1662 Organometallics 1994, 13, 1662–1668

Reactions of $OsHCl(CO)(PiPr_3)_2$ with Alkyn-1-ols: Synthesis of (Vinylcarbene)osmium(II) Complexes

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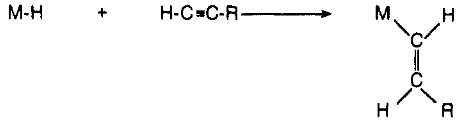
Received October 29, 1993[⊗]

The monohydride complex $OsHCl(CO)(PiPr_3)_2$ (**1**) reacts with 2-propyn-1-ol to give the vinyl compound $Os(CH{=}CHCH_2OH)Cl(CO)(PiPr_3)_2$ (**2a**). The reaction of **1** with 1-phenyl-2-propyn-1-ol leads to a mixture of products, from which the complexes $OsCl_2({=}CHCH{=}CHPh)(CO)(PiPr_3)_2$ (**3a**) and $Os(CHCHC(O)Ph)Cl(CO)(PiPr_3)_2$ (**4a**) were separated. The molecular structures of complexes **3a** and **4a** were determined by X-ray crystallography. Crystals of **3a** are monoclinic, space group $P2_1/c$, with unit cell dimensions a = 15.671(3) Å, b = 12.507(2) Å, c = 16.632(3) Å, and β = 108.95(1°). The structure was refined to the R and R_w values 0.0202 and 0.0239 on 5080 observed data. The coordination around the osmium atom can be described as a distorted octahedron with the two triisopropylphosphine ligands occupying *trans* positions; the perpendicular plane is defined by the vinylcarbene and a carbonyl ligand, mutually *cis* disposed, and by two chloride atoms. Crystals of **4a** are orthorhombic, space group $P2_12_12_1$, with a = 8.797(1) Å, b = 15.268(2) Å and c = 22.275(3) Å. The structure was refined to the R and R_w values 0.0198 and 0.0223 on 5532 reflections. The osmium coordination environment can also be rationalized as a distorted octahedron with the two phosphine ligands disposed mutually *trans*. The remaining coordination sites of the octahedron are occupied by the carbonyl ligand, the chloride atom, and the chelate CHCHC(O)Ph ligand. The reaction of **1** with 1,1-diphenyl-2-propyn-1-ol also leads to a mixture of products, from which the complex $OsCl_2({=}CHCH{=}CPh_2)(CO)(PiPr_3)_2$ (**3b**) was isolated and characterized.

Introduction

One of the most typical reactions of transition-metal hydrides is the insertion of alkynes into the metal–hydride bond, which leads to vinyl derivatives (eq 1).[1]



In agreement with this general trend, we have previously observed that the monohydride complexes $OsHCl(CO)(PiPr_3)_2$[2,3] and $[OsH(\eta^1\text{-}OCMe_2)(CO)_2(PiPr_3)_2]BF_4$[4] react with alkynes $RC{\equiv}CCO_2Me$ (R = Me, CO_2Me) and $HC{\equiv}CR$ (R = H, Me, Ph) by insertion to yield the corresponding vinylmetal compounds. However, we have also observed that it is possible to get different and, furthermore, specific organometallic compounds by direct reaction of osmium hydrides with alkynes.

Reactions of $OsH_2Cl_2(PiPr_3)_2$[5] with terminal alkynes lead to hydride–carbyne complexes. When the alkyne contains a hydroxy group, hydride–vinylcarbyne compounds can be obtained. These reactions proceed via hydroxycarbyne compounds, which undergo a dehydration process to give the corresponding hydride–vinylcarbyne derivatives. The formation of hydride–carbyne complexes from $OsH_2Cl_2(PiPr_3)_2$ and terminal alkynes seems to be due to the formation of dihydrogen–vinylidene intermediates. The hydride–vinylidene species $OsH(\eta^2\text{-}O_2CCH_3)({=}C{=}CHPh)(PiPr_3)_2$ has been recently isolated by reaction of $OsH_3(\eta^2\text{-}O_2CCH_3)(PiPr_3)_2$ with $HC{\equiv}CPh$ in our laboratory.[6]

The tetrahydride complex $OsH_4(CO)(PiPr_3)_2$, in contrast to the compounds $OsH_2Cl_2(PiPr_3)_2$ and $OsH_3(\eta^2\text{-}O_2CCH_3)(PiPr_3)_2$, reacts with $HC{\equiv}CR$ to give hydride–alkynyl-dihydrogen complexes of formula $OsH(C_2R)(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ (R = Ph, Me_3Si), which react with further alkyne to form the five-coordinated bis(alkynyl) derivatives $Os(C_2R)_2(CO)(PiPr_3)_2$.[7] Reactions of the tetrahydride complexes with $HC{\equiv}CCO_2Me$, $PhC{\equiv}CPh$, and $EtO_2CC{\equiv}CCO_2Et$ lead to $Os(C_2CO_2Me)(CH{=}C(H)COOMe)(CO)(PiPr_3)_2$,[7b] $Os(\eta^2\text{-}C_2Ph)(CO)(PiPr_3)_2$,[8] and $OsH(C(COOEt){=}CC(H)CO_2Et)(CO)(PiPr_3)_2$,[8] respectively.

As a continuation of our work on the chemical properties of osmium–hydride complexes in the presence of alkynes, we have now studied the reactivity of monohydride compound $OsHCl(CO)(PiPr_3)_2$ toward $HC{\equiv}CCH_2OH$, $HC{\equiv}CCH(OH)Ph$, and $HC{\equiv}CC(OH)Ph_2$. During this study, we have isolated vinylcarbene complexes.

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1994.

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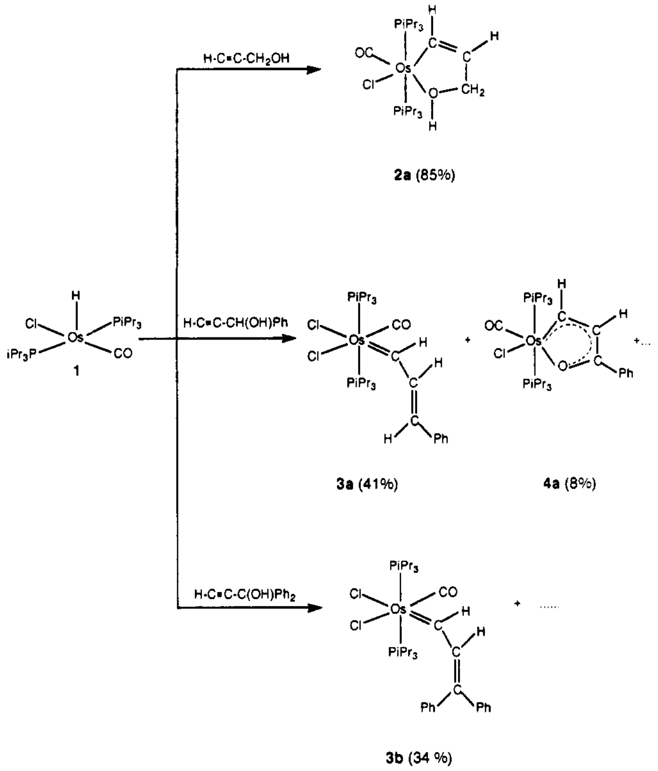
Vinylcarbene complexes are compounds[9] that can play an important role in many interesting transformations, including Diels–Alder reactions,[10] cyclohexadienone annulations,[11] cyclopropanations,[12] catalytic polymerization of alkynes,[13] conversions to pyrrole,[14] δ-carboline,[15] or 3-imidazoline[16] complexes, transmetalations,[17] formation of dinuclear compounds containing μ-η^1:η^3-allylidene[18] or bis(carbene)[19] ligands, and polymerizations to organometallic polymers.[20]

The potential of the vinylcarbene derivates is often limited by the difficulty in building the unsaturated group. These compounds are usually prepared either by multistep procedures[21] or in one step by photolysis.[22] Recently some compounds of this type have also been obtained in one step without photolysis.[20a,22–24] In the present article, we describe the synthesis and characterization of the vinylcarbene complexes $OsCl_2(=CHCH=CRPh)(CO)(P\textit{i}Pr_3)_2$ (R = H, Ph). In addition, the preparations of the complexes $Os(CH=CHCH_2OH)Cl(CO)(P\textit{i}Pr_3)_2$ and $Os(CHCHC(O)Ph)Cl(CO)(P\textit{i}Pr_3)_2$ are also reported.

Results and Discussion

Synthesis and Characterization of the New Compounds. The investigations aimed at elucidating the reactivity of the carbonyl–hydride complex $OsHCl(CO)(P\textit{i}Pr_3)_2$ (**1**) toward alkyn-1-ols are summarized in Scheme 1.

Scheme 1



Treatment of a toluene solution of **1** with the stoichiometric amount of 2-propyn-1-ol leads to a green solution, from which the vinylmetal complex **2a** can be isolated as a pale green solid in 85% yield. The IR spectrum of **2a** in Nujol contains a resonance at 3400 cm^{-1}, characteristic of ν(OH) absorption, while the ^{1}H NMR spectrum shows resonances at 8.49 and 5.04 ppm due to the vinylic hydrogen atoms of the vinyl ligand. The *cis* stereochemistry at the carbon–carbon double bond is strongly supported by the proton–proton coupling constant of 9.8 Hz, which is a typical value for this arrangement.[25] The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 9.57 ppm, indicating that the two phosphine ligands are equivalent.

The reaction of **1** with 1-phenyl-2-propyn-1-ol gives a mixture of products, from which the complexes **3a** and **4a** were separated by column chromatography as pure solids in 41% and 8% yield, respectively. These compounds were fully characterized by elemental analysis, IR, and ^{1}H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy, and X-ray diffraction.

The IR spectrum of **3a** in Nujol shows a strong ν(C=C) band at 1589 cm^{-1}, assigned to the olefinic bond of the vinylcarbene ligand. In the ^{1}H NMR spectrum, this ligand exhibits resonances at 17.74, 8.14, and 7.70 ppm. The Os=CH– carbon atom appears in the $^{13}C\{^1H\}$ NMR spectrum as a triplet at 269.19 ppm with a P–C coupling constant of 6.9 Hz, while the vinylic carbon atoms appear as singlets at 150.72 and 141.80 ppm. The $^{31}P\{^1H\}$ NMR shows a singlet at 12.94 ppm.

A view of the molecular geometry of **3a** is shown in Figure 1. Selected bond distances and angles are listed in Table 1. The geometry of the complex can be rationalized as a distorted octahedron with the two phosphorus atoms of the triisopropylphosphine ligands occupying two *trans* positions (P(1)–Os–P(2) = 171.98(3)°). The alkylidene and carbonyl ligands are mutually *cis* disposed (C(1)–Os–C(10) = 93.0(1)°, as are the two chloride atoms (Cl-

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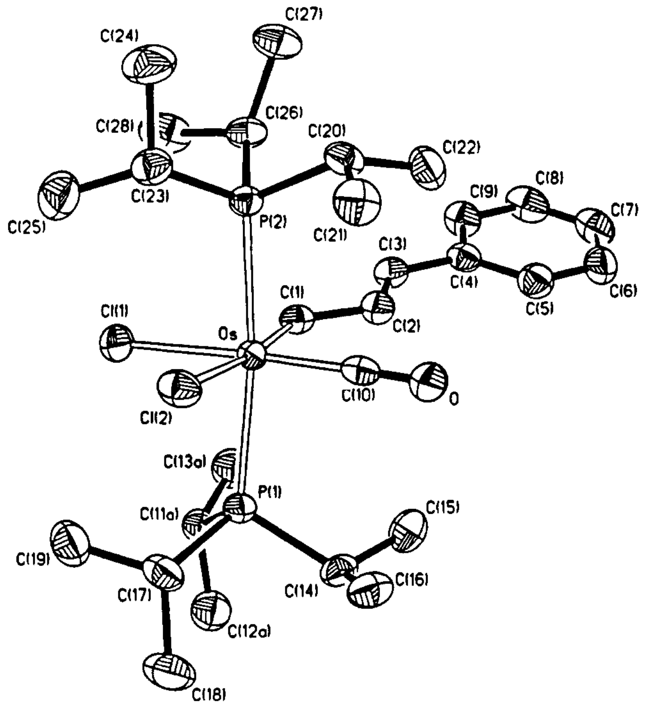

Figure 1. Molecular representation of $OsCl_2(=CHCH=CHPh)(CO)(PiPr_3)_2$ (**3a**) with the labeling scheme used.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex $OsCl_2(=CHCH=CHPh)(CO)(PiPr_3)_2$ (3a)

Os-P(1)	2.487(1)	C(3)-C(4)	1.452(5)
Os-P(2)	2.475(1)	C(4)-C(5)	1.395(5)
Os-Cl(1)	2.461(1)	C(4)-C(9)	1.399(5)
Os-Cl(2)	2.513(1)	C(5)-C(6)	1.381(5)
Os-C(1)	1.921(3)	C(6)-C(7)	1.367(7)
Os-C(10)	1.853(3)	C(7)-C(8)	1.375(5)
C(1)-C(2)	1.438(4)	C(8)-C(9)	1.393(5)
C(2)-C(3)	1.346(5)	C(10)-O	1.116(4)
P(1)-Os-P(2)	171.98(3)	Cl(1)-Os-Cl(2)	92.12(3)
P(1)-Os-Cl(1)	84.83(3)	Cl(1)-Os-C(1)	86.03(9)
P(1)-Os-Cl(2)	88.68(3)	Cl(1)-Os-C(10)	176.5(1)
P(1)-Os-C(1)	97.6(1)	Cl(2)-Os-C(1)	173.2(1)
P(1)-Os-C(10)	92.0(1)	Cl(2)-Os-C(10)	89.3(1)
P(2)-Os-Cl(1)	90.76(3)	C(1)-Os-C(10)	93.0(1)
P(2)-Os-Cl(2)	84.79(3)	Os-C(1)-C(2)	132.2(2)
P(2)-Os-C(1)	88.7(1)	C(1)-C(2)-C(3)	122.3(3)
P(2)-Os-C(10)	92.6(1)	C(2)-C(3)-C(4)	128.0(3)

(1)-Os-Cl(2) = 92.12(3)°). The most conspicuous features of the structure are first the Os-C(1) bond length (1.921(3) Å), which is consistent with a Os-C(1) double-bond formulation, and second the Os-C(1)-C(2) bond angle (132.2(2)°), which indicates sp^2 hybridization for the C(1) carbon atom. Similar values have been reported for related osmium-carbene complexes.[26] The alkylidene ligand is observed to be nearly planar (maximum deviation 0.035(4) Å). The bond lengths within this group are consistent with the vinylcarbene proposal; e.g., C(1) and C(2) are separated by 1.438(4) Å and C(2) and C(3) by 1.346(5) Å.

It should be also mentioned that the Os-Cl(1) bond distance (Cl *trans* to CO) is significantly shorter (0.05 Å approximately) than the Os-Cl(2) bond distance (Cl *trans* to carbene), possibly due to the different *trans* influences of the carbonyl and alkylidene ligands. Surprisingly, the Os-P bond lengths (2.487(1) and 2.475(1) Å) are about 0.1 Å longer than the Os-P distances reported for two phosphine ligands similarly disposed in osmium(II) complexes.[27]

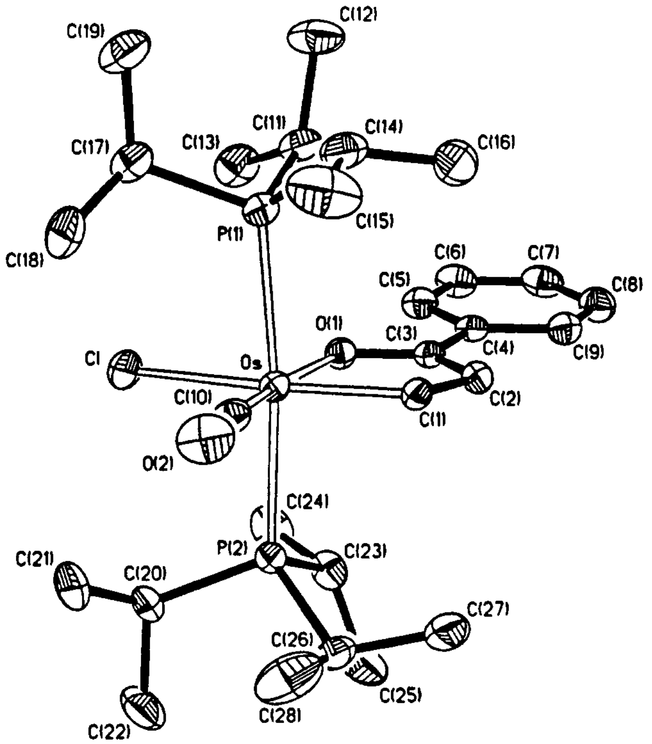

Figure 2. Molecular representation of $\overline{\text{Os(CHCHC(O}}\text{)Ph)Cl(CO)(P}i\text{Pr}_3)_2$ (**4a**) with the atomic numbering scheme.

The IR spectrum of **4a** in KBr shows a very strong ν(C=O) band at 1451 cm^{-1}, assigned to the CHCHC(Ph)O ligand. In contrast to the IR spectrum of **3a**, however, it does not contain a ν(C=C) absorption. In the ^1H NMR spectrum the CHCHC(Ph)O ligand shows signals at 12.94 and 7.49 ppm, which appear as doublets with an H-H coupling constant of 7.2 Hz. The OsCH carbon atom appears in the $^{13}C\{^1H\}$ NMR spectrum at 230.13 ppm as a triplet, with a P-C coupling constant of 5.1 Hz. The remaining vinylic carbon atoms were located at 187.93 (OsOC) and 131.00 (OsCC) ppm. The first signal appears as a triplet with a P-C coupling constant of 1.6 Hz, whereas the second one is observed as a singlet. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 14.87 ppm, indicating the relative *trans* position of the two phosphine ligands.

A molecular representation of **4a** is shown in Figure 2. Selected bond distances and angles are listed in Table 2. The coordination geometry around the osmium atom can also be rationalized as a distorted octahedron with the two phosphorus atoms occupying relative *trans* positions (P(1)-Os-P(2) = 173.16(3)°). The remaining coordination sites involve the C(1) and O(1) atoms of the chelate CHCH(Ph)O ligand—forming with the osmium atom a five-membered ring (O(1)-Os-C(1) = 76.9(1)°)—a chloride atom *trans* to C(1) (Cl-Os-C(1) = 162.0(1)°), and a CO ligand located *trans* to O(1) (O(1)-Os-C(10) = 171.8(1)°). The five-membered metallacycle is almost planar (max-

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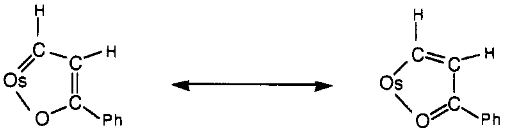
Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Complex $\overline{Os(CHCHC(O}Ph)Cl(CO)(PiPr_3)_2$ (4a)

Os-P(1)	2.424(1)	C(3)-C(4)	1.474(5)
Os-P(2)	2.407(1)	C(4)-C(5)	1.389(5)
Os-Cl	2.482(1)	C(4)-C(9)	1.395(5)
Os-O(1)	2.126(3)	C(5)-C(6)	1.373(6)
Os-C(1)	1.971(3)	C(6)-C(7)	1.381(6)
Os-C(10)	1.814(4)	C(7)-C(8)	1.376(6)
C(1)-C(2)	1.376(5)	C(8)-C(9)	1.381(6)
C(2)-C(3)	1.394(5)	C(10)-O(2)	1.172(5)
C(3)-O(1)	1.283(4)		
P(1)-Os-P(2)	173.16(3)	Cl-Os-C(1)	162.0(1)
P(1)-Os-Cl	85.93(3)	Cl-Os-C(10)	103.0(1)
P(1)-Os-O(1)	88.05(7)	O(1)-Os-C(1)	76.9(1)
P(1)-Os-C(1)	95.0(1)	O(1)-Os-C(10)	171.8(1)
P(1)-Os-C(10)	91.4(1)	C(1)-Os-C(10)	95.0(2)
P(2)-Os-Cl	87.23(3)	Os-O(1)-C(3)	113.7(2)
P(2)-Os-O(1)	91.31(7)	Os-C(1)-C(2)	117.7(3)
P(2)-Os-C(1)	91.5(1)	C(1)-C(2)-C(3)	113.7(3)
P(2)-Os-C(10)	90.2(1)	C(2)-C(3)-O(1)	117.9(3)
Cl-Os-O(1)	85.15(7)	Os-C(10)-O(2)	176.6(4)

Scheme 2

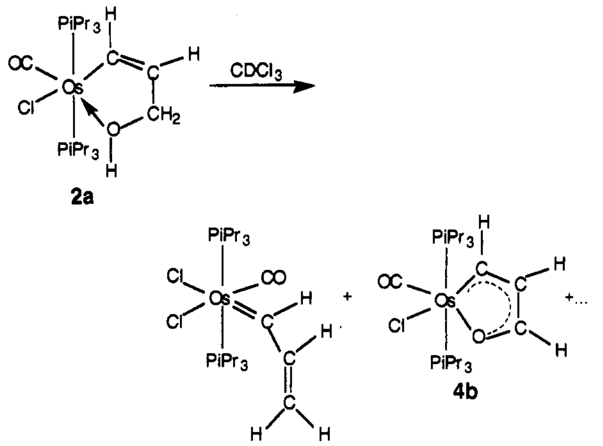


imum deviation 0.096(3) Å). The Os-C(1) distance is 1.971(3) Å, about 0.13 Å shorter than the Os-C bond length found for the related vinyl complex $\overline{Os(C_2CO_2Me)(CH{=}C(H)C}OOMe)(CO)(PiPr_3)_2$ (2.103(4) Å)[7a] but slightly longer than the Os-C(1) bond length found for **3a**. The C(1)-C(2) and C(2)-C(3) distances are 1.376(5) and 1.394(5) Å, respectively. These values are between those expected for single and double carbon-carbon bonds. The O(1)-C(3) (1.283(4) Å) and Os-O(1) (2.126(3) Å) values are quite similar to those found in the cation $[\overline{Os(CH{=}C(I)-C}OOMe)(\eta^6\text{-}C_6H_6)(PiPr_3)_2]^+$ (1.25(2) and 1.111(8) Å, respectively), where the two resonance forms shown in Scheme 2 have been suggested for the bonding pattern of the heterocycle.[28]

The Os-P, Os-CO, and Os-Cl distances are clearly in the expected range and deserve no further comment.

The reaction of **1** with 1,1-diphenyl-2-propyn-1-ol also leads to a mixture of organometallic compounds. In this case, in contrast to the reaction of **1** with 1-phenyl-2-propyn-1-ol, the only compound that can be isolated is the complex **3b**, as a dark brown solid in 34% yield. The presence of the vinylcarbene ligand in this complex was inferred from the ^1H and $^{13}C\{^1H\}$ NMR spectra. The former shows two characteristic resonances at 18.27 and 8.62 ppm, while the $^{13}C\{^1H\}$ NMR spectrum contains absorptions at 268.11 (Os=CH), 151.10 (CH=), and 145.74 (=CPh$_2$) ppm.

Comments on the Formation of $OsCl_2({=}CHCH{=}CRPh)(CO)(PiPr_3)_2$. Complex **2a** decomposes slowly in chloroform-*d* solution to a mixture of products. The ^1H NMR spectrum of the mixture contains two resonances at about 17.3 and 13.0 ppm, which can be assigned to the compounds **3c** and **4b** (eq 2) by comparison of these spectra with those of the complexes **3a,b** and **4a**. This decomposition process, together with the reaction of the monohydride **1** with 2-propyn-1-ol to afford **2a**, suggests that the formations of **3a,b** and **4a** involve the initial insertions of the alkynes into the Os-H bond of the starting complex.



2a **3c** **4b** (2)

Scheme 3 illustrates a sequence of elementary reactions that allows the formation of **2**–**4** to be rationalized. The insertion of $HC{\equiv}CR^1(OH)R^2$ into the Os—H bond of **1** to give **2** must involve the initial coordination of the corresponding alkyne to the osmium atom followed by the migration of the hydride from the metal to the HC≡*C*– carbon atom of the corresponding alkyn-1-ol.

Previous spectroscopic studies on the insertion reaction of acetylenedicarboxylic acid dimethyl ester into the Os—H bond of **1** prove that the alkyne coordinates to **1** *trans* to the hydride at room temperature, and then the rearrangement to a *cis* isomer takes place, followed by insertion to yield vinyl species.[3] The same sequence of events is operative in the formation of the styryl compounds $M((E)\text{-}CH{=}CHPh)Cl(CO)(PiPr_3)_2$ (M = Ru, Os).[2,29] The migration of a hydride ligand from the metallic center to a coordinated alkyne is generally viewed as a concerted process involving a four-center intermediate, which leads regioselectively to a $M((E)\text{-}CH{=}CHR)$ or $M(CR{=}CH_2)$ isomer.[1] Therefore, it is reasonable to assume that the insertions of $HC{\equiv}CR^1(OH)R^2$ into the Os—H bond of **1** give initially the (*E*)-vinyl intermediates **5**, which subsequently isomerize to **2**. The key to these isomerizations is probably the fact that the five-coordinated intermediates **5** are 16-electron species, while the intermediates **2** are 18-electron species. The isomerization of vinyl compounds has been previously observed.[4,25,30] In some cases, it has been suggested that the process may occur by formation of zwitterionic carbene intermediates.[30a,d]

The formation of the complexes **4a,b** from the corresponding species **2** could initially involve the elimination of HCl to give the five-coordinated intermediates **6**, which by a subsequent hydrogen *β*-elimination (R^1 = H) should give **7**. Then the protonation with HCl of the hydride ligands of the intermediates **7**, followed by displacement of the formed dihydrogen ligands by Cl^-, could give **4**.

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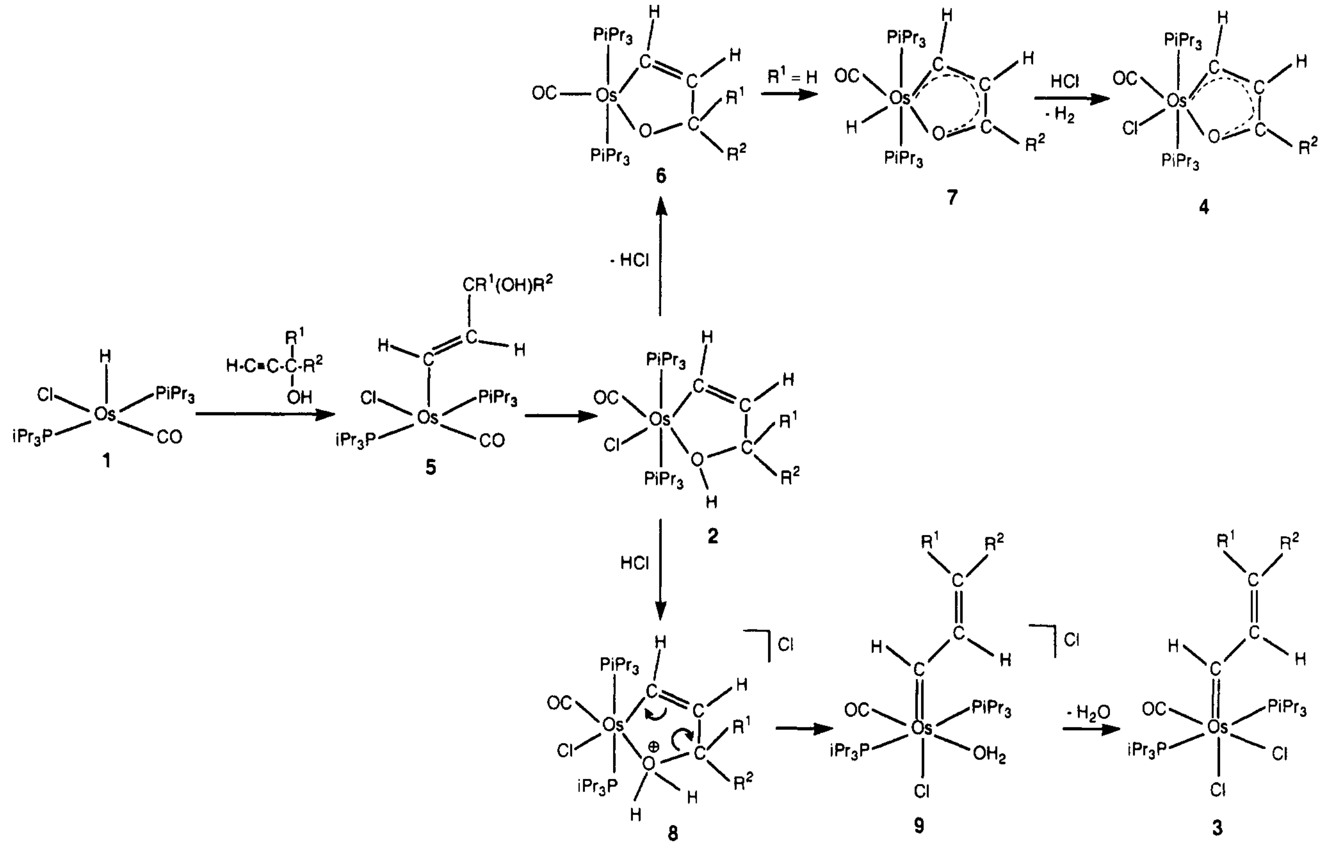
Scheme 3



Indications in favor of the participation of the hydride intermediates **7** were found in the ^{1}H NMR spectrum of the reaction mixture of **1** and 1-phenyl-2-propyn-1-ol, before the addition of the mixture to the chromatographic column. This spectrum shows the signals of the complexes **3a** and **4a** together with resonances due to other products. Among these signals, it is useful to point out a doublet at 13.62 ppm with a H-H coupling constant of 7.2 Hz and a triplet at −4.88 ppm with a P-H coupling constant of 24.0 Hz. The position, multiplicity, and value of the coupling constant of the signal at lower field are indicative of the presence of a CHCHC(O)Ph ligand, while the same parameters for the signal at higher field are indicative of the presence of a hydride ligand. With regard to the intensity ratio between the two signals (1:1), there is no doubt that the two ligands are parts of the same compound, most probably complex **7** with R^1 = Ph.

In addition, it should be mentioned that the formation of the complexes **4a,b** from the corresponding species **2** is a result of the dehydrogenation of the alcohol group of the vinyl ligand. The dehydrogenation of primary and secondary alcohols is a process which plays a main role in the homogeneous catalytic reduction of unsaturated organic substrates.[31] From a mechanistic point of view, it has been proved that the alcohol dehydrogenation proceeds by initial heterolytic activation of the H—O bond, followed by a β-elimination process of hydrogen at the C—H bond of a M—O—CHR group.[32] Although the tertiary alcohols can undergo heterolytic activation of the H—O bond, as in the mechanism mentioned above, they are not suitable as source of hydrogen, because they do not contain a geminal hydrogen. The process of dehydrogenation of the species **2**, proposed in Scheme 3, involves the same sequence of events as that proposed for the catalytic dehydrogenation of alcohols. In agreement with this proposal, detectable amounts of **4** were not observed from the reaction of **1** with 1,1-diphenyl-2-propyn-1-ol.

The loss of HCl in the **2** → **6** step could be the key to the formation of **3a–c**. Thus, the protonation of the OH group of the metallacycle of the species **2** could yield the cationic vinylcarbene intermediates **9** via **8**. Subsequently, the displacement of the water molecule by Cl^- should give the complexes **3a–c**. There is a precedent for this process. Previously, it has been reported that the reaction of Fe(η^5-C_5H_5)((*E*)-CH=CHC$(CH_3)_2$OH)$(CO)_2$ with HBF_4 gives the vinylcarbene complex [Fe(η^5-C_5H_5)(=CHCH=C$(CH_3)_2$)$(CO)_2$]BF_4.[21c]

Concluding Remarks. This study has shown that it is possible to get vinylcarbene complexes of the type $OsCl_2$(=CHCH=CR^1R^2)(CO)(P*i*Pr_3)$_2$ in about 40% yield in one step by the reaction of the monohydride OsHCl(CO)(P*i*Pr_3)$_2$ with HC≡CCR^1(OH)R^2. When R^1 is hydrogen, small amounts of the complexes Os(CHCHC(O)R^2)(CO)(P*i*Pr_3)$_2$ can also be obtained. The reactions proceed by initial formation of the vinyl complexes Os(CH=CHCR^1(OH)R^2)Cl(CO)(P*i*Pr_3)$_2$, which are a result of the insertion of the alkynes into the Os—H bond of the starting compound.

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Previously, we have reported[2-7] evidence proving that the reactions of osmium hydride complexes with terminal alkynes, HC≡CR, allow the preparation of specific organometallic compounds if the number of the hydride ligands and the electronic properties of the starting complexes are appropriately selected. In addition, we now show that the choice of the nature of the group R of the alkyne also determines the nature of the organometallic complexes obtained.

Experimental Section

General Considerations. All reactions were carried out with rigorous exclusion of air by using Schlenk tube techniques. Solvents were dried by known procedures and distilled under argon prior to use. 2-Propyn-1-ol (Aldrich), 1-phenyl-2-propyn-1-ol (ABCR), and 1,1-diphenyl-2-propyn-1-ol (ABCR) were used without further purification. $OsHCl(CO)(PiPr_3)_2$ was prepared by a published method.[33]

Physical Measurements. NMR spectra were recorded on a Varian XL-200 or on a Varian UNITY 300 spectrophotometer. Chemical shifts are expressed in ppm upfield from Me_4Si (^{13}C, ^1H) and 85% H_3PO_4 (^{31}P). Coupling constants J and N ($N = J(HP) + J(HP')$ for ^1H and $N = J(CP) + J(CP')$ for ^{13}C) are given in hertz. Infrared spectra were recorded with a Perkin-Elmer 783 spectrophotometer or a Perkin-Elmer 883 spectrophotometer, as solids (Nujol mulls on polyethylene sheets or KBr). C and H analyses were carried out with a Perkin-Elmer 240C microanalyzer or a Perkin-Elmer 2400 CHNS/O analyzer.

Reaction of 1 with 2-Propyn-1-ol: Preparation of $\overline{Os(CH{=}CHCH_2O}H)Cl(CO)(PiPr_3)_2$ (2a). A solution of 1 (140 mg, 0.24 mmol) in 10 mL of toluene was treated with 2-propyn-1-ol (15 μL, 0.26 mmol). After the mixture was stirred for 15 min at room temperature, it was filtered and the solvent was removed. The residue was washed repeatedly with hexane. The product is a pale green solid. Yield: 128 mg (85%). Anal. Calcd for $OsC_{22}H_{47}ClO_2P_2$: C, 41.86; H, 7.50. Found: C, 41.65; H, 7.98. IR (Nujol): ν(OH) 3400 (br), ν(C≡O) 1895 (vs) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.49 (d, J(HH) = 9.8; OsCH=), 5.04 (d, J(HH) = 9.8; =CH–), 4.85 (s; $-CH_2OH$), 2.89 (s; OH), 2.70 (m; PCH), 1.38 (dvt, N = 12.8, J(HH) = 6.4; $PCCH_3$), 1.30 (dvt, N = 12.9, J(HH) = 6.7; $PCCH_3$). $^{31}P\{^1H\}$ NMR (80.90 MHz, CH_2Cl_2): δ 9.57 (s).

Table 3. Atomic Coordinates (×10⁴; ×10⁵ for Os, P(1), P(2), Cl(1), and Cl(2) Atoms) and Equivalent Isotropic Displacement Coefficients (Å² × 10³; ×10⁴ for Os, P(1), P(2), Cl(1), and Cl(2) Atoms) for the Compound $OsCl_2({=}CHCH{=}CHPh)(CO)(PiPr_3)_2$ (3a)

atom	x/a	y/b	z/c	$U_{eq}{}^a/U_{iso}{}^b$
Os	26274(1)	21828(1)	15062(1)	229(1)
P(1)	41000(5)	18064(6)	12983(5)	273(2)
P(2)	11753(6)	28066(5)	16277(5)	252(3)
Cl(1)	34188(5)	37110(6)	23572(5)	380(3)
Cl(2)	21859(5)	32622(6)	1593(5)	355(3)
O	1799(2)	263(2)	506(2)	44(1)
C(1)	2858(2)	1451(2)	2572(2)	29(1)
C(2)	2657(2)	383(2)	2777(2)	32(1)
C(3)	2748(2)	82(3)	3577(2)	32(1)
C(4)	2556(2)	−956(2)	3870(2)	31(1)
C(5)	2290(2)	−1840(3)	3335(2)	40(1)
C(6)	2127(3)	−2811(3)	3653(3)	50(2)
C(7)	2208(3)	−2924(3)	4492(3)	50(2)
C(8)	2464(3)	−2063(3)	5030(3)	48(1)
C(9)	2649(2)	−1079(3)	4730(2)	41(1)
C(10)	2099(2)	991(3)	880(2)	30(1)
C(11a)	5111(7)	1994(8)	2229(6)	30(3)[b]
C(12a)	5989(5)	1510(11)	2150(5)	46(3)[b]
C(13a)	5019(6)	1561(11)	3063(5)	46(3)[b]
C(11b)	5061(7)	1983(8)	2354(8)	38(3)[b]
C(12b)	5990(5)	1998(10)	2217(5)	45(3)[b]
C(13b)	5058(5)	1124(9)	3014(4)	39(2)[b]
C(14)	4216(2)	458(3)	872(2)	35(1)
C(15)	4038(2)	−458(3)	1403(2)	43(1)
C(16)	3623(2)	349(3)	−53(2)	43(1)
C(17)	4335(3)	2716(3)	503(2)	39(1)
C(18)	5064(3)	2385(4)	138(3)	58(2)
C(19)	4483(3)	3866(3)	816(3)	52(2)
C(20)	200(2)	1946(3)	1071(2)	33(1)
C(21)	−2(3)	1931(3)	106(2)	42(1)
C(22)	286(3)	802(3)	1432(2)	43(1)
C(23)	778(2)	4131(3)	1141(2)	35(1)
C(24)	−147(3)	4483(3)	1183(3)	53(2)
C(25)	1444(3)	5053(3)	1420(3)	51(1)
C(26)	1159(2)	2790(2)	2744(2)	33(1)
C(27)	228(3)	2727(3)	2865(2)	46(1)
C(28)	1690(3)	3687(3)	3285(2)	55(1)

[a] Equivalent isotropic U, defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Isotropic thermal parameters have been used for disordered atoms.

Reaction of 1 with 1-Phenyl-2-propyn-1-ol: Preparation of $OsCl_2({=}CHCH{=}CHPh)(CO)(PiPr_3)_2$ (3a) and $\overline{Os(CHCH}C(\overline{O})Ph)Cl(CO)(PiPr_3)_2$ (4a). A solution of 1 (157 mg, 0.27 mmol) in 12 mL of toluene/methanol (1:5) was treated with 1-phenyl-2-propyn-1-ol (37 mg, 0.28 mmol). After the mixture was stirred for 2 h at room temperature, the solvent was removed. Chromatography of the dark brown residue on silica gel (0.063–0.200 mm; 10 × 2 cm) with toluene led initially to an orange solution and subsequently to a brown solution, which gave after removing the solvent orange and dark brown crude products, respectively. Recrystallization of the orange product from hexane led to compound **4a** as an orange solid, and recrystallization of the dark brown product from methanol at −20 °C led to compound **3a** as a brown solid. Yield: 80 mg (41%) **3a**; 15 mg (8‰) **4a**. Anal. Calcd for $OsC_{28}H_{50}Cl_2OP_2$ (**3a**): C, 46.33; H, 6.94. Found: C, 46.17; H, 7.23. IR (Nujol): ν(C≡O) 1918 (vs), ν(C=C) 1589 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 17.74 (d, J(HH) = 12.9; Os=CH–), 8.14 (dd, J(HH) = 14.8, J(HH) = 12.9; CH=), 7.75 (d, J(HH) = 7.7; H_{oPh}), 7.70 (d, J(HH) = 14.8; =CHPh), 7.55 (t, J(HH) = 7.7; H_{pPh}), 7.37 (t, J(HH) = 7.7; H_{mPh}), 2.85 (m; PCH), 1.36 (dvt, N = 14.3, J(HH) = 7.1; $PCCH_3$), 1.19 (dvt, N = 13.5, J(HH) = 6.6; $PCCH_3$). $^{13}C\{^1H\}$ NMR (75.43 MHz, $CDCl_3$): δ 269.19 (t, J(CP) = 6.9, Os=CH–), 179.50 (t, J(CP) = 8.9; OsCO), 150.72, 141.80 (both s; C_{vinyl}), 136.53, 130.26, 129.99, 128.31 (all s; C_{Ph}), 24.51 (vt, N = 30.8; PCH), 20.13, 19.10 (both s; $PCCH_3$). $^{31}P\{^1H\}$ NMR (80.90 MHz, C_6D_6): δ 12.94 (s). Anal. Calcd for $OsC_{28}H_{49}ClO_2P_2$ (**4a**): C, 47.68; H, 7.00. Found: C, 47.56; H, 7.44. IR (KBr): ν(C≡O) 1901 (vs), ν(C=O) 1451 (vs) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 12.94 (d, J(HH) = 7.2; OsCH=), 7.49 (d, J(HH) = 7.2; =CH–), 2.29 (m; PCH), 1.45 (dvt, N = 14.5, J(HH) = 7.1; $PCCH_3$), 0.76 (dvt, N = 12.5, J(HH) = 6.8; $PCCH_3$). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6): δ 230.16 (t, J(CP) = 5.1; OsCH), 191.96 (t, J(CP) = 1.6; OsOC), 187.93 (t, J(CP) = 10.1; OsCO), 136.69 (s; C_{ipsoPh}), 131.30 (s; =CHCO), 128.90 (s; C_{mPh}), 125.13 (s; $C_{o\text{-}Ph}$), 22.96 (vt, N = 12.4; PCH), 20.76, 19.10 (both s; $PCCH_3$). $^{31}P\{^1H\}$ NMR (80.90 MHz, C_6D_6): δ 14.87 (s).

Reaction of 1 with 1,1-Diphenyl-2-propyn-1-ol: Preparation of $OsCl_2({=}CHCH{=}CPh_2)(CO)(PiPr_3)_2$ (3b). A solution of 1 (155 mg, 0.27 mmol) in 12 mL of toluene/methanol (1:5) was treated with 1,1-diphenyl-2-propyn-1-ol (56 mg, 0.27 mmol). After the mixture was stirred for 1 h at room temperature, the solvent was removed. Crystallization from methanol led to a dark brown solid. Yield: 72 mg (34%). Anal. Calcd for $OsC_{34}H_{54}Cl_2OP_2$ (**3b**): C, 50.93; H, 6.79. Found: C, 50.72; H, 7.01. IR (Nujol): ν(C≡O) 1920 (s) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 18.27 (dt, J(HH) = 14.1, J(HP) = 1.5; Os=CH–), 8.62 (d, J(HH) = 14.1; –CH=), 7.33 (C_6H_5), 2.75 (m; PCH), 1.33 (dvt, N = 14.4, J(HH) = 7.2; $PCCH_3$), 1.07 (dvt, N = 13.5, J(HH) = 6.6; $PCCH_3$). $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6): δ 268.11 (t, J(CP) = 7.4; Os=CH–), 180.99 (t, J(CP) = 9.2; OsCO), 151.13 (s; –CH=), 145.74, 142.66, 129.70, 128.72, 128.49 (all s; unambiguous as-

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(33) Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 221.

Table 4. Atomic Coordinates (×10⁴; ×10⁵ for Os, Cl, P(1), and P(2) Atoms) and Equivalent Isotropic Displacement Coefficients (Å² × 10³; ×10⁴ for Os, Cl, P(1), and P(2) Atoms) for the Compound Os(CHCHC(O)Ph)Cl(CO)(P*i*Pr₃)₂ (4a)

atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]
Os	25891(1)	57299(1)	12480(1)	185(1)
Cl	50188(11)	52795(7)	17230(5)	298(3)
P(1)	32287(11)	71995(6)	15737(4)	230(3)
P(2)	22331(10)	42166(5)	9803(4)	201(2)
O(1)	1625(3)	5514(2)	2111(1)	20(1)
O(2)	3432(4)	6145(2)	−18(1)	39(1)
C(1)	416(4)	5982(2)	1120(2)	20(1)
C(2)	−551(4)	5876(2)	1600(2)	22(1)
C(3)	183(4)	5638(2)	2130(2)	20(1)
C(4)	−541(4)	5552(2)	2724(2)	21(1)
C(5)	342(5)	5374(2)	3227(2)	28(1)
C(6)	−307(5)	5302(3)	3785(2)	31(1)
C(7)	−1856(5)	5409(2)	3854(2)	33(1)
C(8)	−2747(5)	5581(2)	3360(2)	33(1)
C(9)	−2105(4)	5658(2)	2797(2)	28(1)
C(10)	3148(5)	5979(2)	483(2)	28(1)
C(11)	2809(5)	7372(2)	2380(2)	29(1)
C(12)	2836(6)	8318(3)	2601(2)	45(2)
C(13)	3802(5)	6808(3)	2790(2)	39(1)
C(14)	2131(5)	8095(2)	1218(2)	34(1)
C(15)	2326(7)	8121(3)	546(2)	58(2)
C(16)	454(5)	8052(3)	1382(3)	55(2)
C(17)	5264(5)	7507(3)	1480(2)	30(1)
C(18)	5986(5)	7133(3)	916(2)	35(1)
C(19)	5574(5)	8506(3)	1494(2)	41(1)
C(20)	4043(4)	3621(3)	865(2)	28(1)
C(21)	5165(5)	4085(3)	448(2)	38(1)
C(22)	3866(6)	2662(3)	678(2)	44(2)
C(23)	1241(5)	3617(3)	1591(2)	29(1)
C(24)	2271(5)	3495(3)	2126(2)	38(1)
C(25)	420(6)	2770(3)	1425(2)	47(2)
C(26)	1038(5)	3953(3)	316(2)	29(1)
C(27)	−587(5)	4292(3)	381(3)	50(2)
C(28)	1710(6)	4226(3)	−286(2)	54(2)

[a] Equivalent isotropic *U*, defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

signment was not possible), 25.01 (vt, *N* = 13.0; PCH), 20.10, 19.19 (both s; $PCCH_3$). $^{31}P\{^1H\}$ NMR (80.90 MHz, C_6D_6): δ 11.60 (s).

X-ray Structure Analysis of OsCl₂(=CHCH=CHPh)(CO)(P*i*Pr₃)₂ (3a) and Os(CHCHC(O)Ph)Cl(CO)(P*i*Pr₃)₂ (4a). Crystals suitable for X-ray diffraction experiments were obtained by slow diffusion of hexane into a concentrated solution of **3a** in CH_2Cl_2 and from a saturated solution of hexane for **4a**. Atomic coordinates and U_{eq} values are listed in Table 3 for **3a** and Table 4 for **4a**. The crystals studied were glued on glass fibers and mounted on a Siemens AED-2 diffractometer. Cell constants were obtained from the least-squares fit of the setting angles of 57 reflections in the range 20 ≤ 2*θ* ≤ 50° for **3a** and 49 reflections in the range 20 ≤ 2*θ* ≤ 45° for **4a**. The recorded reflections (7070 for **3a** and 10 127 for **4a**) were corrected for Lorentz and polarization effects. Three orientation and intensity standards were monitorized every 55 min of measuring time; no variation was observed. Reflections were also corrected for absorption by a semiempirical (Ψ-scan) method.[34]

The structures were solved by Patterson (Os atom) and conventional Fourier techniques. An isopropyl group of a phosphine ligand was observed as disordered in **3a**. The disordered group was modeled with two different isopropyl groups refined with a complementary occupancy factor assigned on the basis of the thermal parameters (0.484 for the C(11a), C(12a), and C(13a) atoms and 0.516 for C(11b), C(12b), and C(13b)) and with the internal C–C bond distances restrained to 1.54(1) Å. Refinement, in both cases, 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, except those involved in disorder (complex **3a**). Hydrogen atoms were located from difference Fourier maps and included in the refinement riding on carbon atoms with a common isotropic thermal parameter (hydrogens bonded to disordered atoms were not included in the refinement). Atomic scattering factors, corrected for anomalous dispersion for Os, P and Cl, were taken from ref 35. The function minimized was $\Sigma w([F_0] - [F_c])^2$, with the weight defined as $w^{-1} = \sigma^2[F_0] + g[F_0{}^2]$ (*g* = 0.000 726 for **3a** and *g* = 0.000 187 for **4a**). Final *R* and R_w values were 0.0202 and 0.0239 for **3a** and 0.0198 and 0.0223 for **4a**. All calculations were performed by the use of the SHELXTL-PLUS system of computer programs.[36]

Table 5. Crystal Data and Data Collection and Refinement for OsCl₂(=CHCH=CHPh)(CO)(P*i*Pr₃)₂ (3a) and Os(CHCHC(O)Ph)Cl(CO)(P*i*Pr₃)₂ (4a)

	3a	**4a**
	Crystal Data	
formula	$C_{28}H_{50}Cl_2OOsP_2$	$C_{28}H_{49}ClO_2OsP_2$
mol wt	725.76	705.29
color and habit	dark red, prismatic block	red, prismatic block
cryst size, mm	0.287 × 0.406 × 0.798	0.200 × 0.200 × 0.494
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)
a, Å	15.671(3)	8.797(1)
b, Å	12.507(2)	15.268(2)
c, Å	16.632(3)	22.275(3)
β, deg	108.95(1)	
V, Å³	3083(1)	2991(1)
Z	4	4
D(calcd), g cm⁻³	1.564	1.566
temp, K	233	173
	Data Collection and Refinement	
diffractometer	4-circle Siemens-STOE AED	
λ(Mo K*α*), Å; technique	0.710 73; bisecting geometry	
monochromator	graphite oriented	
μ, mm⁻¹	4.44	4.49
scan type	*ω*/2*θ*	
2*θ* range, deg	3 ≤ 2*θ* ≤ 50	3 ≤ 2*θ* ≤ 52
no. of data collect	9394	10 127
no. of unique data	5422 (R_{int} = 0.027)	5884 (R_{int} = 0.019)
no. of unique obsd data	5080 ($F_o \geq 5.0\sigma(F_o)$)	5532 ($F_o \geq 4.0\sigma(F_o)$)
no. of params refined	307	316
R, R_w[a]	0.0202, 0.0239	0.0198, 0.0223

[a] $w^{-1} = \sigma^2(F_o) + g(F_o)^2$; *g* = 0.000 187 for **3a** and 0.000 726 for **4a**.

Acknowledgment. We thank the DGICYT (Project BP 92-0092, Programa de Promoción General del Conocimiento) for financial support. B. Z. thanks the Ministerio de Educación y Ciencia and E. O. the Diputación General de Aragón (DGA) for a grant.

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 for **3a** and **4a** (23 pages). Ordering information is given on any current masthead page.

OM930742J

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