One-Pot Synthesis for Osmium(II) Azavinylidene−Carbyne and Azavinylidene−Alkenylcarbyne Complexes Starting from an Osmium(II) Hydride−Azavinylidene Compound

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Treatment at room temperature of the complex $OsHCl_2(=N=CMe_2)(P^iPr_3)_2$ (**1**) with $Ag[CF_3SO_3]$ and the subsequent stirring of the resulting solution under an acetylene atmosphere gives the azavinylidene−carbyne derivative $[OsCl(=N=CMe_2)(\equiv CCH_3)(P^iPr_3)_2][CF_3SO_3]$ (**2**). The related complexes $[OsCl(=N=CMe_2)(\equiv CCH_2R)(P^iPr_3)_2][CF_3SO_3]$ (R = Cy (**3**), $(CH_2)_2CH_3$ (**4**)) have been prepared by reaction of **1** with $Ag[CF_3SO_3]$ and cyclohexylacetylene or 1-pentyne. The structure of **2** in the solid state has been determined by an X-ray diffraction study. The geometry around the metal center could be described as a distorted trigonal bipyramid with apical phosphines and inequivalent angles within the Y-shaped equatorial plane. The azavinylidene coordinates in a bent fashion with an Os−N−C angle of 152.0(8)°. Complexes **2**−**4** react with MeLi to afford the five-coordinate azavinylidene−vinylidenes $OsCl(=N=CMe_2)(=C=CHR)(P^iPr_3)_2$ (R = H (**5**), Cy (**6**), $(CH_2)_2CH_3$ (**7**)), as a result of the deprotonation of the β-CH_2 group of the carbyne ligands in **2**−**4**. The formation of **2**−**4** involves azavinylidene−alkenyl and imine−vinylidene intermediates. In agreement with this, it is also reported that, at −25 °C, the addition of cyclohexylacetylene to the solution resulting from the treatment of **1** with $Ag[CF_3SO_3]$ affords $[Os\{(E)\text{-}CH=CHCy\}Cl(=N=CMe_2)(P^iPr_3)_2][CF_3SO_3]$ (**8**), where the H_β atom of the alkenyl ligand interacts with the osmium atom to form an agostic bond. At −30 °C, the addition of NaCl to tetrahydrofuran solutions of **8** gives $OsCl_2(=C=CHCy)(NH=CMe_2)(P^iPr_3)_2$ (**9**), which evolves into **6** in solution at room temperature. Complex **1** also reacts with $Ag[CF_3SO_3]$ and 2-methyl-1-buten-3-yne. The reaction leads to the azavinylidene−alkenylcarbyne $[OsCl(=N=CMe_2)(\equiv CCH=CMe_2)(P^iPr_3)_2][CF_3SO_3]$ (**10**), which by deprotonation with MeLi yields the azavinylidene−alkenylvinylidene $OsCl(=N=CMe_2)\{=C=CHC(Me)=CH_2\}(P^iPr_3)_2$ (**11**). The formation of **10** proceeds similarly to those of **2**−**4**. Thus, it has been observed that, at −25 °C, the addition of 2-methyl-1-buten-3-yne to the solution resulting from the treatment of **1** with $Ag[CF_3SO_3]$ gives $[Os\{(E)\text{-}CH=CHC(Me)=CMe_2\}Cl(=N=CMe_2)(P^iPr_3)_2][CF_3SO_3]$ (**12**), which in solution at room temperature evolves into **10**. The complexes $[OsCl(=N=CMe_2)(\equiv CCH=CPhR)(P^iPr_3)_2][CF_3SO_3]$ (R = H (**13**), CH_3 (**14**), Ph (**15**)) have been prepared by reaction of **1** with $Ag[CF_3SO_3]$ and 1-phenyl-2-propyn-1-ol, 2-phenyl-3-butyn-2-ol, and 1,1-diphenyl-2-propyn-1-ol, respectively. The deprotonation of **14** with MeLi affords $OsCl(=N=CMe_2)\{=C=CHC(Ph)=CH_2\}(P^iPr_3)_2$ (**15**).

Introduction

The synthesis of Fischer type carbyne complexes has been traditionally a laborious process, which has involved the formation of transition-metal-bonded sp^2- or sp-hybridized carbon atoms and their subsequent transformation into sp carbyne carbon atoms.[1]

In 1993, we showed that the carbynes $OsHCl_2(\equiv C\text{-}CH_2R)(P^iPr_3)_2$ and alkenylcarbynes $OsHCl_2(\equiv CCH=CR_2)(P^iPr_3)_2$ can be prepared in a one-pot synthesis by treatment of the dihydride−dichloro complex $OsH_2Cl_2(P^iPr_3)_2$ with terminal alkynes, alkynols, and 1-en-3-ynes. The key intermediates of these reactions are dihydrogen−vinylidene species, which evolve by electrophilic attack of the acidic hydrogen proton of the dihydrogen on the C_β atom of the vinylidene.[2]

The behavior of the complex $OsH_2Cl_2(P^iPr_3)_2$ in the presence of alkynes cannot be extrapolated to other osmium compounds containing two hydrogen atoms bonded to the metallic center. Up until now, in addition to $OsH_2Cl_2(P^iPr_3)_2$, the reactivity of three complexes has been studied: the dihydrogen $OsCl_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$,[3] the neutral seven-coordinate dihydride $OsH_2(\kappa^2\text{-}O_2\text{-}$

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$CCH_3)\{\kappa^1\text{-}OC(O)CH_3\}(P^iPr_3)_2$,[4] and the cationic seven-coordinate dihydride $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]^+$,[5] and between them serious differences of behavior are observed. It appears that the formed organometallic compound is a result of a sophisticated combination of electronic factors involving the metal and the alkyne. Thus, the dihydrogen complex $OsCl_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ reacts with phenylacetylene to give the carbene derivative $OsCl_2(=CHCH_2Ph)(CO)(P^iPr_3)_2$,[3] whereas the neutral dihydride $OsH_2(\kappa^2\text{-}O_2CCH_3)\{\kappa^1\text{-}OC(O)CH_3\}(P^iPr_3)_2$ affords the hydride−vinylidene $OsH(\kappa^2\text{-}O_2CCH_3)\{=C=CHC(CH_3)=CH_2\}(P^iPr_3)_2$ in the presence of 2-methyl-1-buten-3-yne,[4] and the cation $[OsH_2(\kappa^2\text{-}O_2CCH_3)(H_2O)(P^iPr_3)_2]^+$ gives hydride−osmacyclopropenes, hydride−carbynes,[5] or mixtures of both types of compounds depending upon the nature of the alkyne.[6]

In contrast to the osmium compounds containing two hydrogen atoms bonded to the metal, the chemistry of osmium monohydrides in the presence of terminal alkynes is very clear. Via vinylidene[7] or π-alkyne[8] intermediates, they afford alkenyl derivatives.[9] When alkynols are used, alkenylcarbene compounds are also obtained.[10] However, the formation of carbyne complexes has not been observed.

Azavinylidene complexes are an interesting class of transition-metal compounds containing an M−N double bond.[11,12] Some of them have even been proposed as intermediates in the catalytic and stoichiometric reduction of nitriles[13,11s,x] and in the ammoxidation of propylene.[11o] Hydride−azavinylidene complexes are very rare, and only two mononuclear species had been reported before 2000: the five-coordinate d^6 derivatives $MH(=N=CPh_2)(CO)(P^iPr_3)_2$ (M = Ru,[14] Os[15]).

We have recently shown that the dihydride−dichloro complex $OsH_2Cl_2(P^iPr_3)_2$ reacts, in a one-pot synthesis, not only with terminal alkynes but also with oximes. The reactions lead to the six-coordinate d^4 hydride−azavinylidene derivatives $OsHCl_2(=N=CR_2)(P^iPr_3)_2$,[16] which are related to the carbynes $OsHCl_2(\equiv CCH_2R)(P^iPr_3)_2$ containing an azavinylidene ligand instead of a carbyne group.

These hydride−azavinylidene complexes do not react with phenylacetylene due to their saturated character. However, the treatment of dichloromethane solutions of $OsHCl_2(=N=CR_2)(P^iPr_3)_2$ with $Ag[CF_3SO_3]$ at room temperature and the subsequent addition at −25 °C of phenylacetylene affords the alkenyl derivatives $[Os\{(E)\text{-}CH=CHPh\}Cl(=N=CR_2)(P^iPr_3)_2]^+$. These compounds are the result of the addition of the M−H bond of the starting materials to the carbon−carbon triple bond of the alkyne, in agreement with the general tendency shown by the osmium monohydride complexes. In solution at room temperature, the azavinylidene−styryl compounds are unstable and evolve into a novel type of derivative, containing the imine and vinylidene functional groups, by the novel hydrogen transfer reaction from styryl groups to azavinylidene ligands.[17]

In this paper, we report the formation of other two novel types of difunctional organometallic compounds, azavinylidene−carbyne and azavinylidene−alkenyl-

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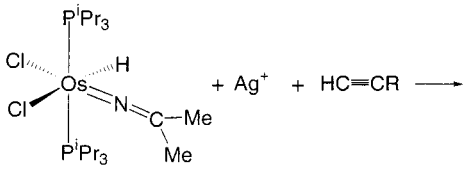
carbyne, and show that not only the reaction products from dihydrides and alkynes are the result of a sophisticated combination of electronic factors involving the metal and the alkyne but also those formed from monohydrides and alkynes.

Results and Discussion

1. Reactions of $OsHCl_2(=N=CMe_2)(P^iPr_3)_2$ with HC≡CR. Treatment at room temperature of dichloromethane solutions of $OsHCl_2(=N=CMe_2)(P^iPr_3)_2$ (**1**) with 1.0 equiv of $Ag[CF_3SO_3]$, and the subsequent stirring of the resulting solution under an acetylene atmosphere, gives rise to the five-coordinate azavinylidene−carbyne complex $[OsCl(=N=CMe_2)(\equiv CCH_3)(P^iPr_3)_2][CF_3SO_3]$ (**2**). The related compounds $[OsCl(=N=CMe_2)(\equiv CCH_2R)(P^iPr_3)_2][CF_3SO_3]$ (R = Cy (**3**), $(CH_2)_2CH_3$ (**4**)) were similarly prepared by reaction of **1** with $Ag[CF_3SO_3]$ and the corresponding alkyne (eq 1).



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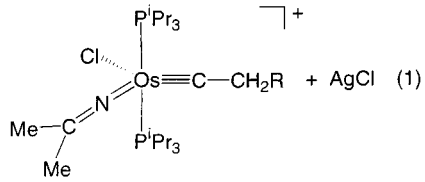

R = H (**2**), Cy (**3**), $(CH_2)_2CH_3$ (**4**)

Complexes **2**−**4** were isolated as yellow solids in about 80% yield, and they were characterized by MS, elemental analysis, and IR and $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectroscopy. Complex **2** was further characterized by an X-ray crystallographic study. A view of the molecular geometry of the cation of the complex is shown in Figure 1. Selected bond distances and angles are listed in Table 1.

The geometry around the osmium atom can be rationalized as a distorted trigonal bipyramid with apical phosphines (P(1)−Os−P(2) = 165.60(11)°) and inequivalent angles within the Y-shaped equatorial plane. The angles C(22)−Os−N, C(22)−Os−Cl, and N−Os−Cl are 111.6(5), 108.8(5), and 139.6(3)°, respectively. This Y structure is similar to that found in the vinylidene complex $OsCl(=N=CMe_2)(=C=CHPh)(P^iPr_3)_2$[18] and the calculated structure for $RuHCl(=C=CH_2)(PH_3)_2$.[19] However, it contrasts with the structure of the carbene complexes $RuCl_2(=CR_2)(P^iPr_3)_2$, in which the carbene ligand occupies the apical position of a square pyramid.[20]

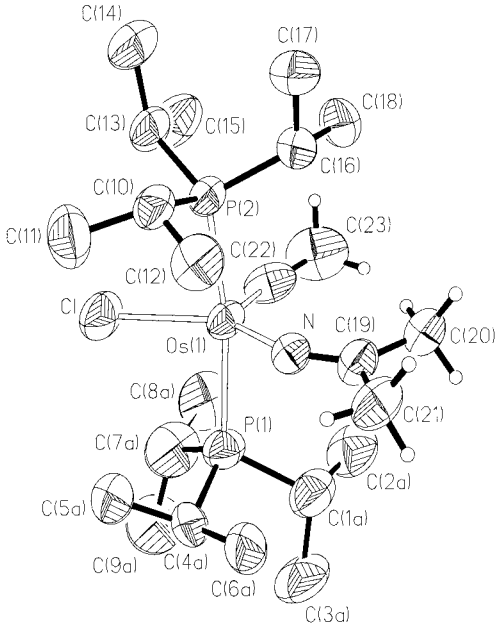

Figure 1. Molecular diagram for the cation of $[OsCl(=N=CMe_2)(\equiv CCH_3)(P^iPr_3)_2][CF_3SO_3]$ (**2**). Thermal ellipsoids are shown at 50% probability.

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complex $[OsCl(=N=CMe_2)(\equiv CCH_3)(P^iPr_3)_2][CF_3SO_3]$ (2)

Os(1)−Cl	2.401(3)	Os(1)−N	1.871(8)
Os(1)−P(1)	2.426(3)	N−C(19)	1.267(13)
Os(1)−P(2)	2.434(3)	C(22)−C(23)	1.488(19)
Os(1)−C(22)	1.720(13)		
Cl−Os(1)−P(1)	87.25(11)	P(1)−Os(1)−N	88.3(3)
Cl−Os(1)−P(2)	86.21(11)	P(2)−Os(1)−C(22)	97.9(4)
Cl−Os(1)−C(22)	108.8(5)	P(2)−Os(1)−N	88.4(3)
Cl−Os(1)−N	139.6(3)	C(22)−Os(1)−N	111.6(5)
P(1)−Os(1)−P(2)	165.60(11)	Os−N−C(19)	152.0(8)
P(1)−Os(1)−C(22)	96.3(4)	Os−C(22)−C(23)	169.4(12)

The very short Os−C(22) bond length of 1.720(13) Å is fully consistent with an Os−C(22) triple-bond formulation. Similarly to other metal carbyne compounds,[21] a slight bending in the Os−C(22)−C(23) moiety is also present (Os−C(22)−C(23) = 169.4(12)°).

The azavinylidene ligand coordinates to the osmium atom in a bent fashion with an Os−N−C(19) angle of 152.0(8)°. A similar coordination mode has been observed for the azavinylidene ligands of the osmium complexes $OsCl(=N=CMe_2)(=C=CHPh)(P^iPr_3)_2$ (157.2(6)°),[18] $[Os\{=N=C(Me)^tBu\}(\eta^6\text{-}C_6H_6)(P^iPr_3)][PF_6]$ (167(2), 168(2), and 155(2)°),[12m] and *cis*-$[OsCl_2\{=N=C(Ph)(2\text{-}PhCOC_6H_4)\}(terpy)][PF_6]$ (168.3(3)°).[12t] The Os−N distance of 1.871(8) Å is similar to that of $OsCl(=N=CMe_2)(=C=CHPh)(P^iPr_3)_2$ (1.873(5) Å)[18] and intermediate between those found in $OsCl_2(=C=CHPh)(NH=CMe_2)(P^iPr_3)_2$ (2.072(7) Å)[17] and in the complexes $[Os\{=N=C(Me)^tBu\}(\eta^6\text{-}C_6H_6)(P^iPr_3)][PF_6]$ (1.81(2) and 1.83(2)Å),[12m] and in *cis*-$[OsCl_2\{=N=C(Ph)(2\text{-}PhCOC_6H_4)\}(terpy)][PF_6]$ (1.812(6) Å),[12t] while the N−C(19) distance of 1.267(13) Å is similar to those found in the aforementioned compounds.

In addition, it should be mentioned that the methyl carbon atoms C(20) and C(21) form a plane with the

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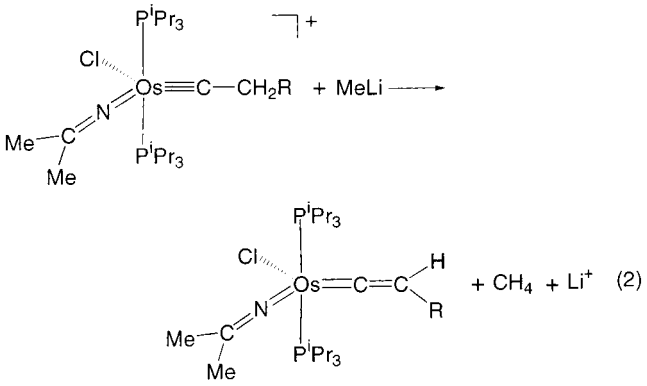
Os−C−N unit, which is perpendicular to the best plane containing the phosphorus atoms of the phosphine ligands and the osmium atom (89.8(3)°).

The IR and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra of **2**−**4** are consistent with the structure shown in Figure 1. The IR spectra in KBr contain a ν(C═N) band at about 1670 cm^{-1}, along with the characteristic stretching bands of the free $[CF_3SO_3]^-$ anion[22] (see Experimental Section), in agreement with the salt character of the complexes. Because the azavinylidene ligand lies in the Y plane, the methyl groups are inequivalent and, in the ^{1}H NMR spectrum, they display two singlets between 2.6 and 2.2 ppm. The resonances corresponding to the hydrogen atoms bonded to the C_β atom of the carbyne groups are observed between 2.9 and 2.5 ppm. The ^{13}C{^{1}H} NMR spectra show the characteristic Os≡C resonance of the carbyne ligands, which appear at about 290 ppm as triplets with C−P coupling constants of about 5 Hz. The ^{31}P{^{1}H} NMR spectra contain singlets between 36 and 33 ppm.

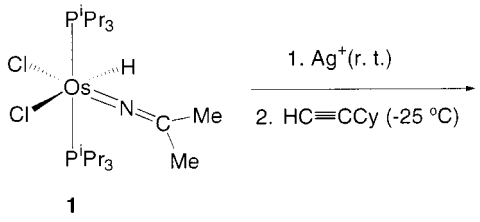
Complexes **2**−**4** react with MeLi to give the azavinylidene−vinylidene derivatives OsCl(═N═CMe$_2$)(═C═CHR)(P^{i}Pr$_3$)$_2$ (R = H (**5**), Cy (**6**), (CH$_2$)$_2$CH$_3$ (**7**)), as a result of the extraction of a proton of the β-CH$_2$ groups (eq 2).



R = H (**2, 5**), Cy (**3, 6**), (CH$_2$)$_2$CH$_3$ (**4, 7**)

Complexes **5** and **6** were obtained as orange solids in 73% and 80% yields, respectively, whereas complex **7** was obtained as an orange oil in quantitative yield. The spectroscopic data of these complexes agree well with those previously reported for the related compound OsCl(═N═CMe$_2$)(═C═CHPh)(P^{i}Pr$_3$)$_2$, where the trigonal-bipyramidal geometry around the osmium atom and the bent coordination of the azavinylidene have been proved by an X-ray diffraction analysis.[18] In agreement with the presence of the azavinylidene and vinylidene ligands, the IR spectra in KBr of the three compounds show ν(C═N) and ν(Os═C═C) bands at about 1660 cm^{-1} and between 1625 and 1605 cm^{-1}, respectively. As in **2**−**4** the azavinylidene ligand of **5**−**7** lies in the Y plane. Thus, the ^{1}H NMR spectra show two methyl resonances between 2.2 and 1.9 ppm, corresponding to the inequivalent methyl groups of the azavinylidene. The resonance due to the ═CH hydrogen atom of the vinylidene ligands appears between 1.6 and 2.3 ppm. The ^{13}C{^{1}H} NMR spectra show the characteristic C_α and C_β resonances of the vinylidenes, which are observed at about 270 ppm, as triplets with C−P coupling constants of about 11 Hz and between 110 and 90 ppm as singlets. The ^{31}P{^{1}H} NMR spectra contain singlets at about 3 ppm.

2. Azavinylidene−Alkenyl and Imine−Vinylidene Species as Intermediates in the Formation of 2−4. To obtain information about the formation of **2**−**4**, we have carried out at −25 °C the addition of cyclohexylacetylene to the solution resulting from the treatment of **1** with [AgCF$_3$SO$_3$]. Under these conditions the alkenyl derivative [Os{(*E*)-CH═CHCy}Cl(═N═CMe$_2$)(P^{i}Pr$_3$)$_2$][CF$_3$SO$_3$] (**8**) was obtained after 5 h, as a green solid in 70% yield (eq 3).



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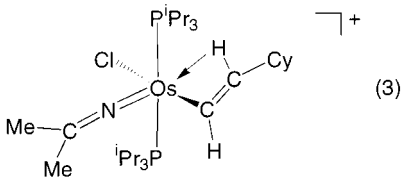


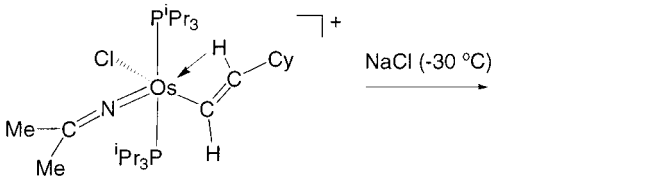
8

The unsaturated character of **8** is strongly supported by its IR spectrum in KBr, which contains the characteristic stretching bands of the free $[CF_3SO_3]^-$ anion at 1274, 1223, 1150, and 1032 cm^{-1}. The ^{1}H NMR spectrum in dichloromethane-d_2 at −30 °C confirms the presence of the alkenyl group with an *E* stereochemistry and suggests that the H$_\beta$ atom interacts with the metal to form an agostic bond. Thus, the resonance corresponding to the vinylic H$_\alpha$ atom is observed at 6.08 ppm, in agreement with the chemical shift reported for Os{(*E*)-CH═CHCy}Cl(CO)(P^{i}Pr$_3$)$_2$ (6.80 ppm).[7a] However, according to a ^{1}H−^{1}H COSY spectrum, the resonance due to the H$_\beta$ atom lies at about 2.70 ppm, shifted about 2 ppm to higher field in comparison with that found in the carbonyl complex (4.60 ppm), which does not show agostic interaction. In agreement with the agostic interaction the value of the H$_\alpha$−H$_\beta$ coupling constant in **8** (9.5 Hz) is lower than that found in Os{(*E*)-CH═CHCy}Cl(CO)(P^{i}Pr$_3$)$_2$ (12.6 Hz). The ^{13}C NMR spectrum is also consistent with a weak interaction between the H$_\beta$ atom of the alkenyl ligand and the osmium atom. The C_β resonance appears at 138.0 ppm with a C−H coupling constant of 142.5 Hz, a significantly low value compared to the ^1J(C−H) value of 154.5 Hz corresponding to the C_α resonance, which is observed at 143.1 ppm. The ^{31}P{^{1}H} NMR spectrum shows a singlet at −1.7 ppm. These spectroscopic data agree well with those previously reported for the styryl complex [Os{(*E*)-CH═CHPh}Cl(═N═CMe$_2$)(P^{i}Pr$_3$)$_2$][CF$_3$SO$_3$], where the H$_\beta$ atom of the styryl ligand also interacts with the metal.[17]

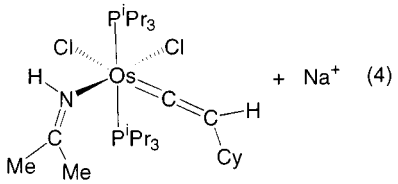
In solution at room temperature there is a marked difference in behavior between the aforementioned styryl compound and **8**. While the former species evolves into mixtures of five products, none of them are azavinylidene−carbyne derivatives; complex **8** affords **3** as

(22) Lawrence, G. A. *Chem. Rev.* **1986**, *86*, 17.

a consequence of a 1,2-hydrogen shift within the alkenyl group. However, at −30 °C the behavior is not very different. The addition of NaCl to tetrahydrofuran solutions of **8** gives rise to the imine−vinylidene derivative $OsCl_2(=C=CHCy)(NH=CMe_2)(P^iPr_3)_2$ (**9**), as a result of the hydrogen transfer from the alkenyl group to the azavinylidene ligand (eq 4). Under the same conditions, the styryl compound initially affords $Os\{(E)\text{-}CH=CHPh\}Cl_2(=N=CMe_2)(P^iPr_3)_2$, which evolves into the corresponding imine−vinylidene at room temperature.



8



9

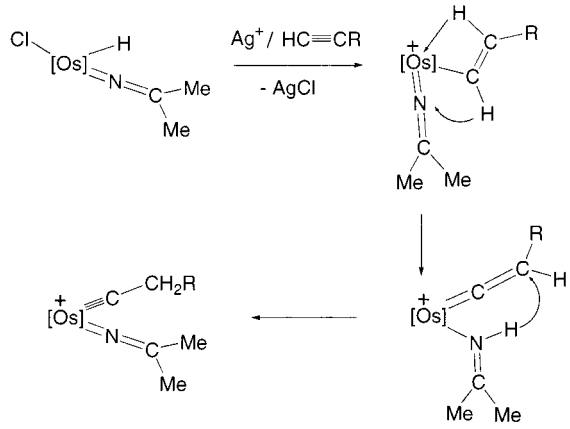
Complex **9** was isolated as an orange solid in 86% yield. In agreement with the presence of the imine ligand, the IR spectrum in KBr contains a ν(N−H) band at 3201 cm^{-1}. In the ^1H NMR spectrum in toluene-d_8 at −20 °C, the NH resonance appears at 11.33 ppm. The spectrum is in accordance with the mutually cis disposition of the chloride ligands, showing two ^{i}Pr methyl chemical shifts. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance due to the C_α atom of the vinylidene is observed at 287.6 ppm as a triplet with a C−P coupling constant of 9.7 Hz, whereas the C_β atom displays a singlet at 110.3 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at −21.2 ppm.

In dichloromethane-d_2, at room temperature, complex **9** dissociates a chloride and evolves into **3**, as a result of the hydrogen transfer from the imine to the C_β atom of the vinylidene. After 24 h, the transformation is quantitative. This reaction along with those showed in eqs 3 and 4 suggest that the formation of **2**−**4**, according to eq 1, proceeds via the elemental steps summarized in Scheme 1. The extraction of a chloride ligand from **1** activates the metallic center for the insertion of the alkyne into the Os−H bond. The formed alkenyl ligand evolves into a carbyne group by a double hydrogen transfer reaction involving the azavinylidene ligand. The first step of this formal 1,2-hydrogen shift takes place between the C_α atom of the alkenyl and the N atom of the azavinylidene, whereas the second one involves the N and C_β atoms of the resulting imine and vinylidene ligands. The latter step is in agreement with the expected electrophilic character of the hydrogen atom of the imine and the well-known nucleophilic nature of the C_β atoms of the vinylidene ligands.[23]

In contrast to **9**, the imine−phenylvinylidene complexes $OsCl_2(=C=CHPh)(NH=CR_2)(P^iPr_3)_2$ do not evolve into the corresponding azavinylidene−carbyne species.[17]

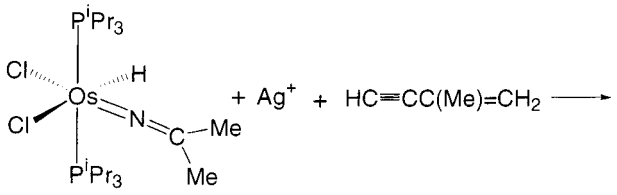
(23) Kostic, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974.

Scheme 1

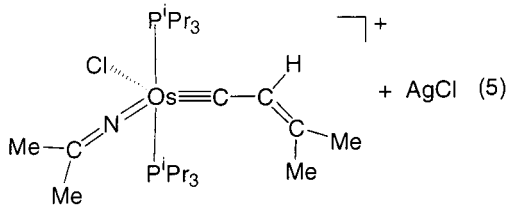


Moreover, their protonation affords imine−carbyne derivatives, which regenerate the imine−vinylidenes by deprotonation. This suggests that for R = Ph the imine−vinylidene form is thermodynamically more stable than the azavinylidene−carbyne form. The higher stability of the imine−vinylidene form could be related to a conjugating effect between the phenyl group and the π-system of the vinylidene. A similar situation has been previously observed between osmacyclopropene and osmium carbyne species. While for R = H and alkyl the osmium carbyne form is thermodynamically more stable than the cyclic one, there is a reversal in the relative energy of the isomers for R = Ph.[5]

3. Reactions of $OsHCl_2(=N=CMe_2)(P^iPr_3)_2$ with 2-Methyl-1-buten-3-yne. Treatment at room temperature of dichloromethane solutions of **1** with 1.0 equiv of $Ag[CF_3SO_3]$ and the subsequent addition of 1.0 equiv of 2-methyl-1-buten-3-yne leads after 4 h to the azavinylidene−alkenylcarbyne derivative $[OsHCl(=N=CMe_2)(\equiv C-CH=CMe_2)(P^iPr_3)_2][CF_3SO_3]$ (**10**), according to eq 5.



1

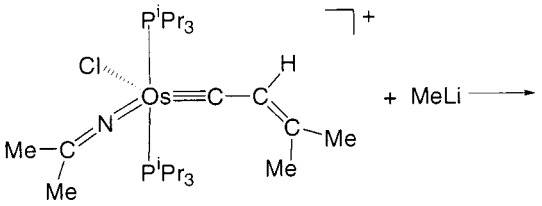


10

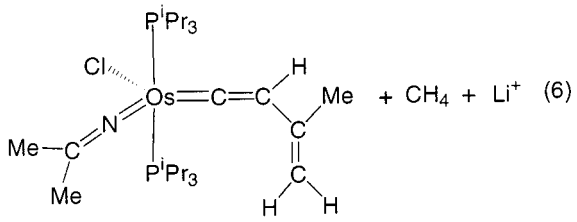
Complex **10** was isolated as a yellow solid in 77% yield. In the ^1H NMR spectrum in chloroform-*d* at room temperature, the most noticeable resonances are those corresponding to the alkenylcarbyne group, which appear as singlets at 6.07 (=CH) and 2.09 and 1.88 ppm (CH_3). As in **2**−**5**, the methyl groups of the azavinylidene display two resonances, indicating that the

disposition of this ligand is as shown in Figure 1. The $^{13}C\{^1H\}$ NMR spectrum shows the resonance due to the C(sp) atom of this ligand at 278.9 ppm, as a triplet with a C−P coupling constant of 5.5 Hz, whereas those corresponding to the C(sp^2) atoms are observed as singlets at 170.5 and 136.9 ppm. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 32.1 ppm.

Similarly to **2**−**4**, complex **10** can be deprotonated by MeLi. However, the deprotonation does not occur at the C_β atom of the carbyne but at one of the two methyl groups of the alkenyl unit. As a result, the treatment at room temperature of tetrahydrofuran solutions of **10** with MeLi affords the novel azavinylidene−alkenylvinylidene compound $OsCl(=N=CMe_2)\{=C=CHC(Me)=CH_2\}(P^iPr_3)_2$ (**11**), according to eq 6.



10



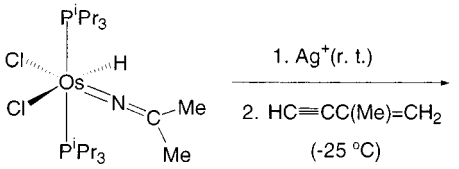
(6)

11

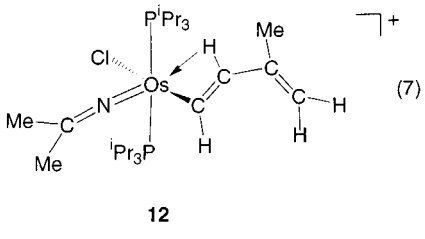
Complex **11** was isolated as an orange microcrystalline solid in 73% yield. The presence of the alkenylvinylidene ligand in **11** is strongly supported by the ^1H and $^{13}C\{^1H\}$ NMR spectra of this complex in dichloromethane-d_2, at room temperature. In the ^1H NMR spectrum, the unsaturated η^1-carbon ligand gives rise to three singlets at 4.56 and 4.08 ppm (=CH_2) and 2.11 ppm (CH_3) and a triplet at 3.27 ppm with a H−P coupling constant of 3.3 Hz, which corresponds to the β-CH proton. In the $^{13}C\{^1H\}$ NMR spectrum, the C_α and C_β resonances of the vinylidene unit appear at 275.2 and 116.6 ppm, the first of them as a triplet with a C−P coupling constant of 10.5 Hz, whereas the second one is observed as a singlet. The C(sp^2) atoms of the alkenyl unit display singlets at 137.9 and 100.6 ppm. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 2.9 ppm.

To obtain information about the formation of **10**, we carried out at −25 °C the addition of 2-methyl-1-buten-3-yne to the solution resulting from the treatment of **1** with $Ag[CF_3SO_3]$. Under these conditions the butadienyl derivative $[Os\{(E)\text{-}CH=CHC(Me)=CH_2\}(=N=CMe_2)(P^iPr_3)_2][CF_3SO_3]$ (**12**) was obtained after 5 h as a green solid in 74% yield (eq 7).

Complex **12** is the result of the extraction of a chloride ligand from **1** and the selective addition of the Os−H bond to the carbon−carbon triple bond of the enyne. A similar addition has been previously observed for the five-coordinate monohydrides $MHCl(CO)(P^iPr_3)_2$ (M = Ru,[24] Os[3]) and $RhH(SnPh_3)(acac)(PCy_3)$.[25] In contrast, the reaction of *cis*-$(Me_3Si)CH=CHC=CSiMe_3$ with the six-coordinate $RuHCl(CO)(PPh_3)_3$ gives a stable complex



1



(7)

12

whose molecular structure is formally regarded as the result of either 1,2-addition of the Ru−H to the double bond or 1,4-addition of the Ru−H to the conjugated enyne.[26]

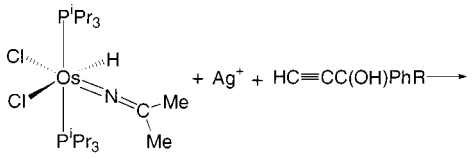
The structure proposed for **12** in eq 7 is consistent with the IR and ^1H, ^{13}C, and $^{31}P\{^1H\}$ NMR spectra of this compound. The IR in KBr contains the characteristic stretching bands of the free $[CF_3SO_3]^-$ anion, at 1281, 1221, 1140, and 1031 cm^{-1}, in agreement with the salt nature of the compound. The ^1H NMR spectrum, in dichloromethane-d_2 at −30 °C, suggest that the OsCH=CHR unit has an *E* stereochemistry and that, in a manner similar to **8**, the H_β atom interacts with the metal to form an agostic bond. Thus, this resonance appears at 3.73 ppm, shifted between 2 and 4 ppm to higher field in comparison with those found in other butadienyl compounds without agostic interactions.[3,4,24,25] The value of the H−H coupling constant (10.5 Hz) is similar to that found in **8** and between 3 and 8 Hz lower than those observed in other (*E*)-butadienyl derivatives. In the ^{13}C NMR spectrum the resonances of the butadienyl ligand appear at 145.2 (C_β), 141.5 (C_α), 137.3 (C_γ), and 115.9 (C_δ) ppm. In agreement with the H_β−Os interaction, the $^1J(C_\beta-H)$ value of 137.3 Hz is significantly lower than the $^1J(C_\alpha-H)$ and $^1J(C_\delta-H)$ values of 154.1 and 158.5 Hz, respectively. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at −0.6 ppm.

In solution at room temperature, complex **12** evolves into **10**, indicating that **12** is an intermediate in the formation of **10**, as **8** is intermediate in the formation of **3**. However, it should be noted that while the formation of **3** involves a formal 1,2-hydrogen shift in the alkenyl ligand of **8**, the formation of **10** involves a formal 1,4-hydrogen shift in the butadienyl ligand of **12**.

This 1,4-hydrogen shift is the result of the hydrogen transfer from the C_α atom of the butadienyl ligand to the nitrogen atom of the azavinylidene group and the subsequent hydrogen transfer from the nitrogen atom of the resulting imine to the C_δ atom of the resulting alkenylvinylidene. In this context, it should be mentioned that the addition of H^+ to the C_δ atom of alkenylvinylidene ligands is a general method to prepare alkenylcarbyne compounds.[27]

(24) Esteruelas, M. A.; Liu, F.; Oñate, E.; Sola, E.; Zeier, B. *Organometallics* **1997**, *16*, 2919.
(25) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E. Oro, L. A.; Rodriguez, L. *Organometallics* **1996**, *15*, 3670.
(26) Wakatsuki, Y.; Yamazaki, H.; Maraguma, Y.; Shimizu, I. *J. Chem. Soc., Chem. Commun.* **1991**, 261.

4. Reactions of $OsHCl_2(=N=CMe_2)(P^iPr_3)_2$ with HC≡CC(OH)PhR. Azavinylidene−alkenylcarbyne complexes related to **10** can be also obtained from alkynols. At room temperature, the addition of 1-phenyl-2-propyn-1-ol, 2-phenyl-3-butyn-2-ol, and 1,1-diphenyl-2-propyn-1-ol to the solutions resulting from the treatment of **1** with $Ag[CF_3SO_3]$ leads to the complexes $[OsCl(=N=CMe_2)(\equiv CCH=CPhR)(P^iPr_3)_2][CF_3SO_3]$ (R = H (**13**), CH_3 (**14**), Ph (**15**)), according to eq 8. The formation of



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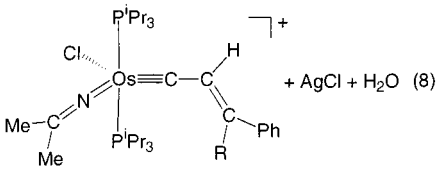
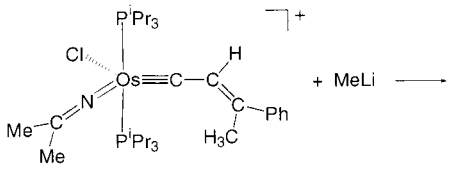


R = H (**13**), CH_3 (**14**), Ph (**15**)

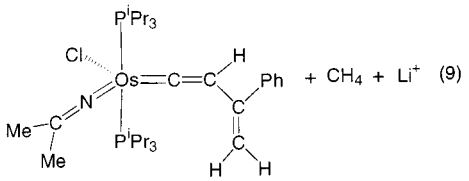
these compounds probably involves imine−hydroxyvinylidene intermediates related to **9**, which evolves into the corresponding carbyne derivatives by protonation of the OH group with the N−H of the imine.

Complexes **13**−**15** were isolated as brown (**13** and **15**) or light pink (**14**) solids in about 80% yield. In the ^1H NMR spectra, the most noticeable resonances are those corresponding to the β-CH hydrogen atom of the carbyne ligands, which appear at about 7 ppm. The $^{13}C\{^1H\}$ NMR spectra agree well with that of **10**. The resonances due to the C(sp) atom of the unsaturated η^1-carbon ligands are observed at about 280 ppm, as triplets with C−P coupling constants of about 6 Hz, whereas the resonances corresponding to the $C(sp^2)$ atoms appears at about 160 and 130 ppm as singlets. The $^{31}P\{^1H\}$ NMR spectra show singlets between 28 and 34 ppm.

Similarly to **10**, the addition of MeLi to tetrahydrofuran solutions of **14** produces the deprotonation of the methyl group of the alkenyl unit, to afford the azavinylidene−alkenylvinylidene $OsCl(=N=CMe_2)\{=C=CHC(Ph)=CH_2\}(P^iPr_3)_2$ (**16**), according to eq 9. The



14



16

(27) Esteruelas, M. A.; López, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1997**, *16*, 4657 and references therein.

deprotonation of the C_β atom of the alkenylcarbyne of **14** is not observed. In agreement with this, complexes **13** and **15** are inert in the presence of MeLi.

Complex **16** was isolated as an orange microcrystalline solid in 72% yield. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **16** agree well with that of **11**. In the ^1H NMR spectrum, the =CH resonance of the vinylidene unit is observed at 3.23 ppm, as a triplet with a H−P coupling constant of 3.0 Hz, whereas the $=CH_2$ group of the alkenyl unit displays two singlets at 5.40 and 5.19 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the C_α and C_β resonances of the vinylidene appear at 275.7 and 112.0 ppm, respectively, the first of them as a triplet with a C−P coupling constant of 11.0 Hz, whereas the second one is observed as a singlet. The vinyl carbon atoms of the alkenyl unit display singlets at 131.9 and 105.4 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 4.6 ppm.

Concluding Remarks

This paper reveals the existence of two novel types of difunctional organometallic compounds: the five-coordinate azavinylidene−carbyne $[OsCl(=N=CMe_2)(\equiv CCH_2R)(P^iPr_3)_2][CF_3SO_3]$ (R = H, alkyl) and the five-coordinate azavinylidene−alkenylcarbyne $[OsCl(=N=CMe_2)(\equiv CCH=CRR')(P^iPr_3)_2][CF_3SO_3]$ (R, R′ = H, alkyl, phenyl), which by deprotonation yield the corresponding five-coordinate azavinylidene−vinylidene $OsCl(=N=CMe_2)(=C=CHR)(P^iPr_3)_2$ and azavinylidene−alkenylvinylidene $OsCl(=N=CMe_2)\{=C=CHC(R)=CH_2\}(P^iPr_3)_2$.

The formation of the carbyne ligand of $[OsCl(=N=CMe_2)(\equiv CCH_2R)(P^iPr_3)_2][CF_3SO_3]$ is the result of the extraction of a chloride from the complex $OsHCl_2(=N=CMe_2)(P^iPr_3)_2$ and the subsequent addition of the Os−H bond to the alkynes HC≡CR (R = H, alkyl). The reactions initially give azavinylidene−alkenyl intermediates, which evolve by a formal 1,2-hydrogen shift within the alkenyl group into the carbynes. This hydrogen shift involves (i) the hydrogen transfer from the C_α atom of the alkenyl ligand to the nitrogen atom of the azavinylidene group to afford imine−vinylidene species and (ii) the NH hydrogen migration from the imine to the C_β atom of the vinylidene.

Azavinylidene−alkenylcarbynes are similarly formed from $OsHCl_2(=N=CMe_2)(P^iPr_3)_2$ and enynes (HC≡CC(Me)=CH_2) or alkynols (HC≡CC(OH)PhR). In this case the reactions initially give azavinylidene−butadienyl or azavinylidene−hydroxyvinylidene intermediates, which evolve into imine−alkenylvinylidenes or imine−hydroxyvinylidenes, respectively. The imine−alkenylvinylidenes afford azavinylidene−alkenylcarbynes by migration of the NH hydrogen atom from the imine to the C_δ atom of the alkenylvinylidene ligand, whereas the imine−hydroxyvinylidenes afford azavinylidene−alkenylcarbynes by protonation of the OH group of the hydroxyvinylidene with the NH of the imine.

In conclusion azavinylidene−carbyne and azavinylidene−alkenylcarbyne complexes can be prepared in a one-pot synthesis by reaction of hydride−azavinylidenes with terminal alkynes and enynes or alkynols, respectively. The formation of these species takes place via a novel hydrogen shift in the alkynes, which is promoted by the azavinylidene ligand.

Experimental Section

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting material $OsHCl_2\{=N=C(CH_3)_2\}(P^iPr_3)_2$ (**1**) was prepared by the published method.[16] ^1H NMR spectra were recorded at 300 MHz, and chemical shifts are expressed in ppm downfield from Me_4Si. $^{13}C\{^1H\}$ NMR spectra were recorded at 75.4 MHz, and chemical shifts are expressed in ppm downfield from Me_4Si. $^{31}P\{^1H\}$ NMR spectra were recorded at 121.4 MHz, and chemical shifts are expressed in ppm downfield from 85% H_3PO_4. Coupling constants, J and N, are given in hertz.

Preparation of $[OsCl\{=N=C(CH_3)_2\}(\equiv CCH_3)(P^iPr_3)_2][CF_3SO_3]$ (2). A pale green solution of **1** (100 mg, 0.157 mmol) in a mixture of dichloromethane (10 mL) and acetone (0.5 mL) was treated with 40 mg (0.157 mmol) of $Ag[CF_3SO_3]$. The suspension was stirred for 3 h and was filtered through Celite to eliminate the AgCl formed. The resulting blue solution was stirred under an acetylene atmosphere for 1 h. After the color changed to yellow, the solvent was concentrated to ca. 0.5 mL. Addition of diethyl ether yielded a yellow precipitate that was washed with diethyl ether (3 × 2 mL) and dried in vacuo. Yield: 90 mg (74%). Anal. Calcd for $C_{24}H_{51}NSClF_3O_3OsP_2$: C, 37.03; H, 6.60; N, 1.79; S, 4.11. Found: C, 37.05; H, 6.21; N, 2.16; S, 3.91. IR (KBr, cm^{-1}): ν(C=N) 1671 (m); $\nu_a(SO_3)$ 1281 (s); $\nu_s(CF_3)$ 1223 (s); $\nu_a(CF_3)$ 1143 (s); $\nu_s(SO_3)$ 1030 (s); $\delta_a(SO_3)$ 638 (s). ^1H NMR (CD_2Cl_2, 20 °C): δ 2.71 (m, 6H, PCH); 2.52 (s, 3H, Os≡CCH_3); 2.43 and 2.34 (both t, J_{H-P} = 2.1, 6H, $\{CH_3\}_2C=N$); 1.36 and 1.33 (both dvt, J_{H-H} = 7.2, N = 13.5, 36H, PCHCH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 290.5 (t, J_{C-P} = 5.5, Os≡C); 162.1 (t, J_{C-P} = 3.6, Os=N=C); 121.4 (q, J_{C-F} = 321.2, CF_3); 43.0 (s, Os≡CCH_3); 25.3 and 22.2 (both s, $\{CH_3\}_2C=N$); 24.2 (vt, N = 26.2, PCH); 19.8 and 19.4 (both s, PCHCH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 36.1 (s). MS (FAB^+): m/z 630 (M^+).

Preparationof$[OsCl\{=N=C(CH_3)_2\}(\equiv CCH_2Cy)(P^iPr_3)_2][CF_3SO_3]$ (3). A pale green solution of **1** (100 mg, 0.157 mmol) in a mixture of dichloromethane (10 mL) and acetone (0.5 mL) was treated with 40 mg (0.157 mmol) of $Ag[CF_3SO_3]$. The suspension was stirred for 3 h and was filtered through Celite to eliminate the AgCl formed. After 20 μL (0.157 mmol) of cyclohexylacetylene was added, the reaction mixture was stirred for 1 h at room temperature. The color changed to yellow, and the solvent was concentrated to ca. 0.5 mL. Addition of diethyl ether yielded a yellow precipitate that was washed with diethyl ether (3 × 2 mL) and dried in vacuo. Yield: 105 mg (77%). Anal. Calcd for $C_{30}H_{61}NSClF_3O_3OsP_2$: C, 41.88; H, 7.15; N, 1.63; S, 3.73. Found: C, 42.03; H, 7.31; N, 1.73; S, 3.68. IR (KBr, cm^{-1}): ν(C=N) 1670 (m); $\nu_a(SO_3)$ 1263 (s); $\nu_s(CF_3)$ 1223 (s); $\nu_a(CF_3)$ 1152 (s); $\nu_s(SO_3)$ 1032 (s); $\delta_a(SO_3)$ 636 (s). ^1H NMR (CD_2Cl_2, 20 °C): δ 2.95 (m, 2H, Os≡CCH_2); 2.89 (m, 6H, PCH); 2.60 and 2.48 (both t, J_{H-P} = 2.1, 6H, $\{CH_3\}_2C=N$); 2.19 (m, 1H, CH Cy); 2.0−1.2 (m, 10H, CH_2 Cy); 1.52 and 1.48 (both dvt, J_{H-H} = 6.9, N = 13.5, 36H, PCHCH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 295.2 (t, J_{C-P} = 5.5, Os≡C); 162.7 (t, J_{C-P} = 3.7, Os=N=C); 120.6 (q, J_{C-F} = 319.3, CF_3); 63.1 (s, Os≡CCH_2); 37.2, 26.2, and 25.8 (all s, CH_2 Cy); 34.0 (s, CH Cy); 25.5 and 22.4 (both s, $\{CH_3\}_2C=N$); 24.1 (vt, N = 26.1, PCH); 19.7 and 19.3 (both s, PCHCH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 34.2 (s). MS (FAB^+): m/z 712 (M^+).

Preparation of $[OsCl\{=N=C(CH_3)_2\}\{\equiv C(CH_2)_3CH_3\}(P^iPr_3)_2][CF_3SO_3]$ (4). This complex was prepared as described for **3**, starting from **1** (100 mg, 0.157 mmol), 40 mg (0.157 mmol) of $Ag[CF_3SO_3]$, and 16 μL (0.158 mmol) of 1-pentyne. A yellow solid was obtained. Yield: 110 mg (85%). Anal. Calcd for $C_{27}H_{57}NSClF_3O_3OsP_2$: C, 39.52; H, 7.00; N, 1.70; S, 3.90. Found: C, 39.55; H, 7.03; N, 1.83; S, 3.83. IR (KBr, cm^{-1}): ν(C=N) 1676 (m); $\nu_a(SO_3)$ 1264 (s); $\nu_s(CF_3)$ 1223 (s); $\nu_a(CF_3)$ 1152 (s); $\nu_s(SO_3)$ 1032 (s); $\delta_a(SO_3)$ 637 (s). ^1H NMR (CD_2Cl_2, 20 °C): δ 2.61 (t, J_{H-H} = 7.2, 2H, β-CH_2); 2.39 (m, 6H, PCH); 2.22 (br, 6H, $\{CH_3\}_2C=N$); 1.70 (tt, J_{H-H} = 7.2, J_{H-H} = 6.9, 2H, γ-CH_2); 1.29 (ct, J_{H-H} = 7.2, J_{H-H} = 6.9, 2H, δ-CH_2); 1.07 and 1.05 (both dvt, J_{H-H} = 7.2, N = 13.5, 36H, PCHCH_3); 0.79 (t, J_{H-H} = 7.2, 3H, CH_3). $^{13}C\{^1H\}$-APT NMR (CD_2Cl_2, 20 °C): δ 295.3 (t, J_{C-P} = 5.2, Os≡C); 162.3 (t, J_{C-P} = 3.0, Os=N=C); 121.4 (q, J_{C-F} = 321.2, CF_3); 55.0, 27.3, and 22.0 (all s, CH_2); 25.4 and 22.2 (both s, $\{CH_3\}_2CN$); 23.4 (vt, N = 26.7, PCH); 19.8 and 19.4 (both s, PCHCH_3); 17.7 (s, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 33.9 (s). MS (FAB^+): m/z 672 (M^+).

Preparation of $OsCl\{=N=C(CH_3)_2\}(=C=CH_2)(P^iPr_3)_2$ (5). A yellow solution of **2** in tetrahydrofuran (100 mg, 0.128 mmol) was treated with a solution of MeLi (80 μL, 1.6 M in diethyl ether, 0.128 mmol) at room temperature. The color changed immediately to orange and the solvent was concentrated to dryness. Then 8 mL of toluene was added to eliminate by filtration the $Li[CF_3SO_3]$ formed. After the toluene was removed, addition of methanol yielded an orange microcrystalline solid that was washed twice with methanol and dried in vacuo. Yield: 65 mg (80%). Anal. Calcd for $C_{23}H_{50}NClOsP_2$: C, 43.97; H, 8.02; N, 2.23. Found: C, 44.12; H, 7.92; N, 2.11. IR (KBr, cm^{-1}): ν(C=N) 1658 (m); ν(Os=C=C) 1607 (s). ^1H NMR (C_6D_6, 20 °C): δ 2.76 (m, 6H, PCH); 2.19 and 1.93 (both s, 6H, $\{CH_3\}_2C=N$); 2.01 (t, J_{H-P} = 3.6, 2H, Os=C=CH_2); 1.37 and 1.23 (both dvt, J_{H-H} = 6.6, N = 13.5, 36H, PCHCH_3). $^{13}C\{^1H\}$-APT NMR (C_6D_6, 20 °C): δ 271.3 (t, J_{C-P} = 11.1, Os=C); 152.6 (t, J_{C-P} = 3.2, C=N); 91.2 (s, Os=C=CH_2); 23.0 and 21.0 (both t, J_{C-P} = 2.0, $\{CH_3\}_2C=N$); 22.8 (vt, N = 28.5, PCH); 19.7 and 19.6 (both s, PCHCH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): δ 3.6 (s). MS (FAB^+): m/z 629 (M^+).

Preparation of $OsCl\{=N=C(CH_3)_2\}(=C=CHCy)(P^iPr_3)_2$ (6). This complex was prepared as described for **5**, starting from **3** (100 mg, 0.116 mmol) and MeLi (75 μL, 1.6 M in diethyl ether, 0.120 mmol). An orange solid was obtained. Yield: 60 mg (73%). Anal. Calcd for $C_{29}H_{60}NClOsP_2$: C, 49.03; H, 8.51; N, 1.97. Found: C, 48.65; H, 8.74; N, 1.99. IR (KBr, cm^{-1}): ν(C=N) 1655 (m); ν(Os=C=C) 1621 (s). ^1H NMR (C_6D_6, 20 °C): δ 2.81 (m, 6H, PCH); 2.22 and 1.95 (both s, 6H, $\{CH_3\}_2C=N$); 2.02 (m, 4H, Cy); 1.80 (m, 4H, Cy); 1.64 (m, 1H, Os=C=CHCy); 1.4−1.1 (m, 3H, Cy); 1.40 and 1.23 (both dvt, J_{H-H} = 6.9 Hz, N = 13.2, 36H, PCHCH_3). $^{13}C\{^1H\}$-APT NMR (C_6D_6, 20 °C): δ 267.8 (t, J_{C-P} = 11.4, Os=C); 152.6 (t, J_{C-P} = 3.2, C=N); 113.9 (s, Os=C=CHCy); 37.6, 27.0, and 26.6 (all s, CH_2 Cy); 32.7 (s, CH Cy); 22.8 and 20.7 (both s, $\{CH_3\}_2C=N$); 22.3 (vt, N = 23.0, PCH); 19.6 and 19.4 (both s, PCHCH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): δ 2.8 (s). MS (FAB^+): m/z 711 (M^+).

Preparation of $OsCl\{=N=C(CH_3)_2\}\{=C=CH(CH_2)_2CH_3\}(P^iPr_3)_2$ (7). This complex was prepared as described for **5**, starting from **4** (100 mg, 0.122 mmol) and MeLi (77 μL, 1.6 M in diethyl ether, 0.123 mmol). An orange oil was obtained. IR (Nujol, cm^{-1}): ν(C=N) 1659 (m); ν(Os=C=C) 1610 (s). ^1H NMR (C_6D_6, 20 °C): δ 2.76 (m, 8H, PCH and γ-CH_2); 2.23 (t, J_{H-P} = 2.0, Os=C=CH); 2.20 and 1.96 (both s, 6H, $\{CH_3\}_2C=N$); 1.48 (ct, J_{H-H} = 7.2, J_{H-H} = 7.0, 2H, δ-CH_2), 1.38 and 1.23 (both dvt, J_{H-H} = 6.9, N = 12.6, 36H, PCHCH_3); 0.99 (t, J_{H-H} = 7.2, 3H, CH_3). $^{13}C\{^1H\}$-APT NMR (C_6D_6, 20 °C): δ 268.5 (t, J_{C-P} = 12.0, Os=C); 152.5 (t, J_{C-P} = 3.2, C=N); 106.7 (s, Os=C=C); 26.1 and 24.7 (both s, CH_2); 22.0 and 20.8 (both s, $\{CH_3\}_2C=N$); 22.5 (vt, N = 23.1, PCH); 19.6 and 19.5 (both s, PCHCH_3); 14.1 (s, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): δ 2.9 (s). MS (FAB^+): m/z 671 (M^+).

Preparation of $[Os\{(E)\text{-}CH=CHCy\}Cl\{=N=C(CH_3)_2\}(P^iPr_3)_2][CF_3SO_3]$ (8). A pale green solution of **1** (100 mg, 0.157 mmol) in a mixture of dichloromethane (10 mL) and acetone (0.5 mL) was treated with 40 mg (0.157 mmol) of $Ag[CF_3SO_3]$. The suspension was stirred for 3 h and was filtered through Celite to eliminate the AgCl formed. The blue solution was cooled to −25 °C, and 30 μL (0.235 mmol) of cyclohexylacetylene was added. The reaction mixture was stirred for 5 h at a temperature between −25 and −10 °C. The color changed to green, and the solvent was concentrated to dryness,

keeping the temperature lower than −10 °C. Addition of diethyl ether at −50 °C yielded a green precipitate that was washed three times with cold diethyl ether and dried in vacuo. Yield: 95 mg (70%). Anal. Calcd for $C_{30}H_{61}NSClF_3O_3OsP_2$: C, 41.88; H, 7.15; N, 1.63; S, 3.73. Found: C, 41.65; H, 7.10; N, 1.72; S, 3.62. IR (KBr, cm^{-1}): ν(C═N) 1671 (m); $\nu_a(SO_3)$ 1274 (s); $\nu_s(CF_3)$ 1223 (s); $\nu_a(CF_3)$ 1150 (s); $\nu_s(SO_3)$ 1032 (s); $\delta_a(SO_3)$ 637 (s). ^{1}H NMR (CD_2Cl_2, −30 °C): δ 6.08 (d, J_{H-H} = 9.5 Hz, 1H, Os−C*H*═CHCy); 3.89 and 3.68 (both s, 6H, {CH_3}$_2$C═N); 2.70 (m, 7H, PCH and Os−CH═C*H*Cy); 1.7−1.2 (m, 11H, Cy); 1.32 and 1.24 (both dvt, J_{H-H} = 7.0, N = 13.7, 36H, PCHC*H*$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, −30 °C): δ 160.0 (s, Os═N═C); 143.1 (s {d, J_{C-H} = 154.5 in ^{13}C NMR (CD_2Cl_2, −30 °C)}, Os−*C*H═CHCy); 138.0 (s {d, J_{C-H} = 142.5 in ^{13}C NMR (CD_2Cl_2, −30 °C)}, Os−CH═*C*HCy); 120.6 (q, J_{C-F} = 318.7, CF_3); 42.8, 26.3, and 25.8 (all s, CH_2 Cy); 35.1 (s, CH Cy); 22.8 (vt, N = 23.0, PCH); 19.2 and 19.0 (both s, PCH*C*H$_3$); 10.1 and 7.8 (both s, {*C*H$_3$}$_2$C═N). ^{31}P{^{1}H} NMR (CD_2Cl_2, −30 °C): δ −1.7 (s). MS (FAB$^+$): *m*/*z* 712 (M^+).

Preparation of $OsCl_2$(═C═CHCy){NH═C(CH_3)$_2$}(P^iPr_3)$_2$ (9). A green solution of **8** (100 mg, 0.116 mmol) at −30 °C in tetrahydrofuran was treated with NaCl (25 mg, 0.428 mmol) and was kept stirring during 3 h at this temperature. The color changed to orange, and the solvent was concentrated to dryness at −30 °C. Then 8 mL of toluene was added to eliminate by filtration the Na[CF_3SO_3] formed and the excess NaCl. After the toluene was removed again at −30 °C, addition of pentane at −50 °C yielded an orange precipitate that was washed three times with cold pentane and dried in vacuo. Yield: 75 mg (86%). Anal. Calcd for $C_{29}H_{61}NCl_2OsP_2$: C, 46.64; H, 8.23; N, 1.88. Found: C, 46.58; H, 8.08; N, 1.70. IR (KBr, cm^{-1}): ν(N−H) 3201 (m); ν(C═N) 1656 (m); ν(Os═C═C) 1609 (s). ^{1}H NMR (toluene-d_8, −20 °C): δ 11.33 (s, 1H, N−H); 2.93 (m, 6H, PCH); 2.7−1.0 (m, 12H, Os═C═C*H*Cy and Cy); 1.60 and 1.53 (both s, 6H, {CH_3}$_2$C═N); 1.33 (m, 36H, PCHC*H*$_3$). ^{13}C{^{1}H} NMR (toluene-d_8, −20 °C): δ 287.6 (t, J_{C-P} = 9.7, Os═C); 173.6 (s, C═N); 110.3 (s, Os═C═*C*); 47.8, 24.8, and 24.3 (all s, CH_2 Cy); 36.0 (s, CH Cy); 27.8 and 22.2 (both s, {*C*H$_3$}$_2$C═N); 21.3 (br, PCH); 17.8 (br, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (toluene-d_8, −20 °C): δ −21.2 (s). MS (FAB$^+$): *m*/*z* 712 (M^+ − Cl).

Preparation of [OsCl{═N═C(CH_3)$_2$}{≡CCH═C(CH_3)$_2$}(P^iPr_3)$_2$][CF_3SO_3] (10). This complex was prepared as described for **3**, starting from **1** (100 mg, 0.157 mmol), 40 mg (0.157 mmol) of Ag[CF_3SO_3], and 15 μL (0.158 mmol) of 2-methyl-1-buten-3-yne. A orange solid was obtained. Yield: 100 mg (77%). Anal. Calcd for $C_{27}H_{55}NSClF_3O_3OsP_2$: C, 39.63; H, 6.77; N, 1.71; S, 3.91. Found: C, 39.56; H, 6.50; N, 1.82; S, 3.96. IR (KBr, cm^{-1}): ν(C═N) 1673 (m); $\nu_a(SO_3)$ 1270 (s); $\nu_s(CF_3)$ 1221 (s); $\nu_a(CF_3)$ 1144 (s); $\nu_s(SO_3)$ 1031 (s); $\delta_a(SO_3)$ 636 (s). ^{1}H NMR ($CDCl_3$, 20 °C): δ 6.07 (s, 1H, CH═); 2.69 (m, 6H, PCH); 2.47 and 2.37 (both t, J_{H-P} = 2.0, 6H, {CH_3}$_2$C═N); 2.09 and 1.88 (both s, 6H, ═C{CH_3}$_2$); 1.32 and 1.30 (both dvt, J_{H-H} = 7.2, N = 13.5, 36H, PCHC*H*$_3$). ^{13}C{^{1}H}-APT NMR ($CDCl_3$, 20 °C): δ 278.9 (t, J_{C-P} = 5.5, Os≡C); 170.5 (s, ═*C*{CH_3}$_2$); 162.0 (t, J_{C-P} = 3.0, Os═N═C); 136.9 (s, CH═); 121.4 (q, J_{C-F} = 322.8, CF_3); 26.6 and 24.6 (both s, ═C{*C*H$_3$}$_2$); 24.8 and 22.0 (both t, J_{C-P} = 1.8, {*C*H$_3$}$_2$C═N); 23.7 (vt, N = 26.7, PCH); 19.6 and 19.2 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C): δ 32.1 (s). MS (FAB$^+$): *m*/*z* 670 (M^+).

Preparation of OsCl{═N═C(CH_3)$_2$}{═C═CHC(CH_3)═CH_2}(P^iPr_3)$_2$ (11). A orange solution of **10** in tetrahydrofuran (100 mg, 0.122 mmol) was treated with a solution of MeLi (77 μL, 1.6 M in diethyl ether, 0.123 mmol) at room temperature. After 5 min of reaction the solvent was concentrated to dryness. Then 8 mL of toluene was added to eliminate by filtration the Li[CF_3SO_3] formed. After the toluene was removed, addition of 2 mL of methanol at −78 °C yielded an orange microcrystalline solid that was washed with cold methanol (2 × 1 mL) and pentane (3 × 2 mL) and dried in vacuo. Yield: 60 mg (73%). Anal. Calcd for $C_{26}H_{54}NClOsP_2$: C, 46.73; H, 8.14; N, 2.10. Found: C, 46.52; H, 7.98; N, 2.07. IR (KBr, cm^{-1}): ν(C═N) 1671 (m); ν(Os═C═C) 1600 (s). ^{1}H NMR (C_6D_6, 20 °C): δ 4.56 and 4.08 (both s, 2H, ═CH_2); 3.27 (t, J_{H-P} = 3.3, 1H, Os═C═CH); 2.75 (m, 6H, PCH); 2.16 and 1.94 (both s, 6H, {CH_3}$_2$C═N); 2.11 (s, 3H, C{CH_3}═); 1.34 and 1.18 (both dvt, J_{H-H} = 6.9, N = 13.5, 36H, PCHC*H*$_3$). ^{13}C-{^{1}H} NMR (C_6D_6, 20 °C): δ 275.2 (t, J_{C-P} = 10.5, Os═C); 153.8 (s, C═N); 137.9 (s, *C*{CH_3}═); 116.6 (s, Os═C═*C*); 100.6 (s, ═CH_2); 30.2 (s, C{*C*H$_3$}═); 23.1 (vt, N = 23.0, PCH); 22.3 and 20.6 (both s, {*C*H$_3$}$_2$C═N); 19.9 and 19.6 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ 2.9 (s). MS (FAB$^+$): *m*/*z* 670 (M^+ − H).

Preparation of [Os{(*E*)-CH═CHC(CH_3)═CH_2}Cl{═N═C(CH_3)$_2$}(P^iPr_3)$_2$][CF_3SO_3] (12). This complex was prepared as described for **8**, starting from **1** (100 mg, 0.157 mmol), 40 mg (0.157 mmol) of Ag[CF_3SO_3], and 15 μL (0.158 mmol) of 2-methyl-1-buten-3-yne. A green solid was obtained. Yield: 95 mg (74%). Anal. Calcd for $C_{27}H_{55}NSClF_3O_3OsP_2$: C, 39.63; H, 6.77; N, 1.71; S, 3.91. Found: C, 39.53; H, 6.42; N, 1.67; S, 3.81. IR (KBr, cm^{-1}): ν(C═N) 1648 (m); $\nu_a(SO_3)$ 1281 (s); $\nu_s(CF_3)$ 1221 (s); $\nu_a(CF_3)$ 1140 (s); $\nu_s(SO_3)$ 1031 (s); $\delta_a(SO_3)$ 637 (s). ^{1}H NMR (CD_2Cl_2, −30 °C): δ 7.25 (d, J_{H-H} = 10.5, 1H, Os−C*H*═CH); 4.05 and 4.00 (both s, 2H, ═CH_2); 3.8 (br, 6H, {CH_3}$_2$C═N); 3.73 (dt, J_{H-H} = 10.5, J_{H-P} = 4.5, 1H, Os−CH═C*H*); 2.8 (m, 6H, PCH); 1.55 (s, 3H, C{CH_3}═); 1.36 and 1.34 (both dvt, J_{H-H} = 7.5, N = 14.1, 36H, PCHC*H*$_3$). ^{13}C{^{1}H}-APT NMR (CD_2Cl_2, −30 °C): δ 160.4 (s, Os═N═C); 145.2 (s, {d, J_{C-H} = 137.3 in ^{13}C NMR (CD_2Cl_2, −30 °C)}, Os−CH═*C*H); 141.5 (s, {d, J_{C-H} = 154.1 in ^{13}C NMR (CD_2Cl_2, −30 °C)}, Os-*C*H═CH); 137.3 (s, {t, J_{C-H} = 158.5 in ^{13}C NMR (CD_2Cl_2, −30 °C)}, *C*{CH_3}═); 120.6 (q, J_{C-F} = 318.7, CF_3); 115.9 (s, ═*C*H$_2$); 22.8 (br, PCH); 22.6 (s, C{*C*H$_3$}═); 19.2 and 19.0 (both s, PCH*C*H$_3$); 10.1 and 7.8 (both s, {*C*H$_3$}$_2$C═N). ^{31}P{^{1}H} NMR (CD_2Cl_2, −30 °C): δ −0.6 (s). MS (FAB$^+$): *m*/*z* 670 (M^+).

Preparation of [OsCl{═N═C(CH_3)$_2$}(≡CCH═CHPh)(P^iPr_3)$_2$][CF_3SO_3] (13). This complex was prepared as described for **3**, starting from **1** (100 mg, 0.157 mmol), 40 mg (0.157 mmol) of Ag[CF_3SO_3], and 21 mg (0.158 mmol) of 1-phenyl-2-propyn-1-ol. A brown solid was obtained. Yield: 110 mg (80%). Anal. Calcd for $C_{31}H_{55}NSClF_3O_3OsP_2$: C, 42.97; H, 6.39; N, 1.61; S, 3.69. Found: C, 42.72; H, 6.18; N, 1.79; S, 3.69. IR (KBr, cm^{-1}): ν(C═N) 1670 (m); $\nu_a(SO_3)$ 1275 (s); $\nu_s(CF_3)$ 1223 (s); $\nu_a(CF_3)$ 1148 (s); $\nu_s(SO_3)$ 1036 (s); $\delta_a(SO_3)$ 637 (s). ^{1}H NMR ($CDCl_3$, 20 °C): δ 7.75 (d, J_{H-H} = 7.5, 2H, $H_{ortho-Ph}$); 7.73 (d, J_{H-H} = 15.8, 1H, CH═C*H*Ph); 7.59 (t, J_{H-H} = 7.8, 1H, $H_{para-Ph}$); 7.45 (t, J_{H-H} = 7.8, 2H, $H_{meta-Ph}$); 7.12 (d, J_{H-H} = 15.8, 1H, C*H*═CHPh); 2.71 (m, 6H, PCH); 2.53 and 2.50 (both t, J_{H-P} = 2.0, 6H, {CH_3}$_2$C═N); 1.36 and 1.33 (both dvt, J_{H-H} = 7.2, N = 14.1, 36H, PCHC*H*$_3$). ^{13}C{^{1}H}-APT NMR ($CDCl_3$, 20 °C): δ 278.9 (t, J_{C-P} = 6.4, Os≡C); 162.4 (t, J_{C-P} = 3.6, Os═N═C); 151.7 (s, = *C*HPh); 135.8, 130.2, and 129.5 (all s, Ph); 133.6 (s, CH═); 133.0 (s, $C_{ipso-Ph}$); 121.6 (q, J_{C-F} = 322.1, CF_3); 25.2 and 21.8 (both s, {*C*H$_3$}$_2$C═N); 24.2 (vt, N = 25.5, PCH); 19.8 and 19.5 (both s, PCH*C*H$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C): δ 28.6 (s). MS (FAB$^+$): *m*/*z* 718 (M^+).

Preparation of [OsCl{═N═C(CH_3)$_2$}{≡CCH═C(CH_3)Ph}(P^iPr_3)$_2$][CF_3SO_3] (14). This complex was prepared as described for **3**, starting from **1** (100 mg, 0.157 mmol), 40 mg (0.157 mmol) of Ag[CF_3SO_3], and 23 mg (0.158 mmol) of 2-phenyl-3-butyn-2-ol. A light pink solid was obtained. Yield: 110 mg (79%). Anal. Calcd for $C_{32}H_{57}NSClF_3O_3OsP_2$: C, 43.65; H, 6.53; N, 1.59; S, 3.64. Found: C, 43.65; H, 6.86; N, 1.60; S, 3.64. IR (KBr, cm^{-1}): ν(C═N) 1670 (m); $\nu_a(SO_3)$ 1272 (s); $\nu_s(CF_3)$ 1224 (s); $\nu_a(CF_3)$ 1147 (s); $\nu_s(SO_3)$ 1031 (s); $\delta_a(SO_3)$ 637 (s). ^{1}H NMR ($CDCl_3$, 20 °C): δ 7.71 (d, J_{H-H} = 7.8, 2H, $H_{ortho-Ph}$); 7.58 (t, J_{H-H} = 6.9, 1H, $H_{para-Ph}$); 7.47 (t, J_{H-H} = 7.8, 2H, $H_{meta-Ph}$); 6.60 (s, 1H, CH═); 2.71 (m, 6H, PCH); 2.47 (br, {CH_3}$_2$C═N); 2.42 (s, 3H, ═C{*C*H$_3$}Ph); 1.33 and 1.29 (both dvt, J_{H-H} = 7.2, N = 14.1, 36H, PCHC*H*$_3$). ^{13}C{^{1}H}-APT NMR ($CDCl_3$, 20 °C): δ 277.6 (t, J_{C-P} = 5.6, Os≡C); 162.5 (t, J_{C-P} = 3.2, Os═N═C); 162.4 (s, ═*C*{CH_3}Ph); 137.6 (s, $C_{ipso-Ph}$); 134.6,

130.0, and 126.8 (all s, Ph); 132.8 (s, CH═); 121.6 (q, J_{C-F} = 320.1, CF_3); 25.2 and 21.9 (both s, $\{CH_3\}_2C$═N); 23.8 (vt, N = 25.8, PCH); 21.2 (s, ═C{CH_3}Ph); 19.7 and 19.2 (both s, PCHCH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): δ 28.6 (s). MS (FAB^+): m/z 732 (M^+).

Preparation of [OsCl{═N═C(CH₃)₂}{≡CCH═C(Ph)₂}-(P^{i}Pr₃)₂][CF₃SO₃] (15). This complex was prepared as described for **3**, starting from **1** (100 mg, 0.157 mmol), 40 mg (0.157 mmol) of Ag[CF_3SO_3], and 33 mg (0.158 mmol) of 1,1-diphenyl-2-propyn-1-ol. A brown solid was obtained. Yield: 115 mg (77%). Anal. Calcd for $C_{37}H_{59}NSClF_3O_3OsP_2$: C, 47.15; H, 6.31; N, 1.49; S, 3.40. Found: C, 46.87; H, 6.45; N, 1.52; S, 3.49. IR (KBr, cm^{-1}): ν(C═N) 1676 (m); $\nu_a(SO_3)$ 1271 (s); $\nu_s(CF_3)$ 1222 (s); $\nu_a(CF_3)$ 1147 (s); $\nu_s(SO_3)$ 1031 (s); $\delta_a(SO_3)$ 636 (s). ^1H NMR (acetone-d_6, 20 °C): δ 7.7−7.4 (m, 10H, Ph); 6.86 (s, 1H, CH═); 2.86 (m, 6H, PCH); 2.65 (br, 6H, $\{CH_3\}_2C$═N); 1.36 and 1.32 (both dvt, J_{H-H} = 7.5, N = 14.5, 36H, PCHCH_3). $^{13}C\{^1H\}$ plus APT NMR (acetone-d_6, 20 °C): δ 281.4 (t, J_{C-P} = 6.0, Os≡C); 164.2 (t, J_{C-P} = 3.6, Os═N═C); 162.2 (s, ═C{Ph}$_2$); 140.5 and 139.0 (both s, $C_{ipso-Ph}$); 136.3 (s, CH═); 136.0, 132.5, 132.3, 130.5, and 130.1 (all s, Ph); 121.6 (q, J_{C-F} = 322.1, CF_3); 24.9 and 21.2 (both s, $\{CH_3\}_2C$═N); 23.8 (vt, N = 22.5, PCH); 19.9 and 19.4 (both s, PCHCH_3). $^{31}P\{^1H\}$ NMR (acetone-d_6, 20 °C): δ 33.9 (s). MS (FAB^+): m/z 794 (M^+).

Preparation of OsCl{═N═C(CH₃)₂}{═C═CHC(Ph)═CH₂}(P^{i}Pr₃)₂ (16). This complex was prepared as described for **11**, starting from **14** (100 mg, 0.113 mmol) and MeLi (72 μL, 1.6 M in diethyl ether, 0.115 mmol). An orange solid was obtained. Yield: 60 mg (72%). Anal. Calcd for $C_{31}H_{56}NClOsP_2$: C, 50.98; H, 7.73; N, 1.92. Found: C, 50.80; H, 7.72; N, 1.79. IR (KBr, cm^{-1}): ν(C═N) 1676 (m); ν(Os═C═C) 1603 (s). ^1H NMR (C_6D_6, 20 °C): δ 7.71 (d, J_{H-H} = 7.5, 2H, $H_{ortho-Ph}$); 7.21 (t, J_{H-H} = 7.5, 2H, $H_{meta-Ph}$); 7.11 (t, J_{H-H} = 7.2, 1H, $H_{para-Ph}$); 5.40 and 5.19 (both s, 2H, ═CH_2); 3.23 (t, J_{H-P} = 3.0, 1H, Os═C═CH); 2.77 (m, 6H, PCH); 2.16 and 1.93 (both s, 6H, $\{CH_3\}_2C$═N); 1.35 and 1.20 (both dvt, J_{H-H} = 6.9, N = 13.5, 36H, PCHCH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 20 °C): δ 275.7 (t, J_{C-P} = 11.0, Os═C); 153.8 (s, C═N); 145.2 (s, $C_{ipso-Ph}$); 139.1 (s, C){Ph}═); 127.6, 126.9, and 126.6 (all s, C_{Ph}); 112.0 (s, Os═C═C); 105.4 (s, ═CH_2); 22.8 (vt, N = 23.0, PCH); 22.3 and 20.6 (both s, $\{CH_3\}_2C$═N); 19.7 and 19.4 (both s, PCHCH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): δ 4.6 (s). MS (FAB^+): m/z 732 (M^+ − H).

X-ray Structure Analysis of Complex 2. Crystals suitable for X-ray diffraction analysis were mounted onto a glass fiber and transferred to an Bruker-Siemens P4 automatic diffractometer (200 K, Mo Kα radiation, graphite monochromator, λ = 0.710 73 Å). A summary of crystal data and refinement parameters is reported in Table 2. Accurate unit cell parameters were determined by least-squares fitting from the setting of high-angle reflections. Data were collected by the ω scan method. Lorentz and polarization corrections were applied. Decay was monitored by measuring three standards throughout data collection. Corrections for decay and absorption (semiempirical ψ-scan method) were applied.

The structure was solved by Patterson methods and refined by full-matrix least squares on F^2.[28] A phosphine ligand (P(1)) and the triflate anion were observed to be severely disordered. The triisopropylphosphine group was refined as two moieties with complementary occupancy factors, with the same free geometry, and isotropic thermal parameters. The triflate anion was refined with common sulfur and carbon atoms but with two moieties for each of the fluorine and oxygen atoms. The complementary occupancy factors were restrained to amount to 1; isotropic thermal parameters and restrained geometry were also used. The rest of the non-hydrogen atoms were anisotropically refined, and the hydrogen atoms of nondisordered groups were observed or included at idealized positions.

Table 2. Crystal Data and Data Collection and Refinement Details for the Complex [OsCl(═N═CMe₂)(≡CCH₃)(P^{i}Pr₃)₂][CF₃SO₃] (2)

Crystal Data	
formula	$C_{24}H_{51}ClF_3NO_3OsP_2S$
mol wt	778.31
habit	irregular block
space group	monoclinic, $P2_1/n$
a, b, c, Å	13.146(1), 8.978(1), 28.245(4)
α, β, γ, deg	90, 94.28(1), 90
V, Å^3; Z	3324.3(7), 4
D_{calcd}, g cm^{-3}	1.555
Data Collection and Refinement Details	
diffractometer	Bruker-Siemens P4
λ(Mo Kα), Å	0.710 73
monochromator	graphite oriented
μ, mm^{-1}	4.116
scan type	w
2θ range, deg	$3 \le 2\theta \le 50$
temp, K	200.0(2)
no. of data collect	6385
hkl limits	0 to 15, −10 to +2, −33 to +33
no. of unique data	5776 (merging R factor 0.0449)
no. of params refined/restraints	478/359
R1($F^2 > 2\sigma(F^2)$)[a]	0.0615
wR2(all data)[b]	0.1655
S(all data)[c]	1.025

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] $GOF = S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray studies, and bond distances and angles for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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