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Hydride-Alkenylcarbyne to Alkenylcarbene Transformation in Bisphosphine-Osmium Complexes

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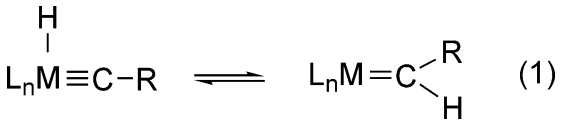
Abstract: The elongated dihydrogen complex [Os{$C_6H_4C(O)CH_3$}(η^2-H_2)(H_2O)(P^iPr_3)$_2$]BF_4 (**1**) reacts with 1,1-diphenyl-2-propyn-1-ol and 2-methyl-3-butyn-2-ol to give the hydride-hydroxyvinylidene-π-alkynol derivatives [OsH{=C=CHC(OH)R_2}{η^2-HC≡CC(OH)R_2}(P^iPr_3)$_2$]BF_4 (R = Ph (**2**), Me (**3**)), where the π-alkynols act as four-electron donor ligands. Treatment of **2** and **3** with HBF_4 and coordinating solvents leads to the dicationic hydride-alkenylcarbyne compounds [OsH(≡CCH=CR_2)S_2(P^iPr_3)$_2$][BF_4]$_2$ (R = Ph, S = H_2O (**4**), CH_3CN (**5**); R = Me, S = CH_3CN (**6**)), which in acetonitrile evolve into the alkenylcarbene complexes [Os(=CHCH=CR_2)(CH_3CN)$_3$(P^iPr_3)$_2$][BF_4]$_2$ (R = Ph (**7**), Me (**8**)) by means of a concerted 1,2-hydrogen shift from the osmium to the carbyne carbon atom. Treatment of 2-propanol solutions of **5** with NaCl affords $OsHCl_2$(≡CCH=CPh_2)(P^iPr_3)$_2$ (**10**), which reacts with $AgBF_4$ and acetonitrile to give [OsHCl(≡CCH=CPh_2)(CH_3CN)(P^iPr_3)$_2$]BF_4 (**11**). In this solvent complex **11** is converted to [OsCl(=CHCH=CPh_2)(CH_3CN)$_2$(P^iPr_3)$_2$]BF_4 (**12**). Complex **5** reacts with CO to give [Os(=CHCH=CPh_2)(CO)(CH_3CN)$_2$-(P^iPr_3)$_2$][BF_4]$_2$ (**15**). DFT calculations and kinetic studies for the hydride-alkenylcarbyne to alkenylcarbene transformation show that the difference of energy between the starting compounds and the transition states, which can be described as η^2-carbene species (Os=C(R)H), increases with the basicity of the metallic center. The X-ray structures of **4** and **7** and the rotational barriers for the carbene ligands of **7**, **8**, and **12** are also reported.

Introduction

Complexes containing M=C and M≡C bonds are attracting much attention, due to their use as tools in organic synthesis and homogeneous catalysis.[1] Among the transformations involving both types of compounds, the equilibrium between hydride-carbyne and carbene species (eq 1) is one of the most fascinating processes.[2]



(1)

A large number of carbene complexes have been prepared by protonating carbyne compounds.[3] However, not in all cases it has been clear the participation of the metallic center. Evidences for 1,2-hydrogen shift from the metal to the carbyne carbon atom have been found in the tungsten complex WH(≡C−Mes)(CO){$P(OMe)_3$}$_3$, which affords W(=CH−Mes)(CO)L-{$P(OMe)_3$}$_3$ (L = CO, $P(OMe)_3$, PMe_3) via a five-coordinate carbene intermediate.[4] The 1,2-hydrogen shift has been mainly observed in the opposite sense. The extraction of the chloride ligand from the cyclopentadienyl-osmium-carbene complexes 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 (R = P^iPr_3,[5] P^iPr_2[$C(CH_3)$=CH_2][6]). The related compounds [OsH(η^5-C_5H_5)-(≡CCH_2Ph)(P^iPr_3)]BF_4[7] and [OsH(η^5-$C_5H_4SiPh_3$){≡CCH-

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$(Ph)R\}(P^iPr_3)]BF_4$ (R = H, CH_3)[8] are also known. Similarly, the rhenium-hydride-carbyne complexes $ReH(\equiv CCH_3)(\eta^2\text{-}CH_2{=}CH_2)(PNP)$ (PNP = $N(SiMe_2CH_2PCy_2)_2$),[9] $[ReH_2(\equiv CCH_2R)(mq)(PPh_3)_2]PF_6$, and $ReH(\equiv CCH_2R)(mq)(PPh_3)_2$ (mq = the anion of 2-mercaptoquinoline)[10] are stable, and the migratory insertion of the carbyne ligands into the Re—H bond is not observed. On the other hand, analogous ruthenium compounds prefer the carbene form.[11]

The formation of $[OsH(\eta^5\text{-}C_5H_5)(\equiv CPh)(PR_3)]^+$ by means of the creation of a coordination vacancy in $Os(\eta^5\text{-}C_5H_5)Cl(=CHPh)(PR_3)_2$ agrees well with the existence of $[OsH\{\kappa\text{-}N,\kappa\text{-}O[ON{=}C(CH_3)_2]\}(\equiv CCH_2R)(P^iPr_3)_2]BF_4$,[12] $[OsH(\kappa^2\text{-}O_2CCH_3)(\equiv CCH_2R)(P^iPr_3)_2]BF_4$,[13] $[OsHX(\equiv CCH_2Ph)(Hpz)(P^iPr_3)_2]BF_4$ (X = F, Cl),[14] and $OsHCl_2(\equiv CR)(PR'_3)_2$.[15] The latter are isomers of the unknown compounds $OsCl_2(=CHR)(PR'_3)_2$, which should be the osmium counterparts to the Grubbs-type carbene ruthenium derivatives $RuCl_2(=CHR)(PR'_3)_2$.[16] DFT calculations indicate that although the energies of hydride-carbyne and carbene isomers are similar, the energy for the hydride migration is too large. Thus, the formation of $OsCl_2(=CHEt)(CO)(P^iPr_3)_2$[17] from $OsHCl_2(\equiv CEt)(P^iPr_3)_2$ is associative in CO.[18]

As a part of our work on the capacity of high valent metal complexes to activate C—H bonds,[19] we have recently shown that the d^2 hexahydride $OsH_6(P^iPr_3)_2$ activates an *ortho*-CH bond of acetophenone to yield $\overline{OsH_3\{C_6H_4C(O)}CH_3\}(P^iPr_3)_2$,[20] which affords the cationic elongated dihydrogen derivate $[\overline{Os\{C_6H_4C(O)}CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$ by reaction with $HBF_4{\cdot}OH_2$.[21] This complex reacts with terminal alkynes, RC≡CH, to give in a competitive manner hydride-vinylidene-π-alkyne compounds $[OsH(=C{=}CHR)(\eta^2\text{-}HC{\equiv}CR)(P^iPr_3)_2]BF_4$ and hydride-osmacyclopropene species $[\overline{OsH\{C_6H_4C(O)}CH_3\}\{=C(R)CH_2\}(P^iPr_3)_2]BF_4$. The preferred formation of one of the two types of compounds depends on the substituent R of the alkyne.[22] Hydrogen and alkyl groups exclusively afford hydride-vinylidene-π-alkyne complexes, while phenyl gives rise to a mixture of both types of derivates. The reaction 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 structure of 1,2,4-cyclohexatriene $\overline{Os\{=C{=}C(Ph)CH(Ph)CH{=}C(CH_2Ph)\}}Cl(P^iPr_3)_2$.[23] Now, we have observed that the reactions of $[\overline{Os\{C_6H_4C(O)}CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$ with alkynols lead to hydride-hydroxyvinylidene-π-alkynol complexes, which generate dicationic hydride-alkenylcarbyne derivatives.

In this paper we report the following: (i) the preparation and characterization of novel hydride-hydroxyvinylidene-π-alkynol and dicationic hydride-alkenylcarbyne complexes, (ii) the transformation of the latter into dicationic alkenylcarbene derivatives, (iii) the mechanism of the transformation, and (iv) the influence of the co-ligands on the activation parameters of the 1,2-hydrogen shift.

Results and Discussion

1. Preparation and Characterization of $[OsH\{=C{=}CHC(OH)R_2\}\{\eta^2\text{-}HC{\equiv}CC(OH)R_2\}(P^iPr_3)_2]BF_4$ and $[OsH(\equiv CCH{=}CR_2)S_2(P^iPr_3)_2][BF_4]_2$ (R = Ph, Me; S = H_2O, CH_3CN). The chemical bonding in transition-metal alkyne complexes is described in a way similar to that for transition-metal alkene compounds. The bonding is considered to arise from donor−acceptor interactions between the alkyne and the metal. A major difference between alkene and alkyne is that the latter has a second occupied π orbital orthogonal to the MC_2 plane ($M_\perp$) which, in some cases, engages in the transition-metal-alkyne bonding. In that case, the alkyne is a four-electron-donor ligand by means of its $M_{||}$ and $M_\perp$ orbitals.

In dichloromethane, the elongated dihydrogen complex $[\overline{Os\{C_6H_4C(O)}CH_3\}(\eta^2\text{-}H_2)(H_2O)(P^iPr_3)_2]BF_4$ (**1**) releases acetophenone to afford the highly unsaturated monohydride $[OsH(H_2O)(P^iPr_3)_2]^+$,[22] which rapidly coordinates two alkynol mol-

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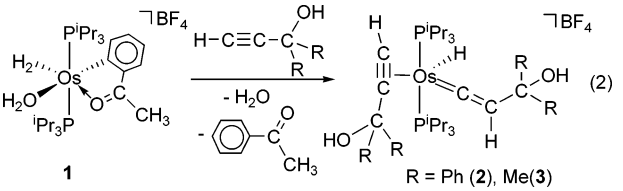
ecules. Thus, the treatment of dichloromethane solutions of **1** with 2.5 equiv of 1,1-diphenyl-2-propyn-1-ol and 2-methyl-3-butyn-2-ol, at 243 K, leads to $[OsH\{=C=CHC(OH)R_2\}\{\eta^2\text{-}HC\equiv CC(OH)R_2\}(P^iPr_3)_2]BF_4$ (R = Ph (**2**), Me (**3**)), containing a hydroxyvinylidene group and a four-electron donor π-alkynol ligand (eq 2).



Complexes **2** and **3** are notable because they are rare examples of five-coordinate cationic hydride-hydroxyvinylidene derivatives. With the exception of the neutral six-coordinate compound $OsH(\kappa^2\text{-}O_2CCH_3)\{=C=CHC(OH)Ph_2\}(P^iPr_3)_2$,[24] as far as we know, species of this type have not been previously reported in the osmium chemistry, in particular those containing at the same time hydride, hydroxyvinylidene, and π-alkynol ligands.

The chemistry of four-electron-donating alkynes has been centered at early transition metals, mainly molybdenum and tungsten. A wide variety of six-coordinate Mo(II) and W(II) complexes have been synthesized.[25] Four-coordinate d^6 complexes of the types $ML(alkyne)_3$[26] and $ML_2(alkyne)_2$[27] have been also reported. However, five-coordinate d^6 monoalkyne complexes with the general formula $ML_4(alkyne)$ are very scarce.[28] In addition to $[OsH\{=C=CHR\}\{\eta^2\text{-}HC\equiv CR\}(P^iPr_3)_2]BF_4$ (R = H, Cy, Ph),[22] we have reported the cyclopentadienyl-osmium derivatives $[Os(\eta^5\text{-}C_5H_5)\{\eta^2\text{-}HC\equiv CC(OH)R_2\}(P^iPr_3)]PF_6$ (R = Ph, Me).[29]

Complexes **2** and **3** were isolated as orange and brown solids, respectively, in almost quantitative yield and characterized by elemental analysis, MS, IR, and ^1H, $^{31}P\{H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy. The NMR spectra strongly support the presence in these compounds of π-alkynol groups acting as four-electron donor ligands. Furthermore, they indicate that the structure of **2** and **3** is like that of $[OsH\{=C=CHR\}\{\eta^2\text{-}HC\equiv CR\}(P^iPr_3)_2]BF_4$ which, on the basis of an X-ray diffraction study on the acetylene derivative, has been described as a trigonal bipyramid with apical phosphines and inequivalent angles within the equatorial plane.[22]

In the ^1H NMR spectra in dichloromethane-d_2, the resonances corresponding to the H−C(sp)-proton of the alkynols appear at 9.91 (**2**) and 10.09 (**3**) ppm. These chemical shifts agree well with those found for the cyclopentadienyl complexes $[Os(\eta^5\text{-}C_5H_5)\{\eta^2\text{-}HC\equiv CC(OH)R_2\}(P^iPr_3)]PF_6$ (δ, 9.43 (R = Ph) and 9.17 (R = Me)). On the other hand, they are strongly shifted toward lower field with regard to the H−C(sp) resonances observed for the two-electron-donor alkynols of the compounds $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HC\equiv CC(OH)R_2\}(P^iPr_3)$ (δ, 4.32 (R = Ph) and 3.72 (R = Me)).[29] A similar relationship is observed between the $^{13}C\{^1H\}$ NMR spectra of these compounds. The C(sp) resonances are observed at 158.6 and 142.3 (**2**) and 163.0 and 138.0 (**3**) ppm, in agreement with the chemical shifts found for the cationic cyclopentadienyl complexes (δ, 179.0 and 146.0 (R = Ph) and 182.8 and 143.3 (R = Me)). However, they appear strongly shifted toward lower field with regard to those observed for $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HC\equiv CC(OH)R_2\}(P^iPr_3)$ (δ, 82.2 and 57.5 (R = Ph) and 69.1 and 49.6 (R = Me)).[30]

In agreement with a parallel disposition of the carbon−carbon triple bond of the alkynols with regard to the P−P direction, the $^{31}P\{^1H\}$ NMR spectra show AB spin systems centered at 32.9 (**2**) and 31.5 (**3**) ppm and defined by $\Delta\nu = 664$ Hz and $J_{A-B} = 117.9$ Hz (**2**) and $\Delta\nu = 956$ Hz and $J_{A-B} = 120.5$ Hz (**3**). This disposition imposes a high steric hindrance between the $C(OH)R_2$ substituents and one of the phosphines. As a result, the stability of **2** and **3** is very low. In solution at room temperature, both compounds decompose to give a complex mixture of unidentified species.

The hydride ligands display doublet of doublets at −3.89 (**2**) and −4.09 (**3**) ppm with H−P coupling constants of 29.7 and 22.2 (**2**) and 30.7 and 23.8 (**3**) Hz, in the ^1H NMR spectra, whereas the resonances corresponding to the C_β−H hydrogens of the hydroxyvinylidene ligands appear at 3.63 (**2**) and 2.64 (**3**) ppm as triplets with H−P coupling constants of about 4.5 Hz. In the $^{13}C\{^1H\}$ NMR spectra, the Os−C_α resonances of the η^1-carbon donor ligands are observed at 279.9 (**2**) and 282.4 (**3**) ppm, as triplets with C−P coupling constants of 14.4 and 15.1 Hz, respectively.

The hydroxy groups of the hydroxyvinylidene ligands of **2** and **3** are easily extracted from the organic skeletons by reaction with H^+. The hydroxyvinylidene-alkenylcarbyne transformation is accompanied by the release of the π-alkynol ligand from the osmium atom. The resulting highly unsaturated hydride-alkenylcarbyne species are stabilized by action of coordinating solvents. Thus, the treatment of dichloromethane solutions of **2** and **3** with 2 equiv of HBF_4 at 243 K, and the subsequent addition of water or acetonitrile, at room temperature, leads to $[OsH(\equiv CCH=CR_2)S_2(P^iPr_3)_2][BF_4]_2$ (R = Ph, S = H_2O (**4**), CH_3CN (**5**); R = Me, S = CH_3CN (**6**)), which are isolated in high yield according to eq 3.

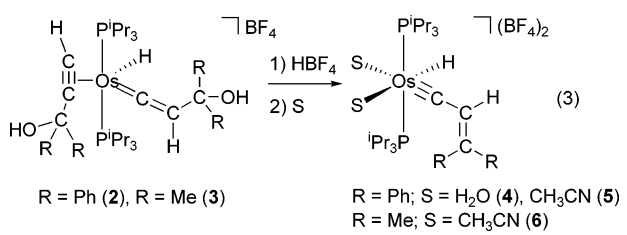


Figure 1 shows a view of the geometry of the cation of **4**. Selected bond distances and angles are listed in Table 1. The

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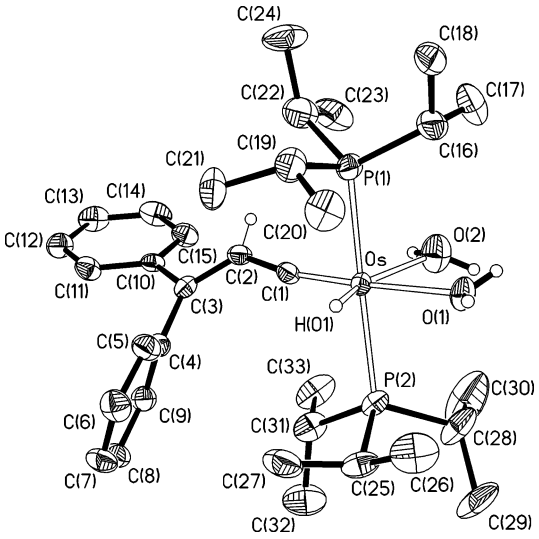


Figure 1. Molecular diagram of the cation of complex $[OsH\{\equiv CCH{=}CPh_2\}(H_2O)_2(P^iPr_3)_2][BF_4]_2$ (**4**).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[OsH(\equiv CCH{=}CPh_2)(H_2O)_2(P^iPr_3)_2][BF_4]_2$ (**4**)

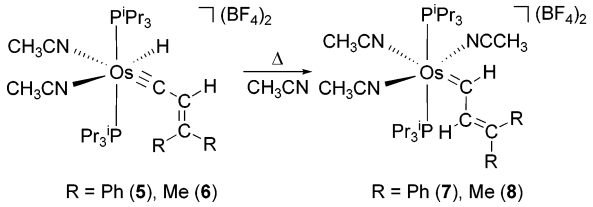
Os−P(1)	2.4197(17)	Os−C(1)	1.733(6)
Os−P(2)	2.4410(17)	C(1)−C(2)	1.406(8)
Os−O(1)	2.198(4)	C(2)−C(3)	1.352(8)
Os−O(2)	2.272(5)		
P(1)−Os−P(2)	170.16(6)	O(1)−Os−O(2)	77.12(18)
P(1)−Os−O(1)	88.30(13)	O(1)−Os−C(1)	176.5(2)
P(1)−Os−O(2)	94.50(15)	O(1)−Os−H(01)	78(3)
P(1)−Os−C(1)	90.5(2)	O(2)−Os−C(1)	99.7(2)
P(1)−Os−H(01)	82(3)	O(2)−Os−H(01)	155(3)
P(2)−Os−O(1)	85.86(13)	C(1)−Os−H(01)	105(3)
P(2)−Os−O(2)	91.91(15)	Os−C(1)−C(2)	168.0(5)
P(2)−Os−C(1)	95.7(2)	C(1)−C(2)−C(3)	128.6(6)
P(2)−Os−H(01)	89(3)		

coordination around the osmium atom can be rationalized as a distorted octahedron with the phosphorus atoms of the phosphine ligands occupying trans positions (P(1)−Os−P(2) = 170.16(6)°). The perpendicular plane is formed by the water molecules cis disposed (O(1)−Os−O(2) = 77.12(18)°), the hydride ligand trans disposed to O(2), and the carbyne group trans disposed to O(1) (O(1)−Os−C(1) = 176.5(2)°).

The most conspicuous feature of the structure is the very short Os−C(1) bond length of 1.733(6) Å, which is fully consistent with an Os−C(1) triple bond formulation.[31] Similarly to other carbyne-metal compounds,[32] a slight bending in the Os−C(1)−C(2) moiety is also present (Os−C(1)−C(2) = 168.0(5)°). The alkenyl carbyne proposal is supported by the bond lengths and angles within the η^1-carbon donor ligand; e.g., C(1) and C(2) are separated by 1.406(8) Å and C(2) and C(3), by 1.352(8) Å, and the angles around C(2) and C(3) are in the range 111°−128°.

In agreement with the presence of a hydride ligand in **4**−**6**, their ^{1}H NMR spectra in the high field region show triplets at −9.86 (**4**), −6.44 (**5**), and −6.66 (**6**) ppm, with H−P coupling constants of about 16 Hz. In the low field region the most noticeable signal is a singlet between 4.8 and 5.5 ppm corresponding to the C(sp^2)-H proton of the alkenyl group of the carbyne ligands. In the $^{13}C\{^1H\}$ spectra the Os−C$_\alpha$ resonances appear between 260 and 281 ppm, as triplets with C−P coupling constants of about 8 Hz. The $^{31}P\{^1H\}$ NMR spectra contain singlets between 25 and 50 ppm.

2. Formation and Characterization of $[Os(=CHCH=CR_2)(CH_3CN)_3(P^iPr_3)_2][BF_4]_2$ (R = Ph, Me). Dicationic alkenylcarbyne complexes are rare.[33] In the osmium chemistry, they have been previously isolated as half-sandwich derivatives.[34] As far as we know dicationic osmium-hydride-alkenylcarbyne complexes were unknown until now. In contrast to the neutral and monocationic derivatives previously reported, they show a high tendency to evolve into alkenylcarbene compounds. Thus, in acetonitrile under reflux, complexes **5** and **6** give rise to the dicationic alkenylcarbene derivatives $[Os(=CHCH=CR_2)(CH_3CN)_3(P^iPr_3)_2][BF_4]_2$ (R = Ph (**7**), Me (**8**)), which are isolated as green (**7**) and gray (**8**) solids in almost quantitative yield, according to eq 4.



(4)

Complexes **7** and **8** are also rare examples of dicationic species containing an Os−C double bond, in the osmium chemistry.[35] They were characterized by elemental analysis, IR, and ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. Complex **7** was further characterized by an X-ray crystallographic study. A view of the structure of the cation of this species is shown in Figure 2. Selected bond distances and angles are listed in Table 2.

The geometry around the osmium atom can be described as a distorted octahedron with the phosphorus atoms of the phosphine ligands occupying trans positions (P(1)−Os−P(2) = 173.95(4)°). The perpendicular plane is formed by the acetonitrile molecules *mer* disposed (N(1)−Os−N(3) = 174.97(14)°) and the carbene group trans disposed to N(2) (N(2)−Os−C(1) = 172.05(16)°).

In this case, the most noticeable feature of the structure is the Os−C(1) bond length of 1.890(5) Å, which supports the Os−C double bond formulation.[36] In agreement with the sp^2 hybridization at C(1), the angles around this atom are between 112(3)° and 132.0(3)°. The parameters of the alkenyl moiety agree well with those of **4**. The C(1)−C(2) distance is 1.428(6)

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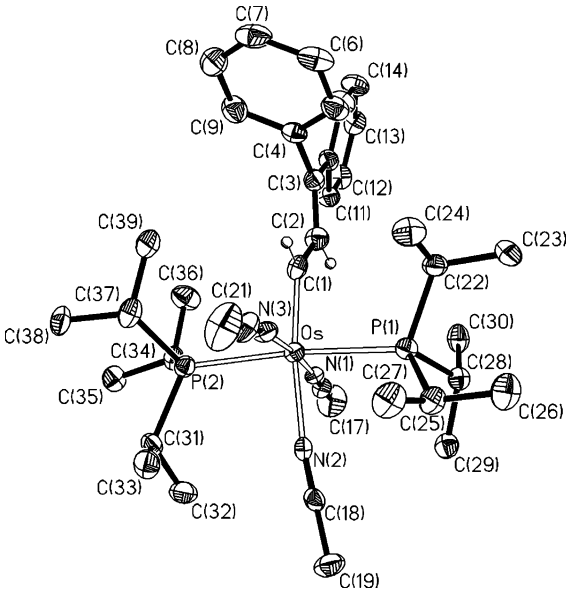

Figure 2. Molecular diagram of the cation of complex $[Os(=CHCH=CPh_2)(CH_3CN)_3(P^iPr_3)_2][BF_4]_2$ (**7**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Os(=CHCH=CPh_2)(CH_3CN)_3(P^iPr_3)_2][BF_4]_2$ (**7**)

Os−P(1)	2.4575(12)	Os−C(1)	1.890(5)
Os−P(2)	2.4638(12)	C(1)−C(2)	1.428(6)
Os−N(1)	2.003(3)	C(2)−C(3)	1.355(6)
Os−N(2)	2.129(3)		
Os−N(3)	2.011(3)		
P(1)−Os−P(2)	173.95(4)	N(1)−Os−N(2)	90.22(12)
P(1)−Os−N(1)	93.56(9)	N(1)−Os−N(3)	174.97(14)
P(1)−Os−N(2)	82.23(9)	N(1)−Os−C(1)	91.59(15)
P(1)−Os−N(3)	90.60(10)	N(2)−Os−N(3)	87.55(13)
P(1)−Os−C(1)	89.93(14)	N(2)−Os−C(1)	172.05(16)
P(2)−Os−N(1)	87.90(9)	N(3)−Os−C(1)	91.23(15)
P(2)−Os−N(2)	91.89(9)	Os−C(1)−C(2)	132.0(3)
P(2)−Os−N(3)	87.68(10)	C(1)−C(2)−C(3)	127.1(4)
P(2)−Os−C(1)	95.91(13)		

Å, whereas the C(2)−C(3) bond length is 1.355(6) Å, and the angles around C(2) and C(3) are in the range 116°−128°.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **7** and **8** are temperature dependent. Figure 3 shows the acetonitrile region of the $^1H\{^{31}P\}$ NMR spectrum of **7** in dichloromethane-d_2, as a function of the temperature. The spectrum of **8** is similar. According to Figure 2, the hydrogen and alkenyl substituents of the carbene carbon atom lie in the plane containing the nitrogen atoms. As a result, the acetonitrile molecules cis disposed to the alkenylcarbene ligand are chemically inequivalent. In agreement with this, the spectrum at 223 K contains three resonances for the acetonitrile methyl groups at 3.2 (cis to carbene), 2.95 (trans to carbene), and 2.88 (cis to carbene) ppm. On raising the temperature, the cis acetonitrile methyl resonances coalesce, until finally only one resonance is observed. This behavior can be understood as the result of the rotation of the alkenylcarbene ligand around the Os−C double bond.

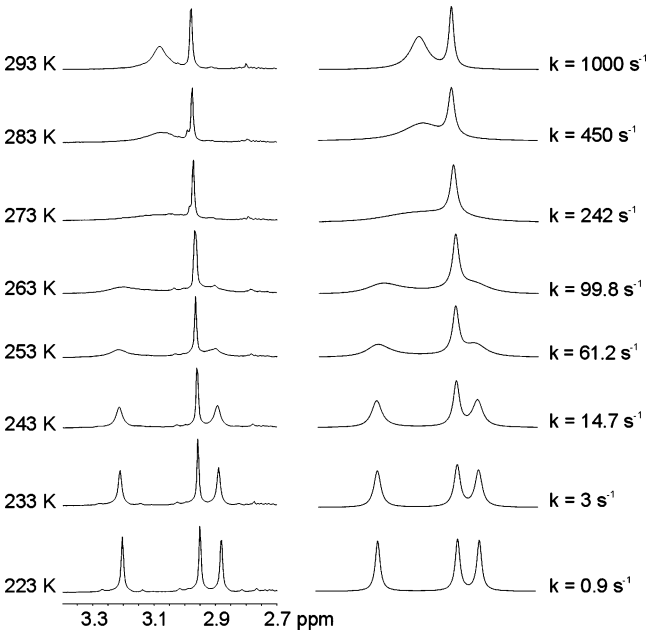

Figure 3. Variable-temperature $^1H\{^{31}P\}$ NMR spectra in the acetonitrile region of $[Os(=CHCH=CPh_2)(CH_3CN)_3(P^iPr_3)_2][BF_4]_2$ (**7**): experimental in CD_2Cl_2 (left) and calculated (right).

Line shape analysis of the *cis* acetonitrile methyl resonances of **7** and **8** allows the calculation of the rate constants for the rotation processes. The activation parameters obtained from the corresponding Eyring analysis are $\Delta H^{\ddagger} = 12.8 \pm 0.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -0.6 \pm 1.0$ cal mol^{-1} K^{-1} for **7** and $\Delta H^{\ddagger} = 13.7 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = 1.4 \pm 1.0$ cal mol^{-1} K^{-1} for **8**. The values of the activation entropy, near zero, are consistent with a rotational process, whereas the values of the activation enthalpy lie within the range reported for other transition-metal-carbene complexes[37] and indicate that the substituents of the alkenyl moiety have not any significant influence in the rotation.

In the ^1H NMR spectra the most noticeable resonances of the alkenylcarbene ligands are those corresponding to the C_α−H and C_β−H protons, which appear at 19.13 and 8.24 (**7**) and 19.04 and 7.57 (**8**) ppm, respectively, as doublets with H−H coupling constants of about 14 Hz. In the $^{13}C\{^1H\}$ NMR spectra the Os−C_α resonances are observed at 267.9 (**7**) and 265.3 (**8**) ppm, as triplets with C−P coupling constants of about 7 Hz. The $^{31}P\{^1H\}$ NMR spectra shows singlets at 3.1 (**7**) and 2.5 (**8**) ppm.

3. Mechanism of the Hydride-Alkenylcarbyne to Alkenylcarbene Transformation. The reactions shown in eq 4 were followed by ^1H NMR spectroscopy by measuring the appearance of the C_α−H resonance of the alkenylcarbene ligands of **7** and **8** as a function of time. As shown in Figure 4 for the transformation from **5** to **7**, in acetonitrile as solvent, the increases of **7** and **8** (with the corresponding decreases of **5** and **6**) are exponential functions of time, in agreement with *pseudo* first-order processes.

To determine the role of acetonitrile during these reactions, we have also followed the transformation from **5** to **7** in chloroform-*d* as solvent and in the presence of acetonitrile concentrations between 0.83 and 3.34 M. Interestingly, at 363

(36) For example, see: (a) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 1662. (b) Brumaghim, J. L.; Girolami, G. S. *Chem. Commun*. **1999**, 953. (c) Werner, H.; Stüer, W.; Wolf, J.; Laubender, M.; Weberndörfer, B.; Herbst-Irmer, R.; Lehmann, C. *Eur. J. Inorg. Chem*. **1999**, 1889. (d) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 2294. (e) Gusev, D. G.; Lough, A. J. *Organometallics* **2002**, *21*, 2601. (f) Weberndörfer, B.; Henig, G.; Hockless, D. C. R.; Bennett, M. A.; Werner, H. *Organometallics* **2003**, *22*, 744.

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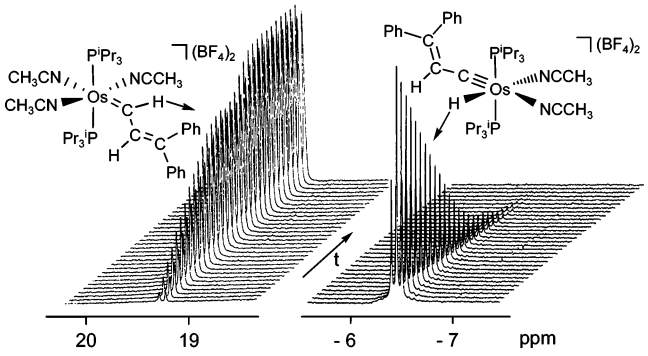


Figure 4. Stacked ^{1}H NMR spectra illustrating the transformation from **5** to **7** in CD_3CN at 323 K.

Table 3. Rate Constants for the Hydride-Alkenylcarbyne to Alkenylcarbene Transformations

			k_{obs} (10^5 s^{-1})		
T (K)	solvent	[CH_3CN]	**7**	**8**	**12**
313	CD_3CN		3.5 ± 0.03	1.0 ± 0.03	
323	CD_3CN		11.6 ± 0.1	3.4 ± 0.2	
333	CD_3CN		44.2 ± 0.5	9.6 ± 0.3	0.6 ± 0.01
333	$CDCl_3$	3.3	53.1 ± 0.4		
333	$CDCl_3$	2.1	42.9 ± 0.4		
333	$CDCl_3$	0.8	33.5 ± 1.3		
338	CD_3CN				1.1 ± 0.1
343	CD_3CN		137.0 ± 1.4	30.5 ± 0.4	1.8 ± 0.1
348	CD_3CN				4.1 ± 0.2
353	CD_3CN		264.5 ± 2.3	89.7 ± 0.5	6.4 ± 0.3

K, the value of k_{obs} for the reaction carried out in acetonitrile as solvent (4.4×10^{-4} s^{-1}) lies within the range of values found for the reactions carried out in chloroform-*d* and in the presence of acetonitrile, between 3.3×10^{-4} and 5.3×10^{-4} s^{-1}. This result clearly shows that the formation rates of the alkenylcarbene ligands of **7** and **8** are independent of the acetonitrile amount in the reaction medium. So, acetonitrile does not play any role in the formation of the alkenylcarbene ligands. Its role in the reactions is to trap the five-coordinate intermediates $[Os(=CHCH=CR_2)(CH_3CN)_2(P^iPr_3)_2]^{2+}$ (**9**), which are generated as a result of the 1,2-hydrogen shift from the osmium atom to the carbon atom of the carbyne ligands of **5** and **6**.

The values obtained for k_{obs} in the temperature range studied are collected in Table 3. The activation parameters for the formation of both **7** and **8** have been obtained from the corresponding Eyring analysis (Figure 5). The values found for the formation of **7**, $\Delta H^{\ddagger} = 23.8 \pm 1.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -2.8 \pm 2.3$ cal mol^{-1} K^{-1}, are similar to those obtained for the formation of **8**, $\Delta H^{\ddagger} = 23.9 \pm 1.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -5.3 \pm 2.3$ cal mol^{-1} K^{-1}. This indicates that the substituents of the alkenyl moiety of the alkenylcarbyne ligands have not any significant influence in the reaction shown in eq 4.

The slightly negative values of the activation entropy suggest that the insertion of the alkenylcarbyne ligands into the Os−H bond of **5** and **6** is an intramolecular process, which occurs by a concerted mechanism with a geometrically highly oriented transition state. To obtain information about the nature of this transition state, we have performed DFT calculations on the process shown in eq 4, using PH_3 and $CCH=CH_2$ as models of the triisopropylphosphine and alkenylcarbyne ligands, respectively (Figure 6).

The formation of the six-coordinate alkenylcarbene complex $[Os(=CHCH=CH_2)(CH_3CN)_3(PH_3)_2]^{2+}$ (**7t**) from the hydride-

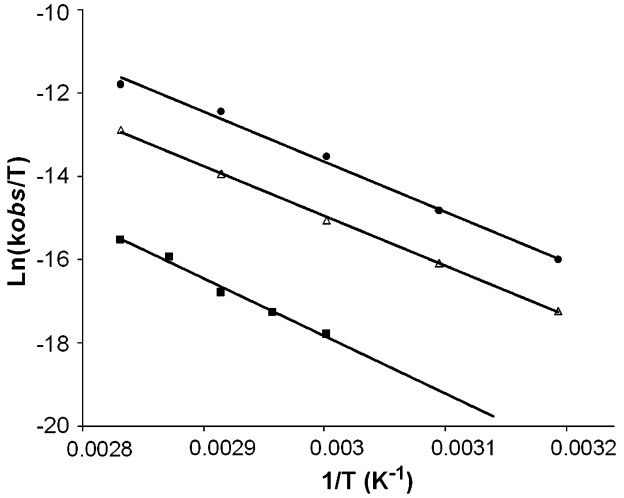


Figure 5. Eyring plot of k_{obs} for the formation of **7** (●), **8** (△), and **12** (■).

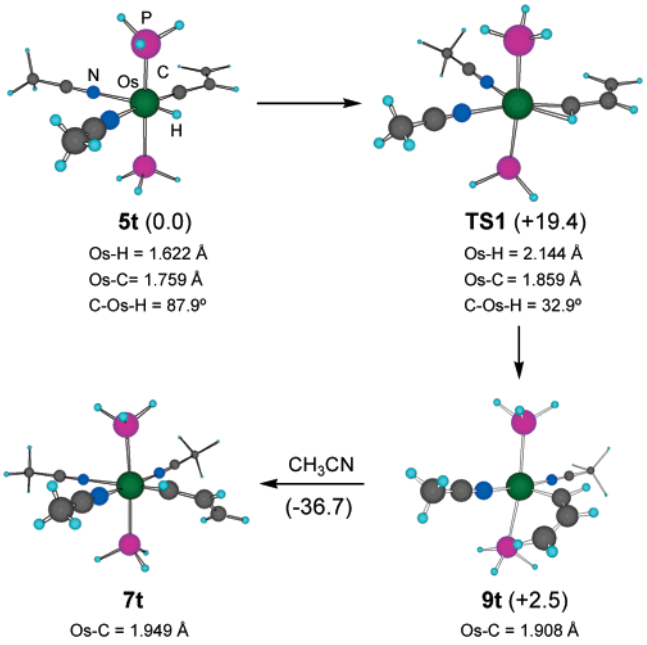


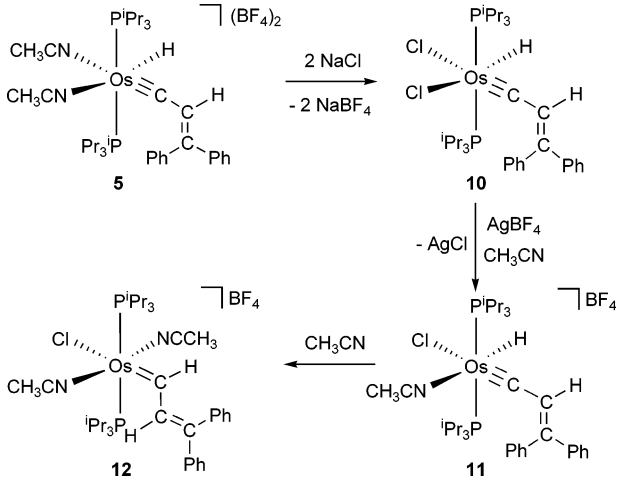
Figure 6. Optimized structures and relative energies (kcal mol^{-1}) of $[OsH(\equiv CCH=CH_2)(CH_3CN)_2(PH_3)_2]^{2+}$ (**5t**), $[Os(=CHCH=CH_2)(CH_3CN)_2(PH_3)_2]^{2+}$ (**9t**), $[Os(=CHCH=CH_2)(CH_3CN)_3(PH_3)_2]^{2+}$ (**7t**), and the transition state **TS1**.

alkenylcarbyne starting compound $[OsH(\equiv CCH=CH_2)(CH_3CN)_2(PH_3)_2]^{2+}$ (**5t**) takes place via the five-coordinate intermediate $[Os(=CHCH=CH_2)(CH_3CN)_2(PH_3)_2]^{+}$ (**9t**), which lies 2.5 kcal mol^{-1} above **5t**. The coordination of an acetonitrile molecule to **9t** is exothermic by 36.7 kcal mol^{-1}.

The geometry around the osmium atom of **9t** can be rationalized as a square pyramid with the alkenylcarbene ligand located at the apex, trans phosphines (169.0°) and trans acetonitriles (173.4°). The Os−C distance of 1.908 Å agrees well with that found by X-ray diffraction analysis for **7**.

The transition state **TS1** connecting **5t** with the intermediate **9t** was located. It results from the approach of the hydride ligand to the carbyne carbon atom in **5t**. As a consequence of the approach process the osmium-hydride-carbyne unit forms an (Os=C(R)H) system. The Os−C distance of 1.859 Å is 0.1 Å longer than that found in **5t** (1.759 Å) and 0.049 Å shorter than the calculated one in **9t**. The Os−H and C−H distances are

Scheme 1



2.144 and 1.165 Å, respectively, whereas the C−Os−H angle is 32.9°. This distorted η^2-coordination mode has been observed in alkylidene complexes of electron-deficient transition metals.[38] In agreement with the values obtained by ^{1}H NMR spectroscopy for the activation enthalpy of the reactions shown in eq 4, the energy of **TS1** is 19.4 kcal mol^{-1} above **5t**.

4. Influence of the Co-ligands on the Activation Parameters of the 1,2-Hydrogen Shift. Treatment of 2-propanol solutions of **5** with 5.0 equiv of NaCl produces the replacement of the acetonitrile molecules by chloride ligands. The substitution leads to OsHCl$_2$(≡CCH═CPh$_2$)(P^{i}Pr$_3$) (**10**), which is isolated as a green solid in 69%, according to Scheme 1.

The ^{1}H NMR spectrum of **10** in dichloromethane-d_2 shows a singlet at 4.91 ppm, due to the C$_\beta$−H proton of the alkenylcarbyne group. The hydride ligand gives rise to a triplet at −7.28 ppm, with a H−P coupling constant of 17.1 Hz. In the ^{13}C{^{1}H} NMR spectrum the Os−C$_\alpha$ resonance of the η^1-carbon donor ligand appears at 254.1 ppm, as a triplet with a C−P coupling constant of 10.8 Hz. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 18.3 ppm.

In acetonitrile as solvent, complex **10** reacts with 1.0 equiv of AgBF$_4$ to give the monocationic derivative [OsHCl(≡CCH═CPh$_2$)(CH$_3$CN)(P^{i}Pr$_3$)$_2$]BF$_4$ (**11**) as a result of the extraction of one of the chloride ligands and the coordination of an acetonitrile molecule. Complex **11** is isolated as an orange solid in 89% yield.

The ^{1}H NMR spectrum of **11** in dichloromethane-d_2 shows the C$_\beta$−H resonance corresponding to the alkenylcarbyne ligand at 5.14 ppm, as a singlet, whereas the hydride resonance appears at −6.51 ppm as a triplet with a H−P coupling constant of 16.8 Hz. In the ^{13}C{^{1}H} NMR spectrum the Os−C$_\alpha$ resonance is observed at 256.9 ppm, as a triplet with a C−P coupling of 13.2 Hz. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 25.5 ppm.

Like **5** and **6**, in acetonitrile under reflux, complex **11** evolves into an alkenylcarbene species, [OsCl(═CHCH═CPh$_2$)(CH$_3$CN)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (**12**), as a result of the 1,2-hydrogen shift of the hydride ligand from the osmium to the carbyne carbon atom. Complex **12** is isolated as a yellow solid in 91% yield.

(38) (a) Schultz, A. J.; Williams, J. M.; Schrock, R. R.; Rupprecht, G. A.; Fellmann, J. D. *J. Am. Chem. Soc.* **1979**, *101*, 1593. (b) Goddard, R. J.; Hoffmann, R.; Jemmis, E. D. *J. Am. Chem. Soc.* **1980**, *102*, 7667.

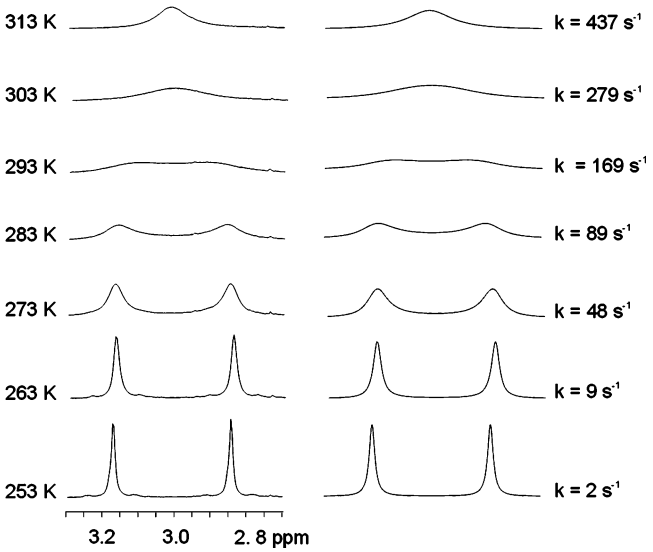


Figure 7. Variable-temperature ^{1}H{^{31}P} NMR spectra in the acetonitrile region of [OsCl(═CHCH═CPh$_2$)(CH$_3$CN)$_2$(P^{i}Pr$_3$)$_2$]BF$_4$ (**12**): experimental in CD$_2$Cl$_2$ (left) and calculated (right).

As a consequence of the inequivalence of the acetonitrile molecules and the rotation of the alkenylcarbene ligand around the Os−C double bond, the acetonitrile resonances of **12** are temperature dependent in the ^{1}H and ^{13}C{^{1}H} NMR spectra. Line shape analysis of the observed ones in the ^{1}H{^{31}P} NMR spectrum (Figure 7) allows the calculation of the rate constants for the rotation process. The activation parameters obtained from the corresponding Eyring analysis are $\Delta H^{\ddagger} = 13.3 \pm 0.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -3.2 \pm 1.3$ cal mol^{-1} K^{-1}. These values agree well with those obtained for **7** and **8**.

In the ^{1}H NMR spectrum of **12** in dichloromethane-d_2, the most noticeable resonances of the alkenylcarbene ligand are those due to the C$_\alpha$-H and C$_\beta$-H protons, which appear at 20.29 and 7.98 ppm, respectively, as doublets with a H−H coupling constant of 13.2 Hz. In the ^{13}C{^{1}H} NMR spectrum, the Os−C$_\alpha$ resonance is observed at 252.0 ppm, as a triplet with a C−P coupling constant of 8.3 Hz. The ^{31}P{^{1}H} NMR spectrum contains a singlet at −6.3 ppm.

The formation of **12** was followed by ^{1}H NMR spectroscopy (Table 3) by measuring the appearance of the C$_\alpha$−H resonance of the alkenylcarbene ligand as a function of time. The reaction is a first-order process, with activation parameters of $\Delta H^{\ddagger} = 27.6 \pm 3.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -0.4 \pm 4.8$ cal mol^{-1} K^{-1} (Figure 5). The value of the activation enthalpy, which is slightly higher than that obtained for the formation of **7**, suggests that, in **5**, the substitution of an acetonitrile molecule by a chloride ligand produces an increase of the activation barrier for the 1,2-hydrogen shift from the osmium to the carbyne carbon atom. This is also supported by DFT calculations (Figure 8).

The insertion of the alkenylcarbyne ligand into the Os−H bond of the model compound [OsHCl(≡CCH═CH$_2$)(CH$_3$CN)(PH$_3$)$_2$]$^+$ (**11t**) leads to the five-coordinate complex [OsCl(═CHCH═CH$_2$)(CH$_3$CN)(PH$_3$)$_2$]$^+$ (**13t**), which lies 1.9 kcal mol^{-1} above **11t**. The process takes place via the transition state **TS2**, which is 22.8 kcal mol^{-1} above **11t**. In agreement with the spectroscopic results, this value is slightly higher (3.2 kcal mol^{-1}) than the energy difference between **TS1** and **5t**.

The structure of the five-coordinate intermediate **13t** is similar to that of **9t** with P−Os−P and Cl−Os−N angles of 173.3°

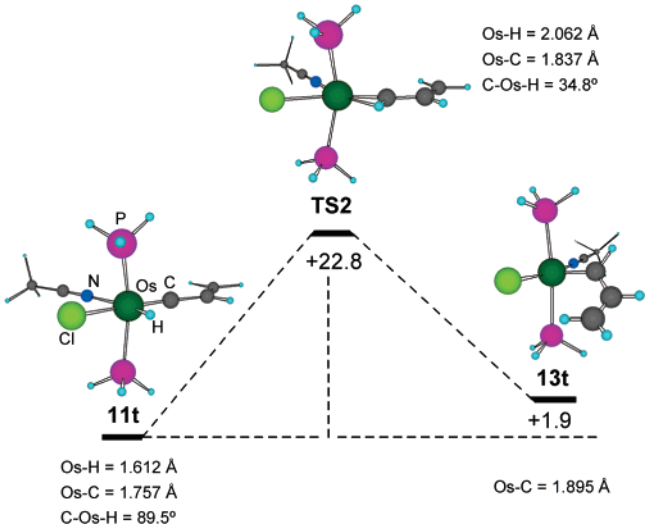


Figure 8. Optimized structures and relative energies (kcal mol^{-1}) of $[OsHCl(\equiv CCH{=}CH_2)(CH_3CN)(PH_3)_2]^+$ (**11t**), $[OsCl(=CHCH{=}CH_2)(CH_3CN)(PH_3)_2]^+$ (**13t**), and the transition state **TS2**.

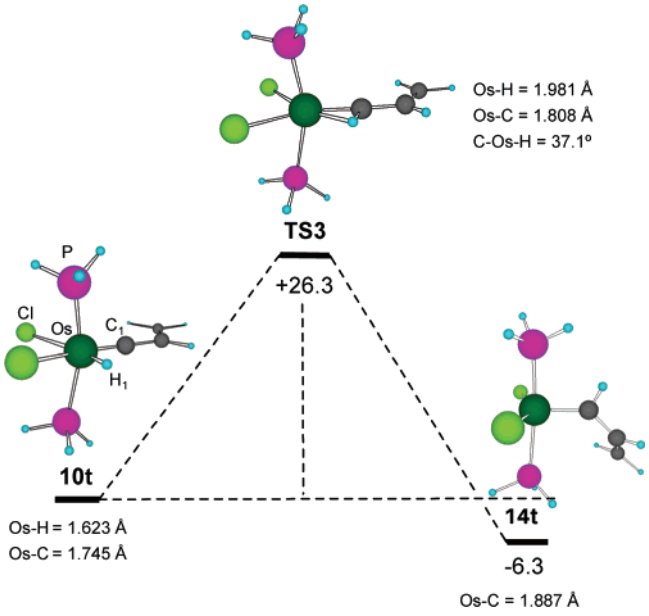
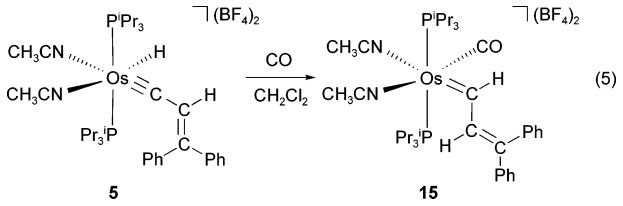


Figure 9. Optimized structures and relative energies (kcal mol^{-1}) of $OsHCl_2(\equiv CCH{=}CH_2)(PH_3)_2$ (**10t**), $OsCl_2(=CHCH{=}CH_2)(PH_3)_2$ (**14t**), and the transition state **TS3**.

and 159.4°, respectively, and an Os−C bond length of 1.895 Å. The geometry around the osmium atom of **TS2** also agrees well with that of **TS1**. As in the latter, the osmium-hydride-carbyne unit form an (Os=C(R)H) system with Os−C, Os−H, and C−H distances of 1.837, 2.062, and 1.185 Å, respectively, and a C−Os−H angle of 34.8°.

The replacement of the acetonitrile molecule of **11** by a chloride ligand (the substitution of the second acetonitrile molecule of **5** by a chloride ligand) produces a new increase of the activation barrier for the 1,2-hydrogen shift from the osmium to the carbyne carbon atom. Thus, DFT calculations show that the transformation of the model compound $OsHCl_2(\equiv CCH{=}CH_2)(PH_3)_2$ (**10t**) into the five-coordinate species $OsCl_2(=CHCH{=}CH_2)(PH_3)_2$ (**14t**) occurs via **TS3**, related to **TS1** and **TS2**, which lies 26.3 kcal mol^{-1} above **10t** (Figure 9). The height of the activation barrier in **10** makes impossible the hydride carbyne to carbene transformation from an experimental point of view, 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. In fact, in acetonitrile at 353 K complex **10** evolves into $[OsCl(=CHCH{=}CPh_2)(CH_3CN)_2(P^iPr_3)_2]Cl$ via $[OsHCl(\equiv CCH{=}CPh_2)(CH_3CN)(P^iPr_3)_2]Cl$.

The increase of the activation barrier is certainly a consequence of the increase of electron density on the metallic center. The substitution of an acetonitrile molecule in **5** by carbon monoxide, which in contrast to chloride is a π-acceptor ligand, produces a rapid hydride-carbyne to carbene transformation. Thus, at room temperature under carbon monoxide atmosphere, complex **5** affords $[Os(=CHCH{=}CPh_2)(CO)(CH_3CN)_2(P^iPr_3)_2][BF_4]_2$ (**15**), which is isolated as an orange solid in 90% yield according to eq 5.



(5)

The presence of a carbonyl ligand in **15** is strongly supported by its IR and $^{13}C\{^1H\}$ NMR spectrum. The IR spectrum in Nujol shows a ν(CO) band at 1970 cm^{-1}, whereas the $^{13}C\{^1H\}$ NMR spectrum in dichloromethane-d_2 contains a triplet at 179.8 ppm, with a C−P coupling constant of 8.3 Hz. The resonance due to the Os−C_α carbon atom of the alkenylcarbene appears at 270.5 ppm, also as a triplet but with a C−P coupling constant of 4.7 Hz. In agreement with the mutually cis disposition of the acetonitrile molecules, the spectrum also contains four resonances for these ligands at 134.8 and 128.1 (C≡N) and 4.3 and 4.0 (CH_3) ppm. The ^1H NMR spectrum is consistent with the $^{13}C\{^1H\}$ NMR spectrum. Thus it shows two acetonitrile methyl singlets at 2.81 and 2.74 ppm. The C_α−H and C_β−H resonances of the alkenylcarbene ligand are observed at 16.27 and 8.48 ppm, respectively, as doublets with a H−H coupling constant of 13.9 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 21.1 ppm. These spectra are temperature invariant between 183 and 333 K. This is in agreement with theoretical calculations on d^6 carbene-metal complexes, suggesting that a carbonyl ligand cis disposed to the carbene gives rise to high activation energy for the carbene rotation.[39]

The transformation from **5** to **15** has been also analyzed by means of DFT calculations (Figure 10). Initially, the reaction appears to involve the substitution of an acetonitrile molecule by the carbonyl group. From a thermodynamic point of view, the substitution of the acetonitrile ligand disposed trans to the hydride is favored with regard to the replacement of the acetonitrile molecule disposed trans to the Os−C triple bond. Thus, the *cis*-hydride-carbonyl isomer of the model compound $[OsH(\equiv CCH{=}CH_2)(CO)(CH_3CN)(PH_3)_2]^{2+}$ (**16t**) lies 7.6 kcal mol^{-1} above the trans isomer. The 1,2-hydrogen shift in the latter affords the five-coordinate derivative $[Os(=CHCH{=}CH_2)(CO)(CH_3CN)(PH_3)_2]^{2+}$ (**17t**). This species is 9.5 kcal mol^{-1} more stable than **16t-trans**. The migration takes place via the transition state **TS4**. Accordingly with the experimental observations the difference in energy between **TS4** and

(39) Maouche, B.; Volatron, F.; Jean, Y. *New J. Chem.* **1993**, *17*, 449.

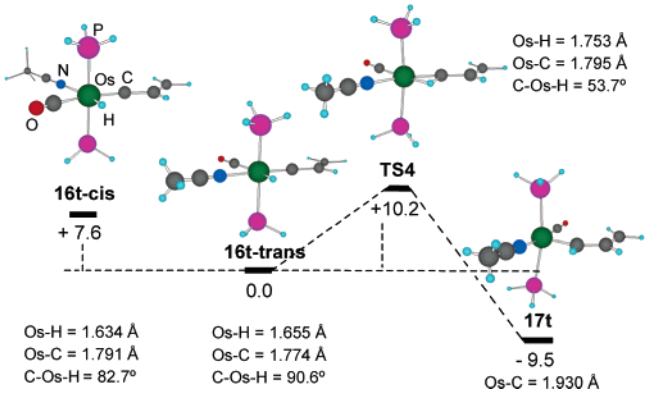


Figure 10. Optimized structures and relative energies (kcal mol^{-1}) of [OsH(≡CCH═CH$_2$)(CO)(CH$_3$CN)(PH$_3$)$_2$]$^{2+}$ (**16t**), [Os(═CHCH═CH$_2$)(CO)(CH$_3$CN)(PH$_3$)$_2$]$^{2+}$ (**17t**), and the transition state **TS4**.

16t-trans (10.2 kcal mol^{-1}) is significantly smaller than that between **TS1** and **5t** (19.4 kcal mol^{-1}).

Concluding Remarks

This study reveals that the elongated dihydrogen complex [Os{C$_6$H$_4$C(O)CH$_3$}{η^2-H$_2$)(H$_2$O)(P^{i}Pr$_3$)$_2$BF$_4$ is a synthon for the 12-valence electron monohydride [OsH(P^{i}Pr$_3$)$_2$]$^+$, which coordinates two alkynol molecules to afford the novel hydride-hydroxyvinyliedene-π-alkynol derivatives [OsH{═C═CHC(OH)R$_2$}{η^2-HC≡CC(OH)R$_2$}(P^{i}Pr$_3$)$_2$]BF$_4$ (R = Ph, Me), where the π-alkynol acts as a four-electron donor ligand.

These species are the entry to the dicationic hydride-alkenylcarbyne complexes [OsH(≡CCH═CR$_2$)S$_2$(P^{i}Pr$_3$)$_2$][BF$_4$]$_2$ (R = Ph, Me; S = H$_2$O, CH$_3$CN) which, in contrast to the previously reported neutral hydride-carbyne compounds OsHCl$_2$(≡C-alkyl)(P^{i}Pr$_3$)$_2$, undergo 1,2-hydrogen shift from the osmium to carbyne carbon atom. Thus, in acetonitrile, they evolve into the corresponding dicationic alkenylcarbene derivatives [Os(═CHCH═CR$_2$)(CH$_3$CN)$_3$(P^{i}Pr$_3$)$_2$][BF$_4$]$_2$.

Kinetic studies suggest that the formation of these six-coordinate alkenycarbene complexes takes place via the five-coordinate intermediates [Os(═CHCH═CR$_2$)(CH$_3$CN)$_2$(P^{i}Pr$_3$)$_2$]$^{2+}$, which coordinate an acetonitrile molecule. In agreement with the kinetic results, DFT calculations on the model system [OsH(≡CCH═CH$_2$)(CH$_3$CN)$_2$(PH$_3$)$_2$]$^{2+}$ have located the transition state connecting the hydride-alkenylcarbyne and five-coordinate alkenylcarbene intermediate [Os(═CHCH═CH$_2$)(CH$_3$CN)$_2$(PH$_3$)$_2$]$^{2+}$ at 19.4 kcal mol^{-1} above the starting compound. It can be described as an η^2-carbene species (Os═C(R)H).

The sequential substitution of acetonitrile molecules by chloride ligands in the dicationic hydride-alkenylcarbyne compounds produces a sequential increase of the activation energy for the hydride migration. This is a consequence of the gradual increase of the electron richness of the metal center. While two chloride ligands inhibit the hydride-alkenylcarbyne to carbene transformation, the latter is favored by a carbonyl group.

In conclusion, we show an easy access to novel dicationic hydride-alkenylcarbyne and alkenylcarbene complexes, study the mechanism of the transformation between both types of species, and analyze the influence of the coligands on the activation energy of the hydride-alkenylcarbyne to carbene transformation.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried according to the usual procedures and distilled under argon prior to use. The starting material [Os{C$_6$H$_4$C(O)CH$_3$}(η^2-H$_2$O)(P^{i}Pr$_3$)$_2$]BF$_4$ (**1**) was prepared according to the published method.[12] ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on a Varian Gemini 2000, a Bruker AXR 300, or a Bruker Avance 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}) or external H$_3$PO$_4$ (^{31}P{^{1}H}). Coupling constants, *J* and *N*, are given in hertz. Infrared spectra were run on a Perkin-Elmer 1730 spectrometer (Nujol mulls on polyethylene sheets). C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. Mass spectra analyses were performed with a VG Austospec instrument in LSIMS$^+$ mode, ions were produced with the standard Cs$^+$ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used in the matrix.

Preparation of [OsH{═C═CHC(OH)Ph$_2$}{η^2-HC≡CC(OH)Ph$_2$}(P^{i}Pr$_3$)$_2$]BF$_4$ (2). An orange solution of **1** (568 mg, 0.77 mmol) in 7 mL of dichloromethane was treated with 1,1-diphenyl-2-propyn-1-ol (401 mg, 1.92 mmol) and stirred for 1 min at room temperature. The resulting mixture was cooled to 243 K and concentrated to dryness. Subsequent addition of diethyl ether (5 mL) at 243 K caused the precipitation of an orange solid, which was washed with diethyl ether and dried in vacuo. Yield: 727 mg (93%). Anal. Calcd for C$_{48}$H$_{67}$BF$_4$O$_2$OsP$_2$: C, 56.80; H, 6.65. Found: C, 56.85; H, 6.67. IR (Nujol, cm^{-1}): ν(OH) 3461 (br); ν(OsH) 2119 (w); ν(BF) 1059 (vs). MS: *m*/*z* 928 [M + H]$^+$. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 293 K): δ 9.91 (d, J_{H-P} = 28.8, 1H, ≡CH), 7.70−7.07 (m, 20H, Ph), 4.22 (s, 1H, OH), 3.63 (t, J_{H-P} = 4.5, 1H, ═CH−), 3.27 and 2.79 (both m, 6H, PCH), 1.16 (dvt, *N* = 13.6, J_{H-H} = 7.0, 18H, PCHC*H*$_3$), 1.12 (s, 1H, OH),[40] 1.07 (dvt, *N* = 15.9, J_{H-H} = 6.9, 18H, PCHC*H*$_3$), −3.89 (dd, J_{H-P} = 29.7 and 22.2, 1H, OsH). ^{31}P{^{1}H} NMR (121.4 MHz, CD$_2$Cl$_2$, 293 K): δ 32.9 (AB spin system, $\Delta\nu$ = 664, J_{A-B} = 117.9, P^{i}Pr$_3$). ^{19}F NMR (282.3 MHz, CD$_2$Cl$_2$, 293 K): δ −152.8 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.4 MHz, CD$_2$Cl$_2$, 243 K): δ 279.9 (t, J_{C-P} = 14.4, Os═C), 158.6 (t, J_{C-P} = 2.3, ≡CR), 148.2 and 146.7 (both s, C$_{ipso}$—Ph), 147.4 and 141.1 (both s, C$_{ipso}$—Ph), 134.6−123.5 (all s, CH$_{Ph}$), 142.3 (s, ≡CH), 114.5 (t, J_{C-P} = 5.5, ═CH−), 81.9 (d, J_{C-P} = 7.4, C(OH)), 68.9 (s, C(OH)), 25.2 (br, PCH), 17.5 (br, PCH*C*H$_3$).

Preparation of [OsH{═C═CHC(OH)Me$_2$}{η^2-HC≡CC(OH)Me$_2$}(P^{i}Pr$_3$)$_2$]BF$_4$ (3). This complex was prepared as described for **2** starting from 305 mg (0.41 mmol) of **1** and 2-methyl-3-butyn-2-ol (101 μL, 1.03 mmol). A light brown solid was obtained. Yield: 300 mg (95%). Anal. Calcd for C$_{28}$H$_{59}$BF$_4$O$_2$OsP$_2$: C, 43.86; H, 7.76. Found: C, 43.91; H, 7.74. IR (Nujol, cm^{-1}): ν(OH) 3512 (br); ν(OsH) 2118 (w); ν(BF) 1056 (vs). MS: *m*/*z* 680 [M + H]$^+$. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 293 K): δ 10.09 (dd, J_{H-H} = 1.8, J_{H-P} = 29.4, 1H, ≡CH), 3.34 and 3.09 (both m, 6H, PCH), 2.94 (s, 1H, OH), 2.64 (t, J_{H-P} = 4.6, 1H, ═CH−), 1.78 and 1.60 (both s, 6H, CH$_3$), 1.36 (dvt, *N* = 13.6, J_{H-H} = 7.0, 18H, PCHC*H*$_3$), 1.65 (s, 1H, OH),[40] 1.18 (dvt, *N* = 15.4, J_{H-H} = 7.0, 18H, PCHC*H*$_3$), 1.08 and 1.04 (both s, 6H, CH$_3$), −4.09 (dd, J_{H-P} = 30.7 and 23.8, 1H, OsH). ^{31}P{^{1}H} NMR (121.4 MHz, CD$_2$Cl$_2$, 293 K): δ 31.5 (AB spin system, $\Delta\nu$ = 956, J_{A-B} = 120.5, P^{i}Pr$_3$). ^{19}F NMR (282.3 MHz, CD$_2$Cl$_2$, 293 K): δ −152.6 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (100.5 MHz, CD$_2$Cl$_2$, 243 K): δ 282.4 (t, J_{C-P} = 15.1, Os═C), 163.0 (t, J_{C-P} = 10.5, ≡CR), 138.0 (br, ≡CH), 116.0 (t, J_{C-P} = 6.0, ═CH−), 75.2 (d, J_{C-P} = 7.0, C(OH)), 65.8 (s, C(OH)), 34.0, 32.5, 31.1 and 30.0 (all s, CH$_3$), 23.6 (d, J_{C-P} = 29.1, PCH), 19.9 (s, PCH*C*H$_3$), 18.8 (d, J_{C-P} = 2.0, PCH*C*H$_3$).

(40) Masked by the triisopropylphosphine methyl resonances. Assigned on the basis of a correlated ^{1}H−^{13}C{^{1}H} HMBC experiment.

Preparation of [OsH(≡CCH═CPh$_2$)(H$_2$O)$_2$(P^{i}Pr$_3$)$_2$][BF$_4$]$_2$ (4).[41] An orange solution of **2** (150 mg, 0.15 mmol) in 5 mL of dichloromethane at 243 K was treated with HBF_4·OH_2 (22 μL, 0.30 mmol). Immediately, the reaction mixture became green. After 30 min at 243 K, the solvent was removed and the green residue was washed with diethyl ether and dried in vacuo. The crude product was recrystallized from a mixture CH_2Cl_2/Et_2O at 243 K to afford orange crystals of **4**. Yield: 65 mg (48%). IR (Nujol, cm^{-1}): ν(OH) 3423 (br); ν(OsH) 2166 (m); ν(C═C) 1541 (m); ν(BF) 1060 (vs). MS: *m*/*z* 723 [M − 2H$_2$O + F]$^+$, 563 [M − P^{i}Pr$_3$ − 2H$_2$O]$^+$. ^{1}H NMR (300 MHz, CD_2Cl_2, 233 K): δ 7.69−7.14 (m, 10H, Ph), 5.40 (s, 1H, ═CH−), 4.23 (br, 4H, H_2O), 2.38 (m, 6H, PCH), 1.25 (m, 36H, PCHC*H*$_3$), −9.86 (t, J_{H-P} = 15.7, 1H, OsH). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 46.1 (s). ^{19}F NMR (282.3 MHz, CD_2Cl_2, 293 K): δ −151.6 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.4 MHz, CD_2Cl_2, 293 K): δ 264.1 (br, Os≡C), 158.6 (s, ═*C*Ph$_2$), 137.7 and 138.8 (both s, C$_{ipso}$−Ph), 130.7, 130.5, 129.7, 128.7, 128.6 and 128.2 (all s, CH$_{Ph}$), 130.2 (s, −CH═), 24.9 (vt, *N* = 12.2, PCH), 18.5 and 18.3 (both s, PCH*C*H$_3$).

Preparation of [OsH(≡CCH═CPh$_2$)(CH$_3$CN)$_2$(P^{i}Pr$_3$)$_2$][BF$_4$]$_2$ (5). An orange solution of **2** (316 mg, 0.31 mmol) in 5 mL of dichloromethane at 243 K was treated with HBF_4·OEt_2 (85 μL, 0.62 mmol). Immediately, the reaction mixture became green. After 30 min at 243 K, the solvent was removed and the residue was washed with diethyl ether and dried in vacuo. The crude product was treated with 10 mL of acetonitrile and stirred for 4 h at room temperature. The brown solution was filtered through Celite and evaporated to dryness. Subsequent addition of diethyl ether caused the precipitation of a red solid, which was washed with diethyl ether and dried in vacuo. Yield: 250 mg (84%). Anal. Calcd for $C_{37}H_{60}B_2F_8N_2OsP_2$: C, 46.36; H, 6.31; N, 2.92. Found: C, 46.29; H, 6.67; N, 2.79. IR (Nujol, cm^{-1}): ν(C≡N) 2316 (w), 2286 (w); ν(OsH) 2151 (m); ν(C═C) 1531 (m); ν(BF) 1056 (vs). MS: *m*/*z* 960 [M + 2BF$_4$]$^+$. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.81−7.29 (m, 10H, Ph), 5.18 (s, 1H, ═CH−), 2.87 and 2.59 (s, 6H, CH_3CN), 2.51 (m, 6H, PCH), 1.39 (dvt, *N* = 14.8, J_{H-H} = 7.1, 18H, PCHC*H*$_3$), 1.35 (dvt, *N* = 14.9, J_{H-H} = 6.9, 18H, PCHC*H*$_3$), −6.44 (t, J_{H-P} = 15.9, 1H, OsH). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 30.2 (s). ^{19}F NMR (282.3 MHz, CD_2Cl_2, 293 K): δ −151.2 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.4 MHz, CD_2Cl_2, 293 K): δ 277.9 (t, J_{C-P} = 7.7, Os≡C), 169.7 (s, ═*C*Ph$_2$), 137.6 and 137.7 (both s, C$_{ipso}$−Ph), 135.3 (s, CN), 133.4, 133.1, 130.8, 129.6, 129.5, and 129.4 (all s, CH$_{Ph}$), 131.3 (d, J_{C-P} = 2.0, CN), 130.5 (s, −CH═), 27.7 (vt, *N* = 13.4, PCH), 19.0 and 18.8 (both s, PCH*C*H$_3$), 4.1 and 3.4 (both s, *C*H$_3$CN).

Preparation of [OsH(≡CCH═CMe$_2$)(CH$_3$CN)$_2$(P^{i}Pr$_3$)$_2$][BF$_4$]$_2$ (6). This complex was prepared as described for **5**, starting from **3** (150 mg, 0.20 mmol) and HBF_4·OEt_2 (53 μL, 0.40 mmol). A brown solid was obtained. Yield: 103 mg (63%). Anal. Calcd for $C_{27}H_{56}B_2F_8N_2OsP_2$: C, 38.86; H, 6.76; N, 3.36. Found: C, 39.36; H, 6.69; N, 3.54. IR (Nujol, cm^{-1}): ν(C≡N) 2321 (w), 2290 (w); ν(OsH) 2174 (m); ν(C═C) 1575 (m); ν(BF) 1054 (vs). MS: *m*/*z* 834 [M + H]$^+$, 599 [M − 2CH$_3$CN + F]$^+$. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 4.84 (s, 1H, ═CH−), 2.89 and 2.56 (both s, 6H, CH_3CN), 2.54 (m, 6H, PCH), 2.14 and 1.81 (both s, 6H, ═C(Me)$_2$), 1.44 (dvt, *N* = 15.0, J_{H-H} = 7.4, 18H, PCHC*H*$_3$), 1.39 (dvt, *N* = 14.8, J_{H-H} = 7.2, 18H, PCHC*H*$_3$), −6.66 (t, J_{H-P} = 15.6, 1H, OsH). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 29.1 (s). ^{19}F NMR (282.3 MHz, CD_2Cl_2, 293 K): δ −151.9 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.42 MHz, CD_2Cl_2, 293 K): δ 280.6 (t, J_{C-P} = 8.1, Os≡C), 178.9 (s, ═*C*Me$_2$), 136.2 and 131.5 (both s, CN), 133.7 (s, −CH═), 27.8 and 25.7 (both s, Me), 27.5 (vt, *N* = 13.6, PCH), 19.5 and 18.3 (both s, PCH*C*H$_3$), 4.4 and 3.7 (both s, *C*H$_3$CN).

Preparation of [Os(═CHCH═CPh$_2$)(CH$_3$CN)$_3$(P^{i}Pr$_3$)$_2$][BF$_4$]$_2$ (7). A red solution of **5** (600 mg, 0.63 mmol) in 12 mL of acetonitrile were heated under reflux for 2 h. The solution was filtered through Celite, and the solvent was removed in vacuo. The addition of diethyl ether to the resulting residue led to a green solid, which was washed with diethyl ether and dried in vacuo. Yield: 594 mg (95%). Anal. Calcd for $C_{39}H_{63}B_2F_8N_3OsP_2$: C, 46.86; H, 6.35; N, 4.20. Found: C, 46.64; H, 6.19; N, 4.20. IR (Nujol, cm^{-1}): ν(C≡N) 2323 (w), 2271 (w); ν(C═C) 1528 (m); ν(BF) 1055 (vs). MS: *m*/*z* 413 (M^{2+}). ^{1}H NMR (300 MHz, CD_2Cl_2, 233 K): δ 19.13 (d, J_{H-H} = 13.6, 1H, Os═CH), 8.24 (d, J_{H-H} = 13.6, 1H, −CH═), 7.71−7.18 (m, 10H, Ph), 3.20, 2.95 and 2.88 (all s, 9H, CH_3CN), 2.39 (m, 6H, PCH), 1.23 (br, 36H, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 3.1 (s). ^{19}F NMR (282.3 MHz, CD_2Cl_2, 293 K): δ −151.6 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.4 MHz, CD_2Cl_2, 233 K): δ 267.9 (t, J_{C-P} = 7.0, Os═CH), 149.2 (s, ═*C*Ph$_2$), 147.5 (s, −CH═), 140.9 and 139.6 (both s, C$_{ipso}$−Ph), 137.4, 125.4 and 124.4 (s, CN), 131.2, 130.0, 129.5, 128.8, 128.6 and 127.9 (all s, CH$_{Ph}$), 25.4 (br, PCH), 18.9 and 18.5 (both s, PCH*C*H$_3$), 4.8, 4.3 and 4.0 (all s, *C*H$_3$CN).

Preparation of [Os(═CHCH═CMe$_2$)(CH$_3$CN)$_3$(P^{i}Pr$_3$)$_2$][BF$_4$]$_2$ (8). This complex was prepared as described for **7** starting from 200 mg (0.24 mmol) of **6**. A gray solid was obtained. Yield: 206 mg (98%). Anal. Calcd for $C_{29}H_{59}B_2F_8N_3OsP_2$: C, 39.78; H, 6.79; N, 4.80. Found: C, 39.97; H, 6.69; N, 4.31. IR (Nujol, cm^{-1}): ν(C≡N) 2320 (w), 2276 (w); ν(C═C) 1577 (m); ν(BF) 1059 (vs). ^{1}H NMR (300 MHz, CD_2Cl_2, 233 K): δ 19.04 (d, J_{H-H} = 13.9, 1H, Os═CH), 7.57 (d, J_{H-H} = 13.9, 1H, −CH═), 3.02, 2.96 and 2.90 (all s, 9H, CH_3CN), 2.41 (br, 6H, PCH), 1.54 and 1.32 (both s, 6H, Me), 1.19 (m, 36H, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 2.5 (s). ^{19}F NMR (282.3 MHz, CD_2Cl_2, 293 K): δ −151.8 (br). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.4 MHz, CD_2Cl_2, 233 K): δ 265.3 (d, J_{C-P} = 7, Os═CH), 154.8 (s, ═*C*Me$_2$), 149.8 (s, −CH═), 135.8, 124.0 and 123.9 (all s, CN), 29.0 and 22.4 (both s, Me), 24.6 (vt, *N* = 12.4, PCH), 18.8 and 18.7 (both s, PCH*C*H$_3$), 4.9, 4.6 and 4.0 (all s, *C*H$_3$CN).

Preparation of OsHCl$_2$(≡CCH═CPh$_2$)(P^{i}Pr$_3$)$_2$ (10). A red solution of **5** (150 mg, 0.16 mmol) in 10 mL of 2-propanol were treated with sodium chloride (46 mg, 0.78 mmol). After stirring the mixture for 6 h at room temperature, the solvent was removed in vacuo. Then, 10 mL of dichloromethane were added, the suspension was filtered through Celite, and the filtrate was evaporated to dryness. The residue was washed with pentane to afford a light green solid. Yield: 83 mg (69%). Anal. Calcd for $C_{33}H_{54}Cl_2OsP_2$: C, 51.22; H, 7.03. Found: C, 51.12; H, 6.97. IR (Nujol, cm^{-1}): ν(OsH) 2168 (m); ν(C═C) 1536 (m). MS: *m*/*z* 774 (M$^+$), 739 [M − Cl]$^+$, 579 [M − Cl − P^{i}Pr$_3$]$^+$. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.70−7.25 (m, 10H, Ph), 4.91 (s, 1H, ═CH−), 2.60 (m, 6H, PCH), 1.35 (dvt, *N* = 13.3, J_{H-H} = 7.0, 18H, PCHC*H*$_3$), 1.33 (dvt, *N* = 13.5, J_{H-H} = 6.9, 18H, PCHC*H*$_3$), −7.28 (t, J_{H-P} = 17.1, 1H, OsH). ^{31}P{^{1}H} NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 18.3 (s). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.4 MHz, CD_2Cl_2, 293 K): δ 254.1 (t, J_{C-P} = 10.8, Os≡C), 157.2 (s, ═*C*Ph$_2$), 141.2 and 138.1 (s, C$_{ipso}$−Ph), 135.3 (s, −CH═), 131.2, 130.9, 130.2, 129.6, 129.1 and 128.5 (all s, CH$_{Ph}$), 27.9 (vt, *N* = 12.8, PCH), 19.9 and 19.2 (both s, PCH*C*H$_3$).

Preparation of [OsHCl(≡CCH═CPh$_2$)(CH$_3$CN)(P^{i}Pr$_3$)$_2$]BF$_4$ (11). A green solution of **10** (407 mg, 0.53 mmol) in 12 mL of acetonitrile was treated with $AgBF_4$ (102 mg, 0.53 mmol) in the absence of light. Immediately, the reaction mixture became orange. After stirring the mixture for 1 h at room temperature, the suspension was filtered through Celite and the filtrate was evaporated to dryness. The residue was washed with diethyl ether to afford an orange solid. Yield: 386 mg (89%). Anal. Calcd for $C_{35}H_{57}BF_4ClNOsP_2$: C, 48.53; H, 6.63; N, 1.62. Found: C, 48.29; H, 6.58; N, 1.44. IR (Nujol, cm^{-1}): ν(C≡N) 2313 (w); ν(OsH) 2178 (m); ν(C═C) 1532 (m) ν(BF) 1055 (vs). MS: *m*/*z* 739 [M − CH$_3$CN]$^+$, 579 [M − CH$_3$CN − P^{i}Pr$_3$]$^+$. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.79−7.04 (m, 10H, Ph), 5.14 (s, 1H, ═CH−

(41) All our attempts to achieve a valid elemental analysis determination for complex **4** were unsuccessful. Even when we tried with crystals of the same crop that was used for the X-ray diffraction study, we could not obtain a satisfactory value.

), 2.74 (s, 3H, CH_3CN), 2.69 (m, 6H, PCH), 1.37 (dvt, $N = 15.8$, $J_{H-H} = 7.2$, 18H, $PCHCH_3$), 1.34 (dvt, $N = 16.0$, $J_{H-H} = 7.2$, 18H, $PCHCH_3$), −6.51 (t, $J_{H-P} = 16.8$, 1H, OsH). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 25.5 (s). ^{19}F NMR (282.3 MHz, CD_2Cl_2, 293 K): δ −153.0 (br). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (75.4 MHz, CD_2Cl_2, 293 K): δ 256.9 (t, $J_{C-P} = 13.2$, Os≡C), 164.0 (s, $=CPh_2$), 138.9 and 138.2 (both s, C_{ipso}—Ph), 132.3, 132.2, 132.0, 129.5, 129.3 and 128.8 (all s, CH_{Ph}), 130.6 (s, —CH═), 128.8 (s, CN), 27.0 (vt, $N = 17.8$, PCH), 19.2 and 18.8 (both s, $PCHCH_3$), 3.8 (s, CH_3CN).

Preparation of $[OsCl(=CHCH=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (12). An orange solution of **11** (300 mg, 0.35 mmol) in 12 mL of acetonitrile was heated under reflux 5 h. The solution was filtered through Celite, and the solvent was removed in vacuo. The addition of diethyl ether to the resulting residue led to a yellow solid, which was washed with diethyl ether and dried in vacuo. Yield: 286 mg (91%). Anal. Calcd for $C_{39}H_{60}BF_4N_2ClOsP_2$: C, 48.98; H, 6.66; N, 3.09. Found: C, 48.48; H, 6.60; N, 3.01. IR (Nujol, cm^{-1}): ν(C≡N) 2323 (w), 2269 (w); ν(C═C) 1527 (m); ν(BF) 1061 (vs). MS: m/z 739 $[M - 2CH_3CN]^+$, 661 $[M - P^iPr_3]^+$, 579 $[M - 2CH_3CN - P^iPr_3]^+$. ^1H NMR (300 MHz, CD_2Cl_2, 233 K): δ 20.29 (d, $J_{H-H} = 13.2$, 1H, Os═CH), 7.98 (d, $J_{H-H} = 13.3$, 1H, —CH═), 7.65−7.21 (m, 10H, Ph), 3.18 and 2.85 (both s, 6H, CH_3CN), 2.48 (m, 6H, PCH), 1.20 (m, 36H, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ −6.3 (s). ^{19}F NMR (282.3 MHz, CD_2Cl_2, 293 K): δ −152.6 (br). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (75.4 MHz, CD_2Cl_2, 233 K): δ 252.0 (t, $J_{C-P} = 8.3$, Os═CH), 148.8 (s, —CH═), 143.1 and 142.4 (both s, C_{ipso}—Ph), 140.6 (s, $=CPh_2$), 129.8, 129.6, 128.62, 128.4, 127.7 and 127.6 (all s, CH_{Ph}), 123.0 and 122.7 (both s, CN), 24.9 (br, PCH), 19.1 and 18.6 (both s, $PCHCH_3$), 5.1 and 4.5 (both s, CH_3CN).

Preparation of $[Os(=CHCH=CPh_2)(CH_3CN)_2(CO)(P^iPr_3)_2][BF_4]_2$ (15). A solution of **5** (150 mg, 0.16 mmol) in 8 mL of dichloromethane was stirred under carbon monoxide atmosphere for 1 h. The color turned from red to orange, and the solution was filtered through Celite. The solvent was removed in vacuo. The residue was washed with diethyl ether to afford an orange solid. Yield: 130 mg (90%). Anal. Calcd for $C_{38}H_{60}B_2F_8N_2OOsP_2$: C, 46.26; H, 6.13; N, 2.84. Found: C, 46.15; H, 6.56; N, 2.93. IR (Nujol, cm^{-1}): ν(C≡N) 2323 (w), 2289 (w); ν(C═O) 1970 (s); ν(C═C) 1509 (m); ν(BF) 1059 (vs). MS: m/z 751 $[M - 2CH_3CN + F]^+$, 723 $[M - 2CH_3CN + F - CO]^+$. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 16.27 (d, $J_{H-H} = 13.9$, 1H, Os═CH), 8.48 (d, $J_{H-H} = 13.9$, 1H, —CH═), 7.77−7.17 (m, 10H, Ph), 2.81 and 2.74 (both s, 6H, CH_3CN), 2.52 (m, 6H, PCH), 1.32 (dvt, $N = 15.1$, $J_{H-H} = 7.0$, 18H, $PCHCH_3$), 1.31 (dvt, $N = 14.2$, $J_{H-H} = 7.0$, 18H, $PCHCH_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 21.1 (s). ^{19}F NMR (282.3 MHz, CD_2Cl_2, 293 K): δ −151.8 (br). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (75.4 MHz, CD_2Cl_2, 293 K): δ 270.5 (t, $J_{C-P} = 4.7$, Os═CH), 179.8 (t, $J_{C-P} = 8.3$, C≡O), 161.2 (s, $=CPh_2$), 148.6 (s, —CH═), 139.0 and 137.9 (both s, C_{ipso}—Ph), 134.8 and 128.1 (both s, CN), 133.7, 131.1, 130.8, 130.2, 129.2 and 128.9 (all s, CH_{Ph}), 26.3 (vt, $N = 12.7$, PCH), 19.5 and 18.8 (both s, $PCHCH_3$), 4.3 and 4.0 (both s, CH_3CN).

Kinetic Analysis for the Hydride-Alkenylcarbyne to Alkenylcarbene Transformations. Formation of **7**, **8**, and **12** was followed quantitatively by ^1H NMR spectroscopy in CD_3CN. The increase of the intensity of low field carbene-proton was measured automatically at intervals in a Varian Gemini 2000 spectrometer. Rate constants and errors were obtained fitting the data to an exponential decay function using the routine programs of the spectrometer. Activation parameters $\Delta H^‡$ and $\Delta S^‡$ were obtained by least-squares fit of the Eyring plot. Errors were computed according to published methods.[42]

Determination of the Rotational Barrier of Carbene Ligands of Complexes 7, 8, and 12. Complete line-shape analyses of the acetonitrile region of $^1H\{^{31}P\}$ NMR spectra of these compounds were achieved using the program gNMR (Cherwell Scientific Publishing Limited). The rate constants for various temperatures were obtained by fitting calculated to experimental spectra by full line-shape iterations. The transverse relaxation time, T_2, was estimated at the lowest temperature. Activation parameters $\Delta H^‡$ and $\Delta S^‡$ were obtained by least-squares fit of the Eyring plot. Errors were computed by published methods.[42]

Table 4. Crystal Data and Data Collection and Refinement for **4** and **7**

	4	**7**
	Crystal Data	
formula	$C_{33}H_{58}B_2F_8O_2OsP_2 \cdot CH_2Cl_2$	$C_{39}H_{63}B_2F_8N_3OsP_2$
molecular wt	997.48	999.68
color and habit	irregular block red	irregular block red
symmetry, space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/c$
a, Å	12.3817(8)	18.2946(17)
b, Å	11.1746(7)	10.9593(10)
c, Å	30.4532(19)	21.991(2)
β, deg	100.8100(10)	92.074(2)
V, Å^3	4138.7(5)	4406.2(7)
Z	4	4
D calcd, g cm^{-3}	1.601	1.507
	Data Collection and Refinement	
diffractometer	Bruker Smart APEX	
λ(Mo Kα), Å	0.710 73	
monochromator	graphite oriented	
scan type	ω scans	
μ, mm^{-1}	3.353	3.031
2θ, range deg	3, 57	3, 57
temp, K	100	100
no. of data collect	50 882	46 145
no. of unique data	10 313 ($R_{int} = 0.0544$)	10 876 ($R_{int} = 0.0730$)
no. of params/restrains	475/40	517/0
$R_1{}^a$ [$F^2 > 2\sigma(F^2)$]	0.0553	0.0392
$wR_2{}^b$ [all data]	0.1276	0.0564
S^c [all data]	1.103	0.819

[a] $R_1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $\omega R_2(F^2) = \{\Sigma[\omega(F_o^2 - F_c^2)^2]/\sigma\upsilon\beta\upsilon\Sigma[\omega(F_o^2)^2]\}^{1/2}$. [c] GOF $= S = \{\Sigma[(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

Computational Details. The calculations have been carried out using the Gaussian 03 computational package.[43] All the structures have been optimized using DFT and the B3LYP functional. The 6-31 g** basis set has been used for all the atoms but the Os,[44] where the LANL2DZ basis and pseudopotential has been used instead. The transition states found have been confirmed by frequency calculations, and the connection between the starting and final reactants has been checked by slightly perturbing the TS geometry toward the minima geometries and reoptimizing.

X-ray Analysis of 4 and 7. Two irregular crystals of size 0.38 × 0.10 × 0.08 mm^3 (**4**) and 0.34 × 0.10 × 0.04 mm^3 (**7**) were mounted on a Bruker Smart APEX CCD diffractometer at 100.0(2) K equipped with a normal focus, 2.4 kW sealed tube source (Molybdenum radiation, $\lambda = 0.710\ 73$ Å) operating at 50 kV and 30 mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s covering 0.3° in ω. The cell parameters were determined and refined by least-squares fit of 9710 (**4**) or 5041 (**7**) collected reflections. The first 100 frames were collected at the end of the data collection to monitor crystal decay. Absorption correction was performed with the SADABS program (this is based on the method of

(42) Morse, P. M.; Spencer, M. O.; Wilson, S. R.; Girolami; G. S. *Organometallics* **1994**, *13*, 1646.

(43) Pople, J. A. et al. *Gaussian 03*, revision B.05; Gaussian, Inc., Wallingford CT, 2004.

(44) Following the suggestion of one of the referees, we have checked the influence of an additional f polarization function on Os (see ref 45). The difference in energy between compound **10t** and **TS3** is 26.6 kcal mol^{-1}, only 0.3 kcal mol^{-1} higher than that reported in the text. No further recalculations have been made given the small difference found.

Blessing[46]). Lorentz and polarization corrections were also performed. The structures were solved by Patterson and Fourier methods and refined by full matrix least-squares using the Bruker SHELXTL program package[47] minimizing $\omega(F_o^2 - F_c^2)^2$. The hydrogen atoms were observed or calculated and refined riding to bonded carbon atoms. The hydride ligand of **4** was observed in the difference Fourier maps but not refined properly. Finally a restrained geometry was used for the last cycles of refinement. For **4** a molecule of dichloromethane was observed in the unit cell, and a molecule of BF_4 is disordered over two sites. Weighted R factors (R_w) and goodness of fit (S) are based on F^2, and conventional R factors are based on F. Crystal data and details of the data collection and refinement are given in Table 4.

(45) Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 111.
(46) Blessing, R. H. *Acta Crystallogr., Sect. A.* **1995**, *51*, 33.
(47) *SHELXTL* program v. 6.1; Bruker Analytical, X-ray Systems: Madison, Wisconsin, 2000.

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Supporting Information Available: Crystal structure determinations, including bond lengths and angles of compounds **4** and **7**. Full authors of ref 43. This material is available free of charge via the Internet at http://pubs.acs.org.

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