Influence of the Group 14 Element on the Deprotonation of $OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CPh)(EPh_3)(P^iPr_3)$ (E = Si, Ge): Two Different Organometallic Chemistries

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The complexes $OsH(\eta^5\text{-}C_5H_5)Cl(EPh_3)(P^iPr_3)$ (E = Si (**1**), Ge (**2**)) react with lithium phenylacetylide to give the hydride−alkynyl derivatives $OsH(\eta^5\text{-}C_5H_5)(C{\equiv}CPh)(EPh_3)(P^iPr_3)$ (E = Si (**3**), Ge (**4**)). The structure of **4** has been determined by X-ray diffraction analysis. The distribution of ligands around the osmium atom can be described as a four-legged piano-stool geometry with the monodentate ligands lying in the four-membered face. Treatment of **3** with *n*-butyllithium and the subsequent addition of methanol, methanol-d_4, and methyl iodide to the resulting solution leads to $OsH(\eta^5\text{-}C_5H_4SiPh_3)\{{=}C{=}C(H)Ph\}(P^iPr_3)$ (**5**), $OsH(\eta^5\text{-}C_5H_4SiPh_3)\{{=}C{=}C(D)Ph\}(P^iPr_3)$ (**5-*d***), and $OsH(\eta^5\text{-}C_5H_4SiPh_3)\{o\text{-}C_6H_4C(CH_3){=}CH\}(P^iPr_3)$ (**6**), respectively. Similarly to **3**, the reaction of the perdeuterated cyclopentadienyl complex $OsH(\eta^5\text{-}C_5D_5)(C{\equiv}CPh)(SiPh_3)(P^iPr_3)$ (**3-*d*$_5$**) with *n*-butyllithium and methanol gives $OsH(\eta^5\text{-}C_5D_4SiPh_3)\{{=}C{=}C(H)Ph\}(P^iPr_3)$ (**5-*d*$_4$**). The structure of **6** has been also determined by X-ray diffraction analysis. In this case, the distribution of ligands around the osmium atom can be described as a piano-stool geometry with the metalated carbon atom transoid to the phosphine and cisoid to the hydride. Complex **5** reacts with HBF_4 to give the hydride−carbyne derivative $[OsH(\eta^5\text{-}C_5H_4SiPh_3)({\equiv}CCH_2Ph)(P^iPr_3)]BF_4$ (**7**), which is stable. Initially, the addition of HBF_4 to diethyl ether solutions of **6** also leads to a hydride−carbyne complex, $[OsH(\eta^5\text{-}C_5H_4SiPh_3)\{{\equiv}CCH(CH_3)Ph\}(P^iPr_3)]BF_4$ (**8**). However, in solution, complex **8** evolves into the hydride−allyl compound $[OsH(\eta^5\text{-}C_5H_4SiPh_3)\{\eta^3\text{-}CH_2C(Ph)CH_2\}(P^iPr_3)]BF_4$ (**9**). The structure of **9** has been determined by X-ray diffraction analysis. The distribution of ligands around the osmium atom can be described as a piano-stool geometry, where the allyl ligand occupies two cisoid positions. Treatment of **4** with *n*-butyllithium and the subsequent addition of methanol, methanol-d_4, and methyl iodide to the resulting solution gives the germyl−vinylidene complexes $Os(\eta^5\text{-}C_5H_5)(GePh_3)\{{=}C{=}C(H)Ph\}(P^iPr_3)$ (**10**), $Os(\eta^5\text{-}C_5H_4D)(GePh_3)\{{=}C{=}C(D)Ph\}(P^iPr_3)$ (**10-*d*$_2$**), and $Os(\eta^5\text{-}C_5H_4CH_3)(GePh_3)\{{=}C{=}C(CH_3)Ph\}(P^iPr_3)$ (**11**), respectively. The protonation of **10** and **11** with HBF_4 affords the corresponding carbyne derivatives $[Os(\eta^5\text{-}C_5H_5)(GePh_3)({\equiv}CCH_2Ph)(P^iPr_3)]BF_4$ (**12**) and $[Os(\eta^5\text{-}C_5H_4CH_3)(GePh_3)\{{\equiv}CCH(CH_3)Ph\}(P^iPr_3)]BF_4$ (**13**).

Introduction

Transition-metal hydride complexes are involved in many stoichiometric and catalytic processes.[1] Therefore, a knowledge of the chemical properties of the metal−hydrogen bonds is of great interest. Of these, acid−base properties are among the most important and fundamental. They depend on the electron density of the metallic fragment. For a given metal, the electron density is modulated by the coligands.[2]

The acidity of the hydride ligand in the hydride−alkynyl intermediates appears to be the key for the π-alkyne−vinylidene transformation by 1,3-hydrogen shift. For group 8, Puerta and co-workers[3] have proved that half-sandwich ruthenium−vinylidene compounds can be formed from hydride−alkynyl species in a dissociative two-step process (elimination−addition). The first step consists of the dissociation of a proton, and the second one is the protonation of the resulting alkynyl intermediate.

In many cases the hydride complex bears a cyclopentadienyl ligand, which is known to have rather acidic C−H bonds. In agreement with the acidity of the η^5-C_5H_5 group, cyclopentadienyl complexes of molybdenum,

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tungsten,[4] rhenium,[5] iron,[6] and ruthenium[7] undergo base-induced migration reactions of a monodentate ligand from the metal to a neighboring cyclopentadienyl carbon atom. It is widely accepted that such reactions involve the initial deprotonation of the cyclopentadienyl ring followed by the ligand migration. The produced anion is quenched by reaction with an electrophile.

Despite the known kinetic inertia of the Os(η^5-C_5R_5)-L_3 species,[8] we have previously reported that the complex Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$ reacts with HER_3 molecules to afford the osmium(IV)-hydride derivatives OsH(η^5-C_5H_5)Cl(ER_3)(P^iPr_3) (E = Si, Ge).[9] The nature of E has a marked influence on the reactivity of these types of compounds. Treatment of OsH(η^5-C_5H_5)Cl(EPh_3)(P^iPr_3) with alkyllithium reagents produces the replacement of the chlorine ligand by the alkyl group, to afford OsH-(η^5-C_5H_5)(EPh_3)R(P^iPr_3). These intermediates are unstable and evolve into two different types of substituted cyclopentadienyl complexes, depending on the nature of E.[10] The intermediates OsH(η^5-C_5H_5)($GePh_3$)R(P^iPr_3) afford the dihydride−germyl derivatives OsH_2(η^5-C_5H_4R)($GePh_3$)(P^iPr_3) (R = CH_3, ^{n}Bu, ^{s}Bu) by R(Os)/H(C_5H_5) exchange while, under the same conditions, the silyl species OsH(η^5-C_5H_5)R($SiPh_3$)(P^iPr_3) undergo $SiPh_3$-(Os)/H(C_5H_5) exchange. The resulting dihydride−alkyl compounds are unstable toward the reductive elimination of alkane. As a result, the metallic center of the unsaturated intermediate that forms, OsH(η^5-C_5H_4-$SiPh_3$)(P^iPr_3), is capable of a C−H activation reaction on one of the phenyl groups of the $SiPh_3$ fragment, to give the dihydride cyclometalated complex OsH_2(η^5-$C_5H_4Si(C_6H_4)Ph_2$)(P^iPr_3).

We have now prepared the hydride−alkynyl compounds OsH(η^5-C_5H_5)(C≡CPh)(EPh_3)(P^iPr_3) (E = Si, Ge), which, in contrast to the previously mentioned hydride−alkyl species, are stable. The high stability of these compounds prompted us to investigate the influence of E in their deprotonation reactions. In this paper, we report the synthesis and X-ray structure of the new hydride−alkynyl complexes, their transformation into vinylidenes, and the conversion of the latter species to carbyne or allyl derivatives.

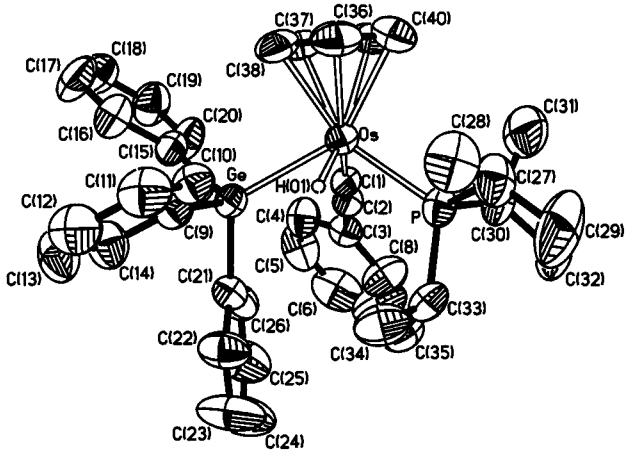


Figure 1. Molecular diagram of the complex OsH(η^5-C_5H_5)(C≡CPh)($GePh_3$)(P^iPr_3) (**4**).

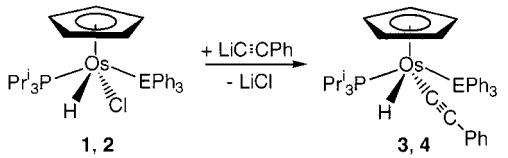
Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complex OsH(η^5-C_5H_5)(C≡CPh)($GePh_3$)(P^iPr_3) (4)

Os−Ge	2.5033(4)	Os−C(37)	2.204(4)
Os−P	2.3459(10)	Os−C(38)	2.222(4)
Os−C(1)	2.008(4)	Os−C(39)	2.278(4)
Os−C(36)	2.240(4)	Os−C(40)	2.283(4)
C(1)−C(2)	1.214(4)	C(2)−C(3)	1.424(5)
Ge−Os−P	115.97(3)	P−Os−C(1)	83.59(10)
Ge−Os−M[a]	115.35(14)	P−Os−H(01)	76.7(15)
Ge−Os−C(1)	79.06(9)	M−Os−C(1)	119.7(2)
Ge−Os−H(01)	59.1(13)	M−Os−H(01)	120.0(5)
P−Os−M	126.65(13)	C(1)−Os−H(01)	117.1(13)
Os−C(1)−C(2)	175.4(3)	C(1)−C(2)−C(3)	171.1(4)

[a] M is the centroid of the C(36)−C(40) Cp ligand.

Results and Discussion

1. Synthesis and Characterization of OsH(η^5-C_5H_5)(C≡CPh)(EPh_3)(P^iPr_3) (E = Si, Ge). Treatment of tetrahydrofuran solutions of OsH(η^5-C_5H_5)Cl(EPh_3)(P^iPr_3) (E = Si (**1**), Ge (**2**)) with lithium phenylacetylide produces the replacement of the chlorine ligand by the alkynyl group to give the hydride−alkynyl derivatives OsH(η^5-C_5H_5)(C≡CPh)(EPh_3)(P^iPr_3) (E = Si (**3**), Ge(**4**)), which are isolated as brown solids in about 60% yield (eq 1).



(1)

Complexes **3** and **4** were characterized by MS, elemental analysis, and IR and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. Furthermore, complex **4** was characterized by X-ray diffraction analysis. A view of its molecular geometry is shown in Figure 1. Selected bond distances and angles are listed in Table 1.

The distribution of ligands about the osmium atom can be described as a piano-stool geometry, with the

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cyclopentadienyl ligand occupying the three-membered face, while the four monodentate ligands lie in the four-membered face.

The most noticeable feature of the structure is the transoid positions of the bulky ligands triisopropylphosphine and triphenylgermyl. The angle Ge−Os−P is 115.97(3)°, whereas the C(1)−Os−H(01) angle is 117.1(13)°. The Os−Ge bond length (2.5033(4) Å) is about 0.06 Å shorter than that found in OsH{Ge(*p*-tolyl)$_3$}(CO)$_2$(PPh$_3$)$_2$ (2.5600(3) Å).[11] This could be related to the different oxidation states of the metallic centers, IV in **4** and II in the above-mentioned carbonyl derivative. The environment of the germanium atom is tetrahedral, with angles between 102.26(15) and 119.50(10)°.

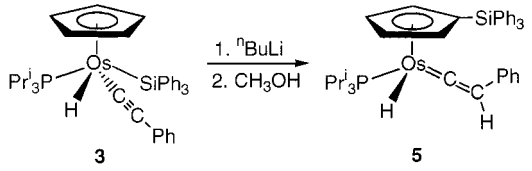
The Os−C(1) distance of 2.008(4) Å is consistent with a single bond from Os(IV) to a C(sp) atom and indicates a low degree of metal-to-ligand back-bonding.[12] The C(1)−C(2) bond length and the Os−C(1)−C(2) and C(1)−C(2)−C(3) angles are 1.424(5) Å and 175.4(3) and 171.1(4)°, respectively. Similar values have been found in the cationic complex [OsH(η^5-C_5H_5)(C≡CPh)(P^iPr_3)$_2$]PF$_6$ for the related parameters.[13]

In agreement with the presence of an alkynyl ligand in **3**, its IR spectrum in Nujol shows a band at 2093 cm^{-1}, corresponding to the ν(C≡C) vibration. The presence of the hydride ligand is supported by the ^{1}H NMR spectrum in benzene-d_6, which contains a doublet at −13.35 ppm with a H−P coupling constant of 32.1 Hz. In the ^{13}C{^{1}H} NMR spectrum the resonances corresponding to the C$_\alpha$ and C$_\beta$ atoms of the alkynyl group appear at 78.4 and 111.9 ppm, respectively. The first of them is observed as a doublet with a C−P coupling constant of 21.8 Hz, while the second one is a singlet. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 18.1 ppm, which under off-resonance conditions is split into a doublet as a consequence of the spin coupling with the hydride.

The spectroscopic data of **4** agree well with those of **3** and are consistent with the structure shown in Figure 1. In the IR spectrum, the ν(C≡C) band is observed at 2081 cm^{-1}. The ^{1}H NMR spectrum shows the hydride resonance as a doublet at −13.42 ppm, with a H−P coupling constant of 34.2 Hz. In the ^{13}C{^{1}H} NMR spectrum, the resonances corresponding to the C(sp) atoms appear at 75.0 (C$_\alpha$) and 112.6 (C$_\beta$) ppm, as a doublet with a C−P coupling constant of 22.6 Hz and a singlet, respectively. The ^{31}P{^{1}H} NMR spectrum contains a singlet at 20.2 ppm, which is split into a doublet under off-resonance conditions.

Species containing simultaneously hydride, alkynyl, and silyl ligands have shown to be key intermediates in the formation of *cis*-alkenylsilanes and alkynylsilanes, by hydrosilylation and dehydrogenative silylation of terminal alkynes.[14] However, only a few compounds of this type, or related complexes with stannyl or germyl instead of silyl, have been isolated and characterized.[14c,15] As far as we know, complexes **3** and **4** are the first derivatives of this class in osmium chemistry.

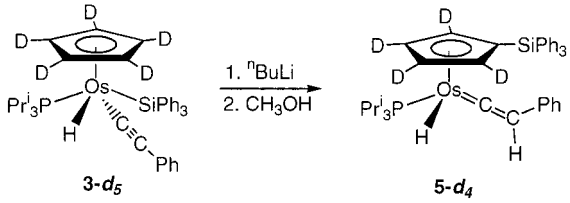
2. Reactions of OsH(η^5-C_5H_5)(C≡CPh)($SiPh_3$)(P^iPr_3). Treatment of a solution of **3** in tetrahydrofuran with 3.0 equiv of *n*-butyllithium over 5 h leads to a solution which reacts with methanol to give the hydride−vinylidene complex OsH(η^5-$C_5H_4SiPh_3$){=C=C(H)Ph}(P^iPr_3) (**5**). This compound, containing a substituted cyclopentadienyl ligand, was isolated as a pale yellow solid in 75% yield (eq 2).



(2)

In agreement with the presence of the substituted cyclopentadienyl ligand, the resonances of the C_5H_4 protons in the ^{1}H NMR spectrum appear as an ABCD spin system, between 5.36 and 4.99 ppm. The =CH proton of the vinylidene displays at 2.50 ppm a double doublet by spin coupling with the hydride (2.4 Hz) and the phosphorus of the phosphine (2.4 Hz). The spin coupling with the hydride ligand was confirmed by a ^{1}H COSY spectrum. The hydride ligand gives rise to a double doublet with a H−P coupling constant of 29.1 Hz at −14.15 ppm. In the ^{13}C{^{1}H} NMR spectrum the resonances due to the C$_\alpha$ and C$_\beta$ of the vinylidene appear at 290.8 and 111.7 ppm, respectively. The first of them is observed as a doublet with a C−P coupling constant of 12.8 Hz, while the second one is a singlet. The ^{31}P{^{1}H} NMR spectrum shows at 41.8 ppm a singlet, which is split into a doublet by spin coupling with the hydride.

Under the same conditions as those previously mentioned for the formation of **5**, the perdeuterated cyclopentadienyl complex OsH(η^5-C_5D_5)(C≡CPh)($SiPh_3$)(P^iPr_3) (**3-*d*$_5$**) affords OsH(η^5-$C_5D_4SiPh_3$){=C=C(H)Ph}(P^iPr_3) (**5-*d*$_4$**), according to eq 3.



(3)

The presence of hydrogen atoms at the metallic center and the C$_\beta$ atom of the vinylidene of **5-*d*$_4$** is supported by the ^{1}H and ^{2}H NMR spectra of this compound. The ^{1}H NMR spectrum contains hydride and =CH resonances at −14.50 and 2.51 ppm, respectively, while the ^{2}H NMR spectrum only shows a broad resonance at 5.00 ppm, corresponding to the $C_5D_4SiPh_3$ group.

The formation of **5** and **5-*d*$_4$** can be rationalized according to Scheme 1. Although complexes **3** and **3-*d*$_5$** could undergo deprotonation at the metallic center and at the cyclopentadienyl group, by action of ^{n}BuLi, the deprotonation selectively occurs at the cyclopentadienyl

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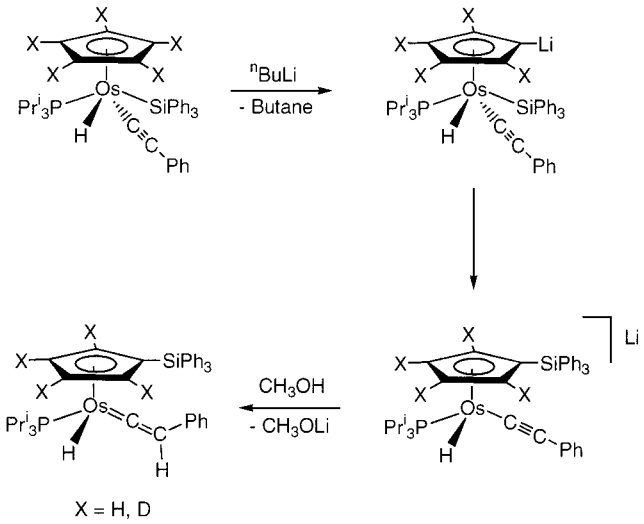
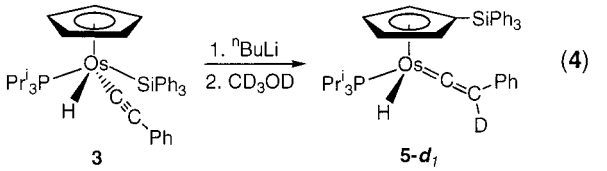
Scheme 1



ligand. The resulting species evolve by migration of the silyl group from the osmium to the cyclopentadienyl ligand, to afford the anion $[OsH(\eta^5\text{-}C_5X_4SiPh_3)(C{\equiv}CPh)(P^iPr_3)]^-$. Then, the acidic proton of methanol attacks the C_β atom of the alkynyl group of this anionic species, to give **5** and **5-*d*$_4$**. The formation of the vinylidene ligand agrees well with the known high nucleophility of the C_β atom of the alkynyl groups in late-transition-metal alkynyl complexes.[16]

In agreement with Scheme 1, we have also observed that the addition of methanol-d_4 to the solution resulting from the treatment of **3** with ^{n}BuLi leads to $OsH(\eta^5\text{-}C_5H_4SiPh_3)\{{=}C{=}C(D)Ph\}(P^iPr_3)$ (**5-*d***), according to eq 4.

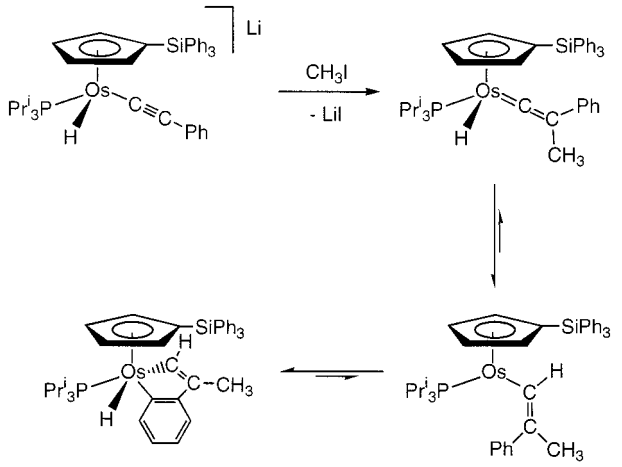


(4)

The presence of a deuterium atom at the C_β atom of the vinylidene ligand of **5-*d*** is strongly supported by the ^{2}H NMR spectrum of this compound, which shows a singlet at 2.52 ppm. In accordance with the ^{2}H NMR spectrum, the ^{1}H NMR spectrum does not contain any ═CH resonance corresponding to the vinylidene.

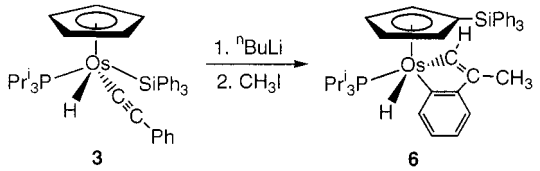
Hydride−vinylidene complexes are considered important intermediates in several homogeneous and heterogeneous catalytic reactions, including alkene oligomerization, polymerization, methatesis of olefins,[17] and Fischer−Tropsch synthesis.[18] However only a few complexes of this type have been isolated.[19] For metals of group 8, with the exception of those containing chelate ligands, the six-coordinate hydride−vinylidene complexes appear to be unstable and in solution evolve to the corresponding five-coordinate alkenyl derivatives,

Scheme 2



as a result of the migratory insertion of the vinylidene group into the M−H bond. As far as we know, complex **5** is the first half-sandwich hydride−vinylidene compound with a metal of group 8.

The stability of the vinylidene in this type of half-sandwich complexes depends on its substituents. The addition of methyl iodide to the solution resulting from the treatment of **3** with *n*-butyllithium does not give the corresponding hydride−methyl−phenylvinylidene, as one should expect, but the metalated derivative $OsH(\eta^5\text{-}C_5H_4SiPh_3)\{o\text{-}C_6H_4C(CH_3){=}CH\}(P^iPr_3)$ (**6**), which was isolated as a white solid in 60% yield (eq 5).



(5)

The formation of **6** can be rationalized according to Scheme 2. The anion $[OsH(\eta^5\text{-}C_5H_4SiPh_3)(C{\equiv}CPh)(P^iPr_3)]^-$, generated from the reaction of **3** with *n*-butyllithium, reacts with methyl iodide to give initially the expected hydride−vinylidene $OsH(\eta^5\text{-}C_5H_4SiPh_3)\{{=}C{=}C(CH_3)Ph\}(P^iPr_3)$, in a manner similar to the formation of **5**. The presence of a methyl group at the C_β atom of the vinylidene increases the electrophilic character of the C_α atom, favoring the migratory insertion of the vinylidene into the Os−H bond. The insertion generates the unsaturated five-coordinate alkenyl intermediate $Os(\eta^5\text{-}C_5H_4SiPh_3)\{CH{=}C(CH_3)Ph\}(P^iPr_3)$, which evolves

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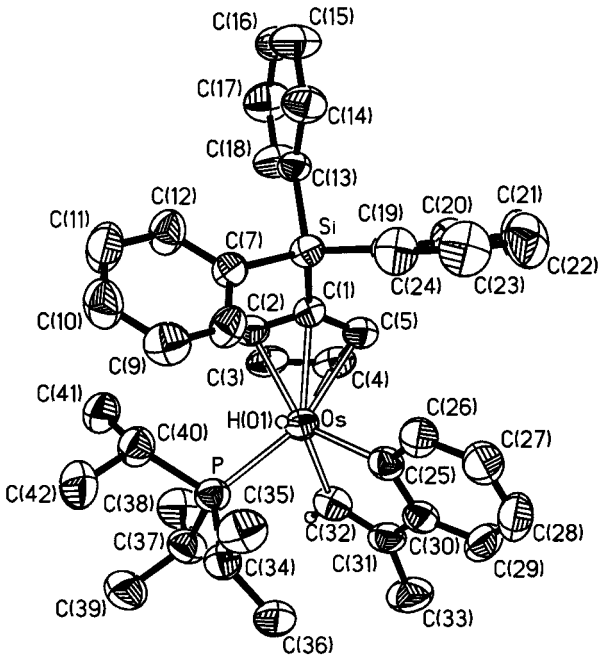


Figure 2. Molecular diagram of the complex OsH(η^5-C_5H_4-$SiPh_3$){*o*-$C_6H_4C(CH_3)$=CH}(P^iPr_3) (**6**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Complex OsH(η^5-$C_5H_4SiPh_3$){*o*-$C_6H_4C(CH_3)$=CH}(P^iPr_3) (6)

Os−P	2.3136(14)	Os−C(4)	2.279(5)
Os−C(1)	2.270(5)	Os−C(5)	2.292(5)
Os−C(2)	2.217(4)	Os−C(25)	2.084(5)
Os−C(3)	2.245(5)	Os−C(32)	2.082(5)
Si−C(1)	1.863(5)	C(31)−C(32)	1.346(7)
C(25)−C(30)	1.419(6)	C(31)−C(33)	1.518(6)
C(30)−C(31)	1.441(7)		
P−Os−M[a]	130.76(16)	M−Os−C(32)	117.6(2)
P−Os−C(25)	107.35(13)	M−Os−H(01)	113.4(8)
P−Os−C(32)	82.42(16)	C(25)−Os−C(32)	74.3(2)
P−Os−H(01)	69.0(13)	C(25)−Os−H(01)	74.9(13)
M−Os−C(25)	121.0(2)	C(32)−Os−H(01)	128.6(13)
Os−C(25)−C(30)	118.6(4)	C(30)−C(31)−C(32)	113.2(5)
Os−C(32)−C(31)	121.3(5)	C(30)−C(31)−C(33)	122.0(5)
C(25)−C(30)−C(31)	112.4(5)	C(32)−C(31)−C(33)	124.6(6)

[a] M is the centroid of the C(1)−C(5) Cp ligand.

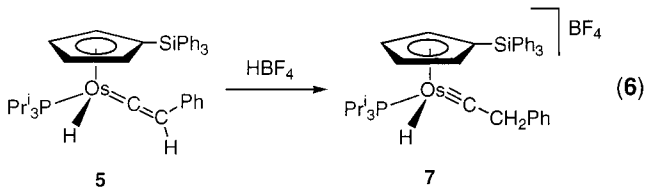
by C−H activation of an ortho CH−aryl bond into **6**. The activation of the phenyl instead of the methyl group of the alkenyl ligand agrees well with the kinetic and thermodynamic preference of the aromatic C−H activation.[20]

A view of the molecular geometry of **6** is shown in Figure 2. Selected bond distances and angles are listed in Table 2. The distribution of ligands around the osmium atom can be described as a four-legged pianostool geometry with the metalated carbon atom C(25) transoid to the phosphine and cisoid to the hydride ligand. The P−Os−C(25) and C(25)−Os−H(01) angles are 107.35(13) and 74.9(13)°, respectively.

The orthometalated alkenyl ligand acts with a bite angle of 74.3(2)°. The five-membered heterometallacycle is almost planar. The deviations (in Å) from the best plane are −0.0001(3) (Os), 0.034(5) (C(25)), −0.028(5) (C(30)), −0.011(5) (C(31)), and 0.034(5) (C(32)). The distances Os−C(25) (2.084(5) Å) and Os−C(32) (2.082(5) Å) are statistically identical and typical for C−(sp^2) single bonds.[21] The C(32)−C(31) bond length (1.346(7) Å) is similar to those found in other alkenyl complexes[22] and agrees well with the average carbon−carbon double-bond distances (1.32(1) Å).[23] The angles around C(31) and C(32) are between 113.2(5) and 124.6(6)°, which indicate an sp^2 hybridization for these atoms.

In agreement with the presence of the hydride ligand disposed cisoid to the phosphine, the ^{1}H NMR spectrum of **6** shows at −13.93 ppm a doublet with a H−P coupling constant of 44.7 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances corresponding to the C(25) and C(32) atoms appear at 160.9 and 130.5 ppm, respectively, as doublets with C−P coupling constants of 2.4 and 20.0 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains at 22.0 ppm a singlet, which under off-resonance conditions is split into a doublet.

3. Protonation of 5 and 6. Theoretical studies on vinylidene transition-metal complexes have identified the electron density on the C_β atom.[24] In agreement with this, the addition of 1.0 equiv of HBF_4·OEt_2 to diethyl ether solutions of **5** affords the hydride−carbyne derivative [OsH(η^5-$C_5H_4SiPh_3$)(≡CCH_2Ph)(P^iPr_3)]BF_4 (**7**), as a result of the protonation of the C_β atom of the vinylidene ligand of **5** (eq 6). Transition-metal hydride−



(6)

carbyne complexes are rare,[25] and as far as we know, half-sandwich osmium complexes have not been previously reported.

Complex **7** was isolated as a brown solid in 87% yield. The presence of a hydride ligand in this compound is supported by its ^{1}H NMR spectrum, which shows at −12.00 ppm a doublet with a H−P coupling constant of 24.3 Hz. In addition, we should mention a singlet at 2.39 ppm, due to the CH_2 group of the carbyne ligand. In the $^{13}C\{^1H\}$ NMR spectrum, the most noticeable resonance is that corresponding to the Os≡C carbon atom, which is observed at 290.6 ppm, as a doublet with a C−P coupling constant of 15.1 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains at 47.2 ppm a singlet, which under off-resonance conditions is split into a doublet.

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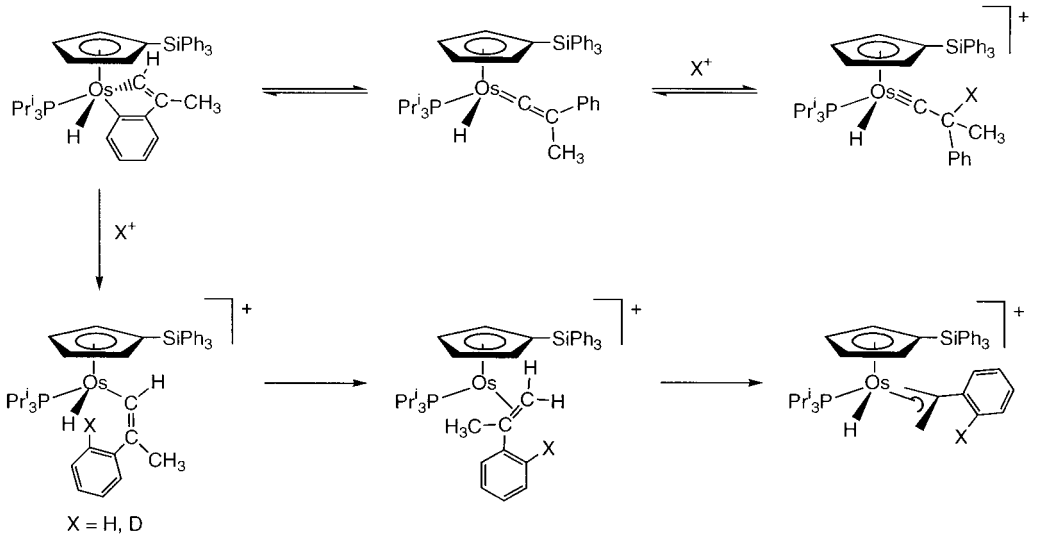
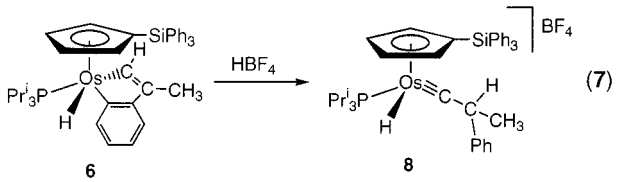
Scheme 3



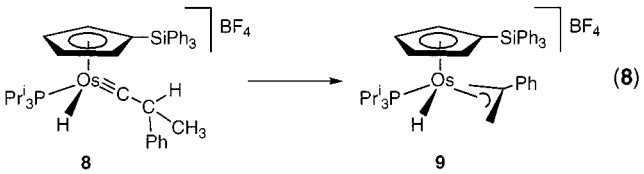
The addition of 1.0 equiv of $HBF_4 \cdot OEt_2$ to diethyl ether solutions of **6** initially gives the hydride−carbyne derivative $[OsH(\eta^5\text{-}C_5H_4SiPh_3)\{\equiv CCH(CH_3)Ph\}(P^iPr_3)]BF_4$ (**8**). The formation of this complex according to eq 7 proves that in fact, as is shown in Scheme 2, in solution complex **6** is in equilibrium with no detectable concentrations of the hydride−vinylidene $OsH(\eta^5\text{-}C_5H_4SiPh_3)\{=C=C(CH_3)Ph\}(P^iPr_3)$.



(7)

As a result of the chirality of the metallic center and the C_β atom of the carbyne ligand, complex **8** was isolated as a 1:1 mixture of the racemic forms of two diastereoisomers. In the ^1H NMR spectrum of the mixture, the most noticeable resonances are those corresponding to the hydride ligands, which appear at −11.60 and −11.68 ppm as doublets with H−P coupling constants of about 25 Hz. In the $^{13}C\{^1H\}$ NMR spectrum the OsC_α atoms display doublets at 294.2 and 294.9 ppm, with C−P coupling constants of about 8 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains two singlets at 47.9 and 47.8 ppm.

In solution, complex **8** evolves into the hydride−allyl isomer $[OsH(\eta^5\text{-}C_5H_4SiPh_3)\{\eta^3\text{-}CH_2C(Ph)CH_2\}(P^iPr_3)]BF_4$ (**9**). At 45 °C, the conversion shown in eq 8 is quantitative after 96 h. This indicates that **8** is the product of kinetic control in the protonation of **6**, whereas **9** is the product of thermodynamic control.



(8)

The protonation of **6** with DBF_4 affords $[OsH(\eta^5\text{-}C_5H_4SiPh_3)\{\equiv CCD(CH_3)Ph\}(P^iPr_3)]BF_4$ (**8-*d***). The presence of the deuterium atom at the C_β atom of the carbyne ligand is supported by the ^2H NMR spectrum of **8-*d***, which contains a broad singlet at 2.58 ppm, as only one resonance. Similarly to **8**, in solution, **8-*d*** evolves into $[OsH(\eta^5\text{-}C_5H_4SiPh_3)\{\eta^3\text{-}CH_2C(C_6H_4D)CH_2\}(P^iPr_3)]BF_4$ (**9-*d***), containing the deuterium atom at one of the ortho carbon atoms of the phenyl group of the allyl ligand. Its position is strongly supported by the ^2H NMR spectrum of **9-*d***, which contains, as only one resonance, a singlet at 7.35 ppm.

The previously mentioned observations suggest that, although the protonation of the hydride−vinylidene is kinetically favored, it is reversible and that the protonation on **6** occurs at the metalated carbon atom of the aryl group (Scheme 3). Thus, once the unsaturated hydride−alkenyl $[OsH(\eta^5\text{-}C_5H_4SiPh_3)\{CH=C(CH_3)Ph\}(P^iPr_3)]BF_4$ is formed, the reductive elimination of the olefin affords $[Os(\eta^5\text{-}C_5H_4SiPh_3)\{\eta^2\text{-}CH_2=C(CH_3)Ph\}(P^iPr_3)]BF_4$, which evolves by C−H activation of the methyl group of the alkene into **9** or **9-*d***. The reductive elimination in $[OsH(\eta^5\text{-}C_5H_4SiPh_3)\{CH=C(CH_3)Ph\}(P^iPr_3)]BF_4$ is probably favored by its unsaturated character,[26] whereas the higher stability of a $M(\eta^3\text{-allyl})$ bond with regard to an M−aryl bond appears to be the driving force for the activation of the methyl instead the phenyl group, in the intermediate $[Os(\eta^5\text{-}C_5H_4SiPh_3)\{\eta^2\text{-}CH_2=C(CH_3)Ph\}(P^iPr_3)]BF_4$.[27]

Figure 3 shows a view of the molecular geometry of **9**. Selected bond distances and angles are listed in Table 3. The distribution of ligands around the osmium atom can be described as a four-legged piano-stool geometry, where the allyl ligand occupies two cisoid positions with a bite angle of 64.2(2)°. The atoms C(24), C(25), C(26), and C(27) of the allyl ligand are coplanar (maximum deviation 0.017(5) Å for C(25)) and form a dihedral angle of 28.04(18)° with the cyclopentadienyl ring. As a result of the disposition of the allyl ligand, the separation between the central carbon atom, C(25), and the metal (2.184(4) Å) is shorter than the separation between the metal and the terminal carbon atoms C(24) (2.217(4) Å) and C(26) (2.196(4) Å). The carbon−carbon distances

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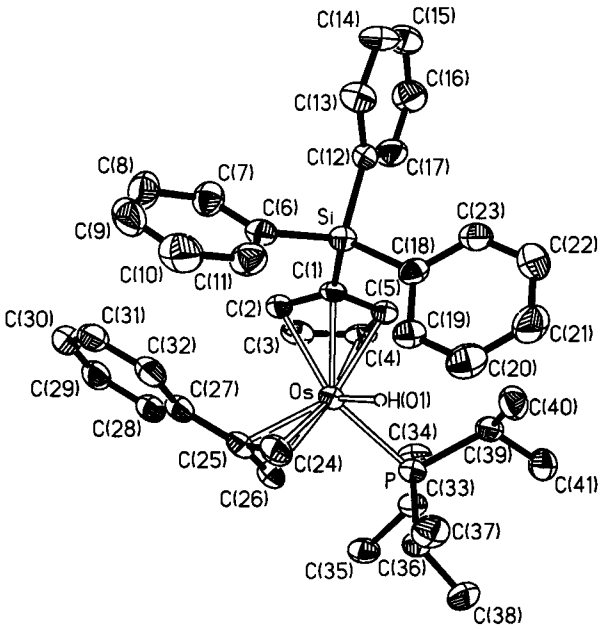


Figure 3. Molecular diagram of the complex [OsH(η^5-$C_5H_4SiPh_3$){η^3-$CH_2C(Ph)CH_2$}(P^iPr_3)]BF_4 (**9**).

Table 3. Selected Bond Distances (Å) and Angles (deg) for the Complex [OsH(η^5-$C_5H_4SiPh_3$){η^3-$CH_2C(Ph)CH_2$}(P^iPr_3)]BF_4 (9)

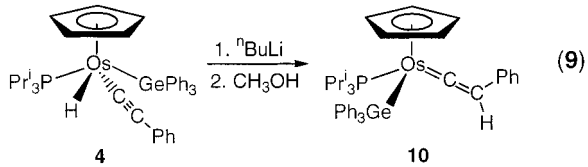
Os−P	2.3500(11)	Os−C(5)	2.188(4)
Os−C(1)	2.255(4)	Os−C(24)	2.217(4)
Os−C(2)	2.266(4)	Os−C(25)	2.184(4)
Os−C(3)	2.266(4)	Os−C(26)	2.196(4)
Os−C(4)	2.246(4)		
Si−C(1)	1.869(4)	C(25)−C(26)	1.415(6)
C(24)−C(25)	1.411(6)	C(25)−C(27)	1.483(6)
P−Os−M[a]	122.89(16)	M−Os−H(01)	108.6(16)
P−Os−C(24)	100.97(15)	C(24)−Os−C(25)	37.39(17)
P−Os−C(25)	112.59(12)	C(24)−Os−C(26)	64.2 (2)
P−Os−C(26)	83.85(13)	C(24)−Os−H(01)	75.3(19)
P−Os−H(01)	70.3(17)	C(25)−Os−C(26)	37.70(16)
M−Os−C(24)	135.1(2)	C(25)−Os−H(01)	112.7(19)
M−Os−C(25)	118.84(18)	C(26)−Os−H(01)	126.2(19)
M−Os−C(26)	125.0(2)		
Os−C(24)−C(25)	70.1(2)	Os−C(26)−C(25)	70.7(2)
Os−C(25)−C(24)	72.6(2)	C(24)−C(25)−C(26)	112.2(4)
Os−C(25)−C(26)	71.6(2)	C(24)−C(25)−C(27)	124.2(4)
Os−C(25)−C(27)	120.8(3)	C(26)−C(25)−C(27)	123.6(4)

[a] M is the centroid of the C(1)−C(5) Cp ligand.

within the allylic moiety are 1.411(6) Å for C(24)−C(25) and 1.415(6) Å for C(25)−C(26). Both bond lengths are about 0.07 Å shorter than the C(25)−C(27) distance (1.483(6) Å), which corresponds to a carbon−carbon single bond. The angle C(24)−C(25)−C(26) is 112.2(4)°.

In agreement with the structure shown in Figure 3, the ^{1}H NMR spectrum shows four resonances for the allylic protons at 4.46, 3.77, 2.15, and 1.82 ppm. In the high-field region the hydride displays a doublet at −13.37 ppm, with a H−P coupling constant of 30.0 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the resonances corresponding to the allyl carbon atoms are observed at 86.2 (C(25)), 28.4 (C(24)), and 18.7 (C(26)) ppm. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 19.3 ppm, which under off-resonance conditions is split into a doublet.

4. Reactions of OsH(η^5-C_5H_5)(C≡CPh)($GePh_3$)(P^iPr_3). There are significant differences in behavior between the silyl complex **3** and its germyl counterpart **4**. The treatment of **4** in tetrahydrofuran with 3.0 equiv of *n*-butyllithium and the subsequent addition of methanol to the resulting solution do not lead to a hydride−vinylidene derivative, containing a germyl-substituted cyclopentadienyl ligand (similar to **5**), but afford the germyl−vinylidene Os(η^5-C_5H_5)($GePh_3$){=C=C(H)Ph}(P^iPr_3) (**10**), according to eq 9.

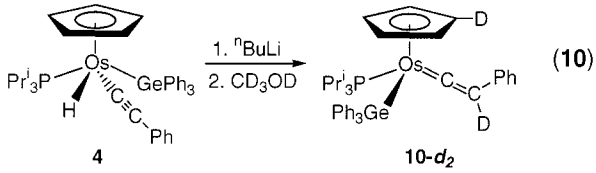


(9)

Complex **10** was isolated as a pale brown solid in 65% yield. In the ^{1}H NMR spectrum, the most noticeable resonances are a singlet at 5.04 ppm, corresponding to the intact cyclopentadienyl ligand, and a doublet at 3.14 ppm with a H−P coupling constant of 1.2 Hz, due to the =CH proton of the vinylidene. In the $^{13}C\{^1H\}$ spectrum, the C_α resonance of the unsaturated η^1-carbon ligand appears at 299.5 ppm, as a doublet with a C−P coupling constant of 12.0 Hz, whereas the C_β resonance is observed at 124.2 ppm, as a singlet. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 19.9 ppm.

Interestingly, the addition of methanol-d_4 to the solution resulting from the treatment of **4** with *n*-butyllithium gives the double-deuterated complex Os(η^5-C_5H_4D)($GePh_3$){=C=C(D)Ph}(P^iPr_3) (**10-*d*$_2$**). The positions of the deuterium atoms at the cyclopentadienyl and vinylidene ligands are strongly supported by the ^{2}H NMR spectrum of the compound, which shows two singlets at 5.01 and 3.21 ppm with a 1:1 intensity ratio.

The formation of **10-*d*$_2$** according to eq 10 indicates that the treatment of **4** with *n*-butyllithium produces a double deprotonation, at the metallic center and at the cyclopentadienyl ligand. Furthermore, it should be noted



(10)

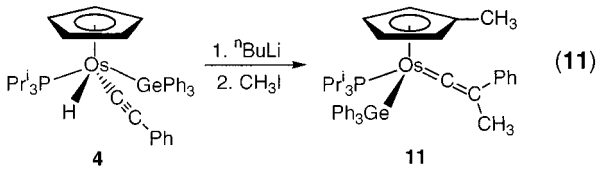
that, in contrast to the silyl complex **3**, the deprotonation of the cyclopentadienyl ligand of **4** does not give way to the migration of the germyl group from the osmium atom to the cyclopentadienyl ligand. This agrees well with the previously determined higher thermodynamic stability of the Os−Ge bond in comparison with the Os−Si bond.[9]

Theoretical studies[28] suggest that in these types of compounds, in addition to the M−ER_3 σ bond there is an important π-bonding, as a result of the donation of electron density from d orbitals of the metal to a linear combination of E−R σ^* orbitals. The higher acidity of the hydride of **4** with regard to the hydride of **3** suggests that the larger fortress of the Os−Ge bond is a result of a more efficient d−π^* donation to the germyl than to the silyl group: i.e., the $GePh_3$ group is a better π-ac-

(28) See for example: Hübler, K.; Hunt, P. A.; Maddock, S. M.; Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Schwerdtfeger, P.; Wright, L. J. *Organometallics* **1997**, *16*, 5076.

ceptor ligand than the $SiPh_3$ group. As a result, the electron density at the metallic center of **4** is lower than at the metallic center of **3**. Thus, the Os−H bond is more polarized in **4** than in **3**, and therefore, the hydride of **4** is more acidic than the hydride of **3**.

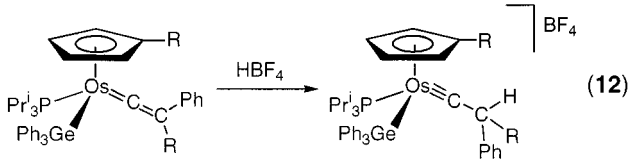
In agreement with the double deprotonation of **4**, the addition of methyl iodide to the solution resulting from the treatment of **4** with *n*-butyllithium gives $Os(\eta^5\text{-}C_5H_4CH_3)(GePh_3)\{=C=C(CH_3)Ph\}(P^iPr_3)$ (**11**), according to eq 11.



4 **11** (**11**)

Complex **11** was isolated as a pale red solid in 72% yield. The presence of the substituted cyclopentadienyl ligand in the complex is supported by its ^1H NMR spectrum, which shows between 5.01 and 4.07 ppm an ABCD spin system corresponding to the cyclopentadienyl protons. In addition, the spectrum contains two singlets due to the $C_5H_4CH_3$ and $=CCH_3$ methyl groups at 2.15 and 1.95 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the C_α and C_β resonances of the vinylidene appear at 303.4 and 115.1 ppm, respectively. The first of them is observed as a doublet with a C−P coupling constant of 12.0 Hz and the second one as a singlet. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 18.7 ppm.

5. Protonation of 10 and 11. Similarly to **5**, the vinylidene ligands of **10** and **11** are capable of undergoing the attack of electrophiles. Thus, the addition of 1.0 equiv of $HBF_4{\cdot}OEt_2$ to diethyl ether solutions of **10** and **11** leads to the corresponding germyl−carbyne derivatives $[Os(\eta^5\text{-}C_5H_5)(GePh_3)(\equiv CCH_2Ph)(P^iPr_3)]BF_4$ (**12**) and $[Os(\eta^5\text{-}C_5H_4CH_3)(GePh_3)\{\equiv CCH(CH_3)Ph\}(P^iPr_3)]BF_4$ (**13**), as a result of the addition of the proton of the acid to the C_β atom of the vinylidene ligands (eq 12).



10, 11 **12, 13** (**12**)

R = H (**10**, **12**), CH_3 (**11**, **13**)

Complex **12** was isolated as a pale brown solid in 83% yield. In the ^1H NMR spectrum the CH_2 group of the carbyne ligand gives rise to an AB spin system, defined by δ_A 3.04, δ_B 2.85 ppm, and J_{AB} = 18.9 Hz. In the $^{13}C\{^1H\}$ spectrum, the resonance corresponding to the Os≡C carbon atom is observed at 297.6 ppm, as a doublet with a C−P coupling constant of 8.8 Hz. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 31.2 ppm.

Complex **13** was isolated as a pale yellow solid in 87% yield. In solution, it exists as a 2:1 mixture of the racemic forms of two diastereoisomers, as a result of the chirality of the metallic center and the C_β atom of the carbyne ligand. Thus, the ^1H NMR spectrum shows two quartets at about 3 ppm with H−H coupling constants of about 7 Hz, corresponding to the CH proton of the carbyne. In the $^{13}C\{^1H\}$ NMR spectrum, the most noticeable resonances are two doublets at about 300 ppm, with C−P coupling constants of about 8 Hz, due to the Os≡C resonances. The $^{31}P\{^1H\}$ NMR spectrum shows two singlets at 28.6 and 30.8 ppm.

In contrast to **8**, in solution, complex **13** is stable and does not evolve into an allyl species related to **9**. This indicate that the migratory insertion of the methylphenylvinylidene into an Os−$GePh_3$ bond is less favored than the insertion into an Os−H bond, which can be related to the lower nucleophilic power of a germyl group with regard to a hydride ligand.

Concluding Remarks

This paper reveals that the group 14 element Si or Ge has a marked influence on the deprotonation reactions of the hydride−alkynyl complexes $OsH(\eta^5\text{-}C_5H_5)(C\equiv CPh)(EPh_3)(P^iPr_3)$ (E = Si, Ge). While the deprotonation of the silyl derivative with *n*-butyllithium is single and selectively occurs at the cyclopentadienyl ligand, the deprotonation of the germyl compound is double and takes place both at the cyclopentadienyl group and at the metallic center. Furthermore, the deprotonation of $OsH(\eta^5\text{-}C_5H_5)(C\equiv CPh)(SiPh_3)(P^iPr_3)$ is accompanied by the migration of the silyl group from the osmium atom to the cyclopentadienyl ligand.

As a consequence of these differences, depending on the group 14 element, different types of vinylidene derivatives are obtained from the reactions of $OsH(\eta^5\text{-}C_5H_5)(C\equiv CPh)(EPh_3)(P^iPr_3)$ with *n*-butyllithium and electrophiles. While the silyl complex leads to hydride−vinylidenes containing a silyl-substituted cyclopentadienyl ligand, $OsH(\eta^5\text{-}C_5H_4SiPh_3)\{=C=C(X)Ph\}(P^iPr_3)$, the germyl complex gives rise to germyl−vinylidenes of the type $Os(\eta^5\text{-}C_5H_4X)(GePh_3)\{=C=C(X)Ph\}(P^iPr_3)$ (X = electrophile). Both types of vinylidene compounds afford carbyne derivatives by protonation with HBF_4.

The germyl−vinylidene complexes are stable with regard to the migratory insertion of the vinylidene into the Os−Ge bond. However, the stability of the hydride−vinylidenes, with regard to the migratory insertion of the vinylidene into the Os−H bond, depends on the substituents of the vinylidene. Thus, in solution, the complex $OsH(\eta^5\text{-}C_5H_4SiPh_3)\{=C=C(CH_3)Ph\}(P^iPr_3)$ is unstable and evolves into the metalated species $OsH(\eta^5\text{-}C_5H_4SiPh_3)\{o\text{-}C_6H_4C(CH_3)=CH\}(P^iPr_3)$, which results from the migratory insertion of the methylphenylvinylidene into the Os−H bond of $OsH(\eta^5\text{-}C_5H_4SiPh_3)\{=C=C(CH_3)Ph\}(P^iPr_3)$ and the subsequent C−H activation of an ortho C−H bond of the aryl group of the alkenyl ligand, in the resulting unsaturated intermediate $[Os(\eta^5\text{-}C_5H_4SiPh_3)\{CH=C(CH_3)Ph\}(P^iPr_3)$.

The protonation of the vinylidene of $OsH(\eta^5\text{-}C_5H_4SiPh_3)\{=C=C(CH_3)Ph\}(P^iPr_3)$ is kinetically favored with regard to the protonation of the metalated aryl group of $OsH(\eta^5\text{-}C_5H_4SiPh_3)\{o\text{-}C_6H_4C(CH_3)=CH\}(P^iPr_3)$. However, the product of thermodynamic control of the reaction is the hydride−allyl derivative $[OsH(\eta^5\text{-}C_5H_4SiPh_3)\{\eta^3\text{-}CH_2C(Ph)CH_2\}(P^iPr_3)]^+$, which results from the protonation of the metalated aryl group of $OsH(\eta^5\text{-}C_5H_4SiPh_3)\{o\text{-}C_6H_4C(CH_3)=CH\}(P^iPr_3)$. The formation of this allyl complex involves the C−H activation of the

methyl group of the coordinated olefin, in the intermediate $[Os(\eta^5\text{-}C_5H_4SiPh_3)\{\eta^2\text{-}CH_2{=}C(CH_3)Ph\}(P^iPr_3)]^+$.

In conclusion, there are strong differences between the organometallic chemistry of the complexes OsH(η^5-C_5H_5)(C≡CPh)($SiPh_3$)(P^iPr_3) and OsH(η^5-C_5H_5)(C≡CPh)($GePh_3$)(P^iPr_3). These differences are a direct consequence of the different natures of the group 14 elements of the complexes.

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 OsH(η^5-C_5H_5)Cl($SiPh_3$)(P^iPr_3) (**1**) and OsH(η^5-C_5H_5)Cl($GePh_3$)(P^iPr_3) (**2**) were prepared by the published methods.[9] The starting materials OsH(η^5-C_5D_5)Cl($SiPh_3$)(P^iPr_3) (**1-*d*$_5$**) and OsH(η^5-C_5D_5)(C≡CPh)($SiPh_3$)(P^iPr_3) (**3-*d*$_5$**) were prepared by using procedures similar to those for the nondeuterated counterparts. The precursor Os(η^5-C_5D_5)Cl(P^iPr_3)$_2$ was prepared by the same method described for Os(η^5-C_5H_5)Cl(P^iPr_3)$_2$, but using TlC_5D_5.[29] TlC_5D_5 was prepared as previously described.[30]

In the NMR spectra, chemical shifts are expressed in ppm downfield from Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants, *J*, are given in Hertz.

Preparation of OsH(η^5-C_5H_5)(C≡CPh)($SiPh_3$)(P^iPr_3) (3). To a solution of OsH(η^5-C_5H_5)Cl($SiPh_3$)(P^iPr_3) (326 mg, 0.46 mmol) in 10 mL of THF was added an excess of lithium phenylacetylide (102 mg, 0.94 mmol). The mixture was stirred for 18 h, and methanol (1 mL) was added. After 1 min of stirring, the solution was vacuum-dried, and the resulting sticky residue was washed with methanol (3 × 5 mL), leading to a pale brown solid. Yield: 217 mg (61%). Anal. Calcd. for $C_{40}H_{47}SiOsP$: C, 61.81; H, 6.11. Found: C, 61.44; H, 6.28. IR (Nujol, cm^{-1}): ν(Os−H) 2179 (vw); ν(C≡C) 2093 (s). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.20−6.90 (20 H, Ph); 4.77 (s, 5 H, η^5-C_5H_5); 2.07 (m, 3 H, PCH); 0.91 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 13.8 Hz, $^3J_{HH}$ = 7.2 Hz); 0.78 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 13.8 Hz, $^3J_{HH}$ = 7.2 Hz); −13.35 (d, 1 H, OsH, $^2J_{HP}$ = 32.1 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 293 K, plus APT): δ 145.8 (−, s, C_{ipso} Ph in $SiPh_3$); 137.2, 127.0 (+, both s, C_{ortho} and C_{meta} Ph in $SiPh_3$); 136.0 (−, s, C_{ipso} Ph in CPh); 131.4, 128.2 (+, both s, C_{ortho} and C_{meta} Ph in C−Ph); 127.7 (+, s, C_{para} Ph in $SiPh_3$); 124.3 (+, s, C_{para} Ph in C−Ph); 111.9 (−, s, OsC≡*C*); 83.3 (+, s, η^5-C_5H_5); 78.4 (−, d, OsC, $^2J_{CP}$ = 21.8 Hz); 28.9 (+, d, PCH, $^1J_{CP}$ = 29.1 Hz); 20.3, 19.7 (+, both s, PCH*C*H_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 18.1 (s, d in off-resonance). MS (FAB^+): *m*/*z* 778 (M^+).

Preparation of OsH(η^5-C_5H_5)(C≡CPh)($GePh_3$)(P^iPr_3) (4). To a solution of OsH(η^5-C_5H_5)Cl($GePh_3$)(P^iPr_3) (427 mg, 0.56 mmol) in 20 mL of THF was added an excess of lithium phenylacetylide (160 mg, 1.48 mmol). The mixture was stirred for 24 h, and methanol (1 mL) was added. After 1 min of stirring, the solution was vacuum-dried, and the resulting sticky residue was washed with methanol (3 × 5 mL), leading to a pale brown solid. Yield: 286 mg (62%). Anal. Calcd for $C_{40}H_{47}GeOsP$: C, 58.48; H, 5.77. Found: C, 58.27; H, 5.67. IR (Nujol, cm^{-1}): ν(Os−H) 2158 (vw); ν(C≡C) 2081 (s). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.20−6.90 (20 H, Ph); 4.79 (s, 5 H, η^5-C_5H_5); 2.15 (m, 3 H, PCH); 0.88 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 14.1 Hz, $^3J_{HH}$ = 7.2 Hz); 0.77 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 14.1 Hz, $^3J_{HH}$ = 7.2 Hz); −13.42 (d, 1 H, Os−H, $^2J_{HP}$ = 34.2 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 293 K, plus APT): δ 147.4 (−, s, C_{ipso} Ph in $GePh_3$); 137.2, 127.8 (+, both s, C_{ortho} and C_{meta} Ph in $GePh_3$); 136.6 (−, s, C_{ipso} Ph in CPh); 135.8, 131.5, 129.4, 128.6, 124.4 (+, all s, C's of phenyl group in CPh); 127.5 (+, s, C_{para} Ph in $GePh_3$); 112.6 (−, s, OsC≡*C*); 82.8 (+, s, η^5-C_5H_5); 75.0 (−, d, OsC, $^2J_{CP}$ = 22.6 Hz); 28.9 (+, d, PCH, $^1J_{CP}$ = 29.8 Hz); 20.3, 19.7 (+, both s, PCH*C*H_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 20.2 (s, d in off-resonance). MS (FAB^+): *m*/*z* 822 (M^+), 745 (M^+ − Ph).

Preparation of OsH(η^5-$C_5H_4SiPh_3$)\{=C=C(H)Ph\}(P^iPr_3) (5). To a cold solution (−30 °C) of OsH(η^5-C_5H_5)(C≡CPh)($SiPh_3$)(P^iPr_3) (201 mg, 0.26 mmol) in 15 mL of THF was added *n*-butyllithium (0.30 mL, 2.6 M, 0.78 mmol), and the mixture was left to react for 5 h, keeping the temperature at −30 °C. Methanol (1 mL) was then added, and the solution was vacuum-dried. The resulting residue was washed with methanol (3 × 3 mL), leading to a pale yellow solid. Yield: 151 mg (75%). Anal. Calcd for $C_{40}H_{47}OsPSi$: C, 61.81; H, 6.11. Found: C, 61.65; H, 6.34. IR (Nujol, cm^{-1}): ν(Os−H) 2108 (w); ν(Os=C=C) 1614 (m). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.90−6.80 (20 H, Ph); 5.36−4.99 (ABCD system, 4 H, signals of η^5-C_5H_4); 2.50 (dd, 1 H, Os=C=CH, $^4J_{HP}$ = 2.4 Hz, $^4J_{HH}$ = 2.4 Hz); 1.94 (m, 3 H, PCH); 0.86 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 14.1 Hz, $^3J_{HH}$ = 7.2 Hz); 0.84 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 14.1 Hz, $^3J_{HH}$ = 7.2 Hz); −14.15 (dd, 1 H, OsH, $^2J_{HP}$ = 29.1 Hz, $^4J_{HH}$ = 2.4 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 293 K): δ 290.8 (d, Os=C, $^2J_{CP}$ = 12.8 Hz); 137.0, 127.9 (both s, C_{ortho}, C_{meta} of Ph in $GePh_3$); 136.3 (s, C_{ipso} of Ph in $SiPh_3$); 135.4 (s, C_{ipso} of Ph in =CPh); 129.7, 127.7 (both s, C_{ortho} and C_{meta} of Ph in =CPh); 128.1 (s, C_{para} of Ph in $SiPh_3$); 124.9 (s, C_{para} of Ph in =CPh); 111.7 (s, Os=C=*C*); 91.8, 88.8, 86.7, 86.1 (all s, tertiary C's in η^5-C_5H_4); 84.1 (d, quaternary C in η^5-C_5H_4, $^2J_{CP}$ = 6.3 Hz); 27.9 (d, PCH, $^1J_{CP}$ = 30.8 Hz); 19.9, 19.7 (both s, PCH*C*H_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 41.8 (s, d in off-resonance). MS (FAB^+): *m*/*z* 778 (M^+).

Preparation of OsH(η^5-$C_5D_4SiPh_3$)\{=C=C(H)Ph\}(P^iPr_3) (5-*d*$_4$). To a cold solution (−30 °C) of OsH(η^5-C_5D_5)(C≡CPh)($SiPh_3$)(P^iPr_3) (161 mg, 0.21 mmol) in 10 mL of THF was added *n*-butyllithium (0.20 mL, 2.6 M, 0.52 mmol), and the mixture was left to react for 5 h, keeping the temperature at −30 °C. Methanol (1 mL) was then added, and the solution was vacuum-dried. The resulting residue was washed with methanol (3 × 3 mL), leading to a pale yellow solid. Yield: 119 mg (74%). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.10−6.80 (20 H, Ph); 2.51 (br s, 1 H, Os=C=CH); 1.94 (m, 3 H, PCH); 0.88 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 14.1 Hz, $^3J_{HH}$ = 7.2 Hz); 0.84 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 14.1 Hz, $^3J_{HH}$ = 7.2 Hz); −14.15 (dd, 1 H, OsH, $^2J_{HP}$ = 30.0 Hz, $^4J_{HH}$ = 2.7 Hz). ^2H NMR (46.1 MHz, C_6H_6, 293 K): δ 5.01 (br signal, η^5-C_5D_4). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 42.2 (s, d in off-resonance).

Preparation of OsH(η^5-C_5H_4-$SiPh_3$)\{=C=C(D)Ph\}(P^iPr_3) (5-*d*). To a cold solution (−30 °C) of OsH(η^5-C_5H_5)(C≡CPh)($SiPh_3$)(P^iPr_3) (180 mg, 0.23 mmol) in 12 mL of THF was added *n*-butyllithium (0.20 mL, 2.6 M, 0.52 mmol), and the mixture was left to react for 5 h, keeping the temperature at −30 °C. Methanol-d_4 (1 mL) was then added, and the solution was vacuum-dried. The resulting residue was washed with methanol (3 × 3 mL), leading to a pale yellow solid. Yield: 130 mg (72%). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 7.90−6.80 (20 H, Ph); 5.36−4.99 (ABCD system, 4 H, signals of η^5-C_5H_4); 1.94 (m, 3 H, PCH); 0.86 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 14.1 Hz, $^3J_{HH}$ = 7.2 Hz); 0.84 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 14.1 Hz, $^3J_{HH}$ = 7.2 Hz); −14.15 (d, 1 H, OsH, $^2J_{HP}$ = 29.1 Hz). ^2H NMR (46.1 MHz, C_6H_6, 293 K): δ 2.52 (s, 1 D, Os=C=CD). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 42.2 (s, d in off-resonance).

Preparation of OsH(η^5-$C_5H_4SiPh_3$)\{*o*-$C_6H_4C(CH_3){=}CH$\}(P^iPr_3) (6). To a solution of OsH(η^5-C_5H_5)(C≡CPh)($SiPh_3$)(P^iPr_3) (186 mg, 0.24 mmol) in 10 mL of THF was added an excess of *n*-butyllithium (0.25 mL, 2.6 M, 0.65 mmol), and the mixture was left to react for 10 min. Methyl iodide (0.40 mL) was then added, and the solution was vacuum-dried. The resulting residue was washed with methanol (3 × 3 mL), leading to a white solid. Yield: 112 mg (60%). Anal. Calcd for $C_{41}H_{49}$-

(29) Esteruelas, M. A.; López, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1997**, *16*, 4657.

(30) Anderson, G. K.; Cross, R. J.; Phillips, I. G. *J. Chem. Soc., Chem. Commun.* **1978**, 709.

OsPSi: C, 62.25; H, 6.24. Found: C, 61.90; H, 6.45. IR (Nujol, cm^{-1}): ν(Os−H) 2149 (s). ^1H NMR (300 MHz, C_6D_6, 293 K): δ 8.00−6.80 (20 H, signals corresponding to CH's of aryl groups and OsCH=); 5.17−4.90 (ABCD system, 4 H, signals of η^5-C_5H_4); 2.25 (s, 3 H, =CCH_3); 1.98 (m, 3 H, PCH); 0.74 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 13.8 Hz, $^3J_{HH}$ = 7.2 Hz); 0.61 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 13.8 Hz, $^3J_{HH}$ = 7.2 Hz); −13.93 (d, 1 H, OsH, $^2J_{HP}$ = 44.7 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 293 K, plus APT): δ 160.9 (−, d, C_α in OsC_6H_4, $^2J_{CP}$ = 2.4 Hz); 151.9, 149.8 (−, both d, the other two quaternary C's in Os{*o*-$C_6H_4C(CH_3)$=CH}, $^3J_{CP}$ = 3.9, 3.8 Hz respectively); 147.0, 122.9, 122.3, 122.1 (+, all s, tertiary C's in C_6H_4); 137.3, 128.3 (+, both s, C_{ortho} and C_{meta} of Ph in $SiPh_3$); 135.0 (−, s, C_{ipso} of Ph in $SiPh_3$); 130.5 (+, d, OsCH=C(CH_3), $^2J_{CP}$ = 20.0 Hz); 130.0 (+, s, C_{para} of Ph in $SiPh_3$); 92.2 (−, d, quaternary C in η^5-C_5H_4, $^2J_{CP}$ = 4.4 Hz); 91.2, 87.2, 85.1, 81.5 (+, all s, tertiary C's in η^5-C_5H_4); 28.7 (+, d, PCH, $^1J_{CP}$ = 31.3 Hz); 20.6, 18.9 (+, both s, PCHCH_3); 1.6 (+, s, =CCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): δ 22.0 (s, d in off-resonance). MS (FAB^+): *m*/*z* 792 (M^+).

Preparation of [OsH(η^5-$C_5H_4SiPh_3$)(≡CCH_2Ph)(P^iPr_3)]BF_4 (7). To a solution of OsH(η^5-$C_5H_4SiPh_3$){=C=C(H)Ph}(P^iPr_3) (112 mg, 0.14 mmol) in 10 mL of diethyl ether was added the stoichiometric amount of a 54% solution of HBF_4 in diethyl ether (20 μL, 0.15 mmol). The subsequent precipitate was decanted and washed twice with diethyl ether (2 × 4 mL). A dark brown solid was obtained. Yield: 108 mg (87%). Anal. Calcd for $C_{40}H_{48}BF_4OsPSi$: C, 55.55; H, 5.59. Found: C, 55.80; H, 5.41. IR (Nujol, cm^{-1}): ν(Os−H) 2071 (vw); $\nu(BF_4)$ 1059 (m). ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.70−6.80 (20 H, Ph); 6.39−5.09 (ABCD system, 4 H, signals of η^5-C_5H_4); 2.39 (s, 2 H, Os≡CCH_2); 1.91 (m, 3 H, PCH); 1.08 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 15.9 Hz, $^3J_{HH}$ = 7.2 Hz); 1.01 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 15.9 Hz, $^3J_{HH}$ = 7.2 Hz); −12.00 (d, 1 H, OsH, $^2J_{HP}$ = 24.3 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 293 K, plus APT): δ 290.6 (−, d, Os≡C, $^2J_{CP}$ = 15.1 Hz); 136.1, 128.3 (+, both s, C_{ortho}, C_{meta} of Ph in $SiPh_3$); 132.8 (−, s, C_{ipso} of Ph in $SiPh_3$); 130.6 (+, s, C_{para} of Ph in $SiPh_3$); 129.1, 128.9 (+, both s, C_{ortho} and C_{meta} of Ph in =CPh); 128.4 (−, s, C_{ipso} of Ph in CH_2Ph); 128.0 (+, s, C_{para} of Ph in CH_2Ph); 102.3, 94.3, 93.4, 90.5 (+, all s, tertiary C's in η^5-C_5H_4); 88.4 (−, d, quaternary C in η^5-C_5H_4, $^2J_{CP}$ = 5.8 Hz); 57.5 (−, s, CH_2); 30.1 (+, d, PCH, $^1J_{CP}$ = 31.4 Hz); 19.2, 19.0 (+, both s, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 293 K): δ 47.2 (s, d in off-resonance). MS (FAB^+): *m*/*z* 779 (M^+).

Preparation of [OsH(η^5-$C_5H_4SiPh_3$){≡$CCH(CH_3)Ph$}(P^iPr_3)]BF_4 (8). To a solution of OsH(η^5-$C_5H_4SiPh_3$){*o*-$C_6H_4C(CH_3)$=CH}(P^iPr_3) (115 mg, 0.15 mmol) in 10 mL of diethyl ether was added the stoichiometric amount of a 54% solution of HBF_4 in diethyl ether (20 μL, 0.15 mmol). The solution changed immediately into a suspension. The solid was then decanted and washed with diethyl ether (2 × 5 mL), leading to a white solid which was a 1:1 mixture of the two pairs of enantiomers. Yield: 110 mg (85%). Anal. Calcd for $C_{41}H_{50}BF_4OsPSi$: C, 56.02; H, 5.73. Found: C, 56.18; H, 6.01. IR (KBr, cm^{-1}): ν(Os−H) 2180, 2128 (w); $\nu(BF_4)$ 1054 (s). NMR data for pair a are as follows. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.80−6.80 (20 H, signals of Ph groups); 6.30−4.74 (ABCD system, 4 H, signals of η^5-C_5H_4); 2.47 (q, 1 H, ≡CCH, $^3J_{HH}$ = 6.9 Hz); 1.93 (m, 3 H, PCH); 1.30−0.80 (21H, signals of PCHCH_3 and CH(Ph)CH_3); −11.60 (d, 1 H, OsH, $^2J_{HP}$ = 24.9 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 293 K): δ 294.2 (d, Os≡C, $^2J_{CP}$ = 7.6 Hz); 137.0−127.0 (all s, C signals of Ph groups); 105.2, 93.5, 91.1, 88.7 (all s, tertiary C's in η^5-C_5H_4); 89.6 (d, quaternary C in η^5-$C_5H_4SiPh_3$, $^2J_{CP}$ = 4.3 Hz); 61.4 (s, ≡C*C*H); 30.0 (d, PCH, $^1J_{CP}$ = 31.7 Hz); 20.0−19.0 (all s, signals of PCHCH_3); 16.5 (s, CH(Ph)CH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 293 K): δ 47.9 (s). NMR data for pair b are as follows. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.80−6.80 (20 H, signals of Ph groups); 6.60−4.66 (ABCD system, 4 H, signals of η^5-C_5H_4); 2.61 (q, 1 H, ≡CCH, $^3J_{HH}$ = 6.9 Hz); 1.84 (m, 3 H, PCH); 1.30−0.80 (21H, signals of PCHCH_3 and CH(Ph)CH_3); −11.68 (d, 1 H, OsH, $^2J_{HP}$ = 24.9 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 293 K): δ 294.9 (d, Os≡C, $^2J_{CP}$ = 7.6 Hz); 137.0−127.0 (all s, C signals of Ph groups); 104.9, 92.9, 92.0, 88.6 (all s, tertiary C's in η^5-C_5H_4); 90.1 (d, quaternary C in η^5-$C_5H_4SiPh_3$, $^2J_{CP}$ = 4.3 Hz); 61.9 (s, ≡C*C*H); 30.5 (d, PCH, $^1J_{CP}$ = 31.9 Hz); 20.0−19.0 (all s, signals of PCHCH_3); 18.1 (s, CH(Ph)CH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 293 K): δ 47.8 (s). MS (FAB^+): *m*/*z* 793 (M^+).

Preparation of [OsH(η^5-$C_5H_4SiPh_3$){η^3-$CH_2C(Ph)CH_2$}(P^iPr_3)]BF_4 (9). A solution of [OsH(η^5-$C_5H_4SiPh_3$){≡C−CH(CH_3)Ph}(P^iPr_3)]BF_4 (72 mg, 0.082 mmol) in 8 mL of dichloromethane was heated to 45 °C for 96 h. Afterward, the mixture was vacuum-dried and washed with diethyl ether (4 × 5 mL), leading to a white solid. Yield: 65 mg (91%). Anal. Calcd for $C_{41}H_{50}BF_4OsPSi$: C, 56.02; H, 5.73. Found: C, 56.05; H, 5.58. IR (Nujol, cm^{-1}): ν(Os−H) 2189 (vw); $\nu(BF_4)$ 1054 (s). ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.60−7.10 (20 H, signals of Ph groups); 6.76−3.26 (ABCD system, 4 H, signals of η^5-C_5H_4); 4.46, 3.77 (both dd, 1 H each, two protons of the allyl group, $^3J_{HP}$ < 1 Hz, $^2J_{HH}$ < 1 Hz); 2.15 (m, 3 H, PCH); 2.03 (dd, 1 H, one proton of the allyl group, $^3J_{HP}$ < 1 Hz, $^2J_{HH}$ < 1 Hz); 1.82 (dd, 1 H, one proton of the allyl group, $^3J_{HP}$ = 18.3 Hz, $^3J_{HH}$ < 1 Hz); 1.12 (dd, 9 H, PCHCH_3, $^2J_{HP}$ = 14.1 Hz, $^2J_{HH}$ = 7.2 Hz); 1.08 (dd, 9 H, PCHCH_3, $^2J_{HP}$ = 14.1 Hz, $^2J_{HH}$ = 7.2 Hz); −13.37 (d, 1 H, OsH, $^2J_{HP}$ = 30.0 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 293 K, plus APT): δ 136.2, 128.4 (+, both s, C_{ortho}, C_{meta} of Ph in $SiPh_3$); 135.6 (−, s, C_{ipso} of Ph in CPh); 131.9 (−, s, C_{ipso} of Ph in $SiPh_3$); 130.6 (+, s, C_{para} in $SiPh_3$); 129.9, 129.1 (+, both s, C_{ortho} and C_{meta} of Ph in CPh); 125.1 (+, s, C_{para} of Ph in CPh); 106.7, 97.6, 88.9, 79.7 (+, all s, tertiary C's in η^5-C_5H_4); 90.3 (−, s, quaternary C in η^5-C_5H_4-$SiPh_3$); 86.2 (−, s, CPh); 28.4 (−, s, one of the secondary C atoms of the allyl group); 27.8 (+, d, PCH, $^1J_{CP}$ = 30.6 Hz); 19.6, 19.1 (+, both s, PCHCH_3); 18.7 (−, d, one of the secondary C atoms of the allyl group, $^2J_{CP}$ = 29.1 Hz). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 293 K): δ 19.3 (s, d in off-resonance). MS (FAB^+): *m*/*z* 793 (M^+).

Preparation of [OsH(η^5-$C_5H_4SiPh_3$){≡$CCD(CH_3)Ph$}(P^iPr_3)]BF_4 (8-*d*). To a solution of OsH(η^5-$C_5H_4SiPh_3$){*o*-$C_6H_4C(CH_3)$=CH}(P^iPr_3) (102 mg, 0.13 mmol) in 10 mL of diethyl ether was added the stoichiometric amount of a 1:1 mixture composed of a solution of HBF_4 in diethyl ether and deuterium oxide (D_2O). The solution, which changed immediately into a suspension, was vacuum-dried, and the resulting residue washed with diethyl ether (3 × 4 mL), leading to a white solid which was a 1:1 mixture of the two pairs of enantiomers. Yield: 94 mg (82%). NMR data for pair a are as follows. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.80−6.80 (20 H, signals of Ph groups); 6.31−4.74 (ABCD system, 4 H, signals of η^5-C_5H_4); 1.93 (m, 3 H, PCH); 1.30−0.80 (21H, signals of PCHCH_3 and CD(Ph)CH_3); −11.59 (d, 1 H, OsH, $^2J_{HP}$ = 24.9 Hz). ^2H NMR (46.1 MHz, $CHCl_3$, 293 K): δ 2.58 (s, ≡CCD). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 293 K): δ 48.0 (s, d in off-resonance). NMR data for pair b are as follows. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.80−6.80 (20 H, signals of Ph groups); 6.61−4.65 (ABCD system, 4 H, signals of η^5-C_5H_4); 1.84 (m, 3 H, PCH); 1.30−0.80 (21H, signals of PCHCH_3 and CD(Ph)CH_3); −11.68 (d, 1 H, OsH, $^2J_{HP}$ = 24.9 Hz). ^2H NMR (46.1 MHz, $CHCl_3$, 293 K): δ 2.58 (s, ≡CCD). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 293 K): δ 47.8 (s, d in off-resonance).

Preparation of [OsH(η^5-$C_5H_4SiPh_3$){η^3-$CH_2C(C_6H_4D)CH_2$}(P^iPr_3)]BF_4 (9-*d*). A solution of [OsH(η^5-$C_5H_4SiPh_3$){≡CCD(CH_3)Ph}(P^iPr_3)]BF_4 (12 mg) in 0.5 mL of chloroform-*d* was heated to 42 °C over 72 h. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.60−7.10 (19 H, signals of Ph groups); 6.77−3.27 (ABCD system, 4 H, signals of η^5-C_5H_4); 4.46, 3.78 (both dd, 1 H each, two protons of the allyl group, $^3J_{HP}$ < 1 Hz, $^2J_{HH}$ < 1

Table 4. Crystal Data and Data Collection and Refinement Details for OsH(η^5-C_5H_5)(C≡CPh)($GePh_3$)(P^iPr_3) (4), OsH(η^5-$C_5H_4SiPh_3$){*o*-$C_6H_4C(CH_3)$=CH}(P^iPr_3) (6), and [OsH(η^5-$C_5H_4SiPh_3$){η^3-$CH_2C(Ph)CH_2$}(P^iPr_3)]BF_4 (9)

	4	6	9
		Crystal Data	
formula	$C_{40}H_{47}GeOsP$	$C_{41}H_{49}OsPSi$	$C_{41}H_{50}BF_4OsPSi{\cdot}CH_2Cl_2$
mol wt	821.54	791.06	963.81
color and habit	yellow block	colorless block	colorless block
sym, space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$
a, Å	11.0904(5)	13.3545(9)	11.7348(6)
b, Å	19.2109(8)	14.5873(12)	12.2783(6)
c, Å	16.5775(7)	18.4672(12)	16.9051(12)
α, deg	90	90	101.215(1)
β, deg	97.017(1)	95.837(1)	98.952(1)
γ, deg	90	90	115.796(1)
V, Å^3; *Z*	3505.5(3), 4	3578.9(4), 4	2070.0(2), 2
D_{calcd}, g cm^{-3}	1.557	1.468	1.546
		Data Collection and Refinement	
diffractometer		Bruker Smart APEX	
λ(Mo Kα), Å		0.710 73	
monochromator		graphite oriented	
μ, mm^{-1}	4.55	3.668	3.324
2θ range, deg	$4 \le 2\theta \le 60$	$4 \le 2\theta \le 60$	$4 \le 2\theta \le 60$
temp, K	296.0(2)	296.0(2)	173.0(2)
no. of data collected	31 992	23 748	19 647
no. of unique data ($R_{merging}$)	8366 (0.0611)	8499 (0.0807)	9639 (0.0626)
no. of params/restraints	398/1	412/1	496/1
R1[a] ($F^2 > 2\sigma(F^2)$)	0.0340	0.0424	0.0407
wR2[b] (all data)	0.0541 ($a = 0.0180$, $b = 0$)	0.0579 ($a = 0.0078$, $b = 0$)	0.0762 ($a = 0.0255$, $b = 0$)
S[c]	0.804	0.684	0.901

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; where $w^{-1} = \sigma^2(F_o^2) + ((aP)^2 + bP$, $P = (F_o^2 + 2F_c^2)/3$. [c] GOF $= S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where *n* is the number of reflections and *p* is the number of refined parameters.

Hz); 2.14 (m, 3 H, PCH); 2.03 (dd, 1 H, one proton of the allyl group, $^3J_{HP} < 1$ Hz, $^2J_{HH} < 1$ Hz); 1.82 (dd, 1 H, one proton of the allyl group, $^3J_{HP} = 18.3$ Hz, $^2J_{HH} < 1$ Hz); 1.12 (dd, 9 H, PCHC*H*$_3$, $^2J_{HP} = 14.1$ Hz, $^2J_{HH} = 7.2$ Hz); 1.08 (dd, 9 H, PCHC*H*$_3$, $^2J_{HP} = 14.1$ Hz, $^2J_{HH} = 7.2$ Hz); −13.37 (d, 1 H, OsH, $^2J_{HP} = 29.7$ Hz). ^{2}H NMR (46.1 MHz, $CHCl_3$, 293 K): *δ* 7.35 (s, C_6H_4D). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 293 K): *δ* 19.3 (s, d in off-resonance).

Preparation of Os(η^5-C_5H_5)($GePh_3$){=C=C(H)Ph}(P^iPr_3) (10). To a solution of OsH(η^5-C_5H_5)(C≡CPh)($GePh_3$)(P^iPr_3) (176 mg, 0.21 mmol) in 15 mL of THF was added *n*-butyllithium (0.25 mL, 2.6 M, 0.68 mmol), and the mixture was left to react for 30 min. Methanol (1 mL) was then added, and the solution was vacuum-dried. The resulting residue was washed with methanol (3 × 3 mL), leading to a pale brown solid. Yield: 114 mg (65%). Anal. Calcd for $C_{40}H_{47}GeOsP$: C, 58.48; H, 5.77. Found: C, 58.13; H, 5.47. IR (Nujol, cm^{-1}): *ν*(Os=C=C) 1609 (s). ^{1}H NMR (300 MHz, C_6D_6, 293 K): *δ* 7.90−6.80 (20 H, Ph); 5.04 (s, 5 H, η^5-C_5H_5); 3.14 (d, 1 H, Os=C=CH, $^4J_{HP} = 1.2$ Hz); 2.07 (m, 3 H, PCH); 0.81 (dd, 9 H, PCHC*H*$_3$, $^3J_{HP} = 13.5$ Hz, $^3J_{HH} = 6.9$ Hz); 0.76 (dd, 9 H, PCHC*H*$_3$, $^3J_{HP} = 13.5$ Hz, $^3J_{HH} = 6.9$ Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 293 K, plus APT): *δ* 299.5 (−, d, Os=C, $^2J_{CP} = 12.0$ Hz); 148.7 (−, s, C_{ipso} Ph in $GePh_3$); 137.0, 127.7 (+, both s, C_{ortho} and C_{meta} Ph in $GePh_3$); 131.5(−, s, C_{ipso} Ph in =CPh); 128.7, 127.7 (+, both s, C_{ortho} and C_{meta} Ph in CPh); 125.5 (+, s, C_{para} Ph in $GePh_3$); 124.2 (+, s, C_{para} Ph in =CPh); 115.6 (+, s, Os=C=*C*); 84.9 (+, s, η^5-C_5H_5); 30.6 (+, d, PCH, $^1J_{CP} = 28.2$ Hz); 21.0, 20.5 (+, both s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): *δ* 19.9 (s). MS (FAB$^+$): *m*/*z* 822 (M$^+$).

Preparation of Os(η^5-C_5H_4D)($GePh_3$){=C=C(D)Ph}(P^iPr_3) (10-*d*$_2$). To a solution of OsH(η^5-C_5H_5)(C≡CPh)($GePh_3$)(P^iPr_3) (125 mg, 0.15 mmol) in 10 mL of THF was added *n*-butyllithium (0.15 mL, 2.6 M, 0.39 mmol), and the mixture was left to react for 30 min. Methanol-d_4 (0.5 mL) was then added, and the solution was vacuum-dried. The resulting residue was washed with methanol (3 × 2 mL), leading to a pale brown solid. Yield: 75 mg (60%). ^{1}H NMR (300 MHz, C_6D_6, 293 K): *δ* 7.90−6.80 (20 H, −Ph); 5.04 (s, 4 H, η^5-C_5H_4D); 2.07 (m, 3 H, PCH); 0.81 (dd, 9 H, PCHC*H*$_3$, $^3J_{HP} = 13.5$ Hz, $^3J_{HH} = 6.9$ Hz); 0.76 (dd, 9 H, PCHC*H*$_3$, $^3J_{HP} = 13.5$ Hz, $^3J_{HH} = 6.9$ Hz). ^{2}H NMR (46.1 MHz, C_6H_6, 293 K): *δ* 5.01 (s, 1 D, η^5-C_5H_4D); 3.21 (s, 1 D, Os=C=CD). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): *δ* 19.8 (s).

Preparation of Os(η^5-$C_5H_4CH_3$)($GePh_3$){=C=C(CH_3)Ph}(P^iPr_3) (11). To a solution of OsH(η^5-C_5H_5)(C≡CPh)($GePh_3$)(P^iPr_3) (115 mg, 0.14 mmol) in 10 mL of THF was added an excess of *n*-butyllithium (0.25 mL, 2.6 M, 0.65 mmol), and the mixture was left to react for 10 min. Methyl iodide (*0*.40 mL, 6.4 mmol) was then added, and the solution was vacuum-dried. The resulting residue was washed with methanol (3 × 3 mL), leading to a pale red solid. Yield: 86 mg (72%). Anal. Calcd for $C_{42}H_{51}GeOsP$: C, 59.37; H, 6.05. Found: C, 59.71; H, 6.11. IR (Nujol, cm^{-1}): *ν*(Os=C=C) 1625 (s). ^{1}H NMR (300 MHz, C_6D_6, 293 K): *δ* 8.00−6.80 (20 H, Ph); 5.01−4.07 (ABCD system, 4 H, signals of η^5-C_5H_4); 2.45 (s, 3 H, =CCH_3); 2.15 (m, 3 H, PCH); 1.95 (s, 3 H, η^5-$C_5H_4CH_3$); 0.83 (dd, 9 H, PCHC*H*$_3$, $^3J_{HP} = 13.2$ Hz, $^3J_{HH} = 6.0$ Hz); 0.81 (dd, 9 H, PCHC*H*$_3$, $^3J_{HP} = 13.2$ Hz, $^3J_{HH} = 6.0$ Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 293 K, plus APT): *δ* 304.3 (−, d, Os=C, $^2J_{CP} = 12.0$ Hz); 150.2 (−, s, C_{ipso} Ph in $GePh_3$); 137.3, 127.6 (+, both s, C_{ortho} and C_{meta} Ph in $GePh_3$); 134.7 (−, s, C_{ipso} Ph in =CPh); 128.2, 124.4 (+, both s, C_{ortho} and C_{meta} Ph in CPh); 127.5 (+, s, C_{para} Ph in $GePh_3$); 124.1 (+, s, C_{para} Ph in =CPh); 115.1 (−, s, Os=C=*C*); 100.4 (−, d, quaternary C in η^5-$C_5H_4CH_3$, $^2J_{CP} = 6.0$ Hz); 91.9, 86.3, 84.2, 80.5 (+, all s, tertiary C's in η^5-C_5H_4); 30.8 (+, d, PCH, $^1J_{CP} = 27.6$ Hz); 20.9, 20.3 (+, both s, PCH*C*H$_3$); 12.0, 8.7 (+, both s, CH_3 in cyclopentadienyl and vinylidene groups). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 293 K): *δ* 18.7 (s). MS (FAB$^+$): *m*/*z* 850 (M$^+$).

Preparation of [Os(η^5-C_5H_5)($GePh_3$)(≡CCH_2Ph)(P^iPr_3)]BF_4 (12). To a solution of Os(η^5-C_5H_5)($GePh_3$){=C=C(H)Ph}(P^iPr_3) (109 mg, 0.13 mmol) in 10 mL of diethyl ether was added the stoichiometric amount of a 54% solution of HBF_4 in diethyl ether (20 *μ*L, 0.15 mmol). The subsequent precipitate was decanted and washed twice with diethyl ether (2 × 4 mL). A pale brown solid was obtained. Yield: 100 mg (83%). Anal. Calcd for $C_{40}H_{48}BF_4GeOsP$: C, 52.82; H, 5.33. Found: C, 52.75;

H, 5.51. IR (Nujol, cm^{-1}): $\nu(BF_4)$ 1054 (s). ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.50−7.00 (20 H, −Ph); 5.59 (5 H, s, η^5-C_5H_5); 3.04 (part A of AB system, 1 H, Os≡CCH_2, J_{AB} = 18.9 Hz); 2.85 (part B of AB system, 1 H, Os≡CCH_2, J_{AB} = 18.9 Hz); 2.27 (m, 3 H, PCH); 1.09 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 16.5 Hz, $^3J_{HH}$ = 7.5 Hz); 1.06 (dd, 9 H, PCHCH_3, $^3J_{HP}$ = 16.5 Hz, $^3J_{HH}$ = 7.5 Hz). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_3COCD_3, 293 K, plus APT): δ 297.6 (−, d, Os≡C, $^2J_{CP}$ = 8.8 Hz); 144.3 (−, s, C_{ipso} Ph in $GePh_3$); 136.3 (−, s, C_{ipso} Ph in CH_2Ph); 136.2, 129.1 (+, both s, C_{ortho} and C_{meta} Ph in $GePh_3$); 130.7, 129.8 (+, both s, C_{ortho} and C_{meta} Ph in CH_2Ph); 129.8 (+, s, C_{ipso} Ph in =CPh); 129.0 (+, s, C_{para} in CH_2Ph); 91.6 (+, s, η^5-C_5H_5); 39.1 (−, s, CH_2); 31.8 (+, d, PCH, $^1J_{CP}$ = 28.6 Hz); 20.8 (+, s, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 293 K): δ 31.2 (s). MS (FAB^+): *m*/*z* 823 (M^+).

Preparation of [Os(η^5-$C_5H_4CH_3$)($GePh_3$){≡CCH(CH_3)Ph}(P^iPr_3)]BF_4 (13). To a solution of Os(η^5-$C_5H_4CH_3$)($GePh_3$){=C=C(CH_3)Ph}(P^iPr_3) (88 mg, 0.10 mmol) in 10 mL of diethyl ether was added the stoichiometric amount of a 54% solution of HBF_4 in diethyl ether (15 μL, 0.11 mmol). The solution changed immediately into a suspension, and the solid was decanted and washed with diethyl ether (2 × 5 mL), leading to a pale yellow solid which was a 2:1 mixture of the two pairs of enantiomers. Yield: 84 mg (87%). Anal. Calcd for $C_{42}H_{52}BF_4GeOsP$: C, 53.81; H, 5.59. Found: C, 53.70; H, 5.79. IR (Nujol, cm^{-1}): $\nu(BF_4)$ 1054 (s). NMR data for pair a was as follows. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.60−7.00 (20 H, signals of Ph groups); 6.32−5.00 (ABCD system, 4 H, signals of η^5-C_5H_4); 3.07 (q, 1 H, ≡CCH, $^3J_{HH}$ = 7.2 Hz); 2.19 (m, 3 H, PCH); 1.71 (s, 3 H, η^5-$C_5H_4CH_3$); 1.26 (d, 3 H, CHCH_3, $^3J_{HH}$ = 7.2 Hz); 1.20−0.90 (18 H, signals of PCHCH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 293 K): δ 301.1 (−, d, Os≡C, $^2J_{CP}$ = 8.3 Hz); 145.0−127.0 (all s, C signals of Ph groups); 110.2 (−, s, quaternary C in η^5-$C_5H_4CH_3$); 96.7, 91.9, 87.4, 83.0 (+, all s, tertiary C's in η^5-C_5H_4); 65.1 (+, s, ≡C*C*H); 30.9 (+, d, PCH, $^1J_{CP}$ = 28.8 Hz); 19.6, 19.5 (+, both s, PCHCH_3); 16.7, 13.6 (+, both s, signals of η^5-$C_5H_4CH_3$ and CHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 293 K): δ 28.6 (s). NMR data for pair b are as follows. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.60−7.00 (20 H, signals of Ph groups); 6.32−5.11 (ABCD system, 4 H, signals of η^5-C_5H_4); 3.40 (q, 1 H, ≡CCH, $^3J_{HH}$ = 7.2 Hz); 2.24 (m, 3 H, PCH); 1.87 (s, 3 H, η^5-$C_5H_4CH_3$); 1.53 (d, 3 H, CHCH_3, $^3J_{HH}$ = 7.2 Hz); 1.20−0.90 (18 H, signals of PCHCH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 293 K): δ 301.3 (−, d, Os≡C, $^2J_{CP}$ = 8.3 Hz); 145.0−127.0 (all s, C signals of Ph groups); 110.1 (−, s, quaternary C in η^5-$C_5H_4CH_3$); 96.2, 91.1, 87.4, 84.4 (+, all s, tertiary C's in η^5-C_5H_4); 64.6 (+, s, ≡C*C*H); 30.8 (+, d, PCH, $^1J_{CP}$ = 28.8 Hz); 19.9, 19.6 (+, both s, PCHCH_3); 17.7, 13.6 (+, both s, signals of η^5-$C_5H_4CH_3$ and CHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 293 K): δ 30.8 (s). MS (FAB^+): *m*/*z* 852 (M^++H).

X-ray Structure Analysis of Complexes OsH(η^5-C_5H_5)(C≡CPh)($GePh_3$)(P^iPr_3) (4), OsH(η^5-$C_5H_4SiPh_3$){*o*-C_6H_4C(=CHCH_3)}(P^iPr_3) (6), and [OsH(η^5-$C_5H_4SiPh_3$){η^3-CH_2C(Ph)CH_2}(P^iPr_3)]BF_4 (9). Crystal data for **4**, **6**, and **9** were measured on a Bruker Smart APEX diffractometer equipped with a fine-focus, 2.4 kW sealed-tube X-ray source (molybdenum radiation, λ = 0.710 73 Å) operating at 50 kV and 30 mA (**4** and **9**) or 50 kV and 35 mA (**6**). Data were collected over a hemisphere by a combination of three sets. The cell parameters were determined and refined by least-squares fits of 7187 (**4**), 2764 (**6**), and 6321 (**9**) collected reflections. Each frame exposure was 10 s, covering 0.3° in ω. The first 100 frames were collected at the end of the data collection to monitor crystal decay. The absorption correction was made using a multiscan method with SADABS.[31] The structures were solved by standard Patterson and conventional Fourier procedures. The positions and anisotropic thermal parameters of the nonhydrogen atoms were refined satisfactorily by full-matrix least-squares calculations on F^2 (SHELXL-97).[31] In all cases the hydride ligands were refined as free isotropic atoms converged too close to the metal center. Finally, a mixed refinement with the distance restrained to 1.59(1) Å was used (from the Cambridge Crystallographic Data Center, mean of 81 terminal osmium−hydride distances obtained by X-ray analysis).[32] Crystal data and data collection and refinement details are given in Table 4.

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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 **4**, **6**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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