Meyer's Complex $OsH_2Cl_2(P^iPr_3)_2$ as a Precursor for the Preparation of New Cyclopentadienylosmium Compounds

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The six-coordinate complex $OsH_2Cl_2(P^iPr_3)_2$ (**1**) reacts with cyclopentadienylthallium to give $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (**2**). In methanol and acetone, **2** dissociates the chlorine ligand and the resulting metallic fragment is capable of activating a methyl C−H bond of a triisopropylphosphine to afford $[OsH(\eta^5\text{-}C_5H_5)\{CH_2CH(CH_3)P^iPr_2\}(P^iPr_3)]^+$ (**3**), which can be isolated as the PF_6 salt by addition of either $NaPF_6$ or $TlPF_6$. Treatment of a 1:10 mixture of **2** and $NaBH_4$ in toluene with 1.0 mL of methanol affords $OsH(\eta^5\text{-}C_5H_5)(P^iPr_3)_2$ (**4**) , which by protonation with $HBF_4{\cdot}OEt_2$ yields $[OsH_2(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]BF_4$ (**5**). In pentane, complex **2** reacts with trimethyl phosphite to give $Os(\eta^5\text{-}C_5H_5)Cl\{P(OMe)_3\}(P^iPr_3)$ (**6**). Similarly, the addition of methyl vinyl ketone and dimethyl acetylenedicarboxylate to toluene solutions of **2** produces the displacement of a phosphine ligand from **2** and the formation of $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}CH_2{=}CHC(O)CH_3\}(P^iPr_3)$ (**7**) and $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}C(CO_2CH_3){\equiv}CCO_2CH_3\}(P^iPr_3)$ (**8**), respectively. Complex **2** also reacts with ethyl diazoacetate to give $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}(Z)\text{-}CH(CO_2C_2H_5){=}CHCO_2C_2H_5\}(P^iPr_3)$ (**9**) and with 1-ethynyl-1-cyclohexanol and 2-methyl-3-butyn-2-ol to afford $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HC{\equiv}C{-}C(OH)(CH_2)_4CH_2\}(P^iPr_3)$ (**10**) and $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HC{\equiv}C{-}C(OH)(CH_3)_2\}(P^iPr_3)$ (**11**). In toluene at 85 °C, complexes **10** and **11** evolve to the corresponding alkenylvinylidene derivatives $Os(\eta^5\text{-}C_5H_5)Cl\{{=}C{=}CH{-}C{=}CH\text{-}(CH_2)_3CH_2\}(P^iPr_3)$ (**12**) and $Os(\eta^5\text{-}C_5H_5)Cl\{{=}C{=}CH{-}C(CH_3){=}CH_2\}(P^iPr_3)$ (**13**). Complex **13** can also be prepared by reaction of **2** with 2-methyl-1-buten-3-yne at room temperature. In this case, a π-alkyne intermediate related to **10** and **11** was not detected even at −60 °C. However, the reaction of **2** with phenylacetylene initially gives $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HC{\equiv}CPh\}(P^iPr_3)$ (**14**), which subsequently evolves into $Os(\eta^5\text{-}C_5H_5)Cl\{{=}C{=}CHPh\}(P^iPr_3)$ (**15**). Protonation of **12**, **13**, and **15** with HBF_4 afford the carbyne derivatives $[Os(\eta^5\text{-}C_5H_5)Cl\{{\equiv}C{-}CH{=}C(CH_2)_4CH_2\}(P^iPr_3)]BF_4$ (**16**), $[Os(\eta^5\text{-}C_5H_5)Cl\{{\equiv}C{-}CH{=}C(CH_3)_2\}(P^iPr_3)]BF_4$ (**17**), and $[Os(\eta^5\text{-}C_5H_5)Cl({\equiv}C{-}CH_2Ph)(P^iPr_3)]BF_4$ (**18**), respectively. The structure of **16** was determined by an X-ray investigation. The Os≡C bond length is 1.756(8) Å, while the Os−C−C angle is 167.8(6)°.

Introduction

Half-sandwich pentamethylcyclopentadienyl- and cyclopentadienylruthenium complexes exhibit a particularly rich and interesting chemistry, which has formed one of the cornerstones in the development of the organometallic field.[1] The chemistry of the related half-sandwich osmium complexes has attracted comparatively less attention,[2] in particular that containing the $Os(\eta^5\text{-}C_5H_5)$ unit.[3] This is in part due to the lack of convenient osmium synthetic precursors[4] and the higher kinetic stability of the $CpOsL_3$ compounds in comparison with the related iron and ruthenium complexes.[5]

In 1985, U. Meyer, a member of Werner's group, found that the treatment of $OsCl_3{\cdot}xH_2O$ with triisopropylphosphine in refluxing 2-propanol leads to $OsH_2Cl_2(P^iPr_3)_2$ (**1**). The solid-state structure of this compound, significantly distorted from octahedral, has only a C_2 symmetry and can be described as a square antiprism with two missing vertices.[6] In solution, it exits as two rapidly interconverting isomers, one having C_2 sym-

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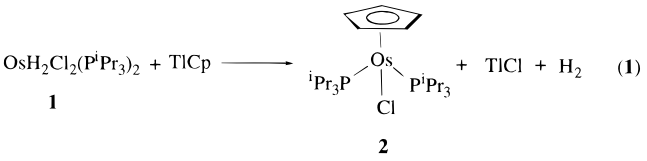
metry and the other with no symmetry.[7] In recent years, Werner, Caulton, and our group have proved that complex **1** is a unique species with a completely different chemical behavior than that of previously reported compounds. In this sense, it should be mentioned that it catalyzes the reduction of ketones, olefins, and diolefins[6b] and is a useful starting material to prepare dihydrogen,[8] polyhydrido,[9] carbyne,[10] and diolefin[11] derivatives of osmium II and IV.

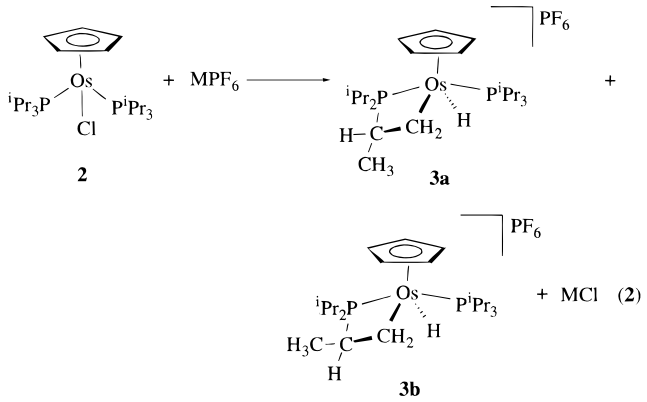
Some months ago, we reported that $OsHCl(CO)(P^iPr_3)_2$, which is prepared similarly to **1** but in methanol,[12] reacts with cyclopentadiene to afford $OsH(\eta^5\text{-}C_5H_5)(CO)(P^iPr_3)$. This complex has been the starting point for new half-sandwich osmium complexes including hydrido, halide, vinylidene, and vinylvinylidene derivatives.[13] In the search for new cyclopentadienylosmium synthetic precursors, and as a continuation of our work in the study of the chemical properties of complex **1**, we have now carried out the reaction of **1** with cyclopentadienylthallium in order to obtain $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$. In this paper, we report the synthesis and some of the potential chemistry of this compound.

Results and Discussion

Synthesis and Characterization of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$. Treatment of a toluene solution of $OsH_2Cl_2(P^iPr_3)_2$ (**1**) with cyclopentadienylthallium in a 1:1 mol ratio for 2 h gives, after filtration and solvent removal, a sticky residue. Pentane extraction of the residue and subsequent filtration of the resulting suspension leads to an orange solution, which affords the cyclopentadienyl complex $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (**2**) as an orange solid in 52% yield, by cooling at −78 °C (eq 1). The most characteristic spectroscopic fact of **2** is a singlet at −1.2 ppm in the $^{31}P\{^1H\}$ NMR spectrum. Complex **2**, which is an air-sensitive solid, is stable for a week if kept under argon at −20 °C. It is easily soluble in solvents such as pentane, toluene, and



benzene, and its solutions are stable under argon for a matter of days. However, in methanol and acetone, complex **2** dissociates the chlorine ligand and the resulting metallic fragment is capable of activating a methyl C−H bond of a triisopropylphosphine to afford a 1:1 mixture of isomers **a** and **b** (eq 2) of the cationic derivative $[OsH(\eta^5\text{-}C_5H_5)\{CH_2CH(CH_3)P^iPr_2\}(P^iPr_3)]^+$ (**3**). Complex **3** was isolated as the PF_6 salt either by



addition of $NaPF_6$ to the methanol solution (61% yield) or by addition of $TlPF_6$ to the acetone solution (86% yield). Complex **3** is a white solid. In solution, the presence of isomers **3a** and **3b** is supported by the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **3**. In the ^1H NMR spectrum, the most noticeable resonances are those due to the hydrido ligands, which appear at −13.81 and −13.98 ppm as double doublets with P−H coupling constants of 36.0 and 27.9 and 38.0 and 25.4 Hz, respectively. Similar P−H coupling constants have been observed for the monohydrido $RuH(\eta^5\text{-}C_5Me_5)\{CH_2CH(CH_3)P^iPr_2\}\{Si(CH_3)Ph_2\}$ (22.5 Hz)[14] and dihydrido $[OsH_2(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+$ (29.0 Hz),[3e] whose *cis*-(P,H) four-legged piano-stool geometries have been determined by X-ray diffraction. In the $^{13}C\{^1H\}$ NMR spectrum, the $OsCH_2$ and $PCH(CH_3)$ resonances of the metalated isopropyl group are observed at −36.9 and −37.4 and 49.9 and 46.9 ppm, respectively, in agreement with the chemical shift previously reported for the compounds $RuH(\eta^5\text{-}C_5Me_5)\{CH_2CH(CH_3)P^iPr_2\}\{Si(CH_3)Ph_2\}$ (−3.15 and 42.80 ppm)[14] and $RuH(\eta^6\text{-}C_6H_6)\{CH_2CH(CH_3)P^iPr_2\}$ (−10.74 and 42.80 ppm).[15] The $^{31}P\{^1H\}$ NMR spectrum of **3** shows four doublets at 8.0 and 4.4 (P^iPr_3) and −33.1 and −37.4 ($PCHCH_2Os$) ppm, with P−P coupling constants of about 20 Hz. Under off-resonance conditions, each doublet is split into a virtual triplet as a result of the P−H coupling with only one hydrido ligand.

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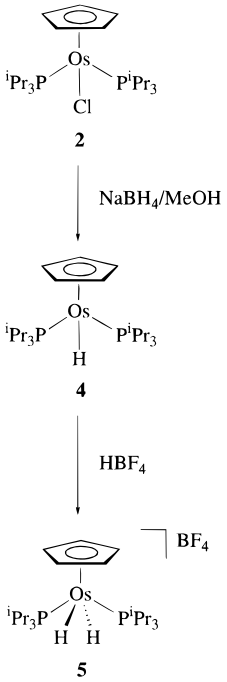
Scheme 1

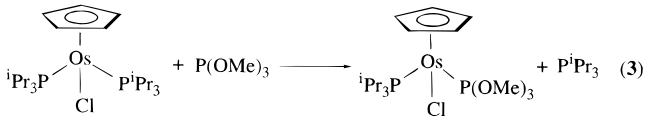


We note that the metalated-phosphine complexes $MH(\eta^2\text{-}CH_2PMe_2)(PMe_3)_3$ (M = Fe,[16] Os[17]) react with methanol to give the corresponding dihydrido derivatives $MH_2(PMe_3)_4$. In contrast to these compounds, complex **3** is stable in a methanol solution and the formation of the dihydrido $[OsH_2(\eta^5\text{-}C_5H_5)(P^{i}Pr_3)_2]^+$ does not take place, even after a week at 60 °C. However, this dihydrido complex, **5**, can be prepared according to Scheme 1. Treatment of a 1:10 mixture of **2** and $NaBH_4$ in toluene with 1.0 mL of methanol affords the monohydrido $OsH(\eta^5\text{-}C_5H_5)(P^{i}Pr_3)_2$ (**4**) in quantitative yield. The protonation of this monohydrido with $HBF_4{\cdot}OEt_2$ in diethyl ether gives the dihydrido **5**. Related cyclopentadienylosmium phosphine hydrido complexes have been previously reported.[3c−f,13]

Complex **4** was isolated as a yellow oil and characterized by MS analysis and IR and ^1H and $^{31}P\{^1H\}$ NMR spectroscopies. In the ^1H NMR spectrum, the most noticeable resonance is a triplet with a P−H coupling constant of 31.1 Hz at −16.10 ppm, which was assigned to the hydrido ligand. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 29.4 ppm, which under off-resonance conditions splits into a doublet due to the P−H coupling.

Complex **5** was isolated as a white solid in 76% yield and characterized by elemental analysis and IR and ^1H and $^{31}P\{^1H\}$ NMR spectroscopies. The IR spectrum in Nujol shows the absorption due to the $[BF_4]^-$ anion with T_d symmetry between 1030 and 1080 cm^{-1}, along with two weak ν(OsH) bands at 2146 and 2203 cm^{-1}. The *trans* disposition of the hydrido ligands is proposed on the basis of the ^1H NMR spectrum in chloroform-*d*, where the complex is stable. This spectrum, which is temperature invariant between 293 and 213 K, contains a single triplet at −14.26 ppm in the high-field region with a P−H coupling constant of 28.8 Hz. Similar *J*(PH) coupling constants have been observed for the *trans*-dihydrido cations $[OsH_2(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+$ (29.0 Hz)[3e] and $[OsH_2(\eta^5\text{-}C_5H_5)(CO)(P^{i}Pr_3)]^+$ (28.8 Hz).[13] In addition, it should be noted that a *cis*-dihydrido structure should give rise to an AA′XX′ spin system. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 32.2 ppm, which is split into a triplet under off-resonance conditions as a result of the P−H coupling with two hydrido ligands.

Although complex **2** is easily soluble in pentane and its solutions are stable for a matter of days, in this solvent the complex shows a high tendency to release a phosphine ligand, most probably, as a consequence of the large steric hindrance experienced by the triisopropylphosphine groups, which is a result of their large cone angle (160°).[18] Thus, in pentane, one of the triisopropylphosphine ligands of **2** can be quantitatively displaced (according to the NMR spectroscopy) by trimethyl phosphite to afford $Os(\eta^5\text{-}C_5H_5)Cl\{P(OMe)_3\}(P^{i}Pr_3)$ (**6**), which was isolated as a yellow solid, only in 36% yield due to its high solubility in pentane (eq 3).



(3)

The presence of the trimethyl phosphite ligand in **6** is supported by the $^{31}P\{^1H\}$ NMR spectrum, which shows two doublets at 103.7 ($P(OMe)_3$) and 14.4 ($P^{i}Pr_3$) ppm, with a P−P coupling constant of 34.6 Hz.

Reactions of 2 with Olefins and Internal Alkynes: Synthesis of π-Olefin and π-Alkyne Complexes. In toluene, complex **2** also shows a high tendency to release a phosphine ligand. Thus, the treatment of toluene solutions of **2** with methyl vinyl ketone and dimethyl acetylenedicarboxylate affords the derivatives $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}CH_2{=}CHC(O)CH_3\}(P^{i}Pr_3)$ (**7**) and $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}C(CO_2CH_3){\equiv}CCO_2CH_3\}(P^{i}Pr_3)$ (**8**) (Scheme 2). The reactions proceed at room temperature and do not lead to displacement of the second phophine, even if excess of unsaturated organic substrate is used.

Complex **7** was isolated as a yellow solid in 83% yield. The presence of the α,β-unsaturated ketone in the complex is supported by the IR spectrum in Nujol, which shows a ν(CO) band at 1661 cm^{-1}. This value is lower than the frequency for free methyl vinyl ketone observed at 1681 cm^{-1}. The resonances of the olefinic protons of this ligand (Figure 1a) can be simulated using an ABMX (X = P) spin system (Figure 1b). The low value (9.4 Hz) of the *J*(AB) coupling constant (A and B, hydrogen protons mutually *trans* disposed) should be noted, which is reduced by 8 Hz with regard to the H−H coupling constant between the hydrogen protons mutually *trans* disposed in the free methyl vinyl ketone (17.4 Hz). This suggests that the coordination of the carbon−carbon double bond of the α,β-unsaturated ketone to the osmium center of **2** produces a weaker intraligand carbon−carbon double bond than that expected, as a result of the unusually strong π-donor power of the metallic center. This is also revealed by the $^{13}C\{^1H\}$ NMR spectrum, which shows the resonances of the olefinic carbon atoms at 46.7 and 19.6 ppm, shifted

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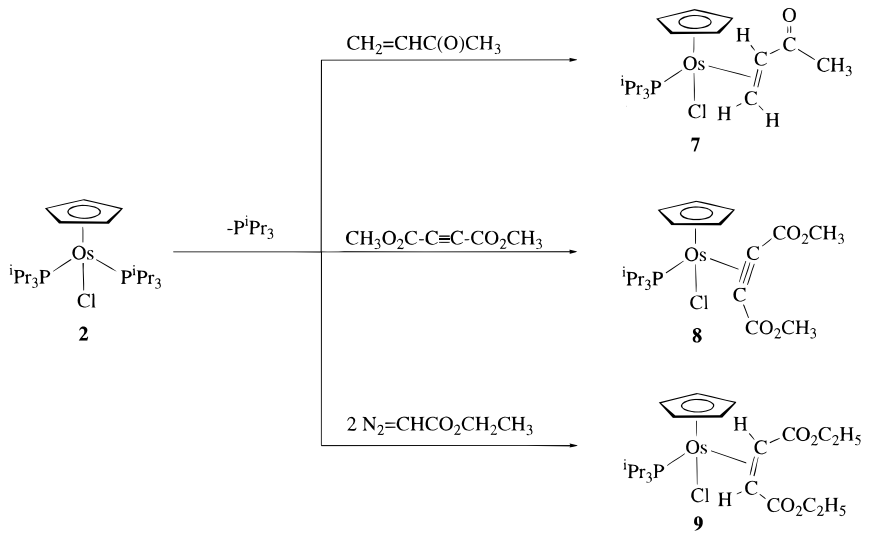
Scheme 2



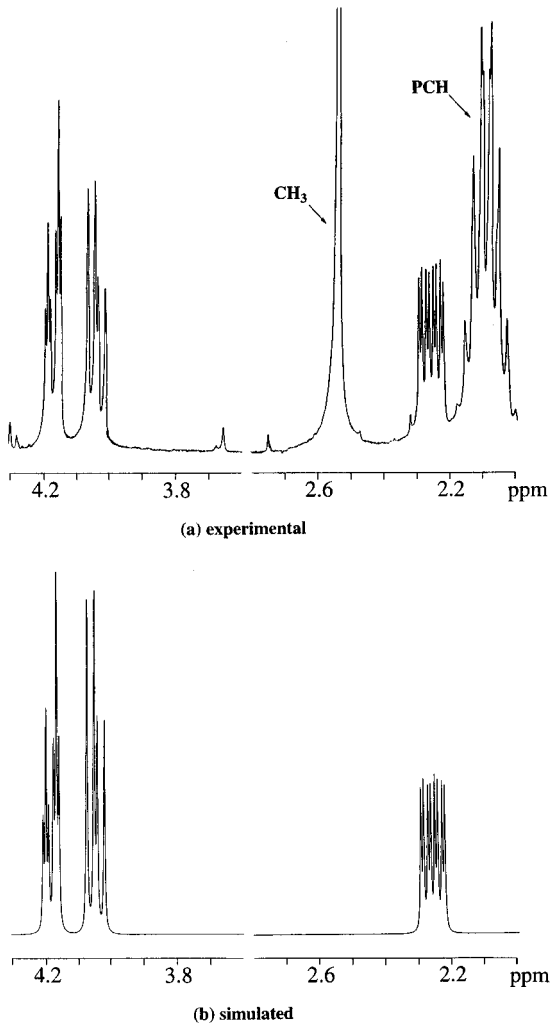


Figure 1. (a) Observed ^{1}H NMR resonances for the olefinic protons of **7**. (b) Simulated ^{1}H NMR resonances for the olefinic protons of **7**.

toward high field by about 100 ppm in comparison with the resonances of the free ligand (137.43 and 128.75 ppm). The electron-rich behavior of the metallic center of this system, which is also confirmed by the reaction shown in eq 2, is in agreement with the metal-based character of the half-sandwich complexes of type (C_5R_5)-ML_2.[19] The $^{31}P\{^1H\}$ NMR spectrum of **7** contains a singlet at 5.7 ppm.

Complex **8** was isolated as a brown solid in 73% yield. The π-coordination of the alkyne in this complex is supported by its IR spectrum in Nujol, in which the C≡C stretching frequency is found at 1825 cm^{-1}, shifted 325 cm^{-1} to lower wavenumbers if compared with the free alkyne. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances of the acetylenic carbon atoms appear at 70.2 and 69.8 ppm. The first resonance appears as a broad signal, while the second resonance is observed as a doublet with a P−C coupling constant of 8.3 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 17.3 ppm.

A particularly noteworthy carbon−carbon coupling reaction takes place in the presence of **2** (Scheme 2). Treatment of a toluene solution of **2** with ethyl diazoacetate in a 1:3 mol ratio at room temperature after 15 h leads to the π-olefin complex Os(η^5-C_5H_5)Cl{η^2-(*Z*)-CH($CO_2C_2H_5$)=$CHCO_2C_2H_5$}(P^iPr_3) (**9**), which was isolated as a yellow solid in 52% yield. Previously, it has been reported that the *meso*-tetra-*p*-tolylporphyrin complex $[Os(TTP)]_2$ reacts with diazoalkenes to give the corresponding carbene derivatives, which catalytically convert ethyl diazoacetate to diethyl maleate and diethyl fumarate in high yields and high stereoselectivity.[20] In contrast to this osmium complex, the rhodium compound $[RhCl(P^iPr_3)_2]_2$ reacts with diazomethane to give RhCl(η^2-CH_2=CH_2)(P^iPr_3)$_2$.[21]

The presence of the olefin ligand in **9** is mainly supported by the ^{1}H and $^{13}C\{^1H\}$ NMR spectra. In the ^{1}H NMR spectrum, the resonances of the olefinic protons are observed as the AB part of an ABX (X = P) spin system with δ_A = 4.35, δ_B = 4.31, J(AB) = 9.9 Hz, and J(XA) = J(XB) = 4.3 Hz. The value of the J(AB) coupling constant is similar to the values obtained for J(AB) (9.4 Hz) and J(MB) (6.5 Hz) in the case of the methyl vinyl ketone complex **7**. So in order to assign the stereochemistry to the olefin ligand of **9**, we carried out an X-ray diffraction analysis of a monocrystal of **9**. Although the low quality of the monocrystals obtained has not allowed the perfect refinement of the structure, from the X-ray diffraction analysis it is inferred that

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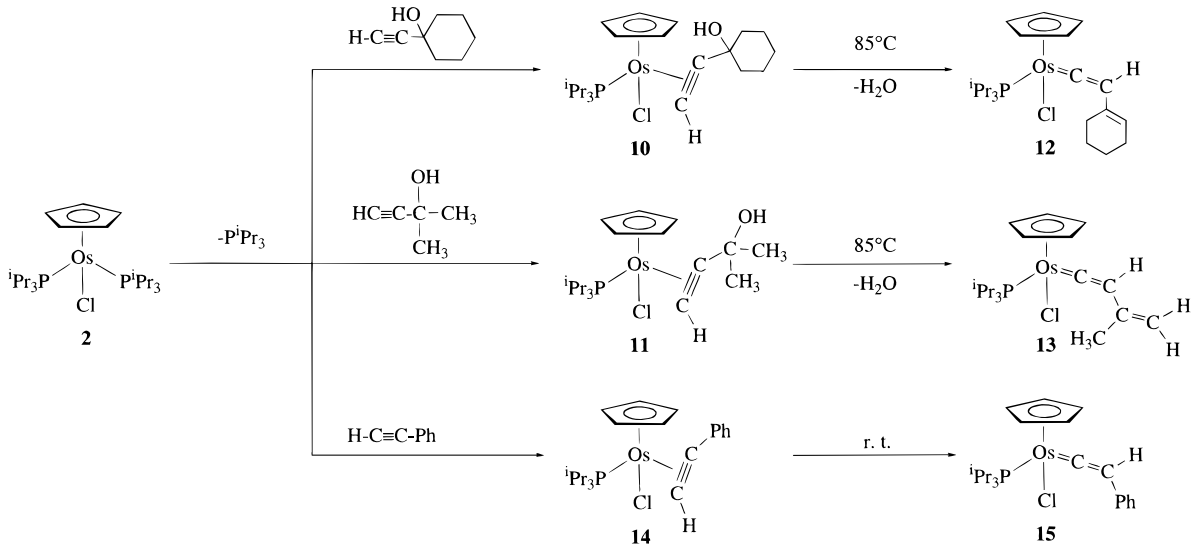
Scheme 3



the olefin ligand has a *cis*-stereochemistry. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances of the olefinic carbon atoms appear at 34.5 and 29.8 ppm, similar to the olefinic resonances of **7**, shifted toward high field by about 100 ppm in comparison with that found in the free olefin (129.8 ppm). The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 2.0 ppm.

Reactions of 2 with Alkynols and Terminal Alkynes: Synthesis of Alkenylvinylidene and Vinylidene Derivatives. The investigations aimed to elucidate the reactivity of complex **2** toward alkynols and terminal alkynes are summarized in Scheme 3. In agreement with the tendency shown by **2** to release a triisopropylphosphine ligand, the treatment of this compound with 1-ethynyl-1-cyclohexanol and 2-methyl-3-butyn-2-ol in pentane leads to the π-alkyne compounds $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HC{\equiv}C{-}\overline{C(OH)(CH_2)_4CH_2}\}(P^iPr_3)$ (**10**) and $Os(\eta^5\text{-}C_5H_5)Cl\{\eta^2\text{-}HC{\equiv}C{-}C(OH)(CH_3)_2\}(P^iPr_3)$ (**11**), which evolve to the corresponding alkenylvinylidene derivatives $Os(\eta^5\text{-}C_5H_5)Cl\{{=}C{=}CH{-}\overline{C{=}CH(CH_2)_3CH_2}\}(P^iPr_3)$ (**12**) and $Os(\eta^5\text{-}C_5H_5)Cl\{{=}C{=}CH{-}C(CH_3){=}CH_2\}(P^iPr_3)$ (**13**) by loss of a water molecule, in toluene at 85 °C.

The behavior of **2** toward 1-ethynyl-1-cyclohexanol and 2-methyl-3-butyn-2-ol agrees well with that previously observed for the carbonyl complex $Os(\eta^5\text{-}C_5H_5)Cl(CO)(P^iPr_3)$, which reacts with 1-ethynyl-1-cyclohexanol in the presence of $AgBF_4$ to give $[Os(\eta^5\text{-}C_5H_5)\{{=}C{=}CH{-}\overline{C{=}CH(CH_2)_3CH_2}\}(CO)(P^iPr_3)]BF_4$.[13] The formation of these alkenylvinylidene compounds most probably involves hydroxyvinylidene intermediates which spontaneously dehydrate. The dehydration of hydroxyvinylidenes, containing hydrogen atoms adjacent to the hydroxy group, can occur in two different directions to afford either alkenylvinylidene or allenylidene derivatives, mainly, depending on the electronic properties of the metallic center. The metallic fragments $[RuCl(\eta^6\text{-arene})(PR_3)]^+$ and $[Ru(\eta^5\text{-}C_5H_5)(CO)(P^iPr_3)]^+$, which are weak Lewis bases, appear to promote dehydration to allenylidene. Thus, Dixneuf has observed that in the presence of NH_4PF_6/MeOH, the reactions of $RuCl_2(\eta^6\text{-}C_6H_6)(PMe_3)$ with 1,1-dimethyl-2-propyn-1-ol and 1-ethynyl-1-cyclohexanol lead to α,β-unsaturated methoxycarbene compounds, via allenylidene intermediates.[22] In the same sense, we have recently reported that the solvato complex $[Ru(\eta^5\text{-}C_5H_5)\{\eta^1\text{-}OC(CH_3)_2\}(CO)(P^iPr_3)]BF_4$ reacts with 1-ethynyl-1-cyclohexanol to give the hydroxycarbene complex $[Ru(\eta^5\text{-}C_5H_5)\{C(OH)CH{=}\overline{C(CH_2)_4CH_2}\}(CO)(P^iPr_3)]BF_4$.[23] In contrast to these systems, the rich-electron fragments $[Ru(\eta^5\text{-}C_5H_5)(PMe_3)_2]^+$ [24] and $[RhCl(P^iPr_3)_2]_2$[25] preferentially afford alkenylvinylidene derivatives. The formation of **12** and **13** from **2** is in agreement with the previously mentioned strong Lewis base character of the $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)$ moiety, which could be a consequence of both the high basicity of the phosphine and the large π-donor power of the chlorine. Furthermore, it should be noted that osmium shows an intrinsically higher basicity than ruthenium.[26]

The π-alkyne complexes **10** and **11** were isolated as brown solids in 52% and 76% yield, respectively. The presence of the π-alkyne ligand in these compounds was mainly inferred from the $^{13}C\{^1H\}$ NMR spectra, which contains resonances at 71.8 and 53.1 (**10**) and 69.1 and 49.6 (**11**) ppm.

The alkenylvinylidene compounds **12** and **13** were isolated as red solids in 50% and 63% yield, respectively. In the $^{13}C\{^1H\}$ NMR spectra, the most noticeable resonances are those corresponding to the carbon atoms of the η^1-unsaturated ligand. In the spectrum of **12**, the resonance of the C_α carbon atom appears at 292.7 ppm as a doublet, with a P−C coupling constant of 13.4 Hz, whereas that corresponding to the C_β carbon atom is observed at 114.5 ppm as a singlet. The carbon atoms of the alkenyl group give rise to singlets at 126.2 and

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118.7 ppm. In the spectrum of **13**, the resonance of the C_α carbon atom appears at 291.4 ppm as a doublet, with a P−C coupling constant of 13.2 Hz, and the C_β atom is observed at 119.3 ppm as a singlet. The carbon atoms of the alkenyl group also display singlets, in this case at 134.2 and 103.7 ppm.

Complex **13** can be also prepared in 64% yield by reaction of **2** with 2-methyl-1-buten-3-yne at room temperature. In this case, a π-alkyne intermediate related to **10** and **11** was not detected, even at −60 °C. However, when the alkyne is phenylacetylene, the π-alkyne intermediate can be detected. Thus, after 5 min, the ^{1}H and ^{31}P{^{1}H} NMR spectra of the solution formed by addition of 1 equiv of phenylacetylene to **2** in benzene-d_6 show resonances corresponding to the starting complex **2**, the π-alkyne Os(η^5-C_5H_5)Cl(η^2-HC≡CPh)(P^iPr_3) (**14**), the vinylidene Os(η^5-C_5H_5)Cl(=C=CHPh)(P^iPr_3) (**15**), and free triisopropylphosphine. After 30 min, the spectra contain only resonances due to **2** and **15** in a 5:95 molar ratio and free triisopropylphosphine. From this solution the vinylidene complex **15** was isolated as a red solid in 64% yield, after benzene-d_6 removal and addition of pentane. The above-mentioned observations suggest that for 2-methyl-1-buten-3-yne and phenylacetylene the isomerization π-alkyne−vinylidene is faster than the substitution of the phosphine by the alkyne. However for the alkynols, the replacement of the phosphine seems to be favored. This could be a result of the presence of an OH group on the alkyne ligand, which should increase the π-acceptor capacity of the ligand and, therefore, the stability of the π-alkyne intermediate.

The π-alkyne−vinylidene transformation is generally viewed either as a 1,2-hydrogen shift or as a 1,3-hydrogen shift via hydrido−alkynyl intermediates.[27] Theoretical studies suggest that the use of energy to promote the concerted migration of the hydrido ligand from the metal to the β-carbon atom of the alkyne group in the 1,3-hydrogen shift is prohibitive.[28] However, experimental evidence suggest that the intermediacy of alkynyl(hydrido) complexes could also be possible in some cases.[25a,29] Thus, for example, Puerta has reported that the half-sandwich compound Ru(η^5-C_5Me_5)Cl(dippe) (dippe = 1,2-bis(diisopropylphosphino)ethane) reacts with terminal alkynes in methanol in the presence of $NaBPh_4$ yielding the metastable hydrido(alkynyl) derivatives [Ru(η^5-C_5Me_5)(H)(C≡CR)(dippe)]BPh_4, which are intermediates in the formation of the corresponding vinylidene complexes.[30] Very recently, theoretical calculations on Werner's system, RhCl(η^2-HC≡CR)(P^iPr_3)$_2$, appear to indicate that the isomerization proceeds via the oxidative addition products RhHCl(C≡CR)(P^iPr_3)$_2$, followed by a bimolecular hydrogen shift from the metal to the C_β alkynyl carbon atom of a second molecule.[31] During the isomerization of π-alkyne complex **14** into the vinylidene derivative **15**, we have not found spectroscopic evidence of the participation of a hydrido(alkynyl) intermediate, related to those reported by Puerta.

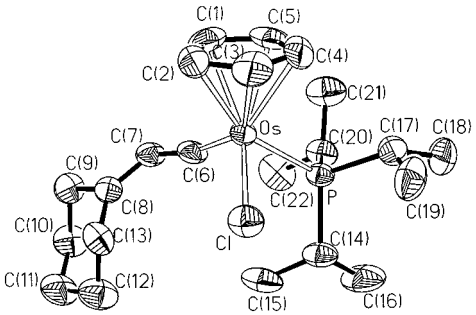
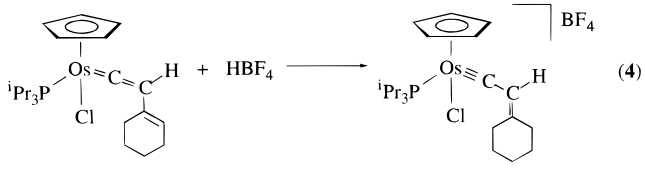


Figure 2. Molecular diagram of complex [Os(η^5-C_5H_5)Cl{≡C−CH=C(CH$_2$)$_4$CH$_2$}(P^iPr_3)]BF_4 (**16**). Thermal ellipsoids are shown at 50% probability.

Characteristic resonances of **14** are, in the ^{1}H NMR spectrum, a doublet at 8.18 ppm, with a P−H coupling constant of 7.8 Hz, assigned to the HC≡ proton and in the ^{31}P{^{1}H} NMR spectrum a relatively broad singlet at 11.5 ppm. The most noticeable feature in the ^{1}H NMR spectrum of **15** is a singlet at 2.83 ppm, corresponding to the =CH vinylidene proton. In the ^{13}C{^{1}H} NMR spectrum, the resonance corresponding to the C_α carbon atom of the vinylidene ligand appears at 291.6 ppm as a doublet with a P−C coupling constant of 13.6 Hz, whereas the resonance due to the C_β carbon atom is observed at 116.1 ppm as a singlet. The ^{31}P{^{1}H} NMR spectrum of **15** shows a singlet at 19.4 ppm.

Protonation of 12, 13, and 15: Synthesis of Alkenylcarbyne and Carbyne Derivatives. Treatment of complex **12** with a stoichiometric amount of HBF_4·OEt_2 in chloroform-*d* leads to the alkenylcarbyne compound [Os(η^5-C_5H_5)Cl{≡C−CH=C(CH$_2$)$_4$CH$_2$}(P^iPr_3)]BF_4 (**16**), which was isolated as a red solid in 90% yield, after solvent removal and addition of diethyl ether (eq 4). Complex **16** was characterized by elemental



analysis, IR and ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectroscopies, and an X-ray diffraction study. The molecular structure is presented in Figure 2, while selected bond distances and angles are listed in Table 1. The geometry around the osmium center is close to octahedral, with the cyclopentadienyl ligand occupying three sites of a face. The angles P−Os−Cl, P−Os−C(6), and Cl−Os−C(6) are 88.74(7)°, 94.1(3)°, and 104.8(3)°, respectively. The most conspicuous feature of the structure is the very short Os−C(6) bond length of 1.756(8)

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for [Os(η^5-C_5H_5)Cl-{≡C−CH=C(CH$_2$)$_4$CH$_2$}(P^{i}Pr$_3$)]BF$_4$ (16)

Bond Lengths			
Os−C(1)	2.217(8)	Os−P	2.374(2)
Os−C(2)	2.262(8)	Os−Cl	2.375(2)
Os−C(3)	2.350(8)	Os−C(6)	1.756(8)
Os−C(4)	2.348(8)	C(6)−C(7)	1.410(11)
Os−C(5)	2.203(8)	C(7)−C(8)	1.327(11)

Bond Angles			
P−Os−Cl	88.74(7)	Os−C(6)−C(7)	167.8(6)
P−Os−C(6)	94.1(3)	C(6)−C(7)−C(8)	123.7(8)
P−Os−G(1)[a]	125.5(3)	C(7)−C(8)−C(9)	121.4(8)
Cl−Os−C(6)	104.8(3)	C(7)−C(8)−C(13)	124.9(7)
Cl−Os−G(1)[a]	114.9(3)	C(9)−C(8)−C(13)	113.6(7)
C(6)−Os−G(1)[a]	122.3(4)		

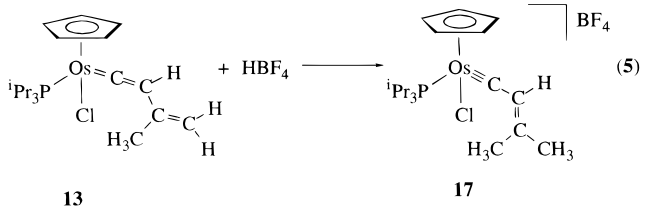
[a] G(1) is the midpoint of the C(1)−C(5) Cp ligand.

Å, which is fully consistent with a Os−C(6) triple bond formulation.[32] A slight bending in the Os−C(6)−C(7) moiety is also observed. The value of this angle (167.8(6)°) agrees well with those found in other carbyne−osmium derivatives.[33] The bond lengths and angles within the η^1-unsaturated ligand are consistent with the alkenylcarbyne proposal, e.g., C(6) and C(7) are separated by 1.410(11) Å and C(7) and C(8) by 1.327(11) Å, and the angles around C(7) and C(8) are in the range 121.4(8)−124.9(7)°. Similar values have been reported for related compounds.[34]

In agreement with the X-ray diffraction study, the $^{13}C\{^1H\}$NMR spectrum of **16** shows a doublet at 290.0 ppm with a P−C coupling constant of 10.1 Hz, corresponding to the sp-carbon atom of the alkenylcarbyne ligand. The resonances due to the sp^2-carbons appear at 187.2 and 134.6 ppm as singlets. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 33.6 ppm.

Although binuclear μ-alkenylcarbyne complexes are well-known,[35] the mononuclear alkenylcarbyne compounds are rare. Kolobova and co-workers[36] have reported that the protonation of the allenylidene complexes Mn(η^5-C_5H_5)(CO)$_2$(=C=C=CR$_2$) yields [Mn(η^5-C_5H_5)(CO)$_2$(≡C−CH=CR$_2$)]BF$_4$. In addition, related manganese,[34a,37] rhodium,[25a] and tungsten[34d] derivatives have been prepared using proton and methyl additions to alkenylvinylidenes. Werner[34c] and our group[10] have observed that some reactions of dihydrido−osmium(IV) complexes with alkynols also lead to derivatives of this type.

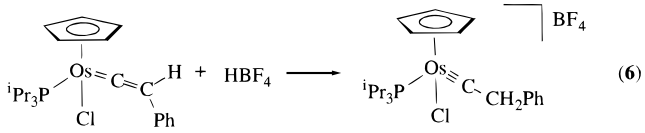
Similar to the reaction shown in eq 4, the protonation of complex **13** with a 1 equiv of HBF$_4$ affords [Os(η^5-C_5H_5)Cl{≡C−CH=C(CH$_3$)$_2$}(P^{i}Pr$_3$)]BF$_4$ (**17**), which was isolated as a red oil in quantitative yield (eq 5).



13 **17**

Complex **17** was characterized by MS analysis and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopies. In the ^1H NMR spectrum, the most noticeable resonances are three singlets at 5.45, 2.32, and 2.01 ppm, with a 1:3:3 intensity ratio, which were assigned to the CH= and methyl protons of the η^1-carbon ligand, respectively. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance due to the sp-carbon atom of the η^1-unsaturated ligand appears at 289.8 ppm as a doublet, with a P−C coupling constant of 10.6 Hz, whereas the resonances of the sp^2-carbon atoms are observed at 181.8 and 137.9 ppm as singlets. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 36.0 ppm.

Complex **2** is not only the starting point to prepare half-sandwich alkenylcarbyne−osmium complexes, but also allows one to obtain simple carbyne derivatives. Thus, the addition of a stoichiometric amount of HBF$_4$ to the vinylidene complex **15** gives [Os(η^5-C_5H_5)Cl(≡C−CH$_2$Ph)(P^{i}Pr$_3$)]BF$_4$ (**18**), which was isolated as a green solid in 90% yield (eq 6). The most characteristic



15 **18**

spectroscopic features of **18** are an AB spin system (δ_A = 3.92, δ_B = 3.52, and J(AB) = 19.9 Hz) for the CH_2−Ph protons in the ^1H NMR spectrum, a doublet with a P−C coupling constant of 9.8 Hz at 304.9 ppm for the sp-carbon atom in the $^{13}C\{^1H\}$ NMR spectrum, and a singlet at 38.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum.

Concluding Remarks

This study has revealed that Meyer's complex OsH$_2$Cl$_2$(P^{i}Pr$_3$)$_2$ is a useful starting material for the preparation of new cyclopentadienylosmium compounds including hydrido, dihydrido, π-olefin, π-alkyne, alkenylvinylidene, vinylidene, alkenylcarbyne, and carbyne derivatives. Thus, it reacts with cyclopentadienylthallium to give Os(η^5-C_5H_5)Cl(P^{i}Pr$_3$)$_2$, which is the starting point of the above-mentioned chemistry.

The chemical behavior of this complex seems to be a result of two factors: the high basicity of the metallic

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center, as a consequence of the presence of the strong donor phosphine and the chlorine ligands in the complex, and the large steric hindrance experienced by the triisopropylphosphine groups, which are mutually *cis* disposed. This mixture allows access to reactive points on the cyclopentadienylosmium center by activation of the Os−P and Os−Cl bonds. In polar solvents such as methanol and acetone, the dissociation of the chlorine ligand occurs and the resulting metallic fragment is capable of activating a methyl C−H bond of a triisopropylphosphine to give $OsH(\eta^5\text{-}C_5H_5)\{CH_2CH(CH_3)P^iPr_2\}(P^iPr_3)]^+$. On the other hand, in pentane and toluene, the splitting of a phosphorous−osmium bond is favored and the reactions of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ with olefins and alkynes lead to π-olefin and π-alkyne complexes. When the alkynes are 1-ethynyl-1-cyclohexanol and 2-methyl-3-butyn-2-ol, the π-alkyne complexes evolve by loss of a water molecule into the corresponding alkenylvinylidene compounds, in agreement with the rich-electron character of the metallic center. These alkenylvinylidene complexes afford alkenylcarbyne derivatives by protonation with $HBF_4{\cdot}OEt_2$.

In conclusion, we report the preparation of a labile cyclopentadienylosmium synthetic precursor, which is allowing the development of extensive organometallic chemistry in a little-known field.

Experimental Section

Physical Measurements. Infrared spectra were recorded as Nujol mulls on polyethylene sheets using a Nicolet 550 spectrometer. NMR spectra were recorded on a Varian UNITY 300, Varian GEMINI 2000 300 MHz, or on a Bruker ARX 300 spectrometer. ^1H 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 ($N = J(PH) + J(P'H)$) are given in Hertz. C, H analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. Mass spectra analyses were performed with a VG Auto Spec instrument. The ions were produced, FAB^+ mode, with the standard Cs^+ gun at *ca.* 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix.

Synthesis. All reactions were carried out with the exclusion of air using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use. The complex $OsH_2Cl_2(P^iPr_3)_2$ (**1**) was prepared according to the literature method.[6b]

Preparation of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (2). A solution of $OsH_2Cl_2(P^iPr_3)_2$ (1.2 g, 2.04 mmol) in 30 mL of toluene was treated with 566 mg (2.04 mmol) of cyclopentadienylthallium. The mixture was stirred for 2 h at room temperature and filtered through Kieselguhr. The resulting orange solution was concentrated to dryness. The product was extracted with 60 mL of pentane, which was filtered through Kieselguhr. The solution was concentrated to about 4 mL, and an orange precipitate was obtained. The solid was separated by decantation, and 3 mL of pentane was added. The suspension was stored at −78 °C for 30 min. The orange solid was separated by decantation and dried *in vacuo*: yield 650 mg (52%). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 4.73 (s, 5 H, Cp), 2.46 (m, 6 H, PCH), 1.22 (dvt, $J(HH) = 7.2$ Hz, $N = 12.0$ Hz, 18 H, $PCCH_3$), 1.13 (dvt, $J(HH) = 7.2$ Hz, $N = 12.0$ Hz, 18 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 293 K): δ −1.2 (s). Anal. Calcd for $C_{23}H_{47}ClOsP_2$: C, 45.19; H, 7.75. Found: C, 44.95; H, 7.20. MS (FAB^+): m/e 577 ($M^+ - Cl$).

Preparation of $[OsH(\eta^5\text{-}C_5H_5)\{CH_2CH(CH_3)P^iPr_2\}(P^iPr_3)]PF_6$ (3). A solution of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (128 mg, 0.21 mmol) in 10 mL of acetone was treated with 73.9 mg (0.21 mmol) of thallium hexafluorophosphate. The color of the solution changed from orange to yellow. After the mixture was stirred for 5 min at room temperature, the solution was filtered through Kieselguhr and concentrated to dryness. Addition of 6 mL of diethyl ether caused the precipitation of a white solid, which was separated by decantation, washed with diethyl ether and dried *in vacuo*: yield 130 mg (86%). IR (Nujol): ν(OsH) 2108 cm^{-1}; $\nu(PF_6)$ 838 cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 5.44 (s, 10 H, Cp), 3.22, 3.07 (both m, 1 H each), 2.76 (dt, $J(HH) = 9.9$ Hz, $J(PH) = 29.7$ Hz, 1 H), 2.54−2.04 (m, 4 H), 2.42 (m, 6 H, PCH P^iPr_3), 2.17, 1.97, 1.55 (all m, 1 H each), 1.51−1.13 (m, 66 H, CH_3), −13.81 (dd, $J(PH) = 36.0$ Hz, $J(PH) = 27.9$ Hz, 1 H, OsH), −13.98 (dd, $J(PH) = 38.0$ Hz, $J(PH) = 25.4$ Hz, 1 H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 8.0 (d, $J(PP) = 20.5$ Hz, vt in off resonance, P^iPr_3), 4.4 (d, $J(PP) = 23.9$ Hz, vt in off resonance, P^iPr_3), −33.1 (d, $J(PP) = 20.5$ Hz, vt in off resonance, $P^iPr_2CH(CH_3)CH_2$), −37.4 (d, $J(PP) = 23.9$ Hz, vt in off resonance, $P^iPr_2CH(CH_3)CH_2$), −144.8 (sept, $J(FP) = 713.6$ Hz, PF_6). $^{13}C\{^1H\}$ NMR (75.42 MHz, CD_2Cl_2, 293 K, plus APT): δ 84.2 (+, s, Cp), 84.1 (+, s, Cp), 49.9 (+, d, $J(PC) = 35.6$ Hz, $P^iPr_2CHCH_3$), 46.9 (+, d, $J(PC) = 36.0$ Hz, $P^iPr_2CHCH_3$), 34.8 (+, d, $J(PC) = 23.5$ Hz, PCH P^iPr_2), 34.7 (+, d, $J(PC) = 22.5$ Hz, PCH P^iPr_2), 31.1 (+, d, $J(PC) = 27.8$ Hz, PCH P^iPr_3), 29.3 (+, d, $J(PC) = 28.3$ Hz, PCH P^iPr_3), 28.7 (+, d, $J(PC) = 21.0$ Hz, PCH P^iPr_2), 26.4 (+, d, $J(PC) = 19.6$ Hz, PCH P^iPr_2), 24.7 (+, d, $J(PC) = 6.5$ Hz, $PCH(CH_3)CH_2$), 24.2 (+, d, $J(PC) = 6.3$ Hz, $PCH(CH_3)CH_2$), 21.7 (+, d, $J(PC) = 3.8$ Hz, $PCCH_3$), 20.9, 20.8 (+, both s, $PCCH_3$), 20.6 (+, d, $J(PC) = 3.0$ Hz, $PCCH_3$), 20.3 (+, s, $PCCH_3$), 20.2 (+, d, $J(PC) = 2.2$ Hz, $PCCH_3$), 19.1 (+, d, $J(PC) = 5.2$ Hz, $PCCH_3$), 18.8, 18.1 (+, both s, $PCCH_3$), −36.9 (−, dd, $J(PC) = 37.1$ Hz, $J(PC) = 9.3$ Hz, $OsCH_2$), −37.4 (−, dd, $J(PC) = 36.1$ Hz, $J(PC) = 9.2$ Hz, $OsCH_2$). Anal. Calcd for $C_{23}H_{47}F_6OsP_3$: C, 38.32; H, 6.57. Found: C, 38.03; H, 6.21. MS (FAB^+): m/e 577 (M^+).

Preparation of $OsH(\eta^5\text{-}C_5H_5)(P^iPr_3)_2$ (4). A solution of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (150 mg, 0.25 mmol) in 10 mL of toluene was treated with 94 mg (2.5 mmol) of $NaBH_4$ and, after 3 min, dropwise with 1.0 mL of methanol. After the mixture was stirred for 15 min at room temperature, the solution was filtered through Kieselguhr. The solvent was removed to dryness, and 10 mL of pentane was added. The yellow solution was filtered through Kieselguhr and concentrated to dryness. The product was isolated as a yellow oil. IR (toluene): ν(OsH) 2075 cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 293 K): δ 4.59 (s, 5 H, Cp), 1.91 (m, 6 H, PCH), 1.14 (dvt, $J(HH) = 6.6$ Hz, $N = 12.6$ Hz, 36 H, $PCCH_3$), −16.10 (t, $J(PH) = 31.1$ Hz, 1 H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, C_6D_6, 293 K): δ 29.4 (s, d in off resonance). MS (FAB^+): m/e 579 ($M^+ + H$).

Preparation of $[OsH_2(\eta^5\text{-}C_5H_5)(P^iPr_3)_2]BF_4$ (5). A solution of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (150 mg, 0.25 mmol) in 10 mL of toluene was treated with 94 mg (2.5 mmol) of $NaBH_4$ and, after 3 min, dropwise with 1.0 mL of methanol. After the mixture was stirred for 15 min at room temperature, the solution was filtered through Kieselguhr. The solvent was removed to dryness, and 10 mL of pentane was added. The yellow solution was filtered through Kieselguhr and concentrated to dryness. Over a diethyl ether solution (5 mL) of the yellow oil obtained, 33.5 μL (0.25 mmol) of HBF_4 was added, and a white solid precipitated. The white solid was separated by decantation, washed with diethyl ether, and dried *in vacuo*: yield 126.5 mg (76%). IR (Nujol): ν(OsH) 2146, 2203 cm^{-1}; $\nu(BF_4)$ 1030−1081 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 5.48 (s, 5 H, Cp), 2.06 (m, 6 H, PCH), 1.21 (dd, $J(HH) = 7.0$ Hz, $J(PH) = 14.2$ Hz, 36 H, $PCCH_3$), −14.26 (t, $J(PH) = 28.8$ Hz, 2 H, OsH). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$, 293 K): δ 32.2 (s, t in off resonance). Anal. Calcd for $C_{23}H_{49}BF_4OsP_2$: C, 41.56; H, 7.43. Found: C, 42.06; H, 7.28. MS (FAB^+): m/e 579 (M^+).

Preparation of $Os(\eta^5\text{-}C_5H_5)Cl\{P(OMe)_3\}(P^iPr_3)$ (6). A suspension of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (65 mg, 0.11 mmol) in 8 mL of pentane was treated with 12.5 μL (0.11 mmol) of

trimethyl phosphite. The mixture was stirred at room temperature for 7 h. The yellow solution was concentrated to dryness. Addition of 3 mL of pentane caused the precipitation of a yellow solid, which was separated by decantation and dried *in vacuo*: yield 22.8 mg (36%). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 4.80 (s, 5 H, Cp), 3.44 (d, J(PH) = 11.1 Hz, 9 H, OCH_3), 2.61 (m, 3 H, PCH), 1.19 (dd, J(HH) = 7.2 Hz, J(PH) = 12.9 Hz, 9 H, $PCCH_3$), 1.08 (dd, J(HH) = 7.2 Hz, J(PH) = 12.9 Hz, 9 H, $PCCH_3$). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 103.7 (d, J(PP) = 34.6 Hz, $P(OMe)_3$), 14.4 (d, J(PP) = 34.6 Hz, P^iPr_3). Anal. Calcd for $C_{17}H_{35}ClO_3OsP_2$: C, 35.50; H, 6.13. Found: C, 35.73; H, 6.06. MS (FAB$^+$): m/e 577 (M^+), 541 ($M^+ - Cl$).

Preparation of Os(η^5-C_5H_5)Cl{η^2-CH_2=CHC(O)CH_3}-(P^iPr_3) (7). A solution of Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$ (125 mg, 0.20 mmol) in 8 mL of toluene was treated with 18.4 μL (0.22 mmol) of methyl vinyl ketone. The mixture was heated at 85 °C for 15 h. After the sample was cooled to room temperature, the yellow solution obtained was filtered through Kieselguhr and concentrated to dryness. Addition of pentane caused the precipitation of a yellow solid, which was separated by decantation, washed with 3 mL of pentane, and dried *in vacuo*: yield 86.8 mg (83%). IR (Nujol): ν(CO) 1661 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 4.85 (s, 5 H, Cp), 4.17, 4.04 (AB part of ABMX system, J(AB) = 9.4 Hz, J(MA) = 2.5 Hz, J(MB) = 6.5 Hz, J(XA) = 2.5 Hz, J(XB) = 0 Hz, 2 H, *trans* protons, =CH), 2.53 (s, 3 H, CH_3), 2.26 (M part of ABMX system, J(BM) = 6.5 Hz, J(AM) = 2.5 Hz, J(XM) = 12.6 Hz, 1 H, $=CH_2$), 2.09 (m, 3 H, PCH), 0.93 (dd, J(HH) = 7.2 Hz, J(PH) = 13.8 Hz, 9 H, $PCCH_3$), 0.76 (dd, J(HH) = 7.2 Hz, J(PH) = 11.7 Hz, 9 H, $PCCH_3$). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 5.7 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 205.9 (−, s, −CO), 84.4 (+, d, J(PC) = 2.2 Hz, Cp), 46.7 (+, d, J(PC) = 1.4 Hz, =CH), 30.9 (+, s, CH_3), 22.9 (+, d, J(PC) = 27.1 Hz, PCH), 20.4 (+, s, $PCCH_3$), 19.6 (−, d, J(PC) = 5.0 Hz, $=CH_2$), 19.2 (+, d, J(PC) = 3.2 Hz, $PCCH_3$). Anal. Calcd for $C_{18}H_{32}ClOOsP$: C, 41.49; H, 6.19. Found: C, 40.94; H, 6.19. MS (FAB$^+$): m/e 523 (M^+), 487 ($M^+ - Cl$).

Preparation of Os(η^5-C_5H_5)Cl{η^2-C(CO_2CH_3)≡CCO_2-CH_3}(P^iPr_3) (8). A solution of Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$ (118 mg, 0.19 mmol) in 8 mL of toluene was treated with 23.6 μL (0.19 mmol) of dimethyl acetylenedicarboxylate and stirred at room temperature for 45 min. After removal of the solvent, the addition of pentane caused the precipitation of a brown solid. The solid was separated by decantation, washed with 4 mL of pentane and dried *in vacuo*: yield 82.3 mg (73%). IR (Nujol): ν(C≡C) 1825 cm^{-1}; ν(C=O) 1705, 1683 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 5.20 (s, 5 H, Cp), 3.59, 3.38 (both s, 3 H each, OCH_3), 2.46 (m, 3 H, PCH), 1.05 (dd, J(HH) = 7.2 Hz, J(PH) = 13.9 Hz, 9 H, $PCCH_3$), 0.88 (dd, J(HH) = 7.2 Hz, J(PH) = 12.3 Hz, 9 H, $PCCH_3$). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 17.3 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K): δ 164.1, 161.2 (both s, CO_2CH_3), 84.2 (d, J(PC) = 3.2, Cp), 70.2 (br s, −C≡), 69.8 (d, J(PC) = 8.3 Hz, −C≡), 51.7, 51.5 (both s, CO_2CH_3), 22.8 (d, J(PC) = 28.0 Hz, PCH), 19.8 (s, $PCCH_3$), 18.6 (d, J(PC) = 3.0 Hz, $PCCH_3$). Anal. Calcd for $C_{20}H_{32}ClO_4OsP$: C, 40.50; H, 5.43. Found: C, 40.08; H, 5.48. MS (FAB$^+$): m/e 558 ($M^+ - H - Cl$).

Preparation of Os(η^5-C_5H_5)Cl{η^2-(*Z*)-CH($CO_2C_2H_5$)=CH$CO_2C_2H_5$}(P^iPr_3) (9). A solution of Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$ (125 mg, 0.20 mmol) in 10 mL of toluene was treated with 64.5 μL (0.60 mmol) of ethyl diazoacetate. The sample was stirred at room temperature for 15 h. The dark yellow solution obtained was filtered through Kieselguhr and concentrated to dryness. Twenty milliliters of pentane was added, and the yellow solution was filtered through Kieselguhr and concentrated until a yellow solid began to precipitate. After the suspension was kept at −78 °C for 1 h, the yellow solid was separated by decantation and dried *in vacuo*: yield 64.7 mg (52%). IR (Nujol): ν(CO) 1718, 1702 cm^{-1}; ν(C=C) 1622 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 5.40 (s, 5 H, Cp), 4.35, 4.31 (AB part of ABX spin system, J(AB) = 9.9 Hz, J(XA) = 4.3 Hz, J(XB) = 4.3 Hz, 2 H, =CH), 4.26−3.93 (m, 4 H, CH_2), 2.07 (m, 3 H, PCH), 1.14, 1.08 (both t, J(HH) = 7.2 Hz, 3 H each, CH_3), 0.92 (dd, J(HH) = 7.3 Hz, J(PH) = 14.0 Hz, 9 H, $PCCH_3$), 0.82 (dd, J(HH) = 7.1 Hz, J(PH) = 11.8 Hz, 9 H, $PCCH_3$). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 2.0 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K): δ 176.7, 176.5 (both s, $CO_2CH_2CH_3$), 86.9 (d, J(PC) = 2.3 Hz, Cp), 60.4, 59.9 (both s, $CO_2CH_2CH_3$), 34.5, 29.8 (both br s, =CH), 23.6 (d, J(PC) = 26.6 Hz, PCH), 20.6 (s, $PCCH_3$), 19.2 (d, J(PC) = 2.3 Hz, $PCCH_3$), 14.8, 14.3 (both s, $CO_2CH_2CH_3$). Anal. Calcd for $C_{22}H_{38}ClO_4OsP$: C, 42.47; H, 6.14. Found: C, 42.87; H, 5.89. MS (FAB$^+$): m/e 625 ($M^+ + 2$ H), 589 ($M^+ - Cl + H$).

Preparation of Os(η^5-C_5H_5)Cl{η^2-HC≡C−$\overline{C(OH)(CH_2)_4C}$-$H_2$}($P^iPr_3$) (10). A suspension of Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$ (125 mg, 0.20 mmol) in 15 mL of pentane was treated with 28 mg (0.20 mmol) of 1-ethynyl-1-cyclohexanol. After the mixture was stirred for 30 min at room temperature, the red solution obtained was filtered through Kieselguhr and concentrated to dryness. Addition of 3 mL of pentane caused the precipitation of a brown solid, which was separated by decantation and dried *in vacuo*: yield 56.2 mg (52%). IR (toluene): ν(C≡C) 1869 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 5.42 (br s, 1 H, OH), 4.99 (s, 5 H, Cp), 3.88 (d, J(PH) = 9.0 Hz, 1 H, ≡CH), 2.39 (m, 3 H, PCH), 2.12−1.20 (m, 10 H, Cy), 0.93 (dd, J(HH) = 7.2 Hz, J(PH) = 12.9 Hz, 18 H, $PCCH_3$). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 9.5 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 79.8 (+, d, J(PC) = 2.3 Hz, Cp), 71.8 (−, d, J(PC) = 10.6 Hz, ≡C−), 53.3 (+, br, ≡CH), 39.9 (−, s, −C(OH)), 26.0, 25.3, 23.5, 23.1 (−, all s, Cy), 24.1 (+, d, J(PC) = 28.1 Hz, PCH), 19.6 (+, s, $PCCH_3$). MS (FAB$^+$): m/e 541 ($M^+ - Cl$). Elemental analysis was not available because of the high instability of the product out of the argon atmosphere.

Preparation of Os(η^5-C_5H_5)Cl{η^2-HC≡C−C(CH_3)$_2$(OH)}-(P^iPr_3) (11). A suspension of Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$ (125 mg, 0.20 mmol) in 10 mL of pentane was treated with 21.2 μL (0.21 mmol) of 2-methyl-3-butyn-2-ol. The color of the solution changed from orange to red, and a brown solid began to precipitate. After the mixture was stirred for 30 min at room temperature, the brown solid was separated by decantation, washed with 4 mL of pentane, and dried *in vacuo*: yield 81.5 mg (76%). IR (Nujol): ν(OH) 3162 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 5.26 (s, 1 H, OH), 4.97 (s, 5 H, Cp), 3.72 (d, J(PH) = 8.4 Hz, 1 H, ≡CH), 2.38 (m, 3 H, PCH), 1.90 (br, 6 H, CH_3), 0.92 (dd, J(HH) = 7.5 Hz, J(PH) = 12.9 Hz, 18 H, $PCCH_3$). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 9.5 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K): 80.2 (s, Cp), 69.1 (br, ≡C−), 49.6 (br, ≡CH), 35.1 (br, −C(OH)), 24.3 (d, J(PC) = 27.7 Hz, PCH), 22.7 (s, CH_3), 19.8 (s, $PCCH_3$), 14.2 (s, CH_3). Anal. Calcd for $C_{19}H_{34}ClOOsP$: C, 42.64; H, 6.40. Found: C, 42.78; H, 6.42. MS (FAB$^+$): m/e 501 ($M^+ - Cl$)

Preparation of Os(η^5-C_5H_5)Cl{=C=CH−$\overline{C=CH(CH_2)_3C}$-H_2}(P^iPr_3) (12). A solution of Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$ (150 mg, 0.25 mmol) in 8 mL of toluene was treated with 33.5 mg (0.27 mmol) of 1-ethynyl-1-cyclohexanol. The mixture was heated at 85 °C for 15 h, and a red solution was obtained. The resulting red solution was cooled to room temperature and filtered through Kieselguhr. The solution was concentrated to dryness, and 8 mL of methanol was added. The solvent was partially evaporated until a red solid began to precipitate, and the suspension was stored at −78 °C for 1 h. The red solid was separated by decantation and dried *in vacuo*: yield 69.6 mg (50%). IR (Nujol): ν(=C=C) 1635, 1613 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ 5.47 (s, 5 H, Cp), 4.83 (br s, 1 H, $C=CH(CH_2)_3CH_2$), 2.76 (m, 3 H, PCH), 2.44 (br, 2 H, $-CH_2$ Cy), 2.30 (s, 1 H, =C=CH), 2.05 (m, 2 H, $-CH_2$ Cy), 1.60 (m, 2 H, $-CH_2$ Cy), 1.52 (m, 2 H, $-CH_2$ Cy), 1.19 (dd, J(HH) = 7.2 Hz, J(PH) = 14.4 Hz, 9 H, $PCCH_3$), 1.14 (dd, J(HH) = 7.2 Hz, J(PH) = 14.4 Hz, 9 H, $PCCH_3$). ^{31}P{^{1}H} NMR (121.42 MHz, $CDCl_3$, 293 K): δ 18.5 (s). ^{13}C{^{1}H} NMR (75.42

Table 2. Crystal Data and Data Collection and Refinement for $[Os(\eta^5\text{-}C_5H_5)Cl\{\equiv C-CH=C(CH_2)_4CH_2\}(P^iPr_3)]BF_4$ (16)

Crystal Data			
formula	$C_{22}H_{37}BClF_4OsP$	c, Å	13.250(2)
mol wt	644.95	α, deg	87.27(2)
color and habit	orange, irregular prism	β, deg	68.68(1)
cryst size, mm	0.21 × 0.13 × 0.25	γ, deg	85.57(1)
symmetry	triclinic	V, Å^3	1276.6(3)
space group	$P\bar{1}$ (No. 2)	Z	2
a, Å	9.805(1)	D_{calcd}, g cm^{-3}	1.678
b, Å	10.582(2)		

Data Collection and Refinement			
diffractometer	four-circle Siemens-STOE AED	no. of data collcd	7043
λ(Mo Kα), Å; technique	0.710 73; bisecting geometry	no. of unique data	4502 (R_{int} = 0.0335)
monochromator	graphite oriented	no. of params refined	272
μ, mm^{-1}	5.20	R1[a] ($F^2 > 2\sigma(F^2)$)	0.0412
scan type	$\omega/2\theta$	wR2[b] (all data)	0.0964
2θ range, deg	$3 \le 2\theta \le 50$	S[c] (all data)	1.034
temp, K	200		

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

MHz, $CDCl_3$, 293 K, plus APT): δ 292.7 (−, d, J(PC) = 13.4 Hz, Os=C), 126.2 (−, s, C=CH(CH$_2$)$_3$CH$_2$), 118.7 (+, s, C=CH-(CH$_2$)$_3$CH$_2$), 114.5 (+, s, =C=CH), 87.3 (+, d, J(PC) = 2.3 Hz, Cp), 28.0, 24.9, 22.9, 22.7 (−, all s, Cy), 24.6 (+, d, J(PC) = 29.5 Hz, PCH), 19.5, 19.4 (+, both s, PCCH$_3$). Anal. Calcd for $C_{22}H_{36}ClOsP$: C, 47.42; H, 6.51. Found: C, 47.59; H, 5.97. MS (FAB$^+$): m/e 558 (M$^+$).

Preparation of $Os(\eta^5\text{-}C_5H_5)Cl\{=C=CH-C(CH_3)=CH_2\}(P^iPr_3)$ (13). Method A. A solution of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (125 mg, 0.20 mmol) in 8 mL of toluene was treated with 21.2 μL (0.21 mmol) of 2-methyl-3-butyn-2-ol. The mixture was heated at 85 °C for 20 h, and a red solution was obtained. The resulting red solution was cooled to room temperature and filtered through Kieselguhr. The solution was concentrated to dryness, and 20 mL of pentane was added. The solution was filtered through Kieselguhr. The solvent was partially evaporated until a red solid began to precipitate, and the suspension was stored at −78 °C for 1 h. The red solid was separated by decantation and dried *in vacuo*: yield 65.1 mg (63%).

Method B. A suspension of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (150 mg, 0.25 mmol) in 20 mL of pentane was treated with 23.4 μL (0.25 mmol) of 2-methyl-1-buten-3-yne. The mixture was stirred at room temperature for 3 h, and a red solution was obtained, which was filtered through Kieselguhr. The solvent was partially evaporated until a red solid began to precipitate, and the suspension was stored at −78 °C for 1 h. The red solid was separated by decantation and dried *in vacuo*: yield 82.7 mg (64%). IR (Nujol): ν(=C=C) 1613 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 5.09 (s, 5 H, Cp), 4.55, 4.05 (both s, 1 H each, =CH$_2$), 2.75 (s, 1 H, =CH), 2.58 (m, 3 H, PCH), 2.21 (s, 3 H, CH$_3$), 1.05 (dd, J(HH) = 7.2 Hz, J(PH) = 13.8 Hz, 9 H, PCCH$_3$), 0.92 (dd, J(HH) = 7.2 Hz, J(PH) = 13.5 Hz, 9 H, PCCH$_3$). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 19.1 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K, plus APT): δ 291.4 (−, d, J(PC) = 13.2 Hz, Os=C), 134.2 (−, s, CH−C=CH$_2$), 119.3 (+, s, CH−C=CH$_2$), 103.7 (−, s, CH−C=CH$_2$), 87.6 (+, d, J(PC) = 1.5 Hz, Cp), 24.9 (+, d, J(PC) = 29.4 Hz, PCH), 22.7 (+, s, CH$_3$), 19.6, 19.5 (+, both s, PCCH$_3$). Anal. Calcd for $C_{19}H_{32}ClOsP$: C, 44.13; H, 6.23. Found: C, 44.41; H, 6.50. MS (FAB$^+$): m/e 519 (M$^+$ + H).

Preparation of $Os(\eta^5\text{-}C_5H_5)Cl\{=C=CHPh\}(P^iPr_3)$ (15). A solution of $Os(\eta^5\text{-}C_5H_5)Cl(P^iPr_3)_2$ (150 mg, 0.25 mmol) in 20 mL of pentane was treated with 25.0 μL (0.25 mmol) of phenylacetylene. The mixture was stirred at room temperature for 3 h. The red solution obtained was filtered through Kieselguhr and concentrated to dryness. Addition of 4 mL of pentane caused the precipitation of a red solid, which was separated by decantation and dried *in vacuo*: yield 88.5 mg (64%). IR (Nujol): ν(=C=C) 1619 cm^{-1}; ν(Ph) 1592 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 7.48 (d, J(HH) = 7.5 Hz, 2 H, *o*-Ph), 7.25 (vt, J(HH) = 7.8 Hz, J(HH) = 7.8 Hz, 2 H, *m*-Ph), 6.83 (vt, J(HH) = 7.5 Hz, J(HH) = 7.5 Hz, 1 H, *p*-Ph), 5.11 (s, 5 H, Cp), 2.83 (s, 1 H, =CH), 2.57 (m, 3 H, PCH), 0.99 (dd, J(HH) = 7.2 Hz, J(PH) = 13.8 Hz, 9 H, PCCH$_3$), 0.92 (dd, J(HH) = 7.5 Hz, J(PH) = 13.5 Hz, 9 H, PCCH$_3$). ^{31}P{^{1}H} NMR (121.42 MHz, C_6D_6, 293 K): δ 19.4 (s). ^{13}C{^{1}H} NMR (75.42 MHz, C_6D_6, 293 K): δ 291.6 (d, J(PC) = 13.6 Hz, Os=C), 131.0, 128.5, 125.0, 124.3 (all s, Ph), 116.1 (s, =CH), 87.8 (d, J(PC) = 2.3 Hz, Cp), 24.95 (d, J(PC) = 29.5 Hz, PCH), 20.1 (s, PCCH$_3$), 19.7 (d, J(PC) = 1.0 Hz, PCCH$_3$). Anal. Calcd for $C_{22}H_{32}ClOsP$: C, 47.77; H, 5.83. Found: C, 47.64; H, 6.09. MS (FAB$^+$): m/e 554 (M$^+$).

Preparation of $[Os(\eta^5\text{-}C_5H_5)Cl\{\equiv C-CH=C(CH_2)_4CH_2\}(P^iPr_3)]BF_4$ (16). A solution of $Os(\eta^5\text{-}C_5H_5)Cl\{=C=CH-C=CH(CH_2)_3CH_2\}(P^iPr_3)$ (37.6 mg, 0.07 mmol) in 0.5 mL of $CDCl_3$ was treated with 9.2 μL (0.07 mmol) of HBF_4. After 2 min at room temperature, the NMR spectra showed only the presence of the compound $[Os(\eta^5\text{-}C_5H_5)Cl\{\equiv C-CH=C(CH_2)_4CH_2\}(P^iPr_3)]BF_4$. The red solution was then transferred to a Schlenk tube and concentrated to dryness. The addition of diethyl ether caused the precipitation of a red solid, which was separated by decantation, washed with diethyl ether, and dried *in vacuo*: yield 40.6 mg (90%). IR (Nujol): $\nu(BF_4)$ 1103−1020 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): δ 6.14 (s, 5 H, Cp), 5.59 (s, 1 H, =CH), 2.81 (br, 2 H, −CH$_2$ Cy), 2.65 (m, 3 H, PCH), 2.29 (br, 2 H, −CH$_2$ Cy), 1.81 (br, 2 H, −CH$_2$ Cy), 1.62 (br, 4 H, −CH$_2$ Cy),1.29 (dd, J(HH) = 6.9 Hz, J(PH) = 15.0 Hz, 9 H, PCCH$_3$), 1.27 (dd, J(HH) = 6.6 Hz, J(PH) = 15.3 Hz, 9 H, PCCH$_3$). ^{31}P{^{1}H} NMR (121.42 MHz, $CDCl_3$, 293 K): δ 33.6 (s). ^{13}C{^{1}H} NMR (75.42 MHz, $CDCl_3$, 293 K, plus APT): δ 290.0 (−, d J(PC) = 10.1 Hz, Os≡C), 187.2 (−, s, CH=C(CH$_2$)$_4$CH$_2$), 134.6 (+, s, CH=C-(CH$_2$)$_4$CH$_2$), 94.1 (+, s, Cp), 37.4, 34.1, 28.4, 28.3 (−, all s, CH$_2$ Cy), 27.3 (+, d, J(PC) = 29.4 Hz, PCH), 25.1 (−, s, −CH$_2$ Cy), 19.5 (+, s, PCCH$_3$), 19.1 (+, d, J(PC) = 2.8 Hz, PCCH$_3$). Anal. Calcd for $C_{22}H_{37}BF_4ClOsP$: C, 40.97; H, 5.78. Found: C, 41.09; H, 5.70. MS (FAB$^+$): m/e 559 (M$^+$).

Preparation of $[Os(\eta^5\text{-}C_5H_5)Cl\{\equiv C-CH=C(CH_3)_2\}(P^iPr_3)]BF_4$ (17). A solution of $Os(\eta^5\text{-}C_5H_5)Cl\{=C=CH-C(CH_3)=CH_2\}(P^iPr_3)$ (31.3 mg, 0.06 mmol) in 0.5 mL of CD_2Cl_2 was treated with 8.2 μL (0.06 mmol) of HBF_4. After 2 min at room temperature, the NMR spectra showed only the presence of the compound $[Os(\eta^5\text{-}C_5H_5)Cl\{\equiv C-CH=C(CH_3)_2\}(P^iPr_3)]BF_4$. The product was isolated as a red oil. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 6.12 (s, 5 H, Cp), 5.45 (br s, 1 H, =CH),

2.66 (m, 3 H, PCH), 2.32, 2.01 (both s, 3 H each, CH_3), 1.34−1.24 (m, 18 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, CD_2Cl_2, 293 K): δ 36.0 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, $CDCl_3$, 293 K, plus APT): δ 289.8 (−, d, J(PC) = 10.6 Hz, Os≡C), 181.8 (−, s, −CH=*C*), 137.9 (+, s, −*C*H=C), 94.6 (+, s, Cp), 27.8 (+, d, J(PC) = 29.9 Hz, PCH), 27.5, 24.1 (+, both s, CH_3), 19.0 (+, s, PC*C*H_3), 19.4 (+, d, J(PC) = 3.0 Hz, PC*C*H_3). MS (FAB^+): *m*/*e* 519 (M^+).

Preparation of [Os(η^5-C_5H_5)Cl(≡C−CH_2Ph)(P^iPr_3)]BF_4 (18). A solution of Os(η^5-C_5H_5)Cl{=C=CHPh}(P^iPr_3) (37.9 mg, 0.07 mmol) in 0.5 mL of $CDCl_3$ was treated with 9.4 μL (0.07 mmol) of HBF_4. After 2 min at room temperature, the color of the solution changed from red to green and the NMR spectra showed only the presence of the compound [Os(η^5-C_5H_5)Cl(≡C−CH_2Ph)(P^iPr_3)]BF_4. The green solution was then transferred to a Schlenk tube and concentrated to dryness. The addition of diethyl ether caused the precipitation of a green solid, which was separated by decantation, washed with diethyl ether, and dried *in vacuo*: yield 39.5 mg (90%). IR (Nujol): $\nu(BF_4)$ 1061 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.39−7.30 (m, 5 H, Ph), 6.10 (s, 5 H, Cp), 3.92, 3.52 (AB spin system, J(AB) = 19.9 Hz, 2 H, $-CH_2$), 2.61 (m, 3 H, PCH), 1.30 (dd, J(HH) = 6.9 Hz, J(PH) = 10.2 Hz, 9 H, $PCCH_3$), 1.25 (dd, J(HH) = 7.2 Hz, J(PH) = 11.4 Hz, 9 H, $PCCH_3$). $^{31}P\{^1H\}$ NMR (121.42 MHz, $CDCl_3$, 293 K): δ 38.3 (s). $^{13}C\{^1H\}$ NMR (75.42 MHz, $CDCl_3$, 293 K, plus APT): δ 304.9 (−, d, J(PC) = 9.8 Hz, Os≡C), 129.9, 129.7, 128.7 (+, all s, Ph), 127.9 (−, s, C_{ipso} Ph), 95.0 (+, s, Cp), 62.08 (−, s, CH_2), 27.4 (+, d, J(PC) = 29.5 Hz, PCH), 20.0 (+, s, PC*C*H_3), 19.2 (+, d, J(PC) = 2.7 Hz, PC*C*H_3). Anal. Calcd for $C_{22}H_{33}BF_4ClOsP$: C, 41.22; H, 5.14. Found: C, 41.19; H, 5.44. MS (FAB^+): *m*/*e* 555 (M^+).

X-ray Structure Analysis of Complex [Os(η^5-C_5H_5)Cl{≡C−CH=C(CH_2)$_4$$CH_2$}($P^iPr_3$)]$BF_4$ (16). Crystals suitable for the X-ray diffraction study were obtained by slow diffusion of ether into a concentrated solution of **16** in CH_2Cl_2. A summary of the crystal data and refinement parameters is reported in Table 2. The orange irregular crystal, of approximate dimensions 0.21 × 0.13 × 0.25 mm, was glued on a glass fiber and mounted on a Siemens-STOE AED-2 diffractometer. A group of 87 reflections in the range 20° ≤ 2θ ≤ 35° were carefully centered at 200 K and used by least-squares methods to obtain the unit cell dimensions. A total of 7043 reflections were measured, from which 4502 unique reflections (R_{merg} = 0.03) were used in the refinement. Three standard reflections were monitored at periodic intervals throughout data collection: no significant variations were observed. All data were corrected for absorption using a semiempirical method.[38] The structure was solved by Patterson (Os atom, SHELXTL-PLUS[39]) and conventional Fourier techniques, and refined by full-matrix least-squares on F^2 (SHELXL93[40]). Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were calculated (C−H = 0.96 Å) and refined riding on carbon atoms with a common isotropic thermal parameter. Atomic scattering factors, corrected for anomalous dispersion for Os and P, were implemented by the program. The refinement converged to R1 = 0.0412 ($F^2 > 2\sigma(F^2)$) and wR2 = 0.0964 (all data), with weighting parameters x = 0.0562 and y = 0.

All assays for preparing monocrystals of **9** were unsuccessful. The only apparently suitable crystal was grown in a saturated solution of complex **9** in pentane left at 253 K for several days. The structure was solved by Patterson (Os atom, SHELXTL-PLUS[39]) and conventional Fourier techniques and refined by full-matrix least-squares on F^2 (SHELXL93[40]). Further refinement, with anisotropic thermal parameters, was not allowed because of the low quality of the data.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray study, bond distances and angles, and interatomic distances for **16** (8 pages). Ordering information is given on any current masthead page.

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