

An Osmium-Carbene Complex with Fischer–Schrock Ambivalent Behavior

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Complex $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)_2$ (**1**) reacts with N_2CHPh to give the carbene derivative $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(=\text{CHPh})\text{Cl}(\text{P}^i\text{Pr}_3)$ (**2**). Complex **2** affords the carbene-plus-organic fragment coupling products $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-CHPhC}_6\text{H}_5)(\text{P}^i\text{Pr}_3)$ (**3**), $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)(\text{CH}_2=\text{CHPh})(\text{P}^i\text{Pr}_3)$, (**4**) and $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\{\eta^2\text{-}(E)\text{-CHPh}=\text{CHCH}=\text{CH}_2\}(\text{P}^i\text{Pr}_3)$ (**5**) by reaction with PhLi , MeLi , and $\text{CH}_2=\text{CHCH}_2\text{MgCl}$, respectively. In solution, the phenyl groups of **3** exchange their positions. The fluxional process takes place via an alkyl intermediate, which can be trapped as $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\text{CHPh}_2)(\text{CO})(\text{P}^i\text{Pr}_3)$ (**6**) under CO atmosphere. In toluene at 60 °C, complex **5** evolves into its allyl isomer $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\{\eta^3\text{-CH}_2\text{CHCH}(\text{CH}_2\text{Ph})\}(\text{P}^i\text{Pr}_3)$ (**7**). Complex **2** also reacts with HBF_4 and NaOCH_3 . The reaction with HBF_4 leads to $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**8**), which loses HCl to give the hydride-carbyne derivative $[\text{OsH}(\eta^5\text{-C}_5\text{H}_5)(\equiv\text{CPh})(\text{P}^i\text{Pr}_3)]^+$ (**9**), while the reaction with NaOCH_3 affords the carbyne compound $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\equiv\text{CPh})(\text{P}^i\text{Pr}_3)$ (**10**). In methanol as solvent, complex **10** evolves into the hydride-alkoxycarbene species $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{OMe})\text{Ph}\}(\text{P}^i\text{Pr}_3)$ (**11**). The reaction of **10** with phenol in pentane leads to $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\{\text{CH}(\text{Ph})\text{OC}_6\text{H}_4\}(\text{P}^i\text{Pr}_3)$ (**12**). The X-ray structures of **3**, **5**, **7**, **9**, and **12** are also reported.

Introduction

Transition-metal carbene complexes are one of the most useful tools in organic synthesis and homogeneous catalysis, including cyclopropanation reactions, olefin metathesis, and Fischer–Tropsch synthesis.¹

These compounds have been divided into two classes: the Fischer-type and the Schrock-type.²

Fischer-type complexes are viewed as a singlet-state carbene donating to the metal from its sp^2 -hybrid orbital, with a corresponding amount of back-donation from the metal to the empty π orbital. The distances between the carbene-carbon and its substituents (heteroatoms or phenyl groups) are short relative to single bonds. They contain a metal from groups VI to VIII, which is present in a low oxidation state, and it is stabilized by a series of other ligands with pronounced acceptor properties.

Complexes of the Schrock-type are viewed as a triplet-state carbene spin-coupled to two electrons on the metal

center.³ These compounds contain an early transition metal in high oxidation state and have hydrogen or alkyl substituents on the carbene.

In the Fischer-type complexes the π electrons appear to be polarized toward the metal, while in the complexes of the Schrock-type the π electrons appear to be nearly equally distributed.^{3a} This electronic situation is in agreement with the observed dichotomy in behavior between these systems. Characteristic of the Fischer-type derivatives is the electrophilicity of the carbene-carbon atom, which is the preferred site of attack for nucleophilic reagents, while, in contrast to the Fischer carbenes, electrophiles add to the carbene-carbon of the Schrock-type. Likewise, strong bases result in deprotonation of the carbene-carbon atom.⁴

One of the most significant recent developments in the area of carbene chemistry has been the synthesis of the ruthenium carbene complexes $\text{RuCl}_2(=\text{CR}_2)(\text{PR}'_3)_2$ and their use as olefin metathesis catalysts.⁵ Since the advent of these systems, a great deal of interest has been given to the synthesis of carbene derivatives of the iron triad with non-Fischer-type substituents.⁶ Various osmium(0) and osmium(II) compounds containing an $\text{Os}=\text{CR}_2$ unit have been prepared;⁷ however, half-sandwich-type osmium complexes with a carbene ligand are very scarce.⁸ Despite the carbene ligands bearing

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no stabilizing heteroatoms, these compounds are generally viewed as Fischer-type derivatives.

We have previously reported overwhelming evidence showing that the complex $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)_2$ is a useful starting material for the development of the osmium-cyclopentadienyl chemistry.^{8b,9} The large steric hindrance experienced by the triisopropylphosphine groups, which are mutually *cis* disposed, labilizes an Os–P bond. As a result, this complex reacts with weak donor ligands, including olefins, alkynes, molecular

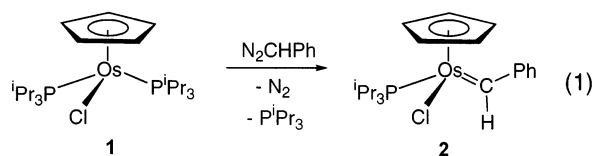
hydrogen, or group 14 element hydride compounds, to give a wide range of novel organometallic derivatives. Recently, we have observed that complex $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)_2$ also reacts with phenyldiazomethane, to afford $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(=\text{CHPh})\text{Cl}(\text{P}^i\text{Pr}_3)$.

The easy accessibility to this compound prompted us to investigate the electrophilicity or nucleophilicity of the carbene-carbon of the new derivative, as a part of our work on the capacity of the osmium–carbon multiple bonds to promote carbon–carbon and carbon–heteroatom coupling reactions.¹⁰ In this paper, we report the Fischer–Schrock ambivalent nature of $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(=\text{CHPh})\text{Cl}(\text{P}^i\text{Pr}_3)$.

Results and Discussion

Preparation of $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(=\text{CHPh})\text{Cl}(\text{P}^i\text{Pr}_3)$.

Treatment of a toluene solution of $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)_2$ (**1**) with a toluene solution of phenyldiazomethane at room temperature produces a rapid evolution of gas (N_2) and a change of color in the starting solution from orange to green. Removal of the solvent and recrystallization of the residue from hexane affords complex $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(=\text{CHPh})\text{Cl}(\text{P}^i\text{Pr}_3)$ (**2**) as a dark blue solid in about 70% yield (eq 1).



We note that recently the synthesis of the related ruthenium complex $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{C}=\text{CPh}_2)(\text{PPh}_3)$ has been reported. In contrast to **2**, the formation of this compound requires higher temperature and a large excess of N_2CPh_2 , which must be added in several portions during the reaction.^{6a} Previous attempts to obtain $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}\{\text{C}(\text{aryl})_2\}(\text{PPh}_3)$ and $\text{Os}(\eta^6\text{-mes})\text{Cl}_2\{\text{C}(\text{aryl})_2\}$ from $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)_2$ and $[\text{Os}(\eta^6\text{-mes})\text{Cl}_2]_n$ (*mes* = 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$), respectively, and the corresponding diazomethanes had failed. Their syntheses require multistep procedures, using the carboxylate compound $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\kappa^2\text{-O}_2\text{CCH}_3\}(\text{PPh}_3)$ or $\text{Os}(\eta^6\text{-mes})\{\kappa^1\text{-OC}(\text{O})\text{CF}_3\}(\kappa^2\text{-O}_2\text{CCF}_3)$ as synthetic intermediate species.^{8b,11}

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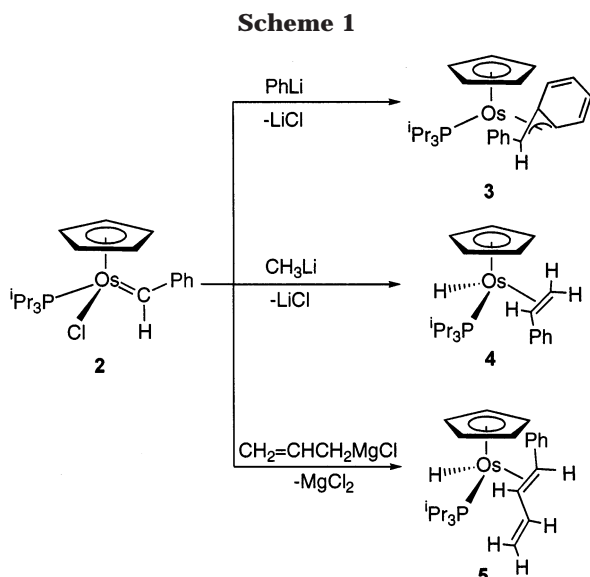
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In the ^1H NMR spectrum of **2** in benzene- d_6 , the most noticeable resonance is that corresponding to the CH-carbene proton, which appears at 19.17 ppm as a doublet with a H–P coupling constant of 12.9 Hz. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the C_α resonance of the carbene ligand is observed as a broad signal at 235 ppm. This resonance is considerably shifted to higher field compared with $\text{Os}(\eta^5\text{-mes})\{\kappa^1\text{-OC(O)CF}_3\}_2\{\text{C(aryl)}_2\}$ (δ , 306–310), $\text{Os}(\eta^5\text{-mes})\text{Cl}_2\{\text{C(aryl)}_2\}$ (δ , 300–303), $[\text{Os}(\eta^5\text{-mes})\text{Cl}\{\text{C(aryl)}_2\}(\text{PPh}_3)]\text{PF}_6$ (δ , 291–293),^{8b} and $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)(=\text{CHCH}_2\text{Ph})\{\text{P(OMe)}_3\}(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (δ , 285.7).^{8c,9} The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains a singlet at 20.7 ppm.

Reactions of $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(=\text{CHPh})\text{Cl}(\text{P}^i\text{Pr}_3)$ with RLi ($\text{R} = \text{Ph, Me}$) and $\text{CH}_2=\text{CHCH}_2\text{MgCl}$. The carbene-carbon atom of **2** shows a marked electrophilicity, characteristic of the Fischer-type derivatives. Thus complex **2** reacts with main group organometallic compounds, such as phenyllithium, methyllithium, and allylmagnesium chloride, to afford novel carbene-plus-organic fragment coupling processes (Scheme 1).

The addition at 0 °C of a cyclohexane/diethyl ether (7:3) solution of phenyllithium to the stoichiometric amount of **2** in tetrahydrofuran leads to the benzoallyl complex $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-CHPhC}_6\text{H}_5)(\text{P}^i\text{Pr}_3)$ (**3**), which was isolated as orange crystals in 65% yield. At the same temperature, the treatment of the tetrahydrofuran solutions of **2** with the stoichiometric amount of methyllithium in diethyl ether affords the hydride-styrene derivative $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)(\text{CH}_2=\text{CHPh})(\text{P}^i\text{Pr}_3)$ (**4**), as a dark brown oil in 75% yield, whereas the reaction of **2** with allylmagnesium chloride in tetrahydrofuran gives rise to the hydride- η^2 -phenylbutadiene compound $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\{\eta^2\text{-}(E)\text{-CHPh=CHCH=CH}_2\}(\text{P}^i\text{Pr}_3)$ (**5**). Complex **5** was isolated as a pale yellow solid in 75% yield.

The reactions shown in Scheme 1 can be rationalized as the addition of the nucleophilic organic fragments to the carbene-carbon atom of **2**, followed by the elimination of chloride and subsequent η^1/η^3 benzyl rearrangement in **3** or β -hydrogen extraction in **4** and **5**. An alternative pathway involving carbene- $(\eta^1\text{-organic fragment})$ metal species, which evolve into the same intermediates as those resulting from the direct attack of

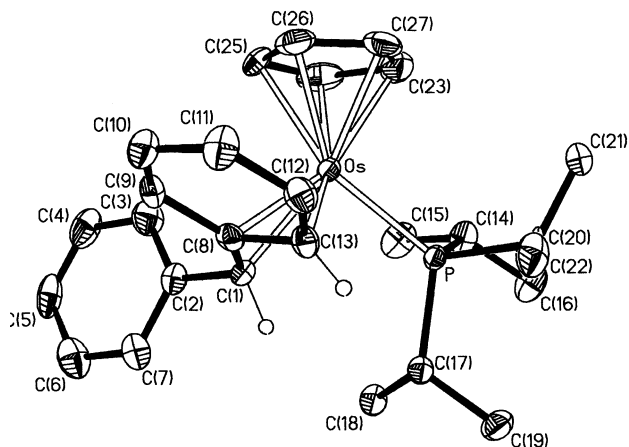


Figure 1. Molecular diagram of the complex $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-CHPhC}_6\text{H}_5)(\text{P}^i\text{Pr}_3)$ (**3**).

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complex $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-CHPhC}_6\text{H}_5)(\text{P}^i\text{Pr}_3)$ (**3**)

| | | | |
|-------------------------|------------|--------------------------|------------|
| Os–P | 2.3360(10) | Os–C(26) | 2.181(4) |
| Os–C(1) | 2.185(4) | Os–C(27) | 2.217(4) |
| Os–C(8) | 2.157(4) | C(1)–C(2) | 1.500(5) |
| Os–C(13) | 2.246(4) | C(1)–C(8) | 1.429(5) |
| Os–C(23) | 2.195(4) | C(8)–C(13) | 1.435(5) |
| Os–C(24) | 2.195(4) | | |
| Os–C(25) | 2.202(4) | | |
| P–Os–M ^a | 123.52(4) | M ^a –Os–C(8) | 125.93(16) |
| P–Os–C(1) | 89.30(11) | M ^a –Os–C(13) | 129.33(17) |
| P–Os–C(8) | 110.31(11) | C(1)–Os–C(8) | 38.43(14) |
| P–Os–C(13) | 91.42(11) | C(1)–Os–C(13) | 66.63(16) |
| M ^a –Os–C(1) | 138.21(17) | C(8)–Os–C(13) | 37.98(14) |
| | | C(2)–C(1)–C(8) | 119.9(4) |

^a M represents the midpoint of the C(23)–C(27) Cp ring.

the organic fragment to the carbene-carbon atom, may be also considered.

Figure 1 shows a view of the molecular geometry of the benzoallyl complex **3**. Selected bond distances and angles are listed in Table 1. The coordination geometry around the osmium atom can be rationalized as being derived from a highly distorted octahedron with the cyclopentadienyl ligand occupying a face.

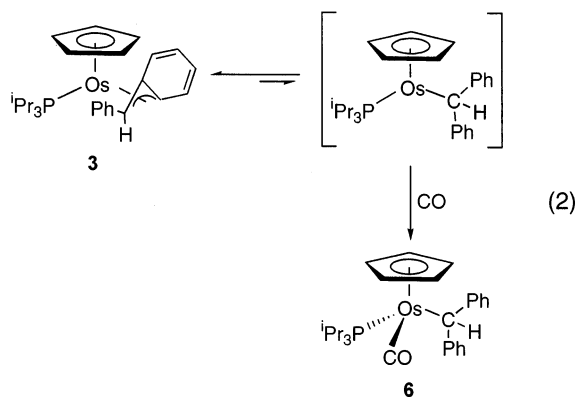
The structure proves the formation of the diphenylmethyl ligand, which is η^3 -coordinated to the osmium center through the methine carbon atom (C(1)) and two of the arene carbon atoms of one of the phenyl substituents, the *ipso* C(8) and one of the *ortho*-arene carbon atoms (C(13)). The C–C bond lengths inside of the allyl unit are 1.429(5) Å (C(1)–C(8)) and 1.435(5) Å (C(8)–C(13)). The phenyl substituent is *syn* disposed with regard to C(8), with an angle of 119.9(4)°. As it has been previously observed for other transition-metal benzoallyl complexes,¹² the allyl moiety of **3** is unsymmetrically bonded to the metal center. However, in this case, the strongest interaction corresponds to the *ipso* carbon atom (Os–C(8) = 2.157(4) Å), whereas the difference

(12) See for example: (a) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 902. (b) Carmona, E.; Marin, J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1987**, *6*, 1757. (c) Werner, H.; Schäfer, M.; Nürnberg, O.; Wolf, J. *Chem. Ber.* **1994**, *127*, 27. (d) Debad, J. D.; Legzdins, P.; Lumb, S. A.; Rettig, S. J.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1999**, *18*, 3414. (e) Pflug, J.; Erker, G.; Kehr, G.; Fröhlich, R. *Eur. J. Inorg. Chem.* **2000**, 1795. (f) Nettekoven, U.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 1166. (g) Ortman, D. A.; Weberndörfer, B.; Ilg, K.; Laubender, M.; Werner, H. *Organometallics* **2002**, *21*, 2369.

between the interactions of osmium-methine carbon ($\text{Os}-\text{C}(1) = 2.185(4) \text{ \AA}$) and osmium-*ortho* carbon ($\text{Os}-\text{C}(13) = 2.246(4) \text{ \AA}$) is relatively small. This unusual finding is probably related with the steric hindrance experienced by the phenyl group bonded at C(1). The coordination of C(8) and C(13) to the osmium atom produces a slight alteration in the six-membered ring containing these atoms. Thus, the bond lengths C(8)–C(9), C(10)–C(11), and C(12)–C(13) (1.450(5), 1.422(5), and 1.438(6) \AA , respectively) are considerably longer than the distances C(9)–C(10) and C(11)–C(12) (1.347(5) and 1.351(5) \AA , respectively), which have more double-bond character.

In solution, complex **3** is fluxional. The process involves the phenyl groups, which exchange their positions. According to this, at room temperature, the ^1H NMR spectrum in dichloromethane- d_2 shows a doublet at 1.84 ppm, with a H–P coupling constant of 14.1 Hz due to the C(1)–H proton, and a broad resonance between 6 and 8 ppm corresponding to the aromatic protons. At -40°C , the broad resonance is resolved and, in addition, the spectrum contains a double doublet at 3.86 ppm, with H–P and H–H coupling constants of 14.4 and 5.6 Hz, respectively, due to the C(13)–H proton. The resonance at 1.84 ppm does not show significant changes. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in dichloromethane- d_2 at -40°C is consistent with the ^1H NMR spectrum and is in agreement with the structure shown in Figure 1. The most noticeable resonances are two doublets at 33.4 and 40.7 ppm, with C–P coupling constants of 7.2 and 4.3 Hz, respectively, and a singlet at 78.2 ppm. On the basis of a $^1\text{H}-^{13}\text{C}$ HMQC spectrum, these resonances are assigned to C(1), C(13), and C(8), respectively. At -40°C , the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at 15.3 ppm.

The exchange process of the phenyl groups takes place via an unsaturated η^1 -diphenylmethyl intermediate, which is trapped when the dichloromethane solutions of **3** are stirred at room temperature under 1 atm of carbon monoxide. Under these conditions, complex $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\text{CHPh}_2)(\text{CO})(\text{P}^i\text{Pr}_3)$ (**6**) is formed. Complex **6** was isolated as a white solid in 73% yield (eq 2).



The presence of a carbonyl ligand in **6** is strongly supported by the IR spectrum of this compound in Nujol, which contains a $\nu(\text{CO})$ absorption at 1895 cm^{-1} . In the ^1H NMR spectrum in benzene- d_6 at room temperature, the most noticeable resonance is a doublet with a H–P coupling constant of 3.5 Hz, at 5.35 ppm, corresponding to the $\text{C}(\text{sp}^3)\text{-H}$ proton of the alkyl group. The displace-

ment of this resonance toward lower field with regard to those expected for alkyl protons is probably a consequence of the negative shielding contribution produced by the ring current effect of the phenyl substituents of the diphenylmethyl group. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the resonance due to the $\text{C}(\text{sp}^3)$ atom of the alkyl group appears at 10.0 ppm, as a doublet with a C–P coupling constant of 5.5 Hz. In addition, it should be mentioned the resonance corresponding to the carbonyl group, which is observed at 189.2 ppm, as a doublet with a C–P coupling constant of 12.9 Hz. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains a singlet at 16.9 ppm.

The hydride-styrene complex **4** was characterized by MS, IR, ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopies. In agreement with the presence of a hydride ligand in this complex, the IR spectrum in Nujol contains a $\nu(\text{Os}-\text{H})$ absorption at 2107 cm^{-1} . At -10°C , the ^1H NMR spectrum in dichloromethane- d_2 strongly supports the stereochemistry proposed for **4** in Scheme 1. In the high-field region of the spectrum (δ , -16.30), the hydride ligand gives rise to a double doublet by spin coupling with the phosphorus atom of the phosphine (33.6 Hz) and the olefinic CH-hydrogen disposed *trans* to the phenyl group (3.9 Hz). This hydrogen atom gives rise to a double doublet of doublets at 2.00 ppm by spin coupling with the hydride and the olefinic hydrogens ($J_{\text{gem}} = 3.2 \text{ Hz}$, $J_{\text{cis}} = 7.6 \text{ Hz}$), whereas the resonance corresponding to the CH-hydrogen disposed *cis* to the phenyl group appears at 2.60 ppm as a double doublet with a *trans* H–H coupling constant of 9.0 Hz. The resonance due to the CHPh-hydrogen is observed as a double doublet of doublets with a H–P coupling constant of 8.3 Hz. It should be noted that the hydrogen atoms of the coordinated olefin disposed *cisoid-syn* with regard to the hydride and phosphine ligands undergo spin coupling with the respective active nuclei of these ligands. At room temperature, the olefinic hydrogen atoms display broad resonances, as a result of the rotation of the olefin around the osmium–olefin axis. According to the $^1\text{H}-^{13}\text{C}$ HMQC spectrum at -10°C , in the $^{13}\text{C}\{^1\text{H}\}$, the olefinic resonances appear at 20.5 (CHPh) and 1.28 (CH_2) ppm, as singlets. These chemical shifts, which are typical for $\text{C}(\text{sp}^3)$ atoms, suggest that the acceptor component of the osmium–styrene bond has a very important contribution to the structure of **4**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains a singlet at 31.4 ppm.

Complex **5** was characterized by elemental analysis, IR, ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopies, and X-ray diffraction analysis. Figure 2 shows a view of the molecular geometry, whereas selected bond distances and angles are listed in Table 2. The hydride ligand H(01) was located in the difference Fourier maps and refined as an isotropic atom together with the rest of the non-hydrogen atoms of the structure, giving an Os–H(01) distance of $1.570(1) \text{ \AA}$. The distribution of ligands around the osmium atom can be described as a four-legged piano-stool geometry with the hydride and phosphine ligands mutually *cisoid* disposed ($\text{P}-\text{Os}-\text{H}(01) = 74.3(12)^\circ$).

The most remarkable features of the structure are, first, the coordination of the C(3) and C(4) atoms of the styryl moiety of the phenylbutadiene and, second, the

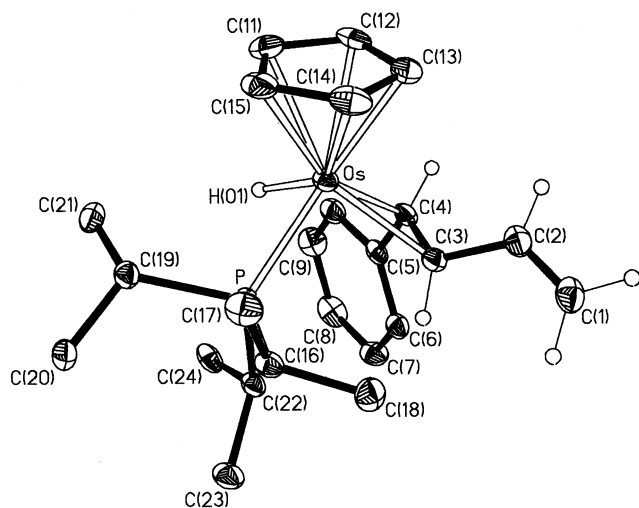


Figure 2. Molecular diagram of the complex $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\{\eta^2\text{-}(E)\text{-CHPh=CHCH=CH}_2\}(\text{P}^i\text{Pr}_3)$ (**5**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Complex

| $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-}(E)\text{-PhCH=CHCH=CH}_2)(\text{P}^i\text{Pr}_3)$ (5) | | | |
|--|------------|----------------|----------|
| Os–P | 2.2887(8) | Os–C(15) | 2.242(3) |
| Os–C(3) | 2.181(3) | Os–H(01) | 1.57(1) |
| Os–C(4) | 2.148(3) | C(1)–C(2) | 1.312(5) |
| Os–C(11) | 2.262(3) | C(2)–C(3) | 1.467(4) |
| Os–C(12) | 2.270(3) | C(3)–C(4) | 1.436(4) |
| Os–C(13) | 2.244(3) | C(4)–C(5) | 1.487(4) |
| Os–C(14) | 2.245(3) | | |
| M(1) ^a –Os–M(2) ^b | 127.53(14) | C(1)–C(2)–C(3) | 127.4(3) |
| M(1) ^a –Os–P | 128.20(10) | C(2)–C(3)–C(4) | 121.5(3) |
| M(1) ^a –Os–H(01) | 115.1(9) | C(3)–C(4)–C(5) | 124.2(3) |
| M(2) ^b –Os–P | 99.04(9) | | |
| M(2) ^b –Os–H(01) | 97(1) | | |
| P–Os–H(01) | 74.3(12) | | |

^{a,b} M(1) and M(2) represent the midpoints of the C(11)–C(15) Cp ring and C(3)–C(4) double bond, respectively.

E-stereochemistry at the coordinated carbon–carbon double bond with the phenyl group *cisoid-syn* disposed to the hydride and the C(3)–H hydrogen atom *cisoid-syn* disposed to the phosphine ligand.

The styryl moiety coordinates to the osmium atom in an asymmetrical fashion with Os–C(3) and Os–C(4) bond lengths of 2.181(3) and 2.148(3) Å, respectively. These distances agree well with those found in other osmium-olefin complexes (between 2.13 and 2.28 Å).¹³ Similarly, the olefinic bond distance C(3)–C(4) (1.436(4) Å) is within the range reported for transition-metal olefin complexes (between 1.340 and 1.445 Å).¹⁴ As a consequence of the contributions of the acceptor component of the osmium-olefin bond to the structure of the complex, the C(3)–C(4) bond length is about 0.12 Å longer than the C(1)–C(2) distance (1.312(5) Å), corresponding to the noncoordinated carbon–carbon double bond of the vinyl moiety. The separation between the styryl and vinyl fragments of the diene is 1.467(4) Å.

(13) (a) Johnson, T. J.; Albinati, A.; Koetzle, T. F.; Ricci, J.; Eisenstein, O.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 4966. (b) Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A.; Tolosa, J. I. *Organometallics* **1997**, *16*, 1316. (c) Edwards, A. J.; Elipse, S.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Valero, C. *Organometallics* **1997**, *16*, 3828. (d) Esteruelas, M. A.; García-Yebra, C.; Oliván, M.; Oñate, E. *Organometallics* **2000**, *19*, 3260.

The disposition of the coordinated olefinic bond in the coordination sphere of the osmium is consistent with the spectroscopic data obtained for **5**, which are in full agreement with those of **4**. The IR spectrum of **5** contains a $\nu(\text{Os-H})$ absorption at 2111 cm^{-1} . Because the hydride ligand is *cisoid-syn* disposed to the phenyl group, and the phosphine ligand is *cisoid-syn* disposed to the C(3)H-hydrogen, in the ¹H spectrum in benzene-*d*₆ at room temperature, the hydride resonance (δ , –16.06) only shows spin coupling with the phosphorus of the phosphine (35.1 Hz), whereas the C(3)–H resonance (δ , 3.33) shows spin coupling with the phosphorus (9.3 Hz) and with the C(4)H- and C(2)H-hydrogens of the diene (9.3 Hz in both cases). The C(4)H-hydrogen displays a doublet at 4.70 ppm. The resonances due to the hydrogen atoms of the vinyl moiety of the diene are observed at 5.78 (C(2)H), 5.14 (C(1)H *trans* to C(2)H), and 4.79 (C(1)H *cis* to C(2)H) ppm, with *cis*-, *trans*-, and *gem*-H–H coupling constants of 10.2, 16.8, and 2.1 Hz, respectively. In the ¹³C{¹H} NMR spectrum the resonances corresponding to the coordinated C(sp²) atoms appear at 24.3 (C(4)) and 23.4 (C(3)), as doublets with C–P coupling constants of 2 and 5 Hz, respectively, while the vinyl carbon atoms give rise to singlets at 151.8 (C(2)) and 103.9 (C(1)). The ³¹P{¹H} NMR spectrum contains a singlet at 31.9 ppm.

In contrast to **4**, in solution at room temperature, the osmium–olefin bond in **5** is rigid. When we tried to force the rotation of the olefin, the formation of a new compound was observed. The heating at 60 °C of the toluene or benzene-*d*₆ solutions of **5** gives rise to the allyl complex $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\{\eta^3\text{-CH}_2\text{CHCH}(\text{CH}_2\text{Ph})\}(\text{P}^i\text{Pr}_3)$ (**7**), as a result of the migratory insertion of C(4) into the Os–H bond. After 6 h, the conversion of **5** into **7** is quantitative. Complex **7** was isolated as a white solid by addition of methanol (eq 3).

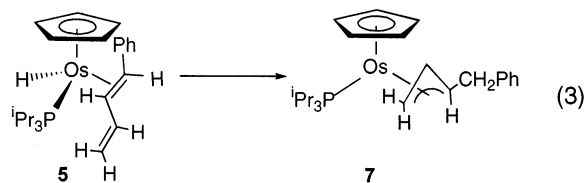


Figure 3 shows a view of the molecular geometry of **7**, whereas selected bond distances and angles are listed in Table 3. The coordination geometry around the osmium atom can be rationalized as being derived from a highly distorted octahedron with the cyclopentadienyl ligand occupying a face. The structure proves the formation of the allyl ligand, which is coordinated by the C(1), C(2), and C(3) carbon atoms. The angles C(1)–Os–C(3) and C(1)–C(2)–C(3) are 67.87(16)° and 118.3(4)°, respectively. The benzyl substituent is *syn* disposed with regard to C(2), with a C(2)–C(3)–C(4) angle of 117.7(4)°. The allyl moiety coordinates in an asymmetrical fashion, with the separation between the central carbon atom, C(2), and the metal (2.112(4) Å) shorter than the separation between the metal and the terminal carbon atoms C(1) (2.183(4) Å) and C(3) (2.193-

(14) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187.

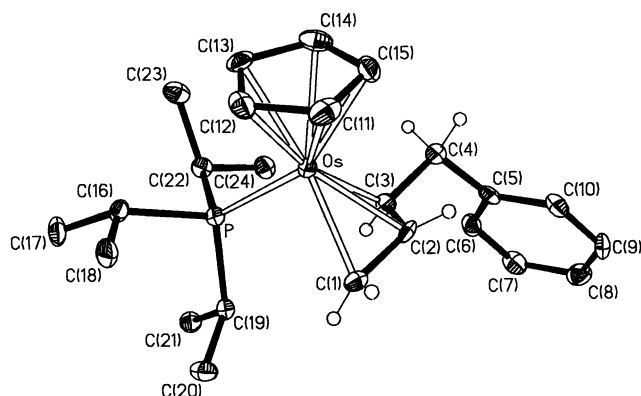


Figure 3. Molecular diagram of the complex $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\{\eta^3\text{-CH}_2\text{CHCH}(\text{CH}_2\text{Ph})\}(\text{P}^i\text{Pr}_3)$ (**7**).

Table 3. Selected Bond Distances (Å) and Angles (deg) for the Complex $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\{\eta^3\text{-CH}_2\text{CHCH}(\text{CH}_2\text{Ph})\}(\text{P}^i\text{Pr}_3)$ (**7**)

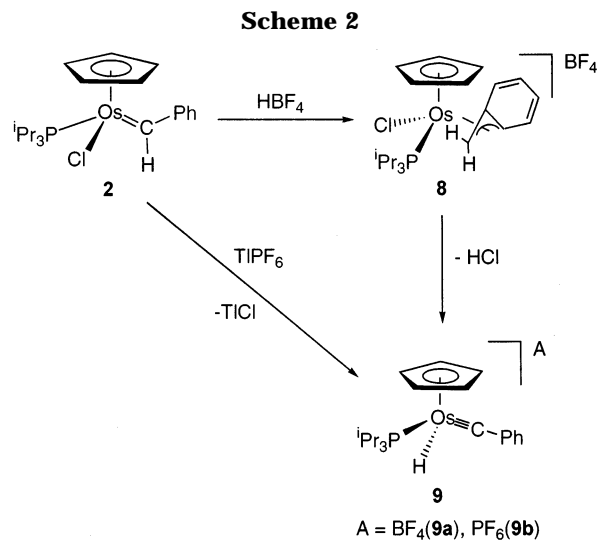
| | | | |
|----------------------|------------|----------------|-----------|
| Os–P | 2.3124(11) | Os–C(13) | 2.219(4) |
| Os–C(1) | 2.183(4) | Os–C(14) | 2.236(4) |
| Os–C(2) | 2.112(4) | Os–C(15) | 2.228(4) |
| Os–C(3) | 2.193(4) | C(1)–C(2) | 1.416(6) |
| Os–C(11) | 2.182(4) | C(2)–C(3) | 1.429(6) |
| Os–C(12) | 2.214(4) | C(3)–C(4) | 1.515(6) |
| | | C(4)–C(5) | 1.510(5) |
| $M^a\text{-Os-P}$ | 124.86(14) | C(1)–Os–C(2) | 38.46(16) |
| $M^a\text{-Os-C(1)}$ | 130.71(16) | C(1)–Os–C(3) | 67.87(16) |
| $M^a\text{-Os-C(2)}$ | 124.04(16) | C(2)–Os–C(3) | 38.71(16) |
| $M^a\text{-Os-C(3)}$ | 133.13(17) | C(1)–C(2)–C(3) | 118.3(4) |
| P–Os–C(1) | 93.20(13) | C(2)–C(3)–C(4) | 117.7(4) |
| P–Os–C(2) | 111.08(13) | C(3)–C(4)–C(5) | 110.3(3) |
| P–Os–C(3) | 93.01(12) | | |

^a M represents the midpoint of the C(11)–C(15) Cp ring.

(4) Å). The carbon–carbon distances within the allylic moiety are 1.416(6) Å for C(1)–C(2) and 1.429(6) Å for C(2)–C(3). These values agree well with those found for **3** and the osmium(IV) derivative $[\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\{\eta^3\text{-CH}_2\text{C}(\text{Ph})\text{CH}_2\}(\text{P}^i\text{Pr}_3)]\text{BF}_4$.^{9j}

In agreement with the structure shown in Figure 3, the ¹H NMR spectrum in benzene-*d*₆ at room temperature shows four resonances for the allylic protons at 3.73 (C(2)H), 2.83 (C(1)H *syn* to C(2)H), 1.44 (C(3)H), and 0.73 (C(1)H *anti* to C(2)H) ppm. The different coupling constants mixed up in these multiplets have been deduced by means of the ¹H{³¹P} NMR spectrum and selective homonuclear irradiation in the ¹H NMR spectrum and are reported in the Experimental Section. In the ¹³C{¹H} NMR spectrum the most noticeable resonances are a singlet at 52.8 ppm and two doublets at 36.0 and 11.0 ppm with a C–P coupling constant of 6 Hz, in both cases. On the basis of the ¹H–¹³C HMQC spectrum, these resonances are assigned to the C(2), C(3), and C(1) atoms of the allyl ligand, respectively. The ³¹P{¹H} NMR spectrum contains a singlet at 21.9 ppm.

3. Reaction of $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{=CHPh})(\text{P}^i\text{Pr}_3)$ with HBF_4 . Although the reactions shown in Scheme 1 prove the electrophilicity of the carbene-carbon atom of **2**, it must be pointed out that this atom also undergoes the attack of electrophiles.¹⁵ The addition of 1.0 equiv of $\text{HBF}_4\cdot\text{OEt}_2$ to an NMR tube containing a dichloromethane-*d*₂ solution of **2** leads to a 7:1 mixture of the η^3 -benzyl complex $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**8**) and the hydride-carbyne derivative $[\text{OsH}(\eta^5\text{-C}_5\text{H}_5)(\text{=CPh})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**9a**).



$(\eta^5\text{-C}_5\text{H}_5)(\text{=CPh})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**9a**). When the reaction is carried out in a Schlenk-tube using diethyl ether as solvent, the molar ratio is 1:1. The successive recrystallizations of the mixture from dichloromethane/diethyl ether increase the amount of **9a**.

These observations can be rationalized according to Scheme 2. The initial protonation of the carbene-carbon atom of **2** affords **8**, which eliminates HCl to give **9**. The higher polarity and/or basicity of diethyl ether with regard to dichloromethane favors the loss of HCl and, therefore, the formation of the hydride-carbyne derivative. The PF_6^- -salt of **9** can be obtained by treatment of acetone solutions of **2** with a stoichiometric amount of thallium hexafluorophosphate, at room temperature. By this procedure, complex **9b** (Scheme 2) was obtained as a yellow solid in 66% yield.

In the ¹H NMR spectrum of the mixture, the –CH₂– protons of the benzyl ligand of **8** display two resonances, at 5.23 and 5.04 ppm. The first of them appears as a doublet with a H–H coupling constant of 4.8 Hz, while the second one is observed as a double doublet by spin coupling with the phosphorus of the phosphine (11.2 Hz) and the other CH₂-hydrogen. The spin coupling between one of the CH₂-hydrogens and the phosphorus of the phosphine suggests that in a four-legged piano-stool arrangement of ligands around the osmium atom the CH₂ group is *cisoid* disposed to the phosphine. The aromatic protons of the η^3 -benzyl ligand give rise to five resonances at 8.49 (H_{para}), 7.59 (both H_{ortho}), 7.22 (H_{meta}), and 6.83 (H_{meta}) ppm. In the ¹³C{¹H} NMR spectrum, the resonance due to the CH₂-carbon of the benzyl ligand is observed at 22.5 ppm as a doublet with a C–P coupling constant of 26 Hz. The aromatic carbon atoms of the benzyl ligand display singlets between 109 and 140 ppm. A singlet at –7.1 ppm in the ³¹P{¹H} is also characteristic of **8**. These spectroscopic data are in accordance with those reported previously for other η^3 -benzyl complexes.¹⁶

(15) We note that the complexes $\text{Ru}(\text{=CF}_2)(\text{CO})_2(\text{PPh}_3)_2$, $\text{Re}(\text{C}_5\text{H}_5)(\text{=CHCH}_2\text{CH}_2\text{CMe}_3)(\text{CO})_2$, and $\text{Re}\{\text{=C}(\text{CH}_3)\text{C}(\text{CH}_3)_2\text{CH}_2\text{-}(\eta^5\text{-C}_5\text{H}_4)\}(\text{CO})_2$ also show amphiphilic reactivity at the carbene carbon atom. See: (a) Clark, G. R.; Hoskins, S. V.; Jones, T. C.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1983**, 719. (b) Casey, C. P.; Vosejka, P. C.; Askham, F. R. *J. Am. Chem. Soc.* **1990**, *112*, 3713. (c) Casey, C. P.; Czerwinski, C. J.; Powell, D. R.; Hayashi, R. K. *J. Am. Chem. Soc.* **1997**, *119*, 5750.

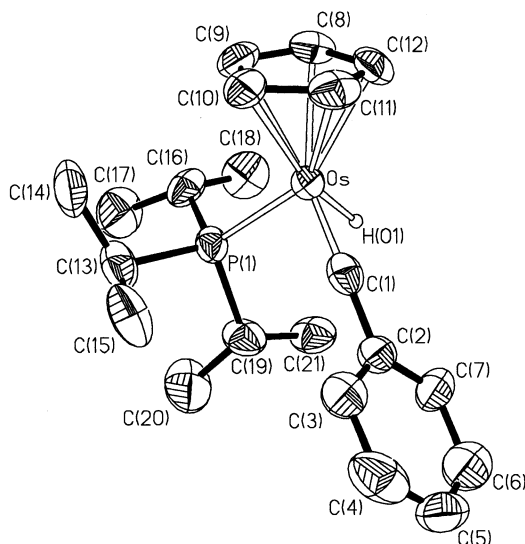


Figure 4. Molecular diagram of the cation of $[\text{OsH}(\eta^5\text{-C}_5\text{H}_5)(=\text{CPh})(\text{P}^i\text{Pr}_3)]\text{PF}_6$ (**9b**).

Table 4. Selected Bond Distances (Å)^a and Angles (deg) for the Complex $[\text{OsH}(\eta^5\text{-C}_5\text{H}_5)(=\text{C-Ph})(\text{P}^i\text{Pr}_3)]\text{PF}_6$ (**9b**)

| | | | |
|-----------------|----------|---------------|-----------|
| Os–P(1) | 2.347(2) | Os–C(10) | 2.253(8) |
| Os–C(1) | 1.733(9) | Os–C(11) | 2.238(8) |
| Os–C(8) | 2.328(9) | Os–C(12) | 2.249(8) |
| Os–C(9) | 2.350(9) | C(1)–C(2) | 1.449(12) |
| M^b –Os–P(1) | 124.4(3) | P(1)–Os–H(01) | 79(3) |
| M^b –Os–C(1) | 135.9(4) | C(1)–Os–H(01) | 73(4) |
| M^b –Os–H(01) | 132(2) | Os–C(1)–C(2) | 176.9(7) |
| P(1)–Os–C(1) | 92.5(3) | | |

^a The Os–H(01) was fixed to 1.59(1) Å. ^b M represents the midpoint of the C(8)–C(12) Cp ring.

Figure 4 shows a view of the structure of the cation of **9b**. Table 4 collects selected bond distances and angles. The coordination geometry around the metallic center can be rationalized as being derived from a highly distorted octahedron with the cyclopentadienyl ligand occupying a face of the octahedron. The angle between the phosphine and carbyne ligand is close to 90° (C(1)–Os–P(1) = 92.5(3)°). However the angles C(1)–Os–H(01) (73(4)°) and P(1)–Os–H(01) (79(3)°) strongly deviate from the ideal value of 90°. The very short Os–C(1) bond length of 1.733(9) Å and the angle Os–C(1)–C(2) of 176.9(7)° are fully consistent with an Os–C(1) triple-bond formulation.¹⁷

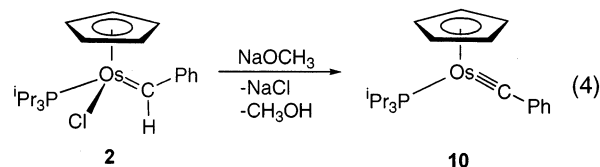
In agreement with the presence of a hydride ligand in **9b**, the IR spectrum in Nujol shows a $\nu(\text{OsH})$ absorption at 2129 cm^{-1} . In the ^1H NMR spectrum in dichloromethane- d_2 at room temperature, the hydride ligand gives rise to a doublet at –11.94 ppm with a H–P coupling constant of 24.0 Hz. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the most noticeable resonance is a doublet at 280.5 ppm, with a C–P coupling constant of 9 Hz, corresponding to C(1). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains a singlet at 45.1 ppm and a septuplet at –146.2 ppm for the hexafluorophosphate anion.

The formation of **9a** by means of the creation of a coordination vacancy in **2** agrees well with the existence of the hydride-carbyne derivatives $\text{OsHCl}_2(=\text{CR})(\text{PR}'_3)_2$.¹⁸ These bis(phosphine) complexes are isomers of the unknown compounds $\text{OsCl}_2(=\text{CHR})(\text{PR}'_3)_2$, which should be the osmium counterparts to the Grubbs-type carbene-

ruthenium derivatives, $\text{RuCl}_2(=\text{CHR})(\text{PR}'_3)_2$. To rationalize the higher stability of these saturated hydride-carbyne species with regard to the unsaturated carbene isomers, it can be argued that the migration of the hydrogen from the carbene to the metal involves a highly intramolecular oxidative addition. It is well-known that this process is more favored for the 5d metals than for the 4d ones.

The fact that the α -hydrogen migration in these osmium systems leads to carbyne complexes where the metal could be viewed as being in a high formal oxidation state suggests that the carbyne ligand could be considered as a trianionic group. So, the previously mentioned hydride-carbyne complexes could be considered as osmium(VI) species. Thus, since the oxidative addition process involves an increase in two units of the oxidation state, the carbene precursors could be considered as osmium(IV) derivatives. This means that complex **2** could be viewed as a triplet-state carbene spin coupled to two electrons on the metal center. In other words, complex **2** could be a Schrock-type carbene derivative. This possibility prompted us to carry out the reaction of **2** with sodium methoxide.

4. Reaction of $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(=\text{CHPh})(\text{P}^i\text{Pr}_3)$ with Sodium Methoxide. Treatment of tetrahydrofuran solutions of **2** with sodium methoxide produces the deprotonation of the carbene carbon atom and the formation of the neutral carbyne derivative $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(=\text{CPh})(\text{P}^i\text{Pr}_3)$ (**10**), according to the reactivity expected for a Schrock-type carbene compound (eq 4). Complex **10** can also be prepared as a dark purple solid in high yield (about 77%) by addition of sodium methoxide to the tetrahydrofuran solutions of the cationic hydride-carbyne **9b** (Scheme 3).



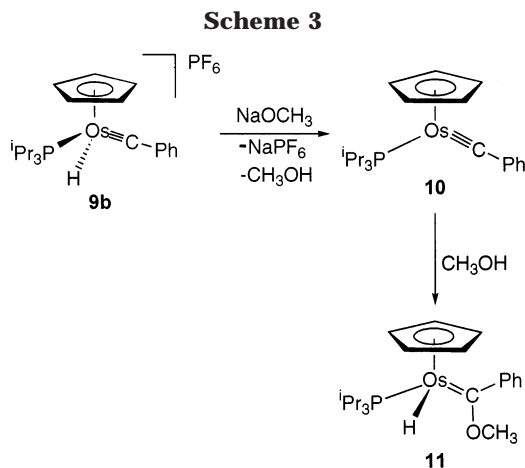
The most noticeable feature in the ^1H spectrum of **10** in benzene- d_6 is the absence of any hydride resonance. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum displays at 262.0 a doublet with a C–P coupling constant of 13.8 Hz due to the C(sp) carbon of the carbyne ligand. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains a singlet at 53.5 ppm.

Complex **10** is soluble in hydrocarbon solvents. Its solutions are stable for up to several days if kept under argon. However, in methanol, it evolves into the hydride-alkoxycarbene derivative $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{-}\{\text{C}(\text{OMe})\text{Ph}\}(\text{P}^i\text{Pr}_3)$ (**11**), as a consequence of the addition of the O–H bond of the alcohol to the Os–C triple bond of **10** (Scheme 3). Complex **11** can be prepared in a one-pot synthesis by reaction of **2** with KOH in methanol.

(16) See for example: (a) Lee, B. Y.; Bazan, G. C.; Vela, J.; Komon, Z. J. A.; Bu, X. *J. Am. Chem. Soc.* **2001**, *123*, 5352. (b) Carmona, E.; Paneque, M.; Poveda, M. L. *Polyhedron* **1989**, *8*, 285.

(17) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2001**, *20*, 3283, and references therein.

(18) (a) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N. *J. Am. Chem. Soc.* **1993**, *115*, 4683. (b) Spivak, G. J.; Coalter, J. N.; Oliván, M.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 999. (c) Werner, H.; Jung, S.; Weberndörfer, B.; Wolf, J. *Eur. J. Inorg. Chem.* **1999**, 951.



Complex **11** was isolated as a dark orange oil in about 88% yield. The presence of a hydride ligand in this complex is strongly supported by the ^1H NMR spectrum in benzene- d_6 at room temperature, which contains at -14.99 ppm a doublet with a H–P constant of 32.1 Hz. In the low-field region of the spectrum, the most noticeable resonance is a singlet at 3.09 ppm, corresponding to the methoxy group. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum the resonance due to the C_α atom of the carbene ligand appears at 242.6 ppm, as a doublet with a C–P coupling constant of 9 Hz. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at 46.5 ppm.

Complex **10** also reacts with phenol. Treatment of pentane solutions of **10** with 1.0 equiv of phenol at room temperature affords the hydride, metallacyclic-osmium-(IV) complex $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\{\text{CH}(\text{Ph})\text{OC}_6\text{H}_4\}(\text{P}^i\text{Pr}_3)$ (**12**), which was isolated as a yellow solid in about 66% yield (eq 5).

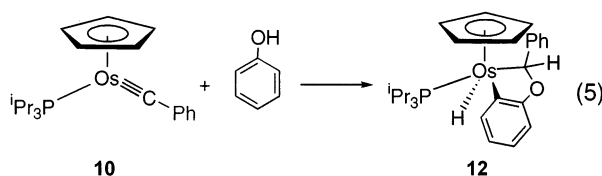


Figure 5 shows a view of the structure of **12**. Table 5 collects selected bond distances and angles. The distribution of ligands around the osmium atom can be described as a four-legged piano-stool geometry with the carbon atom C(1) of the metalated phenyl group disposed *transoid* to the hydride ligand. The C(1)–Os–H(01) and C(7)–Os–P angles are $126.8(17)^\circ$ and $103.10(15)^\circ$, respectively.

The bidentate carbon donor ligand acts with a bite angle of $75.5(2)^\circ$. The Os–C(1) and Os–C(7) bond lengths are 2.109(5) and 2.159(6) Å, respectively. The five-membered metallacycle shows an envelope conformation with the osmium atom displaced by 0.217(8) Å from the plane defined by the oxygen and the carbon atoms.

In agreement with the presence of a hydride ligand in **12**, the ^1H NMR spectrum of this compound in benzene- d_6 at room temperature contains at -13.94 ppm a doublet with a H–P coupling constant of 41.1 Hz. In the low-field region of the spectrum, the most noticeable resonance is a singlet at 8.36 ppm, corre-

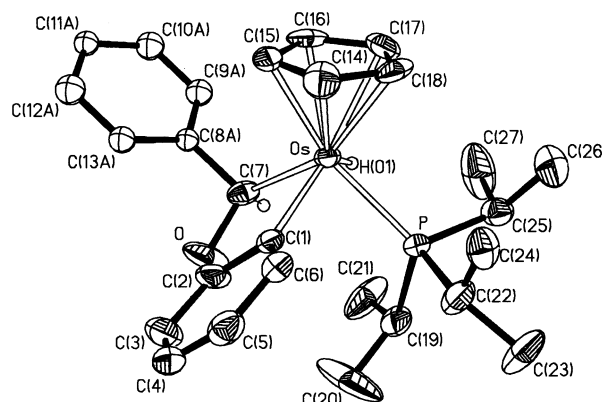


Figure 5. Molecular diagram of the complex $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\{\text{CH}(\text{Ph})\text{OC}_6\text{H}_4\}(\text{P}^i\text{Pr}_3)$ (**12**).

Table 5. Selected Bond Distances (Å)^a and Angles (deg) for the Complex

| $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\{\text{CH}(\text{Ph})\text{OC}_6\text{H}_4\}(\text{P}^i\text{Pr}_3)$ (12) | | | |
|---|------------|---------------|-----------|
| Os–P | 2.3228(14) | Os–C(17) | 2.242(5) |
| Os–C(1) | 2.109(5) | Os–C(18) | 2.296(6) |
| Os–C(7) | 2.159(6) | O–C(2) | 1.354(6) |
| Os–C(14) | 2.266(5) | O–C(7) | 1.435(6) |
| Os–C(15) | 2.220(5) | C(1)–C(2) | 1.397(3) |
| Os–C(16) | 2.207(5) | | |
| M^b –Os–P | 129.62(18) | C(1)–Os–C(7) | 75.5(2) |
| M^b –Os–C(1) | 115.8(2) | C(1)–Os–H(01) | 126.8(17) |
| M^b –Os–C(7) | 125.7(2) | C(7)–Os–H(01) | 68.7(17) |
| M^b –Os–H(01) | 116(2) | Os–C(1)–C(2) | 115.8(4) |
| P–Os–C(1) | 85.36(14) | Os–C(7)–O | 114.5(4) |
| P–Os–C(7) | 103.10(15) | O–C(2)–C(1) | 118.6(5) |
| P–Os–H(01) | 66.8(17) | C(2)–O–C(7) | 113.6(4) |

^a The Os–H(01) was fixed to 1.59(1) Å. ^b M represents the midpoint of the C(14)–C(18) Cp ring.

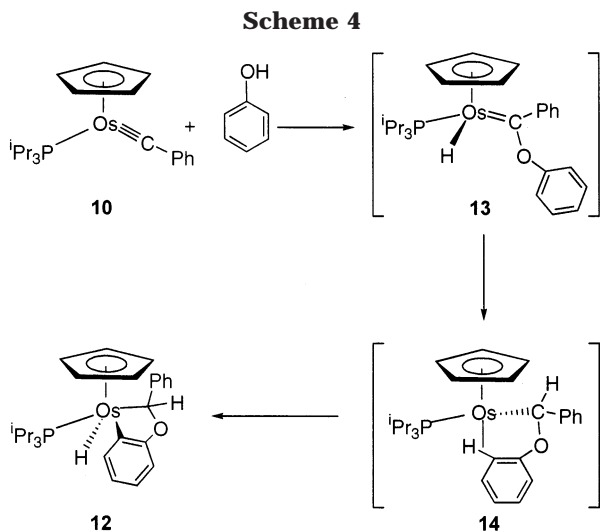
sponding to the OsCH-hydrogen atom. The chemical shift of the latter agrees with the reported one for the related resonance of the ruthenium complex $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{9\text{-phenyl-1,3-dihydronaphtho}[2,3\text{-}c\text{-}1\text{-furanyl}\}(\text{CO})(\text{P}^i\text{Pr}_3)$ (7.50 ppm). These unusual chemical shifts seem to be a consequence of the ring current effect of the aromatic rings of these polycyclic systems.¹⁹ In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, the resonances corresponding to the C(1) and C(7) carbon atoms are observed, at 172.7 and 67.3 ppm, as singlets. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at 19.0 ppm.

The formation of **12** can be rationalized according to Scheme 4. The initial addition of the O–H bond of phenol to the Os–C triple bond of **10** should give the hydride-alkoxycarbene intermediate **13**, similar to that isolated from the reaction of **10** with methanol (Scheme 3). The subsequent migration of the hydride ligand from the metallic center to the C_α atom of the carbene ligand should afford the unsaturated species **14**, which could evolve into **12** by C–H activation of one of the *ortho*-CH bonds of the OPh group.

Concluding Remarks

This paper reports the preparation and reactivity of the osmium-carbene complex $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(=\text{CHPh})\text{Cl}(\text{P}^i\text{Pr}_3)$, which shows a Fischer–Schrock ambivalent behavior.

(19) Esteruelas, M. A.; Gómez, A. V.; López, A. M.; Oliván, M.; Oñate, E.; Ruiz, N. *Organometallics* **2000**, *19*, 4.



As it should be expected for a Fischer-type carbene derivative, the complex $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(=\text{CHPh})\text{Cl}(\text{P}^i\text{Pr}_3)$ reacts with phenyllithium, methyllithium, and allylmagnesium chloride to afford carbene-plus-organic fragment coupling products. As a result, the benzoallyl complex **3**, the hydride-styrene derivative **4**, and the compounds hydride- η^2 -butadiene **5** and allyl **7** have been obtained and characterized.

The behavior of $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(=\text{CHPh})\text{Cl}(\text{P}^i\text{Pr}_3)$ as a Schrock-type carbene complex is supported by three reactions: (i) the formation of the benzoallyl derivative **8** as a consequence of the protonation of the carbene ligand with HBF_4 , (ii) the formation of the hydride-carbyne **9** by extraction of the chlorine ligand and migration of the hydrogen-carbene atom from the carbene-carbon atom to the metallic center, and (iii) the deprotonation of the carbene to give the five-coordinate carbyne **10**.

It is assumed that the Fischer or Schrock character of a carbene derivative depends on the ground state of the carbene ligand in its coordination to the metal (singlet or triplet). So, according to the results reported here, it must be assumed that there is a class of carbene derivatives without heteroatom substituents, for which both modes of coordination are accessible under the usual experimental conditions.

The chemistry of this type of species and their derivatives is very versatile. This study reveals that complex $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(=\text{CHPh})\text{Cl}(\text{P}^i\text{Pr}_3)$, in addition to affording carbon-carbon coupling reactions and interesting carbyne derivatives, provides access to the novel hydride-alkoxycarbene compound **11** and the hydride-heterometallacycle species **12**.

Experimental Section

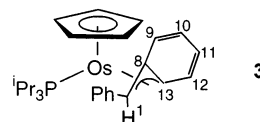
All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting materials $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)_2$ ^{9a} (**1**) and $\text{N}_2=\text{CHPh}$ ²⁰ were prepared by the published methods.

NMR spectra were recorded on a Varian Unity, a Varian Gemini 2000, and a Bruker ARX 300 MHz instrument. ¹H (300 MHz) and ¹³C (75.19 MHz) NMR chemical shifts were referenced to TMS by using known shifts of residual proton or carbon signals in the solvents. ³¹P (121 MHz) NMR were measured relative to external 85% phosphoric acid. Coupling

constants, *J*, are given in hertz. MS data were recorded on a VG Austospec double-focusing mass spectrometer operating in the positive mode; ions were produced with the Cs^+ gun at ca. kV, and 3-nitrobenzyl alcohol (NBA) was used.

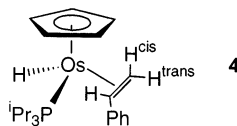
Preparation of $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{=CHPh})(\text{P}^i\text{Pr}_3)$ (2**).** An orange solution of **1** (300 mg, 0.49 mmol) in 4 mL of toluene was treated with 12.5 mL of a red solution of $\text{N}_2=\text{CHPh}$ in toluene (0.078 M, 1.96 mmol). The reaction mixture was allowed to react at room temperature for 4 h, and the solvent was removed. Then, 15 mL of pentane was added and the solution was filtered through Kieselguhr. The resultant green solution was concentrated to about 5 mL and was kept at -50°C for 1.5 h. The dark blue solid formed was washed twice with 2 mL of cold pentane and, finally, dried in vacuo. Yield: 175 mg (66%). Anal. Calcd for $\text{C}_{21}\text{H}_{32}\text{ClOsP}$: C, 46.64; H, 5.92. Found: C, 46.84; H, 5.97. ¹H NMR (C_6D_6 , 293 K): δ 19.17 (d, $J_{\text{H-P}} = 12.9$, 1H, $\text{Os}=\text{CHPh}$), 7.93 (d, $J_{\text{H-H}} = 7.4$, 2H, *o*-Ph), 7.39 (t, $J_{\text{H-H}} = 7.4$, 1H, *p*-Ph), 7.15 (vt, $J_{\text{H-H}} = 7.4$, 2H, *m*-Ph), 4.96 (s, 5H, C_5H_5), 2.56 (m, 3H, *PCH*), 1.05 (dd, $J_{\text{H-P}} = 12.9$, $J_{\text{H-H}} = 7.2$, 9H, *PCHCH}_3*), 0.97 (dd, $J_{\text{H-P}} = 13.2$, $J_{\text{H-H}} = 7.2$, 9H, *PCHCH}_3*). ³¹P{¹H} NMR (C_6D_6 , 293 K): δ 20.7 (s). ¹³C{¹H} NMR (C_6D_6 , 293 K): δ 235 (br, $\text{Os}=\text{C}$), 167.7 (s, $\text{C}_{\text{ipso}}\text{Ph}$), 130.2, 126.5, and 125.7 (all s, Ph), 85.1 (s, Cp), 25.2 (d, $J_{\text{C-P}} = 27$, *PCH*), 20.1 and 19.6 (both s, *PCHCH}_3*).

Preparation of $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-CHPhC}_6\text{H}_5)(\text{P}^i\text{Pr}_3)$ (3**).** A bluish green solution of **2** (100 mg, 0.18 mmol) in tetrahydrofuran at 0°C was treated with phenyllithium (103 μL , 0.18 mmol, 1.8 M in cyclohexane/diethyl ether, 70:30). The solution became orange immediately, and after 30 min, the solvent was removed. The product was extracted with 20 mL of pentane, which was filtered through Kieselguhr. The solution was concentrated to dryness, and an orange solid was obtained. Pentane was added (2 mL), and the solution was stirred at 0°C for 30 min, until an orange solid precipitated. It was separated by decantation and dried in vacuo. Yield: 70 mg (65%). Anal. Calcd for $\text{C}_{27}\text{H}_{37}\text{OsP}$: C, 55.64; H, 6.40. Found: C, 56.10; H, 6.38. IR (Nujol, cm^{-1}): $\nu(\text{Ph})$ 1594 (m). ¹H NMR (CD_2Cl_2 , 233 K): δ 7.37 (d, $J_{\text{H-H}} = 7.3$, 2H, *o*-Ph), 7.23 (t, $J_{\text{H-H}} = 7.3$, 2H, *m*-Ph), 7.13 (t, $J_{\text{H-H}} = 7.3$, 1H, *p*-Ph), 6.98 (m, 2H, $\text{H}^9\text{-H}^{12}$), 6.38 (m, 2H, $\text{H}^{10}\text{-H}^{11}$), 3.99 (s, 5H, C_5H_5), 3.86 (dd, $J_{\text{H-P}} = 14.4$, $J_{\text{H}^{12}\text{-H}^{13}} = 5.6$, 1H, H^{13}), 2.13 (m, 3H, *PCH*), 1.84 (d, $J_{\text{H-P}} = 14.1$, 1H, *CHPh}_2*), 1.22 (dd, $J_{\text{H-P}} = 12.3$, $J_{\text{H-H}} = 7.2$, 9H, *PCHCH}_3*), 1.18 (dd, $J_{\text{H-P}} = 12.3$, $J_{\text{H-H}} = 7.2$, 9H, *PCHCH}_3*). ³¹P{¹H} NMR (CD_2Cl_2 , 233 K): δ 15.3 (s). ¹³C{¹H} NMR (CD_2Cl_2 , 233 K): δ 148.6 (s, $\text{C}_{\text{ipso}}\text{Ph}$), 142 (s, C^9 or C^{12}), 131.1 (s, *o*-Ph), 129.3 (s, C^9 or C^{12}), 128.2 (s, *m*-Ph), 124.6 (s, C^{10} or C^{11}), 124 (s, *p*-Ph), 116.8 (s, C^{10} or C^{11}), 78.2 (s, C^8), 74.7 (s, Cp), 40.7 (d, $J_{\text{C-P}} = 4$, C^{13}), 33.4 (d, $J_{\text{C-P}} = 7$, $-\text{CHPh}_2$), 26.4 (br, *PCH*), 20.5 (s, *PCHCH}_3*), 20.3 (s, *PCHCH}_3*). ¹H NMR (CD_2Cl_2 , 293 K): δ 7.6–6.2 (br, Ph), 3.99 (s, 5H, C_5H_5), 2.20 (m, 3H, *PCH*), 1.84 (br d, $J_{\text{H-P}} = 14.1$, 1H, *CHPh}_2*), 1.20 (dd, $J_{\text{H-P}} = 12$, $J_{\text{H-H}} = 7$, 18H, *PCHCH}_3*).

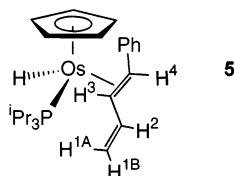


Preparation of $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)(\text{CH}_2=\text{CHPh})(\text{P}^i\text{Pr}_3)$ (4**).** A bluish green solution of **2** (110 mg, 0.20 mmol) in tetrahydrofuran at 0°C was treated with methyllithium (127 μL , 0.20 mmol, 1.6 M in diethyl ether). Immediately, the reaction mixture became brown. It was allowed to react at 0°C for 45 min. Then, the solvent was removed, and the resultant oil was extracted in toluene and filtered through Kieselguhr. The toluene solution was dried in vacuo, and a dark brown oil was obtained. Yield: 79.4 mg (75%). IR (Nujol, cm^{-1}): $\nu(\text{OsH})$ 2107 (w), $\nu(\text{Ph})$ 1599 (m). ¹H NMR (CD_2Cl_2 , 263 K): δ 7.13 (vt, $J_{\text{H-H}} = 7.6$, 2H, *m*-Ph), 7.01 (d, $J_{\text{H-H}} = 7.6$, 2H, *o*-Ph), 6.87 (t, $J_{\text{H-H}} = 7.6$, 1H, *p*-Ph), 4.53 (s, 5H, C_5H_5), 3.18 (ddd, $J_{\text{H-P}} = 8.3$,

$J_{H-H_{trans}} = 9.0$, $J_{H-H_{cis}} = 7.6$, 1H, *CHPh*), 2.60 (dd, $J_{H-H_{trans}} = 9.0$, $J_{H_{cis}-H_{trans}} = 3.2$, 1H, *CHH_{trans}*), 2.14 (m, 3H, *PCH*), 2.00 (ddd, $J_{H_{cis}-H_{trans}} = 3.2$, $J_{H-H_{cis}} = 7.6$, $J_{H_{cis}-H_{hyd}} = 3.9$, 1H, *CHH_{cis}*), 1.20 (dd, $J_{H-P} = 13.3$, $J_{H-H} = 7.2$, 9H, *PCHCH_3*), 1.11 (dd, $J_{H-P} = 12$, $J_{H-H} = 7.1$, 9H, *PCHCH_3*), -16.30 (dd, $J_{H-P} = 33.6$, $J_{H-H} = 3.9$, 1H, Os-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 263 K): δ 31.4 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 263 K): δ 153.9 (s, C_{ipso}Ph), 128.1 and 125.1 (both s, Ph), 122.7 (s, *p*-Ph), 80.1 (s, Cp), 28.4 (d, $J_{C-P} = 28$, *PCH*), 21.5 (s, *PCHCH_3*), 20.5 (s, *CHPh*), 19.9 (s, *PCHCH_3*) 1.28 (s, CH_2). MS (FAB $^+$): m/z 522 ($\text{M}^+ + \text{H}$).

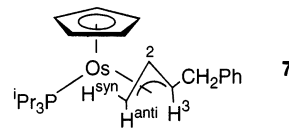


Preparation of $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\{\eta^2\text{-}(E)\text{-CHPh=CHCH=CH}_2\}(\text{P}^i\text{Pr}_3)$ (5). A bluish green solution of **2** (100 mg, 0.18 mmol) in 5 mL of tetrahydrofuran at 0 °C was treated with allylmagnesium chloride (92.4 μL , 0.18 mmol, 2 M in tetrahydrofuran). The solution was stirred for 1 h, after which it became brown. The solvent was removed. The product was extracted with 20 mL of pentane, and the solution was filtered through Kieselguhr. The resultant yellow solution was concentrated to 2 mL, and a pale yellow solid was obtained. The solid was separated by decantation and dried in vacuo. Yield: 75.8 mg (75%). Anal. Calcd for $\text{C}_{24}\text{H}_{37}\text{OsP}$: C, 52.72; H, 6.82. Found: C, 52.97; H, 6.79. IR (Nujol, cm^{-1}): $\nu(\text{OsH})$ 2111 (w), $\nu(\text{Ph})$ 1610 (m). ^1H NMR (C_6D_6 , 293 K): δ 7.53 (d, $J_{H-H} = 7.5$, 2H, *o*-Ph), 7.12 (vt, $J_{H-H} = 7.5$, 2H, *m*-Ph), 6.97 (t, $J_{H-H} = 7.5$, 1H, *p*-Ph), 5.78 (ddd, $J_{H^2-H^3} = 9.3$, $J_{H^2-H^{1A}} = 10.2$, $J_{H^2-H^{1B}} = 16.8$, 1H, H^2), 5.14 (dd, $J_{H^{1A}-H^{1B}} = 2.1$, $J_{H^{1A}-H^2} = 16.8$, 1H, H^{1A}), 4.79 (dd, $J_{H^{1A}-H^{1B}} = 2.1$, $J_{H^{1B}-H^2} = 10.2$, 1H, H^{1B}), 4.71 (s, 5H, C_5H_5), 4.70 (d, $J_{H^4-H^3} = 9.3$, 1H, H^4), 3.33 (ddd, $J_{H^3-H^2} = J_{H^3-H^4} = J_{H^3-P} = 9.3$, 1H, H^3), 1.65 (m, 3H, *PCH*), 1.02 (dd, $J_{H-P} = 12.6$, $J_{H-H} = 7.5$, 9H, *PCHCH}_3*), 0.65 (dd, $J_{H-P} = 12.9$, $J_{H-H} = 7.2$, 9H, *PCHCH}_3*), -16.06 (d, $J_{H-P} = 35.1$, 1H, Os-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 293 K): δ 31.9 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 293 K): δ 153.5 (s, C_{ipso}Ph), 151.8 (s, C^2), 130.7, 127, 124.3 (all s, Ph), 103.9 (s, C^1), 80.4 (s, Cp), 29.6 (d, $J_{C-P} = 28$, *PCH*), 24.3 (d, $J_{C-P} = 2$, C^4), 23.4 (d, $J_{C-P} = 5$, C^3), 20.4 and 19.4 (both s, *PCHCH}_3*).

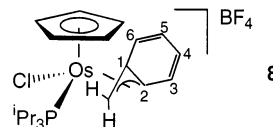


Preparation of $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\text{CHPh}_2)(\text{CO})(\text{P}^i\text{Pr}_3)$ (6). An orange solution of **3** (100 mg, 0.17 mmol) in 5 mL of dichloromethane was stirred under 1 atm of CO for 4 h, at room temperature. The resultant light yellow solution was concentrated to dryness, pentane was added (2 mL), and a white solid precipitated. The solid was separated by decantation and dried in vacuo. Yield: 76 mg (73%). Anal. Calcd for $\text{C}_{28}\text{H}_{37}\text{OOsP}$: C, 55.07; H, 6.11. Found: C, 54.85; H, 6.03. IR (Nujol, cm^{-1}): $\nu(\text{C=O})$ 1895 (vs). ^1H NMR (C_6D_6 , 293 K): δ 7.54 (d, $J_{H-H} = 7.6$, 2H, *o*-Ph), 7.29 (d, $J_{H-H} = 7.6$, 2H, *o*-Ph), 7.21 (vt, $J_{H-H} = 7.6$, 2H, *m*-Ph), 7.13 (vt, $J_{H-H} = 7.6$, 2H, *m*-Ph), 6.97 (t, $J_{H-H} = 7.6$, 1H, *p*-Ph), 6.91 (t, $J_{H-H} = 7.6$, 1H, *p*-Ph), 5.35 (d, $J_{H-P} = 3.5$, -*CHPh}_2*), 4.63 (s, 5H, C_5H_5), 2.10 (m, 3H, *PCH*), 0.94 (dd, $J_{H-P} = 13.7$, $J_{H-H} = 7.2$, 9H, *PCHCH}_3*), 0.71 (dd, $J_{H-P} = 12.8$, $J_{H-H} = 7.1$, 9H, *PCHCH}_3*). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 293 K): δ 16.9 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 293 K): δ 189.2 (d, $J_{C-P} = 13$, CO), 159.3 (s, C_{ipso}Ph), 155.3 (s, C_{ipso}Ph), 131, 123.6, 122.6 (all s, Ph), 82.9 (s, Cp), 27.2 (d, $J_{C-P} = 28$, *PCH*), 20.2 and 19.1 (s, *PCHCH}_3*), 10.0 (d, $J_{C-P} = 5$, -*CHPh}_2*).

Preparation of $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\{\eta^3\text{-CH}_2\text{CHCH}(\text{CH}_2\text{Ph})\}(\text{P}^i\text{Pr}_3)$ (7). A yellow solution of **5** (100 mg, 0.18 mmol) in 5 mL of toluene was heated at 60 °C for 6 h. After the sample was cooled to room temperature, the yellow solution obtained was concentrated to dryness and MeOH was added (about 2 mL). A white solid was obtained, and the suspension was stored at -78 °C for 30 min. The solid was separated by decantation, washed with cold MeOH, and dried in vacuo. Yield: 90 mg (90%). Anal. Calcd for $\text{C}_{24}\text{H}_{37}\text{OsP}$: C, 52.72; H, 6.82. Found: C, 52.51; H, 6.38. ^1H NMR (C_6D_6 , 293 K): δ 7.50 (d, $J_{H-H} = 7.5$, 2H, *o*-Ph), 7.29 (t, $J_{H-H} = 7.5$, 2H, *m*-Ph), 6.99 (t, $J_{H-H} = 7.5$, 1H, *p*-Ph), 4.55 (s, 5H, C_5H_5), 3.73 (dddd, $J_{H^{1syn}-H^2} = 6.0$, $J_{H^{1anti}-H^2} = J_{H^2-H^3} = 8.3$, $J_{H-P} = 3.6$, 1H, H^2), 3.32 (dd, $J_{gem} = 14.4$, $J_{H-H} = 3$, 1H, - CH_2Ph), 2.83 (dd, $J_{H^{1syn}-H^2} = 6.0$, $J_{H^{1syn}-H^{1anti}} = 1.8$, 1H, H^{1syn}), 2.73 (dd, $J_{gem} = 14.4$, $J_{H-H} = 9.9$, 1H, - CH_2Ph), 1.74 (m, 3H, *PCH*), 1.44 (m, 1H, H^3), 0.98 (dd, $J_{H-P} = 12.0$, $J_{H-H} = 7.0$, 9H, *PCHCH}_3*), 0.97 (dd, $J_{H-P} = 12.0$, $J_{H-H} = 7.1$, 9H, *PCHCH}_3*), 0.73 (ddd, $J_{H-P} = 14.0$, $J_{H^{1anti}-H^2} = 8.3$, $J_{H^{1syn}-H^{1anti}} = 1.8$, 1H, H^{1anti}). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 293 K): δ 21.9 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 293 K): δ 146.3 (s, C_{ipso}Ph), 128.5, 128.5, and 125.6 (all s, Ph), 72 (s, Cp), 52.8 (s, C^2), 46.8 (s, - CH_2Ph), 36.0 (d, $J_{C-P} = 6$, C^3), 27.0 (d, $J_{C-P} = 25$, *PCH*), 20.4 and 20.0 (both s, *PCHCH}_3*), 11.0 (d, $J_{C-P} = 6$, C^1).



Reaction of **2 with HBF_4 .** A bluish green solution of **2** (13 mg, 0.02 mmol) in dichloromethane- d_2 (0.4 mL) was treated with a tetrafluoroboric acid/diethyl ether complex (3.2 μL , 0.02 mmol). Immediately, the solution became dark red. After 2 min at room temperature, the NMR spectra showed the presence of $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**8**) and $[\text{OsH}(\eta^5\text{-C}_5\text{H}_5)(\equiv\text{CPh})(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**9a**) in a molar ratio 7:1. Spectroscopic data for **8**: ^1H NMR (CD_2Cl_2 , 293 K): δ 8.49 (vt, $J_{H-H} = 7.8$, 1H, H^4), 7.59 (d, $J_{H-H} = 7.8$, 1H, H^2), 7.59 (d, $J_{H-H} = 7.8$, 1H, H^6), 7.22 (vt, $J_{H-H} = 7.8$, 1H, H^3), 6.83 (vt, $J_{H-H} = 7.8$, 1H, H^5), 6.29 (s, 5H, C_5H_5), 5.23 (d, $J_{H-H} = 4.8$, 1H, - CH_2 -allyl), 5.04 (dd, $J_{H-P} = 11.2$, $J_{H-H} = 4.8$, 1H, - CH_2 -allyl), 2.71 (m, 3H, *PCH*), 1.38 (dd, $J_{H-P} = 12.9$, $J_{H-H} = 7.2$, 9H, *PCHCH}_3*), 1.16 (dd, $J_{H-P} = 13.2$, $J_{H-H} = 7.2$, 9H, *PCHCH}_3*). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 293 K): δ -7.1 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 293 K): 21 δ 139.8 (s, C^4), 136.5 (s, C^3), 134.3 (s, C^2 or C^6), 130.5 (s, C^5), 109.9 (s, C^2 or C^6), 89.5 (s, Cp), 27.1 (d, $J_{C-P} = 25$, *PCH*), 22.5 (d, $J_{C-P} = 26$, - CH_2 -allyl), 20.9 and 20.1 (both s, *PCHCH}_3*).



Preparation of $[\text{OsH}(\eta^5\text{-C}_5\text{H}_5)(\equiv\text{CPh})(\text{P}^i\text{Pr}_3)]\text{PF}_6$ (9b**).** An orange solution of **1** (300 mg, 0.49 mmol) in 4 mL of toluene was treated with 12.5 mL of a red solution of $\text{N}_2=\text{CHPh}$ in toluene (0.078 M, 1.96 mmol). The reaction mixture was allowed to react at room temperature for 4 h. The solvent was removed in vacuo, and the resultant green oil was treated with 6 mL of acetone and 171 mg (0.49 mmol) of thallium(I) hexafluorophosphate. The resulting mixture was stirred for 15 min in the absence of light, during which it became brown. The suspension was filtered through Kieselguhr. The resultant solution was concentrated to ca. 1 mL and cooled to 0 °C. Diethyl ether was added (15 mL) and 30 min later, a yellow

(20) Jiménez, A. I.; López, P.; Oliveros, L.; Cativiela, C. *Tetrahedron* **2001**, *57*, 6019.

(21) The resonance due to C(1) was not observed.

Table 6. Crystal Data and Data Collection and Refinement for 3, 5, 7, 9b, and 12

| | 3 | 5 | 7 | 9b | 12 |
|--|--|---|---|--|--|
| Crystal Data | | | | | |
| formula | C ₂₇ H ₃₇ OsP | C ₂₄ H ₃₇ OsP | C ₂₄ H ₃₇ OsP | C ₂₁ H ₃₂ F ₆ OsP ₂ ·0.5H ₂ O | C ₂₇ H ₃₇ OOSp |
| molecular wt | 582.74 | 546.71 | 546.71 | 659.61 | 598.74 |
| color and habit | orange, irregular block | yellow, irregular block | needle, irregular block | yellow, irregular block | yellow, irregular block |
| size, mm | 0.18, 0.18, 0.08 | 0.20, 0.18, 0.16 | 0.12, 0.06, 0.06 | 0.30, 0.30, 0.06 | 0.12, 0.08, 0.07 |
| symmetry, space group | monoclinic, <i>P</i> 2 ₁ / <i>c</i> | triclinic, <i>P</i> $\bar{1}$ | orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁ | monoclinic, <i>P</i> 2/ <i>c</i> | monoclinic, <i>P</i> 2 ₁ / <i>c</i> |
| <i>a</i> , Å | 9.1858(6) | 9.1744(5) | 7.6276(4) | 14.3655(16) | 10.7954(8) |
| <i>b</i> , Å | 14.2596(10) | 10.8883(6) | 9.6814(5) | 9.3630(10) | 13.0172(10) |
| <i>c</i> , Å | 18.4529(13) | 11.1237(6) | 29.1843(15) | 18.247(2) | 16.8056(12) |
| α , deg | | 97.945(1) | | | |
| β , deg | 102.582(2) | 93.635(1) | | 101.232(2) | 93.673(1) |
| γ , deg | | 94.429(1) | | | |
| <i>V</i> , Å ³ | 2359.0(3) | 1094.14(10) | 2155.14(19) | 2407.3(5) | 2356.8(3) |
| <i>Z</i> | 4 | 2 | 4 | 4 | 4 |
| <i>D</i> _{calc} , g cm ⁻³ | 1.641 | 1.659 | 1.685 | 1.822 | 1.682 |
| Data Collection and Refinement | | | | | |
| diffractometer | Bruker Smart APEX | | | | |
| λ (Mo K α), Å | 0.71073 | | | | |
| monochromator | graphite oriented | | | | |
| scan type | ω scans | | | | |
| μ , mm ⁻¹ | 5.48 | 5.91 | 6.00 | 5.49 | 5.50 |
| 2 θ , range deg | 3, 57 | 3, 57 | 3, 57 | 3, 57 | 3, 57 |
| temp, K | 100.0(2) | 100.0(2) | 100.0(2) | 173.0(2) | 100.0(2) |
| no. of data collect | 21596 | 13436 | 28479 | 15246 | 21483 |
| no. of unique data | 5584 (<i>R</i> _{int} = 0.0501) | 5094 (<i>R</i> _{int} = 0.037) | 5185 (<i>R</i> _{int} = 0.068) | 5690 (<i>R</i> _{int} = 0.0461) | 5608 (<i>R</i> _{int} = 0.0520) |
| no. of params/restraints | 274/0 | 265/1 | 260/0 | 285/10 | 256/0 |
| Flack param | | | 0.162(6) | | |
| <i>R</i> ₁ ^a [<i>F</i> ² > 2 σ (<i>F</i> ²)] | 0.0282 | 0.0228 | 0.0242 | 0.0546 | 0.0354 |
| <i>wR</i> ₂ ^b [all data] | 0.0433 | 0.0423 | 0.0382 | 0.1319 | 0.0611 |
| <i>S</i> ^c [all data] | 0.776 | 0.933 | 0.841 | 1.038 | 0.814 |

^a $R_1(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR_2(F^2) = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$. ^c $Goof = S = \{ \sum [F_o^2 - F_c^2]^2 / (n - p) \}^{1/2}$, where *n* is the number of reflections, and *p* is the number of refined parameters.

solid appeared, which was separated by decantation, washed with 2 mL of tetrahydrofuran, and dried in vacuo. Yield: 210 mg (66%). Anal. Calcd for C₂₁H₃₂F₆OsP₂: C, 38.77; H, 4.96. Found: C, 38.65; H, 4.90. IR (Nujol, cm⁻¹): ν (OsH) 2129 (w), ν (Ph) 1586 (m), ν (PF₆) 845 (vs). ¹H NMR (CD₂Cl₂, 293 K): δ 7.86 (tt, *J*_{H-H} = 7.6, *J*_{H-H} = 1.3, 1H, *p*-Ph), 7.79 (dd, *J*_{H-H} = 7.6, *J*_{H-H} = 1.3, 2H, *o*-Ph), 7.47 (vt, *J*_{H-H} = 7.6, 2H, *m*-Ph), 5.86 (s, 5H, C₅H₅), 2.15 (m, 3H, PCH), 1.29 (dd, *J*_{H-P} = 10.2, *J*_{H-H} = 7.2, 9H, PCHCH₃), 1.24 (dd, *J*_{H-P} = 10.2, *J*_{H-H} = 7.2, 9H, PCHCH₃), -11.94 (d, *J*_{H-P} = 24.0, 1H, Os-H). ³¹P{¹H} NMR (CD₂Cl₂, 293 K): δ -146.2 (sept, *J*_{F-P} = 714, PF₆), 45.1 (s, PⁱPr₃). ¹³C{¹H} NMR (CD₂Cl₂, 293 K): δ 280.5 (d, *J*_{C-P} = 9, Os=C), 145.6 (s, C_{ipso}Ph), 135.1, 132, and 129.6 (all s, Ph), 88.5 (s, Cp), 30.1 (d, *J*_{C-P} = 33, PCH), 20.1 and 19.6 (both s, PCHCH₃).

Preparation of Os(η^5 -C₅H₅)(=CPh)(PⁱPr₃) (10). A slurry of **9b** (240 mg, 0.37 mmol) in 7 mL of tetrahydrofuran was treated with 20 mg (0.37 mmol) of sodium methoxide. The mixture was stirred for 12 h at room temperature. The resulting dark brown solution was concentrated to dryness. The product was extracted with 20 mL of pentane, which was filtered through Kieselguhr. The resulting dark purple solution was concentrated to about 1 mL and cooled to -78 °C, and a dark purple precipitate was obtained. The solid was separated by decantation and dried in vacuo. Yield: 144 mg (77%). Anal. Calcd for C₂₁H₃₁OsP: C, 49.98; H, 6.19. Found: C, 50.37; H, 5.87. IR (Nujol, cm⁻¹): ν (Ph) 1583 (m). ¹H NMR (C₆D₆, 293 K): δ 7.85 (m, 2H, *o*-Ph), 7.11 (tt, *J*_{H-H} = 7.5, *J*_{H-H} = 1.2, 1H, *p*-Ph), 6.88 (vt, *J*_{H-H} = 7.5, 2H, *m*-Ph), 4.83 (s, 5H, C₅H₅), 1.69 (m, 3H, PCH), 1.17 (dd, *J*_{H-P} = 14, *J*_{H-H} = 6.9, 18H, PCHCH₃). ³¹P{¹H} NMR (C₆D₆, 293 K): δ 53.5 (s). ¹³C{¹H} NMR (C₆D₆, 293 K): δ 262.0 (d, *J*_{C-P} = 14, Os=C), 150.4 (s, C_{ipso}Ph), 129.5, 128.9, and 127.6 (all s, Ph), 76.4 (s, Cp), 30.9 (d, *J*_{C-P} = 29, PCH), 20.7 (s, PCHCH₃). MS (FAB⁺): *m/z* 505 (M⁺).

Preparation of OsH(η^5 -C₅H₅){=C(OCH₃)Ph}(PⁱPr₃) (11).

An orange solution of **10** (150 mg, 0.23 mmol) in 5 mL of methanol was stirred for 1 h at room temperature and filtered through Kieselguhr. The solution was concentrated to dryness, and the product was isolated as a dark orange oil. Yield: 140 mg (88%). ¹H NMR (C₆D₆, 293 K): δ 7.17 (d, *J*_{H-H} = 7.2, 2H, *o*-Ph), 7.04 (vt, *J*_{H-H} = 7.2, 2H, *m*-Ph), 6.95 (t, *J*_{H-H} = 7.5, 1H, *p*-Ph), 4.82 (s, 5H, C₅H₅), 3.09 (s, 3H, -OCH₃), 2.03 (m, 3H, PCH), 1.17 (dd, *J*_{H-P} = 12.9, *J*_{H-H} = 7.2, 9H, PCHCH₃), 1.12 (dd, *J*_{H-P} = 12.9, *J*_{H-H} = 7.2, 9H, PCHCH₃), -14.99 (d, *J*_{H-P} = 32.1, 1H, Os-H). ³¹P{¹H} NMR (C₆D₆, 293 K): δ 46.5 (s). ¹³C{¹H} NMR (C₆D₆, 293 K): δ 242.6 (d, *J*_{C-P} = 9, Os=C), 160.4 (s, C_{ipso}Ph), 126.6, 125.5, and 122.5 (all s, Ph), 83 (s, Cp), 57.2 (s, -OCH₃), 28.8 (d, *J*_{C-P} = 27.3, PCH), 20.1 and 19.8 (both s, PCHCH₃). MS (FAB⁺): *m/z* 538 (M⁺ + H), *m/z* 507 (M⁺ + H - OCH₃).

Preparation of OsH(η^5 -C₅H₅){CH(Ph)OC₆H₄}(PⁱPr₃) (12).

A deep purple solution of **10** (140 mg, 0.28 mmol) in pentane was treated with phenol (26 mg, 0.28 mmol). The sample was stirred at room temperature for 12 h. The resultant light orange solution was filtered through Kieselguhr and concentrated to 2 mL. A yellow solid was obtained. The solid was separated by decantation, and cold pentane was added (1 mL). The suspension was stored at -78 °C for 20 min. The yellow solid was separated by decantation and dried in vacuo. Yield: 110 mg (66%). Anal. Calcd for C₂₇H₃₇OOSp: C, 54.16; H, 6.23. Found: C, 54.07; H, 6.06. ¹H NMR (C₆D₆, 293 K): δ 8.36 (s, 1H, OsCH), 7.45 (d, *J*_{H-H} = 7.5, 2H, *o*-Ph), 7.22 (vt, *J*_{H-H} = 7.5, 2H, *m*-Ph), 7.1 (m, 1H, Ph), 7.04 (vt, *J*_{H-H} = 7.5, 1H, Ph), 6.91 (vt, *J*_{H-H} = 7.5, 1H, Ph), 6.78 (vt, *J*_{H-H} = 7.5, 1H, Ph), 6.64 (d, *J*_{H-H} = 7.5, 1H, Ph), 4.34 (s, 5H, C₅H₅), 2.12 (m, 3H, PCH), 0.79 (dd, *J*_{H-P} = 14.4, *J*_{H-H} = 7.2, 9H, PCHCH₃), 0.75 (dd, *J*_{H-P} = 15.9, *J*_{H-H} = 7.2, 9H, PCHCH₃), -13.94 (d, *J*_{H-P} = 41.1, 1H, Os-H). ³¹P{¹H} NMR (C₆D₆, 293 K): δ 19.0 (s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 293 K): δ 172.7 (s, Os– $\text{C}_{\text{sp}2}$), 159.8 (s, $\text{C}_{\text{ipso}}\text{Ph}$) 143.8, 129.7, 125.6, 124.2, 123.4, and 118.7 (all s, Ph), 115.8 (s, $\text{C}_{\text{ipso}}\text{Ph}$), 107 (s, Ph), 84.7 (s, Cp), 67.3 (s, Os– $\text{C}_{\text{sp}3}$), 26.6 (d, $J_{\text{C-P}} = 29$, PCH), 20 and 19.2 (both s, PCHCH₃).

Structural Analysis of Complexes 3, 5, 7, 9b, and 12.

X-ray data were collected for all complexes at low temperature on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) using ω scans. Data were corrected for absorption by using a multi-scan method applied with the SADABS program.²² The structures for all five compounds were solved by the Patterson method. Refinement, by full-matrix least squares on F^2 with SHELXL97,²³ was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters for all non-hydrogen nondisordered atoms. The hydrogens attached to carbon atoms bonded directly to Os metals were observed in the difference maps and refined as free isotropic atoms in the last cycles of refinement. The hydride ligand of **5** was located and refined freely, but in **9b** and **12** these refinements

(22) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33–38. SADABS: Area-detector absorption correction; Bruker-AXS: Madison, WI, 1996.

were unsuccessful and the distance Os–H was fixed to 1.59–(1) Å.²⁴ The rest of the hydrogen atoms were calculated and refined using a restricted riding mode. All the highest electronic residuals were observed in close proximity of the Os centers and make no chemical sense.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray studies, and bond distances and angles for **3**, **5**, **7**, **9b**, and **12**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(23) SHELXTL Package v. 6.10; Bruker-AXS: Madison, WI, 2000. Sheldrick, G. M. SHELXS-86 and SHELXL-97; University of Göttingen: Göttingen, Germany, 1997.

(24) 3D Search and Research Using the Cambridge Structural Database. Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8* (1), 1, 31–37.