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Synthesis of New Hydride–Carbyne and Hydride–Vinylcarbyne Complexes of Osmium(II) by Reaction of $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ with Terminal Alkynes

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Abstract: The dihydride–dichloro complex $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ (**1**) reacts with phenylacetylene, cyclohexylacetylene, and 1-(trimethylsilyl)-1,4-pentadiyne, in hexane at 60 °C, to give the hydride–carbyne complexes $OsHCl_2(CCH_2R)(P\text{-}i\text{-}Pr_3)_2$ (R = Ph (**2**), Cy (**3**), $CH_2C{\equiv}CSiMe_3$ (**4**)). The molecular structure of complex **2** was determined by X-ray crystallography. Crystals of **2** are orthorhombic, space group $P2_12_12_1$, with unit cell dimensions $a = 8.7490(3)$ Å, $b = 15.4051(5)$ Å, and $c = 22.4257(8)$ Å. The structure was solved and refined using 4615 unique, observed ($F \geq 5.0\sigma(F)$) reflections; $R = 0.022$ and $R_w = 0.023$. The geometry around the osmium can be described as a distorted octahedron with the two triisopropylphosphine ligands occupying the apical positions. The equatorial plane is formed by the carbyne and the hydride ligands mutually cis disposed and two chlorine atoms. The reaction of **1** with trimethylsilylacetylene leads to $OsHCl_2(CCH_3)(P\text{-}i\text{-}Pr_3)_2$ (**5**), suggesting that the key intermediates of these processes are dihydrogenvinylidene species of osmium(II). The hydride–vinylcarbyne complexes $OsHCl_2(CCH{=}CH(CH_3)CH_2CH_3)(P\text{-}i\text{-}Pr_3)_2$ (**8**), $OsHCl_2(CCH{=}CCH_2CH_2CH_2CH_2CH_2)(P\text{-}i\text{-}Pr_3)_2$ (**9**), and $OsHCl_2(CCH{=}C(CH_3)_2)(P\text{-}i\text{-}Pr_3)_2$ (**11**) were prepared by reaction of **1** with 3-methyl-1-pentyn-3-ol, 1-ethynyl-1-cyclohexanol, and 2-methyl-1-buten-3-yne, respectively. Complexes **8** and **9** were formed via the hydroxycarbyne intermediates $OsHCl_2(CCH_2C(OH)(CH_3)CH_2CH_3)(P\text{-}i\text{-}Pr_3)_2$ (**6**) and $OsHCl_2(CCH_2C(OH)CH_2CH_2CH_2CH_2CH_2)(P\text{-}i\text{-}Pr_3)_2$ (**7**). The synthesis of the hydroxycarbyne $OsHCl_2(CCH_2C(OH)Ph_2)(P\text{-}i\text{-}Pr_3)_2$ (**10**) is also reported.

Introduction

The reactions of alkynes with transition metal hydride complexes generally result in the formation of vinyl derivatives by an insertion of the alkyne into the M–H bonds.[1] In this respect, we observed, during our investigations directed toward the determination of the reaction mechanisms of the hydrogenation[2] and hydrosilylation[3] of terminal alkynes catalyzed by $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$, that this compound and the cation $[OsH(CO)_2(\eta^1\text{-}O{=}CMe_2)(P\text{-}i\text{-}Pr_3)_2]^+$ react with alkynes such as PhC_2H, C_2H_2, MeC_2CO_2Me, and HC_2CO_2Me to give vinyl derivatives by insertion of the alkynes into the Os–H bond of these complexes.[4,5]

We also reported, as a part of our work in the field of homogeneous catalysis,[6] that the tetrahydride $OsH_4(CO)(P\text{-}i\text{-}Pr_3)_2$ complex catalyzes the hydrogen transfer reaction from 2-propanol to phenylacetylene.[7] During the study designed to determine the mechanism of this reaction, we found that the tetrahydride $OsH_4(CO)(P\text{-}i\text{-}Pr_3)_2$ complex reacts with the stoichiometric amount of phenylacetylene to give molecular hydrogen and the alkynyl–dihydrogen complex $OsH(C_2Ph)(CO)(\eta^2\text{-}H_2)(P\text{-}i\text{-}Pr_3)_2$.[8] The complex $OsH_4(CO)(P\text{-}i\text{-}Pr_3)_2$ is coordinatively saturated, and its activation involves the loss of one hydrogen molecule per molecule of tetrahydride.[9] In this way, the formation of $OsH(C_2Ph)(CO)(\eta^2\text{-}H_2)(P\text{-}i\text{-}Pr_3)_2$ could be rationalized as the formal oxidative addition of a terminal alkyne to a dihydride complex of 16 electrons and subsequent intramolecular reduction. Because $RC{\equiv}CH$ is fairly acidic and the $OsH_2(CO)(P\text{-}i\text{-}Pr_3)_2$ fragment is probably rich in electrons, the formation of $OsH(C_2Ph)(CO)(\eta^2\text{-}H_2)(P\text{-}i\text{-}Pr_3)_2$ could involve the initial protonation of $OsH_2(CO)(P\text{-}i\text{-}Pr_3)_2$ to give the cationic intermediate $[OsH(CO)(\eta^2\text{-}H_2)(P\text{-}i\text{-}Pr_3)_2]^+$ [10] and subsequent coordination of $[PhC{\equiv}C]^-$.[8]

The complex $OsH(C_2Ph)(CO)(\eta^2\text{-}H_2)(P\text{-}i\text{-}Pr_3)_2$ is isoelectronic and isostructural with $OsHCl(CO)(\eta^2\text{-}H_2)(P\text{-}i\text{-}Pr_3)_2$.[11] However, they show a marked difference in reactivity toward phenylacetylene. Whereas the hydride–chloro compound reacts with phenylacetylene to give the vinyl complex $Os((E)\text{-}CH{=}CHPh)Cl(CO)(P\text{-}i\text{-}Pr_3)_2$,[2] the alkynyl analogue leads to the bis(alkynyl) derivative $Os(C_2Ph)_2(CO)(P\text{-}i\text{-}Pr_3)_2$.[8] This derivative, which can also be obtained directly by reaction of $OsH_4(CO)(P\text{-}i\text{-}Pr_3)_2$ with

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(10) This complex was recently isolated in our laboratory by reaction of $[(P\text{-}i\text{-}Pr_3)_2(CO)HOs(\mu,\mu^4\text{-}BH_4)OsH(CO)(P\text{-}i\text{-}Pr_3)_2]^+$ with H_2. See: Esteruelas, M. A.; García, M. P.; López, A. M.; Oro, L. A.; Ruiz, N.; Schlünken, C.; Valero, C.; Werner, H. *Inorg. Chem.* **1992**, *31*, 5580.

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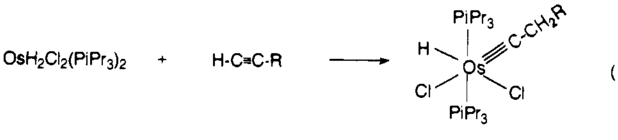
excess phenylacetylene,[12] was detected during the hydrogen transfer reaction from 2-propanol to phenylacetylene.[7,12]

Two years ago, the synthesis, molecular structure, and catalytic activity of the dihydride–dichloro complex $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ (**1**) were reported.[13] This compound catalyzes the hydrogenation of olefins, dienes and α,β-unsaturated ketones. When we attempted the hydrogenation of phenylacetylene in the presence of **1**, we observed that rapid deactivation of the catalyst occurs. This unexpected finding prompted us to explore the reactivity of this complex toward terminal alkynes. During these studies, we discovered an unusual reaction pattern. The reaction of **1** with terminal alkynes leads to hydride–carbyne complexes.

In this paper, we report the synthesis and characterization of new hydride–carbyne and hydride–vinylcarbyne osmium(II) complexes, which have been obtained by direct reaction between a transition metal dihydride compound and terminal alkynes. Recently, the synthesis of some hydride–carbyne rhenium complexes which were prepared by reaction of rhenium polyhydrides and alkynes, was reported. However, in this case, the addition of an electrophile was necessary.[14]

Results and Discussion

Treatment of a suspension of $OsH_2Cl_2(Pr\text{-}i\text{-}Pr_3)_2$ (**1**) with phenylacetylene, cyclohexylacetylene, or 1-(trimethylsilyl)-1,4-pentadiyne in hexane at 60 °C results in the formation of solids, which according to the elemental analysis, correspond apparently to 1:1 adducts of the starting material and the alkynes. The IR, ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra of these solids suggest that the products obtained from these reactions are the carbyne complexes **2**–**4** (eq 1).



(1)

R= Ph (**2**); Cy (**3**); $CH_2C{\equiv}CSiMe_3$ (**4**)

The presence of a hydride ligand in these complexes is inferred from the IR and ^1H NMR spectra. The IR spectra in Nujol show a strong ν(Os–H) absorption between 2160 and 2185 cm^{-1}, while the ^1H NMR spectra in benzene-d_6 all contain a triplet between −6.57 and −6.88 ppm, with a P–H coupling constant of about 16 Hz. The sp-carbon atom of the carbyne ligands appears in the $^{13}C\{^1H\}$ NMR spectra as a triplet between 264 and 270 ppm, with a P–C coupling constant of about 11 Hz. The $^{31}P\{^1H\}$ NMR spectra show a singlet, indicating that the two phosphine ligands are equivalent.

The definitive characterization of **2**–**4** as hydride–carbyne compounds came from an X-ray diffraction experiment on a single crystal of **2**. A view of the molecular geometry of this complex is shown in Figure 1. Selected bond distances and angles are listed in Table I.

The geometry of the complex can be rationalized as a distorted octahedron with the two phosphorus atoms of the triisopropylphosphine ligands occupying the apical positions (P(1)–Os–P(2) = 168.50(4)°). The equatorial plane is formed by the carbyne and the hydride ligands mutually cis disposed (H–Os–C(19) = 94(2)°) and the two chlorine atoms also cis disposed (Cl(1)–Os–Cl(2) = 88.65(5)°).

The most conspicuous feature of the structure is the very short Os–C(19) bond length at 1.711(4) Å, which is fully consistent with a Os–C(19) triple bond formulation. Os–C (carbyne) bond lengths previously reported are between 1.75(1) and 1.84(2) Å.[15] So, the Os–C(19) bond length is the shortest known osmium–carbyne distance. The C(19)–C(20) distance and C(19)–C(20)–C(21) angle are 1.475(7) Å and 117.7(4)°, respectively. A slight bending in the Os–C(19)–C(20) moiety is present (Os–C(19)–C(20) = 172.4(4)°); similar values were found for related complexes.[16]

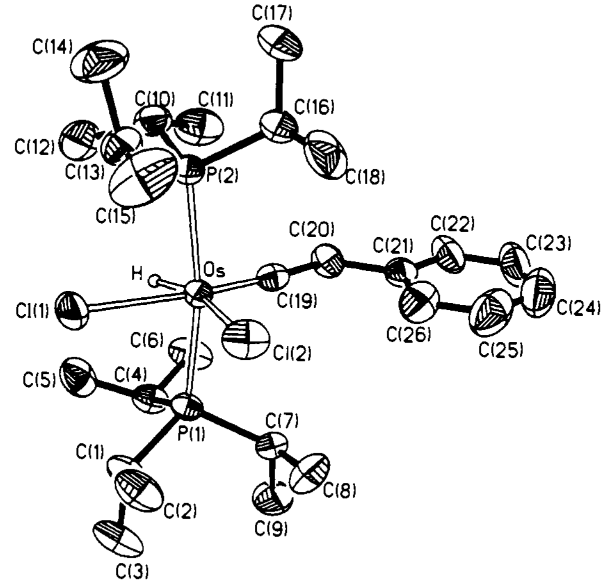


Figure 1. ORTEP diagram of complex **2**. Thermal ellipsoids are shown at 50%.

Table I. Selected Bond Distances (Å) and Angles (deg) for the Complex $[OsHCl_2(CCH_2Ph)(P\text{-}i\text{-}Pr_3)_2]$ (**2**)

Os–P(1)	2.429(1)	Os–P(2)	2.424(1)
Os–Cl(1)	2.488(1)	Os–Cl(2)	2.498(1)
Os–C(19)	1.711(4)	Os–H	1.437(40)
C(19)–C(20)	1.475(7)	C(22)–C(23)	1.373(8)
C(20)–C(21)	1.532(7)	C(23)–C(24)	1.351(12)
C(21)–C(22)	1.364(8)	C(24)–C(25)	1.367(13)
C(21)–C(26)	1.375(8)	C(25)–C(26)	1.399(8)
P(1)–C(1)	1.846(5)	P(2)–C(10)	1.847(5)
P(1)–C(4)	1.863(5)	P(2)–C(13)	1.865(6)
P(1)–C(7)	1.857(5)	P(2)–C(16)	1.857(6)
P(1)–Os–P(2)	168.50(4)	P(2)–Os–H	91(2)
P(1)–Os–Cl(1)	86.50(4)	Cl(1)–Os–Cl(2)	88.65(5)
P(1)–Os–Cl(2)	95.04(4)	Cl(1)–Os–C(19)	168.7(2)
P(1)–Os–C(19)	92.7(2)	Cl(1)–Os–H	75(2)
P(1)–Os–H	78(2)	Cl(2)–Os–C(19)	102.6(2)
P(2)–Os–Cl(1)	87.41(4)	Cl(2)–Os–H	163(2)
P(2)–Os–Cl(2)	94.56(4)	C(19)–Os–H	94(2)
P(2)–Os–C(19)	91.4(2)		
Os–C(19)–C(20)	172.4(4)	C(21)–C(22)–C(23)	119.9(6)
C(19)–C(20–C(21)	117.7(4)	C(22)–C(23)–C(24)	121.1(7)
C(20)–C(21)–C(22)	118.3(4)	C(23)–C(24)–C(25)	119.7(6)
C(20)–C(21)–C(26)	121.5(5)	C(24)–C(25)–C(26)	120.2(8)
C(22)–C(21)–C(26)	120.2(5)	C(21)–C(26)–C(25)	118.9(6)

Furthermore, it should be mentioned that the Os–Cl(1) bond distance (Cl trans to C(19)) is 0.01 Å shorter than the Os–Cl(2) distance (Cl trans to H), which can be assigned to the different trans-influence of the carbyne and hydride ligands. The Os–P and Os–H distances are clearly in the expected range and deserve no further comment.

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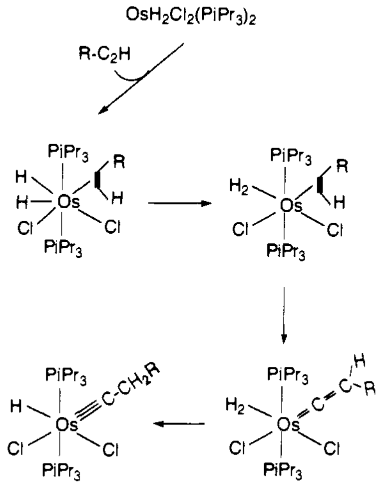
Scheme I



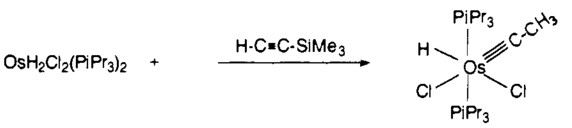
The reactions shown in eq 1 merit further consideration. It was previously reported that the addition of an electrophile to an octahedral alkyenylidene complex results in transformation of the alkenylidene group into a carbyne ligand.[17] MO calculations predict that the regioselectivity of the reaction is governed by a significant charge localized on the β-C atom of the M=C=CHR unit,[18] which should therefore undergo electrophilic attack. In this respect, the formation of **2**–**4** could be rationalized as the electrophilic attack of an acidic hydrogen atom to the β-C atom of an Os=C=CHR unit. Scheme I summarizes a reaction mechanism, which is consistent with our proposal for the formation of **2**–**4** from **1**. Since we had a 16-electron complex (**1**), it could thus undergo the nucleophilic attack of the alkyne to give dihydride–π-alkyne–osmium(IV) intermediates, in equilibrium with dihydrogen–π-alkyne–osmium(II) species. This formal reduction $d^4 \rightarrow d^6$ should favor isomerization from the π-alkyne complexes into vinylidene intermediates, most probably, via a concerted mechanism. The subsequent electrophilic attack of the acidic hydrogen of the dihydrogen ligands to the β-C atom of the vinylidenes could lead to the hydride–carbyne complexes **2**–**4**.

In favor of the mechanism shown in Scheme I, the following should be noted. (i) Complex **1** is a useful starting material in preparing dihydrogen complexes. Recent studies carried out in our laboratory have shown that the simple coordination of pyrazole (Hpz) to **1** gives rise to the complex $OsCl_2(\eta^2\text{-}H_2)(Hpz)(P\text{-}i\text{-}Pr_3)_2$, which has been characterized by X-ray analysis.[19] So, it is reasonable to assume that the necessary π-coordination of the alkyne to the osmium atom in **1** produces the transformation of $Os(H)_2$ into $Os(\eta^2\text{-}H_2)$.

(ii) The preparation of vinylidene complexes from terminal alkynes via a formal 1,2-hydrogen shift is a well-established process,[20] which is very usual in octahedral d^6 complexes. In these types of compounds, the alkyne–vinylidene rearrangement is promoted by an unfavorable $4e^-$ 2-center d_π-π conflict, because they have no vacant d orbitals.[21] However, in d^4 complexes, this isomerization is rarely observed, and, to the best of our knowledge, only one example has been previously reported.[22] The isomerization dihydride → dihydrogen, shown in Scheme I, involves a formal two-electron reduction of the osmium center ($d^4 \rightarrow d^6$), which therefore, must favor the alkyne → vinylidene transformation.

(iii) The electrophilic character of the dihydrogen complexes has been previously demonstrated. A common property of these compounds seems to be that the coordinated dihydrogen ligand is readily deprotonated.[23]

Experimental indications in favor of the participation of vinylidene intermediates, in the formation of **2**–**4** from **1**, were also found. Treatment of a suspension of **1** in hexane with (trimethylsilyl)acetylene in a 1:3 molar ratio leads to the complex $OsHCl_2(CCH_3)(P\text{-}i\text{-}Pr_3)_2$ (**5**) according to eq 2.



(2)

There are precedents for the cleavage of the Si–C bond in related processes. The vinylidene ligand $C{=}CH_2$ of the complex $[OsI(\eta^6\text{-}C_6H_6)(C{=}CH_2)(PMe^tBu_2)]PF_6$ is produced from the reaction of $OsI_2(\eta^6\text{-}C_6H_6)(PMe^tBu_2)$ with $AgPF_6$ in the presence of (trimethylsilyl)acetylene.[24] The same alkyne and the complex $IrCl(P\text{-}i\text{-}Pr_3)_2$ have been used to prepare $IrCl(C{=}CH_2)(P\text{-}i\text{-}Pr_3)_2$.[25] It has been suggested that these desilylation processes are due to the presence, in the reaction media, of slight traces of H_2O, which act as an electrophilic reagent.[24] In contrast to the vinylidene–silyl ligands, the alkynyl–silyl ligands seem to be extremely stable in an aqueous medium. Thus, the complex $Rh(C{\equiv}CSiMe_3)(PMe_3)_3$ was prepared from *cis*-$[RhH(C{\equiv}CSiMe_3)(PMe_3)_3]Cl$ in concentrated aqueous KOH.[26] The different behavior of the groups $C{=}CHSiMe_3$ and $C{\equiv}CSiMe_3$ toward the electrophilic substitution could also explain why the alkyne 1-(trimethylsilyl)-1,4-pentadiyne does not undergo desilylation during its reaction with **1**.

Werner[27] previously reported that the square-planar iridium–vinylidene complexes $IrCl(C{=}CHR)(P\text{-}i\text{-}Pr_3)_2$ react with HBF_4 in diethyl ether to give the cations $[IrHCl(C{=}CHR)(P\text{-}i\text{-}Pr_3)_2]^+$, which are in equilibrium with the carbyne compounds $[IrCl(CCH_2R)(P\text{-}i\text{-}Pr_3)_2]^+$. These reactions could be considered as a precedent for our reactions; however, there are significant differences between both processes. Werner's reaction must be rationalized as the nucleophilic attack of a hydride ligand (H^-) on the vinylidene group, while our reaction must be rationalized as the electrophilic attack of a proton (H^+) on the vinylidene ligand. This difference could be related to the different nature of the fragments $IrCl(C{=}CHR)(P\text{-}i\text{-}Pr_3)_2$ and $OsCl_2(C{=}CHR)(P\text{-}i\text{-}Pr_3)_2$. While the first shows a Lewis base character reacting with Brønsted acids, the second could have Lewis acid character, coordinating a weak Lewis base such as the dihydrogen ligand. The different charge on the metallic centers of both fragments

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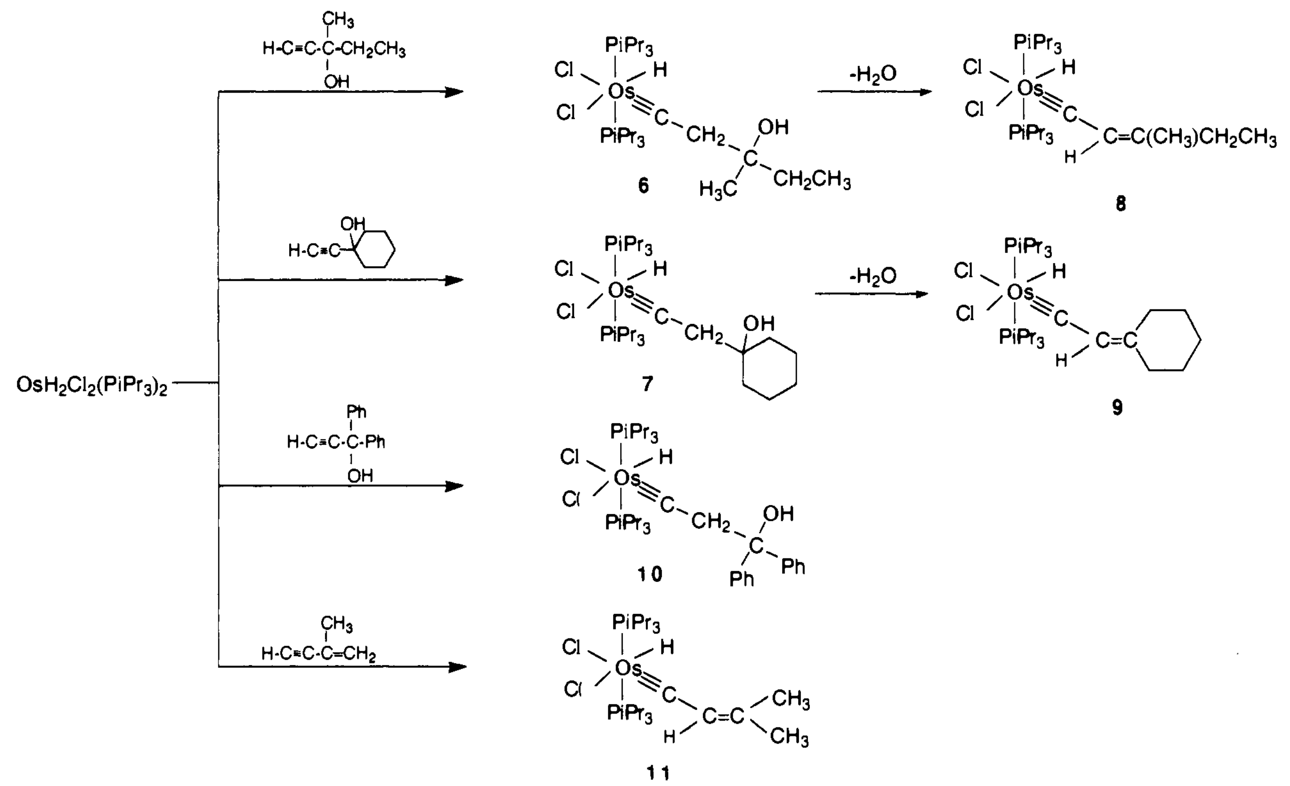
Scheme II



could change the charge distribution on the carbon atoms of the vinylidene ligands, therefore, determining the nature of the attack.

Hydride–Vinylcarbyne Complexes. Reactions of **1** with 3-methyl-1-pentyn-3-ol and 1-ethynyl-1-cyclohexanol lead to hydride–vinylcarbyne complexes, in toluene at 65 °C. The reactions, which can be easily monitored by $^{31}P\{^1H\}$ spectroscopy, proceed via the hydroxycarbyne intermediates **6** and **7** (Scheme II). The hydride–vinylcarbyne **8** was obtained as a pink solid in 70% yield, after 20 h. The presence of the vinyl group in the vinylcarbyne ligand of **8** was confirmed by the $^{13}C\{^1H\}$ NMR spectrum that shows in the olefinic resonances region two singlets at 166.4 and 134.3 ppm. When the reaction between **1** and 3-methyl-1-pentyn-3-ol was carried out in hexane at 60 °C, a violet solid was obtained after 24 h. The IR, ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra of this solid indicate that it is a mixture of **6** and **8** in a 1:1 molar ratio. The IR spectrum of the solid contains a broad resonance at about 3450 cm^{-1}, characteristic of ν(OH) absorption, while the $^{13}C\{^1H\}$ spectrum shows two singlets at 71.29 and 61.56 ppm for the aliphatic $\equiv CCH_2$ and -COH carbon atoms of **6**.

Complex **9** was obtained as a dark solid in 60% yield after 4 days. The presence of the vinyl group in the vinylcarbyne ligand of this compound was also inferred from the $^{13}C\{^1H\}$ NMR spectrum that shows two singlets at 169.90 and 132.61 ppm. Similar to the reaction of **1** with 3-methyl-1-pentyn-3-ol, the treatment of **1** with 1-ethynyl-1-cyclohexanol for 18 h in hexane, at 60 °C, leads to a mixture of the hydroxycarbyne **7** and the vinylcarbyne **9** in a 2:1 molar ratio. Although the complexes **6** and **7** were completely characterized by IR, ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy, they were not isolated as pure solids. Attempts to separate the mixtures **6**–**8** and **7**–**9** by fractional crystallization or column chromatography were unsuccessful. In contrast to **6** and **7**, the hydroxycarbyne **10** was obtained as a pure yellow solid in 61% yield by reaction of **1** with 1,1-diphenyl-2-propyn-1-ol for 24 h in toluene, at 65 °C. A subsequent dehydration of the hydroxycarbyne ligand was not observed.

Selegue et al. previously reported that reactions of 1-alkyn-3-ols with Ru(η^5-C_5H_5)Cl$(PR_3)_2$ in polar media lead to hydroxyvinylidene intermediates, which spontaneously dehydrate in situ.[28-30] In the case of 1,1-diphenyl-2-propyn-1-ol, allenylidene complexes are formed exclusively.[28] However, when hydrogen atoms adjacent to the hydroxy group are present, dehydration can give either allenylidene or vinylvinylidene.[29] Kolobova[31] and co-workers observed that the action of SiO_2 or Al_2O_3 on hydroxyvinylidene manganese compounds causes their dehydration to allenylidenes. Dixneuf[32] and co-workers described that the complex $RuCl_2(\eta^6\text{-}C_6Me_5)(PMe_3)$ reacts at room temperature with HC≡CCR$_2$OH (R ≠ H) and NaPF$_6$ in methanol to produce vinylcarbenes. Some platinum(II) alkynyls with tertiary hydroxy groups can also be dehydrated to enynyls.[33]

Although the vinylcarbyne complexes are interesting compounds which could have important applications in organic synthesis, their number and the synthetic routes that lead to them are limited. In this context, it is interesting to note that vinylcarbynes could also be obtained starting from enynes. Thus, working under similar conditions to those mentioned above for **2**–**5**, we isolated the hydride–vinylcarbyne **11** by reaction of **1** with 2-methyl-1-buten-3-yne. The IR, ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra of this complex (see Experimental Section) are in accordance with the structure proposed in Scheme II. This reaction that can be rationalized according to the mechanism shown in Scheme I further involves the isomerization of the olefinic bond of the starting alkyne, probably on a vinylvinylidene intermediate, which could afford linear allenylidene species clearly preferred by steric conflicts between the vinylvinylidene group

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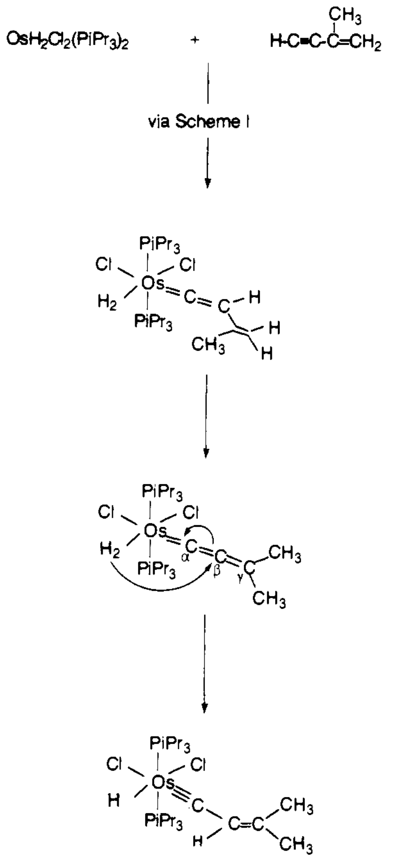
Scheme III



and the triisopropylphosphine ligands (Scheme III). In this context, it is interesting to note that the protonation of compounds of the type $Mn(CCCPh_2)(CO)_2(\eta^5\text{-}C_5H_5)$ leads to cationic vinylcarbyne complexes.[34] In agreement with this, MO calculations suggest that the C_α and C_γ atoms of the $C{=}C{=}CPh_2$ group are electrophilic centers and the C_β atom is nucleophilic.[20,35]

Concluding Remarks. The present study reports a new synthetic route for preparing hydride–carbyne complexes. The complex $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ (**1**) reacts with phenylacetylene, cyclohexylacetylene, and 1-(trimethylsilyl)-1,4-pentadiyne to give the complexes $OsHCl_2(CCH_2R)(P\text{-}i\text{-}Pr_3)_2$ (R = Ph (**2**); Cy (**3**); $CH_2C{\equiv}CSiMe_3$ (**4**); H (**5**)). The reaction of **1** with 1-alkyn-3-ols and unsaturated alkynes leads to the formation of hydride-vinylcarbyne complexes. Thus, the complexes $OsHCl_2(CCH{=}C(CH_3)CH_2CH_3)(P\text{-}i\text{-}Pr_3)_2$ (**8**), $OsHCl_2(CCH{=}CCH_2CH_2CH_2CH_2CH_2)(P\text{-}i\text{-}Pr_3)_2$ (**9**), and $OsHCl_2(CCH{=}C(CH_3)_2)(P\text{-}i\text{-}Pr_3)_2$ (**11**) were prepared. The key intermediates of these processes seem to be dihydrogen–vinylidene species of osmium(II); in this way, the reactions could be rationalized as the electrophilic attack of the acidic hydrogen proton of the dihydrogen ligands on the β-C atom of the vinylidene ligands.

In addition, it is interesting to note that the reactions described in this paper illustrate a new reaction pattern between hydride transition metal complexes and terminal alkynes. In general, these reactions lead to vinyl complexes by an insertion reaction of the alkyne into the M–H bond. Furthermore, we recently observed that when the metallic fragment is rich in electrons, an oxidative addition of the alkyne can also take place to give dihydrogen–alkynyl complexes. We have now shown that the reaction of an alkyne with a dihydride complex can afford hydride–carbyne compounds. The reason for this unusual finding seems to be due to the tendency shown by the starting dihydride $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ to form dihydrogen complexes.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of argon by using Schlenk tube techniques. Solvents were dried and purified by known procedures and distilled under argon prior to use. The reagents cyclohexylacetylene (Merck), 1-ethynyl-1-cyclohexanol (Fluka), 3-methyl-1-pentyn-3-ol (Koch. Light Laboratories Ltd), (trimethylsilyl)acetylene 98% (Aldrich), and 1,1-diphenyl-2-propyn-1-ol (ABCR) were obtained from commercial sources as indicated and used without further purification. 2-Methyl-1-buten-3-yne (ABCR), phenylacetylene (Merk), and 1-(trimethylsilyl)-1,4-pentadiyne (ABCR) were distilled prior to use. The starting complex $OsH_2Cl_2(P\text{-}i\text{-}Pr_3)_2$ (**1**) was prepared by a published method.[13]

Physical Measurements. NMR spectra were recorded on a Varian 200 XL or on a Varian UNYT 300 spectrophotometer at room temperature. Chemical shifts are expressed in parts per million, upfield from $Si(CH_3)_4$ (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants J and N [$N = J(PH) + J(P'H)$] are given in hertz. Infrared spectra were recorded on a Perkin-Elmer 783 instrument. C and H analyses were carried out on a Perkin-Elmer 240 C microanalyzer.

Preparation of $OsHCl_2(CCH_2Ph)(P\text{-}i\text{-}Pr_3)_2$ (2). A suspension of compound **1** (150 mg, 0.26 mmol) in 10 mL of hexane was treated with phenylacetylene (85 μL, 0.77 mmol). The mixture was stirred for 17 h at 60 °C, and after the mixture was cooled to room temperature, a brown solid was formed. The solvent was decanted, and the solid was repeatedly washed with hexane and then dried in vacuo. Yield: 103 mg (58%). Anal. Calcd for $C_{26}Cl_2H_{50}OsP_2$: C, 45.67; H, 7.09. Found: C, 45.48; H, 7.08. IR (Nujol): $\nu(OsH)$ 2160 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 7.10 (m, 5 H, Ph), 2.58 (m, 6 H, $PCHCH_3$), 2.04 (s, 2 H, $Os{\equiv}CCH_2$), 1.42 (dvt, N = 13.5, $J(HH)$ = 7.2 Hz, 18 H, $PCHCH_3$), 1.31 (dvt, N = 13.8, $J(HH)$ = 7.0 Hz, 18 H, $PCHCH_3$), –6.57 (t, $J(PH)$ = 16 Hz, 1 H, OsH). $^{31}P\{^1H\}$ NMR (80.98 MHz, C_6D_6): δ 19.51 (s, d in off-resonance). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6): δ 264.68 (t, $J(PC)$ = 11.05 Hz, $Os{\equiv}C$), 129.39, 129.06, and 127.82 (each s, Ph), 56.95 (s, CH_2), 27.04 (vt, N = 25.8 Hz, $PCHCH_3$), 19.85 and 19.66 (both s, $PCHCH_3$).

Preparation of $OsHCl_2(CCH_2Cy)(P\text{-}i\text{-}Pr_3)_2$ (3). This complex was prepared analogously to that described for **2**, starting from **1** (150 mg, 0.26 mmol) and cyclohexylacetylene (99.28 μL, 0.77 mmol). A yellow solid was formed. Yield: 88 mg (49%). Anal. Calcd for $C_{26}Cl_2H_{56}OsP_2$: C, 45.33; H, 8 17. Found: C, 45.62; H, 8.91. IR (Nujol): $\nu(OsH)$ 2160 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 2.70 (m, 6 H, $PCHCH_3$), 1.96 (br, 2 H, $Os{\equiv}CCH_2$), 1.52 (dvt, N = 13.7, $J(HH)$ = 7.0 Hz, 18 H, $PCHCH_3$), 1.38 (dvt, N = 13.8, $J(HH)$ = 7.0 Hz, 18 H, $PCHCH_3$), 1.9–0.6 (br, 11 H, Cy), –6.88 (t, $J(PH)$ = 16.5 Hz, 1 H, OsH). $^{31}P\{^1H\}$ NMR (80.98 MHz, C_6D_6): δ 18.99 (s). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6): δ 270.09 (t, $J(PC)$ = 10.8 Hz, $Os{\equiv}C$), 58.96 (s, ${\equiv}CCH_2$), 34.71 (s, CH), 34.03 (s, Cy ortho carbons), 27.38 (vt, N = 25.8 Hz, $PCHCH_3$), 26.27 (s, Cy meta carbons), 26.00 (s, Cy para carbon), 19.86 and 19.77 (both s, $PCHCH_3$).

Preparation of $OsHCl_2(CCH_2CH_2C{\equiv}CSiMe_3)(P\text{-}i\text{-}Pr_3)_2$ (4). This complex was prepared analogously to that described for **2**, starting from **1** (150 mg, 0.26 mmol) and 1-(trimethylsilyl)-1,4-pentadiyne (110 μL, 0.77 mmol). After being cooled to room temperature, the solution was concentrated to ca. 5 mL in vacuo and stored at –78 °C. A dark brown solid was formed. The solvent was decanted, and the solid was washed twice with hexane and then dried in vacuo. Yield: 60 mg (33%). Anal. Calcd for $C_{26}Cl_2H_{56}OsP_2Si$: C, 43.37; H, 7.86. Found: C, 43.40; H, 8.43. IR (Nujol): $\nu(OsH)$ 2185 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 2.56 (m, 6 H, $PCHCH_3$), 2.67–2.53 (br, 4 H, $Os{\equiv}CCH_2CH_2$), 1.36 (dvt, N = 13.5, $J(HH)$ = 6.9 Hz, 18 H, $PCHCH_3$), 1.23 (dvt, N = 13.8, $J(HH)$ = 6.9 Hz, 18 H, $PCHCH_3$), 0.14 (s, 9 H, $SiCH_3$), –6.60 (t, $J(PH)$ = 16.2 Hz, 1 H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6): δ 20.75 (s). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6): δ 265.04 (t, $J(PC)$ = 10.8 Hz, $Os{\equiv}C$), 103.23 (s, $C{\equiv}$), 87.33 (s, ${\equiv}CSi$), 50.58 (s, $Os{\equiv}CCH_2$), 26.68 (vt, N = 26.3 Hz, $PCHCH_3$), 19.80 and 19.78 (both s, $PCHCH_3$), 12.44 (s, $CH_2C{\equiv}C$), –0.09 (s, $Si(CH_3)_3$).

Preparation of $OsHCl_2(CCH_3)(P\text{-}i\text{-}Pr_3)_2$ (5). This complex was prepared analogously to that described for **2**, starting from **1** (150 mg, 0.26 mmol) and (trimethylsilyl)acetylene (108 μL, 0.77 mmol). An orange

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Table II. Crystal Data and Data Collection and Refinement for $[OsHCl_2(CCH_2Ph)(P\text{-}i\text{-}Pr_3)_2]$ (**2**)

Crystal Data	
formula	$C_{26}H_{50}Cl_2OsP_2$
mol wt	685.73
color, habit	yellow, prismatic block
crystal size, mm	0.205 × 0.277 × 0.563
crystal sys	orthorhombic
space group	$P2_12_12_1$ (No. 19)
a, Å	8.7490(3)
b, Å	15.4051(5)
c, Å	22.4257(8)
V, Å^3	3022.5(2)
Z	4
d(calcd), g cm^{-3}	1.507
Data Collection and Refinement	
diffractometer	4-circle Siemens AED
λ (Mo K_α) radiation, Å, technique	0.71069, bisecting geometry
monochromator	graphite oriented
μ, cm^{-1}	45.19
scan type	ω–2θ
2θ range, deg	3–50
no. of data collected	7149
no. of unique data	5316
unique observed data	4615, $F \geq 5\sigma(F)$
no. of params refined	287
R, R_w[a]	0.022, 0.023
max/min trans fact	0.465, 0.278

[a] $w^{-1} = \sigma^2(F) + 0.000379F^2$.

Table III. Atomic Coordinates (×10^4; ×10^5 for Os Atom) and Equivalent Isotropic Displacement Coefficients (Å^2, ×10^3; Å^2, ×10^4 for Os Atom) for the Compound $[OsHCl_2(CCH_2Ph)(P\text{-}i\text{-}Pr_3)_2]$ (**2**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}[a]
Os	75110(2)	56632(1)	86980(1)	294(5)
Cl(1)	5637(2)	5643(1)	9532(1)	54(1)
Cl(2)	5475(2)	5074(1)	8030(1)	54(1)
P(1)	6797(1)	7174(1)	8559(1)	32(1)
P(2)	8359(2)	4248(1)	9036(1)	36(1)
C(1)	4839(5)	7479(3)	8783(3)	44(2)
C(2)	3575(5)	6930(4)	8497(3)	62(2)
C(3)	4430(7)	8438(4)	8718(3)	69(2)
C(4)	7956(5)	7917(3)	9034(2)	41(2)
C(5)	7618(9)	7796(4)	9703(2)	62(2)
C(6)	9678(6)	7823(3)	8920(3)	54(2)
C(7)	7194(6)	7544(3)	7787(2)	43(2)
C(8)	6107(7)	7159(4)	7335(2)	64(2)
C(9)	7334(9)	8530(3)	7693(2)	65(2)
C(10)	9900(6)	4357(3)	9594(2)	50(2)
C(11)	11331(7)	4824(4)	9353(3)	70(2)
C(12)	9355(9)	4788(5)	10162(2)	78(3)
C(13)	6893(7)	3589(4)	9436(3)	56(2)
C(14)	7489(10)	2793(4)	9779(3)	94(3)
C(15)	5535(8)	3326(5)	9049(4)	100(3)
C(16)	9279(7)	3597(3)	8439(2)	49(2)
C(17)	10214(8)	2814(4)	8640(3)	68(2)
C(18)	8256(8)	3365(5)	7927(3)	81(3)
C(19)	9044(5)	5751(3)	8228(2)	33(1)
C(20)	10478(6)	5870(3)	7892(2)	42(2)
C(21)	10462(6)	5657(3)	7225(2)	42(2)
C(22)	11800(7)	5718(3)	6916(2)	57(2)
C(23)	11824(10)	5547(5)	6315(3)	76(3)
C(24)	10544(12)	5302(5)	6023(3)	85(3)
C(25)	9195(11)	5235(5)	6327(3)	81(3)
C(26)	9140(8)	5414(4)	6938(3)	60(2)
H	8284(50)	6080(27)	9186(17)	68(18)[b]

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Isotropic thermal parameter.

solid was formed. Yield: 71 mg (45%). Anal. Calcd for $C_{20}Cl_2H_{46}OsP_2$: C, 39.39; H, 7.62. Found: C, 39.08; H, 7.76. IR (Nujol): ν(OsH) 2150 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.64 (m, 6 H, PC*H*CH$_3$), 1.37 (dvt, *N* = 13.8, *J*(HH) = 6.9 Hz, 18 H, PCHC*H*$_3$), 1.31 (dvt, *N* = 14.1, *J*(HH) = 7.2 Hz, 18 H, PCHC*H*$_3$), 0.9 (s, 3 H, CH$_3$), −7.56 (t, *J*(PH) = 16 Hz, 1H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$): δ 21.88 (s). $^{13}C\{^1H\}$ NMR (75.43 MHz, $CDCl_3$): δ 265.66 (t, *J*(PC) = 11.8 Hz, Os≡C), 38.23 (s, CH$_3$), 25.67 (vt, *N* = 26.2 Hz, *P*CHCH$_3$), 19.76 and 19.64 (both s, PCH*C*H$_3$).

Preparation of $OsHCl_2(CCH{=}C(CH_3)CH_2CH_3)(P\text{-}i\text{-}Pr_3)_2$ (8). A solution of compound **1** (150 mg, 0.26 mmol) in 10 mL of toluene was treated with 3-methyl-1-pentyn-3-ol (76 μL, 0.77 mmol). The reaction mixture was stirred for 48 h at 65 °C. (The reaction was followed by $^{31}P\{^1H\}$ NMR.) After being cooled to room temperature, the solution was concentrated to ca. 2 mL in vacuo. Addition of hexane caused the precipitation of a pink solid. The solvent was decanted, and the solid was washed twice with hexane and then dried in vacuo. Yield: 108 mg (63%). Anal. Calcd for $C_{24}Cl_2H_{52}OsP_2$: C, 43.42; H, 7.90. Found: C, 43.52; H, 8.27. IR (Nujol): ν(OsH) 2162, ν(C=C) 1594 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): δ 4.30 (s, 1 H, =CH), 2.80 (m, 6 H, PC*H*CH$_3$), 1.99 (s, 3 H, =CCH$_3$), 1.25 (q, *J*(HH) = 7.2 Hz, 2 H, C*H*$_2$CH$_3$), 1.54 and 1.42 (each dvt, *N* = 13.5, *J*(HH) = 6.9 Hz, each 18 H, PCHC*H*$_3$), 0.59 (t, *J*(HH) = 7.2 Hz, 3 H, CH$_2$C*H*$_3$), −6.96 (t, *J*(PH) = 16.3 Hz, 1 H, OsH). $^{31}P\{^1H\}$ NMR (80.98 MHz, C_6D_6): δ 17.80 (s). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6): δ 255.70 (t, *J*(PC) = 11.5 Hz, Os≡C), 166.42 and 134.28 (each s, C=C), 32.40 (s, *C*H$_2$CH$_3$), 26.63 (vt, *N* = 25.27 Hz, P*C*HCH$_3$), 21.98 (s, =C*C*H$_3$), 19.99 and 19.68 (both s, PCH*C*H$_3$), 11.12 (s, CH$_2$*C*H$_3$).

Preparation of $OsHCl_2(CCH{=}CCH_2CH_2CH_2CH_2CH_2)(P\text{-}i\text{-}Pr_3)_2$ (9). This compound was prepared analogously to that described for **8**, starting from **1** (150 mg, 0.26 mmol) and 1-ethynyl-1-cyclohexanol (96 mg, 0.77 mmol). After being stirred for 96 h at 65 °C, the reaction mixture was worked up as described for **8**. A brown solid was formed. Yield: 91 mg (51%). Anal. Calcd for $C_{26}Cl_2H_{54}OsP_2$: C, 45.26; H, 7.90. Found: C, 45.50; H, 8.29. IR (Nujol): ν(OsH) 2170, ν(C=C) 1598 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): δ 4.20 (s, 1H, CH), 2.75 (m, 6 H, PC*H*CH$_3$), 2.0–1.1 (br signals were overlapped, Cy protons), 1.51 and 1.40 (each dvt, *N* = 13.5, *J*(HH) = 6.9 Hz, each 18 H, PCHC*H*$_3$), −6.95 (t, *J*(PH) = 16.5 Hz, 1 H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6): δ 18.10 (s). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6): δ 255.51 (t, *J*(PC) = 11.5 Hz, Os≡C), 167.9 and 132.61 (each s, C=C), 36.48, 33.62, 27.81, 27.76, and 25.6 (each s, ring *C*H$_2$), 26.77 (vt, *N* = 25.34 Hz, P*C*HCH$_3$), 20.10 and 19.65 (each s, PCH*C*H$_3$).

Preparation of a Mixture (1:1) of $OsHCl_2(CCH_2C(OH)(CH_3)CH_2CH_3)(P\text{-}i\text{-}Pr_3)_2$ (6) and $OsHCl_2(CCH{=}C(CH_3)CH_2CH_3)(P\text{-}i\text{-}Pr_3)_2$ (8). A suspension of compound **1** (150 mg, 0.26 mmol) in 10 mL of hexane was treated with 3-methyl-1-pentyn-3-ol (76 μL, 0.77 mmol). The mixture was stirred for 24 h at 60 °C. After the mixture was cooled to room temperature, a solid precipitated. The solvent was decanted, and the solid was washed repeatedly with hexane and then dried in vacuo. A dark purple solid was isolated, which according to the IR, ^{1}H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ spectra turned out to be a mixture of **6** and **8** in a 1:1 ratio. Spectroscopic data for **6** are as follows. IR (Nujol): ν(OH) 3450, ν(OsH) 2162 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): δ 3.96 (s, 1 H, OH), 2.87 (m, 6 H, PC*H*CH$_3$), 1.33 (s, 3 H, =CCH$_3$), 1.66 (q, *J*(HH) = 7.5 Hz, 2 H, C*H*$_2$CH$_3$), 1.54 and 1.42 (each dvt, *N* = 13.5, *J*(HH) = 6.9 Hz, each 18 H, PCHC*H*$_3$), 0.85 (t, *J*(HH) = 7.5 Hz, 3 H, CH$_2$C*H*$_3$), −5.78 (t, *J*(PH) = 16.3 Hz, 1 H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6): δ 20.87 (s). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6): δ 270.49 (t, *J*(PC) = 10.2 Hz, Os≡C), 71.29 (s, Os≡C*C*H$_2$), 61.56 (s, COH), 36.04 (s, *C*H$_2$CH$_3$), 27.39 and 27.35 (both vt, *N* = 26.2, 25.72 Hz, P*C*HCH$_3$), 28.02 (s, =C*C*H$_3$), 19.84 and 19.45 (both d, *J*(PC) = 2.34, 3.70 Hz, PCH*C*H$_3$), 8.03 (s, CH$_2$*C*H$_3$).

Preparation of a Mixture (2:1) of $OsHCl_2(CCH_2C(OH)CH_2CH_2CH_2CH_2CH_2)(P\text{-}i\text{-}Pr_3)_2$ (7) and $OsHCl_2(CCH{=}CCH_2CH_2CH_2CH_2CH_2)(P\text{-}i\text{-}Pr_3)_2$ (9). This mixture was prepared analogously to that described for the mixture of **6**–**8**, starting from **1** (150 mg, 0.26 mmol) and 1-ethynyl-1-cyclohexanol (96 mg, 0.77 mmol). After the mixture was stirred for 18 h at 60 °C, a pale pink solid was isolated, which according to the IR, ^{1}H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ spectra turned out to be a mixture of **7** and **9** in a 2:1 ratio. Spectroscopic data for **7** are as follows. IR (Nujol): ν(OH) 3450, ν(OsH) 2170 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 3.98 (s, 1 H, OH), 2.83 (m, 6 H, PC*H*CH$_3$), 1.8–0.9 (br signals were overlapped, Cy protons), 1.51 and 1.40 (each dvt, *N* = 13.5, *J*(HH) = 6.9 Hz, each 18 H, PCHC*H*$_3$), −5.74 (t, *J*(PH) = 17.1 Hz, 1 H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6): δ 21.16 (s). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6): δ 270.12 (t, *J*(PC) = 10.7 Hz, Os≡C), 70.26 (s, Os≡C*C*H$_2$), 62.91 (s, COH) 38.98, 25.28, and 21.84 (each s, ring *C*H$_2$), 27.37 (vt, *N* = 25.72 Hz, P*C*HCH$_3$), 19.87 and 19.46 (each s, PCH*C*H$_3$).

Preparation of $OsHCl_2(CCH_2C(OH)Ph_2(P\text{-}i\text{-}Pr_3)_2$ (10). A solution of compound **1** (150 mg, 0.26 mmol) in 10 mL of toluene was treated with 1,1-diphenyl-2-propyn-1-ol (166 mg, 0.77 mmol). After the solution was stirred for 24 h at 65 °C, a yellow solid was formed. The solvent was decanted, and the solid was washed three times with hexane and then dried in vacuo. Yield: 125 mg (61%). Anal. Calcd for $C_{33}Cl_2H_{56}OsP_2$: C, 51.07; H, 7.30. Found: C, 50.59; H, 7.43. IR (Nujol): ν(OH) 3400, ν(OsH) 2160 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.4–7.2 (m, 10 H, Ph), 5.2 (s, 1 H, OH), 2.60 (m, 6 H, PC*H*CH$_3$), 2.1 (s, 2 H, Os$\equiv$CCH$_2$), 1.34 (dvt, *N* = 14.4, *J*(HH) = 7.2 Hz, 18 H, PCHC*H*$_3$), 1.29 (dvt, *N* = 13.8, *J*(HH) = 6.9 Hz, 18 H, PCHC*H*$_3$), –5.64 (t, *J*(PH) = 17 Hz, 1 H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, $CDCl_3$): δ 22.82 (s). ^{13}C{^{1}H} NMR (75.43 MHz, $CDCl_3$): δ 267.84 (t, *J*(PC) = 10.4 Hz, Os$\equiv$C), 128.6, 127.4, and 125.0 (each s, Ph), 75.49 (s, Os$\equiv$C*C*H$_2$), 62.8 (s, COH), 27.03 (vt, *N* = 26.25 Hz, P*C*HCH$_3$), 19.51 and 18.9 (each s, PCH*C*H$_3$).

Preparation of $OsHCl_2(CCH{=}C(CH_3)_2)(P\text{-}i\text{-}Pr_3)_2$ (11). The complex was prepared analogously to that described for **3**, starting from **1** (150 mg, 0.26 mmol) and 2-methyl-1-buten-3-yne (75 μL, 0.77 mmol) to give a dark brown solid. Yield: 116 mg (69%). Anal. Calcd for $C_{23}Cl_2H_5OsP_2$: C, 42.51; H, 7.90. Found: C, 43.01; H, 8.27. IR (Nujol): ν(OsH) 2180, ν(C=C) 1600 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 4.19 (s, 1 H, =CH), 2.72 (m, 6 H, PC*H*CH$_3$), 1.93 (s, 3 H, (trans to H)CH$_3$), 1.51 and 1.38 (both dvt, *N* = 13.6, *J*(HH) = 6.9 Hz, 36 H, PCHC*H*$_3$), 0.83 (s, 3H, (cis to H)CH$_3$), –6.94 (t, *J*(PH) = 16.6 Hz, 1 H, OsH). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6): δ 17.57 (s). ^{13}C{^{1}H} NMR (75.43 MHz, C_6D_6): δ 255.28 (t, *J*(PC) = 11.1 Hz, Os$\equiv$C), 161.08 and 135.85 (each s, C=C), 26.72 (vt, *N* = 25.72 Hz, P*C*HCH$_3$), 25.55 and 23.78 (both s, CH$_3$), 19.96 and 19.66 (both s, PCH*C*H$_3$).

X-ray Structure Analysis of 2. Collection and Reduction of Data. Crystals suitable for an X-ray diffraction experiment were obtained by slow diffusion of hexane into a dichloromethane solution of the complex at room temperature. A summary of crystal data, intensity collection procedure, and refinement data is reported in Table II. The prismatic crystal studied was glued on a glass fiber and mounted on a Siemens AED-2 diffractometer. Cell constants were obtained from the least-squares fit of the setting angles of 38 reflections in the range 20° $\le 2\theta \le$ 35°. The 7149 recorded reflections were corrected for Lorentz and polarization effects. Three orientation and intensity standards were monitored every 55 min of measuring time; no variation was observed. Reflections were also corrected for absorption by a numerical method based on indexed morphological faces.

Structure Solution and Refinement. The structure was solved by Patterson (Os atom) and conventional Fourier techniques. Refinement was carried out by full-matrix least squares with initial isotropic thermal parameters. Anisotropic thermal parameters were used in the last cycles of refinement for all non-hydrogen atoms. Since the space group $P2_12_12_1$ leads to a chiral configuration in the structure, an independent cycle of refinement was carried out using the coordinates $-x$, $-y$, $-z$ for the non-hydrogen atoms. A remarkable increase of the *R* value was obtained [$R(x,y,z) = 0.033$; $R(-x,-y,-z) = 0.049$]. The former model was selected, and the reported data refer to this model. Hydrogen atoms are included at their geometrically calculated positions (C–H = 0.97 Å) and were refined with a common isotropic thermal parameter "riding" on the corresponding carbon atoms. At this stage, the hydride ligand is located in the difference Fourier map and was refined subsequently as an isotropic atom. Atomic scattering factors, corrected for anomalous dispersion of Os, Cl, and P, were taken from ref 36. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with the weight defined as $w = 1/[\sigma^2(F) + 0.000379F^2]$. Final R and R_w values are 0.022 and 0.0023, respectively. All calculations were performed by use of the SHELXTL PLUS system of computer programs.[37] The final positional parameters for all non-hydrogen atoms are given in Table III.

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Supplementary Material Available: Tables of anisotropic thermal parameters, atomic coordinates for hydrogen atoms, experimental details of the X-ray study, bond distances and angles, selected least-squares planes, and interatomic distances (17 pages); a table of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page. The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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