Yu, K. P.; Sung, H. H. Y.; Williams, I. D.; Lin, Z.; Jia, G. *J. Am. Chem. Soc.* **2006**, *128*, 13742. (h) Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *J. Am. Chem. Soc.* **2006**, *128*, 3965. (i) Esteruelas, M. A.; Fernández-Alvarez, F. J.; Oliván, M.; Oñate, E. *J. Am. Chem. Soc.* **2006**, *128*, 4596. (j) Bai, T.; Zhu, J.; Xue, P.; Sung, H. H. –Y.; Williams, I. D.; Ma, S.; Lin, Z.; Jia, G. *Organometallics* **2007**, *26,* 5581. (k) Gong, L.; Lin, Y.; He, G.; Zhang, H.; Wang, H.; Wen, T. B.; Xia, H. *Organometallics* **2008**, *27,* 309. (l) Gong, L.; Lin, Y.; Wen, T. B.; Xia, H. *Organometallics* **2009**, *28,* 1101. (m) Bolaño, T.; Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *J. Am. Chem. Soc.* **2009**, *131*, 2064. (n) Gong, L.; Chen, Z.; Lin, Y.; He, X.; Wen, T. B.; Xu, X.;

Xia, H. *Chem. Eur. J.* **2009**, *15*, 6258. (o) Liu, B.; Wang, H.; Xie, H.; Zeng, B.; Chen, J.; Tao, J.; Wen, T. B.; Cao, Z.; Xia, H. *Angew. Chem. Int. Ed.* **2009**, *48*, 5430. (p) Baya, M.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2010**, *29,* 6298.

(22) See for example: (a) Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1994**, *13,* 1669. (b) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1995**, *14,* 3596. (c) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Valero, C.; Zeier, B. *J. Am. Chem. Soc.* **1995**, *117*, 7935. (d) Buil, M. L.; Esteruelas, M. A. *Organometallics* **1999**, *18,* 1798. (e) Bohanna, C.; Buil, M. L.; Esteruelas, M. A.; Oñate, E.; Valero, C. *Organometallics* **1999**, *18,* 5176. (f) Baya, M.; Esteruelas, M. A. *Organometallics* **2002**, *21,* 2332. (g) Esteruelas, M. A.; López, A. M.; Oñate, E. *Organometallics* **2007**, *26,* 3260.

(23) Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *16,* 1646.

(24) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33. SADABS: Area-detector absorption correction; Bruker- AXS, Madison, WI, 1996.

(25) SHELXTL Package v. 6.14; Bruker-AXS, Madison, WI, 2000. Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.

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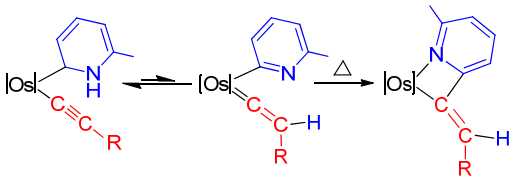

[Os]= OsTp(P^iPr_3); R = Ph, Cy