Reactions of the Dihydrogen Complex $OsCl_2(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ with Terminal Alkynes: Synthesis of Carbene, Vinylcarbene, and μ-Bis-Carbene Osmium(II) Derivatives

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Received January 17, 1995[⊗]

Abstract: The dihydrogen complex $OsCl_2(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ (**1**) has been prepared by reaction of the monohydride $OsHCl(CO)(PiPr_3)_2$ (**2**) with HCl. Complex **1** reacts with carbon monoxide and *tert*-butyl isocyanide to give $OsHCl(CO)(L)(PiPr_3)_2$ (L = CO (**3**), *t*BuNC (**4**)) and HCl. The reaction of **1** with phenylacetylene affords the carbene derivative $OsCl_2(=CHCH_2Ph)(CO)(PiPr_3)_2$ (**5**), which can be also obtained by reaction of $Os\{(E)\text{-}CH=CHPh\}Cl(CO)(PiPr_3)_2$ (**6**) with HCl. The molecular structure of **5** has been determined by X-ray crystallography. Crystals of **5** are orthorhombic, space group *Pbca*, with unit cell dimensions a =13.641(2) Å, b =15.698(2) Å, and c = 29.059(4) Å. The structure was solved and refined using 3185 unique, observed reflections, R = 0.0412 and R_w = 0.0380. The coordination around the osmium atom can be described as a distorted octahedron with the two triisopropylphosphine ligands occupying *trans* positions. The $PhCH_2CH$ moiety, clearly bonded to the metal through an Os−C double bond, is situated in a relative *trans* position to a chloride ligand. Complex **1** reacts with 2-methyl-1-buten-3-yne to give $OsCl_2\{=CHCH=C(CH_3)_2\}(CO)(PiPr_3)_2$ (**7**). The reaction of **2** with 2-methyl-1-buten-3-yne leads to $Os\{(E)\text{-}CH=C(H)(CH_3)=CH_2\}Cl(CO)(PiPr_3)_2$ (**8**), which gives **7** by reaction with HCl. Complex **1** also reacts with 1,7-octadiyne. The reaction produces a mixture of products from which the binuclear μ-bis-carbene compound $[(PiPr_3)_2(CO)Cl_2Os]\{=CH(CH_2)_6CH=\}[OsCl_2(CO)(PiPr_3)_2]$ (**11**) was identified by NMR spectroscopy. Complex **11** can be prepared as an analytically pure solid by reaction of $[(PiPr_3)_2(CO)ClOs]\{CH=CH(CH_2)_4CH=CH\}[OsCl(CO)(PiPr_3)_2]$ (**12**) with HCl. Complex **12** was obtained from the reaction of **2** with 1,7-octadiyne.

Introduction

Since the first report by Kubas *et al.* on the coordination of molecular hydrogen to a transition metal,[1] numerous dihydrogen complexes have been reported. The spectroscopic characterization, some theoretical aspects on the nature and stabilization of the $M(\eta^2\text{-}H_2)$ bond of these compounds, and the roles that they can play during some homogeneous catalytic processes have been also the subject of intensive studies in recent years.[2-3] Concerning reactivity, by far, the largest number of observed reactions involve the loss of molecular hydrogen due to the weak binding of the dihydrogen ligand to the metallic fragment. According to Jessop and Morris,[2d] this class of reaction can be considered in five ways: simple elimination, substitution, substitution followed by insertion, ligand exchange, and elimination followed by dimerization.

The scarce new developments in the reactivity of dihydrogen complexes are probably due to the fact that the reported compounds, and the ancillary ligands contained by them are very similar. This problem is a result of the limited number of useful synthetic routes described for their preparation. These species have been generally prepared either by coordination of molecular hydrogen to an unsaturated metallic fragment or by protonation of saturated dihydrido compounds.[2] Recently, we have observed that coordination of nucleophilic ligands to the unsaturated dihydrido complex $OsH_2Cl_2(PiPr_3)_2$[4] and addition of HX molecules to unsaturated monohydrido compounds[5,6] are also useful pathways toward the formation of dihydrogen complexes. According to this, we have now observed that the monohydrido $OsHCl(CO)(PiPr_3)_2$ reacts with HCl to afford $OsCl_2(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$.

We are also interested in the study of the reactivity of hydridoosmium compounds toward alkynes, and we recently reported that the reactions of these complexes with terminal alkynes allow the preparation of specific organometallic compounds[7] (vinyl,[8] hydrido-carbyne,[9] hydrido-vinylidene,[7] and hydrido-dihydrogen-

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1995.

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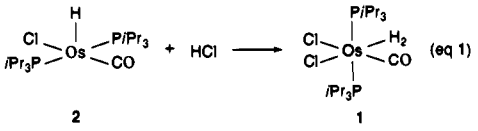
alkynyl[6]) if the number of hydrido ligands and the electronic properties of the starting materials are appropriately selected.

Continuing with our work in the dihydrogen field,[4-6,10] and as a part of our research on the reactivity of hydrido-osmium complexes toward terminal alkynes, we have now investigated the reactivity of the dihydrogen complex $OsCl_2(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ toward phenylacetylene, 2-methyl-1-buten-3-yne, and 1,7-octadiyne. During this study, we have discovered a new, and unexpected, reaction pattern. The reactions of $OsCl_2(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ with terminal alkynes lead to carbene derivatives.

In this paper we report the synthesis and characterization of $OsCl_2(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$, together with new carbene, vinylcarbene, and binuclear μ-bis-carbene osmium(II) complexes. These compounds are the first examples of carbene derivatives obtained by direct reaction between a dihydrogen complex and terminal alkynes. The mechanism of this transformation is also discussed.

Results and Discussion

Synthesis and Characterization of $OsCl_2(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ (1). The dihydrogen complex $OsCl_2(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ (**1**) was prepared as a cream colored solid in 75% yield, by treatment of a toluene solution of the five-coordinate monohydrido compound $OsHCl(CO)(PiPr_3)_2$ (**2**) with other toluene HCl solution (eq 1).



2 1

The IR spectrum of **1** in Nujol shows a strong $\nu(C{\equiv}O)$ absorption at 1957 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum shows at 16.9 ppm a singlet, indicating the equivalence of the two phosphine ligands and their mutually *trans* disposition. At room temperature the ^1H NMR spectrum in benzene-d_6 (Figure 1) shows two doublets of virtual triplets at 1.25 and 1.12 ppm for the methyl groups of the triisopropylphosphine ligands. The presence of two signals for these protons, which is a result of the prochirality of the phosphorous atoms, indicates that the two chloride ligands are mutually *cis* disposed. In the high field region, the spectrum contains a broad triplet at −7.46 ppm due to the dihydrogen ligand. A variable temperature 300 MHz T_1 study of the dihydrogen peak shows a slight broadening of this signal and gives a T_1(min) of 15 ms at 233 K. In agreement with the nonclassical structure, this value corresponds to a hydrogen−hydrogen distance of 0.88 Å (fast spinning) or 1.11 Å (slow spinning).[11] The H−D coupling constant, J(HD), of

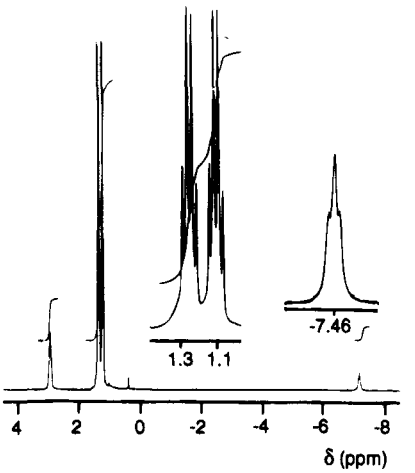
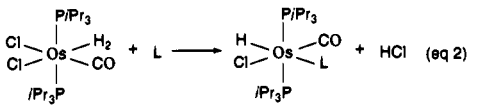


Figure 1. ^1H NMR spectrum of $OsCl_2(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ (**1**) at 293K in benzene-d_6.

20.1 Hz in $OsCl_2(\eta^2\text{-}HD)(CO)(PiPr_3)_2$ (**1-*d***) suggests that the longer distance estimated (1.11 Å) is the most likely one.[21]

Complex **1**[12a] which is an air-sensitive solid, is stable up to 1 month if kept under argon at room temperature. In solution it is stable under argon for a matter of days. However, the coordinated dihydrogen ligand is highly activated toward heterolytic cleavage, as demonstrated by deprotonation with NaH and by reaction with carbon monoxide and *tert*-butyl isocyanide (eq 2). By passing a slow stream of carbon monoxide through a benzene-d_6 solution of **1**, the dicarbonyl complex **3** is formed.[12b] Similarly, the treatment of a toluene solution of **1** with the stoichiometric amount of *tert*-butyl isocyanide affords complex **4**, which was isolated as a white solid in 80% yield.



1 3, 4

L = CO (3), *t*BuNC (4)

The most noticeable absorptions of the IR spectrum of **4** in Nujol are three bands at 2136, 2007, and 1898 cm^{-1}, assigned to the $\nu(C{\equiv}N)$, ν(Os-H), and $\nu(C{\equiv}O)$ vibrations, respectively. The presence of the hydrido ligand is also supported by the ^1H and $^{31}P\{^1H\}$ NMR spectra, in benzene-d_6. The ^1H NMR spectrum shows a triplet at −6.50 ppm with a P−H coupling constant of 20.9 Hz, while the $^{31}P\{^1H\}$ NMR spectrum contains a singlet, which under off resonance conditions splits into a doublet.

Elimination of HCl from chloro−dihydrogen complexes is an important process in order to rationalize the activation of some homogeneous catalysts precursors. Thus, Crabtree has proposed that the ruthenium complex $RuCl_2(PPh_3)_3$, a highly effective hydrogenation catalyst precursor, could activate molecular hydrogen heterolytically via the dihydrogen complex $RuCl_2(\eta^2\text{-}H_2)(PPh_3)_3$.[13] We have found kinetic evidence indicating that during the hydrogenation of benzylideneacetone to 4-phenylbutan-2-one, in the presence of $IrClH_2(PiPr_3)_2$, the

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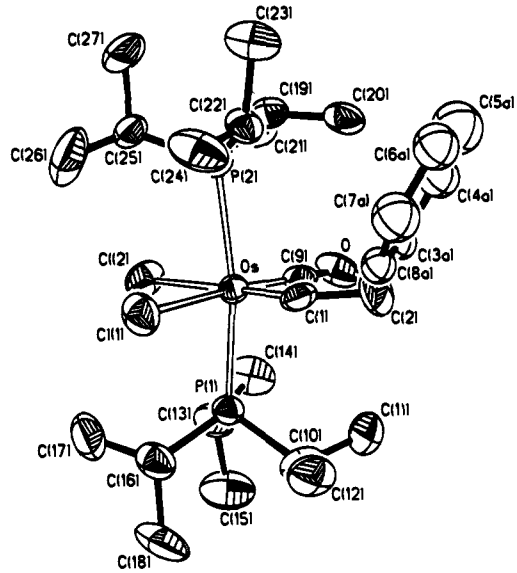
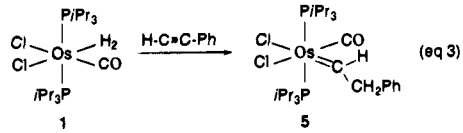


Figure 2. Molecular representation of $OsCl_2(=CHCH_2Ph)(CO)(PiPr_3)_2$ (**5**) with the atomic numbering scheme.

dihydrogen complex $IrClH_2(\eta^2\text{-}H_2)(PiPr_3)_2$ plays a key role in the formation of $IrH_3(PiPr_3)_2$, which is the active species.[10f] These processes most probably involve the deprotonation of the acidic proton of the dihydrogen ligand by the chloride Brönsted base. Since H_2 or HCl is not lost when a solution of **1** is evacuated, the reaction shown in eq 2 may occur by initial dissociation of one of the two chloride anions, followed by the coordination of L, and subsequent dihydrogen deprotonation.

Reaction of $OsCl_2(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ (1) with Phenylacetylene. Treatment of **1** with phenylacetylene in a 1:1 molar ratio, in toluene at room temperature, gives a yellow solution from which the compound $OsCl_2(=CHCH_2Ph)(CO)(PiPr_3)_2$ (**5**, eq 3) is separated as a yellow solid in 75% yield. Complex **5** was fully characterized by elemental analysis, IR, and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy, and X-ray diffraction.



The presence of a carbene ligand in **5** is supported by the ^1H and $^{13}C\{^1H\}$ NMR in benzene-d_6. The ^1H NMR spectrum contains a triplet at 18.99 ppm and a doublet at 3.49 ppm (J(HH) = 6.6 Hz), which were assigned to the Os=CH and $-CH_2Ph$ protons, respectively. The sp^2-carbon atom appears in the $^{13}C\{^1H\}$ NMR spectrum as a triplet at 296.60 ppm with a P−C coupling constant of 6.0 Hz. The chemical shifts of the Os=CH proton and the sp^2-carbon atom show good agreement with those previously observed for related compounds.[14] The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 12.2 ppm.

A view of the molecular geometry of **5** is shown in Figure 2. 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 the apical positions (P(1)-Os−P(2) = 168.45(9)°). The equatorial plane is formed by the carbene and the carbonyl ligands mutually *cis* disposed (C(1)−Os−C(9) = 91.4(5)°) and the two chlorine atoms also in relative *cis* positions (Cl(1)−Os−Cl(2) = 89.03(9)°).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex $OsCl_2(=CHCH_2Ph)(CO)(PiPr_3)_2$ (**5**)

Os−Cl(1)	2.473(3)	Os−Cl(2)	2.495(3)
Os−P(1)	2.475(3)	Os−P(2)	2.482(3)
Os−C(1)	1.887(9)	Os−C(9)	1.861(12)
C(1)−C(2)	1.477(15)	C(9)−O	1.059(14)
C(2)−C(3a)	1.539(16)	C(2)−C(3b)	1.531(21)
Cl(1)−Os−Cl(2)	89.03(9)	P(1)−Os−C(1)	98.8(3)
Cl(1)−Os−P(1)	88.51(9)	P(1)−Os−C(9)	88.8(4)
Cl(1)−Os−P(2)	89.86(9)	P(2)−Os−C(1)	92.5(3)
Cl(1)−Os−C(1)	85.8(3)	P(2)−Os−C(9)	93.5(3)
Cl(1)−Os−C(9)	175.7(4)	C(1)−Os−C(9)	91.4(5)
Cl(2)−Os−P(1)	82.55(9)	Os−C(1)−C(2)	136.9(8)
Cl(2)−Os−P(2)	85.99(9)	C(1)−C(2)−C(3a)	110(1)
Cl(2)−Os−C(1)	174.6(3)	C(1)−C(2)−C(3b)	115(1)
Cl(2)−Os−C(9)	93.9(3)	Os−C(9)−O	177.4(9)
P(1)−Os−P(2)	168.45(9)		

The most conspicuous features of the structure are firstly the Os−C(1) bond length (1.887(9) Å), which is consistent with an Os−C(1) double-bond formulation and secondly the Os−C(1)−C(2) bond angle (136.9(8)°), which indicates a sp^2 hybridization for the C(1) carbon atom. Similar values have been reported for related osmium−carbene complexes.[15] The carbene benzyl substituent points to the P(2) atom. The averaged torsion angle P(2)−Os−C(2)−C(3) is 30(1)°, indicating that the phosphine ligands are chemically inequivalent. In agreement with this, the singlet observed in the $^{31}P\{^1H\}$ spectrum at 293 K is converted into a broad resonance ($w_{1/2}$ = 195 Hz) at 213 K. It should also be mentioned that the Os−Cl(1) bond distance (Cl *trans* to CO) is shorter than the Os−Cl(2) bond distance (Cl *trans* to carbene), possibly due to the different *trans* influence of the carbonyl and alkylidene ligands. The Os−P(1), Os−P(2), Os−C(9), and C(9)−O distances are clearly in the expected range and deserve no further comments.

The unusual reactivity of **1** toward phenylacetylene merits further considerations. It has been previously mentioned that complex **1** reacts with neutral ligands to give six-coordinate hydrido-chloro derivatives and HCl (eq 2). So, it is reasonable to assume that in the presence of phenylacetylene, **1** eliminates HCl to afford initially a six-coordinate hydrido-π-alkyne intermediate, which evolves to the insertion product Os{(*E*)-CH=CHPh}Cl(CO)($PiPr_3$)$_2$ (**6**). This vinyl complex has been previously prepared by reaction of **2** with phenylacetylene and characterized by an X-ray diffraction study.[8a] Furthermore, it should be noted that previous studies on vinyl compounds have identified the localization of electron density at the β-carbon atom of the vinyl ligand. The chemical reactivity at this atom is thus oriented toward electrophiles.[16] In this respect, the formation of **5** could be rationalized as the electrophilic attack of H^+ to the β-carbon atom of the vinyl ligand of **6**, followed by the coordination of Cl^- to the metallic center. In agreement with this, we have observed that complex **6** reacts with the

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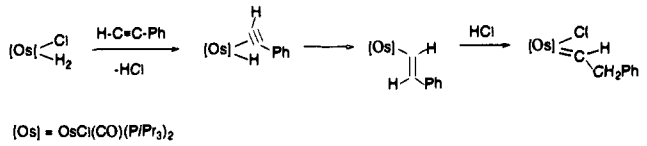
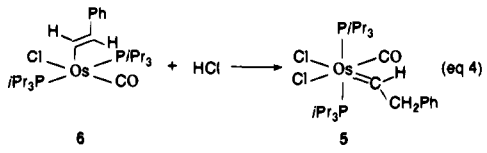
Scheme 1



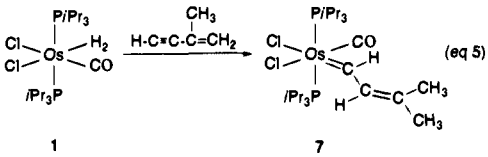
[Os] = OsCl(CO)(P*i*Pr$_3$)$_2$

stoichiometric amount of a toluene HCl solution to give the dichloro-carbene compound **5** (eq 4). Scheme 1 summarizes the sequence of elementary reactions above mentioned, which rationalizes the formation of **5**.



6 **5** (eq 4)

Reaction of OsCl$_2$(η^2-H$_2$)(CO)(P*i*Pr$_3$)$_2$ (1) with 2-Methyl-1-buten-3-yne. Treatment of **1** with the stoichiometric amount of 2-methyl-1-buten-3-yne in toluene at room temperature affords, after 1 h, the vinylcarbene complex **7** (eq 5), as an orange solid in 50% yield.



1 **7** (eq 5)

Complex **7** can also be prepared via the reaction sequence shown in Scheme 2. The vinylvinyl compound **8** was isolated as a dark blue solid in 86% yield, by addition of the stoichiometric amount of 2-methyl-1-buten-3-yne to a toluene solution of **2**. In a similar fashion to the reaction of **6** with HCl to give **5**, the reaction of **8** with the stoichiometric amount of a toluene HCl solution affords the vinylcarbene complex **7**. By this route, **7** was isolated in 60% yield.

In the IR spectrum of **7**, the most prominent feature is a strong ν(C=C) band at 1582 cm^{-1}, which was assigned to the olefinic bond of the vinylcarbene ligand. In the ^{1}H NMR spectrum, this ligand exhibits resonances at 18.20 (dt, J(HH) = 13.8 and J(HP) = 0.9 Hz), 7.70 (d, J(HH) = 13.8 Hz), and 1.11 and 0.81 (both s), which were assigned to the Os=CH, −CH=, and CH$_3$ protons, respectively. The Os=CH carbon atom appears in the ^{13}C{^{1}H} NMR spectrum as a triplet at 265.42 ppm with a P−C coupling constant of 6.5 Hz, while the vinylic carbon atoms appear as singlets at 152.40 and 147.50 ppm. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 12.6 ppm. These spectroscopic data agree well with those previously reported for the compounds MCl$_2$(=CHCH=CR^{1}R^2)(CO)(P*i*Pr$_3$)$_2$ (M = Ru, Os; R^1 = H, Ph; R^2 = Ph),[17] where the *cis* disposition of the two chloro ligands was determined by an X-ray diffraction experiment on a single crystal of OsCl$_2$(=CHCH=CHPh)(CO)(P*i*Pr$_3$)$_2$. The IR spectrum of **8** in Nujol shows two ν(C=C) bands at 1600 and 1562 cm^{-1}, assigned to the vinylvinyl ligand. In the ^{1}H NMR spectrum, this ligand exhibits resonances at 7.93 (d, J(HH) = 13.1 Hz), 5.87 (dt, J(HH) = 13.1 Hz, and J(HP) = 2.1 Hz), 4.63 and 4.34 (both d, J(HH) = 2.4 Hz), and 1.94 (s) ppm, which are assigned to the OsCH=, =CH−, =CH$_2$, and CH$_3$ protons, respectively. The *trans* stereochemistry at the carbon−carbon double bond of the group OsCH=CHR is strongly supported by the proton−proton coupling constant of 13.1 Hz, which is a typical value for this arrangement.[8a,18] The organic ligand carbon atoms were assigned by a DEPT NMR experiment to four signals at 142.38 (−*C*(CH$_3$)=), 138.34 (=CH−), 119.41 (OsCH=), and 105.55 (=CH$_2$). In the ^{13}C-{^{1}H} NMR spectrum the first three signals appear as triplets with P−C coupling constants of 2.3, 3.2, and 7.8 Hz, respectively, whereas the fourth signal appears as a singlet. The ^{31}P-{^{1}H} NMR spectrum shows a singlet at 22.3 ppm.

Although it has been previously mentioned that in a vinyl ligand the electron density is located at the β-carbon atom, it is also true that the protonation of the complex RuCl{(*E*)-CH=CHC=CH(CH$_2$)$_3$CH$_2$}(CO)(P*i*Pr$_3$)$_2$ occurs at the δ carbon atom of the vinylvinyl ligand, suggesting that in this ligand the electron density is located at the δ-carbon atom.[17b] So, the formation of **7** by reaction of **8** with HCl can be rationalized as the electrophilic attack of a proton to the δ-carbon atom of the vinylvinyl ligand of **8**, to afford an unsaturated vinylcarbene intermediate, followed by the coordination of a chloride anion. In order to prove this, we carried out the protonation of **8** with HBF$_4$ and the subsequent treatment of the resulting derivative with NaCl.

Addition of the stoichiometric amount of HBF$_4$·OEt$_2$ to a diethyl ether solution of **8** gives an ochre solid in 80% yield, which according to the elemental analysis, IR, and ^{1}H NMR spectroscopy could be formulated as the expected cationic derivative [OsCl{=CHCH=C(CH$_3$)$_2$}(CO)(P*i*Pr$_3$)$_2$](BF$_4$) (**9**). The IR spectrum in Nujol shows the bands characteristic of the coordinated ligands. Furthermore, it contains the absorption due to the [BF$_4$]$^-$ anion with T_d symmetry, indicating that this anion is not coordinated to the metallic center. The presence of the vinylcarbene ligand was inferred from the ^{1}H NMR spectrum in chloroform-*d*. The resonances of this ligand appear as broad signals at about 16.80 (Os=CH), 7.40 (−CH=), and as two singlets at 1.70 and 1.50 (−CH$_3$) ppm. The ^{31}P{^{1}H} NMR is not very informative, as it exhibits a very broad signal between 48 and 52 ppm. The full spectroscopic characterization of **9** as a cationic species containing a vinylcarbene ligand, was carried out on the six-coordinate derivative [OsCl{=CHCH=C-(CH$_3$)$_2$}(CO)(NCCH$_3$)(P*i*Pr$_3$)$_2$](BF$_4$) (**10**), which was prepared by addition of acetonitrile to a chloroform-*d* solution of **9**.

The ^{1}H NMR spectrum of **10** shows the expected resonances for the vinylcarbene ligand at 17.17 (d, J(HH) = 13.5 Hz), 7.60 (d, J(HH) = 13.5 Hz), and 1.73, and 1.46 (both s) ppm. The Os=CH− carbon atom appears in the ^{13}C{^{1}H} NMR spectrum as a triplet at 261.84 ppm with a P−C coupling constant of 5.3 Hz, while the vinylic carbon atoms appear as singlets at 159.44 and 151.85 ppm. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 14.5 ppm.

As expected, the treatment of **9** with NaCl in methanol affords **7** in 85% yield. The formation of **9** by protonation of **8** with HBF$_4$, and the reaction of **9** with NaCl to give **7** provide very strong evidence in favor of the proposal involving two steps for the formation of **7**, by reaction of **8** with HCl.

Reaction of OsCl$_2$(η^2-H$_2$)(CO)(P*i*Pr$_3$)$_2$ (1) with 1,7-Octadiyne. Treatment of **1** with 1,7-octadiyne in 2:1 molar ratio in toluene yields, after 4 days at room temperature, a mixture of products from which the binuclear μ-bis-carbene complex [(P*i*Pr$_3$)$_2$(CO)Cl$_2$Os]{=CH(CH$_2$)$_6$CH=} [OsCl$_2$(CO)(P*i*Pr$_3$)$_2$] (**11**) (20% yield) was identified by NMR spectroscopy. This compound was prepared as an analytically pure yellow solid via the reactions sequence shown in Scheme 3. Treatment of **2** with 1,7-octadiyne in 2:1 molar ratio in toluene affords, after 6 h at 333 K, the binuclear μ-bis-vinyl complex **12**, which was

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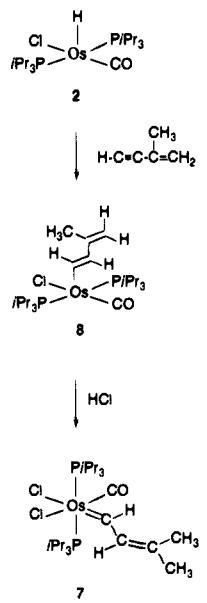
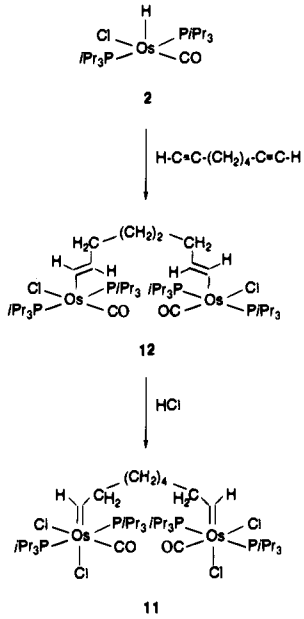
Scheme 2



Scheme 3



isolated by addition of pentane as a dark blue solid in 83% yield. The reaction of **12** with the stoichiometric amount of a toluene HCl solution leads to **11**, which was obtained in excellent yield (80%).

Complexes **11** and **12** were fully characterized by elemental analysis, IR, and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy. The ^1H NMR spectrum of **11** contains a triplet at 18.95 ppm with a H−H coupling constant of 5.6 Hz. This resonance was assigned to the Os=CH protons. The sp^2 carbon atoms of the μ-bis-carbene ligand appear in the $^{13}C\{^1H\}$ NMR spectrum as a broad signal at 300.07 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 12.4 ppm. The IR spectrum of **12** in Nujol contains a ν(C=C) band at 1590 cm^{-1}, which was assigned to the olefinic bonds of the bis-vinyl ligand of this compound. In the ^1H NMR spectrum, the most noticeable resonances of the bis-vinyl ligand are a doublet at 6.84 ppm with a H−H coupling constant of 12.4 Hz, a double triplet at 4.41 ppm with a H−H of 12.4 Hz, and a P−H coupling constant of 6.0 Hz. These signals were assigned to the protons OsCH=, and =CH−, respectively. In the $^{13}C\{^1H\}$ NMR spectrum both α-vinylic carbon atoms appear at 108.08 ppm as a triplet with a P−C coupling constant of 7.8 Hz and the β-vinylic carbon atoms at 133.59 ppm also as a triplet with a P−C coupling constant of 3.2 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 22.3 ppm.

The more common transition metal carbene complexes possess a carbene fragment bonded to a single transition metal. Binuclear μ-bis-carbene complexes are relatively rare. This group of compounds consists of homodimetallic derivatives of chromium,[19] tungsten,[19b,f,j,k,20] molybdenum,[19f,k,20b] manganese,[21] and iron.[22] However none of these compounds possess the simple structure M=CH−$(CH_2)_n$−CH=M. Thus, **11** represents the first complex to contain this unit and the first example of binuclear μ-bis-carbene compound of osmium.

Concluding Remarks. The dihydrogen complex $OsCl_2(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ can be prepared by addition of HCl to the monohydrido $OsHCl(CO)(PiPr_3)_2$. The study of the reactivity of $OsCl_2(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ toward terminal alkynes has revealed a new reaction pattern of the dihydrogen complexes. The reactions of $OsCl_2(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ with terminal alkynes lead to carbene derivatives. The formation of these derivatives goes by elimination of HCl to afford initially a six-coordinate hydrido-π-alkyne intermediate, which evolves to the insertion product. Subsequently, the vinyl complex undergoes the electrophilic attack of the HCl proton at the nucleophilic center of the unsaturated organic ligand (β or δ carbon atom) to give a cationic carbene species, followed by the coordination of the chloride anion to the metallic center.

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. $OsHCl(CO)(PiPr_3)_2$ (**2**),[12b] $OsDCl(CO)(PiPr_3)_2$ (**2-*d***),[8b] and $Os\{(E)\text{-}CH{=}CHPh\}Cl(CO)(PiPr_3)_2$ (**6**)[8a] were prepared by published methods. Unless otherwise stated, the reactions were carried out at room temperature.

Physical Measurements. Infrared spectra were recorded as Nujol mulls on polyethylene sheets using a Perkin-Elmer 883 or a Nicolet 550 spectrometer. NMR spectra were recorded on a Varian UNITY 300 or on a Bruker 300 AXR. ^1H, DEPT, and $^{13}C\{^1H\}$ chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. $^{31}P\{^1H\}$ chemical shifts are reported relative to H_3PO_4 (85%). Coupling constants J and N ($N = J(HP) + J(HP')$ for ^1H, and $N = J(CP) + J(CP')$ for ^{13}C) are given in

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Hertz. T_1 measurements were made at 300 MHz with a standard 180°−τ−90° pulse sequence, and are given in miliseconds. C, H, and N analyses were carried out with a Perkin-Elmer 2400 CHNS/O analyzer.

Preparation of $OsCl_2(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ (1). A solution of **2** (130 mg, 0.23 mmol) in 4 mL of toluene was treated with a toluene HCl solution (0.10 M, 3.5 mL, 0.35 mmol). After the yellow mixture was stirred for 10 min, the solvent was removed *in vacuo*. The cream residue was washed two times with 2 mL of cold pentane and dried *in vacuo*. The product is a cream colored solid: yield 105 mg (75%); IR (Nujol) ν(C≡O) 1957 (s) cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 2.81 (m; PCH), 1.25 (dvt, N = 14.3, J(HH) = 7.1; $PCCH_3$), 1.12 (dvt, N = 13.7, J(HH) = 6.9; $PCCH_3$), −7.46 (t, J(HP) = 8.5, $Os(H_2)$); $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6) δ 16.9 (s); T_1 of Os-(η^2-H_2) (300 MHz, toluene-d_8) 42 (293 K), 30 (273 K), 21 (253 K), 15 (233 K), 16 (213 K), 27 (193 K). Anal. Calcd for $C_{19}H_{44}Cl_2OOsP_2$: C, 37.31; H, 7.25. Found: C, 37.61; H, 6.90.

Preparation of $OsCl_2(\eta^2\text{-}HD)(CO)(PiPr_3)_2$ (1-*d*). The procedure was analogous to that described for **1**; starting materials were **2-*d*** (200 mg, 0.35 mmol) and a toluene HCl solution (0.10 M, 3.8 mL, 0.38 mmol). The product is a cream colored solid: yield 147 mg (67%); $^1H\{^{31}P\}$ NMR (300 MHz,C_6D_6) δ −7.46 (t, J(HD) = 20.1; Os(HD)).

Reaction of 1 with NaH. A solution of **1** (80 mg, 0.137 mmol) in 10 mL of THF was treated with NaH (17 mg, 0.28 mmol). After the mixture was stirred for 24 h, the solvent was removed *in vacuo*. The residue was dissolved in 10 mL of toluene, and after filtration, the solvent was removed *in vacuo*. The resultant residue was washed with 2 mL of pentane and dried *in vacuo*. The product was characterized as a 3:1 mixture of **1** and **2** by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy.

Reaction of $OsCl_2(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ (1) with Carbon Monoxide. Formation of $OsHCl(CO)_2(PiPr_3)_2$ (3). In a 5 mm NMR tube containing a benzene-d_6 solution of **1** (0.033 mmol in 0.7 mL) carbon monoxide was bubbled for 5 min. The reaction was monitored by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy: ^{1}H NMR (300 MHz, C_6D_6) δ 2.65 (m; PCH), 1.35 (dvt, N =14.0, J(HH) = 7.1; $PCCH_3$), −4.70 (t, J(HP) = 20.9, OsH); $^{31}P\{^1H\}$ NMR (121.42 MHz,C_6D_6) δ 27.8 (s, d in off resonance).

Reaction of $OsCl_2(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ (1) with *tert*-Butyl Isocyanide. Preparation of $OsHCl(CNtBu)(CO)(PiPr_3)_2$ (4). A solution of **1** (120 mg, 0.19 mmol) in 4 mL of toluene was treated with *tert*-butyl isocyanide (24.8 μL, 0.22 mmol). The pale yellow solution was stirred for 45 min. The gas evolved during the reaction tainted indicator paper red demonstrating the evolution of acid. The mixture was concentrated to ca. 0.5 mL, and 3 mL of pentane were added. The white precipitate formed was filtered off, washed with 1 mL of pentane, and dried *in vacuo*. The product is a white solid: yield 100 mg (80%); IR (Nujol) ν(C≡N) 2136 (w), ν(OsH) 2007 (m), ν(C≡O) 1898 (s) cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 2.67 (m; PCH), 1.34, 1.32 (both dvt, N = 12.1, J(HH) = 6.9; $PCCH_3$), 1.09 (s; *t*BuNC), −6.50 (t, J(HP) = 20.9; OsH); $^{31}P\{^1H\}$ NMR (121.42 MHz,C_6D_6) δ 28.5 (s, d in off resonance). Anal. Calcd for $C_{24}H_{52}ClNOOsP_2$: C, 43.61; H, 7.91; N, 2.23. Found: C, 43.79; H 7.96; N, 2.12.

Reaction of $OsCl_2(\eta^2\text{-}H_2)(CO)(PiPr_3)_2$ (1) with Phenylacetylene. Preparation of $OsCl_2(=CHCH_2Ph)(CO)(PiPr_3)_2$ (5). A solution of **1** (91 mg, 0.15 mmol) in 4 mL of toluene was treated with phenylacetylene (20 μL, 0.18 mmol). After the mixture was stirred for 1.5 h, the solvent was removed *in vacuo*. The residue was washed twice with 2 mL of cold pentane and dried *in vacuo*. The product is a yellow solid: yield 84 mg (75%); IR (Nujol) ν(C≡O) 1900 (s) cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 18.99 (t, J(HH) = 6.6; Os=CH), 7.2−7.0 (m; Ph), 3.49 (d, J(HH) = 6.6; CH_2Ph), 2.61 (m; PCH), 1.26 (dvt, N = 14.0, J(HH) = 7.14; $PCCH_3$), 0.99 (dvt, N = 13.4, J(HH) = 6.9; $PCCH_3$); $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6) δ 296.60 (t, J(CP) = 6.0; Os=C), 180.61 (t, J(CP) = 8.7; OsCO), 138.73 (s; C_{ipsoPh}), 128.81, 128.20, 127.03 (all s; C_{Ph}), 67.58 (s; CH_2Ph), 25.21 (vt, N = 25.3; PCH), 20.05, 19.33 (both s; $PCCH_3$); $^{31}P\{^1H\}$ NMR (121.42 MHz,C_6D_6) δ 12.2 (s). Anal. Calcd for $C_{27}H_{50}Cl_2OOsP_2$: C, 45.44; H, 7.02. Found: C 44.95; H 6.79.

Reaction of 6 with HCl. Formation of 5. A solution of **6** (130 mg, 0.19 mmol) in 3 mL of toluene was treated dropwise with a toluene HCl solution (0.08 M; 3.5 mL, 0.28 mmol). The mixture turned, immediately, from dark blue to yellow. After stirring for 15 min, it was concentrated to ca. 0.5 mL, and 3 mL of pentane was added. The resulting solution was stirred for 30 min until a yellow precipitate was formed. The solid was filtered off, washed with 2 mL of pentane, and dried *in vacuo*. The product was characterized as **5** by ^{1}H and $^{31}P\{^1H\}$ NMR: yield 94 mg (70%).

Reaction of 1 with 2-Methyl-1-buten-3-yne. Preparation of $OsCl_2\{=CHCH=C(CH_3)_2\}(CO)(PiPr_3)_2$ (7). A solution of **1** (117 mg, 0.19 mmol) in 7 mL of toluene was treated with 2-methyl-1-buten-3-yne (19 μL, 0.23 mmol). After the mixture was stirred for 1 h, it was concentrated to ca. 0.5 mL, and 3 mL of methanol was added. The resultant solution was kept at −30 °C overnight. The orange precipitate formed was filtered off, washed twice with 1 mL of methanol at −30° C, and dried *in vacuo*. The product is an orange solid: yield 75 mg (50%); IR (Nujol) ν(C≡O) 1925 (vs), ν(C=C) 1582 (s) cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 18.20 (dt, J(HH) = 13.8, J(HP) = 0.9; Os=CH), 7.70 (d, J(HH) = 13.8; −CH=C), 2.88 (m; PCH), 1.42 (dvt, N = 14.2, J(HH) = 7.1; $PCCH_3$), 1.11 (s; $=CCH_3$), 1.03 (dvt, N = 14.2, J(HH) = 6.5; $PCCH_3$), 0.81 (s, $=CCH_3$); $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6) δ 265.42 (t, J(CP) = 6.5; Os=CH), 180.90 (t, J(CP) = 9.6; OsCO), 152.40 (s; $=C(CH_3)_2$), 147.50 (s; CH=) [both signals assigned by a DEPT NMR experiment], 27.17 (s, $=CCH_3$), 24.28 (vt, N = 24.8; PCH), 21.27 (s, $=CCH_3$), 20.28, 18.94 (both s, $PCCH_3$); $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6) δ 12.6 (s). Anal. Calcd for $C_{24}H_{50}Cl_2OOsP_2$: C, 42.53; H, 7.44. Found: C, 42.64; H, 8.17.

Reaction of 2 with 2-Methyl-1-buten-3-yne. Preparation of Os-{(*E*)-CH=CHC(CH$_3$)=CH$_2$}Cl(CO)(*Pi*Pr$_3$)$_2$ (8). A solution of **2** (114 mg, 0.20 mmol) in 10 mL of toluene was treated with 2-methyl-1-buten-3-yne (20 μL, 0.20 mmol). After the mixture was stirred for 1 h, the solvent was removed *in vacuo*. The residue was washed twice with 1 mL of cold methanol and dried *in vacuo*. The product is a dark blue solid: yield 122 mg (86%); IR (Nujol) ν(C≡O) 1892 (vs), ν(C=C) 1600 (s), 1562 (s) cm^{-1}; ^{1}H NMR (300 MHz, C_6D_6) δ 7.93 (d, J(HH) = 13.1; OsCH=), 5.87 (dt, J(HH) = 13.1, J(HP) = 2.1; =CH−), 4.63, and 4.34 (both d, J(HH) = 2.4; H of $=CH_2$), 2.78 (m; PCH), 1.94 (s; $C(CH_3)$=), 1.18 (dvt, N = 13.5, J(HH) = 6.2; $PCCH_3$), 1.17 (dvt, N = 14.1, J(HH) = 6.3; $PCCH_3$); $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6) δ 181.89 (t, J(CP) = 8.3; OsCO), 142.38 (t, J(CP) = 2.3; $C(CH_3)$=), 138.34 (t, J(CP) = 3.2; =CH−), 119.41 (t, J(CP) = 7.8; OsCH=), 105.55 (s; $=CH_2$) [the fourth signals assigned by a DEPT NMR experiment], 24.85 (vt, N = 23.9; PCH), 20.03 (s; $C(CH_3)$=), 19.95, 19.52 (both s; $PCCH_3$); $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6) δ 22.3 (s). Anal. Calcd for $C_{24}H_{49}ClOOsP_2$: C, 44.95; H, 7.70. Found: C, 44.92; H, 8.50.

Reaction of 8 with HCl. Formation of 7. The experimental procedure was analogous to that described for the reaction of **6** with HCl; starting materials were **8** (140 mg, 0.22 mmol) and a toluene HCl solution (0.08 M; 3.5 mL, 0.28 mmol). The product was characterized as **7** by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy: yield 85 mg (60%).

Reaction of 8 with HBF_4·OEt_2. Preparation of $[OsCl\{=CH-CH=C(CH_3)_2\}(CO)(PiPr_3)_2]BF_4$ (9). A solution of **8** (198 mg, 0.31 mmol) in 10 mL of diethyl ether was treated dropwise with HBF_4·OEt_2 (54%) (45 μL, 0.31 mmol). After 30 min, the yellow-brown solution obtained was concentrated to 2 mL. The ochre precipitate formed was filtered off, washed with cold diethyl ether and hexane (1:1), and dried *in vacuo*. The product is an ochre solid: yield 182 mg (80%); IR (Nujol) ν(C≡O) 1932 (vs), ν(C=C) 1591 (s), ν(BF) 1050 (br) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 16.80 (br; Os=CH), 7.40 (br; −CH=), 2.65 (m; PCH), 1.70 and 1.50 (both s; $=C(CH_3)_2$), 1.33 (dvt, N = 14.8, J(HH) = 7.1; $PCCH_3$), 1.19 (dvt, N = 13.7, J(HH) = 6.6; $PCCH_3$); $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$) δ 50 (br). Anal. Calcd for $C_{24}H_{50}BClF_4OOsP_2$: C, 39.54; H, 6.91. Found: C, 38.98; H, 7.51.

Reaction of 9 with Acetonitrile. Formation of $[OsCl\{=CH-CH=C(CH_3)_2\}(CO)(NCCH_3)(PiPr_3)_2]BF_4$ (10). To a 5 mm NMR tube containing a chloroform-*d* solution of **9** (0.075 mmol in 0.7 mL) was added acetonitrile (4.0 μL, 0.075 mmol). The reaction was monitored by ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy: ^{1}H NMR (300 MHz, $CDCl_3$) δ 17.17 (d, J(HH) = 13.5; Os=CH), 7.60 (d, J(HH) = 13.5; −CH=), 2.76 (s; $NCCH_3$), 2.63 (m; PCH), 1.73, 1.46 (both s; CCH_3), 1.34 (dvt, N =14.7, J(HH) = 7.7; $PCCH_3$), 1.18 (dvt, N = 14.7, J(HH) = 6.8; $PCCH_3$); $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6) δ 261.84 (t, J(CP) = 5.3; Os=C), 182.80 (t, J(CP) = 9.0; OsCO), 159.44 (s; $=C(CH_3)_2$), 151.85 (s; CH=) [both signals assigned by a DEPT

Table 2. Atomic Coordinates ($\times 10^4$; $\times 10^5$ for Os atom) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$; $\times 10^4$ for Os atom) for the Complex $OsCl_2(=CHCH_2Ph)(CO)(PiPr_3)_2$ (**5**)

atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]/U_{iso}
Os	2670(2)	11551(2)	13044(1)	329(1)
Cl(1)	74(2)	−245(2)	925(1)	60(1)
Cl(2)	−1169(2)	812(2)	1803(1)	58(1)
P(1)	−1023(2)	1722(2)	789(1)	40(1)
P(2)	1278(2)	480(2)	1914(1)	39(1)
O	544(5)	2861(5)	1682(3)	60(3)
C(1)	1358(7)	1304(6)	914(3)	44(3)
C(2)	2097(8)	1973(8)	825(5)	72(5)
C(9)	421(7)	2244(8)	1546(4)	50(4)
C(10)	−564(9)	2429(8)	328(3)	65(5)
C(11)	−53(9)	3232(7)	530(5)	76(5)
C(12)	93(8)	1979(9)	−5(4)	76(5)
C(13)	−2063(8)	2276(8)	1086(4)	60(4)
C(14)	−1767(9)	2857(8)	1468(4)	75(5)
C(15)	−2725(9)	2789(9)	747(4)	91(6)
C(16)	−1644(8)	861(7)	445(4)	59(4)
C(17)	−2251(9)	278(8)	735(5)	86(6)
C(18)	−2189(9)	1157(9)	2(4)	91(6)
C(19)	1682(8)	1232(7)	2369(3)	50(4)
C(20)	2409(8)	1898(7)	2188(4)	59(4)
C(21)	828(9)	1625(9)	2636(3)	76(5)
C(22)	2466(7)	50(7)	1687(4)	47(4)
C(23)	3235(8)	−195(8)	2058(4)	73(5)
C(24)	2386(8)	−687(8)	1353(4)	78(5)
C(25)	630(8)	−332(7)	2256(3)	49(4)
C(26)	273(11)	−1108(8)	2003(5)	103(7)
C(27)	1143(10)	−625(9)	2700(4)	103(7)
C(3A)[b]	3130(9)	1580(10)	801(5)	35(9)
C(4A)	3882	1779	1108	60(6)
C(5A)	4778	1354	1080	88(9)
C(6A)	4922	731	744	63(7)
C(7A)	4170	532	438	71(8)
C(8A)	3273	957	466	40(5)
C(3B)	3163(12)	1670(16)	826(9)	80(22)
C(4B)	3780	2170	1097	49(7)
C(5B)	4740	1906	1182	73(10)
C(6B)	5082	1142	997	73(10)
C(7B)	4465	642	726	114(15)
C(8B)	3505	906	641	92(12)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] From this atom downwards isotropic displacement parameters were used since these atoms were involved in static disorder.

NMR experiment], 124.01 (s; CH_3CN), 28.39 (s, $=CCH_3$), 24.52 (vt, $N = 25.8$; PCH), 22.24 (s, $=CCH_3$), 19.89, and 19.62 (both s, $PCCH_3$), 4.28 (s; CH_3CN); $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$) δ 14.5 (s).

Reaction of 9 with NaCl. Formation of 7. A solution of **9** (183 mg, 0.25 mmol) in 10 mL of methanol was treated with NaCl (17 mg, 0.28 mmol). After the mixture was stirred for 30 min, the solvent was removed *in vacuo*. The residue was dissolved in 10 mL of toluene, and after filtration the solvent was removed *in vacuo*. The resultant dark-brown oil was washed with 1 mL of methanol and dried *in vacuo*. The product was characterized as **7** by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy: yield 161 mg (85%).

Reaction of 1 with 1,7-Octadiyne. Formation of $[(PiPr_3)_2(CO)Cl_2Os]\{=CH(CH_2)_6CH=\}[OsCl_2(CO)(PiPr_3)_2]$ (11). A solution of **1** (131 mg, 0.21 mmol) in 8 mL of toluene was treated with 1,7-octadiyne (15 μL, 0.11 mmol). The reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy over a period of 4 days. After 4 days, the reaction mixture consists of ca. 20% of **11** together with other unidentified products: ^1H NMR (300 MHz, C_6D_6) δ 18.95 (t, J(HH) = 5.6, 2H; Os=CH), 2.77 (m, 24H; PCH), 2.29 (td, J(HH) = 6.8 and 5.6, 4H; $CHCH_2$), 1.55 (m, 4H; CH_2), 1.35, 1.13 (both dvt, $N = 13.4$, J(HH) = 6.7, each 36H; $PCCH_3$), 0.88 (m, 4H; CH_2); $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6) δ 300.07 (br; Os=CH), 180.60 (t, J(PC) = 9.05; OsCO), 61.10, 30.04, 29.30 (all s; $-CH_2-$), 25.10 (vt, $N = 24.96$; PCH), 20.12, 19.43 (both s; $PCCH_3$); $^{31}P\{^1H\}$ NMR (121.42 MHz,C_6D_6) δ 12.4 (s).

Reaction of 2 with 1,7-Octadiyne. Preparation of $[(PiPr_3)_2(CO)ClOs]\{CH=CH(CH_2)_4Os=CH\}[OsCl(CO)(PiPr_3)_2]$ (12). A solution of **2** (174 mg, 0.30 mmol) in 5 mL of toluene was treated with 1,7-octadiyne (24 μL, 0.18 mmol). After the mixture was stirred for 6 h at 333 K, the solvent was removed *in vacuo*. The residue was washed twice with 2 mL of cold pentane and dried *in vacuo*. The product is a dark blue solid: yield 158 mg (83%); IR (Nujol) ν(C≡O) 1885 (s), ν(C=C) 1590 (m) cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 6.84 (d, J(HH) = 12.4, 2 H; OsCH=), 4.41 (dt,J(HH) = 12.4, J(HP) = 6.0 Hz, 2 H; =CH−), 2.90 (m, 12 H; PCH), 2.41, 1.53 (both m, each 4 H; $-CH_2-$), 1.23 (dvt, N = 13,1, J(HH) = 6.8, 72 H; $PCCH_3$); $^{13}C\{^1H\}$ NMR (75.43 MHz, C_6D_6) δ 182.99 (t, J(CP) = 9.2; OsCO), 133.59 (t, J(PC) = 3.2; =CH−), 108.08 (t, J(PC) = 7.8; OsCH=), 36.89, 31.52 (both s; CH_2), 24.80 (vt, N = 23.94; PCH), 20.04, 19.77 (both s; $PCCH_3$); $^{31}P\{^1H\}$ NMR (121.42 MHz,C_6D_6) δ 22.3 (s). Anal. Calcd for $C_{46}H_{96}Cl_2O_2Os_2P_4$: C, 43.94; H, 7.70. Found: C, 43.78; H, 8.15.

Reaction of 12 with HCl. Formation of 11. The experimental procedure was analogous to that described for the reaction of **6** with HCl; starting materials were **12** (138 mg, 0.11 mmol) and a toluene HCl solution (0.08 M; 3.5 mL, 0.28 mmol). The product is a yellow solid and was characterized as **11** by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy: yield 117 mg (80%); IR (Nujol) ν(C≡O) 1933 (s) cm^{-1}. Anal. Calcd for $C_{46}H_{98}Cl_4O_2Os_2P_4$: C, 41.56; H 7.43. Found: C 41.87; H 6.84.

X-ray Structure Analysis of $OsCl_2(=CHCH_2Ph)(CO)(PiPr_3)_2$ (5). Crystals suitable for an X-ray diffraction experiment were obtained from a saturated solution of **5** in pentane at −20 °C. Atomic coordinates and U_{eq} values are listed in Table 2. A summary of crystal data, intensity collection procedure, and refinement is reported in Table 3. The orange 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 56 reflections in the range $20 \le 2\theta \le 34°$. The recorded reflections (5701) 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 an empirical method.[23]

The structures were solved by Patterson (Os atom) and conventional Fourier techniques. The phenyl ligand of the carbene ligand was found to be disordered. The disordered group was modeled with two different moieties refining with a complementary occupancy factor assigned on the basis of the thermal parameters, to final value (0.56(3) for the

Table 3. Crystal, Collection, and Refinement Data for the Complex $OsCl_2(=CHCH_2Ph)(CO)(PiPr_3)_2$ (**5**)

Crystal Data	
formula	$C_{27}H_{50}Cl_2OOsP_2$
mol wt	713.75
color and habit	orange, transparent prism
crys size, mm	0.19 × 0.34 × 0.15
crys syst	orthorhombic
space group	*Pbca* (No.61)
a, Å	13.641(2)
b, Å	15.698(2)
c, Å	29.059(4)
V, Å^3	6223(1)
Z	8
D(calc), g cm^{-3}	1.528
temp, K	233
Data Collection and Refinement	
diffractometer	4-circle Siemens-STOE AED-2
λ(Mo Kα), Å; technique	0.710 73; bisecting geometry
monochromator	graphite oriented
μ, mm^{-1}	4.40
scan type	$\omega/2\theta$
2θ range, degree	$2 \le 2\theta \le 50$
no. of data collect	5701
no. of unique data	5494 (R_{int} = 0.0399)
no. of unique obs data	3185 ($F \ge 4.0\sigma(F)$)
no. of param refined	270
R, R_w[a]	0.0412, 0.0380

[a] $R = (\sum[|F_o| - |F_c|])/\sum F_o$; $R_w = (\sum([|F_o| - |F_c|])w^{1/2})/\sum(|F_o|w^{1/2})$; $w^{-1} = \sigma^2(F_o)^2 + 0.000\,31(F_o)^2$.

(23) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

a-labeled atoms, and 0.44(3) for the *b*-labeled atoms), and with the geometry restrained to a regular hexagon. 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, except those involved in disorder. Hydrogen atoms were calculated (except those bonded to disorded atoms) and included in the refinement riding on carbon atoms with a common isotropic thermal parameter. Atomic scattering factors, corrected for anomalous dispersion for Os, P, and Cl, were taken from ref 24. The function minimized was $\sum w([F_o] - [F_c])^2$, with the weight defined as $w^{-1} = \sigma^2[F_o] - 0.00031[F_o^2]$. Final R and R_w values were 0.0412 and 0.0380. All calculations were performed using SHELXTL-PLUS.[25]

Acknowledgment. We thank the D.G.I.C.Y.T. (Project PB 92-0092, Programa de Promoción General del Conocimiento) and E.U. (Project: Selective Processes and Catalysis Involving Small Molecules) for financial support. B.Z. thanks the Ministerio de Educación y Ciencia de España (M.E.C.) and E.O. the Diputación General de Aragón (D.G.A.) for a grant.

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(25) Sheldrick, G. M. *SHELXTL* PLUS; SIEMENS Analytical X-ray Instruments: Madison, WI, 1990.

Supporting Information 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 **5** (11 pages); tables of observed and calculated structures (20 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA950154S