Dalton Transactions

Pentamethylcyclopentadienyl Osmium Complexes that Contain Diazoalkane, Dioxygen and Allenylidene Ligands: Preparation and Reactivity

Journal:	*Dalton Transactions*
Manuscript ID	DT-ART-01-2019-000223
Article Type:	Paper
Date Submitted by the Author:	16-Jan-2019
Complete List of Authors:	Albertin, Gabriele; UNIVERSITA' CA' FOSCARI VENEZIA, DSMN Antoniutti, Stefano; Università Ca' Foscari Venezia, Dipartimento di Scienze Molecolari e Nanosistemi Castro, Jesus; Universidade de Vigo, Departamento de Química Inorgánica Sibilla, Francesca; Università Ca\' Foscari Venezia, Dipartimento di Scienze Molecolari e Nanosistemi

Pentamethylcyclopentadienyl Osmium Complexes that Contain Diazoalkane, Dioxygen and Allenylidene Ligands: Preparation and Reactivity

Gabriele Albertin,*[†] Stefano Antoniutti,[†] Jesús Castro[‡] and Francesca Sibilla[†]

[†]*Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Via Torino 155, 30172 Venezia Mestre, Italy*

[‡]*Departamento de Química Inorgánica, Universidade de Vigo, Facultade de Química, Edificio de Ciencias Experimentais, 36310 Vigo (Galicia), Spain*

Abstract: Diazoalkane complexes $[Os(\eta^5\text{-}C_5Me_5)(N_2CAr1Ar2)(PPh_3)\{P(OR)_3\}]BPh_4$ (**1, 2**) [R = Me (**1**), Et (**2**); Ar1 = Ar2 = Ph (**a**); Ar1 = Ph, Ar2 = *p*-tolyl (**b**); Ar1Ar2 = $C_{12}H_8$ (fluorenyl) (**c**)] were prepared by reacting bromo-compounds $OsBr(\eta^5\text{-}C_5Me_5)(PPh_3)\{P(OR)_3\}$ with an excess of diazoalkane in ethanol. The treatment of diazoalkane complexes **1** and **2** with acetylene under mild conditions (1 atm, RT) led to dipolar (3+2) cycloaddition affording 3*H*-pyrazole derivatives $[Os(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}N{=}NC(C_{12}H_8)CH{=}CH)(PPh_3)\{P(OR)_3\}]BPh_4$ (**6, 7**) [R = Me (**6**), Et (**7**)] whereas reactions with terminal alkynes R1C≡CH (R1 = Ph, *p*-tolyl, COOMe) gave vinylidene derivatives $[Os(\eta^5\text{-}C_5Me_5)\{{=}CH{-}C(H)R1\}(PPh_3)\{P(OR)_3\}]BPh_4$ (**8b-d, 9b-d**) [R = Me (**8**), Et (**9**); R1 = Ph (**b**), *p*-tolyl (**c**), COOMe (**d**)]. Exposure to air of dichloromethane solutions of

complexes **1** and **2** produced dioxygen derivatives [Os(η^5-C_5Me_5)(η^2-O_2)(PPh_3){$P(OR)_3$}]BPh_4 (**10, 11**) [R = Me (**10**), Et (**11**)]. Allenylidene [Os]=C=C=CR1R2 (**12-14**) [R1 = R2 = Ph (**12, 13**); R1 = Ph, R2 = Me (**14**)], vinylivinylidene [Os]=C=C(H)C(Ph)=CH_2 (**15**) and 3-hydroxyvinylidene [Os]=C=C(H)C(H)R2(OH) (**16, 17**) [R2 = Ph (**16**), H (**17**)] derivatives were also prepared. The vinylidene complex [Os(η^5-C_5Me_5)(=C=CH_2)(PPh_3){$P(OMe)_3$}]BPh_4 (**8a**) reacted with PPh_3 to afford the alkenylphosphonium derivative [Os(η^5-C_5Me_5){η^1-C(H)=C(H)PPh_3}(PPh_3){$P(OMe)_3$}]BPh_4 (**18**) whereas vinylidene complexes **8** and **9** reacted with water leading to the hydrolysis of the alkyne and the formation of carbonyl complexes [Os(η^5-C_5Me_5)(CO)(PPh_3){$P(OR)_3$}]BPh_4 (**19**, **20**). The complexes were characterised by spectroscopic data (IR and NMR) and by X-ray crystal structure determination of [Os(η^5-C_5Me_5){=C=C(H)*p*-tolyl}(PPh_3){$P(OEt)_3$}]BPh_4 (**9c**), [Os(η^5-C_5Me_5)(η^2-O_2)(PPh_3){$P(OMe)_3$}]BPh_4 (**10**) and [Os(η^5-C_5Me_5)(CO)(PPh_3){$P(OMe)_3$}]BPh_4 (**19**).

INTRODUCTION

The preparation and reactivity of the diazoalkane complexes of transition metals has attracted long-standing interest[1-5] not only for the variety of

coordination modes but mainly due to the striking reactivity shown by the metal-bonded $N_2CAr1Ar2$ group. The extrusion of dinitrogen with carbene [M]=CAr1Ar2 formation was observed in η^2-CN-coordinated species,[1,2b,6,7] whereas a η^1-bound diazoalkane, in converting carbene into imine[6g] or cleaving the N-N bond of the $N_2CAr1Ar2$ group,[2i] may yield dinitrogen [M]-N_2 complexes.[2g,k] Dipolar (3+2) cycloaddition of coordinated diazoalkane with alkenes and alkynes affording 3*H*-pyrazole derivatives[5b,e,f,h,i] as well as the hydrolysis of the [M]-$N_2CAr1Ar2$ group yielding η^2-diazene derivatives[5c,g] have recently been reported.

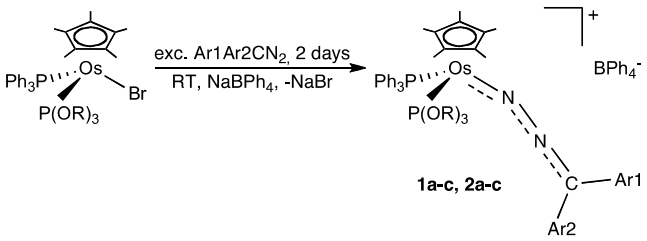
A number of diazoalkane complexes of several metals has been described in recent years[1-5] and their reactivity studies have highlighted various pathways depending on the central metal, the coordination mode and the nature of the ancillary ligands. However, unlike Fe and Ru, the chemistry of diazoalkane complexes of osmium is poorly described and, apart from two brief reports on $[OsH(N_2CAr1Ar2)L_4]BPh_4$ and $[OsCl(\eta^6\text{-}p\text{-cymene})(N_2CAr1Ar2)L]BPh_4$ species (L = phosphine),[5d,5k] no other examples for this metal have been reported.

We are interested in the chemistry of diazoalkane complexes[5] and have recently reported on the synthesis and reactivity of half-sandwich derivatives for iron[5a] and ruthenium[5b-k] of the type $[Fe(\eta^5\text{-}C_5H_5)(N_2CAr1Ar2)(P\text{-}P)]BPh_4$, $[Ru(\eta^5\text{-}$

$C_5H_5)(N_2CAr1Ar2)\{P(OR)_3\}L]BPh_4$, $[Ru(\eta^5\text{-}C_5Me_5)(N_2CAr1Ar2)\{P(OR)_3\}L]BPh_4$, $[Ru(\eta^5\text{-}C_9H_7)(N_2CAr1Ar2)\{P(OR)_3\}L]BPh_4$ and $[Ru(Tp)(N_2CAr1Ar2)\{P(OR)_3\}L]BPh_4$ [L = PPh_3, $P(OR)_3$, CNR; Tp = tris(pyrazolyl)borate; P-P = $Ph_2PCH_2CH_2PPh_2$]. As the diazo group bonded to these metal fragments showed new and interesting properties, we extended our study to osmium to test whether diazoalkane complexes could be prepared and how their properties change. The results are given here.

RESULTS AND DISCUSSION

Diazoalkane complexes of osmium $[Os(\eta^5\text{-}C_5Me_5)(N_2CAr1Ar2)(PPh_3)\{P(OR)_3\}]BPh_4$ (**1, 2**) were prepared by reacting the new bromo-compounds $OsBr(\eta^5\text{-}C_5Me_5)(PPh_3)\{P(OR)_3\}$ with an excess of diazoalkane in the presence of $NaBPh_4$, as shown in Scheme 1.



Scheme 1. R = Me (**1**), Et (**2**); Ar1 = Ar2 = Ph (**a**); Ar1 = Ph, Ar2 = *p*-tolyl (**b**); Ar1Ar2 = $C_{12}H_8$ (fluorenyl) (**c**).

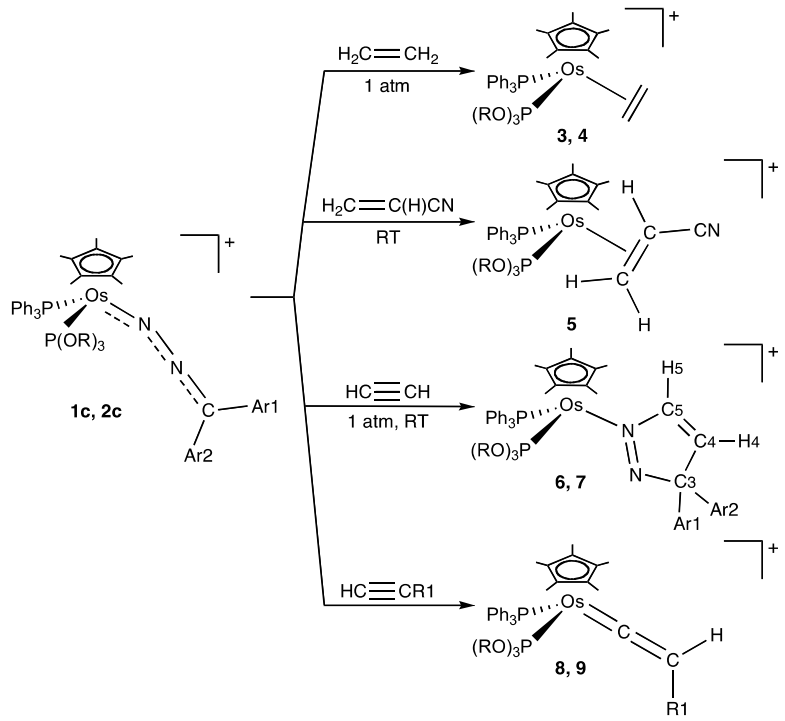
The reaction proceeded by substituting the bromo ligand and the formation of diazoalkane complexes (**1a-c**, **2a-c**) which were isolated in good yields and characterised. Crucial for the success of the syntheses was the presence of the $NaBPh_4$ salt (or $NaPF_6$) which, favouring the substitution of the Br^- ligand, allowed the complexes to separate as solids. However, the reaction was slow at room temperature and took two days to be completed. Reflux conditions could not be used owing to the formation of decomposition products.

The bis(triphenylphosphine) complex $OsBr(\eta^5\text{-}C_5Me_5)(PPh_3)_2$ was also reacted with diazoalkane *via* different conditions, but no reaction occurred, resulting the starting complexes unchanged. Only the mixed-ligands compounds $OsBr(\eta^5\text{-}C_5Me_5)(PPh_3)\{P(OR)_3\}$, prepared by substituting one PPh_3 with phosphite in $OsBr(\eta^5\text{-}C_5Me_5)(PPh_3)_2$, was found to afford diazoalkane derivatives.

The new complexes **1a-c** and **2a-c** were isolated as yellow-orange solids stable in air and in polar organic solvent solutions, where they behave as 1:1 electrolytes.[8] Analytical and spectroscopic (IR, NMR) data supported the proposed formulations. The IR spectra showed a medium-intensity band at 1935-1946 cm^{-1}, attributed to the ν_{N_2} of the coordinate diazoalkane group.[1,5] Besides the signals of the ancillary ligands C_5Me_5, PPh_3, $P(OR)_3$ and the BPh_4 anion, the ^1H NMR

spectra showed resonances characteristic of the substituents $C_{12}H_8$ and 4-$CH_3C_6H_4$ of the diazoalkane Ar1Ar2CN_2. Their presence was further supported by the $^{13}C\{^1H\}$ NMR spectra of **1c** and **2a**, which showed a broad signal at 83.5 (**1c**) and at 88.83 (**2a**) ppm attributed to the CN_2 carbon resonance of the diazoalkane. In the temperature range from +20 to -80 °C, the ^{31}P NMR spectra appeared as two doublets fitting the proposed geometry for the complexes.

Reactivity studies on our diazoalkane complexes **1** and **2** with alkenes and alkynes were undertaken with the aim of testing whether (3+2) cycloaddition may occur. The results are summarised in Scheme 2.



Scheme 2. R = Me (**3, 5, 6, 8**), Et (**4, 7, 9**); R1 = Ph (**b**), *p*-tolyl (**c**), COOMe (**d**).

Under mild conditions (1 atm, RT) ethylene reacted with diazoalkane complexes **1** and **2** to give the ethylene derivatives [Os(η^5-C_5Me_5)(η^2-CH_2=CH_2)(PPh_3){$P(OR)_3$}]BPh_4 [**3** (R = Me), **4** (R = Et)]. However, the reaction was very slow and took several days to complete. Instead, in refluxing 1,2-dichloroethane the η^2-CH_2=CH_2 complexes **3** and **4** formed quickly and were isolated in good yield and characterised. The reaction proceeded with substitution of the diazoalkane ligand and no evidence of cyclisation reaction yielding 3*H*-pyrazole derivatives was observed.

The substitution of diazoalkane also occurred with activated alkenes such as acrylonitrile, affording the complex [Os(η^5-C_5Me_5){η^2-CH_2=C(H)CN}(PPh_3){$P(OMe)_3$}]BPh_4 (**5**) in which the acrylonitrile is proposed as π-coordinated to the metal center.

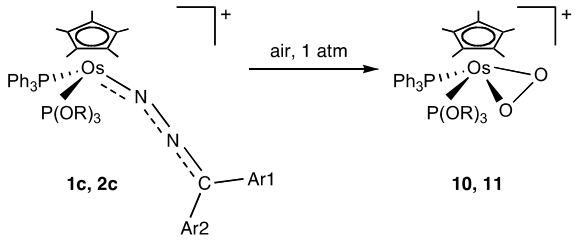
Under mild conditions, acetylene HC≡CH slowly reacted with diazoalkane complexes **1** and **2** to give 3*H*-pyrazole derivatives [Os(η^5-C_5Me_5)(η^1-N=NC($C_{12}H_8$)CH=CH)(PPh_3){$P(OR)_3$}]BPh_4 [**6** (R = Me), **7** (R = Et)] which were isolated and characterised. The reactions proceeded with dipolar (3+2) cycloaddition of acetylene to the coordinated diazoalkane giving the 3*H*-pyrazole complexes **6** and **7**, in which the heterocycle acted as a ligand.

Terminal alkynes R1C≡CH also reacted at room temperature with diazoalkane complexes **1c** and **2c** giving vinylidene complexes [Os(η^5-C_5Me_5){=C=C(H)R1}(PPh_3){$P(OR)_3$}]BPh_4 (**8b-d, 9b-d**) which were isolated and characterised. The substitution of diazoalkane is hypothesised to afford intermediate η^2-alkyne complexes that undergo R1C≡CH ligand tautomerisation[9-11] to afford the vinylidene derivatives. These results highlight the important influence of the substituents on alkyne in determining the cyclisation reaction which only proceeds with acetylene HC≡CH. Differently, with monosubstituted alkynes R1C≡CH only the substitution of the Ar1Ar2CN_2 ligand and the formation of the vinylidene took place.

All our results on the reactivity of diazoalkane complexes **1** and **2** towards alkenes and alkynes indicate that the pentamethylcyclopentadienyl fragment [Os(η^5-C_5Me_5)(PPh_3){$P(OR)_3$}]$^+$ can activate the coordinated diazoalkane towards dipolar (3+2) cycloaddition. However, this may only occur with acetylene HC≡CH, affording 3*H*-pyrazole complexes **6** and **7**. With alkenes and terminal alkynes, substitution only occurs affording η^2-alkene or vinylidene as the final product, respectively. In addition, comparison with previous results[5b] on the pentamethylcyclopentadienyl fragment [Ru(η^5-C_5Me_5)(PPh_3){$P(OR)_3$}]$^+$ indicates that

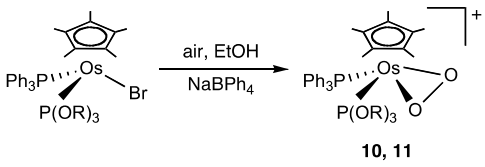
the two metal fragments behave in a similar manner. These are able to activate the coordinated $C_{12}H_8CN_2$ group towards (3+2) cycloaddition, exclusively with acetylene. Substitution of the diazoalkane ligand affording η^2-alkene or vinylidene derivatives is predominant with both metals.

Instead, a different behaviour respect to ruthenium was shown by the diazoalkane derivatives of osmium **1a-c** and **2a-c** in the reaction with air, which yielded dioxygen complexes $[Os(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}O_2)(PPh_3)\{P(OR)_3\}]BPh_4$ [**10** (R = Me), **11** (R = Et)], which were isolated and characterised (Scheme 3).



Scheme 3. R = Me (**10**), Et (**11**).

The reaction proceeded by substituting the $Ar1Ar2CN_2$ group with O_2, affording the η^2-O_2 derivatives in good yields. Of note, dioxygen complexes **10** and **11** can also be prepared by substituting the Br^- ligand in $OsBr(\eta^5\text{-}C_5Me_5)(PPh_3)\{P(OR)_3\}$ and using $NaBPh_4$ as a labilising agent, as shown in Scheme 4.



Scheme 4. R = Me (**10**), Et (**11**).

The coordination of the O_2 molecule to the $[Os(\eta^5\text{-}C_5Me_5)(PPh_3)\{P(OR)_3\}]^+$ fragment is striking as dioxygen complexes of osmium are rare[12] and mainly contain bidentate phosphine ligands. Complexes **10** and **11** are the first members of a new family of $Os(\eta^2\text{-}O_2)$ compounds with pentamethylcyclopentadienyl as a supporting ligand.

The new pentamethylcyclopentadienyl complexes of osmium **3**–**11** were all isolated as their BPh_4^- salts which were stable in air and in solution of polar organic solvents, where they behaved as 1:1 electrolytes.[8] Analytical and spectroscopic (IR, NMR) data support the proposed formulation. In addition, more thoroughly characterisation could be obtained by X-ray crystal structure determination of complexes $[Os(\eta^5\text{-}C_5Me_5)\{=C=C(H)p\text{-tolyl}\}(PPh_3)\{P(OEt)_3\}]BPh_4$ (**9c**) and $[Os(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}O_2)(PPh_3)\{P(OMe)_3\}]BPh_4$ (**10**) the ORTEPs[13] of which are shown in Figures 1 and 2.

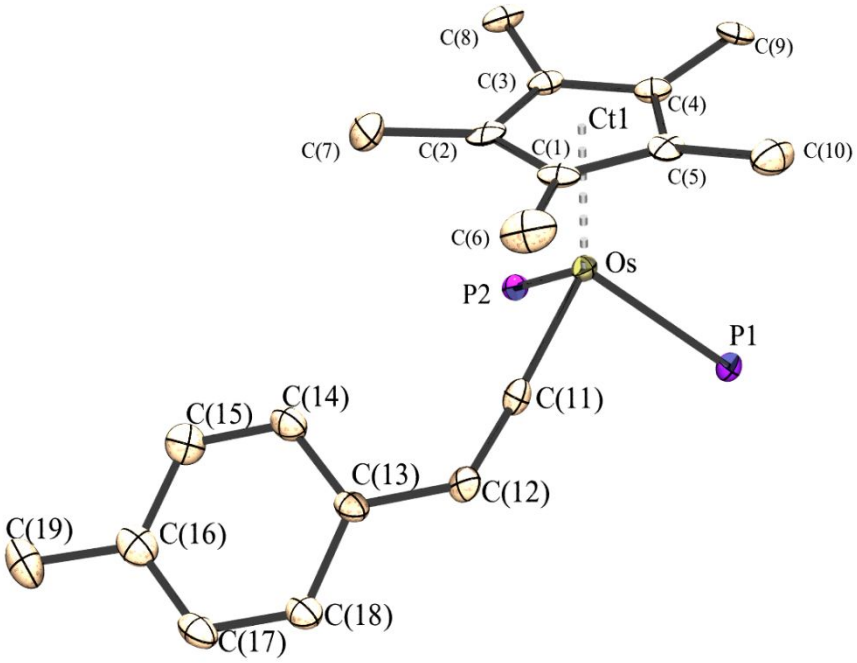


Figure 1. ORTEP[13] scheme of the molecular structure of **9c** cation. P1 represents a PPh_3 and P2 a $P(OEt)_3$.

The **9c** cation complex contained an osmium atom in a half-sandwich piano-stool structure, coordinated by a pentamethylcyclopentadienyl group (Cp^*), one $P(OEt)_3$, one PPh_3 and a *p*-tolylvinylidene ligand. The overall geometry of the complex was a slightly-distorted octahedron where the angles between the centroid of the Cp^* ligand (Ct1) and the legs were close to the theoretical 125.264° [geometrical calculation for the angle between the center of a face of an octahedron an one of its axis, π-arccos(1/√3)].[14d] Angles formed between the legs of the piano-stool were also near 90° (see Table 1). Coordination of the Cp^* ligand showed Os-C distances between 2.267(4) and 2.338(4) Å (average, 2.300

Å), the longest Os-C bond corresponding to that *trans* to the vinylidene ligand. These values are analogous to those found, for example, in $Cp^*OsCl(PPh_3)_2$ with an average Os−Cp^* of 2.247 Å.[15] The ring slippage, calculated as described in the experimental section, 0.077 Å, is in the usual range.[5a] The Os-P bond lengths depend on the nature of the ligand, shorter for the phosphite, 2.2725(11) Å, and longer, 2.3283(11) Å, for the triphenylphosphine, in an usual behaviour of these ligands.[5a] Further, the coordination mode of the vinylidene ligand comprises an Os-C bond length of 1.859(5) Å with an angle of 174.4(4)°, that is, close to linearity. In addition, the C(11)-C(12) bond distance of 1.306(6) Å indicates a double bond character and the C(11)-C(12)-C(13) angle shows an important bending, with a value of 126.2(4)°. Conjunction of these values is indicative of vinylidene formulation,[14] and they are comparable to values found for vinylidene compounds, as the cation $[(^tBu\text{-}BPI^{Me})Os(PPh_3)_2(=C=CHPh)]^+$ [(^tBu-BPI^{Me}) is a 1,3-bis(2-pyridylimino)isoindolate ligand] which show values as Os-C length of 1.867 Å, Os-C-C angle of 176.1°, C-C bond distance 1.321 Å and C-C-C angle of 129.9(2)°;[14a] in compounds as $OsHTp\{=C=CHC(Me)=CH_2\}(P^iPr_3)$, with Os-C(1), 1.796(8) Å; C(1)-C(2), 1.354(10) Å; Os-C(1)-C(2), 173.8(6)°; C(1)-C(2)-C(3), 126.0(7)°,[14b] or for a compound bearing similar vinylidene Ph-CH=C=Os system,

with values of Os-C(1), 1.817(5) Å; C(1)-C(2), 1.328(6) Å; C(2)-C(3), 1.460(6) Å; Os-C(1)-C(2), 170.4(4)°; C(1)-C(2)-C(3) 125.9(4)°.[14d] Related formulations could be excluded since these values are different, for example, the alkynyl compounds show both Os-C-C and C-C-C angles almost linear (for example the values found in neutral (^{t}Bu-BPI^{Me})Os(PPh$_3$)$_2$(C≡CHPh), Os-C-C 172.3° and C-C-C 175.6°).[14a] Also the behaviour found in **9c** is different than that found in alkenylcarbyne derivatives, where Os-Cα bond is shorter but Cα-Cβ bond length is longer, as occurs, for example in the cation [OsHTp(≡CCH=CMe$_2$)(P^{i}Pr$_3$)]$^{+}$, where those values are 1.726(6) and 1.424(8) Å, respectively.[14b]

The asymmetric unit of **10** contained four molecular formulae, that is, four cations and four anions as well as any unknown solvent. Reflections caused by the latter were eliminated in the usual procedure (see Experimental section). In Figure 2 only one cation is sketched and a selection of bond distances and angles are set out in Table 2.

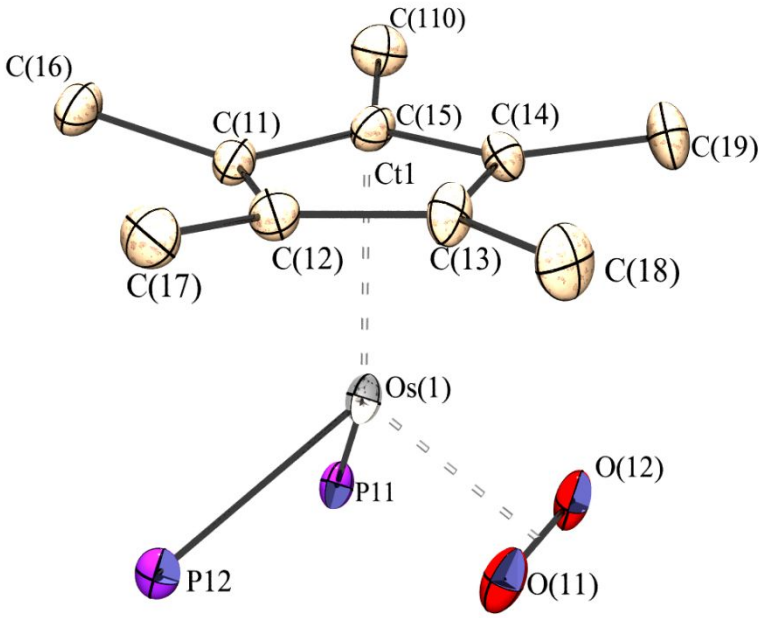


Figure 2. ORTEP[13] scheme of the molecular structure of **10** cation. P11 represents a PPh_3 and P12 a $P(OEt)_3$.

All cation complexes in the asymmetric unit were similar. Table 2 was carefully ordered in the sake to show the small differences between corresponding values for the four molecules. Each one contain an osmium atom in a half-sandwich piano-stool structure coordinated by a pentamethylcyclopentadienyl group (Cp*), one $P(OMe)_3$, one PPh_3 and a dioxygen ligand in a η^2-coordination manner. The coordination of the Cp* (ring slippage between 0.062 to 0.088 Å) showed Os-C distances between 2.222(5) and 2.319(5) Å, with an Os-C average between 2.2656 and 2.275 Å, in a narrower range than that found in **9c**.

Phosphite Os-P bond lengths were between 2.2893(11) and 2.3034(12) Å, shorter than phosphine ones which were between 2.3595(11) and 2.3679(11) Å.

All of these were slightly longer than those of compound **9c**. Os-O bond lengths ranged from 2.020(3) to 2.044(3) Å, while O-O bond distances are between 1.413(5) and 1.430(5) Å. The dπ(Os)→π^*(η^2-O_2) binding component of side-on cation compound [OsX(η^2-O_2)(dcpe)$_2$]$^+$ was recently discussed[12b] concluding that compounds with distances in the upper side of the usual range observed for Os(η^2-O_2) derivatives (1.31 - 1.49 Å)[12-16] should be described as peroxo complexes of Os(IV). The O-O bond distances in **10** are even longer that the found in the peroxide compound Os(η^2-O_2)Cl(acyl-NHC)(P^{i}Pr$_3$)$_2$ (consequently, Os-O bonds are slightly shorter).[12a]

Besides the signals of the ancillary ligands C_5Me_5, PPh_3, $P(OR)_3$ and the BPh_4 anion, the ^{1}H NMR spectra of ethylene complexes **3** and **4** showed two broad signals at 2.36-2.38 and at 2.05 ppm attributed to the protons of the ethylene ligand. Lowering the sample temperature caused a number of variations in the spectra but even at -90 °C the two multiplets that appeared at 2.86 and at 2.25-2.20 ppm remained broad, indicating that a rotation of CH_2=CH_2 still took place at this temperature thus preventing the complete determination of the NMR parameters. However, the presence of the η^2-CH_2=CH_2 ligand was confirmed by the ^{13}C spectra which showed a broad singlet at 26.46-26.43 ppm correlated, in a

HMQC experiment, with the two multiplets at 2.36-2.38 and at 2.05 ppm that appeared in the proton spectra and was so attributed to the ethylene carbon resonance. In the temperature range between +20 and-80 °C, the $^{31}P\{^{1}H\}$ NMR spectra were two doublets fitting the proposed formulation for the complexes.

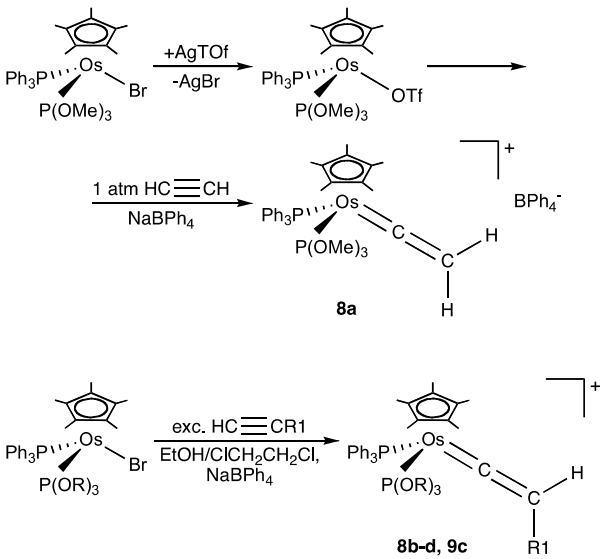
The IR spectrum of nitrile complex **5** showed a weak band at 2207 cm^{-1} that was attributed to the ν_{CN} of the nitrile ligand. The lowering of the ν_{CN} in **5** as compared to the free CH_2=CHCN suggests an η^2-coordination of the nitrile as an N-bond should have resulted in an increase of the ν_{CN} as in compound [Fe(η^5-C_5H_5)(κ^1-NCCH=CH_2)(dppp)]BPh_4.[5a,17] Support for this coordination came from the ^{1}H NMR spectrum which, besides the signals of the ancillary ligands C_5Me_5, PPh_3 and $P(OMe)_3$, showed a multiplet between 6.95 and 5.33 ppm attributed to the CH_2=C(H)CN protons. This multiplet was due to coupling of the nitrile protons with the ^{31}P nuclei of the P-ligands and can be simulated using an ABCXY model (A, B, C = ^{1}H; X, Y = ^{31}P) with the parameters reported in the Experimental section. The good fit between the calculated and experimental spectra strongly suggests an η^2-coordination of the acrylonitrile.

The infrared and NMR spectra (^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$) of 3*H*-pyrazole complexes [Os(η^5-C_5Me_5)(η^1-N=NC($C_{12}H_8$)CH=CH)(PPh_3){$P(OR)_3$}]BPh_4 (**6, 7**) and

vinylidene derivatives [Os(η^5-C_5Me_5){=C=C(H)R1}(PPh_3){$P(OR)_3$}]BPh_4 (**8, 9**) (see ESI) support the proposed formulations.

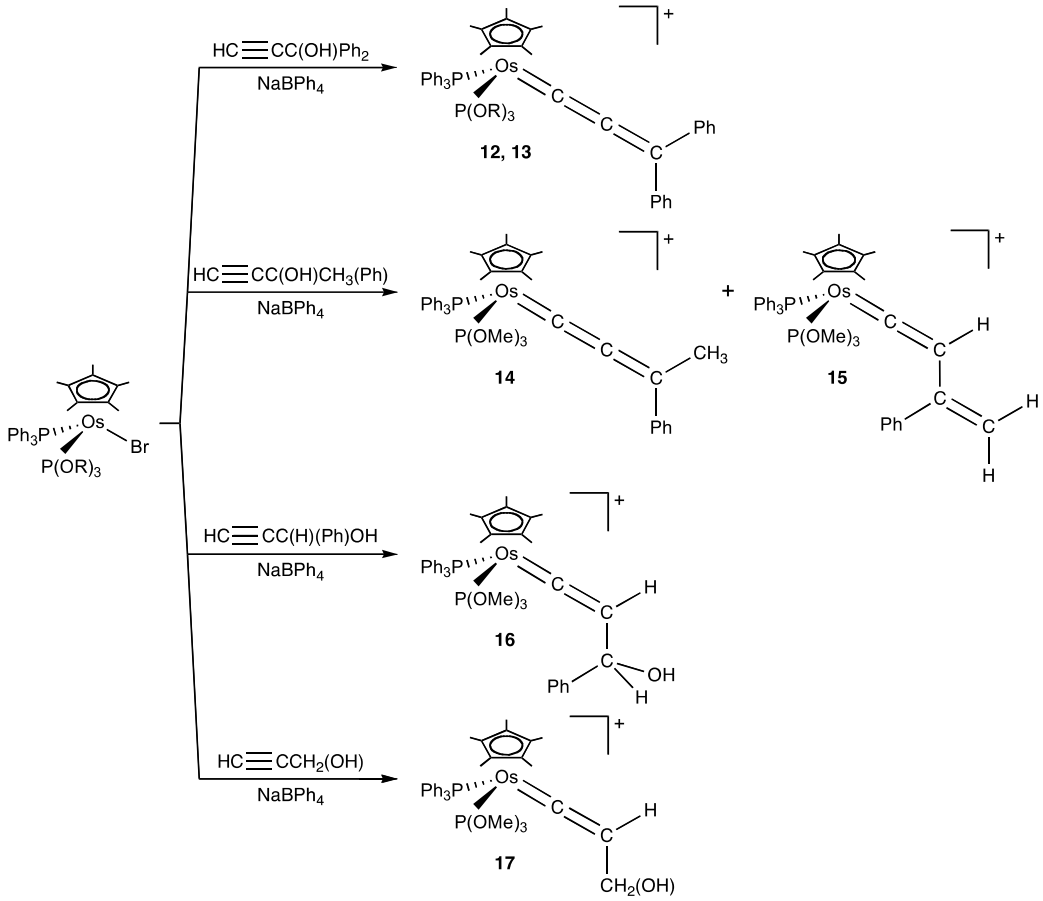
Besides the signals of the phosphines and the BPh_4 anion, the ^1H NMR spectra of dioxygen complexes **10** and **11** showed a singlet at 1.47-1.53 ppm of the methyl protons of the C_5Me_5. However, the $^{31}P\{^1H\}$ NMR spectra are two doublets, suggesting that a geometry similar to that observed in the solid state for **10** also occured in solution.

Vinylidene and allenylidene derivatives. Vinylidene complexes [Os(η^5-C_5Me_5){=CH=C(H)R1}(PPh_3){$P(OR)_3$}]BPh_4 (**8, 9**) were also prepared by reacting bromo-complexes OsBr(η^5-C_5Me_5)(PPh_3){$P(OR)_3$} with terminal alkynes HC≡CR1 in the presence of $NaBPh_4$, as shown in Scheme 5.



Scheme 5. R = Me (**8**), Et (**9**); R1 = Ph (**b**), *p*-tolyl (**c**), COOMe (**d**).

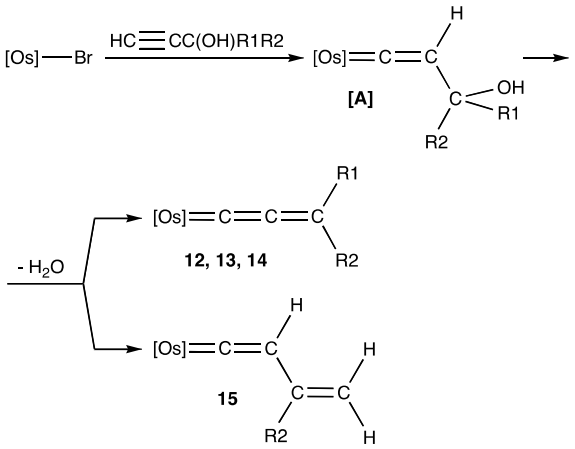
The $NaBPh_4$ salt favoured the substitution of Br^- with alkyne, which tautomerised on the metal centre yielding vinylidene derivatives **8** and **9**. These results prompted us to extend study to propargylic alcohols HC≡CC(OH)R1R2 with the aim of testing whether allenylidene complexes may be prepared. The results are summarised in Scheme 6.



Scheme 6. R = Me (**12**), Et (**13**).

Depending on the nature of substituents R1 and R2, the reaction of bromo-complexes $OsBr(\eta^5\text{-}C_5Me_5)(PPh_3)\{P(OR)_3\}$ with propargylic alcohols HC≡CC(OH)R1R2 afforded allenylidene [Os]=C=C=CR1R2 (**12-14**), vinylvinylidene

[Os]=C=C(H)C(Ph)=CH_2 (**15**) or 3-hydroxyvinylidene [Os]=C=C(H)C(H)R2(OH) (**16, 17**) derivatives, which were isolated and characterised. The presence of $NaBPh_4$ was crucial for successful syntheses as well as labilising the Br^- ligand and favoured the formation of the carbene derivatives. The reactions proceeded with the substitution of the bromo ligand and the formation, after tautomerisation on the metal centre,[9-11] of the hydroxyvinylidene intermediate **[A]** (Scheme 7).



Scheme 7. [Os] = $[Os(\eta^5\text{-}C_5Me_5)(PPh_3)\{P(OR)_3\}]^+$. R = Me (**12, 14, 15**), Et (**13**); R1 = R2 = Ph, (**12, 13**); R1 = Me, R2 = Ph (**14, 15**).

The loss of one water molecule from this 3-hydroxyvinylidene can afford either allenylidene **12-14** or vinylvinylidene **15** derivatives[18] depending on the presence of hydrogen atoms of the substituents in β position with respect to the hydroxy group. In fact, 1,1-diphenyl-2-propyn-1-ol yielded the allenylidene complexes [Os]=C=C=C=Ph_2 (**12, 13**), whereas 2-phenyl-3-butyn-1-ol afforded a

mixture of allenylidene [Os]=C=C=C=(CH_3)(Ph) (**14**) and vinylvinylidene [Os]=C=C(H)C(Ph)=CH_2 (**15**). Surprisingly, the reaction of the bromo-compound OsBr(η^5-C_5Me_5)(PPh_3){$P(OR)_3$} with 1-phenyl-2-propyn-1-ol and 2-propyn-1-ol afforded the hydroxyvinylidene derivatives [Os]=C=C(H)CH(Ph)OH (**16**) and [Os]=C=C(H)CH_2(OH) **(17**) which were very stable and did not undergo water loss giving the corresponding allenylidene derivatives. The reluctance of these 3-hydroxyvinylidene complexes to dehydrate even in protic solvents (EtOH) may be attributed both to the nature of the substituents of the vinylidene and to the properties of the pentamethylcyclopentadienyl osmium fragment, which stabilises 3-hydroxyvinylidene **16** and **17**, preventing the formation of allenylidene [Os]=C=C=C(H)R1 (R1 = H, Ph).

Despite the large number of reported complexes on ruthenium,[9a,19,20] allenylidene of osmium are rather rare and involve mainly η^5-cyclopentadienyl and η^6-arene complexes.[9a,19,20] The use of the mixed-ligands fragments [Os(η^5-C_5Me_5)(PPh_3){$P(OR)_3$}]$^+$ allowed the preparation of the first vinylidene and allenylidene complexes of Os containing the pentamethylcyclopentadienyl as a supporting ligand. [text moved up]

The IR spectra of allenylidene complexes [Os(η^5-C_5Me_5)(=C=C=CPh_2)(PPh_3){$P(OMe)_3$}]BPh_4 (**12**, **13**) showed a strong band at 1921-1925 cm^{-1} that were attributed to the $\nu_{=C=C=C}$ of the allenylidene ligand.[9a,19] This presence was confirmed by the $^{13}C\{^1H\}$ NMR spectra, which showed a doublet of doublets at 259.81 (**12**) and 259.41 (**13**) ppm attributed to the Cα resonance of the =Cα=Cβ=Cγ ligand. The Cβ and Cγ resonances appeared at 217.10 (**12**) and 218.60 (**13**) and at 146.26 (**12**) and145.10 (**13**) ppm, respectively, and their attribution was supported by HMQC and HMBC experiments. The $^{31}P\{^1H\}$ NMR spectra appeared as two doublets fitting the proposed formulation for the complexes.

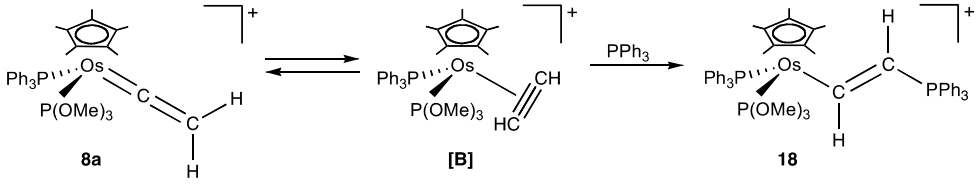
The IR spectra of the non-separable mixture containing the allenylidene **14** and the vinylvinylidene **15** complexes showed two characteristic bands, one at 1933 cm^{-1} attributed to the $\nu_{=C=C=C}$ of **14**, and the other at 1631 cm^{-1} attributed to the $\nu_{=C=C}$ of **15**. However, the presence of the two species was ascertained through $^{13}C\{^1H\}$ NMR spectra, which showed two doublets of doublets at 314.29 and 260.99 ppm assigned to the carbenic Cα of the vinylidene **15** and allenylidene **14**, respectively.[18] These values of chemical shift are strictly comparable with those of vinylidene complexes **8** and **9** and those of allenylidene

12 and **13**, thus supporting the presence of the two derivatives in the mixture. Two signals at 210.52 and 149.68 ppm also appeared in the $^{13}C\{^{1}H\}$ NMR spectra. These were attributed to the Cβ and Cγ of the allenylidene ligands, respectively. Further, a singlet at 114.04 ppm was attributed by HMQC to the Cβ of the vinylidene. In the $^{31}P\{^{1}H\}$ NMR spectra, two doublets of doublets appeared, in agreement with the proposed formulation for the mixture of **14** and **15**.

The presence of the 3-hydroxyvinylidene ligand in the complexes [Os(η^5-C_5Me_5){=C=C(H)C(H)R2(OH)}(PPh_3){$P(OMe)_3$}]BPh_4 (**16, 17**) was mainly confirmed by both IR and $^{13}C\{^{1}H\}$ NMR spectra. In particular, a medium-intensity band at 1647-1653 cm^{-1} due to the $\nu_{=C=C}$ of vinylidene appeared in the IR spectra, whereas one doublet of doublets appeared at 309.65 ppm for **17** and two doublet of doublets at 308.24 and 308.67 ppm for **16** were observed in the $^{13}C\{^{1}H\}$ NMR spectra of the complexes. These were attributed to the carbenic Cα carbon resonance of the =C=C(H)C(H)R2(OH) moiety. The presence of two doublets of doublets in the spectra of complex [Os(η^5-C_5Me_5){=C=C(H)C(H)Ph(OH)}(PPh_3){$P(OMe)_3$}]BPh_4 (**16**) is due to the fact that it was obtained as a mixture of two diastereoisomers, owing to the presence of two chiral centres in the molecule, *i.e.*, the osmium atom and the carbon atom

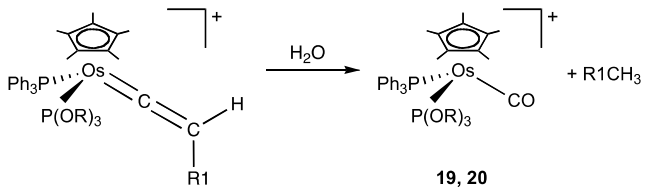
bonded to the Cβ of the vinylidene. In the $^{13}C\{^1H\}$ NMR spectra a singlet at 115.10 (**16**) and 107.95 (**17**) ppm also appeared. This was correlated in a HMQC experiment with the multiplet that appeared in the proton spectra at 2.49 (**16**) and 2.56 (**17**) ppm and was assigned to the Cβ carbon resonance of the vinylidene. Additionally, the signals of the vinylidene substituents CH_2OH and CH(Ph)OH also appeared in the proton spectra as a multiplet (ABCXY spin system) at 4.20-2.56 ppm (**17**) and as two doublets at 5.09 and 5.11 ppm (**16**). In the temperature range between +20 and -80 °C, the $^{31}P\{^1H\}$ NMR spectra appeared as two doublets for **17** and two doublets of doublets for **16**, fitting the proposed formulation for the complexes.

Vinylidene complexes were found to be stable with all substituents except in $[Os(\eta^5\text{-}C_5Me_5)(=C=CH_2)(PPh_3)\{P(OMe)_3\}]BPh_4$ (**8a**) which quickly decomposed in solution preventing complete characterisation. However, in the presence of PPh_3 a reaction occurred affording the alkenylphosphonium[21] derivative $[Os(\eta^5\text{-}C_5Me_5)\{\eta^1\text{-}C(H)=C(H)PPh_3\}(PPh_3)\{P(OMe)_3\}]BPh_4$ (**18**) which was stable and isolable (Scheme 8).



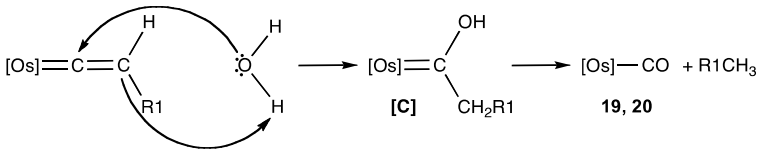
Scheme 8.

As proposed for the comparable alkenylphosphonium derivative [Ru(η^5-1,2,3-$R_3C_9H_4$){η^1-C(H)=C(Ph_3)Ph}(CO)(PPh_3)]BF_4,[21b] **18** is likely to form via a nucleophilic attack of phosphine on one of the two carbon atoms of the η^2-alkyne **[B]** in equilibrium with the vinylidene species (Scheme 8). Noticeably, the other vinylidene complexes with aryl or carboxyl substituents **8** and **9** did not react with phosphine in mild conditions probably owing to the absence of η^2-alkyne intermediate **[B]**. Instead, the vinylidene derivatives [Os]=C=C(H)R1 (R1 = Ph, 4-$CH_3C_6H_4$) underwent easy hydrolysis in solution at room temperature yielding as final products the carbonyl compounds [Os(η^5-C_5Me_5)(CO)(PPh_3){$P(OR)_3$}]BPh_4 (**19**, **20**), which were isolated and characterised (Scheme 9).



Scheme 9. R1 = Ph, R = Me (**19**); R1 = *p*-tolyl, R = Et (**20**).

Further, the formation of carbonyl derivatives **19** and **20** may be the result of the nucleophilic attack of H_2O on the vinylidene,[5f,22] giving an unstable carbene intermediate (**[C]**, Scheme 10).



Scheme 10. [Os] = $[Os(\eta^5\text{-}C_5Me_5)(PPh_3)\{P(OR)_3\}]^+$

Decomposition of intermediate **[C]** may involve the H-shift from the hydroxo group to the alkyl carbon atom of the carbene yielding the carbonyls **19** and **20** and free hydrocarbon $R1CH_3$. The presence of $R1CH_3$ in the reaction mixture was confirmed by GC analysis, thus supporting the reaction path proposed in Scheme 10. The reaction, therefore, entails hydrolysis of the terminal alkyne with C≡C bond cleavage and formation of carbonyl derivatives **19** and **20** and free hydrocarbon.

The reaction of vinylidene with H_2O prompted us to study the reactivity with other nucleophiles such as alcohol and amine in an attempt to prepare stable carbene complexes. Surprisingly, no reaction was observed with alkylamine RNH_2 in refluxing 1,2-dichloroethane as well as in refluxing EtOH or MeOH, indicating some reluctance of our vinylidenes to form oxy- or aminocarbene derivatives. In addition, a comparison of the reactivity of the vinylidene ligand bonded to the pentamethylcyclopentadienyl fragment $[Os(\eta^5\text{-}C_5Me_5)(PPh_3)\{P(OR)_3\}]^+$ with our previous results on $[Ru(\eta^5\text{-}C_5Me_5)(PPh_3)\{P(OR)_3\}]^+$ highlights the peculiar properties

of the osmium which cause both the preparation of the novel alkenylphosphonium derivative **18** and easy hydrolysis of terminal alkyne, with C≡C bond cleavage and formation of carbonyl derivatives **19** and **20**.

The new η^5-C_5Me_5 complexes **18**-**20** were all isolated as solids stable in air and in solution of polar organic solvents where they behaved as 1:1 electrolytes.[8] Analytical and spectroscopic (IR, ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR) data supported the proposed formulations which, in the case of [Os(η^5-C_5Me_5)(CO)(PPh_3){$P(OMe)_3$}]BPh_4 (**19**), was further confirmed by X-ray crystal structure determination, the ORTEP[13] of which is shown in Figure 3.

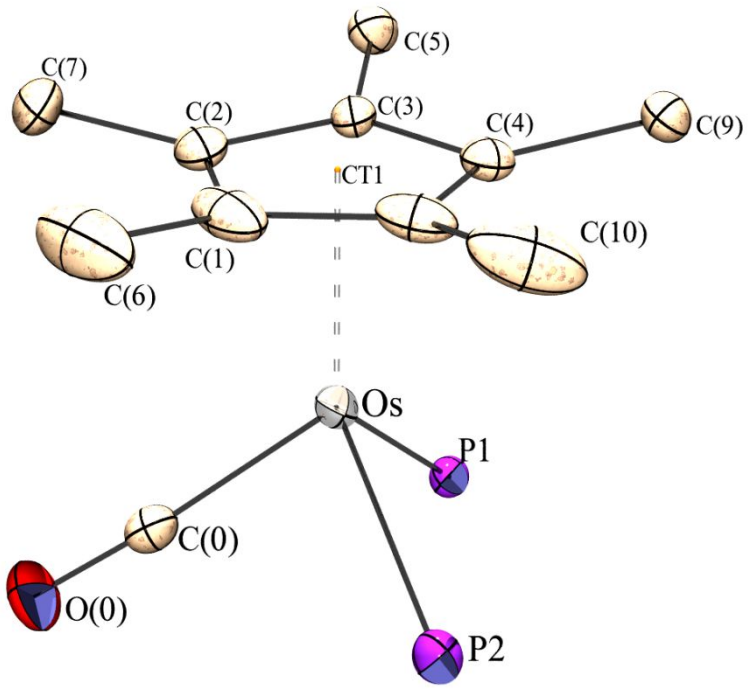


Figure 3. ORTEP[13] scheme of the molecular structure of **19** cation. P1 represents a PPh_3 and P2 a $P(OEt)_3$.

The cation of **19** contained an osmium atom in a half-sandwich piano-stool structure, coordinated by a pentamethylcyclopentadienyl group (Cp*), one $P(OMe)_3$, one PPh_3 and a carbonyl ligand. The overall geometry of the half-sandwich piano-stool complex was a slightly distorted octahedron and was marked by the angles between the centroid of the Cp* ligand (Ct1) and the legs close to the theoretical 125.3°, or by near 90° values for angles formed by the legs of the piano-stool (see Table 3). Coordination of the Cp* ligand (ring slippage, 0.031 Å) showed Os-C distances between 2.258(3) and 2.299(3) Å (average, 2.281 Å). The shorter Os-C bond corresponded to that *trans* to the phosphine ligand where the longer bond was not quite *trans* to the phosphite ligand. These values agree with the Os-P bond lengths, which also depended on the nature of the ligand, 2.2509(7) Å for the phosphite ligand and 2.3365(7) Å for the triphenylphosphine ligand. These values were analogous to those found in the above-mentioned compounds. Carbonyl ligand showing a C-Os bond length of 1.865(3) Å and O-C-Os angle 175.5(3)º. Further, they were close to those found, for example, in [Os(η^1-CH_2Ph)(CO)(η^6-*p*-cymene){$PPh(OEt)_2$}]BPh_4,[23] in Os(η^4-C_4H_5Ph)(CO)(P^iPr_3)$_2$[24] and for the 1-(methylthio)cyclopentadienyl cationic compound [Os(η^5-C_5H_4SMe)(CO)(PPh_3)$_2$]$^+$.[25] Interestingly, the latter is the only half-sandwich piano-

stool compound $Os(CO)P_2$ [that is, one carbonyl and two phosphorus atoms as legs] found in the CCDC data base,[26] either with any kind of cyclopentadienyl derivative (Cp, Cp*, indenyl, etc.) or benzene derivatives, including *p*-cymenes.

The ^1H NMR spectrum of the alkenylphosphonium derivative $[Os(\eta^5\text{-}C_5Me_5)\{\eta^1\text{-}C(H)=C(H)PPh_3\}(PPh_3)\{P(OMe)_3\}]BPh_4$ (**18**) showed two multiplets centred at 11.20 and 6.24 ppm which are attributable to the two vinyl protons of the alkenylphosphonium ligand $C(H)=C(H)PPh_3$. The two multiplets could be simulated using an AXYDE model (A, X, Y = ^{31}P; D, E = ^1H) and the good fit between the calculated and experimental spectra supports the presence of the alkenylphosphonium group. Further support came from the $^{13}C\{^1H\}$ NMR spectrum, which showed a multiplet at 191.09 ppm simulated with an AXYN model (N = ^{13}C) and, in a HMQC experiment, correlated with the multiplet at 11.20 ppm and attributed to the Cα carbon atom of the $C(H)=C(H)PPh_3$ ligand. A doublet at 98.54 ppm with a high $J_{^{13}C^{31}P}$ value of 75.48 Hz, instead, was attributed to the Cβ carbon resonance. In the temperature range between +20 and -80 °C, the $^{31}P\{^1H\}$ NMR spectrum of **18** is an AXY multiplet which may be simulated using the parameters reported in the Experimental section and matching the proposed formulation for the alkenylphosphonium derivative **18**.

The IR spectra of carbonyl complexes $[Os(\eta^5\text{-}C_5Me_5)(CO)(PPh_3)\{P(OR)_3\}]BPh_4$ (**19**, **20**) showed a strong band at 1944-1951 cm^{-1} attributed to the ν_{CO} of the carbonyl ligand, the presence of which was confirmed by the $^{13}C\{^1H\}$ NMR spectrum of **19** showing a doublet of doublets at 183.65 ppm of the CO carbon resonance. The proton spectra showed the characteristic signals of the ancillary ligands, whereas the ^{31}P spectra are two doublets suggesting a geometry in solution similar to those found in the solid state.

Conclusions

In this paper we report several results on the chemistry of half-sandwich pentamethylcyclopentadienyl complexes of osmium. In particular, we demonstrate that the $[Os(\eta^5\text{-}C_5Me_5)(PPh_3)\{P(OR)_3\}]^+$ fragment stabilises diazoalkane complexes which can undergo dipolar (3+2) cycloaddition with acetylene HC≡CH in mild conditions affording 3*H*-pyrazole derivatives. With ethylene and acrylonitrile, instead, diazoalkane substitution occurs yielding η^2-alkene derivatives. Novel dioxygen derivatives $[Os(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}O_2)(PPh_3)\{P(OR)_3\}]BPh_4$ may also be prepared. Vinylidene [Os]=C=C(H)R, allenylidene [Os]=C=C=CR1R2, vinylvinylidene [Os]=C=C(H)C(Ph)=CH_2 and hydroxyvinylidene [Os]=C=C(H)C(H)R(OH) complexes,

stabilised by the pentamethylcyclopentadienyl fragment, were also obtained. Finally, the reaction of osmium vinylidene complexes with water led to hydrolysis with C≡C bond cleavage whereas reaction with triphenylphosphine yielded alkenylphosphonium derivatives $[Os(\eta^5\text{-}C_5Me_5)\{\eta^1\text{-}C(H)=C(H)PPh_3\}(PPh_3)\{P(OR)_3\}]BPh_4$.

EXPERIMENTAL

Materials and Physical Measurements. All reactions were carried out in an inert atmosphere (argon) by means of standard Schlenk techniques or in an inert-atmosphere glove box. Once isolated, the complexes were found to be relatively stable in air, but were stored under nitrogen at -25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. OsO_4 was a Pressure Chemical Co. (USA) product, used as received. The phosphites $P(OMe)_3$ and $P(OEt)_3$ were Aldrich products, purified by distillation under argon. Diazoalkanes were prepared following the known methods.[27] ⌈text moved up⌋ ⌈The complex $OsBr(\eta^5\text{-}C_5Me_5)(PPh_3)_2$ was prepared following the method previously reported.[28] Precursor complexes $OsBr(\eta^5\text{-}C_5Me_5)(PPh_3)\{P(OR)_3\}$ (R = Me, Et) were prepared as follows: an excess

of the appropriate phosphite $P(OR)_3$ (2.1 mmol) was added to a solution of $OsBr(\eta^5\text{-}C_5Me_5)(PPh_3)_2$ (1.0 g, 1.07 mmol) in 50 mL of benzene and the reaction mixture was refluxed for 1 h. The solvent was removed under reduced pressure to give an oil, which was dissolved in diethylether and chromatographed on a silica gel column (80× 5 cm) using diethylether as eluent. The yellow fraction was collected and evaporated to dryness and the oil obtained was triturated with alcohol (2 mL). A yellow solid slowly separated out, which was filtered and dried under vacuum; yield 82% for R = Me, 80% for R = Et. **R = Me:** ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.60-7.25 (m, 15H, Ph), 3.39 (d, 9H, CH_3 phos), 1.41 (dd, 15H, CH_3 Cp*) ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 92.92, δ_X 7.57, J_{AX} = 38.89 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): 165-122 (m, Ph), 95.95 (s br, C_5 Cp*), 54.93 (d, CH_3 phos), 9.75 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{31}H_{39}BrO_3OsP_2$ (791.72): C, 47.03; H, 4.97; Found: C, 47.21; H, 4.90%. **R = Et:** ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.58-7.24 (m, 15H, Ph), 3.80 (m, 6H, CH_2), 1.40 (s, 15H, CH_3 Cp*), 1.01 (t, 9H, CH_3 phos) ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 89.19, δ_X 8.45, J_{AX} = 41.44 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): 165-122 (m, Ph), 96.18 (s br, C_5 Cp*), 65.15 (d, CH_2), 15.70 (d, CH_3 phos), 9.65 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{34}H_{45}BrO_3OsP_2$ (833.80): C, 48.98; H, 5.44;

Found: C, 48.79; H, 5.38%. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Perkin-Elmer Spectrum-One FT-IR spectrophotometer. NMR spectra (^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$) were obtained on an AVANCE 300 Bruker spectrometer at temperatures between -90 and +30 °C, unless otherwise noted. ^{1}H and ^{13}C spectra are referred to internal tetramethylsilane; $^{31}P\{^{1}H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. COSY, HMQC and HMBC NMR experiments were performed with standard programs. The iNMR software package[29] was used to process NMR data. The conductivity of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25 °C was measured on a Radiometer CDM 83. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze Farmaceutiche, University of Padova (Italy).

Synthesis of the complexes.

$[Os(\eta^5\text{-}C_5Me_5)(N_2CAr1Ar2)(PPh_3)\{P(OR)_3\}]BPh_4$ (1, 2) [Ar1 = Ar2 = Ph (a); Ar1 = Ph, Ar2 = *p*-tolyl (b); Ar1Ar2 = $C_{12}H_8$ (c); R = Me (1), Et (2)]. In a 25-mL three-necked round-bottomed flask were placed 0.1 mmol of the appropriate bromo-compound $OsBr(\eta^5\text{-}C_5Me_5)(PPh_3)\{P(OR)_3\}$, an excess of the appropriate

diazoalkane (0.3 mmol), an excess of $NaBPh_4$ (0.2 mmol, 68 mg), 5 mL of ethanol and 5 mL of dichloromethane. The reaction mixture was stirred at room temperature for 48 h and then the solvent removed under reduced pressure leaving an oil, which was triturated with ethanol (1 mL). A yellow-orange solid slowly separated out from the resulting solution, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield 72% for **1**, 75% for **2**.

1a: IR (KBr, cm^{-1}): ν_{N_2} 1941 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.55-6.87 (m, 45H, Ph), 3.29 (d, 9H, CH_3 phos), 1.53 (dd, 15H, CH_3 Cp*) ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 85.87, δ_X 7.43, J_{AX} = 41.20 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): 165-122 (m, Ph), 98.03 (dd, C_5 Cp*), 55.40 (d, CH_3 phos), 9.87 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{68}H_{69}BN_2O_3OsP_2$ (1225.28): C, 66.66; H, 5.68; N, 2.29; Found: C, 66.44; H, 5.75; N, 2.18%; Λ_M = 53.4 Ω^{-1} mol^{-1} cm^2.

1b: IR (KBr, cm^{-1}): ν_{N_2} 1942 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.78-6.88 (m, 44H, Ph), 3.29 (d, 9H, CH_3 phos), 2.43 (s, 3H, CH_3 *p*-tolyl), 1.39 (dd, 15H, CH_3 Cp*) ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 85.90, δ_X 7.51, J_{AX} = 40.98 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): 165-121 (m, Ph), 98.65 (s br, C_5 Cp*), 83.1 (br, C=N), 56.02 (d, CH_3 phos), 20.97 (s, CH_3 *p*-tolyl), 9.89 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{69}H_{71}BN_2O_3OsP_2$ (1239.30): C, 66.87; H, 5.77; N, 2.26;

Found: C, 66.68; H, 5.82; N, 2.20%; Λ_M = 52.7 Ω^{-1} mol^{-1} cm^2.

1c: IR (KBr, cm^{-1}): ν_{N_2} 1946 (m); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.96-6.86 (m, 43H, Ph+fluorene), 3.46 (d, 9H, CH_3 phos), 1.67 (dd, 15H, CH_3 Cp*); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 82.86, δ_X 6.00, J_{AX} = 41.32 Hz; ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): 165-121 (m, Ph+fluorene), 98.32 (dd, C_5 Cp*), 83.5 (br, C=N), 55.66 (d, CH_3 phos), 9.96 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{68}H_{67}BN_2O_3OsP_2$ (1223.26): C, 66.77; H, 5.52; N, 2.29; Found: C, 66.56; H, 5.43; N, 2.37%; Λ_M = 52.5 Ω^{-1} mol^{-1} cm^2.

2a: IR (KBr, cm^{-1}): ν_{N_2} 1935 (m); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.78-6.87 (m, 45H, Ph), 3.70 (m, 6H, CH_2), 1.56 (s, 15H, CH_3 Cp*), 1.08 (t, 9H, CH_3 phos); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 81.26, δ_X 7.38, J_{AX} = 42.28 Hz; ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): 165-122 (m, Ph), 97.06 (dd, C_5 Cp*), 83.83 (s br, C=N), 65.64 (d, CH_2), 15.90 (d, CH_3 phos), 9.87 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{71}H_{75}BN_2O_3OsP_2$ (1267.36): C, 67.29; H, 5.96; N, 2.21; Found: C, 67.13; H, 6.05; N, 2.16%; Λ_M = 51.8 Ω^{-1} mol^{-1} cm^2.

2b: IR (KBr, cm^{-1}): ν_{N_2} 1941 (m); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.75-6.87 (m, 44H, Ph), 3.70 (m, 6H, CH_2), 2.43 (s, 3H, CH_3 *p*-tolyl), 1.55 (s, 15H, CH_3 Cp*), 1.05 (t, 9H, CH_3 phos) ppm; ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A

81.43, δ_X 7.58, J_{AX} = 42.29 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): 165-122 (m, Ph), 97.82 (s br, C_5 Cp*), 65.71 (d, CH_2), 21.03 (s, CH_3 *p*-tolyl), 15.82 (d, CH_3 phos), 9.90 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{72}H_{77}BN_2O_3OsP_2$ (1281.38): C, 67.49; H, 6.06; N, 2.19; Found: C, 67.32; H, 5.98; N, 2.14%; Λ_M = 52.5 Ω^{-1} mol^{-1} cm^2.

2c: IR (KBr, cm^{-1}): ν_{N_2} 1946 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 8.40-6.77 (m, 43H, Ph+fluorene), 3.83 (qnt, 6H, CH_2), 1.66 (s, 15H, CH_3 Cp*), 1.12 (t, 9H, CH_3 phos) ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 77.92, δ_X 6.01, J_{AX} = 41.79 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): 165-121 (m, Ph+fluorene), 97.43 (dd, C_5 Cp*), 84.0 (br, C=N), 65.15 (d, CH_2), 16.03 (d, CH_3 phos), 9.73 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{71}H_{73}BN_2O_3OsP_2$ (1265.34): C, 67.39; H, 5.82; N, 2.21; Found: C, 67.54; H, 5.88; N, 2.13%; Λ_M = 52.9 Ω^{-1} mol^{-1} cm^2.

[Os(η^5-C_5Me_5)(η^2-CH_2=CH_2)(PPh_3){$P(OR)_3$}]BPh_4 (3, 4) [R = Me (3), Et (4)]. A solution of diazoalkane complex [Os(η^5-C_5Me_5)($N_2CC_{12}H_8$)(PPh_3){$P(OR)_3$}]BPh_4 (**1c**, **2c**) (0.1 mmol) in 10 mL of dichloroethane was refluxed under an ethylene CH_2=CH_2 atmosphere (1 atm) for 1 h. The solvent was removed under reduced pressure to leave an oil, which was triturated with ethanol (1 mL) containing $NaBPh_4$ (0.1 mmol, 34 mg). A yellow solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield 80% for **3**, 82% for **4**.

3: ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.43-6.88 (m, 35H, Ph), 3.48 (d, 9H, CH_3 phos), 2.36 (br), 2.05 (t) (4H, CH_2=CH_2), 1.43 (s, 15H, CH_3 Cp*); (-70 °C) δ: 2.86, 2.20 (m br, 4H, CH_2=CH_2); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 78.14, δ_X 4.91, J_{AX} = 34.75 Hz; ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): 164-122 (m, Ph), 96.41 (t, C_5 Cp*), 55.64 (d, CH_3 phos), 26.43 (s br, CH_2=CH_2), 9.08 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{57}H_{63}BO_3OsP_2$ (1059.10): C, 64.64; H, 6.00; Found: C, 64.41; H, 5.91%; Λ_M = 53.6 Ω^{-1} mol^{-1} cm^2.

4: ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.58-6.87 (m, 35H, Ph), 3.84 (d, 6H, CH_2 phos), 2.38 (br), 2.05 (m br) (4H, CH_2=CH_2), 1.42 (s, 15H, CH_3 Cp*), 1.13 (t, 9H, CH_3 phos); (-70 °C) δ: 2.86, 2.25 (m br, 4H, CH_2=CH_2); ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 74.34, δ_X 5.03, J_{AX} = 45.60 Hz; ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C): 165-122 (m, Ph), 96.30 (d, C_5 Cp*), 64.78 (d, CH_2 phos), 26.46 (br, CH_2=CH_2), 15.84 (d, CH_3 phos), 9.10 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{60}H_{69}BO_3OsP_2$ (1101.18): C, 65.44; H, 6.32; Found: C, 65.27; H, 6.24%; Λ_M = 52.1 Ω^{-1} mol^{-1} cm^2.

[Os(η^5-C_5Me_5){η^2-CH_2=C(H)CN}(PPh_3){P(OMe)$_3$}]BPh_4 (5). An exces of acrylonitrile CH_2=C(H)CN (1.0 mmol, 53 μL) was added to a solution of the diazoalkane complex [Os(η^5-C_5Me_5)($N_2CC_{12}H_8$)(PPh_3){P(OMe)$_3$}]BPh_4 (**1c**) (0.1

mmol, 0.122 g) in 8 mL of dichloromethane and the rection mixture was stirred at RT for 48 h. The solvent was removed under reduced pressure to leave an oil, which was triturated with ethanol (1 mL) containing $NaBPh_4$ (0.1 mmol, 34 mg). An orange solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield 76%. IR (KBr, cm^{-1}): ν_{CN} 2207 (w); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.71-6.87 (m, 35H, Ph), ABCXY spin syst (ABC = ^1H; XY = ^{31}P), δ_A = 6.95, δ_B = 6.52, δ_C = 5.33, J_{AB} = 7.1, J_{AC} = 1.4, J_{AX} = 2.1, J_{AY} = 0.2, J_{BC} = 7.6, J_{BX} = 1.7, J_{BY} = 0.1, J_{CX} = 1.0, J_{CY} = 0.1 (3H, CH_2=CH), 3.55 (d, 9H, CH_3 phos), 1.53 (s, 15H, CH_3 Cp^*) ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 88.75, δ_X 10.97, J_{AX} = 40.10 Hz; Anal. Calcd for $C_{58}H_{62}BNO_3OsP_2$ (1084.11): C, 64.26; H, 5.76; N, 1.29; Found: C, 64.09; H, 5.85; N, 1.20%; Λ_M = 51.8 Ω^{-1} mol^{-1} cm^2.

[Os(η^5-C_5Me_5)(η^1-N=CC($C_{12}H_8$)CH=CH)(PPh_3){$P(OR)_3$}]BPh_4 (6, 7) [R = Me (6), Et (7)]. A solution of the appropriate diazoalkane complex [Os(η^5-C_5Me_5)($N_2CC_{12}H_8$)(PPh_3){$P(OR)_3$}]BPh_4 (**1c, 2c**) (0.1 mmol) in 10 mL of dichlorometahne was stirred under acetylene HC≡CH (1 atm) for 48 h. The solvent was removed under reduce pressure to give an oil, which was triturated with ethanol (1 mL) containing an exces of $NaBPh_4$ (0.2 mmol, 68 mg). A yellow-

orange solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield 78% for **6**, 81% for **7**.

6: ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 8.40-6.87 (m, 43H, Ph+fluorene), 7.53 (d, $J_{^1H^1H}$ = 2.8, 1H, C5H), 6.72 (d, $J_{^1H^1H}$ = 2.8 Hz, 1H, C4H), 3.57 (d, 9H, CH_3 phos), 1.47 (s, 15H, CH_3 Cp*); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 89.15, δ_X 7.60, J_{AX} = 40.10 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): 165-122 (m, Ph+fluorene), 158.13 (s, C5), 139.39 (s, C4), 105.38 (br, C3), 95.58 (s, C_5 Cp*), 54.00 (d, CH_3 phos), 9.46 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{70}H_{69}BN_2O_3OsP_2$ (1249.30): C, 67.30; H, 5.57; N, 2.17; Found: C, 67.14; H, 5.66; N, 2.12%; Λ_M = 53.8 Ω^{-1} mol^{-1} cm^2.

7: ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.87 (d, $J_{^1H^1H}$ = 3.0, 1H, C5H), 7.70-6.87 (m, 43H, Ph+fluorene), 6.73 (d, $J_{^1H^1H}$ = 3.0 Hz, 1H, C4H), 3.84 (qnt, 6H, CH_2 phos), 1.31 (s, 15H, CH_3 Cp*), 1.24 (t, 9H, CH_3 phos); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 84.83, δ_X 7.36, J_{AX} = 440.83 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): 165-122 (m, Ph+fluorene), 157.47 (s, C5), 139.50 (s, C4), 105.31 (br, C3), 95.57 (s, C_5 Cp*), 63.01 (d, CH_2), 16.01 (d, CH_3 phos), 9.39 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{73}H_{75}BN_2O_3OsP_2$ (1291.38): C, 67.90; H, 5.85; N, 2.17; Found: C, 67.69; H, 5.77; N, 2.26%; Λ_M = 54.2 Ω^{-1} mol^{-1} cm^2.

[Os(η^5-C_5Me_5)(=C=CH_2)(PPh_3){$P(OMe)_3$}]BPh_4 (8a). In a 25-mL three-necked round-bottomed flask were placed 0.1 mmol (79 mg) of the bromo-compound OsBr(η^5-C_5Me_5)(PPh_3){$P(OMe)_3$}, a slight excess of AgOTf (0.11 mmol, 28.3 mg) and 5 mL of toluene. The reaction mixture was stirred in the dark for 1 h, filtered to remove the AgBr formed and then the solution evaporated to dryness under reduced pressure. Dichloromethane (5 mL) was added and the resulting solution allowed to stand under an acetylene HC≡CH atmosphere (1 atm). After 17 h of stirring, the solvent was removed under reduced pressure leaving an oil, which was triturated with ethanol (1 mL) containing $NaBPh_4$ (0.1 mmol, 34 mg). A gummy solid slowly separated out from the resulting solution, which was filtered and dried under vacuum. IR (KBr, cm^{-1}): $\nu_{C=C}$ 1633 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.80-6.81 (m, 35H, Ph), 4.42 (t, 2H, =CH_2), 3.44 (d, 9H, CH_3 phos), 1.44 (s, 15H, CH_3 Cp*) ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 79.55, δ_X 2.83, J_{AX} = 33.66 Hz.

[Os(η^5-C_5Me_5){=C=C(H)R1}(PPh_3){$P(OR)_3$}]BPh_4 (8, 9) [R1 = Ph (b), *p*-tolyl (c), COOMe (d); R = Me (8), Et (9)].

Method 1: An excess of the appropriate alkyne R1C≡CH (0.3 mmol) was added to a solution of diazoalkane complex [Os(η^5-

$C_5Me_5)(N_2CC_{12}H_8)(PPh_3)\{P(OR)_3\}]BPh_4$ (**1c**, **2c**) (0.1 mmol) in 5 mL of dichloromethane and the reaction mixture was stirred for 48 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (1 mL) containing $NaBPh_4$ (0.1 mmol, 34 mg). A pink solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield 80% for **8**, 83% for **9c**.

Method 2: In a 25-mL three-necked round-bottomed flask were placed 0.1 mmol of bromo-compound $OsBr(\eta^5\text{-}C_5Me_5)(PPh_3)\{P(OR)_3\}$, an excess of $NaBPh_4$ (0.2 mmol, 68 mg), an excess of the appropriate alkyne R1C≡CH (0.3 mmol), 5 mL of ethanol and 5 mL of 1,2-dichloroethane. The reaction mixture was refluxed for 4 h (6 h for **8d**) and then the solvent removed under reduced pressure leaving an oil, which was triturated with ethanol (1 mL) containing $NaBPh_4$ (0.1 mmol, 34 mg). A pink solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield 75% for **8**, 77% for **9c**.

8b: IR (KBr, cm^{-1}): $\nu_{C=C}$ 1650, 1628 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.75-6.86 (m, 40H, Ph), 3.44 (d, 9H, CH_3 phos), 3.15 (m, 1H, =CH), 1.66 (s, 15H, CH_3 Cp^*); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 81.29, δ_X 7.35, J_{AX} = 38.37; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): 316.31 (dd, J_{CP} = 12.7, J_{CP} = 9.1, Cα),

165-122 (m, Ph), 115.69 (s, Cβ), 102.97 (dd, J_{CP} = 1.7, J_{CP} = 1.3 Hz, C_5 Cp*), 55.38 (d, CH_3 phos), 9.84 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{63}H_{65}BO_3OsP_2$ (1133.18): C, 66.77; H, 5.78; Found: C, 66.59; H, 5.70%; Λ_M = 52.6 Ω^{-1} mol^{-1} cm^2.

8c: IR (KBr, cm^{-1}): $\nu_{C=C}$ 1655, 1632 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.47-6.87 (m, 39H, Ph), 3.43 (d, 9H, CH_3 phos), 3.13 (m, 1H, =CH), 2.30 (s, 3H, CH_3 *p*-tolyl), 1.65 (dd, J_{1H31P} = 18, J_{1H31P} = 1.0 Hz, 15H, CH_3 Cp*); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 81.54, δ_X 7.56, J_{AX} = 38.89; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): 317.46 (dd, J_{CP} = 9.04, J_{CP} = 3.77 Hz, Cα), 165-122 (m, Ph), 115.53 (s, Cβ), 102.88 (s, C_5 Cp*), 55.36 (d, CH_3 phos), 21.03 (s, CH_3 *p*-tolyl), 9.84 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{64}H_{67}BO_3OsP_2$ (1147.20): C, 67.01; H, 5.89; Found: C, 66.83; H, 5.97%; Λ_M = 51.7 Ω^{-1} mol^{-1} cm^2.

8d: IR (KBr, cm^{-1}): ν_{CO} 1699 (s), $\nu_{C=C}$ 1662, 1604 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.82-6.90 (m, 35H, Ph), 3.55 (s, 3H, CH_3CO), 3.47 (d, 9H, CH_3 phos), 2.83 (m, 1H, =CH), 1.69 (s, 15H, CH_3 Cp*); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 80.07, δ_X 5.61, J_{AX} = 39.70; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): 310.99 (dd, J_{CP} = 12.8, J_{CP} = 9.10 Hz, Cα), 165-122 (m, Ph), 161.50 (s, CO), 107.43 (s, Cβ), 103.63 (d, C_5 Cp*), 55.25 (d, CH_3 phos), 51.42 (d, $\underline{C}H_3CO$), 9.61 (s, CH_3

Cp*) ppm; Anal. Calcd for $C_{59}H_{63}BO_5OsP_2$ (1115.12): C, 63.55; H, 5.69; Found: C, 63.40; H, 5.76%; Λ_M = 53.0 Ω^{-1} mol^{-1} cm^2.

9c: IR (KBr, cm^{-1}): $\nu_{C=C}$ 1637 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.43-6.87 (m, 39H, Ph), 3.77 (qnt, 6H, CH_2), AXD spin syst (D = ^1H; AX = ^{31}P), δ_D 3.15, J_{AD} = 34.0, J_{XD} = 1.7 (1H, =CH), 2.39 (s, 3H, CH_3 *p*-tolyl), 1.65 (s, 15H, CH_3 Cp*), 1.13 (t, 9H, CH_3 phos); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 77.07, δ_X 7.24, J_{AX} = 37.42; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): 317.27 (dd, J_{CP} = 12.8, J_{CP} = 9.20 Hz, Cα), 165-122 (m, Ph), 115.42 (s, Cβ), 102.57 (s, C_5 Cp*), 64.43 (d, CH_2), 20.00 (d, CH_3 *p*-tolyl), 15.93 (d, CH_3 phos), 9.78 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{67}H_{73}BO_3OsP_2$ (1189.28): C, 67.66; H, 6.19; Found: C, 67.48; H, 6.32%; Λ_M = 52.4 Ω^{-1} mol^{-1} cm^2.

[Os(η^5-C$_5$Me$_5$)(η^2-O$_2$)(PPh$_3$){P(OR)$_3$}]BPh$_4$ (10, 11) [R = Me (10), Et (11)].

Method 1: A solution of diazoalkane complex [Os(η^5-C_5Me_5)(N_2CAr1Ar2)(PPh_3){$P(OR)_3$}]BPh_4 (**1**, **2**) (0.1 mmol) in 5 mL of dichloromethane was stirred under air (1 atm) for 48 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (1 mL) containing $NaBPh_4$ (0.1 mmol, 34 mg). A yellow solid slowly separated out, which was filtered and twice crystallised from CH_2Cl_2 and ethanol; yield 71% for **10**,

72% for **11**.

Method 2: In a 25-mL three-necked round-bottomed flask were placed 0.1 mmol of bromo-compound $OsBr(\eta^5\text{-}C_5Me_5)(PPh_3)\{P(OR)_3\}$, an excess of $NaBPh_4$ (0.2 mmol, 68 mg), 5 mL of CH_2Cl_2 and 5 mL of ethanol. The solution was stirred under air (1 atm) for 48 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (1 mL) containing $NaBPh_4$ (0.1 mmol, 34 mg). A yellow solid slowly separated out, from the resulting solution, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield 74% for **10**, 76% for **11**.

10: ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.48-6.87 (m, 35H, Ph), 3.54 (d, 9H, CH_3 phos), 1.47 (s, 15H, CH_3 Cp*) ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 52.67, δ_X -11.43, J_{AX} = 53.46 Hz; Anal. Calcd for $C_{55}H_{59}BO_5OsP_2$ (1063.04): C, 62.14; H, 5.59; Found: C, 61.93; H, 5.66%; Λ_M = 52.6 Ω^{-1} mol^{-1} cm^2.

11: ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.47-6.87 (m, 35H, Ph), 3.96 (m, 6H, CH_2), 1.53 (s, 15H, CH_3 Cp*), 1.06 (t, 9H, CH_3 phos) ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 47.18, δ_X -11.05, J_{AX} = 53.71 Hz; Anal. Calcd for $C_{58}H_{65}BO_5OsP_2$ (1105.12): C, 63.04; H, 5.93; Found: C, 62.84; H, 5.85%; Λ_M =

52.8 Ω^{-1} mol^{-1} cm^2.

It is worth noting that all diazoalkane complexes **1** and **2** exhibit the same reactivity patterns than **1c** and **2c**. However, in the preparation of compounds **3-11** were used **1c** and **2c** as starting materials because they afforded the best yields.

[Os(η^5-C_5Me_5)(=C=C=CPh_2)(PPh_3){$P(OR)_3$}]BPh_4 (12, 13) [R = Me (12), Et (13)]. In a 25-mL three-necked round-bottomed flask were placed 0.1 mmol of bromo-compound Os$Br(\eta^5$-$C_5Me_5)(PPh_3)${$P(OR)_3$}, an excess of $NaBPh_4$ (0.2 mmol, 68 mg), an excess of the propargylic alcohol HC≡CC(Ph_2)OH (0.4 mmol, 83 mg), 5 mL of ethanol and 5 mL of 1,2-dichloroethane. The reaction mixture was refluxed for 4 h and then the solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (1 mL). A dark-red solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield 70% for **12**, 73% for **13**.

12: IR (KBr, cm^{-1}): $\nu_{C=C=C}$ 1925 (s); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.89-6.87 (m, 45H, Ph), 3.41 (d, 9H, CH_3 phos), 1.65 (s, 15H, CH_3 Cp*); [$(CD_3)_2CO$, 20 °C] δ: 7.94-6.77 (m, 45H, Ph), 3.54 (d, 9H, CH_3 phos), 1.71 (s, 15H, CH_3 Cp*); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 82.71, δ_X 10.39, J_{AX} = 40.59;

[$(CD_3)_2CO$, 20 °C] δ: AX spin syst, δ_A 82.20, δ_X 10.12, J_{AX} = 41.44; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): 259.81 (dd, $J_{^{13}C^{31}P}$ = 10.5, $J_{^{13}C^{31}P}$ = 5.1, Cα), 217.10 (dd, $J_{^{13}C^{31}P}$ = 5.3, $J_{^{13}C^{31}P}$ = 1.5 Hz, Cβ), 165-122 (m, Ph), 146.20 (s, Cγ), 101.94 (d, C_5 Cp*), 54.04 (d, CH_3 phos), 9.79 (s, CH_3 Cp*); [$(CD_3)_2CO$, 20 °C] δ: 260.77 (dd, $J_{^{13}C^{31}P}$ = 10.2, $J_{^{13}C^{31}P}$ = 14.3 Hz, Cα), 219.32 (dd br, Cβ), 165-122 (m, Ph), 149.26 (s, Cγ), 102.61 (s, C_5 Cp*), 54.54 (d, CH_3 phos), 9.85 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{70}H_{69}BO_3OsP_2$ (1221.28): C, 68.84; H, 5.69; Found: C, 68.61; H, 5.58%; Λ_M = 51.5 Ω^{-1} mol^{-1} cm^2.

13: IR (KBr, cm^{-1}): $\nu_{C=C=C}$ 1921 (s); ^{1} ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.86-6.86 (m, 45H, Ph), 3.80 (qnt, 6H, CH_2), 1.63 (s, 15H, CH_3 Cp*), 1.09 (t, 9H, CH_3 phos); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 78.29, δ_X 10.57, J_{AX} = 40.95; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): 259.41 (dd, $J_{^{13}C^{31}P}$ = 10.3, $J_{^{13}C^{31}P}$ = 5.2, Cα), 218.63 (dd, $J_{^{13}C^{31}P}$ = 5.4, $J_{^{13}C^{31}P}$ = 1.4 Hz, Cβ), 165-122 (m, Ph), 145.10 (s, Cγ), 101.98 (d, C_5 Cp*), 63.61 (d, CH_2), 15.86 (d, CH_3 phos), 9.65 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{73}H_{75}BO_3OsP_2$ (1263.36): C, 69.40; H, 5.98; Found: C, 69.26; H, 6.07%; Λ_M = 52.6 Ω^{-1} mol^{-1} cm^2.

[Os(η^5-C_5Me_5){=C=C=C(Me)Ph}(PPh$_3$){P(OMe)$_3$}]BPh$_4$ (14) and [Os(η^5-C_5Me_5)-{=C=C(H)C(Ph)=CH$_2$}(PPh$_3$){P(OMe)$_3$}]BPh$_4$ (15). In a 25-mL three-necked

round-bottomed flask were placed 0.2 mmol (158 mg) of bromo-compound $OsBr(\eta^5\text{-}C_5Me_5)(PPh_3)\{P(OMe)_3\}$, an excess of $NaBPh_4$ (0.4 mmol, 136 mg), an excess of the propargylic alcohol HC≡CC(Me)(Ph)OH (0.8 mmol, 127 μL), 5 mL of ethanol and 10 mL of 1,2-dichloroethane. The reaction mixture was refluxed for 4 h and then the solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (1 mL). The reddish-brown solid that slowly separated out was filtered and fractionally crystallised from CH_2Cl_2 and ethanol. A typical crystallisation involved slow cooling up to -25 °C of a solution of the compound prepared in ethanol (4 mL) and enough dichloromethane to obtain a saturated solution at room temperature. In any case, no separation of the two compounds was observed, since the various fractions always contained the same ratio between the two tautomers; total yield about 70%.

14: IR (KBr, cm^{-1}): $\nu_{C=C=C}$ 1933 (s); ^1H NMR (CD_2Cl_2, 20 °C) δ: 8.14-6.86 (m, 40H, Ph), 3.41 (d, 9H, CH_3 phos), 1.80 (s, 3H, CH_3C=), 1.68 (s, 15H, CH_3 Cp*); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 81.85, δ_X 12.15, J_{AX} = 38.88 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): 260.99 (dd, Cα), 210.52 (dd, Cβ), 165-122 (m, Ph), 149.68 (s, Cγ), 101.18 (d, C_5 Cp*), 54.04 (d, CH_3 phos), 10.02 (s, $\underline{C}H_3C$=), 9.86 (s, CH_3 Cp*) ppm.

15: IR (KBr, cm^{-1}): $\nu_{Os=C=C}$ 1631 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.82-6.87 (m, 40H, Ph), 5.15 (d, 2H, $=CH_2$), 3.36 (d, 9H, CH_3 phos), 2.72 (m, 1H, =CH), 1.66 (s, 15H, CH_3 Cp*); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 82.63, δ_X 6.98, J_{AX} = 40.20; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): 314.29 (dd, $J_{^{13}C^{31}P}$ = 12.6, $J_{^{13}C^{31}P}$ = 9.3 Hz, Cα), 165-122 (m, Ph), 146.68 (s, Cγ), 114.04 (s, Cβ), 113.68 (s, Cδ), 102.40 (d, C_5 Cp*), 55.06 (d, CH_3 phos), 9.79 (s, CH_3 Cp*) ppm.

Anal. Calcd for $C_{65}H_{67}BO_3OsP_2$ (1159.21) *(tautomer mixture)*: C, 67.35; H, 5.83; Found: C, 67.15; H, 5.92%; Λ_M = 52.4 Ω^{-1} mol^{-1} cm^2.

[Os(η^5-C_5Me_5){=C=C(H)C(H)Ph(OH)}(PPh_3){$P(OMe)_3$}]BPh_4 (16) and [Os(η^5-C_5Me_5){=C=C(H)CH_2(OH)}(PPh_3){$P(OMe)_3$}]BPh_4 (17). These complexes were prepared by refluxing Os$Br(\eta^5$-$C_5Me_5)(PPh_3)\{P(OMe)_3\}$ with an excess of the appropriate propargylic alcohol HC≡CC(H)(Ph)OH or HC≡$CC(H_2)$OH (0.8 mmol), following the method used for **12** and **13**; yield 74% for **16**, 75% for **17**.

16: IR (KBr, cm^{-1}): $\nu_{C=C}$ 1653 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.55-6.87 (m, 40H, Ph), 5.09 (5.11) (d, 1H, =CCH), 3.38 (3.37) (d, 9H, CH_3 phos), 2.49 (m, 1H, =CH), 1.61 (1.65) (s, 15H, CH_3 Cp*); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 83.05, δ_X 8.17, J_{AX} = 40.80 (AX spin syst, δ_A 82.62, δ_X 8.31, J_{AX} = 40.40); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): ABX spin syst, δ_X 308.24, J_{AX} = 12.5, J_{BX} =

9.10 (ABX spin syst, δ_X 308.67, J_{AX} = 12.5, J_{BX} = 9.10 Hz) (Cα), 165-125 (m, Ph), 115.10 (114.65) (s, Cβ), 102.40 (br, C_5 Cp*), 70.64 (71.44) (s, Cγ), 54.72 (54.60) (s, CH_3 phos), 9.70 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{64}H_{67}BO_4OsP_2$ (1163.20): C, 66.08; H, 5.81; Found: C, 65.92; H, 5.70%; Λ_M = 53.1 Ω^{-1} mol^{-1} cm^2.

17: IR (KBr, cm^{-1}): $\nu_{C=C}$ 1647 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.59-6.87 (m, 35H, Ph), ABCXY spin syst (AB = CH_2; C = CH; XY = ^{31}P), δ_A = δ_B = 4.20, δ_C = 2.56, J_{AB} = 7.8, J_{AC} = 7.4, J_{AX} = 2.3, J_{AY} = 0.4, J_{BC} = 8.2, J_{BX} = 2.2, J_{BY} = 1.1, J_{CX} = 2.7, J_{CY} = 1.4 (3H, CH_2=CH), 3.41 (d, 9H, CH_3 phos), 1.65 (s, 15H, CH_3 Cp*); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 83.01, δ_X 9.01, J_{AX} = 40.10; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): 309.65 (dd, $J_{^{13}C^{31}P}$ = 8.5, $J_{^{13}C^{31}P}$ = 3.6, Cα), 165-122 (m, Ph), 107.95 (s, Cβ), 102.20 (d, C_5 Cp*), 57.88 (s, Cγ), 54.76 (d, $J_{^{13}C^{31}P}$ = 9.8 Hz, CH_3 phos), 9.58 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{58}H_{63}BO_4OsP_2$ (1087.11): C, 64.08; H, 5.84; Found: C, 63.89; H, 5.93%; Λ_M = 53.5 Ω^{-1} mol^{-1} cm^2.

[Os(η^5-C_5Me_5){η^1-C(H)=C(H)PPh_3}(PPh_3){$P(OMe)_3$}]BPh_4 (18). In a 25-mL three-necked round-bottomed flask were placed 0.1 mmol (79 mg) of the bromo-compound OsBr(η^5-C_5Me_5)(PPh_3){$P(OMe)_3$}, a slight excess of AgOTF (0.11 mmol,

28.3 mg) and 5 mL of toluene. The reaction mixture was stirred in the dark for 1 h, filtered to remove the AgBr formed and, after addition of 5 mL of dichloromethane, allowed to stand under acetylene HC≡CH (1 atm). After 17 h of stirring, an excess of PPh_3 (0.3 mmol, 79 mg) was added and the reaction mixture stirred for another 24 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (1 mL) containing an excess of $NaBPh_4$ (0.2 mmol, 68 mg). A reddish-brown solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield 70%. ^1H NMR (CD_2Cl_2, 20 °C) δ: AXYDE spin syst (DE = ^1H; AXY = ^{31}P), δ_D = 11.20, δ_E = 6.24, J_{AD} = 3.7, J_{AE} = 1.5, J_{XD} = 2.2, J_{XE} = 1.4, J_{YD} = 32.1, J_{YE} = 38.9, J_{DE} = 17.8 (2H, CH=CH), 7.71-6.86 (m, 50H, Ph), 3.22 (d, 9H, CH_3 phos), 1.42 (s, 15H, CH_3 Cp*); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AXY spin syst, δ_A 89.90, δ_X 16.06, δ_Y 10.48, J_{AX} = 38.6, J_{AY} = 4.4, J_{XY} = 5.7; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): AXYN spin syst (N = ^{13}C), δ_N = 191.09, J_{AN} = 10.0, J_{XN} = 8.7, J_{YN} = 12.6 (Cα), 165-122 (m, Ph), 98.54 (d, $J_{^{13}C^{31}P}$ = 75.5 Hz, Cβ), 93.52 (dd, C_5 Cp*), 54.61 (d, CH_3 phos), 9.60 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{75}H_{76}BO_3OsP_3$ (1319.37): C, 68.28; H, 5.81; Found: C, 68.11; H, 5.74%; Λ_M = 51.2 Ω^{-1} mol^{-1} cm^2.

[Os(η^5-C_5Me_5)(CO)(PPh_3){$P(OR)_3$}]BPh_4 (19, 20) [R = Me (19), Et (20)]. An

excess of H_2O (0.4 mmol, 7.2 μL) was added to a solution of the appropriate vinylidene complex [Os(η^5-C_5Me_5){=C=C(H)R1}(PPh_3){$P(OR)_3$}]BPh_4 (**8b, 9c**) [R1 = Ph (**b**), *p*-tolyl **(c)]** (0.1 mmol) in 5 mL of dichloromethane and the reaction mixture was stirred for 24 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (1 mL) containing $NaBPh_4$ (0.1 mmol, 34 mg). A yellow solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield 75% for **19**, 77% for **20**.

19: IR (KBr, cm^{-1}): ν_{CO} 1951 (s); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.70-6.89 (m, 35H, Ph), 3.44 (d, 9H, CH_3 phos), 1.70 (s, 15H, CH_3 Cp*); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 84.82, δ_X 9.27, J_{AX} = 33.79; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): 183.65 (dd, $J_{^{13}C^{31}P}$ = 15.7, $J_{^{13}C^{31}P}$ = 10.7 Hz, CO), 165-122 (m, Ph), 98.69 (dd, C_5 Cp*), 54.61 (d, CH_3 phos), 9.61 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{56}H_{59}BO_4OsP_2$ (1059.05): C, 63.51; H, 5.62; Found: C, 63.36; H, 5.50%; Λ_M = 52.5 Ω^{-1} mol^{-1} cm^2.

20: IR (KBr, cm^{-1}): ν_{CO} 1944 (s); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.70-6.87 (m, 35H, Ph), 3.85 (m, 6H, CH_2), 1.69 (s, 15H, CH_3 Cp*), 1.14 (t, 9H, CH_3 phos); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AX spin syst, δ_A 80.31, δ_X 9.73, J_{AX} = 34.82; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): 182.77 (dd, $J_{^{13}C^{31}P}$ = 16.0, $J_{^{13}C^{31}P}$ = 10.5 Hz, CO),

165-122 (m, Ph), 98.12 (dd, C_5 Cp*), 64.0 (d, CH_2), 16.03 (d, CH_3 phos), 9.65 (s, CH_3 Cp*) ppm; Anal. Calcd for $C_{59}H_{65}BO_4OsP_2$ (1101.13): C, 64.35; H, 5.95; Found: C, 64.19; H, 6.06%; Λ_M = 53.5 Ω^{-1} mol^{-1} cm^2.

Crystal structure determinations. Crystallographic data for compounds **9c**, **10** and **19** were collected at CACTI (Univ. of Vigo) at 100 K (CryoStream 800) using a Bruker D8 Venture Photon 100 CMOS detector and Mo-Kα radiation (λ = 0.71073 Å) generated by a Incoatec high brillance IμS microsource. The software APEX3[30] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT[30] for integration of intensity of reflections, and SADABS[30] for scaling and empirical absorption correction. The crystallographic treatment was performed with the Oscail program.[31] solved by using the SHELXT program.[32] The structure was subsequently refined by a full-matrix least-squares based on F^2, SHELXL program.[33] For compounds **10** and **19**, the *Squeeze* program[34] was used to eliminate the reflections due to a solvent disorder, since the quality of data did not allow to further model these molecules. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters. Other details of crystal data and structural refinement

are given in Table 4. PLATON, Version-230318[35] was used for obtain several geometrical parameters as ring slippage. CCDC 1874036-1874038 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

The financial support of MIUR - PRIN 2016 is gratefully acknowledged. Thanks are also due to Daniela Baldan, from the Università Ca' Foscari Venezia (Italy), for technical assistance.

References

1 *(a)* M. Dartiguenave, M. J. Menu, E. Deydier, Y. Dartiguenave and H. Siebald, *Coord. Chem. Rev.*, 1998, **178-180**, 623-663; *(b)* Y. Mizobe, Y. Ishii and M. Hidai, *Coord. Chem. Rev.*, 1995, **139**, 281-311; *(c)* W. A. Herrmann, *Angew, Chem., Int. Ed. Engl.*, 1978, **17**, 800-812; *(d)* D. Sutton, *Chem. Rev.*, 1993, **93**, 995-1022.

2 *(a)* S. J. Bonyhady, J. M. Goldberg, N. Wedgwood, T. R. Dugan, A. G. Eklund, W. W. Brennessel and P. L. Holland, *Inorg. Chem.*, 2015, **54**, 5148-

5150; *(b)* V. M. Iluc and G. L. Hillhouse, *J. Am. Chem. Soc.*, 2014, **136**, 6479-6488; *(c)* E. M. Matson, P. E. Fanwick and S. C. Bart, *Eur. J. Inorg. Chem.*, 2012, 5471-5478; *(d)* C. Khosla, A. B. Jackson, P. S. White and J. L. Templeton, *Organometallics*, 2012, **31**, 987-994; *(e)* S. K. Russell, E. Lobkovsky and P. J. Chirik, *J. Am. Chem. Soc.*, 2009, **131,** 36-37; *(f)* N. P. Mankad and J. C. Peters, *Chem. Commun.*, 2008, 1061-1063; *(g)* J. Zhang, M. Gandelman, L. J. W. Shimon and D. Milstein, *Organometallics*, 2008, **27**, 3526-3533; *(h)* R. G. Samant, T. W. Graham, B. D. Rowsell, R. McDonald and M. Cowie, *Organometallics*, 2008, **27**, 3070-3081 and references therein; *(i)* S. C. Bart, A. C. Bowman, E. Lobkovsky and P. J. Chirik, *J. Am. Chem. Soc.*, 2007, **129,** 7212-7213; *(j)* T. Schaub and U. Radius, *Z. Anorg. Allg. Chem.*, 2007, **633**, 2168-2172; *(k)* R. Cohen, B. Rybtchinski, M. Gandelman, H. Rozenberg, J. M. L. Martin and D. Milstein, *J. Am. Chem. Soc.*, 2003, **125**, 6532-6546; *(l)* B. D. Rowsell, S. J. Trepanier, R. Lam, R. McDonald and M. Cowie, *Organometallics*, 2002, **21**, 3228-3237; *(m)* Y. Gao, M. C. Jennings, R. J. Puddephatt and H. A. Jenkins, *Organometallics*, 2001, **20**, 3500-3509; *(n)* S. J. Bonyhady, D. E. DeRosha, J. Vela, D. J. Vinyard, R. E. Cowley, B. Q. Mercado, W. W. Brennessel and P. L. Holland, *Inorg. Chem.*, 2018, **57**, 5959-5972; *(o)* M. A. Alvarez, M. E. García, D. García-Vivó, E. Huergo, M. A. Ruiz and M. F. Vega, *Organometallics*, 2015, **34**, 38333841.

3 *(a)* L. Messerle and M. D. Curtis, *J. Am. Chem. Soc.*, 1980, **102**, 7789-7791; *(b)* C. Woodcock and R. Eisenberg, *Organometallics*, 1985, **4**, 4-7; *(c)* M. D. Curtis, L. Messerle, J. J. D'Errico, W. M. Butler and M. S. Hay, *Organometallics*, 1986, **5**, 2283-2294.

4 *(a)* A. Nakamura, T. Yoshida, M. Cowie, S. Otsuka and J. A. Ibers, *J. Am. Chem. Soc.*, 1977, **99**, 2108-2117; *(b)* K. D. Schramm and J. A. Ibers, *Inorg. Chem.*, 1980, **19**, 1231-1236; *(c)* K. D. Schramm and J. A. Ibers, *Inorg. Chem.*, 1980, **19**, 2435-2440; *(d)* K. D. Schramm and J. A. Ibers, *Inorg. Chem.*, 1980, **19**, 2441-2448; *(e)* G. L. Hillhouse, G. L. and B. L. Haymore, *J. Am. Chem. Soc.*, 1982, **104,** 1537-1548; *(f)* M. Cowie, S. J. Loeb and I. R. McKeer, *Organometallics*, 1986, **5**, 854-865; *(g)* M. Hidai, S. Aramaki, K. Yoshida, T. Kodama, T. Takahashi, Y Uchida and Y. Mizobe, *J. Am. Chem. Soc.*, 1986, **108**, 1562-1568; *(h)* A. W. Kaplan, J. L. Polse, G. E. Ball, R. A. Andersen and R. G. Bergman, *J. Am. Chem. Soc.*, 1998, **120,** 11649-11662; *(i)* H. Kwen, V. G. Jr. Young and E. A. Maatta, *Angew. Chem. Int. Ed.*, 1999, **38**, 1145-1146; *(j)* E. L. Dias, M. Brookhart, and P. S. White, *J. Am. Chem. Soc.*, 2001, **123**, 2442-2443; *(k)* H. Werner, N. Mahr, J. Wolf, A. Fries, M. Laubender, E. Bleuel, R. Garde and P. Lahuerta, *Organometallics*, 2003, **22**, 3566-3576.

5 *(a)* G. Albertin, S. Antoniutti, M. Bortoluzzi, A. Botter, J. Castro and F. Sibilla, *RSC Adv.*, 2016, **6**, 97650-97658; *(b)* G. Albertin, S. Antoniutti, M. Bortoluzzi, A. Botter and J. Castro, *J. Organomet. Chem.*, 2016, **822**, 259-268; *(c)* G. Albertin, S. Antoniutti, M. Bortoluzzi, A. Botter and J. Castro, *Inorg. Chem.*, 2016, **55**, 5592-5602; *(d)* G. Albertin, S. Antoniutti, M. Forcolin and D. Gasparato, *Polyhedron*, 2016, **104**, 46-51; *(e)* G. Albertin, S. Antoniutti, M. Bortoluzzi, J. Castro and L. Marzaro, *Dalton Trans.*, 2015, **44**, 15470-15480; *(f)* G. Albertin, S. Antoniutti, J. Castro and G. Dottorello, *Dalton Trans.*, 2015, **44**, 9289-9303; *(g)* G. Albertin, S. Antoniutti, A. Botter and J. Castro, *Inorg. Chem.*, 2015, **54**, 2091-2093; *(h)* G. Albertin, S. Antoniutti, A. Botter,

J. Castro and M. Giacomello, *Organometallics*, 2014, **33**, 3570-3582; *(i)* G. Albertin, S. Antoniutti, D. Baldan, J. Castro and G. Comparin, *Organometallics*, 2013, **32**, 3157-3160; *(j)* G. Albertin, S. Antoniutti, F. Callegaro and J. Castro, *Organometallics*, 2009, **28**, 4475-4479; *(k)* G. Albertin, S. Antoniutti, E. Bordignon and B. Carrera, *Inorg. Chem.*, 2000, **39**, 4646-4650.

6 *(a)* W. Baratta, A. Del Zotto and P. Rigo, *Organometallics*, 1999, **18**, 5091-5096; *(b)* A. Del Zotto, W. Baratta, M. Sandri, G. Verardo and P. Rigo, *Eur. J. Inorg. Chem.*, 2004, 524-529; *(c)* H. Seino, D. Watanabe, T. Ohnishi, C. Arita and Y. Mizobe, *Inorg. Chem.*, 2007, **46**, 4784-4786; *(d)* R. A. Zarkesh and A. F. Heyduk, *Organometallics*, 2009, **28**, 6629-6631; *(e)* M. A. Alvarez, M. E. García, R. Gonzalez and M. A. Ruiz, *Organometallics*, 2010, **29**, 5140-5153; *(f)* W. Ren, E. Zhou, B. Fang, G. Hou, G. Zi, D.-C. Fang and M. D. Walter, *Angew. Chem. Int. Ed.*, 2014, **42**, 11310-11314; *(g)* J. Egloff, M. Ranocchiari, A. Schira, C. Schotes and A. Mezzetti, *Organometallics*, 2013, **32**, 4690-4701.

7 *(a)* J. Louie and R. H. Grubbs, *Organometallics*, 2001, **20**, 481-484; *(b)* S. K. Russell, J. M. Hoyt, S. C. Bart, C. Milsmann, S. C. E. Stieber, S. P. Semproni, S. DeBeer and P. Chirik, *Chem. Sci.*, 2014, **5**, 1168-1174; *(c)* J. A. Bellow, S. A. Stoian, J. van Tol, A. Ozarowski, R. L. Lord and S. Groysman, *J. Am. Chem. Soc.*, 2016, **138**, 5531-5534.

8 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81-122.

9 *(a)* M. I. Bruce, *Chem. Rev.*, 1991, **91**, 197-257; *(b)* M. C. Puerta and P. Valerga, *Coord. Chem. Rev.*, 1999, **193-195**, 977-1025.

10 *(a)* M. Bullock, *J. Chem. Soc., Chem. Commun.*, 1989, 165-167; *(b)* M. A.

Esteruelas, L. A. Oro and C. Valero, *Organometallics*, 1995, **14**, 3596-3599; *(c)* I. de los Rios, M. Jiménez Tenorio, M. C. Puerta and P. Valerga, *J. Am. Chem. Soc.*, 1997, **119**, 6529-6538.

11 *(a)* J. Silvestre and R. Hoffmann, *Helv. Chim. Acta*, 1985, **68**, 1461-1506; *(b)* Y. Wakatsuki, N. Koga, H. Werner and K. Morokuma, *J. Am. Chem. Soc.*, 1997, **119**, 360-366.

12 *(a)* T. Bolaño, M. A. Esteruelas, M. P. Gay, E. Oñate, I. M. Pastor and M. Yus, *Organometallics*, 2015, **34**, 3902-3908; *(b)* P. Barthazy, M. Wörle, H. Rüegger and A. Mezzetti, *Inorg. Chem.*, 2000, **39**, 4903- 4912; *(c)* P. Barthazy, M. Wörle and A. Mezzetti, *J. Am. Chem. Soc.*, 1999, **121**, 480-481; *(d)* T. Y. Bartucz, A. Galombek, A. J. Lough, P. A. Maltby, R. H. Morris, R. Ramachandran and M. Schlaf, *Inorg. Chem.*, 1998, **37**, 1555-1562.

13 *(a)* L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565-565; *(b)* POV-Ray, v. 3.7 for Windows, Persistence of Vision Pty. Ltd. (2016) Persistence of Vision Raytracer (Version 3.7).

14 *(a)* A. L. Muller, H. Wadepohl and L. H. Gade, *Organometallics*, 2015, **34**, 2810-2818; *(b)* R. Castro-Rodrigo, M. A. Esteruelas, A. M. López, S. Mozo and E. Oñate, *Organometallics*, 2010, **29**, 4071-4079; *(c)* R. Castro-Rodrigo, M. A. Esteruelas, A. M. López, F. López, J. L. Mascarenas, M. Olivan, E. Oñate, L. Saya and L. Villarino, *J. Am. Chem. Soc.*, 2010, **132**, 454-455; *(d)* M. Baya, M. L. Buil, M. A. Esteruelas and E. Oñate, *Organometallics*, 2005, **24**, 2030-2038; *(e)* T. B. Wen, W. Y. Hung, Z. Y. Zhou, M. F. Lo, I. D. Williams and G. Jia, *Eur. J. Inorg. Chem.*, 2004, 2837-2846; *(f)* P. Barrio, M. A. Esteruelas and E. Oñate, *Organometallics*, 2002, **21**, 2491-2503; *(g)* D.

G. Gusev, T. Maxwell, F. M. Dolgushin, M. Lyssenko and A. J. Lough, *Organometallics*, 2002, **21**, 1095-1100; *(h)* M. Baya, P. Crochet, M. A. Esteruelas, A. M. Lopez, J. Modrego and E. Oñate, *Organometallics*, 2001, **20**, 4291-4294; *(i)* R. Castarlenas, M. A. Esteruelas, E. Gutierrez-Puebla and E. Oñate, *Organometallics*, 2001, **20**, 1545-1554; *(j)* R. Castarlenas, M. A. Esteruelas and E. Oñate, *Organometallics*, 2000, 19, 5454-5463.

15 S. K. S. Tse, W. Bai, H. H. Y. Sung, I. D. Williams and G. Jia, *Organometallics*, 2010, **29**, 3571-3581.

16 *(a)* S. M. Maddock, C. E. F. Richard, W. R. Roper and L. J. Wright, *J. Organomet. Chem.*, 1996, **510**, 267-279; *(b)* A. Mezzetti, E. Zangrando, A. Del Zotto and P. Rigo, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 1597-1598.

17 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, John Wiley and Sons, Inc., New York, 1963.

18 *(a)* V. Cadierno, S. Cornejero, M. P. Gamasa and J. Gimeno, *Organometallics*, 2002, **21**, 203-209; *(b)* M. A. Esteruelas, A. M. López, N. Ruiz and J. I. Tolosa, *Organometallics*, 1997, **16**, 4567-4667.

19 *(a)* H. Werner, *Chem. Commun.*, 1997, 903-904; *(b)* M. I. Bruce, *Chem. Rev.*, 1998, **98**, 2797-2858; *(c)* D. Touchard and P. H. Dixneuf, *Coord. Chem. Rev.*, 1998, **178-180**, 409-429; *(d)* V. Cadierno, M. P. Gamasa and J. Gimeno, *Eur. J. Inorg. Chem.*, 2001, 571-591.

20 M. A. Esteruelas, A. M. López and M. Oliván, *Coord. Chem. Rev.*, 2007, **251**, 795-840; *(b)* V. Cadierno and J. Gimeno, *Chem. Rev.*, 2009, **109**, 3512-3560.

21 *(a)* V. Cadierno, M. P. Gamasa, J. Gimeno, J. Borge and S. García-Granda,

Organometallics, 1997, **16,** 3178-3187; *(b)* V. Cadierno, M. P. Gamasa, J. Gimeno, C. González-Bernardo, E. Pérez-Carreño and S. García-Granda, *Organometallics*, 2001, **20**, 5177-5188; *(c)* M. J. Cowley, M. J. Lynam, R. S. Moneypenny, A. C. Whitwood and A. J. Wilson, *Dalton Trans.*, 2009, 9529-954.

22 *(a)* M. I. Bruce and A. G. Swincer, *Aust. J. Chem.*, 1980, **33**, 1471-1483; *(b)* B. P. Sullivan, R. S. Smythe, E. M. Kober and T. J. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 4701-4703; *(c)* J. M. O'Connor and L. Pu, *J. Am. Chem. Soc.*, 1990, **112**, 9013-9015; *(d)* C. Mountassir, T. Ben Hadda and H. Le Bozec, *J. Organomet. Chem.*, 1990, **388**, c13-c16; *(e)* W. Knaup and H. Werner, *J. Organomet. Chem.*, 1991, **411**, 471-489; *(f)* C. Bianchini, J. A. Casares, M. Peruzzini, A. Romerosa and F. Zanobini, *J. Am. Chem. Soc.*, 1996, **118**, 4585-4594; *(g)* M. L. Buil, M. A. Esteruelas, A. M. López and E. Oñate, *Organometallics*, 1997, **16**, 3169-3177; *(h)* M. V. Jiménez, E. Sola, A. P. Martínez, F. J. Lahoz and L. A. Oro, *Organometallics*, 1999, **18**, 1125-1136; *(i)* U. Belluco, R. Bertani, F. Meneghetti, R. A. Michelin and M. Mozzon, *J. Organomet. Chem.*, 1999, **583**, 131-135; *(j)* C. S. Chin, D. Chong, B. Maeng, J. Ryu, H. Kim, L. Kim and H. Lee, *Organometallics*, 2002, **21**, 1739-1742.

23 G. Albertin, S. Antoniutti and J. Castro, *Organometallics*, 2011, **30**, 1558-1568.

24 C. Bohanna, M. A. Esteruelas, F. J. Lahoz, E. Oñate, L. A. Oro and E. Sola, *Organometallics*, 1995, **14**, 4825-4831.

25 P. M. Johns, W. R. Roper, S. D. Woodgate and L. J. Wright,

Organometallics, 2010, **29**, 5358-5365.

26 CSD version 5.39 updates (Nov 2017), C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *Acta Crystallogr.*, 2016, **B72**, 171-179.

27 *(a)* L. I. Smith and K. L. Howard, *Organic Syntheses*, Wiley, New York, USA, 1955, vol. III, p. 351; *(b)* J. B. Miller, *J. Org. Chem.*, 1959, **24**, 560; *(c)* R. Baltzly, N. B. Mehta, P. B. Russell, R. E. Brooks, E. M. Grivsky and A. M. Steinberg, *J. Org. Chem.*, 1961, **26**, 3669.

28 C. L. Gross and G. S. Girolami, *Organometallics*, 1996, **15**, 5359-5367.

29 G. Balacco, http://www.inmr.net/

30 Bruker, *APEX3, SMART, SAINT*, Bruker AXS Inc., Madison, Wisconsin, USA, 2015.

31 P. McArdle, K. Gilligan, D. Cunningham, R. Dark and M. Mahon, *CrystEngComm*, 2004, **6**, 303-309.

32 G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3-8.

33 G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

34 A. L. Spek, *Acta Cryst.*, 2015, **C71**, 9-18.

35 A. L. Spek, *Acta Cryst.*, 2009, **D65**, 148-155.

Table 1. Selected list of bond lengths [Å] and angles [º] for **9c**.

Os-C(11)	1.859(5)	Os-CG1	1.9495(2)
Os-P(1)	2.3283(11)	Os-P(2)	2.2725(11)
Os-C(1)	2.274(4)	Os-C(4)	2.338(4)
Os-C(2)	2.267(4)	Os-C(5)	2.306(4)
Os-C(3)	2.315(4)	Os-C_{av}	2.300(4)
C(11)-C(12)	1.306(6)	C(12)-C(13)	1.476(6)
C(11)-Os-CG1	124.04(13)	C(11)-Os-P(1)	91.32(13)
CG1-Os-P(1)	126.23(3)	P(2)-Os-P(1)	93.35(4)
CG1-Os-P(2)	122.14(3)	C(11)-Os-P(2)	89.89(13)
Os-C(11)-C(12)	174.4(4)	C(11)-C(12)-C(13)	126.2(4)

Table 2. Selected bond lengths [Å] and angles [º] for **10**.

Os(1)-CT1	1.91834(14)	Os(3)-CT3	1.9177(2)
Os(1)-O(12)	2.026(3)	Os(3)-O(31)	2.031(3)
Os(1)-O(11)	2.041(3)	Os(3)-O(32)	2.019(3)
Os(1)-P(11)	2.3666(10)	Os(3)-P(31)	2.3678(11)
Os(1)-P(12)	2.2893(11)	Os(3)-P(32)	2.3034(12)
Os(1)-C(11)	2.242(4)	Os(3)-C(31)	2.255(5)
Os(1)-C(12)	2.240(4)	Os(3)-C(32)	2.240(5)
Os(1)-C(13)	2.274(4)	Os(3)-C(33)	2.222(5)
Os(1)-C(14)	2.323(4)	Os(3)-C(34)	2.314(5)
Os(1)-C(15)	2.297(4)	Os(3)-C(35)	2.319(4)
Os(1)-C_{av}	2.2756(4)	Os(3)-C_{av}	2.2702(5)
O(11)-O(12)	1.429(4)	O(31)-O(32)	1.430(5)
Os(2)-CT2	1.9142(2)	Os(4)-CT4	1.9214(2)
Os(2)-O(21)	2.028(3)	Os(4)-O(41)	2.032(3)
Os(2)-O(22)	2.044(3)	Os(4)-O(42)	2.024(3)
Os(2)-P(21)	2.3663(11)	Os(4)-P(41)	2.3595(11)
Os(2)-P(22)	2.2922(12)	Os(4)-P(42)	2.2885(13)
Os(2)-C(21)	2.238(4)	Os(4)-C(41)	2.235(5)
Os(2)-C(22)	2.238(4)	Os(4)-C(42)	2.287(4)
Os(2)-C(23)	2.268(4)	Os(4)-C(43)	2.302(4)
Os(2)-C(24)	2.304(5)	Os(4)-C(44)	2.294(5)
Os(2)-C(25)	2.280(4)	Os(4)-C(45)	2.256(5)
Os(2)-C_{av}	2.2656(5)	Os(4)-C_{av}	2.275(5)
O(21)-O(22)	1.425(5)	O(41)-O(42)	1.413(5)
CT1-Os(1)-O(11)	119.27(9)	CT3-Os(3)-O(31)	120.32(10)
CT1-Os(1)-O(12)	114.60(9)	CT3-Os(3)-O(32)	113.44(9)
CT1-Os(1)-P(11)	129.96(3)	CT3-Os(3)-P(31)	130.84(3)
CT1-Os(1)-P(12)	120.04(3)	CT3-Os(3)-P(32)	120.32(3)
O(11)-Os(1)-P(11)	103.77(9)	O(31)-Os(3)-P(31)	100.69(10)
O(11)-Os(1)-P(12)	85.61(9)	O(31)-Os(3)-P(32)	86.00(10)
O(12)-Os(1)-	41.14(12)	O(32)-Os(3)-	41.35(13)

O(11)		O(31)	
O(12)-Os(1)-P(11)	81.23(9)	O(32)-Os(3)-P(31)	79.26(9)
O(12)-Os(1)-P(12)	117.80(9)	O(32)-Os(3)-P(32)	119.20(10)
P(12)-Os(1)-P(11)	85.52(4)	P(32)-Os(3)-P(31)	86.00(4)
CT2-Os(2)-O(21)	115.27(10)	CT4-Os(4)-O(41)	120.62(10)
CT2-Os(2)-O(22)	120.43(10)	CT4-Os(4)-O(42)	116.13(10)
CT2-Os(2)-P(21)	129.87(3)	CT4-Os(4)-P(41)	129.13(3)
CT2-Os(2)-P(22)	119.24(3)	CT4-Os(4)-P(42)	118.76(3)
O(21)-Os(2)-O(22)	40.96(14)	O(41)-Os(4)-P(41)	103.58(10)
O(21)-Os(2)-P(21)	79.60(9)	O(41)-Os(4)-P(42)	85.70(10)
O(21)-Os(2)-P(22)	118.85(11)	O(42)-Os(4)-O(41)	40.78(13)
O(22)-Os(2)-P(21)	102.15(10)	O(42)-Os(4)-P(41)	80.98(10)
O(22)-Os(2)-P(22)	86.88(11)	O(42)-Os(4)-P(42)	117.75(10)
P(22)-Os(2)-P(21)	85.90(4)	P(42)-Os(4)-P(41)	86.29(4)

Table 3. Selected bond lengths [Å] and angles [º] for **19**.

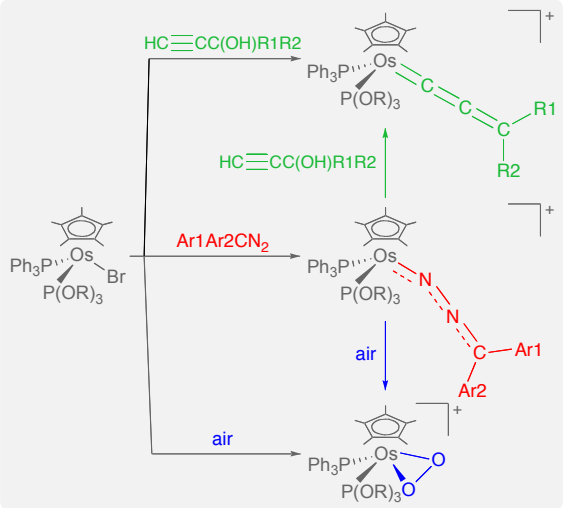
Os-C(0)	1.865(3)	Os-CT1	1.92863(12)
Os-P(1)	2.3365(7)	Os-P(2)	2.2509(7)
Os-C(1)	2.258(3)	Os-C(2)	2.279(3)
Os-C(3)	2.299(3)	Os-C(4)	2.289(3)
Os-C(5)	2.281(3)	Os-C_{av}	2.281(3)
C(0)-O(0)	1.153(3)	P(1)-C(11)	1.827(3)
C(0)-Os-CT1	124.64(9)	C(0)-Os-P(2)	89.10(9)
CT1-Os-P(2)	123.750(18)	P(2)-Os-P(1)	93.24(2)
C(0)-Os-P(1)	90.99(9)	CT1-Os-P(1)	124.975(17)
O(0)-C(0)-Os	175.5(3)		

Table 4. Crystal data and structure refinement.

Compound	**9c**	**10**	**19**
Empirical formula	$C_{67}H_{73}BO_3OsP_2$	$C_{55}H_{59}BO_5OsP_2$	$C_{56}H_{59}BO_4OsP_2$
Moiety formula	$C_{43}H_{53}O_3OsP_2$, $C_{24}H_{20}B$	$C_{31}H_{39}O_5OsP_2$, $C_{24}H_{20}B$	$C_{32}H_{39}O_4OsP_2$, $C_{24}H_{20}B$
Formula weight	1189.20	1062.97	1058.98
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	*P-1*	*P*-1	$P2_1/n$
Unit cell dimensions	a = 10.5543(8) Å b = 16.5381(13) Å c = 16.6482(13) Å α = 92.982(3)º β = 99.500(3)º γ = 94.337(3)º	a = 16.9078(12) Å b = 18.2131(14) Å c = 34.414(3) Å α = 102.266(2)º β = 96.846(2)º γ = 105.345(2)º	a = 17.0342(8) Å b = 16.7169(9) Å c = 18.2980(10) Å α = 90º β = 104.281(2)º γ = 90º
Volume	2851.7(4) $Å^3$	9812.0(13) $Å^3$	5049.5(5) $Å^3$
Z	2	8	4
Density (calculated)	1.385 Mg/m^3	1.439 Mg/m^3	1.393 Mg/m^3
Absorption coefficient	2.338 mm^{-1}	2.712 mm^{-1}	2.633 mm^{-1}
F(000)	1220	4312	2152
Crystal size	0.173 × 0.154 × 0.075 mm	0.231 × 0.043 × 0.025 mm	0.225 × 0.216 × 0.034 mm
Θ range for data collection	2.409 to 28.376º.	2.239 to 28.438º	2.242 to 28.355º
Index ranges	$-14 \le h \le 14$ $-22 \le k \le 22$ $-22 \le l \le 22$	$-22 \le h \le 22$ $-24 \le k \le 24$ $-46 \le l \le 46$	$-22 \le h \le 22$ $-22 \le k \le 22$ $-24 \le l \le 24$
Reflections collected	45360	425186	92143
Independent reflections	14113 [R_{int} = 0.0764]	49260 [R_{int} = 0.0561]	12602 [R_{int} = 0.0430]
Reflections observed (>σ)	11171	40377	10634
Data Completeness	0.988	0.995	0.999
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.5981	0.7457 and 0.6064	0.7457 and 0.6149
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	14113 / 0 / 676	49259 / 0 / 2337	12602 / 0 / 585
Goodness-of-fit on F^2	1.029	1.055	1.118
Final R indices [I>2σ(I)]	R_1 = 0.0493 wR_2 =	$R_1 = 0.0431$ $wR_2 = 0.0918$	R_1 = 0.0261 wR_2 =

R indices (all data)	0.0942 R_1 = 0.0756 wR_2 = 0.1023	$R_1 = 0.0597$ w$R_2 = 0.0977$	0.0633 R_1 = 0.0379 wR_2 = 0.0725
Largest diff. peak and hole	2.963 and -1.450 e.Å^{-3}	6.455 and -2.492 e.Å^{-3}	2.021 and -1.829 e.Å^{-3}

FOR THE TABLE OF CONTENTS ENTRY

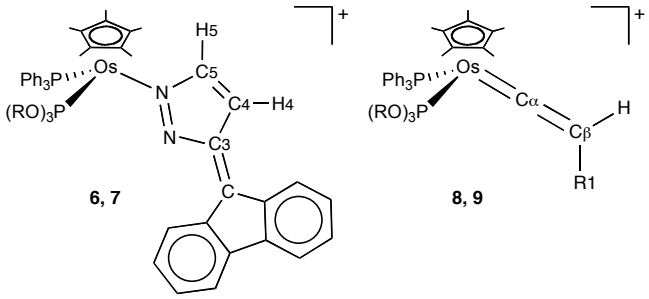


The preparation and reactivity of a series of half-sandwich pentamethylcyclopentadienyl complexes of osmium containing diazoalkane, alkene, dioxygen, vinylidene and allenylidene as ligands are described.

ELECTRONIC SUPPLEMENTARY INFORMATION

Title: Pentamethylcyclopentadienyl Osmium Complexes that Contain Diazoalkane, Dioxygen and Allenylidene Ligands: Preparation and Reactivity

Authors: Gabriele Albertin* *et al*.



The ^{1}H NMR spectra of the 3*H*-pyrazole complexes [Os(η^5-C_5Me_5)(η^1-N=CC($C_{12}H_8$)CH=CH)(PPh_3){$P(OR)_3$}]BPh_4 (**6, 7**) showed two doublets at 7.53 and 6.72 ppm (J_{HH} = 2.8 Hz) for **6** and at 7.87 and 6.73 ppm (J_{HH} = 3.0 Hz) for **7** attributed to H5 and H4 of the heterocycle, and the characteristic signals of the $C_{12}H_8$ substituent at C3. The ^{13}C{^{1}H} NMR spectra confirmed the presence of the 3*H*-pyrazole ligand showing, for **6**, two singlets at 158.13 and 139.39 ppm which, in a HMQC experiment, were correlated with the doublets at 7.53 and 6.72 ppm observed in the proton spectrum and attributed to C5 and C4 carbon resonances of the heterocycle; a singlet at 105.38 ppm was attributed to C3. In the ^{13}C{^{1}H} NMR spectrum of **7**, two singlets appeared at 157.47 and 139.50 ppm which, in a HMQC experiment, were correlated with the doublets at 7.87 and 6.73 ppm observed in the proton spectrum and attributed to C5 and C4 carbon resonances of the heterocycle. In the spectra, the signals of the ancillary ligands and the BPh_4 anion also appeared. The ^{31}P spectra are doublets of doublets fitting the proposed formulation for the complexes.

The IR spectra of vinylidene complexes **8** and **9** showed a medium-intensity band at 1662–1604 cm^{-1} attributed to the $\nu_{Os=C=C}$ of the vinylidene ligand. Its presence was confirmed by the multiplet taht appeared at 3.15 for **8b**, 3.13 for **8c,** 2.83 for **8d** and 3.15 ppm for **9c** in the proton

NMR spectra and attributed to the =C(H)R vinylidene proton. The $^{13}C\{^{1}H\}$ NMR spectra showed a doublet of doublets at 316.31 for **8b**, 317.46 for **8c,** 310.99 for **8d** and 327.17 ppm for **9c** of the Cα carbene carbon resonance =Cα=Cβ(H)[1-4] and a singlet at 115.69 for **8b**, 115.53 for **8c,** 107.47 for **8d** and 115.42 ppm for **9c** which, in a HMQC experiment, was correlated with the multiplet between 3.15 and 2.83 ppm in the ^{1}H NMR spectra and attributed to the Cβ carbon resonance of the =C=C(H)R1 group. The ^{31}P NMR spectra appeared as two doublets in agreement with the proposed formulation for the complexes.

References

1 *(a)* M. I. Bruce, *Chem. Rev.*, 1991, **91**, 197–257; *(b)* M. C. Puerta and P. Valerga, *Coord. Chem. Rev.*, 1999, **193–195**, 977–1025.

2 *(a)* M. Bullock, *J. Chem. Soc., Chem. Commun.*, 1989, 165–167; *(b)* M. A. Esteruelas, L. A. Oro and C. Valero, *Organometallics*, 1995, **14**, 3596–3599; *(c)* I. de los Rios, M. Jiménez Tenorio, M. C. Puerta and P. Valerga, *J. Am. Chem. Soc.*, 1997, **119**, 6529–6538.

3 *(a)* J. Silvestre and R. Hoffmann, *Helv. Chim. Acta*, 1985, **68**, 1461–1506; *(b)* Y. Wakatsuki, N. Koga, H. Werner and K. Morokuma, *J. Am. Chem. Soc.*, 1997, **119**, 360–366.

4 *(a)* A. L. Muller, H. Wadepohl and L. H. Gade, *Organometallics*, 2015, **34**, 2810–2818; *(b)* R. Castro-Rodrigo, M. A. Esteruelas, A. M. López, S. Mozo and E. Oñate, *Organometallics*, 2010, **29**, 4071–4079; *(c)* R. Castro-Rodrigo, M. A. Esteruelas, A. M. López, F. López, J. L. Mascarenas, M. Olivan, E. Oñate, L. Saya and L. Villarino, *J. Am. Chem. Soc.*, 2010, **132**, 454–455; *(d)* M. Baya, M. L. Buil, M. A. Esteruelas and E. Oñate, *Organometallics*, 2005, **24**, 2030–2038; *(e)* T. B. Wen, W. Y. Hung, Z. Y. Zhou, M. F. Lo, I. D. Williams and G. Jia, *Eur. J. Inorg. Chem.*, 2004, 2837–2846; *(f)* P. Barrio, M. A. Esteruelas and E. Oñate, *Organometallics*, 2002, **21**, 2491–2503; *(g)* D. G. Gusev, T. Maxwell, F. M. Dolgushin, M. Lyssenko and A. J. Lough, *Organometallics*, 2002, **21**, 1095–1100; *(h)* M. Baya, P. Crochet, M. A. Esteruelas, A. M. Lopez, J. Modrego and E. Oñate, *Organometallics*, 2001, **20**, 4291–4294; *(i)* R. Castarlenas, M. A. Esteruelas, E. Gutierrez-Puebla and E. Oñate, *Organometallics*, 2001, **20**, 1545–1554; *(j)* R. Castarlenas, M. A. Esteruelas and E. Oñate, *Organometallics*, 2000, 19, 5454–5463.