

Oxidative Addition of HX (X = H, SiR₃, GeR₃, SnR₃, Cl) Molecules to the Complex Os(η^5 -C₅H₅)Cl(PⁱPr₃)₂

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The cyclopentadienyl complex Os(η^5 -C₅H₅)Cl(PⁱPr₃)₂ (**1**) reacts with molecular hydrogen to give a mixture of the isomers *transoid-dihydride* OsH₂(η^5 -C₅H₅)Cl(PⁱPr₃) (**2a**) and *cisoid-dihydride* OsH₂(η^5 -C₅H₅)Cl(PⁱPr₃) (**2b**). Isomer **2a** has a rigid structure in solution. However, the hydride ligands of **2b** undergo a thermally activated site exchange process and show quantum exchange coupling. The reaction of the isomeric mixture of **2a** and **2b** with NaBH₄ and methanol leads to the trihydride OsH₃(η^5 -C₅H₅)(PⁱPr₃) (**3**). In solution, the *cisoid* hydride ligands of this complex also undergo a thermally activated site exchange process. The activation parameters are $\Delta H^\ddagger = 15.1 \pm 0.3$ kcal·mol⁻¹ and $\Delta S^\ddagger = 0.5 \pm 0.7$ cal·mol⁻¹·K⁻¹. Complex **1** also reacts with group 14 element hydride compounds to afford OsH(η^5 -C₅H₅)Cl(ER₃)(PⁱPr₃) [ER₃ = SiEt₃ (**4**), Si(CH₂-CH=CH₂)Me₂ (**5**), SiPh₃ (**6**), SiHPh₂ (**7**), SiH₂-Ph (**8**), GeEt₃ (**9**), GePh₃ (**10**), GeHPh₂ (**11**), SnⁿBu₃ (**12**), SnPh₃ (**13**)]. The structure of **7** has been determined by an X-ray investigation. The distribution of ligands around the metallic center can be described as a piano stool geometry with the triisopropylphosphine and diphenylsilyl ligands disposed mutually *transoid*. Complex **12** reacts with HSnⁿBu₃ to give the dihydride–stannyl derivative OsH₂(η^5 -C₅H₅)(SnⁿBu₃)(PⁱPr₃) (**14**). The reaction of **1** with HCl leads to a mixture of the monohydrides OsH(η^5 -C₅H₅)Cl₂(PⁱPr₃) (**15**) and [OsH(η^5 -C₅H₅)Cl(PⁱPr₃)₂]⁺ (**16**). Complexes **15** and **16** can also be obtained by reaction of **6** with HCl and by protonation of **1** with HBF₄, respectively.

Introduction

In recent years, we have shown that in the iron triad not only iron and ruthenium but also osmium form complexes that behave as good catalysts for the reduction of unsaturated organic substrates¹ and for the addition of group 14 element hydride compounds to terminal alkynes.² In connection with these reactions, the oxidative additions of molecular hydrogen, silanes, germanes, and stannanes to osmium precursors are elementary processes of considerable interest.³

As a part of our study on the chemical properties of the six-coordinate osmium(IV) complex OsH₂Cl₂(PⁱPr₃)₂, we have recently reported the synthesis of the half-sandwich compound Os(η^5 -C₅H₅)Cl(PⁱPr₃)₂ (**1**).⁴ Although, in comparison with the related iron and ruthenium complexes, the Os(η^5 -C₅H₅)L₃ derivatives show a higher kinetic stability,⁵ complex **1** is a useful starting material for the development of new cyclopentadienyl–osmium chemistry.^{4,6} Thus, in polar solvents such as methanol and acetone, the dissociation of the chlorine

ligand occurs, and the resulting fragment is capable of activating a methyl C–H bond of a triisopropylphos-

phine to give [OsH(η^5 -C₅H₅){CH₂CH(CH₃)PⁱPr₂}(PⁱPr₃)]⁺. On the other hand, in pentane and toluene, the dissociation of a phosphine ligand is favored, and the reactions of **1** with olefins and alkynes afford chloro π -olefin and π -alkyne derivatives.⁴ The π -alkyne complexes evolve into vinylidene or alternatively allenylidene derivatives, depending upon the nature of the alkyne.^{6c}

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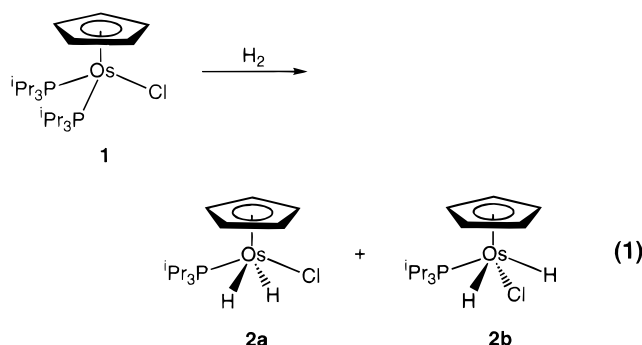
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In the search for new osmium complexes that could be catalytically active in the reduction of unsaturated organic substrates and in the addition of group 14 element hydride compounds to terminal alkynes, we have now studied the reactivity of **1** toward molecular hydrogen, group 14 element hydride compounds, and HCl.

In this paper, we report the resulting products of the reactions of **1** with these molecules. Although the half-sandwich $\text{Ru}(\eta^5\text{-C}_5\text{R}_5)$ ($\text{R} = \text{Me}, \text{H}$) and $\text{Os}(\eta^5\text{-C}_5\text{Me}_5)$ complexes exhibit a particularly rich and interesting chemistry,⁷ which has formed one of the cornerstones in the development of organometallic chemistry, the chemistry of the corresponding $\text{Os}(\eta^5\text{-C}_5\text{H}_5)$ unit is a little-known field.⁸

Results and Discussion

1. Reaction of $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)_2$ with Molecular Hydrogen. Bubbling molecular hydrogen through a pentane solution of the complex $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)_2$ (**1**) produces the displacement of a coordinated triisopropylphosphine ligand and the formation of the osmium(IV) dihydride $\text{OsH}_2(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)$ (**2**), which was isolated as a white solid in 67% yield. The solid is a mixture of the isomers **2a** and **2b** (eq 1), as is proved by the IR spectrum of the solid in Nujol, which shows two $\nu(\text{Os-H})$ bands at 2059 (**2a**) and 2121 (**2b**) cm^{-1} . At room temperature, in solution, the **2a**:**2b** molar ratio depends on the used solvent. In dichloromethane- d_2 this value is 20:1, while in toluene- d_8 it decreases to 9:2.



The ^1H NMR spectrum of **2a** in dichloromethane- d_2 , which is temperature invariant between 293 and 163 K, is consistent with a four-legged piano stool structure with the hydrides *transoid*. Thus, it shows at -10.09 ppm a doublet with a H-P coupling constant of 33.6 Hz, which agrees well with those found in the dihydride-silyl derivative $\text{RuH}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{SiMePh}_2)(\text{P}^i\text{Pr}_3)$

(29 Hz)⁹ and in the dihydride cations $[\text{RuH}_2(\eta^5\text{-C}_5\text{Me}_5)(\text{PMe}_3)_2]^+$ (33 Hz),¹⁰ $[\text{RuH}_2(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)_2]^+$ (29 Hz),¹¹ $[\text{OsH}_2(\eta^5\text{-C}_5\text{H}_5)(\text{P}^i\text{Pr}_3)_2]^+$ (32.2 Hz),⁴ and $[\text{OsH}_2(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]^+$ (29.0 Hz),¹² where hydride and phosphine ligands mutually *cisoid* have been also proposed. Furthermore, in agreement with the presence in the molecule of a mirror plane of symmetry containing the Os-P bond, the spectrum shows only one ^1Pr -methyl chemical shift, in the low-field region.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains at 43.1 ppm a singlet, which is split into a triplet under off-resonance conditions as a result of the P-H coupling with two equivalent hydride ligands.

In contrast to the ^1H NMR spectrum of **2a**, the ^1H NMR spectrum of **2b** is temperature dependent and consistent with the operation of a thermally activated site exchange process involving the hydride ligands. In toluene- d_8 , at room temperature, it exhibits in the hydride region a single doublet resonance at -11.05 ppm with a H-P coupling constant of 15.6 Hz, which is between that found in **2a** and the expected one for a hydride ligand disposed *transoid* to the phosphine (about 8 Hz).¹³ Lowering the sample temperature leads to broadening of the resonance until becoming lost in the baseline of the spectrum, which happens between 223 and 193 K. At temperatures lower than 193 K, the spectra show two broad complex resonances centered at -7.50 and -15.04 ppm. With ^{31}P decoupling, these resonances are simplified to the expected doublets. The values of the chemical shifts show no significant temperature dependence. However, the magnitude of the observed H-H coupling constant is sensitive to temperature, decreasing in the sequence 63 Hz (178 K), 52 Hz (173 K), 40 Hz (168 K), and 30 Hz (163 K).

We note that Caulton et al. have previously reported the reaction of $\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{ORf})(\text{P}^i\text{Pr}_2\text{Ph})$ ($\text{ORf} = \text{OSiPh}_3, \text{NPh}, \text{OCH}_2\text{CF}_3$) with 2 equiv of $\text{HSi}(\text{OMe})_3$ to afford $\text{RuH}_2(\eta^5\text{-C}_5\text{Me}_5)\{\text{Si}(\text{OMe})_3\}(\text{P}^i\text{Pr}_2\text{Ph})$, which has also a four-legged piano stool structure with the hydrides mutually *cisoid*. For this complex, the value of the $^2J_{\text{HH}}$ constant is 10 Hz.¹³ In agreement with this magnitude, Graham has reported a value of 9 Hz for the H-H coupling constant between the inequivalent hydride ligands of $\text{OsH}_3(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})$.¹⁴ For **2b**, the large value of the $^2J_{\text{HH}}$ constant and its dependence with the temperature can be rationalized in terms of quantum exchange coupling between the hydrides. This phenomenon, which is presently attracting considerable interest,¹⁵ is usually observed on trihydride complexes. For osmium, three types of compounds have been shown to display quantum exchange coupling: the cationic arene osmium(IV) derivatives $[\text{OsH}_3(\eta^6\text{-C}_6\text{H}_6)(\text{PR}_3)]^+$ ($\text{PR}_3 = \text{PCy}_3, \text{PPh}_3, \text{MPTB}$),¹⁶ the six-coordinate os-

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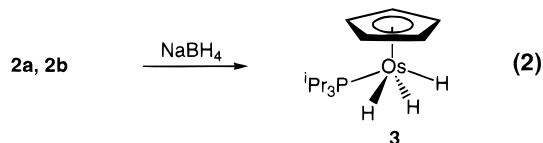
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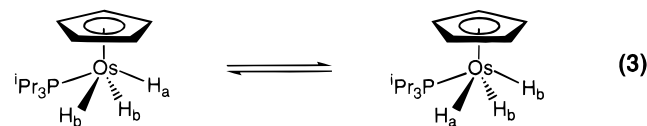
mium(IV) complexes $\text{OsH}_3\text{X}(\text{P}^i\text{Pr}_3)_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$),¹⁷ and the seven-coordinate osmium(IV) compounds $\text{OsH}_3(\text{Hbiim})(\text{P}^i\text{Pr}_3)_2$ ($\text{H}_2\text{biim} = 2,2\text{-biimidazole}$), $(\text{P}^i\text{Pr}_3)_2\text{H}_3\text{Os}(\mu\text{-biim})\text{M}(\text{COD})$ ($\text{M} = \text{Rh}, \text{Ir}$),¹⁸ $[\text{OsH}_3(\text{diolefin})(\text{P}^i\text{Pr}_3)_2]^+$ (diolefin = TFB, NBD),¹⁹ $\text{OsH}_3\{\kappa\text{-N},\kappa\text{-S}-(2\text{-Spy})\}(\text{P}^i\text{Pr}_3)_2$, and $[(\text{P}^i\text{Pr}_3)_2\text{H}_3\text{Os}(\mu\text{-biim})\text{M}(\text{TFB})]_2$ (TFB = tetrafluorobenzobarrelene, $\text{M} = \text{Rh}, \text{Ir}$).²⁰ With the notable exception of the tantalum complexes $[\text{TaH}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{PR}_3)]^+$ ($\text{PR}_3 = \text{P}(\text{OMe})_3, \text{PMe}_2\text{Ph}$),²¹ the phenomenon has not been previously observed on dihydride derivatives.

In contrast to the ^1H NMR spectrum, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2b** is temperature invariant. At 293 K, it shows a singlet at 32.1 ppm, which is split into a broad triplet under off-resonance conditions as a result of the P–H coupling with two inequivalent hydrides undergoing a rapid fluxional process.

Treatment at room temperature of a toluene solution of the isomeric mixture of **2** with NaBH_4 and some drops of methanol leads to the trihydride derivative $\text{OsH}_3(\eta^5\text{-C}_5\text{H}_5)(\text{P}^i\text{Pr}_3)$ (**3**), which was isolated as a colorless oil, according to eq 2.



The IR spectrum of the oil between polyethylene sheets shows a strong $\nu(\text{Os-H})$ band at 2091 cm^{-1} . At room temperature, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in dichloromethane- d_2 as solvent contains at 53.9 ppm a singlet. This spectrum is temperature invariant down to 243 K. However, the ^1H NMR spectrum is temperature dependent. At 363 K, the spectrum exhibits in the hydride region a single broad doublet resonance at -14.97 ppm with a H–P coupling constant of about 16 Hz. This observation is consistent with the operation of the thermally activated site exchange process shown in eq 3, which proceeds at a sufficient rate to lead to a single hydride resonance.



Consistent with this, lowering the sample temperature leads to broadening of the resonance. At 313 K, decoalescence occurs and a pattern corresponding to an

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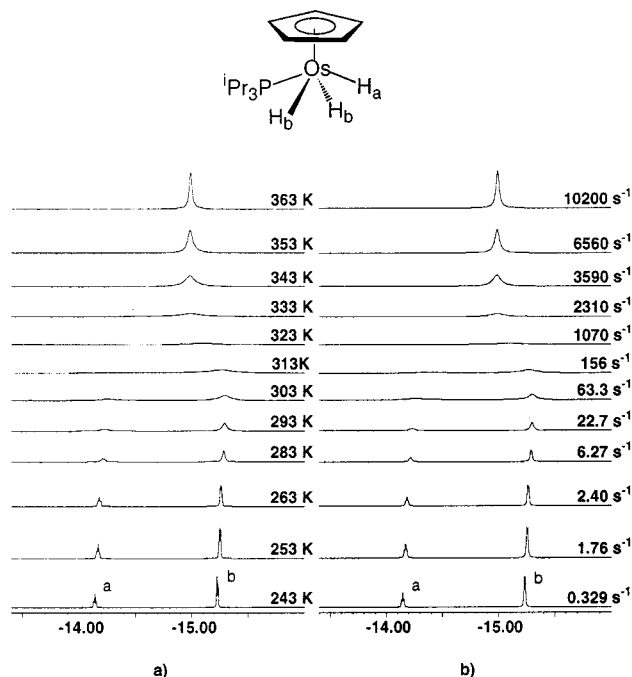


Figure 1. Variable-temperature 300 MHz $^1\text{H}\{^{31}\text{P}\}$ NMR spectra in the high-field region of complex $\text{OsH}_3(\eta^5\text{-C}_5\text{H}_5)(\text{P}^i\text{Pr}_3)$ (**3**) in toluene- d_8 : (a) experimental, (b) simulated.

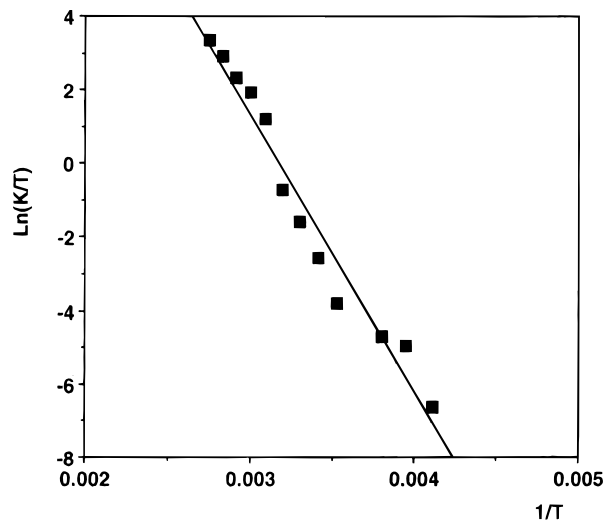


Figure 2. Eyring plot of the rate constants for thermally activated site exchange process of complex $\text{OsH}_3(\eta^5\text{-C}_5\text{H}_5)(\text{P}^i\text{Pr}_3)$ (**3**).

AB_2X spin system ($\text{X} = ^{31}\text{P}$) is observed, which becomes well-resolved at 243 K. The AB_2X spin system is defined by the parameters $\delta_A = -13.9\text{ ppm}$, $\delta_B = -15.0\text{ ppm}$, $J_{\text{AB}} = 3.4\text{ Hz}$, $J_{\text{AX}} = 3\text{ Hz}$, and $J_{\text{BX}} = 33.0\text{ Hz}$, which are temperature invariant. This indicates that, in contrast to **2b**, quantum exchange coupling between H_a and H_b does not take place.

With ^{31}P decoupling (Figure 1a), the spectra are simplified to the expected AB_2 spin system. Line shape analysis of the spectra of Figure 1 allows the calculation of the rate constants for the thermal exchange process at different temperatures. The activation parameters obtained from the Eyring analysis (Figure 2) are $\Delta H^\ddagger = 15.1 \pm 0.3\text{ kcal}\cdot\text{mol}^{-1}$ and $\Delta S^\ddagger = 0.5 \pm 0.7\text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The value for the entropy of activation, close to zero, is in agreement with an intramolecular process,

while the value for the enthalpy of activation lies in the range reported for thermal exchange processes in other trihydride and hydride–dihydrogen derivatives.^{18–20,22} Theoretical studies on the hydride exchange processes in trihydride species suggest that the thermally activated site exchange takes place through dihydrogen transition states, which are reached by a shortening of the H–H distance and a lengthening of the M–H distance. Thus, the barrier for the exchange is the addition of the necessary energy for the dihydrogen formation and the rotation energy of the dihydrogen.²³

Comparison of the ¹H NMR spectra of **3** and **2b** indicates that the barrier for the thermally activate site exchange between the hydrides H_a and H_b of **3** is higher than the barrier for the related process on **2b**. A similar relationship has been previously observed between the barriers for the exchanges of the related hydrogens of the trihydride $\text{OsH}_3\{\text{NH}=\text{C}(\text{Ph})\text{C}_6\text{H}_4\}(\text{P}^i\text{Pr}_3)_2$ and the elongated dihydrogen $\text{OsCl}\{\text{NH}=\text{C}(\text{Ph})\text{C}_6\text{H}_4\}(\eta^2\text{-H}_2)(\text{P}^i\text{Pr}_3)_2$. Although in both cases the hydrogen atoms form dihydrogen ligands in the transition state, the energy barrier for the exchange in the trihydride is significantly higher than the barrier for the exchange in the elongated dihydrogen. The explanation for this fact can be found in the different cost for the dihydrogen formation. The approach of the dihydrogen atoms in the elongated dihydrogen complex costs only 4.0 kcal·mol^{–1}, while 10.5 kcal·mol^{–1} is necessary in the trihydride. The presence of a *cis*-chloride ligand instead of a hydride facilitates the approach between the hydrogen atoms. Once the dihydrogen ligands are formed, the rotational barriers are similar.²⁴

We note that the trihydride $\text{OsH}_3(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)$ has been previously prepared by reaction of $\text{Os}(\eta^5\text{-C}_5\text{Me}_5)\text{Br}_2(\text{PPh}_3)$ with NaBH_4 .²⁵ In contrast to **3**, it is nonfluxional. As it has been previously mentioned, the thermally activated site exchange processes in trihydrido species take place through dihydrogen transition states. Since the dihydrogen character of the H₂ unit is favored by decreasing the basicity of the coligand, and the basicity of triisopropylphosphine is higher than that of triphenylphosphine, the different behavior of the H₃ unit of **3** and $\text{OsH}_3(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)$ can be related with the different electron donor power of the cyclopentadienyl and pentamethylcyclopentadienyl ligands. The lower basicity of the first favors the dihydrogen transition state, giving rise to a lower energy barrier to the hydrogen exchange. The relation between the basicity of these ligands and the energy barriers for the exchange between the hydride ligands of the complexes $\text{RuH}_3(\eta^5\text{-C}_5\text{R}_5)(\text{PR}'_3)$ (R = H, Me) has been elegantly illustrated by Chaudret et al.¹⁵

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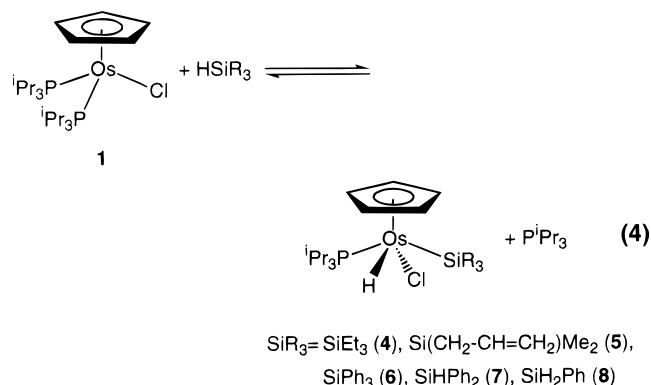
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2. Reactions of $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)_2$ with Silanes. Addition of an excess of HSiEt_3 to a benzene-*d*₆ solution of **1** leads to a mixture of **1** and the hydride–silyl complex $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{SiEt}_3)(\text{P}^i\text{Pr}_3)$ (**4**), according to the equilibrium shown in eq 4. After 30 min the equilibrium is reached, and at 293 K the value of the equilibrium constant is 0.4. In diethyl ether as solvent and in the presence of 1 equiv of HBF_4 , the equilibrium is displaced to the right due to the formation of $[\text{HP}^i\text{Pr}_3][\text{BF}_4]$, which precipitates as a white solid. In this way, complex **4** can be isolated from the diethyl ether solution as a yellow solid.

Similarly to HSiEt_3 , addition of $\text{HSi}(\text{CH}_2\text{-CH=CH}_2)_2\text{-Me}_2$ to a benzene-*d*₆ solution of **1** produces a mixture of **1** and the hydride–silyl compound $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}\{\text{Si}(\text{CH}_2\text{-CH=CH}_2)_2\text{Me}_2\}(\text{P}^i\text{Pr}_3)$ (**5**). In this case, at 293 K the value of the equilibrium constant is 45.2. Under the same conditions, addition of 1 equiv of HSiPh_3 , H_2SiPh_2 , or H_3SiPh to benzene-*d*₆ solutions of **1** leads to the derivatives $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{SiR}_3)(\text{P}^i\text{Pr}_3)$ [$\text{SiR}_3 = \text{SiPh}_3$ (**6**), SiHPh_2 (**7**), SiH_2Ph (**8**)] in quantitative yield, according to the ¹H and ³¹P{¹H} NMR spectra of the reaction mixtures. These compounds were also isolated as yellow solids.



The above-mentioned observations indicate that the constant of the equilibrium shown in eq 4 increases in the sequence $\text{HSiEt}_3 < \text{HSi}(\text{CH}_2\text{-CH=CH}_2)_2\text{Me}_2 < \text{H}_4\text{-x-SiPh}_x$ ($x = 1\text{--}3$). Previously, it has been recognized that the strength of the metal–silyl bond depends on the substituent effects and also on the coordination number and the oxidation state of the metal.²⁶ For basic metallic fragments, the more electronegative substituents appear to give rise to stronger metal–silicon bonds.²⁷ Recently, Hübler, Roper, and co-workers^{3g} have studied from structural and theoretical points of view osmium–silyl complexes of the type $\text{OsCl}(\text{SiR}_3)(\text{CO})(\text{PPh}_3)_2$, with the silyl group changing from SiF_3 to SiCl_3 , $\text{Si}(\text{OH})_3$, and SiMe_3 . The results reveal that, in addition to the Os–Si σ -bond, there is an increasing importance of π -bonding when going from the methyl to the hydroxy, the chloro, and the fluoro derivative. However, no higher d-orbital population on silicon was found in any complex when compared with the corresponding free silanes. The osmium d-orbitals mostly donate into a linear combination of Si–R σ^* -orbitals to form the π -bond. The d-orbitals on silicon serve to polarize the Si–R σ^* -orbitals.

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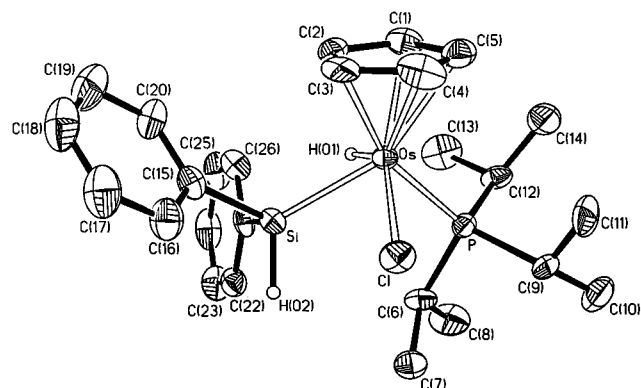


Figure 3. Molecular diagram of complex $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{SiHPh}_2)(\text{P}^i\text{Pr}_3)$ (**7**). Thermal ellipsoids are shown at 50% probability.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of the Complex $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)(\text{SiHPh}_2)$ (7**)**

Os–Cl	2.426(2)	Si–C(15)	1.887(8)
Os–P	2.354(2)	Si–C(21)	1.903(8)
Os–Si	2.406(2)	Si–H(02)	1.32(8)
Os–H(01)	1.69(8)		
G ^a –Os–Cl	113.2(3)	P–Os–H(01)	77(2)
G ^a –Os–P	131.2(3)	Cl–Os–H(01)	136(2)
G ^a –Os–Si	124.2(3)	Os–Si–C(15)	110.3(2)
G ^a –Os–H(01)	108(2)	Os–Si–C(21)	118.2(2)
Si–Os–Cl	80.76(7)	Os–Si–H(02)	116(3)
Si–Os–P	101.96(8)	C(15)–Si–C(21)	107.4(3)
Si–Os–H(01)	64(2)	C(15)–Si–H(02)	107(3)
P–Os–Cl	87.08(8)	C(21)–Si–H(02)	97(3)

^a G is the midpoint of the C(1)–C(5) Cp ligand.

As a result, the π -bonding between osmium and silicon is enhanced and the antibonding between the silicon and the substituents diminishes.

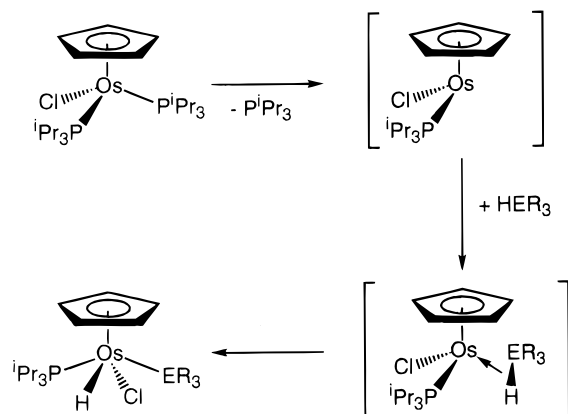
The stability of the Os–Si bond of the complexes $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{SiR}_3)(\text{P}^i\text{Pr}_3)$ is determined not only by the electronic nature of the substituents but also by the cone angle of the silane. Thus, we have also observed that, at room temperature, addition of 1 equiv of H_2SiPh_2 to a benzene- d_6 solution of **6** instantly produces quantitative formation of **7** and HSiPh_3 . The reaction most probably involves the reductive elimination of HSiPh_3 and the subsequent oxidative addition of H_2SiPh_2 to the unsaturated fragment $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)$.

For complexes **4–8**, the structure proposed in eq 4 is supported by the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of these compounds. Furthermore, it was confirmed by an X-ray diffraction analysis on a monocrystal of complex **7**.

A view of the molecular geometry of **7** is shown in Figure 3. Selected bond distances and angles are listed in Table 1. The distribution of ligands around the osmium atom can be described as a piano stool geometry, with the 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 diphenylsilyl. The angle Si–Os–P is 101.96(8)°. This stereochemistry, which is general for the addition of group 14 element hydride compounds to **1** (vide infra), seems to be thermodynamically and kinetically favored and involves the approach of the H–E

Scheme 1



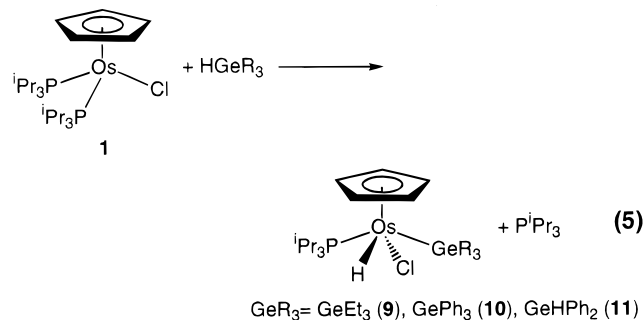
(E = Si, Ge, Sn) bond to the osmium atom of the fragment $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)$ parallel to the Cl–P vector, with the E atom on the chloride (Scheme 1). The basis of this preference is probably steric and involves minimizing nonbonded interactions between the ER_3 ligands and the isopropyl groups of the phosphine.

The Os–Si bond length [2.406(2) Å] is about 0.05 Å shorter than the Os–Si distance found in the trihydride $\text{OsH}_3(\text{SiHPh}_2)(\text{CO})(\text{P}^i\text{Pr}_3)_2$ [2.448(2) Å],^{3b} and about 0.1 Å longer than that reported for $\text{OsH}_3\{\text{Si}(\text{N-pirrolyl})_3\}(\text{PPh}_3)_2$ [2.293(3) Å].^{3e} The environment of the silicon atom is tetrahedral, with angles between 97(3)° and 118.2(2)°.

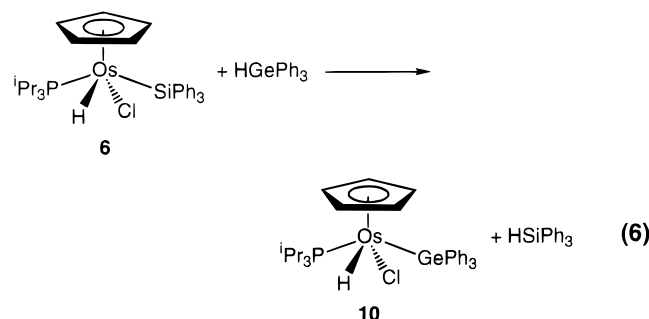
The hydride ligand H(01) was located in the difference Fourier maps and refined as an isotropic atom together with the rest of non-hydrogen atoms of the structure, giving an Os–H(01) distance of 1.69(8) Å. The separation between this ligand and the silyl group (about 2.24 Å) precludes any hydride–silyl interaction and indicates that one of the two H–Si bonds of H_2SiPh_2 has been fully oxidatively added to the metal.

In agreement with the presence of a hydride ligand in the molecules of these compounds, the IR spectra in Nujol show $\nu(\text{Os–H})$ bands between 2096 and 2196 cm^{-1} , and the ^1H NMR spectra contain the corresponding hydride resonances in the high-field region. The hydride ligands of **4–6** give rise, at about –13.5 ppm, to doublets with H–P coupling constants of about 32 Hz, while the hydride ligand of **7** displays a doublet at –14.43 ppm by spin coupling with the phosphorus atom of the phosphine ligand ($J_{\text{HP}} = 32.4$ Hz) and the hydrogen atom of the diphenyl silyl group ($J_{\text{HH}} = 1.2$ Hz). The resonance corresponding to the hydride ligand of **8** appears at –14.82 ppm as a doublet of doublets, by spin coupling with the phosphorus atom of the phosphine ($J_{\text{HP}} = 32.4$ Hz) and the two inequivalent hydrogen atoms of the phenylsilyl group ($J_{\text{HH}} = 3.3$ and 2.1 Hz). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show singlets between 15.0 and 22.4 ppm.

3. Reactions of $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)_2$ with Germanes. The addition of 1 equiv of HGeEt_3 to a benzene- d_6 solution of **1** produces in quantitative yield the hydride–germyl complex $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{GeEt}_3)(\text{P}^i\text{Pr}_3)$ (**9**), according to the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction mixture. Similarly, treatment of **1** with HGePh_3 and H_2GePh_2 affords $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{GePh}_3)(\text{P}^i\text{Pr}_3)$ (**10**) and $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{GeHPh}_2)(\text{P}^i\text{Pr}_3)$ (**11**), respectively, according to eq 5.



The comparison of the yields of the reactions of **1** with HSiEt_3 and HGeEt_3 suggests that the oxidative addition of H–Ge bonds to **1** is more favored than the oxidative addition of H–Si bonds. In agreement with this, we have observed that the addition of 1 equiv of HGePh_3 to a benzene- d_6 solution of **6** instantly leads to **10** in quantitative yield (eq 6).

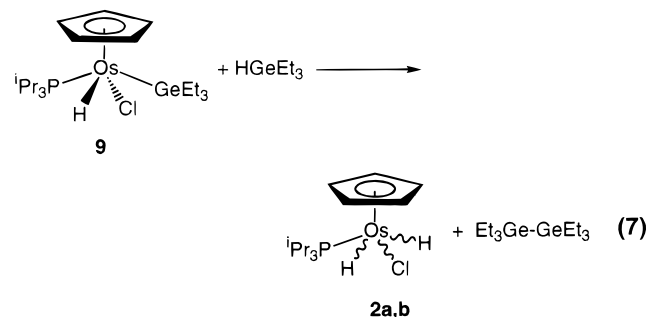


Since the bond dissociation enthalpy for the H–Si bond is only 1.1 times that for the H–Ge bond,²⁸ the above-mentioned observations suggest that, for our system, the Os–Ge bonds are significantly stronger than the Os–Si bonds. Although thermochemical data for the series of transition metal silyl and germyl complexes are quite limited, for basic metal systems, the bond strengths appear to follow the order $\text{M–Ge} > \text{M–Si}$.²⁹ For these systems, bond dissociation energies may be significantly influenced by π -interactions between the transition metal and the group 14 atom, in agreement with the results of Hübler, Roper, and co-workers.

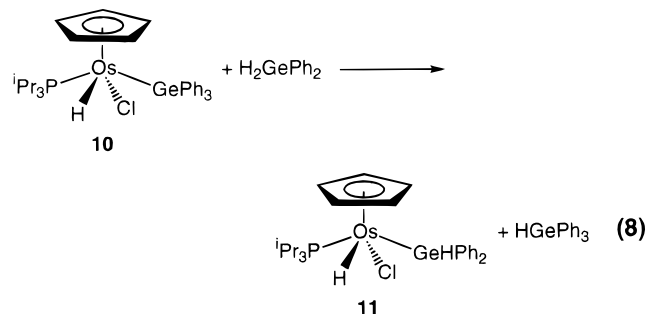
In contrast to the above-mentioned order, Otero and co-workers have found similar bond dissociation enthalpies for the Nb–Si and Nb–Ge bonds in complexes of the type $\text{NbH}_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\text{ER}_3)_2$ ($\text{E} = \text{Si}, \text{Ge}$),³⁰ and Levy and Puddephatt have estimated that the Pt– EMe_3 bond dissociation energies for $[\text{PtX}(\text{Me})_2(\text{EMe}_3)(\text{bpy-}^t\text{Bu}_2)]^+$ are 233 and 182 $\text{kJ}\cdot\text{mol}^{-1}$ for $\text{E} = \text{Si}$ and Ge , respectively.³¹

There is another significant difference between the behavior of HSiEt_3 and HGeEt_3 . While complex **4** does not react with a second molecule of HSiEt_3 , addition of 1 equiv of HGeEt_3 to a benzene- d_6 solution of **9** affords

2 and $\text{Et}_3\text{Ge–GeEt}_3$ (eq 7), which was identified by ^1H NMR spectroscopy.

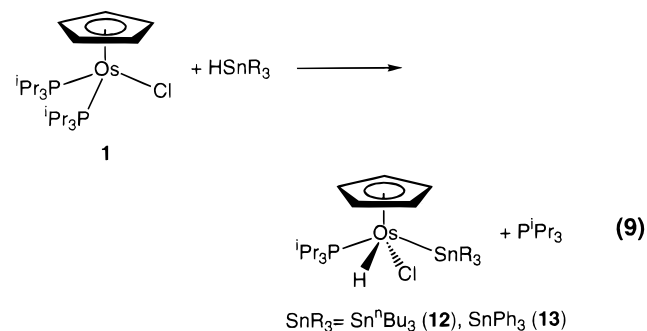


In contrast to **9**, the respective treatments of **10** with HGePh_3 and **11** with H_2GePh_2 do not give rise to reaction. However, addition of 1 equiv of H_2GePh_2 to a benzene- d_6 solution of **10** affords **11** and HGePh_3 in quantitative yield (eq 8). This reaction agrees well with that shown in eq 6 and indicates that the cone angle of the ER_3 groups determines not only the stability of the Os–Si bonds but also the stability of the Os–Ge bonds.



Complexes **9–11** were isolated as yellow solids and characterized by MS, elemental analysis, IR, ^1H , and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopies. The most noticeable absorptions in the IR spectra in Nujol are the $\nu(\text{Os–H})$ bands, which appear between 2084 and 2189 cm^{-1} . The ^1H NMR spectra show the hydride resonance between –13.9 and –15.0 ppm as doublets with H–P coupling constants of about 34 Hz. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra contain singlets between 16 and 22 ppm. Under off-resonance conditions, these singlets are split into doublets, as a result of the P–H coupling with one hydride ligand.

4. Reactions of $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)_2$ with Stannanes. Similarly to the reactions of **1** with germanes, addition of 1 equiv of HSn^nBu_3 or HSnPh_3 to benzene- d_6 solutions of **1** leads to the hydride–stannyl derivatives $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{SnR}_3)(\text{P}^i\text{Pr}_3)$ [$\text{SnR}_3 = \text{Sn}^n\text{Bu}_3$ (**12**), SnPh_3 (**13**)] in quantitative yield, according to eq 9.



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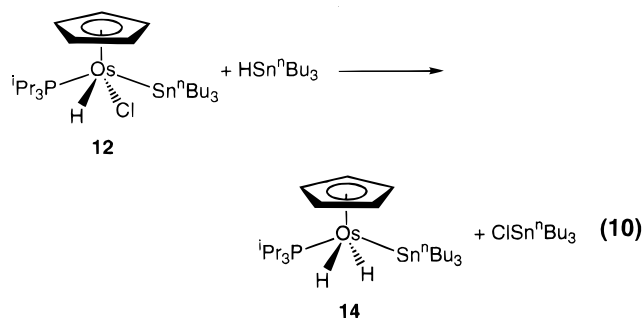
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Complex **12** was isolated as a yellow oil, while complex **13** was isolated as a yellow solid. In the IR spectrum of **13** in Nujol, the most noticeable absorption is the $\nu(\text{Os}-\text{H})$ vibration, which appears at 2138 cm^{-1} . The ^1H NMR spectra of both compounds are similar, showing in the high-field region doublets at -13.29 (**12**) and -14.34 (**13**) ppm, with H-P coupling constants of 34.5 (**12**) and 33.0 (**13**) Hz. Satellites due to the NMR-active Sn isotopes are also observed near the hydride resonance of **12**. The values of the H-Sn coupling constants are 37.2 and 35.0 Hz. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra contain singlets at 23.0 (**12**) and 21.2 (**13**) ppm along with the satellites due to the ^{117}Sn and ^{119}Sn isotopes. The values of the P- ^{119}Sn coupling constants are 133 (**12**) and 144 (**13**) Hz, while the values of the P- ^{117}Sn coupling constants are 127 (**12**) and 137 (**13**) Hz. Under off-resonance conditions the singlets are split into doublets.

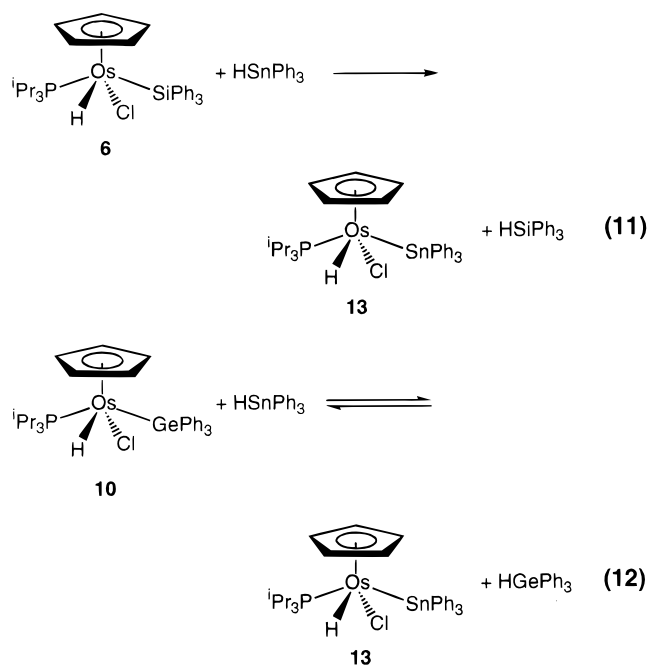
As **9** reacts with HGeEt_3 , **12** reacts with HSn^nBu_3 . However, different reaction products are obtained. The reaction of **12** with HSn^nBu_3 leads to the dihydride-stannyl derivative $\text{OsH}_2(\eta^5\text{-C}_5\text{H}_5)(\text{Sn}^n\text{Bu}_3)(\text{P}^i\text{Pr}_3)$ (**14**) and ClSn^nBu_3 (eq 10) instead of **2**. A similar reaction between **13** and HSnPh_3 is not observed.



Complex **14** was isolated as a colorless oil and characterized by MS and ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. In agreement with the *transoid* disposition of the hydride ligands, the ^1H NMR spectrum, which is temperature invariant, shows only one hydride resonance at -15.53 ppm, as a doublet with a H-P coupling constant of 28.2 Hz. Satellites due to the NMR-active Sn isotopes are also observed near this resonance. The values of the H-Sn coupling constants are 53.4 (H- ^{119}Sn) and 51.0 Hz (H- ^{117}Sn). As the spectrum of **2a**, the spectrum of **14** also shows only one ^iPr -methyl chemical shift in the low-field region. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **14** contains at 46.3 ppm a singlet, along with the satellites due to the ^{117}Sn and ^{119}Sn isotopes. In this case, the value of the P- ^{119}Sn coupling constant is 111 Hz, while the value of the P- ^{117}Sn coupling constant is 106 Hz. Under off-resonance conditions, the singlet is split into a triplet due to the P-H coupling with two equivalent hydride ligands. Traces of an isomer of **14** containing hydride ligands in *cisoid* disposition are not detected.

For these systems, the Os-Sn bond appears to be significantly stronger than the Os-Si bond and slightly weaker than the Os-Ge bond. Thus, we have observed that the addition of 1 equiv of HSnPh_3 to a benzene- d_6 solution of **6** leads to **13** and HSiPh_3 (eq 11), while under the same conditions, addition of 1 equiv of HSnPh_3 to a benzene- d_6 solution of **10** produces a mixture of **13** and

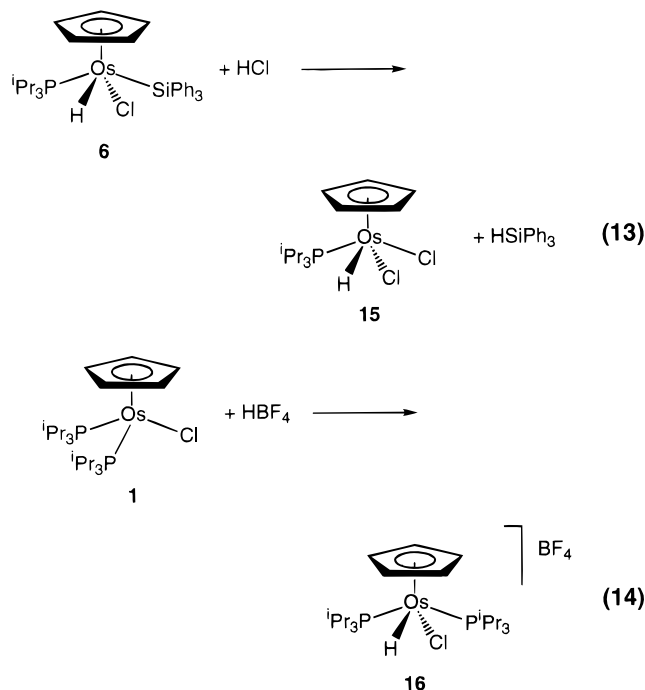
10, according to the equilibrium shown in eq 12. At 293 K , the equilibrium is rapidly reached, and the value of the equilibrium constant is 0.3 .



It has been previously estimated that the H-Ge bond is 1.1 times stronger than the H-Sn bond.²⁸ So, at 293 K , and on the basis of the value of the constant measured for the equilibrium shown in eq 12, one can estimate that, in these systems, the Os-Ge bond is between 3 and 4 times stronger than the Os-Sn bond. M-Ge bonds stronger than the corresponding M-Sn bonds are also found in the previously mentioned systems of Otero and co-workers³⁰ and Levy and Puddephatt.³¹

5. Reactions of $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)_2$ with HCl. Treatment of a toluene solution of **1** with a saturated solution of HCl in toluene in an $1:3$ molar ratio leads to a red suspension, from which a red solid was separated. The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the solid in dichloromethane- d_2 indicate that it is a mixture of the monohydrides $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2(\text{P}^i\text{Pr}_3)$ (**15**) and $[\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)_2]^+$ (**16**). The first of them is the result of the oxidative addition of HCl to the unsaturated metallic fragment $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)$, while the second one is the consequence of the protonation of **1**. In agreement with this, we have also observed that complex **6** reacts with HCl in toluene to afford **15** and HSiPh_3 (eq 13) and that the addition of the stoichiometric amount of a diethyl ether solution of HBF_4 to a dichloromethane- d_2 solution of **1** leads to **16** (eq 14).

Complex **15** was isolated in 84% yield and characterized by MS, elemental analysis, IR, and ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopies. In the IR spectrum in Nujol, the most noticeable absorption is the $\nu(\text{Os}-\text{H})$ vibration, which appears at 2190 cm^{-1} . In the high-field region, the ^1H NMR spectrum shows at -12.83 ppm a doublet with a H-P coupling constant of 33.6 Hz, which supports the *cisoid* disposition of the hydride and the triisopropylphosphine ligands. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains at 22.3 ppm a singlet, which under off-resonance conditions is split into a doublet as a result of the P-H coupling with the hydride.



Cation **16** was characterized in solution by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopies. In the ^1H NMR spectrum in dichloromethane- d_2 , the most characteristic resonance is the corresponding to the hydride ligand, which appears at -14.36 ppm as a triplet with a H-P coupling constant of 33.6 Hz. In agreement with the *transoid* disposition of the phosphine ligands, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains at 4.5 ppm a singlet. Under off-resonance conditions, this signal is split into a doublet.

Concluding Remarks

This study has revealed that the metallic fragment $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)$ is capable of activating by oxidative addition molecules such as H_2 , HSiR_3 , HGeR_3 , HSnR_3 , and HCl to afford osmium(IV) hydride derivatives of the type $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{ClX}(\text{P}^i\text{Pr}_3)$ ($\text{X} = \text{H}$, SiR_3 , GeR_3 , SnR_3 , Cl), with a distribution of ligands around the metallic center that can be described as a four-legged piano stool geometry.

Addition of molecular hydrogen leads to a mixture of the *transoid-dihydride* $\text{OsH}_2(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)$ (**2a**) and *cisoid-dihydride* $\text{OsH}_2(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)$ (**2b**) isomers. Isomer **2a** has a rigid structure in solution. However, the hydride ligands of **2b** undergo a thermally activated site exchange process. Furthermore, they show quantum exchange coupling. The isomeric mixture reacts with NaBH_4 to give the trihydride $\text{OsH}_3(\eta^5\text{-C}_5\text{H}_5)(\text{P}^i\text{Pr}_3)$. The mutually *cisoid* hydrides of this compound also undergo a thermally activated site exchange process. However, they do not show quantum exchange coupling.

The trend to the oxidative addition of silanes increases in the sequence $\text{HSiEt}_3 < \text{HSi}(\text{CH}_2\text{-CH=CH}_2)_2\text{-Me}_2 < \text{H}_4\text{-}_x\text{SiPh}_x$ ($x = 1\text{--}3$). The addition of these molecules, as well as germanes and stannanes, is selective and leads to only one isomer, containing the added fragments in *cisoid* position, and the ER_3 group ($\text{E} = \text{Si}$, Ge , Sn) *transoid* to the phosphine. The thermodynamic stability of the Os-ER_3 bonds depend on the cone angle of the ER_3 group ($\text{Os-EHR}_2 > \text{Os-ER}_3$) and increases in the sequence $\text{Os-Si} \ll \text{Os-Sn} < \text{Os-Ge}$.

The oxidative addition of HCl gives rise to a mixture of the monohydrides $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2(\text{P}^i\text{Pr}_3)$ and $[\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)_2]^+$. The first one is the result of the addition of HCl to the unsaturated fragment $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)$, while the second one is the consequence of the protonation of the precursor $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)_2$.

In conclusion, despite the high kinetic stability of the CpOsL_3 compounds, 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 to prepare not only π -olefin, π -alkyne, vinylidene, allenylidene, and carbyne compounds but also dihydride, trihydride, hydride-silyl, hydride-germyl, hydride-stannyl, and dihydride-stannyl derivatives of osmium(IV). In particular, it should be pointed out that the *cisoid-dihydride* $\text{OsH}_2(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)$ is a rare case of a dihydride compound showing quantum exchange coupling.

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 material $\text{Os}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)_2$ (**1**) was prepared by the published method.⁴

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

Kinetic Analysis. Complete line-shape analysis of the $^1\text{H}\{^{31}\text{P}\}$ NMR spectra was achieved using the program gNMR v3.6 for Macintosh (Cherwell Scientific Publishing Limited). The rate constants (k) for various temperatures were obtained by visually matching observed and calculated spectra. The transverse relaxation time T_2 used was common for the two signals for all temperatures recorded and was obtained from the line width of the exchange-averaged resonance above the fast-exchange limit. The activation parameters ΔH^\ddagger and ΔS^\ddagger were calculated by least-squares fit of $\ln(k/T)$ vs $1/T$ (Eyring equation). Error analysis assumed a 10% error in the rate constant and 1 K in the temperature. Errors were computed by published methods.³²

Preparation of $\text{OsH}_2(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)$ (2**).** Molecular hydrogen was bubbled through a pentane solution (40 mL) saturated with **1** (120.8 mg, 0.20 mmol) during 45 min. The resulting grayish solution was concentrated to ca. 5 mL, and the solvent was decanted, leading to a white solid, which was washed twice with pentane (3 mL). Yield: 60 mg (67%). Anal. Calcd for $\text{C}_{14}\text{H}_{28}\text{ClOsP}$: C, 37.12; H, 6.24. Found: C, 37.49; H, 6.60. Spectroscopic data for **2a**: IR (Nujol): $\nu(\text{Os-H})$: 2059 cm^{-1} (m). ^1H NMR (300 MHz, C_6D_6 , 293 K): δ 4.79 (s, 5H, Cp); 1.94 (m, 3H, PCH); 0.97 (dd, $^2J_{\text{HP}} = 13.8$ Hz, $^2J_{\text{HH}} = 6.9$ Hz, 18H, PCHCH₃); -10.09 (d, $^2J_{\text{HP}} = 33.6$ Hz, 2H, Os-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, C_6D_6 , 293 K): δ 43.1 (s, t in off-resonance). Spectroscopic data for **2b**: IR (Nujol): $\nu(\text{Os-H})$: 2121 cm^{-1} (w). ^1H NMR (300 MHz, C_6D_6 , 293 K): δ 4.89 (s, 5H, Cp); 2.19 (m, 3H, PCH); 1.05-0.90 (m, 18H, PCHCH₃); -11.05 (d, $^2J_{\text{HP}} = 15.6$ Hz, 2H, Os-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, C_6D_6 , 293 K): δ 32.1 (s, br t in off-resonance). MS (FAB⁺): m/e 452 ($\text{M}^+ - \text{HCl}$).

Preparation of $\text{OsH}_3(\eta^5\text{-C}_5\text{H}_5)(\text{P}^i\text{Pr}_3)$ (3**).** An excess of NaBH_4 (89 mg, 2.35 mmol) was added to a toluene solution (10 mL) of **2** (153 mg, 0.34 mmol). Methanol (1 mL) was added dropwise, and the mixture was allowed to react for 15 min. The solution was vacuum-dried, and the resulting residue was extracted with pentane (20 mL). The solvent was again vacuum dried, and an ivory oil was obtained. Yield: 66 mg

(32) Morse, P. M.; Spencer, M. O.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646, and references therein.

(47%). Anal. Calcd for $C_{14}H_{29}OsP$: C, 40.16; H, 7.00. Found: C, 40.42; H, 7.04. IR (Nujol): $\nu(\text{Os-H})$: 2091 cm^{-1} (br, s). ^1H NMR (300 MHz, C_6D_6 , 293 K): δ 4.88 (s, 5H, Cp); 1.64 (m, 3H, PCH); 0.93 (dd, $^3J_{PH} = 13.2$ Hz, $^3J_{HH} = 6.9$ Hz, 18H, PCHCH₃); -14.14 (s br, 1H, Os-H_a); -15.21 (d, $^2J_{HP} = 31.2$ Hz, 2H, Os-H_b). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, C_6D_6 , 293 K): δ 53.9 (s). MS (FAB⁺): m/e 415 ($M^+ - 3H$).

Preparation of $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{SiEt}_3)(\text{P}^i\text{Pr}_3)$ (4). To a diethyl ether solution (10 mL) of **1** (159.1 mg, 0.26 mmol) was added HSiEt_3 (430 μL , 2.63 mmol) and then HBF_4 in ether (35 μL , 0.26 mmol). After 30 min, the suspension was filtered, and the resulting solution was vacuum-dried and then washed twice with cold methanol (2 mL), leading to a yellow solid. Yield: 76 mg (51%). Anal. Calcd for $C_{20}H_{42}ClOsPSi$: C, 42.34; H, 7.48. Found: C, 42.40; H, 7.68. IR (Nujol): $\nu(\text{Os-H})$: 2096 cm^{-1} (m). ^1H NMR (300 MHz, C_6D_6 , 293 K): δ 4.78 (s, 5H, Cp); 2.28 (m, 3H, PCH); 1.4–1.1 (15H, -Et); 0.97 (dd, $^3J_{HP} = 12.9$ Hz, $^3J_{HH} = 7.2$ Hz, 18H, PCHCH₃); -13.45 (d, $^2J_{HP} = 32.1$ Hz, 1H, Os-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, C_6D_6 , 293 K): δ 18.0 (s, d in off-resonance). MS (FAB⁺): m/e 568 (M^+), 452 ($M^+ - \text{HSiEt}_3$).

Preparation of $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}\{\text{Si}(\text{CH}_2\text{-CH=CH}_2)\text{Me}_2\}$ (P^iPr_3) (5). To a solution of **1** (23 mg, 0.038 mmol) in benzene- d_6 (0.5 mL) was added $\text{HSi}(\text{CH}_2\text{-CH=CH}_2)\text{Me}_2$ (5.4 μL , 0.038 mmol). After 1 h, a yellow solution was obtained, in which complex **5** was detected. ^1H NMR (300 MHz, C_6D_6 , 293 K): δ 6.17 (m, 1H, Si-CH₂-CH); 5.1–5.0 (2H, =CH₂); 4.78 (s, 5H, Cp); 2.21 (m, 3H, PCH); 2.2–2.0 (2H, Si-CH₂); 0.95 (dd, $^3J_{HP} = 13.2$ Hz, $^3J_{HH} = 6.9$ Hz, 9H, PCHCH₃); 0.93 (dd, $^3J_{HP} = 13.2$ Hz, $^3J_{HH} = 6.9$ Hz, 9H, PCHCH₃); 0.80 (s, 3H, Si-CH₃); 0.75 (s, 3H, Si-CH₃); -13.76 (dd, $^2J_{HP} = 32.1$ Hz, 1H, Os-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, C_6D_6 , 293 K): δ 19.4 (s, d in off-resonance). MS (FAB⁺): m/e 508 ($M^+ - H - (\text{CH}_2\text{-CH=CH}_2)$), 477 ($M^+ - \text{Cl} - (\text{CH}_2\text{-CH=CH}_2)$).

Preparation of $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{SiPh}_3)(\text{P}^i\text{Pr}_3)$ (6). To a solution of **1** (153 mg, 0.25 mmol) in toluene (10 mL) was added HSiPh_3 (130 mg, 0.50 mmol). The mixture was allowed to react for 2 h and then vacuum-dried. The yellow sticky residue was then washed twice with pentane (3 mL) and later with methanol (3 mL). Yield: 156 mg (88%). Anal. Calcd for $C_{32}H_{42}\text{ClOsPSi}$: C, 54.02; H, 5.96. Found: C, 53.81; H, 5.90. IR (Nujol): $\nu(\text{Os-H})$: 2157 cm^{-1} (m). ^1H NMR (300 MHz, C_6D_6 , 293 K): δ 8.1–7.1 (15H, -Ph); 4.76 (s, 5H, Cp); 2.13 (m, 3H, PCH); 0.81 (dd, $^3J_{PH} = 13.5$ Hz, $^3J_{HH} = 6.9$ Hz, 9H, PCHCH₃); 0.75 (dd, $^3J_{PH} = 13.5$ Hz, $^3J_{HH} = 6.9$ Hz, 9H, PCHCH₃); -13.56 (d, $^2J_{HP} = 32.7$ Hz, 1H, Os-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, C_6D_6 , 293 K): δ 15.0 (s, d in off-resonance). MS (FAB⁺): m/e 452 ($M^+ - \text{HSiPh}_3$).

Preparation of $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{SiHPh}_2)(\text{P}^i\text{Pr}_3)$ (7). $\text{H}_2\text{-SiPh}_2$ (108 μL , 0.58 mmol) was added to a toluene solution (10 mL) of **1** (171.6 mg, 0.28 mmol). The mixture was stirred for 2 h and then vacuum-dried. The resulting residue was washed twice with pentane (3 mL) and then twice with methanol (3 mL), leading to a yellow solid. Yield: 118.9 mg (67%). Anal. Calcd for $C_{26}H_{38}\text{ClOsPSi}$: C, 49.15; H, 6.04. Found: C, 49.20; H, 6.00. IR (Nujol): $\nu(\text{Os-H})$: 2196 cm^{-1} (m); $\nu(\text{Si-H})$: 2117 cm^{-1} (s). ^1H NMR (300 MHz, C_6D_6 , 293 K): δ 8.1–7.1 (10H, -Ph); 6.77 (d, $^3J_{HH} = 1.2$ Hz, 1H, Si-H); 4.76 (s, 5H, Cp); 2.26 (m, 3H, PCH); 0.93 (dd, $^3J_{HP} = 13.8$ Hz, $^3J_{HH} = 7.2$ Hz, 9H, PCHCH₃); 0.81 (dd, $^3J_{HP} = 13.8$ Hz, $^3J_{HH} = 7.2$ Hz, 9H, PCHCH₃); -14.43 (dd, $^2J_{HP} = 32.4$ Hz, $^3J_{HH} = 1.2$ Hz, 1H, Os-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, C_6D_6 , 293 K): δ 21.4 (s, d in off-resonance). MS (FAB⁺): m/e 636 (M^+), 601 ($M^+ - \text{Cl}$), 452 ($M^+ - \text{H}_2\text{SiPh}_2$), 418 ($M^+ - \text{Cl} - \text{HSiPh}_2$).

Preparation of $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{SiH}_2\text{Ph})(\text{P}^i\text{Pr}_3)$ (8). $\text{H}_3\text{-SiPh}$ (50 μL , 0.40 mmol) was added to a toluene solution (10 mL) of **1** (128.3 mg, 0.21 mmol). The mixture was stirred for 30 min and then vacuum-dried. The residue was then washed twice with methanol (3 mL), resulting in a yellow solid. Yield: 71.2 mg (61%). Anal. Calcd for $C_{20}H_{34}\text{ClOsPSi}$: C, 42.95; H, 6.14. Found: C, 42.84; H, 6.10. IR (Nujol): $\nu(\text{Si-H})$: 2104 cm^{-1}

(vs). ^1H NMR (300 MHz, C_6D_6 , 293 K): δ 8.1–7.2 (5H, -Ph); 6.06 (dd, $^2J_{HH} = 6.9$ Hz, $^3J_{HH} = 3.3$ Hz, 1H, Si-H); 5.47 (dd, $^2J_{HH} = 6.9$ Hz, $^3J_{HH} = 2.1$ Hz, 1H, Si-H); 4.73 (s, 5H, Cp); 2.29 (m, 3H, PCH); 0.96 (dd, $^3J_{PH} = 14.4$ Hz, $^3J_{HH} = 7.2$ Hz, 9H, PCHCH₃); 0.91 (dd, $^3J_{PH} = 14.4$ Hz, $^3J_{HH} = 7.2$ Hz, 9H, PCHCH₃); -14.82 (ddd, $^2J_{HP} = 32.4$ Hz, $^3J_{HH} = 3.3$ Hz, $^3J_{HH} = 2.1$ Hz, 1H, Os-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, C_6D_6 , 293 K): δ 22.4 (s, d in off-resonance). MS (FAB⁺): m/e 559 ($M^+ - \text{H}$), 523 ($M^+ - \text{Cl}$).

Preparation of $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{GeEt}_3)(\text{P}^i\text{Pr}_3)$ (9). To a solution of **1** (200.5 mg, 0.33 mmol) in toluene (10 mL) was added HGeEt_3 (75 μL , 0.46 mmol). The mixture was stirred for 10 min and then vacuum-dried. The residue was washed twice with cold methanol (3 mL), resulting in a yellow solid. Yield: 83.6 mg (42%). Anal. Calcd for $C_{20}H_{42}\text{ClGeOsP}$: C, 39.26; H, 6.93. Found: C, 39.41; H, 7.20. IR (Nujol): $\nu(\text{Os-H})$: 2084 cm^{-1} (m). ^1H NMR (300 MHz, C_6D_6 , 293 K): δ 4.84 (s, 5H, Cp); 2.29 (m, 3H, PCH); 1.35 (m, 15H, GeEt₃); 0.97 (dd, $^3J_{PH} = 13.2$ Hz, $^3J_{HH} = 7.2$ Hz, 9H, PCHCH₃); 0.96 (dd, $^3J_{PH} = 13.2$ Hz, $^3J_{HH} = 7.2$ Hz, 9H, PCHCH₃); -14.01 (d, $^2J_{HP} = 34.1$ Hz, 1H, Os-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, C_6D_6 , 293 K): δ 19.0 (s, d in off-resonance). MS (FAB⁺): m/e 612 (M^+), 579 ($M^+ - \text{Cl}$), 517 ($M^+ - 2H - 2Et - \text{Cl}$), 452 ($M^+ - H - \text{GeEt}_3$), 418 ($M^+ - H - \text{Cl} - \text{GeEt}_3$).

Preparation of $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{GePh}_3)(\text{P}^i\text{Pr}_3)$ (10). To a solution of **1** (166 mg, 0.27 mmol) in toluene (10 mL) was added HGePh_3 (176.2 mg, 0.58 mmol). The mixture was left to react for 2 h and then vacuum-dried. The yellow residue was washed twice with pentane (3 mL) and twice with methanol (3 mL). Yield: 117.6 mg (57.3%). Anal. Calcd for $C_{32}H_{42}\text{ClGeOsP}$: C, 50.84; H, 5.61. Found: C, 50.49; H, 5.45. IR (Nujol): $\nu(\text{Os-H})$: 2170 cm^{-1} (m). ^1H NMR (300 MHz, C_6D_6 , 293 K): δ 8.1–7.1 (15H, -Ph); 4.80 (s, 5H, Cp); 2.18 (m, 3H, PCH); 0.79 (dd, $^3J_{PH} = 13.5$ Hz, $^3J_{HH} = 6.9$ Hz, 9H, PCHCH₃); 0.75 (dd, $^3J_{PH} = 13.5$ Hz, $^3J_{HH} = 6.9$ Hz, 9H, PCHCH₃); -14.29 (d, $^2J_{HP} = 33.9$ Hz, 1H, Os-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, C_6D_6 , 293 K): δ 16.9 (s, d in off-resonance). MS (FAB⁺): m/e 756 (M^+), 721 ($M^+ - \text{Cl}$), 677 ($M^+ - \text{Ph}$), 643 ($M^+ - H - \text{Cl} - \text{Ph}$), 452 ($M^+ - \text{HGePh}_3$), 418 ($M^+ - \text{Cl} - \text{GePh}_3$).

Preparation of $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{GeHPh}_2)(\text{P}^i\text{Pr}_3)$ (11). To a solution of **1** (180.3 mg, 0.29 mmol) in toluene (10 mL) was added H_2GePh_2 (110 μL , 0.59 mmol). The mixture was stirred for 2 h and then vacuum-dried. The yellow residue was washed twice with pentane (3 mL) and twice with methanol (3 mL). Yield: 106.7 mg (53%). Anal. Calcd for $C_{26}H_{38}\text{ClOsPGe}$: C, 45.93; H, 5.65. Found: C, 45.85; H, 5.78. IR (Nujol): $\nu(\text{Os-H})$: 2189 cm^{-1} (m); $\nu(\text{Ge-H})$: 1992 cm^{-1} (s). ^1H NMR (300 MHz, C_6D_6 , 293 K): δ 8.0–7.1 (10H, -Ph); 6.70 (s, 1H, Ge-H); 4.77 (s, 5H, Cp); 2.28 (m, 3H, PCH); 0.93 (dd, $^3J_{HP} = 13.8$ Hz, $^3J_{HH} = 7.2$ Hz, 9H, PCHCH₃); 0.81 (dd, $^3J_{HP} = 13.8$ Hz, $^3J_{HH} = 7.2$ Hz, 9H, PCHCH₃); -14.89 (d, $^2J_{HP} = 33.3$ Hz, 1H, Os-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, C_6D_6 , 293 K): δ 21.4 (s, d in off-resonance). MS (FAB⁺): m/e 680 (M^+), 643 ($M^+ - \text{Cl}$), 603 ($M^+ - \text{Ph}$), 452 ($M^+ - \text{H}_2\text{GePh}_2$), 418 ($M^+ - \text{Cl} - \text{HGePh}_2$).

Preparation of $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{Sn}^n\text{Bu}_3)(\text{P}^i\text{Pr}_3)$ (12). HSn^nBu_3 (10 μL , 0.037 mmol) was added to a benzene- d_6 solution (0.5 mL) of **1** (18.2 mg, 0.030 mmol). The mixture was left to react for 15 min, leading to a yellow solution, in which the compound **12** was detected. ^1H NMR (300 MHz, C_6D_6 , 293 K): δ 4.78 (s, 5H, Cp); 2.28 (m, 3H, PCH); 2.0–0.6 (45H, -Bu/PCHCH₃); -13.29 (d, $^2J_{HP} = 34.5$ Hz, 1H, Os-H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, C_6D_6 , 293 K): δ 23.0 (s, d in off-resonance). MS (FAB⁺): m/e 741 ($M^+ - \text{H}$), 649 ($M^+ - H - \text{Cl} - ^n\text{Bu}$), 627 ($M^+ - H - ^n\text{Bu} - ^n\text{Bu}$).

Preparation of $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{SnPh}_3)(\text{P}^i\text{Pr}_3)$ (13). HSnPh_3 (186.0 mg, 0.53 mmol) was added to a toluene solution (10 mL) of **1** (132.6 mg, 0.22 mmol). The mixture was stirred for 2 h and then vacuum-dried. The sticky residue was washed twice with methanol (3 mL), leading to a yellow solid. Yield: 123.2 mg (71%). Anal. Calcd for $C_{32}H_{42}\text{ClOsPSn}$: C, 47.92; H, 5.29. Found: C, 48.00; H, 5.78. IR (Nujol): $\nu(\text{Os-H})$: 2138

cm^{-1} (m). ^1H NMR (300 MHz, C_6D_6 , 293 K): δ 8.1–7.0 (15H, –Ph); 4.81 (s, 5H, Cp); 2.17 (m, 3H, PCH); 0.84 (dd, $^3J_{\text{PH}} = 12.9$ Hz, $^3J_{\text{HH}} = 6.9$ Hz, 9H, PCHCH₃); 0.77 (dd, $^3J_{\text{PH}} = 12.9$ Hz, $^3J_{\text{HH}} = 6.9$ Hz, 9H, PCHCH₃); –14.34 (d, $^2J_{\text{HP}} = 33.0$ Hz, 1H, Os–H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, C_6D_6 , 293 K): δ 21.2 (s, d in off-resonance). MS (FAB⁺): m/e 802 (M^+), 724 ($\text{M}^+ - \text{H} - \text{Ph}$), 689 ($\text{M}^+ - \text{H} - \text{H} - \text{Ph}$), 647 ($\text{M}^+ - \text{H} - \text{Ph} - \text{Ph}$), 418 ($\text{M}^+ - \text{Cl} - \text{SnPh}_3$).

Preparation of $\text{OsH}_2(\eta^5\text{-C}_5\text{H}_5)(\text{Sn}^n\text{Bu}_3)(\text{P}^i\text{Pr}_3)$ (14). To a solution of **1** (22.2 mg, 0.036 mmol) in benzene-*d*₆ was added HSn^nBu_3 (20 μL , 0.074 mmol). The mixture was allowed to react for 7 days, leading to an ivory solution in which the complex **14** was detected. ^1H NMR (300 MHz, C_6D_6 , 293 K): δ 4.69 (s, 5H, Cp); 2.0–0.6 (30H, PCH/-Bu); 0.94 (dd, $^3J_{\text{PH}} = 13.5$ Hz, $^3J_{\text{HH}} = 7.5$ Hz, 18H, PCHCH₃); –15.53 (d, $^2J_{\text{HP}} = 28.2$ Hz, 2H, Os–H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, C_6D_6 , 293 K): δ 46.3 (s, t in off-resonance). MS (FAB⁺): m/e 709 ($\text{M}^+ - \text{H}$), 651 ($\text{M}^+ - ^n\text{Bu}$), 593 ($\text{M}^+ - \text{H} - ^n\text{Bu} - ^n\text{Bu}$), 535 ($\text{M}^+ - \text{H} - \text{H} - ^n\text{Bu} - ^n\text{Bu}$), 491 ($\text{M}^+ - \text{P}^i\text{Pr}_3 - ^n\text{Bu}$).

Preparation of $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2(\text{P}^i\text{Pr}_3)$ (15). To a solution of **6** (423.5 mg, 0.60 mmol) in toluene (3 mL) was added a saturated solution of HCl in toluene (7 mL). The mixture was stirred for 6 h, leading to a red suspension. The suspension was concentrated to ca. 3 mL and then decanted, and the solvent was put away. The red solid was finally washed twice with toluene (3 mL) and twice with diethyl ether (3 mL). Yield: 242.3 mg (84%). Anal. Calcd for $\text{C}_{14}\text{H}_{27}\text{Cl}_2\text{OsP}$: C, 34.49; H, 5.59. Found: C, 34.84; H, 5.05. IR (Nujol): $\nu(\text{Os-H})$: 2190 cm^{-1} (m). ^1H NMR (300 MHz, CCl_2D_2 , 293 K): δ 5.63 (s, 5H, Cp); 2.80 (m, 3H, PCH); 1.26 (dd, $^3J_{\text{PH}} = 13.8$ Hz, $^3J_{\text{HH}} = 6.9$ Hz, 9H, PCHCH₃); 1.24 (dd, $^3J_{\text{PH}} = 13.8$ Hz, $^3J_{\text{HH}} = 6.9$ Hz, 9H, PCHCH₃); –12.83 (d, $^2J_{\text{HP}} = 33.6$ Hz, 1H, Os–H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, CCl_2D_2 , 293 K): δ 22.3 (s, d in off-resonance). MS (FAB⁺): m/e 452 ($\text{M}^+ - \text{H} - \text{Cl}$).

Preparation of $[\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{P}^i\text{Pr}_3)_2]^+$ (16). To a solution of **1** (26.5 mg, 0.043 mmol) in dichloromethane-*d*₂ was added $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (6 μL , 0.043 mmol). The mixture was left to react for 10 min, leading to a reddish solution in which the cationic complex **16** was detected. ^1H NMR (300 MHz, $\text{CD}_2\text{-Cl}_2$, 293 K): δ 5.90 (s, 5H, Cp); 2.66 (m, 6H, PCH); 1.5–1.2 (36H, PCHCH₃); –14.36 (t, $^2J_{\text{HP}} = 33.6$ Hz, 1H, Os–H). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, CD_2Cl_2 , 293 K): δ 4.5 (s, d in off-resonance). MS (FAB⁺): m/e 613 (M^+), 577 ($\text{M}^+ - \text{H} - \text{Cl}$).

X-ray Structure Analysis of Complex $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{SiHPh}_2)(\text{P}^i\text{Pr}_3)$ (7). Crystals suitable for the X-ray diffraction study were obtained by cooling a saturated solution of the complex **7** in pentane. A summary of crystal data and refinement parameters is reported in Table 2. The yellow, prismatic crystal of approximate dimensions $0.36 \times 0.36 \times 0.20$ mm was glued on a glass fiber and mounted on a Siemens-CCD diffractometer (sealed tube 2.4 kW, $\lambda = 0.71073$). Two quadrants of data (3350 reflections) were collected via two runs of 0.3° ω scans at different φ values, over a θ range of $1.7\text{--}23.3^\circ$. All data were corrected for absorption using a semiempirical method.³³ The structure was solved by Patterson (Os atom, SHELXL97³⁴) and conventional Fourier techniques and refined by full-matrix least-squares on F^2 (SHELXL97³⁴). Anisotropic

Table 2. Crystal Data and Data Collection and Refinement for $\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{SiHPh}_2)(\text{P}^i\text{Pr}_3)$ (7)

	Crystal Data
formula	$\text{C}_{26}\text{H}_{38}\text{ClOsPSi}$
molecular wt	635.27
color and habit	yellow, prismatic block
size, mm	$0.36 \times 0.36 \times 0.20$
symmetry	monoclinic
space group	$P2_1$
a, Å	9.9859(9)
b, Å	9.9172(9)
c, Å	13.4605(12)
β , deg	97.462(2)
V, Å ³	1321.7(2)
Z	2
D_{calc} , g cm^{-3}	1.596
	Data Collection and Refinement
diffractometer	Siemens-CCD
$\lambda(\text{Mo K}\alpha)$, Å	0.71073
monochromator	graphite oriented
μ , mm^{-1}	5.042
scan type	0.3° ω scans at different φ values
θ range, deg	$1.7 \leq \theta \leq 23.3^\circ$
temp, K	190.0(2)
no. of data collect	3350 (h , –11, 2; k , –10, 11; l , –9, 14)
no. of unique data	2556 (merging R factor 0.0276)
no. of params refined	286
R_1^a [$F^2 > 2\sigma(F^2)$]	0.0207
wR_2^b [all data]	0.0508
S^c [all data]	1.065

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

parameters were used in the last cycles of refinement for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions and refined riding on their respective carbon atoms with a fixed common thermal parameter. H(01) and H(02) were refined as free isotropic atoms. Atomic scattering factors, corrected for anomalous dispersion, were implemented by the program. The refinement converged to $R_1 = 0.0207$ [$F^2 > 2\sigma(F^2)$] and $wR_2 = 0.0508$ [all data], with weighting parameters $x = 0.0201$ and $y = 1.5777$.

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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 **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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