Dicationic Alkylidene-, Olefin-, and Alkoxyalkenylcarbene-Osmium Complexes Stabilized by a NHC-Ligand.

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RECEIVED DATE

Abstract

Complex $[Os(=CHPh)(CH_3CN)_4(IPr)](OTf)_2$ (**1**) (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolylidene; OTf = CF_3SO_3) exchange the alkylidene group with propylene to give styrene and $[Os(=CHCH_3)(CH_3CN)_4(IPr)](OTf)_2$ (**2**). The reaction of **1** with ethylene leads to $[Os(\eta^2\text{-}CH_2{=}CH_2)(CH_3CN)_4(IPr)](OTf)_2$ (**3**) via the propylene intermediate $[Os(\eta^2\text{-}CH_2{=}CHCH_3)(CH_3CN)_4(IPr)](OTf)_2$ (**4**). Acetoniltrile displaces the olefin ligand of both **3** and **4** to generate the pentakis(solvento) derivative $[Os(CH_3CN)_5(IPr)](OTf)_2$ (**5**). In 2-propanol and methanol, complex **5** reacts with 1,1-diphenyl-2-propyn-1-ol and 2-methyl-3-butyn-2-ol to yield the corresponding alkoxyalkenylcarbene compounds $[Os\{=C(OR)CH{=}CR'_2\}(CH_3CN)_4(IPr)](OTf)_2$ (R = $CH(CH_3)_2$; R' =

Ph (**6**), CH_3 (**7**). R = CH_3; R’ = Ph (**8**), CH_3 (**9**)). The X-ray structures of **4, 5**, and **6** are also reported.

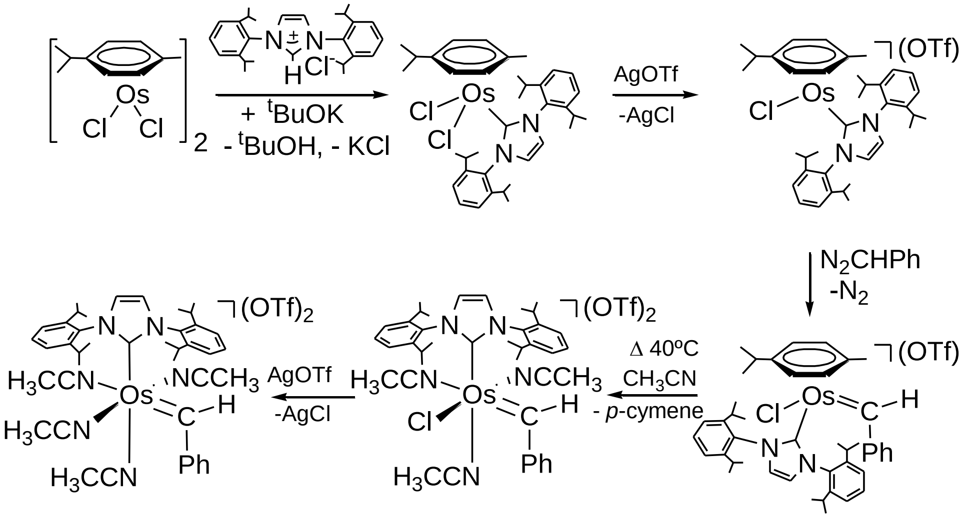
Introduction

Transition-metal complexes containing a metal-carbon double bond are tools of utmost importance in organic chemistry and organometallics, as they represent real catalysts or reactions intermediates for a number of highly valuable processes including carbon-carbon and carbon-heteroatom coupling reactions.[1]

Complexes $M{=}CR^1R^2$ have been traditionally divided into "Schrock-type" and "Fisher-type".[2] "Schrock-type" alkylidenes contain hydrogen and/or alkyl substituents and are viewed as a triplet-state carbene spin-coupled to two electrons on the metal center.[3] "Fisher-type" compounds contain heteroatom-stabilized carbene ligands and are best viewed as single-state carbene donating to the metal center from its sp^2-hybrid orbital, with a corresponding amount of back donation from the metal to the empty π-orbital. As a consequence of multiple bonding between the carbene carbon atom and the heteroatom, the metal carbon bond in this type is longer than a metal-carbon double bond might be expected to be and the carbon heteroatom bond is shorter than expected.[4]

N-Heterocyclic carbenes (NHCs) are cyclic "Fischer-type" ligands bearing at least one α-amino substituent.[5] Although there are significant differences between them, NHCs were initially introduced as analogues to phosphines.[6] During the last few years, their chemistry has experienced explosive development due to the design of diverse homogenous catalytic systems comprising such carbene ligands,[7] mainly ruthenium-catalyzed olefin metathesis[8] and palladium-catalyzed cross-coupling reactions.[9]

The findings with ruthenium have not awakened research interest in the third row counterpart, although osmium has provided catalysts for C-C bond formation[10] and affords stable models of reactive intermediate, proposed in catalytic transformations with ruthenium.[1h,11] As a consequence of this little attention, the NHC-osmium complexes are very scarce,[12] and the most of them have been recently reported.[13] In 2005, as a part of our work on half-sandwich transition-metal compounds,[11b,14] we report that the dimmer [(η^6-*p*-cymene)$OsCl_2$]$_2$ reacts with 1,3-bis(2,6-diisopropylphenyl)imidazolylidene (IPr) to give the mononuclear derivative (η^6-*p*-cymene)$OsCl_2$(IPr), which affords the alkylidene compound [(η^6-*p*-cymene)OsCl(=CHPh)(IPr)]OTf (OTf = CF_3SO_3) by treatment with AgOTf and subsequent addition of phenyldiazomethane to the corresponding 16-electron intermediate [(η^6-*p*-cymene)OsCl(IPr)]OTf.[13a] An alkylidene ligand promotes the dissociation of the arene from octahedral half-sandwich arene-osmium derivatives. Thus, subsequently, we noted that the complex [(η^6-*p*-cymene)OsCl(=CHPh)(IPr)]OTf were a useful starting material to prepare the tris- and tetrakis(solvento)-alkyliden-osmium derivatives, [OsCl(=CHPh)(CH_3CN)$_3$(IPr)]OTf and [Os(=CHPh)(CH_3CN)$_4$(IPr)](OTf)$_2$,[13f] according to Scheme 1. Now, we have studied the reactions of this tetrakis(solvento) complex with propylene and ethylene and observed the formation of new alkylidene- and olefin-tetrakis(solvento) compounds, which are transformed into alkoxyalkenylcarbene derivatives via the novel pentakis(solvento)species [Os(CH_3CN)$_5$(IPr)](OTf)$_2$.

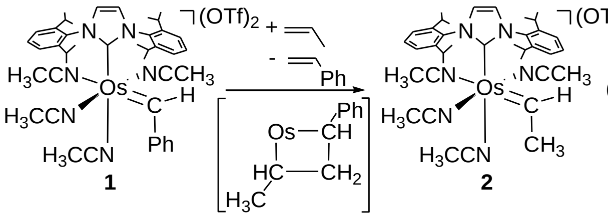


Scheme 1

This paper reports the preparation and characterization of new alkylidene-, olefin-, and alkoxyalkenylcarbene-osmium complexes stabilized with a NHC ligand.

Results and Discussion

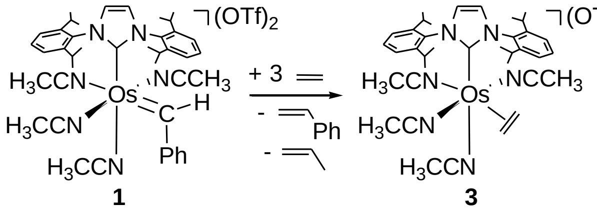
1. Alkylidene and olefin complexes. In dichloromethane at 40 ºC, complex $[Os(=CHPh)(CH_3CN)_4(IPr)](OTf)_2$ (**1**) undergoes alkylidene exchange under 2 atm of propylene to afford styrene and $[Os(=CHCH_3)(CH_3CN)_4(IPr)](OTf)_2$ (**2**)**,** which is isolated after 2 h as a pink solid in 85% yield, according to eq 1.



(1)

The ^1H and $^{13}C\{^1H\}$NMR spectra of **2** in dichloromethane-d_2 at room temperature strongly support the presence of an ethylidene group in the complex. In the ^1H NMR spectrum, this ligand displays at 19.90 ppm a quartet and at 1.01 ppm a doublet (J_{H-H} = 6.9 Hz) due to the CH and CH_3-protons, respectively. In the $^{13}C\{^1H\}$ NMR spectrum, the C(sp^2) and CH_3 resonances are observed at 303.0 and 49.5 ppm, respectively, as singlets. In agreement with **1**, the OsC signal of the NHC-ligand appears at 159.9 ppm.

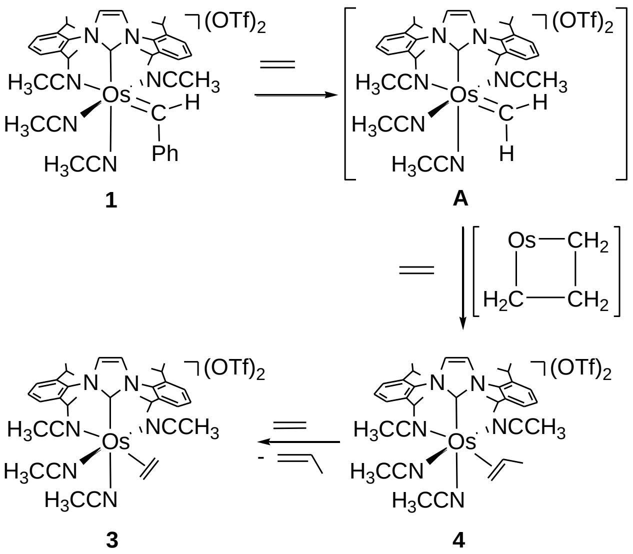
Complex **1** also reacts with ethylene. At 60 ºC under 3 atm of ethylene the dichloromethane solutions of **1** affords styrene, propylene and the ethylene complex $[Os(\eta^2\text{-}CH_2{=}CH_2)(CH_3CN)_4(IPr)](OTf)_2$ (**3**). The latter is isolated after 16 h as a white solid in 88% yield, according to eq 2.



(2)

The ^1H NMR spectrum of **3** in dichloromethane-d_2 at 253 K reveals the absence of any alkylidene resonance and shows at 3.17 ppm a singlet corresponding to the coordinated ethylene molecule. In the $^{13}C\{^1H\}$ NMR spectrum, the olefin gives rise to a singlet at 53.3 ppm. The OsC resonance of the NHC-ligand is observed at 144.3 ppm.

The formation of **3** can be rationalized according to Scheme 2. Under the reaction conditions, complex **1** undergoes an initial alkylidene exchange with ethylene to give styrene and to afford the undetected methylidene $[Os(=CH_2)(CH_3CN)_4(IPr)](OTf)_2$ (**A**). In the absence of an alkyl substituent, the alkylidene increases its reactivity. Thus, in contrast to **2**, the methylidene **A** reacts with a second molecule of olefine to give the propylene derivative $[Os(\eta^2\text{-}CH_2=CHCH_3)(CH_3CN)_4(IPr)](OTf)_2$ (**4**). This species result from a metallacyclobutene intermediate, which undergoes β-hydrogen-elimination and subsequent reductive elimination rather than a metathesis process.[15] Complex **4** can be isolated as a white solid in 80% yield, when the dichloromethane solutions of **1** are stirred under 2 atm of ethylene at 40 ºC for 2 h. At 60 ºC, under 3 atm of ethylene, the propylene ligand of **4** is displaced by ethylene. After 16 h, the ethylene derivative **3** is formed in quantitative yield.



Scheme 2

Complex **4** has been characterized by elemental analysis, IR, and ^1H, and $^{13}C\{^1H\}$ NMR spectroscopy, and by X-ray diffraction analysis. Figure 1 shows a view of the cation of this compound. The coordination geometry around the osmium atom can be rationalized as a distorted octahedron with the olefin molecule *cis* disposed to the NHC ligand. In the ^1H NMR spectrum in dichloromethane-d_2 at 253 K, the coordinated propylene displays at 3.81 ppm a double doublet of quartets due to the CHMe-olefin proton, with $J_{H\text{-}HMe}$, $J_{H\text{-}Hcis}$, and $J_{H\text{-}Htrans}$ coupling constants of 6.0, 8.8 and 12.8 Hz respectively, at

3.13 and 2.99 ppm doublets corresponding to H_{cis} and H_{trans} of the CH_2 group, and at 1.48 ppm a doublet assigned to the methyl protons. In the $^{13}C\{^1H\}$ NMR spectrum the C(sp^2) olefinic resonances appear at 72.6 and 52.6 ppm. In agreement with **3**, the OsC resonance of IPr is observed at 145.5 ppm.

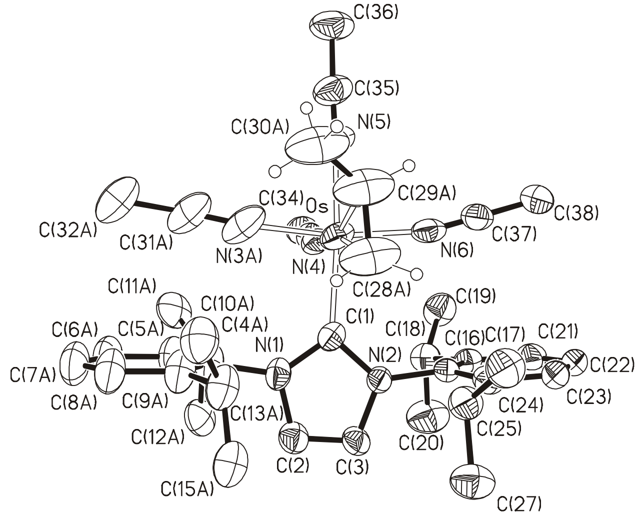
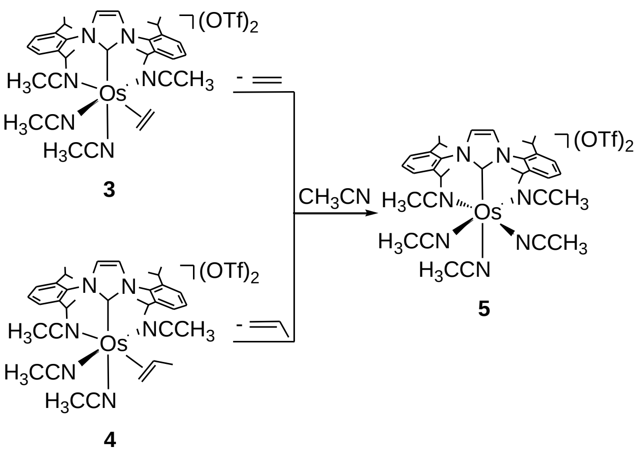


Figure 1. Molecular diagram of the cation of **4**. Selected bond lengths (Å) and angles (deg): Os–C(28A) 2.200(9), Os–C(29A) 2.28(3), C(28A)–C(29A) 1.371(15), Os–C(1) 2.115(7); N(5)–Os–C(1) 168.7(3).

2. Alkoxyalkenylcarbene complexes. Acetonitrile displaces the coordinated olefin molecules of **3** and **4**. Under 1 atm of argon, the stirring at 80 ºC of acetonitrile solutions of both complexes leads after 16 h to the novel pentakis(acetonitrile) derivative $[Os(CH_3CN)_5(IPr)](OTf)_2$ **(5)**, as a result of the release of the olefins and the coordination of a solvent molecule. This pentakis(solvento) derivative is isolated as a white solid in almost quantitative yield, according to Scheme 3.



Scheme 3

Complex **5** is the NHC-Os counterpart to the previously reported Ru-phosphine derivative $[Ru(CH_3CN)_5(PPh_3)](OTf)_2$.[16] Like the latter, it has been characterized by X-ray diffraction analysis. Figure 2 shows a view of the geometry of the cation of this compound. The coordination polyhedron around the osmium atom can be described as a distorted octahedron. The four Os−N bond lengths *cis* to the NHC ligand (2.004(10)-2.032(9) Å) are slight shorter than the one *trans* to the IPr group (2.053(10) Å). The separation between the metal center and the NHC ligand, Os−C(11) = 2.071 (9) Å, agrees well with that found in **4** (Os–C(1) = 2.115(7) Å) and those previously reported for Os-NHC complexes with normal coordination of the NHC unit.[13a,f,g,l,m] The most noticeable spectroscopic feature of **5** is a singlet at 151.3 ppm in the $^{13}C\{^1H\}$ NMR spectrum, corresponding to the OsC resonance of the NHC group.

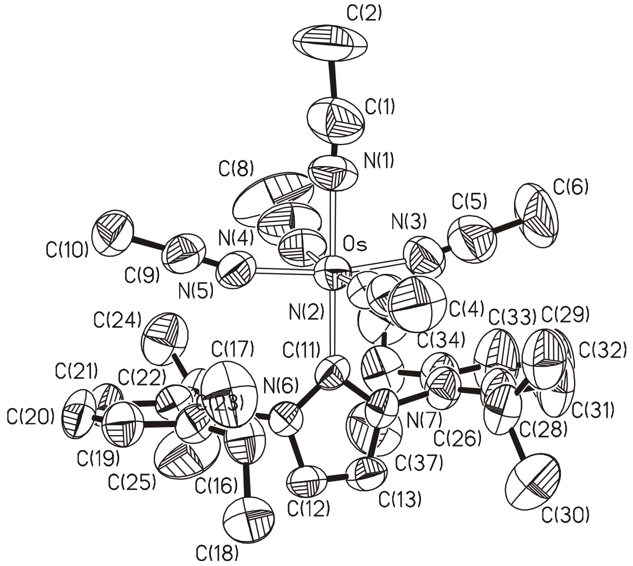
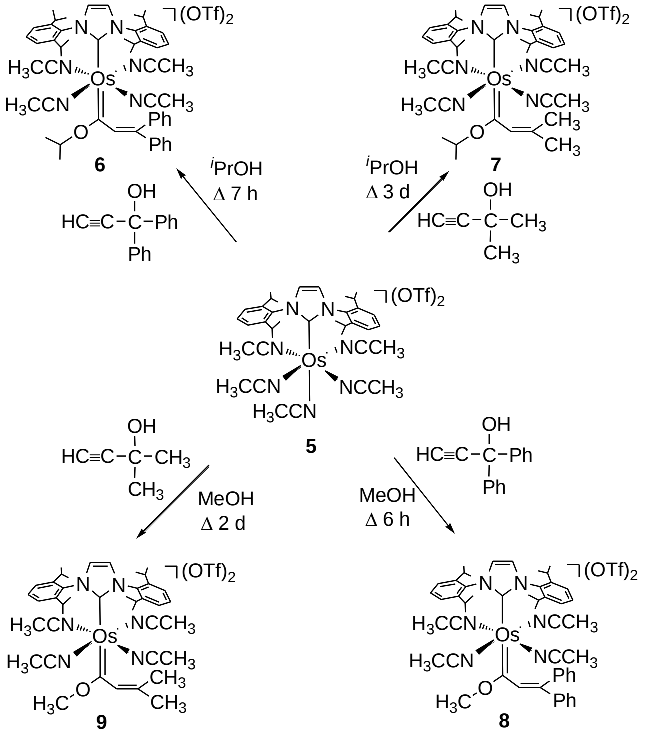


Figure 2. Molecular diagram of the cation of **5**. Selected bond lengths (Å) and angles (deg): Os–N(1) 2.053(10), Os–N(2) 2.018(8), Os–N(3) 2.004(10), Os–N(4) 2.031(9), Os–N(5) 2.032(9); Os–C(11) 2.071(9), N(1)–Os–C(11) 176.5(3).

Complex **5** is a useful material to prepare by a one pot synthesis procedure alkoxyalkenylcarbene derivatives, starting from alkynols and using alcohols as solvent. Thus, under reflux, the treatment of 2-propanol and methanol solutions of this compound with 3.0 eq. of 1,1-diphenyl-2-propyn-1-ol and 2-methyl-3-butyn-2-ol leads to [Os{=C(OR)CH=CR'$_2$}(CH_3CN)$_4$(IPr)](OTf)$_2$ (R = CH(CH_3)$_2$; R' = Ph (**6**), CH_3 (**7**). R = CH_3; R' = Ph (**8**), CH_3 (**9**)), which are isolated as orange (**6** and **8**) and yellow (**7** and **9**) solids in 40-79% yield, according to Scheme 4. The reactions times depends upon the solvent and the alkynol. In methanol the reactions are faster than in 2-propanol, whereas they are faster with 1,1-diphenyl-2-propyn-1-ol than with 2-methyl-3-butyn-2-ol.



Scheme 4

Complexes **6-9** have been characterized by elemental analysis, IR, and ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy. Complex **6** was further characterized by an X-ray crystallographic study. A view of the molecular geometry of the cation of the BF_4 salt is shown in Figure 3.

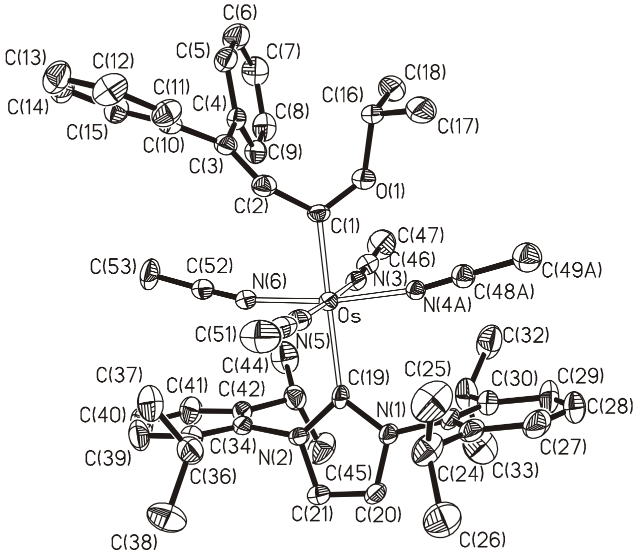


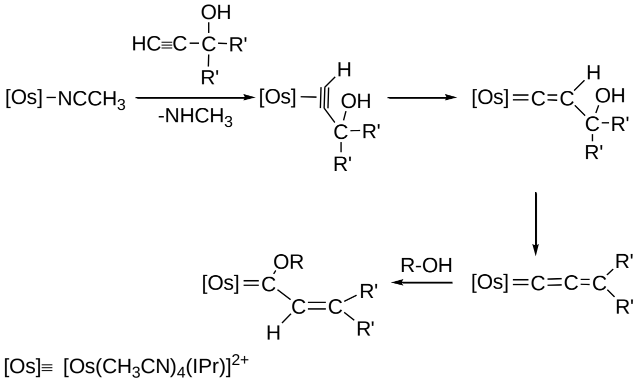
Figure 3. Molecular diagram of the cation of **6**. Selected bond lengths (Å) and angles (deg): Os–C(19) 2.186(5), Os–C(1) 1.995(5), C(1)–C(2) 1.470(7), C(2)–C(3) 1.353(7); C(1)–Os–C(19) 176.48(18), O(1)–C(1)–C(2) 119.8(4), O(1)–C(1)–Os 117.0(3), C(2)–C(1)–Os 123.2(3), C(3)–C(2)–C(1) 129.9(5), C(3)–C(2)–H(2) 115.1, C(1)–C(2)–H(2) 115.1.

The coordination geometry around the osmium atom can be rationalized as a distorted octahedron. In contrast to alkylidene complexes **1** and **2**, the carbon donor ligands are mutually *trans* disposed (C(1)-Os-C(19) = 176.48(18) Å). The difference in disposition of the alkoxyalkenylcarbene ligand with regard to the alkylidene groups of **1** and **2** seems to be a consequence of the bigger steric requirement of the first of them, which would experience a large steric hindrance with the NHC ligand when both of them are mutually *cis* disposed. As expected the methoxy substituent at the carbene carbon atom produces a slight extension of the Os–C double bond in **6**, which is revealed when the Os-C(1) bond length is compared with the Os–C distances in simple alkenylcarbene derivatives. Thus, its value of 1.995(5) Å is similar to those found in the previously reported osmium-alkoxycarbene complexes (1.921(4)-2.034(7)

Å)[17] and about 0.1 Å longer than the Os–C double bond distances in the complexes $[OsH(=CHCH=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (1.892(8) Å),[18] $[Os\{\kappa^1\text{-}OC(O)CH_3\}(=CHCH=CPh_2)(CH_3CN)_2(P^iPr_3)_2]BF_4$ (1.909(3)Å)[19] or $[Os(=CHCH=CPh_2)(CH_3CN)_3(P^iPr_3)_2]BF_4$ (1.890(5) Å).[20] According to the sp^2 hybridization at C(1), the angles around this atom are between 117.0(3)° and 123.2(3)°. The parameters of the alkenyl moiety agree well with those of other alkenylcarbene complexes.[18-21] The C(1)-C(2) distance is 1.470(7) Å, whereas the C(2)-C(3) bond length is 1.353(7) Å, and the angles around C(2) and C(3) are in the range 115-130°. The Os-C(19) bond length of 2.186(5) compares well with the Os-NHC separations in **4** and **5**. In addition it should be noted that is about 0.2 Å longer than the Os-C(1) bond length, in agreement with the presence of two heteroatoms with π-electrons at the carbene carbon atom.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **6-9** in dichloromethane-d_2 at room temperature are consistents with the structure shown in Figure 3. In the ^1H NMR spectra the most noticeable resonance is a singlet at about 5.6 ppm for the methyl derivatives **7** and **9** and at about 6.3 ppm for the phenyl compound **6** and **8,** corresponding to the vinyl CH-proton of the alkenyl unit of the alkoxycarbenes. The $^{13}C\{^1H\}$ NMR spectra show the OsC resonances of these ligands between 283 and 291 ppm, whereas the olefinic resonances of the alkenyl units are observed in the ranges 134-136 (CH) ppm and 137-140 (CR_2) ppm. The OsC resonances of the NHC ligand appear between 166 and 168 ppm.

Complexes **6-9** are the result of the addition of the O-H bond of the solvent to the C_α-C_β double bond of allenylidene[22] intermediates, which are formed according to Scheme 5. EHT-MO calculations indicate that the carbon atoms of the unsaturated chain are alternatively electron-poor and electron-rich, starting from the metal center.[23] Hence electrophilic centers are located at the C_α and the C_γ atoms, while the C_β atom is a nuclephilic site. The type of nucleophilic addition and its regioselectivity is controlled by the electronic and steric properties of the auxiliary ligands on the metal.[24] Thus, electrophilic metal centers with little steric demanding ligands enhances the reactivity associated with the allenylidene spine and favor the addition of the alcohol O-H bond to the C_α-C_β double bond.[25] The coordination of the basic and bulky triisopropylphosphine to osmium inhibits the O-H addition and stabilizes the allenylidene ligand as $[Os(=C=C=CPh_2)(CH_3CN)_3(IPr)(P^iPr_3)]^{2+}$.[131]



Scheme 5

Concluding Remarks.

This study has revealed the ability of the $[Os(CH_3CN)_4(IPr)]^{2+}$ unit to stabilize novel dicationic alkylidene, olefin and alkoxyalkenylcarbene derivatives.

Cation $[Os(=CHPh)(CH_3CN)_4(IPr)]^{2+}$ exchanges the alkylidene group with propylene and ethylene to afford propylidene and methylidene species, respectively. The presence of an alkyl substituent in the alkylidene increases its inertia. Thus, while the first of them is stable, the second one undergoes a [2 + 2] cycloaddition with a new ethylene molecule to give a metallacyclobutane intermediate, which evolves by β-hydrogen elimination and subsequent reductive elimination into a η^2-propylene derivative. Acetonitrile displaces the olefin of the latter and the resulting pentakis(solvento) compound reacts with alkynols in alcohols, as solvent, to give alkoxyalkenylcarbene complexes via allenylidene intermediates.

In conclusion, the 1,3-bis(2,6-diisopropylphenyl)imidazolylidene ligand has a great capacity to stabilize Os-olefin and Os-C double bonds in strongly electrophilic metal fragments, including tetra(solvento) dicationic osmium species.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Organic solvents were dried by standard procedures and distilled under argon prior to use. The starting material **1**, was prepared as previously described in the literature.[19] ^{1}H, and ^{13}C{^{1}H} NMR spectra were recorded on either a Bruker ARX 300, Bruker Avance 300, a Bruker Avance 400, or a Bruker Avance 500 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}). Coupling constants, J 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 either in a Perkin-Elmer 2400 CHNS/O analyzer or a Fisons EA-1108 apparatus.

Preparation of [Os(=CHCH$_3$)(CH$_3$CN)$_4$(IPr)](OTf)$_2$ (2): In a Fisher-Porter reactor, a blue solution of [Os(=CHPh)(CH$_3$CN)$_4$(IPr)](OTf)$_2$ (**1**) (300 mg, 0.265 mmol) in 20 ml of dichloromethane was stirred under 2 atm of propylene at 40 ºC for 2 h. The resulting pink solution was filtrated through celite and evaporated to dryness. The subsequent addition of diethyl ether caused the precipitation of a pink solid which was washed with diethyl ether (3 x 4 mL) and dried in vacuo. Yield: 240 mg (85 %). Anal. Calcd. for $C_{39}H_{52}F_6N_6O_6OsS_2$: C, 43.81; H, 4.90; N, 7.86; S, 6.00. Found: C, 43.73; H, 5.15; N, 7.69; S, 6.29. IR (cm^{-1}): ν(CH$_3$CN) 2303 and 2283 (w); ν_a(SO$_3$) 1261 (s); ν_s(CF$_3$) 1224 (m); ν_a(CF$_3$) 1150 (s); ν_s(SO$_3$) 1029 (s); δ_a(SO$_3$) 637 (s). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 293 K): δ 19.90 (q, $J_{H\text{-}H}$ = 6.9, 1H, Os=CH), 7.6-7.4 (6H, Ph), 7.12 (s, 2H, NCH), 2.91, 2.49 and 2.24 (all s, 12H, CH$_3$CN), 2.52 (m, 4H, C*H*(CH$_3$)$_2$), 1.43 and 1.15 (all d, $J_{H\text{-}H}$ = 6.6, 24H, CH(*CH$_3$*)$_2$), 1.01 (d, $J_{H\text{-}H}$ = 6.9, 3H, Os=CH*CH$_3$*). ^{13}C{^{1}H}-APT NMR plus HSQC and HMBC (75.4 MHz, CD$_2$Cl$_2$, 293 K): δ 303.0 (s, Os=CH), 159.9 (s, NCN), and 146.6 and 146.4 (both s, C_o-2,6-^{i}Pr$_2$Ph), 137.2 (s, C_{ipso}-2,6-^{i}Pr$_2$Ph), 132.4 (s, C_p-2,6-^{i}Pr$_2$Ph), 130.9, 123.3 and 120.9 (all s, CH$_3$*C*N), 124.8 (s, C_m-2,6-^{i}Pr$_2$Ph), 124.6 (s, NCH), 120.6 (q, $J_{C\text{-}F}$ = 320.2, CF$_3$), 49,5 (s, Os=CH*C*H$_3$), 29.2 (s, *C*H(CH$_3$)$_2$), 25.8 and 22.7 (both s, CH(*C*H$_3$)$_2$), 4.8, 3.9 and 3.7 (all s, *C*H$_3$CN).

Preparation of [Os(η^2-CH_2=CH_2)(CH_3CN)$_4$(IPr)](OTf)$_2$ (3): In a Fisher-Porter reactor, a blue solution of **1** (300 mg, 0.277 mmol) in 20 mL of dichloromethane was stirred under 3 atm of ethylene at 60 ºC for 16 h. The resulting uncolored solution was filtrated through celite and evaporated to dryness. The subsequent addition of diethyl ether caused the precipitation of a white solid which was washed with diethyl ether (3 x 4 mL) and dried in vacuo. Yield: 260 mg (88 %). Anal. Calcd. for $C_{39}H_{52}F_6N_6O_6OsS_2$: C, 43.81; H, 4.90; N, 7.86; S, 6.00. Found: C, 44.02; H, 4.56; N, 8.08; S, 6.23. IR (cm^{-1}): ν(CH_3CN) 2280 (w); ν_a(SO_3) 1262 (s); ν_s(CF_3) 1223 (m); ν_a(CF_3) 1151 (s); ν_s(SO_3) 1030 (s); δ_a(SO_3) 639 (s). ^{1}H NMR (400 MHz, CD_3CN, 253 K): δ 7.5-7.3 (6H, Ph), 7.33 (s, 2H, NCH), 3.17 (s, 4H, CH_2=CH_2), 2.90 and 2.56 (both m, 4H, C*H*(CH_3)$_2$), 2.72, 2.46 and 1.98 (all s, 12H, CH_3CN), 1.38, 1.28, 1.12 and 1.09 (all d, $J_{H\text{-}H}$ = 6.8, 24H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H}-APT NMR plus HSQC and HMBC (100.5 MHz, CD_2Cl_2, 253 K): δ 146.4 and 145.6 (both s, C_o-2,6-^{i}Pr$_2$Ph), 144.3 (s, NCN), 136.1 (s, C_{ipso}-2,6-^{i}Pr$_2$Ph), 131.8 (s, C_p-2,6-^{i}Pr$_2$Ph), 127.5 (s, NCH), 124.8 and 124.0 (both s, C_m-2,6-^{i}Pr$_2$Ph), 122.7, 122.1 and 119.2 (all s, CH_3*C*N), 120.5 (q, $J_{C\text{-}F}$ = 320.2, CF_3), 53.3 (s, CH_2=CH_2), 28.9 and 28.7 (both s, *C*H(CH_3)$_2$), 25.5, 25.3, 21.9 and 21.5 (all s, CH(*C*H$_3$)$_2$), 4.6, 3.8 and 3.5 (all s, *C*H$_3$CN).

Preparation of [Os(η^2-CH_2=$CHCH_3$)(CH_3CN)$_4$(IPr)](OTf)$_2$ (4): In a Fisher-Porter reactor, a blue solution of **1** (300 mg, 0.265 mmol) in 20 mL of dichloromethane was stirred under 2 atm of ethylene at 40 ºC for 2 h. The resulting uncolored solution was filtrated through celite and evaporated to dryness. The subsequent addition of diethyl ether caused the precipitation of a white solid which was washed with diethyl ether (3 x 4 mL) and dried in vacuo. Yield: 230 mg (80 %). Anal. Calcd. for $C_{40}H_{54}F_6N_6O_6OsS_2$: C, 44.35; H, 5.02; N, 7.76; S, 5.92. Found: C, 43.97; H, 5.25; N, 7.91; S, 6.03. IR (cm^{-1}): ν(CH_3CN) 2279 (w); ν_a(SO_3) 1260 (s); ν_s(CF_3) 1222 (m); ν_a(CF_3) 1145 (s); ν_s(SO_3) 1029 (s); δ_a(SO_3) 636 (s). ^{1}H NMR (400 MHz, CD_2Cl_2, 253 K): δ 7.5-7.3 (6H, Ph), 7.03 (s, 2H, NCH), 3.81 (ddq, $J_{H\text{-}H}$ = 12.8, 8.8 and 6.0, 1H, C*H*=CH_2), 3.13 (d, $J_{H\text{-}H}$ = 8.8, 1H, CH=C*H*$_2$), 2.99 (d, $J_{H\text{-}H}$ = 12.8, 1H, CH=C*H*$_2$), 2.88 and 2.58 (both m, 4H, C*H*(CH_3)$_2$), 2.83, 2.64, 2.09 and 2.07 (all s, 12H, CH_3CN), 1.48 (d, $J_{H\text{-}H}$ = 6.0, 3H, =CHC*H*$_3$), 1.42, 1.41, 1.32, 1.27, 1.19, 1.18, 1.05 and 1.03 (all d, $J_{H\text{-}H}$ = 6.6, 24H, CH(C*H*$_3$)$_2$).

$^{13}C\{^1H\}$-APT NMR plus HSQC and HMBC (100.5 MHz, CD_2Cl_2, 253 K): δ 146.3, 146.2, 145.4 and 145.2 (all s, C_o-2,6-$^iPr_2Ph$), 145.5 (s, NCN), 136.4 and 136.2 (both s, C_{ipso}-2,6-$^iPr_2Ph$), 131.8 (s, C_p-2,6-$^iPr_2Ph$), 127.4 and 127.3 (both s, NCH), 125.2, 125.1, 124.1 and 124.0 (all s, C_m-2,6-$^iPr_2Ph$), 122.8, 121.4, 120.1 and 119.7 (all s, $CH_3\mathit{C}N$), 120.4 (q, $J_{C\text{-}F}$ = 320.2, CF_3), 72.6 (s, $\mathit{C}HCH_2$), 52.6 (s, $CH\mathit{C}H_2$), 29.4, 29.3, 29.0 and 28.7 (all s, $\mathit{C}H(CH_3)_2$), 26.3, 26.2, 26.0, 25.9, 23.1, 22.9, 22.3 and 22.2 (all s, $CH(\mathit{C}H_3)_2$), 24.2 (s, $CH\mathit{C}H_3$), 5.6, 4.7, 4.6 and 4.4 (all s, $\mathit{C}H_3CN$).

Preparation of $[Os(CH_3CN)_5(IPr)](OTf)_2$ (5): Method a. An uncolored solution of **3** (300 mg, 0.277 mmol) in 10 mL of CH_3CN was stirred at 80 ºC for 16 h. The resulting uncolored solution was filtrated through celite and evaporated to dryness. The subsequent addition of diethyl ether caused the precipitation of a white solid which was washed with diethyl ether (3 x 4 mL) and dried in vacuo. Yield: 280 mg (93 %). **Method b.** An uncolored solution of **4** (250 mg, 0.231 mmol) in 10 mL of CH_3CN was stirred at 80 ºC for 16 h. The resulting uncolored solution was filtrated through celite and evaporated to dryness. The subsequent addition of diethyl ether caused the precipitation of a white solid which was washed with diethyl ether (3 x 4 mL) and dried in vacuo. Yield: 225 mg (90 %). Anal. Calcd. for $C_{39}H_{51}F_6N_7O_6OsS_2$: C, 43.28; H, 4.75; N, 9.06; S, 5.92. Found: C, 42.89; H, 4.58; N, 9.23; S, 6.19. IR (cm^{-1}): $\nu(CH_3CN)$ 2280 (w); $\nu_a(SO_3)$ 1262 (s); $\nu_s(CF_3)$ 1223 (m); $\nu_a(CF_3)$ 1148 (s); $\nu_s(SO_3)$ 1029 (s); $\delta_a(SO_3)$ 637 (s). ^1H NMR (400 MHz, CD_2Cl_2, 253 K): δ 7.5-7.3 (6H, Ph), 6.94 (s, 2H, NCH), 2.74 (s, 6H, CH_3CN), 2.72 (m, 4H, $C\mathit{H}(CH_3)_2$), 2.53 (s, 3H, CH_3CN), 2.14 (s, 6H, CH_3CN), 1.37 and 1.18 (both d, $J_{H\text{-}H}$ = 6.6, 24H, $CH(C\mathit{H}_3)_2$). $^{13}C\{^1H\}$-APT NMR plus HSQC and HMBC (100.5 MHz, CD_2Cl_2, 253 K): δ 151.3 (s, NCN), 146.1 (s, C_o-2,6-$^iPr_2Ph$), 137.2 (s, C_{ipso}-2,6-$^iPr_2Ph$), 131.3 (s, C_p-2,6-$^iPr_2Ph$), 126.3 (s, NCH), 124.1 (s, C_m-2,6-$^iPr_2Ph$), 119.3, 118.5, and 118.4 (both s, $CH_3\mathit{C}N$), 120.4 (q, $J_{C\text{-}F}$ = 320.1, CF_3), 28.9 (s, $\mathit{C}H(CH_3)_2$), 25.5 and 22.7 (both s, $CH(\mathit{C}H_3)_2$), 4.6, 4.3 and 3.4 (all s, $\mathit{C}H_3CN$).

Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of diethylether into a concentrated solution of the BF_4 salt of **5** in dichloromethane. This BF_4-salt was prepared following the procedure described for the OTf-salt starting from the BF_4-salt of **3**.

Preparation of $[Os\{=C(O^iPr)CH=CPh_2\}(CH_3CN)_4(IPr)](OTf)_2$ (6): A mixture of $[Os(CH_3CN)_5(IPr)](OTf)_2$ (**5**) (100 mg, 0.093 mmol) and 1,1-diphenyl-2-propyn-1-ol (43 mg, 0.208 mmol) in isopropanol (8 mL) was stirred at 83ºC for 7 h. The resulting orange-red solution was filtered through celite and evaporated to dryness. The subsequent addition of diethyl ether caused the precipitation of a bright orange solid which was washed with diethyl ether (3 x 3 mL) and dried in vacuo. Yield: 88 mg (73%). Anal. Calcd. for $C_{55}H_{66}F_6N_6O_7OsS_2{\bullet}3CH_2Cl_2$: C, 45.05; H, 4.69; N, 5.4; S, 4.15. Found: C, 45.49; H, 4.67; N, 5.4; S, 4.17. IR (Nujol, cm^{-1}): $\nu(CH_3CN)$ 2330 (w); $\nu_a(SO_3)$ 1272 (s); $\nu_s(CF_3)$ 1225 (m); $\nu_a(CF_3)$ 1152 (s); $\nu_s(SO_3)$ 1017 (s); $\delta_a(SO_3)$ 638 (s). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.55 (t, $J_{H\text{-}H}$ = 7.6, 2H, H_p-2,6-$^iPr_2Ph$), 7.46 (d, $J_{H\text{-}H}$ = 7.6, 4H, H_m-2,6-$^iPr_2Ph$), 7.42-7.35 (4H, H_m-Ph), 7.32 (t, J_{HH} = 7.6, 2H, H_p-Ph), 7.06 (s, 2H, NCH), 6.92 (d, $J_{H\text{-}H}$ = 7.6, 4H, H_o-Ph), 6.30 (s, 1H, $CH{=}CPh_2$), 5.16 (sept, $J_{H\text{-}H}$ = 6.0, 1H, $OCH(CH_3)_2$), 2.79 (sept, $J_{H\text{-}H}$ = 6.7, 4H, $CH(CH_3)_2$), 2.72 and 2.08 (both br s, 6H each, CH_3CN), 1.39 (d, $J_{H\text{-}H}$ = 6.7, 12H, $CH(CH_3)_2$) and 1.20-1.13 (m, 18H, $CH(CH_3)_2$ + $OCH(CH_3)_2$). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (75.4 MHz, CD_2Cl_2, 293 K): 283.8 (s, Os=C), 166.7 (s, NCN), 146.7 (s, C_o-2,6-$^iPr_2Ph$), 141.2 (s, C_{ipso}-Ph), 139.2 (s, C_{ipso}-Ph), 139.0 (s, $CH{=}CPh_2$), 137.7 (s, C_{ipso}-2,6-$^iPr_2Ph$), 135.3 (s, $CH{=}CPh_2$), 132.1 (s, C_p-2,6-$^iPr_2Ph$), 130.5 (s, C_m-Ph), 129.9 (s, C_p-Ph), 129.5 (s, C_o-Ph), 129.4 (s, C_m-Ph), 129.1 (s, C_p-Ph), 129.0 (s, C_o-Ph), 127.7 (s, NCH), 125.0 (s, C_m-2,6-$^iPr_2Ph$), 120.7 (br s, CH_3CN), 85.6 (s, $OCH(CH_3)_2$), 29.2 (s, $CH(CH_3)_2$), 25.9 (s, $CH(CH_3)_2$), 23.3 (s, $OCH(CH_3)_2$), 4.7 (s, CH_3CN).

Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of diethylether into a concentrated solution of the BF_4 salt of **6** in dichloromethane. This BF_4-salt was prepared following the procedure described for the OTf-salt starting from the BF_4-salt of **5**.

Preparation of $[Os\{=C(O^iPr)CH=C(CH_3)_2\}(CH_3CN)_4(IPr)](OTf)_2$ (7): A mixture of

$[Os(CH_3CN)_5(IPr)](OTf)_2$ (**5**) (100 mg, 0.093 mmol) and 2-methyl-3-butyn-2-ol (27.3 mg, 0.325 mmol) in isopropanol (8 mL) was stirred at for 3 d. The resulting yellow solution was filtered through celite and evaporated to dryness. The subsequent addition of diethyl ether caused the precipitation of a yellowish-brown solid which was washed with diethyl ether (3 x 3 mL) and dried in vacuo. Yield: 43.5 mg (40%). Anal. Calcd. for $C_{45}H_{62}F_6N_6O_7OsS_2{\bullet}2CH_2Cl_2$: C, 42.21; H, 4.97; N, 6.28; S, 4.80. Found: C, 42.71; H, 5.00; N, 6.58; S, 5.30**.** IR (Nujol, cm^{-1}): $\nu(CH_3CN)$ 2333 (w); $\nu_a(SO_3)$ 1270 (s); $\nu_s(CF_3)$ 1219 (m); $\nu_a(CF_3)$ 1151 (s); $\nu_s(SO_3)$ 1030 (s); $\delta_a(SO_3)$ 638 (s)**.** ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.59-7.40 (6H, H_m+H_p-2,6-$^iPr_2Ph$), 6.92 (s, 2H, NCH), 5.72 (s, 1H, $CH{=}C(CH_3)_2$), 5.27 (sept, $J_{H\text{-}H}$ = 6.0, 1H, $OCH(CH_3)_2$), 2.79 (sept, $J_{H\text{-}H}$ = 7.0, 4H, $CH(CH_3)_2$), 2.68 and 2.19 (both br s, 6H each, CH_3CN), 1.85 (s, 3H, $CH{=}C(CH_3)_2$), 1.45 (s, 3H, $CH{=}C(CH_3)_2$), 1.42-1.16 (m,, 30H each, $CH(CH_3)_2$ + $OCH(CH_3)_2$). $^{13}C\{^1H\}$-APT NMR plus HMBC and HSQC (75.4 MHz, CD_2Cl_2, 293 K): 289.3 (s, Os=C), 167.2 (s, NCN), 146.6 (s, C_o-2,6-$^iPr_2Ph$), 137.8 (s, $CH{=}C(CH_3)_2$), 134.4 (s, $CH{=}C(CH_3)_2$), 133.7 (s, C_{ipso}-2,6-$^iPr_2Ph$), 132.1 (s, C_p-2,6-$^iPr_2Ph$), 127.5 (s, NCH), 125.0 (s, C_m-2,6-$^iPr_2Ph$), 120.4 (br s, CH_3CN), 83.7 (s, $OCH(CH_3)_2$), 25.9 and 23.3 (both s, $CH(CH_3)_2$), 25.3 (s, $CH{=}C(CH_3)_2$), 22.9 (s, $OCH(CH_3)_2$), 21.6 (s, $CH{=}C(CH_3)_2$), 4.5 (s, CH_3CN).

Preparation of $[Os\{{=}C(OMe)CH{=}CPh_2\}(CH_3CN)_4(IPr)](OTf)_2$ (8): To a colorless solution of $[Os(CH_3CN)_5(IPr)](OTf)_2$ (**5**) (100 mg, 0.093 mmol) in methanol (8 mL), 1,1-diphenyl-2-propyn-1-ol (75 mg, 0.326 mmol) was added and the reaction mixture was stirred at 65ºC for 6 h. The resulting orange-red solution was filtered through celite and evaporated to dryness. The subsequent addition of diethyl ether caused the precipitation of an orange-red solid which was washed with diethyl ether (3 x 3 mL) and dried in vacuo. Yield: 73 mg (62%). Anal. Calcd. for $C_{53}H_{62}F_6N_6O_7OsS_2{\bullet}0.5CH_2Cl_2$: C, 49.20%; H, 4.86; N, 6.43; S, 4.91. Found: C, 48.74; H, 4.86; N, 6.48; S, 4.96. IR (Nujol, cm^{-1}): $\nu(CH_3CN)$ 2330 (w); $\nu_a(SO_3)$ 1270 (s); $\nu_s(CF_3)$ 1223 (m); $\nu_a(CF_3)$ 1153 (s); $\nu_s(SO_3)$ 1018 (s); $\delta_a(SO_3)$ 636 (s)**.** ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.53 (t, $J_{H\text{-}H}$ = 7.6, 2H, H_p-2,6-$^iPr_2Ph$), 7.44 (d, $J_{H\text{-}H}$ = 7.6, 4H, H_m-2,6-$^iPr_2Ph$), 7.43-7.40 (6H, Ph), 7.29 (t, $J_{H\text{-}H}$ = 7.8, 2H, Ph), 7.07 (s, 2H, NCH), 6.86 (d, $J_{H\text{-}H}$ = 7.8, 2H, Ph), 6.29 (s, 1H, C*H*=CPh$_2$), 3.82 (s, 3H, OC*H*$_3$), 2.78 (sept, $J_{\text{H-H}}$ = 6.8, 4H, C*H*(CH$_3$)$_2$), 2.70 and 2.06 (both br s, 6H each, CH$_3$CN), 1.36 and 1.19 (d, $J_{\text{H-H}}$ = 6.8, 12H each, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.4 MHz, CD$_2$Cl$_2$, 293 K): 285.1 (s, Os=C), 166.9 (s, NCN), 146.3 (s, C$_o$-2,6-^{i}Pr$_2$Ph), 141.1 (s, C$_{ipso}$-Ph), 140.5 (s, C$_{ipso}$-Ph), 139.3 (s, CH=*C*Ph$_2$), 137.3 (s, C$_{ipso}$-2,6-^{i}Pr$_2$Ph), 135.7 (s, *C*H=CPh$_2$), 131.8 (s, C$_p$-2,6-^{i}Pr$_2$Ph), 130.4 (s, C$_m$-Ph), 129.7 (s, C$_p$-Ph), 129.4 (s, C$_o$-Ph), 129.3 (s, C$_m$-Ph), 129.1 (s, C$_p$-Ph), 128.4 (s, C$_o$-Ph), 127.3 (s, NCH), 124.6 (s, C$_m$-2,6-^{i}Pr$_2$Ph), 120.4 (s, br, CH$_3$*C*N), 67.8 (s, OCH$_3$), 29.1 (s, *C*H(CH$_3$)$_2$), 25.6 and 23.1 (both s, CH(*C*H$_3$)$_2$), 4.7 (s, *C*H$_3$CN).

Preparation of [Os{=C(OMe)CH=C(CH$_3$)$_2$}(CH$_3$CN)$_4$(IPr)](OTf)$_2$ (9): To a colorless solution of [Os(CH$_3$CN)$_5$(IPr)](OTf)$_2$ (**5**) (100 mg, 0.093 mmol) in methanol (8 mL), 2-methyl-3-butyn-2-ol (23.5 mg, 0.279 mmol) was added and the reaction mixture was stirred at 65ºC for 2 d. The resulting orange-yellow solution was filtered through celite and evaporated to dryness. The subsequent addition 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: 84 mg (79%). Anal. Calcd. for $C_{43}H_{58}F_6N_6O_7OsS_2$: C, 45.33; H, 5.13; N, 7.37; S, 5.63. Found: C, 45.58; H, 5.63; N, 7.43; S, 5.20. IR (Nujol, cm^{-1}): ν(CH$_3$CN) 2330 (w); ν_a(SO$_3$) 1273 (s); ν_s(CF$_3$) 1223 (m); ν_a(CF$_3$) 1148 (s); ν_s(SO$_3$) 1032 (s); δ_a(SO$_3$) 638 (s). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 293 K): δ 7.54 (t, $J_{\text{H-H}}$ = 7.2, 2H, H$_p$-2,6-^{i}Pr$_2$Ph), 7.43 (d, $J_{\text{H-H}}$ = 7.2, 4H, H$_m$-2,6-^{i}Pr$_2$Ph), 7.03 (s, 2H, NCH), 5.67 (s, 1H, C*H*=C(CH$_3$)$_2$), 4.37 (s, 3H, OCH$_3$), 2.75 (sept, $J_{\text{H-H}}$ = 6.8, 4H, C*H*(CH$_3$)$_2$), 2.72 and 2.12 (both br s, 6H each, CH$_3$CN), 1.85 (s, 3H, CH=C(C*H*$_3$)$_2$), 1.46 (s, 3H, CH=C(C*H*$_3$)$_2$), 1.36 and 1.16 (both d, $J_{\text{H-H}}$ = 6.8, 12H each, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H}-APT NMR plus HMBC and HSQC (75.4 MHz, CD$_2$Cl$_2$, 293 K): 290.9 (s, Os=C), 167.4 (s, NCN), 146.5 (s, C$_o$-2,6-^{i}Pr$_2$Ph), 137.9 (s, CH=*C*(CH$_3$)$_2$), 134.6 (s, *C*H=C(CH$_3$)$_2$), 134.1 (s, C$_{ipso}$-2,6-^{i}Pr$_2$Ph), 132.0 (s, C$_p$-2,6-^{i}Pr$_2$Ph), 127.6 (s, NCH), 124.9 (s, C$_m$-2,6-^{i}Pr$_2$Ph), 120.5 (br s, CH$_3$*C*N), 66.4 (s, OCH$_3$), 29.3 (s, *C*H(CH$_3$)$_2$), 26.0 and 23.3 (both s, CH(*C*H$_3$)$_2$), 25.4 (s, CH=C(*C*H$_3$)$_2$), 21.5 (s, CH=C(*C*H$_3$)$_2$), 4.5 (s, *C*H$_3$CN).

Structural Analysis of Complexes 4, 5, and 6. X-ray data were collected for all complexes on a

Bruker Smart Apex CCD diffractometer with graphite monochromated Mo Kα radiation (λ=0.71073 Å) using ω scans. Data were corrected for absorption by using a multiscan method applied with the Sadabs[26] program. The structures for the two compounds were solved by the direct methods. Refinement, by full-matrix least squares on F^2 with SHELXL97,[27] was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were observed or calculated and refined freely or using a restricted riding mode in the last cycles of refinement. For **4** the methyl group of propylene was observed almost equally disordered in two positions related by the acetonitrile-osmium-carbene axis. This disorder is accompanying with the diimino carbene and one acetonitrile ligands, together with the triflate anions. For **5** the BF_4 anions were also observed disordered. For **6** one molecule of solvent isopropanol and one BF_4 anion were observed disordered. This disorder groups were refined with restrained geometry and thermal parameters.

Crystal data for 4: $C_{38}H_{54}N_6Os$ x 2(CF_3SO_3) x 0.25(CH_2Cl_2), M_w 1104.44, colorless, irregular block (0.08 x 0.06 x 0.04 mm), monoclinic, space group $P2_1/n$, a: 12.717(4) Å, b: 18.141(5) Å, c: 21.711(6) Å, β: 104.355(5)°, V = 4852(2) Å^3, Z = 4, D_{calc} = 1.512 g cm^{-3}, F (000) = 2226, T = 100.0(2) K; mu = 2.813 mm^{-1}. 48826 measured reflections (2θ: 3-50°, ω scans 0.3°), 8556 unique (R_{int}= 0.0456); min./max. transm. factors 0.770/0.896. Final agreement factors were R^1 = 0.0578 (7058 observed reflections, I > 2σ(I)) and wR^2 = 0.1538; data/restrains/parameters 8556/1398/951; GoF = 1.078. Largest peak and hole 2.422 and -1.498 e/Å^3. All the highest electronic residuals were observed in the close proximity of the Os centers and make no chemical sense.

Crystal data for 5: $C_{37}H_{51}N_7Os$ x 2(BF_4) x 0.5(CH_2Cl_2), M_w 1000.13, colorless, irregular prism (0.12 x 0.10 x 0.02 mm), monoclinic, space group $P2_1/c$, a: 12.0654(19) Å, b: 12.944(2) Å, c: 31.086(5) Å, β: 100.657(3)°, V = 4771.0(13) Å^3, Z = 4, D_{calc} = 1.392 g cm^{-3} , F (000) = 2004, T = 293.0(2) K; mu = 2.792 mm^{-1}. 49170 measured reflections (2θ: 3-57°, ω scans 0.3°), 8804 unique (R_{int}= 0.0800);

min./max. transm. factors 0.757/0.946. Final agreement factors were R^1 = 0.0634 (5686 observed reflections, I > 2σ(I)) and wR^2 = 0.1856; data/restrains/parameters 8804/85/530; GoF = 1.060. Largest peak and hole 1.245 and -0.692 e/Å^3. All the highest electronic residuals were observed in the close proximity of the Os centers and make no chemical sense.

Crystal data for 6: $C_{53}H_{66}N_6OOs$ x $2(BF_4)$ x $C_3H_8O_1$, M_w 1227.03, red, irregular block (0.12 x 0.10 x 0.06 mm), monoclinic, space group $P2_1/c$, a: 17.849(6) Å, b: 12.263(4) Å, c: 26.548(9) Å, β: 93.405(7)°, V = 5801(3) Å^3, Z = 4, D_{calc} = 1.405 g cm^{-3}, F (000) = 2504 , T = 100.0(2) K; mu = 2.268 mm^{-1}. 71307 measured reflections (2θ: 3-57°, ω scans 0.3°), 14369 unique (R_{int}= 0.0725); min./max. transm. factors 0.718/ 0.876. Final agreement factors were R^1 = 0.0567 (11533 observed reflections, I > 2σ(I)) and wR^2 = 0.1183; data/restrains/parameters 14369/ 48/ 655; GoF = 1.093. Largest peak and hole 2.002 and -2.002 e/Å^3. All the highest electronic residuals were observed in the close proximity of the Os centers and make no chemical sense.

Acknowledgment. Financial support from the MEC of Spain (Project number CTQ2008-00810 and Consolider Ingenio 2010 (CSD2007-00006) and the Diputación General de Aragón (E35) is acknowledged.

Supporting Information Available. This material is available free of charge via the Internet at http://pubs.acs.org.

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Dicationic Alkylidene-, Olefin-, and Alkoxyalkenylcarbene-Osmium Complexes Stabilized by a NHC-Ligand.

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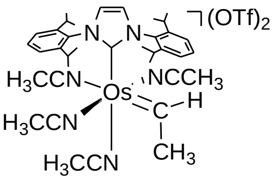

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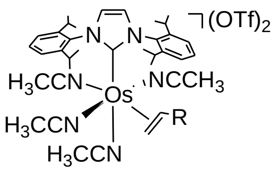

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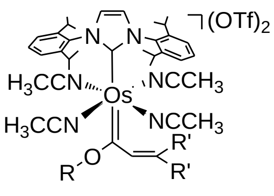

III

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The 1,3-bis(2,6-diisopropylphenyl)imidazolylidene ligand shows a great capacity to stabilize Os-olefin and Os-C double bonds in strongly electrophilic metal fragments. As a consequence of this novel tetra(solvento) dicationic, alkylidene (I), olefin (II), and alkoxycabene (III) species have been isolated and characterized..