1250 *Inorg. Chem.* **1996,** *35,* 1250−1256

Oxidative Addition of Group 14 Element Hydrido Compounds to $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$: Synthesis and Characterization of the First Trihydrido−Silyl, Trihydrido−Germyl, and Trihydrido−Stannyl Derivatives of Osmium(IV)

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The dihydrido−olefin complex $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$ (**2**) reacts with H_2SiPh_2 to give $OsH_3(SiHPh_2)(CO)(P^iPr_3)_2$ (**3**). The molecular structure of **3** has been determined by X-ray diffraction (monoclinic, space group $P2_1/c$ with $a = 16.375(2)$ Å, $b = 11.670(1)$ Å, $c = 18.806(2)$ Å, $\beta = 107.67(1)°$, and $Z = 4$) together with *ab initio* calculations on the model compound $OsH_3(SiH_3)(CO)(PH_3)_2$. The coordination geometry around the osmium center can be rationalized as a heavily distorted pentagonal bipyramid with one hydrido ligand and the carbonyl group in the axial positions. The two other hydrido ligands lie in the equatorial plane, one between the phosphine ligands and the other between the $SiHPh_2$ group and one of the phosphine ligands. Complex **3** can also be prepared by reaction of $OsH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$ (**4**) with H_2SiPh_2. Similarly, the treatment of **4** with $HSiPh_3$ affords $OsH_3(SiPh_3)(CO)(P^iPr_3)_2$ (**5**), while the addition of H_3SiPh to **4** in methanol yields $OsH_3\{Si(OMe)_2Ph\}(CO)(P^iPr_3)_2$ (**6**). Complex **2** also reacts with $HGeR_3$ and $HSnR_3$ to give $OsH_3(GeR_3)(CO)(P^iPr_3)_2$ ($GeR_3 = GeHPh_2$ (**7**), $GePh_3$ (**8**), $GeEt_3$ (**9**)) and $OsH_3(SnR_3)(CO)(P^iPr_3)_2$ (R = Ph (**10**), ^{n}Bu (**11**)), respectively. In solution, compounds **3** and **5**−**11** are fluxional and display similar ^1H and $^{31}P\{^1H\}$ NMR spectra, suggesting that they possess a similar arrangement of ligands around the osmium atom.

Introduction

The fact that the 5d metals form stronger bonds than their 3d and 4d counterparts with the ligands typically involved in catalytic transformations has led in the past to the general assumption that reactions involving third-row transition metal complexes are too slow for catalytic cycles and are thus of no practical use in catalysis. Over the last few years, a number of interesting examples of organic transformations catalyzed by third-row transition metal complexes have emerged in the literature, indicating that a judicious choice of the metal−ligand system may also lead to active third-row catalysts.[1] In this respect, we have reported examples, from the iron triad, which show that not only iron and ruthenium but also osmium form complexes which behave as good catalysts for the addition of silanes to terminal alkynes.[2−4] Thus, the five coordinate hydrido−carbonyl complex $OsHCl(CO)(P^iPr_3)_2$ (**1**) was found to be a very active and highly selective catalyst for the addition of triethylsilane to phenylacetylene. The catalytic reaction proceeds via the silyl−dihydrogen intermediate $Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$, which is formed according to eq 1.[2]

$$OsHCl(CO)(P^iPr_3)_2 + HSiEt_3 \rightarrow OsH_2(SiEt_3)Cl(CO)(P^iPr_3)_2 \rightleftarrows Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2 \quad (1)$$

The design of new catalysts and new processes requires a basic knowledge of the leading factors of the catalytic cycles, that is, the elementary steps of the catalysis. Therefore, in connection with the hydrosilylation reactions, the additions of silanes, and, in general, of group 14 element hydrido compounds to transition metal hydrido complexes are elementary reactions of considerable interest.[5,6]

We recently reported that the reaction of the five-coordinated hydrido−carbonyl complex **1** with ^{n}BuLi affords the dihydrido complex $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$ (**2**).[7] Continuing our study on the interaction of osmium−hydrido complexes with potentially useful molecules in catalysis, we have investigated the addition of group 14 element hydrido compounds to the dihydrido $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$ (**2**). During this study, we have isolated complexes of general formula $OsH_3(ER_3)(CO)(P^iPr_3)_2$ (E = Si, Ge, Sn). Compounds of the type $MLnH_3(ER_3)$ are relatively scarce in the iron triad. Schubert *et al.*[8,9a] have described the synthesis and the spectroscopic properties of the iron−trihydrido−silyl complexes $FeH_3(SiR_3)(PR_3)_3$ and

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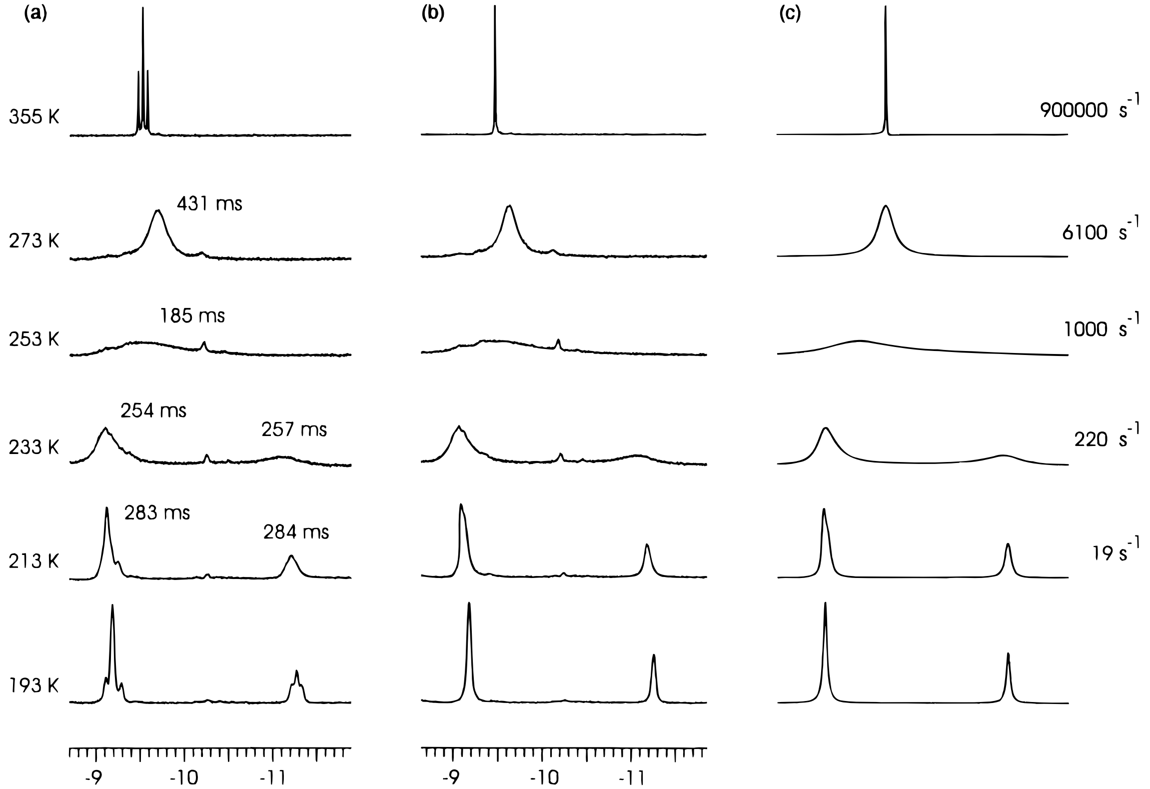

Figure 1. Variable-temperature 300-MHz ^1H NMR spectra in the high-field region of $OsH_3(SiHPh_2)(CO)(P^iPr_3)_2$ (**3**) in toluene-d_8: (a) ^1H; (b) $^1H\{^{31}P\}$; (c) simulated.

$FeH_3(SiR_3)(CO)(dppe)$ (dppe = $Ph_2PCH_2CH_2PPh_2$) and the iron−trihydrido−stannyl derivatives $FeH_3(SnR_3)(PR_3)_3$, which have a pseudotetrahedral heavy-atom skeleton. The same skeleton has been found in the ruthenium−trihydrido−silyl compound $RuH_3(SiMe_3)(PMe_3)_3$.[9] Related ruthenium−trihydrido−silyl derivatives have also been synthetized by Kono *et al.*,[10] Haszeldine *et al.*,[11] and Caulton *et al.*[12] As far as we know, ruthenium−trihydrido−stannyl and iron− and ruthenium−trihydrido−germyl complexes have yet to be reported.

In this paper we report the synthesis and characterization of the first trihydrido−silyl, trihydrido−germyl, and trihydrido−stannyl compounds of osmium. Moreover, the trihydrido−germyl complexes are also the first examples of compounds of this type in the iron triad.

Results and Discussion

Silyl Derivatives. The dihydrido-1-butene complex $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$ (**2**) reacts with 2 equiv of H_2SiPh_2 in hexane to give a colorless solution, from which the trihydrido−silyl complex $OsH_3(SiHPh_2)(CO)(P^iPr_3)_2$ (**3**) was isolated as a white solid in 75% yield.

In the IR spectrum of **3** in Nujol, the most noticeable absorptions are those corresponding to the vibrations ν(Si−H), ν(Os−H), and ν(CO), which appear at 2075, 1995, and 1890 cm^{-1}, respectively. At room temperature, the ^1H NMR spectrum shows the expected resonances for the triisopropylphosphine ligands and the phenyl groups of the diphenylsilyl ligand, along with a triplet at 6.52 ppm (J_{P-H} = 12.1 Hz) assigned to the Si−H proton, and a broad resonance at −9.65 ppm due to the three hydrido ligands. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 37.3 ppm.

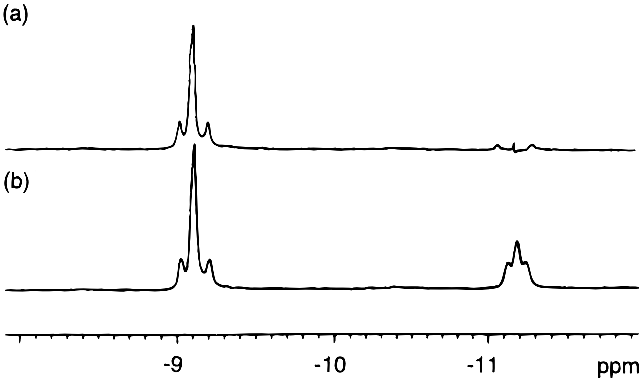

Figure 2. ^1H NMR spectra in the high-field region of $OsH_3(SiHPh_2)(CO)(P^iPr_3)_2$ (**3**) in toluene-d_8: (a) $^1H\ \{^1H\ \}$; (b) ^1H.

The ^1H and $^{31}P\{^1H\}$ NMR spectra are temperature dependent. Figure 1 shows the ^1H and $^1H\{^{31}P\}$ NMR spectra in the hydrido region as a function of the temperature. At 193 K the $^1H\{^{31}P\}$ NMR spectrum (Figure 1b) shows a singlet at −11.18 ppm and another apparent singlet at −9.11 ppm, with a relative intensity ratio of 1:2. These signals are split into a triplet with a P−H coupling constant of 15 Hz and into the AB part of a second order ABXY splitting pattern (Figure 1a) as a result of the P−H coupling. When the temperature is raised, both resonances coalesce to give finally a triplet at 355 K. At 193 K, the $^{31}P\{^1H\}$ NMR spectrum shows a broad resonance between 35 and 39 ppm. The spectra of Figure 1 suggest that complex **3** has a rigid structure only at low temperature. In this structure the hydrido ligands are chemically inequivalent, and one of them is not coupled with the other two, as is proved by Figure 2, which shows that irradiation of the signal at −11.18 ppm leaves unaffected that at −9.11 ppm.

In order to determine the structure of **3**, an X-ray diffraction experiment on a single crystal of this compound was carried out. Unfortunately, from the X-ray diffraction study, it was not possible to locate the hydrido positions. Figure 3 shows a

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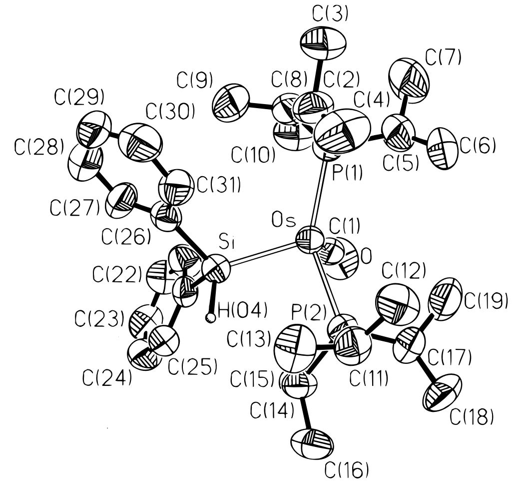

Figure 3. Molecular diagram of complex **3**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex $OsH_3(CO)(SiHPh_2)(P^iPr_3)_2$ (**3**)

Os−P(1)	2.362(2)	Os−C(1)	1.916(9)
Os−P(2)	2.389(2)	C(1)−O	1.142(11)
Os−Si	2.448(2)		
P(1)−Os−P(2)	146.06(7)	Os−Si−C(26)	115.0(3)
P(1)−Os−Si	117.91(7)	Os−Si−H(04)	110(2)
P(1)−Os−C(1)	96.8(3)	C(20)−Si−C(26)	105.5(3)
P(2)−Os−Si	91.23(7)	C(20)−Si−H(04)	102(2)
P(2)−Os−C(1)	89.7(2)	C(26)−Si−H(04)	105(2)
Si−Os−C(1)	107.7(2)	Os−C(1)−O	178.1(7)
Os−Si−C(20)	117.2(3)		

view of the skeleton of the molecule. Selected bond distances and angles are listed in Table 1.

The heavy atom skeleton of **3** can be described as a distorted trigonal pyramid with the carbonyl ligand in the axial site. The silicon and both phosphorus atoms are at the base sites, with the silicon and one of the two phosphorus atoms bent away from the axial ligand (P(1)−Os−C(1) = 96.8(3)°, Si−Os−C(1) = 107.7(2)°). The angles between the basal ligands are P(1)−Os−P(2) = 146.06(7)°, P(1)−Os−Si = 117.91(7)°, and P(2)−Os−Si = 91.23(7)°.

Theoretical studies with geometry optimization have proved to be efficient locating hydrido positions in transition metal complexes.[13] For example, the full structural determination of the complex $ReH_2(SiHPh_2)(CO)(PMe_2Ph)_3$, for which only the position of the heavy atoms were determined by X-ray diffraction, was achieved by means of *ab initio* calculations.[14] With this precedent in mind, we have carried out *ab initio* calculations at the MP2 level, in order to locate the hydrido positions in complex **3**. For this purpose the triisopropylphosphine and diphenylsilyl ligands were replaced by PH_3 and SiH_3, respectively. The positions of the heavy atoms were fixed at the values determined by X-ray diffraction, and energy gradient optimization techniques were used to find the position of the hydrido ligands. Different starting geometries were tested, all converging to the same structure. Figure 4 presents this optimized structure, and Table 2 summarizes the most significant geometrical parameters.[15]

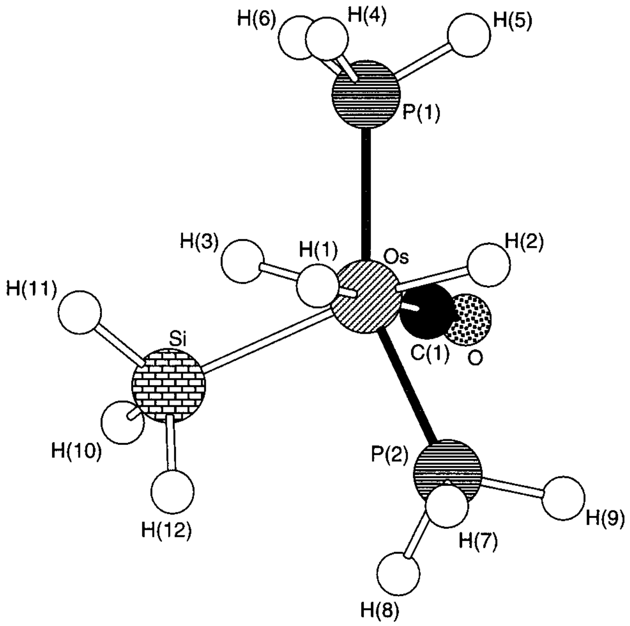

Figure 4. MP2 optimized structure of complex $OsH_3(SiH_3)(CO)(PH_3)_2$.

Table 2. Most Important Optimized Geometrical Parameters[a] of the Complex $OsH_3(SiH_3)(CO)(PH_3)_2$

Os−P(1)	2.362	H(1)···H(3)	2.459
Os−P(2)	2.388	H(2)···H(1)	2.217
Os−Si	2.448	H(2)···H(3)	3.227
Os−C(1)	1.916	Si···H(1)	2.528
C(1)−O	1.142	Si···H(2)	3.981
Os−H(1)	1.685	Si···H(3)	1.869
Os−H(2)	1.668		
Os−H(3)	1.655		
P(1)−Os−P(2)	146.1	C(1)−Os−H(2)	96.2
P(1)−Os−Si	117.9	Si−Os−C(1)	107.6
P(1)−Os−C(1)	96.7	Si−Os−H(1)	72.8
P(1)−Os−H(1)	84.5	Si−Os−H(2)	150.1
P(1)−Os−H(2)	75.4	Si−Os−H(3)	49.7
P(1)−Os−H(3)	70.7	C(1)−Os−H(1)	178.1
P(2)−Os−Si	91.2	C(1)−Os−H(3)	86.9
P(2)−Os−C(1)	89.8	H(1)−Os−H(2)	82.7
P(2)−Os−H(1)	88.4	H(1)−Os−H(3)	94.8
P(2)−Os−H(2)	70.7	H(2)−Os−H(3)	152.3
P(2)−Os−H(3)	136.9		

[a] Distances in Å, angles in deg. Heavy atoms fixed at the positions found in the X-ray determined values of $OsH_3(SiHPh_2)(CO)(P^iPr_3)_2$.

In agreement with the ^1H NMR spectrum of **3** at 193 K, the theoretical calculations localized the hydrido ligands in chemically inequivalent positions, which correspond to vacant positions in the OsP_2CSi core. Thus, one of the hydrido ligands is trans to the carbonyl group (C(1)−Os−H(1) = 178.1°), while the others lie between P(1) and P(2) (H(2)) and between P(1) and Si (H(3)).

The hydrogen−hydrogen separations between the hydrido ligands (more than 2.2 Å) and the T_1 values shown in Figure 1 rule out the possibility of the existence of a dihydrogen ligand. However, the eventual presence of an η^2-$HSiR_3$ group is more arguable. The hydrido ligand H(3) is near the silicon atom (Si−H(3) = 1.869 Å) but with a very elongated distance, compared to the normal Si−H bond length (1.48 Å). The Si−H distances in compounds formulated as η^2-$HSiR_3$ are in the range 1.7−1.8 Å,[16] and in general their structures resemble more closely those of oxidative addition products than those of σ complexes with an unstretched Si−H bond.[17] The bond angles in the model compound $OsH_3(SiH_3)(CO)(PH_3)_2$ (Table 2) can be hardly assigned to an octahedron as should correspond to the presence of an η^2-$HSiR_3$ ligand. On the contrary, all the geometrical parameters are more consistent with heptacoordination around

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(15) A full geometry optimization of complex $OsH_3(SiH_3)(CO)(PH_3)_2$ yielded a very similar geometry to that obtained with the frozen heavy-atom skeleton, differences being smaller than 0.05 Å in the bond distances and 5° in the bond angles.

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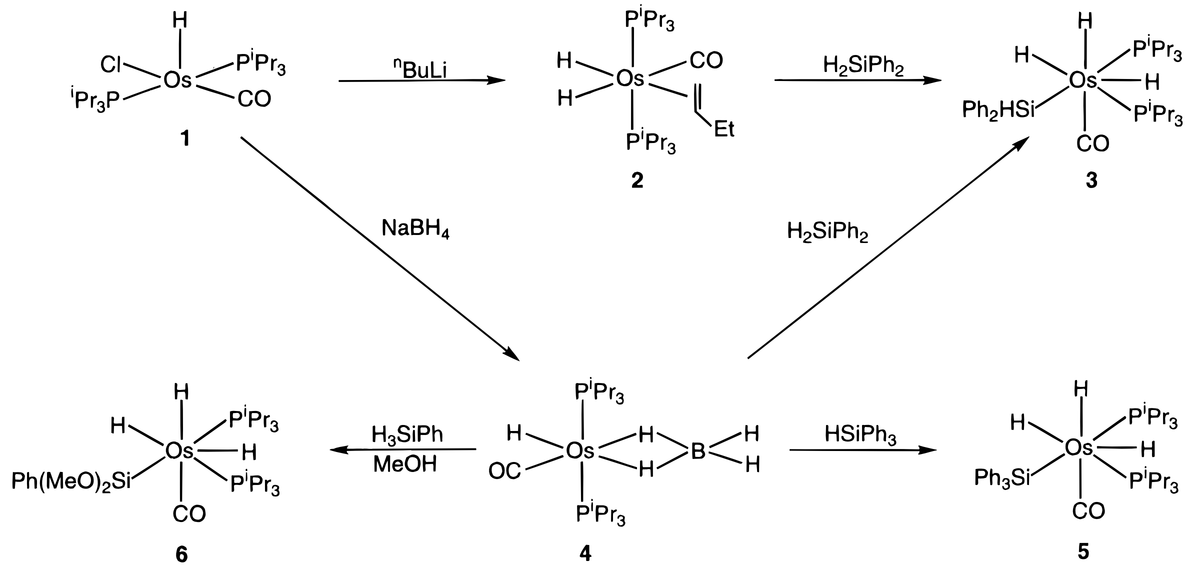
Scheme 1



the metal atom. Moreover the angles between the metal, the silicon atom, and the silyl hydrogens (H(10), H(11), and H(12)) are roughly tetrahedral (between 109 and 117°), whereas the angles between H(3), Si, and the silyl hydrogens deviate much more from the tetrahedral ones (H(3)−Si−H(12) = 151.5°). The environment of the silicon atom of **3** is also tetrahedral with bond angles between 117.1(2) and 102(2)° (Table 1). In addition, it should be mentioned that for hydrido−diphenylsilyl compounds, there exists a relationship between the C−Si−C angle of the diphenylsilyl ligand and the extent of the oxidative addition. Thus, for the complexes $IrH_2(SiHPh_2)(PMe_3)_3$[18] and $RuH(SiHPh_2)(CO)(P^tBu_2Me)_2$[19] the angles C−Si−C are 102.5(4) and 102.5(3) Å, respectively, and the Si−H has been fully oxidatively added to the metal, whereas in the complexes $CrH(SiHPh_2)(\eta^6\text{-}C_6Me_6)(CO)_2$,[20] $Mn(\eta^5\text{-}C_5H_4Me)(H)(SiHPh_2)(CO)(PMe_3)$, $Mn(\eta^5\text{-}C_5Me_5)(H)(SiHPh_2)(CO)_2$,[21] and $Ti(\eta^5\text{-}C_5H_5)_2(H)(SiHPh_2)(CO)(PMe_3)$[22] the related angles are 105.9(2), 106.4(2), 107.0(1), and 105.4(3)°, respectively, and the Si−H bonds interact in an agostic fashion. For complex **3** the value of the angle C(20)−Si−C(26) determined by X-ray diffraction is 105.4(3)°. On the basis of the above mentioned considerations, we formulate complex **3** as a trihydrido−silyl−osmium (IV) derivative, although possibly with some residual Si−H interaction.

Having formulated complex **3** as a heptacoordinate osmium derivative, we can try to relate its structure, on the basis of the theoretical calculations, to the most common regular polyhedra found in seven-coordinate molecules: pentagonal bipyramid (PB), capped octahedron (CO), and capped trigonal prism (CTP).[23] None of these three ideal coordination polyhedra reproduces accurately the bond angles presented in Tables 1 and 2. The most clear structural features of the model compound $OsH_3(SiH_3)(CO)(PH_3)_2$ is the *trans* disposition of the CO group and the H(1) hydrido ligand. If it were a regular PB, the other five ligands (P(1), P(2), H(2), H(3), and Si) would lie in the equatorial plane, with interequatorial ligand angles of 72 and 144°. Taking *XY* as the equatorial plane, the P(2) and H(3) ligands are in the plane (Z = 0.01 and 0.09 Å, respectively), H(2) and P(1) are slightly bent away from this plane (Z = −0.18 and −0.28 Å, respectively) and the silicon atom is far from the regular PB position (Z = −0.75 Å). P(2)−Os−Si and P(1)−Os−Si angles are 91.2 and 117.9°, respectively. An alternative is to describe the model compound as a distorted capped trigonal prism, with H(2) as a capping ligand, P(1), P(2), H(1), and C (from CO) atoms forming the capped quadrilateral face, and Si and H(3) forming the edge of the CTP. However, as it corresponds to different bond lengths, the four ligands of the quadrilateral face are not in a plane. The dihedral angle between the planes P(1)−P(2)−H(1) and P(2)−H(1)−C is 28.8°. Therefore, we think it is more reasonable to describe the coordination polyhedron of the model compound $OsH_3(SiH_3)(CO)(PH_3)_2$, and consequently of **3**, as a heavily distorted pentagonal bipyramid.

Complex **3** can also be obtained by reaction of the octahedral compound $OsH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2$ (**4**) with H_2SiPh_2 in methanol as solvent (Scheme 1). Through this route, complex **3** was isolated in 70% yield. Similarly, the treatment of **4** with $HSiPh_3$ affords $OsH_3(SiPh_3)(CO)(P^iPr_3)_2$ (**5**), while the addition of H_3SiPh to a suspension of **4** in methanol yields $OsH_3\{Si(OMe)_2Ph\}(CO)(P^iPr_3)_2$ (**6**), containing a dialkoxysilyl ligand. The (dialkoxysilyl)iridium (III) compounds $IrH_2\{Si(OR)_2Ph\}(CO)_2(PCy_3)$ (R = Me, Et, ^iPr) have been recently prepared by a similar procedure.[24] Previously, Caulton and co-workers had reported that the reaction of $Cp^*Ru(P^iPr_2Ph)(OCH_2CF_3)$ with H_2SiPh_2 gives two products, one of which is the alkoxysilyl derivative $Cp^*Ru(P^iPr_2Ph)H_2\{Si(OCH_2CF_3)Ph_2\}$.[25]

Complexes **5** and **6** were isolated as white solids in 75 and 65% yield, respectively. In the IR spectra in Nujol the ν(Os−H) and ν(CO) absorptions appear at 2000 (**5** and **6**), 1890 (**5**), and 1900 (**6**) cm^{-1}. The spectrum of **6** also contains a strong band at 1075 cm^{-1}, which was assigned to the ν(Si−O) vibration.[24,26] The ^1H and $^{31}P\{^1H\}$ NMR spectra of these

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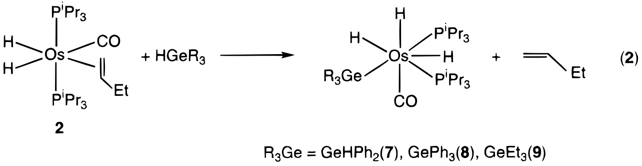
compounds show a dependence on temperature similar to that previously described for **3**. At room temperature, the ^{1}H NMR spectrum of **5** in the hydrido region shows a broad resonance centered at −9.76 ppm. At 193 K this resonance is converted into a triplet at −9.39 ppm, with a P−H coupling constant of 20.5 Hz, and the AB part of a second-order ABXY splitting pattern centered at −9.92 ppm. At room temperature, the ^{1}H NMR spectrum of **6** in the high field region shows a triplet at −10.89 ppm with a P−H coupling constant of 8.8 Hz, while at 193 K, it contains again a new triplet at −10.04 ppm, with a P−H coupling constant of 20.0 Hz and the AB part of a second-order ABXY splitting pattern centered at −10.95 ppm. At room temperature, the ^{31}P{^{1}H} NMR spectra show singlets at 24.6 (**5**) and 30.0 (**6**) ppm. At 193 K, these singlets are broad. The above-mentioned spectroscopic data suggest that **5** and **6** present a coordination polyhedron around the osmium atom similar to **3**.

Germyl and Stannyl Derivatives. The dihydrido−olefin complex **2** also reacts with H_2GePh_2, $HGePh_3$, and $HGeEt_3$ to give the corresponding trihydrido−germyl derivatives **7**−**9** according to eq 2.



Complex **7** was isolated as a yellow oil in quantitative yield, and characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. At room temperature the ^{1}H NMR spectrum in toluene-d_8 shows the expected resonances for the triisopropylphosphine ligands and the phenyl groups of the diphenylgermyl ligand, along with a triplet at 5.78 ppm, with a P−H coupling constant of 11.7 Hz, assigned to the Ge−H proton and a triplet at −9.80 ppm, with a P−H coupling constant of 15 Hz. Below room temperature, a broadening of the latter triplet is observed. The variable temperature 300-MHz T_1 study of the signal at −9.80 ppm gives a T_1(min) of 270 ms at 253 K, in agreement with the trihydrido character of **7**. At room temperature the ^{31}P{^{1}H} NMR spectrum shows a singlet at 38.9 ppm, which becomes broad at 193 K.

Complexes **8** and **9** were isolated as white solids in 62 (**8**) and 60% (**9**) yield. In the IR spectra in Nujol the ν(Os−H) and ν(CO) absorptions appear at 1966 (**8**) and 1957 (**9**) and at 1867 (**8**) and 1870 (**9**) cm^{-1} respectively. The temperature dependent behavior of the ^{1}H NMR spectrum of **8** is as that of **7**. At room temperature, the spectrum contains in the hydrido region a triplet at −9.63 ppm (J_{P-H} = 15 Hz), which is broad at 193 K. However, according to the ^{1}H NMR spectrum **9** behaves in a manner similar to the dialkoxysilyl complex **6** (Figure 5). At room temperature the hydrido resonances appear as only one broad triplet at −10.41 ppm. Below room temperature, the signal broadens, to give finally at 193 K a triplet at −11.20 ppm with a P−H coupling constant of 21 Hz, and the AB part of a second order ABXY spin system centered at −9.90 ppm. In this case, the variable temperature 300-MHz T_1 study rules out also the possibility of dihydrogen association for the trihydride moiety. The spectra of Figure 5 indicate that complex **9** has, as do compounds **3**, **5**, and **6**, three chemically inequivalent hydrido ligands, one of which does not couple with the other two. Therefore, we assume that the structures of the trihydrido−germyl derivatives **7**−**9** are the same as the structures of the trihydrido−silyl complexes **3**, **5**, and **6**. In agreement with this, the ^{31}P{^{1}H} spectra of **8** and **9** at room temperature show singlets at 35.6 (**8**) and 27.7 (**9**) ppm, which under off-resonance conditions split into quartets due to the P−H coupling. At 193 K, both singlets are broad.

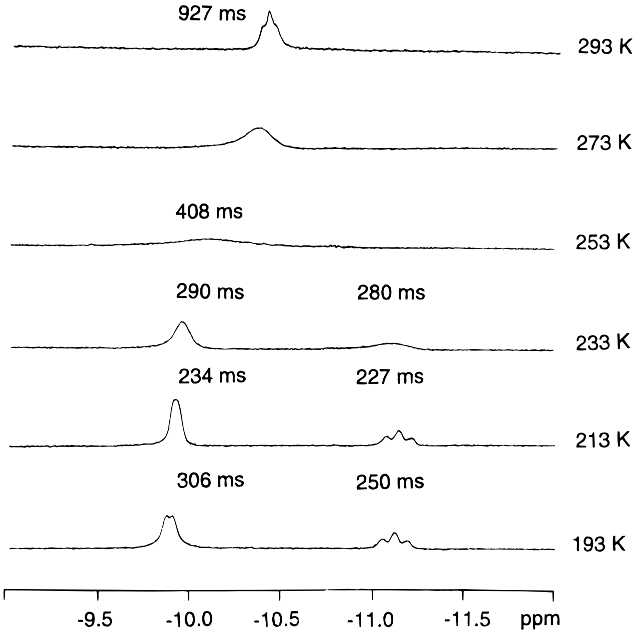
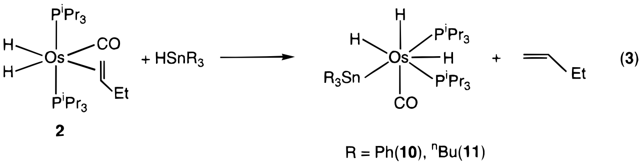


Figure 5. Variable-temperature 300-MHz ^{1}H NMR spectra in the high-field region of $OsH_3(GeEt_3)(CO)(P^iPr_3)_2$ (**9**) in toluene-d_8.

Complex **2** also reacts with and $HSnPh_3$ and HSn^nBu_3. The products of the reactions are the trihydrido−stannyl derivatives $OsH_3(SnPh_3)(CO)(P^iPr_3)_2$ (**10**) and $OsH_3(Sn^nBu_3)(CO)(P^iPr_3)_2$ (**11**), which are formed according to eq 3. We note that the dihydride−distannyl complex $OsH_2(SnMe)_2(CO)(PPh_3)_2$ has been previously synthetized, by oxidative addition of $HSnMe_3$ to $OsH(SnMe_3)(CO)(PPh_3)_2$.[27]



Complex **10** was isolated as a white solid in 75% yield, while complex **11** was isolated as an orange oil in quantitative yield. In the IR spectrum of **10**, the most noticiable absorptions are the ν(Os−H) and ν(CO) vibrations, which appear at 2080 and 1966 cm^{-1}, respectively. In the high field region, the ^{1}H NMR spectra of both compounds are similar. At room temperature, they show triplets at −9.90 (J_{P-H} = 15.1 Hz, **10**) and −10.72 (J_{P-H} = 13.5 Hz, **11**). Satellites due to the Sn isotopes are also observed near these resonances. The values of the Sn−H coupling constants are 52.2 (**10**) and 68.1 (**11**) Hz. Below room temperature, a broadening of the triplets is observed. The triplet of **10** gives finally, at 178 K, two broad resonances at about −10 and −11 ppm with an intensity ratio of 1:2. At room temperature the ^{31}P{^{1}H} NMR spectra show singlets at 39.3 (**10**) and 34.0 (**11**) ppm along with the satellites due to the Sn isotopes, with P−Sn coupling constants of 69.5 (**10**) and 33.4 (**11**) Hz. Under off-resonance conditions, both singlets are split into quartets due to the P−H coupling. At 193 K, both resonances are broad.

The behavior in solution of the three types of compounds $MH_3(ER_3)(CO)(P^iPr_3)_2$ (E = Si, Ge, Sn) described is similar, suggesting that all of them have the same arrangement of ligands around of the osmium atom. However, the interactions of the

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(27) Clark, G. R.; Flower, K. R.; Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. J.*J. Organomet. Chem.* **1993**, *462*, 331.

silyl, germyl, or stannyl groups with one of the three hydrido ligands of the complexes merits further consideration. In solution, complexes **3** and **5**−**11** are fluxional, with the chemically inequivalent hydrido ligands interchanging their positions.[28] Because the hydrido exchange must involve the cleavage of the hydrido−silyl, −germyl, or −stannyl residual interaction and the $\mathrm{R_3E{-}H}$ bond energies decrease in the sequence Si > Ge > Sn,[29] one might expect a higher barrier of activation for the fluxional process in the silyl and germyl compounds than in the stannyl derivatives. In fact, the enthalpies of activation for the silyl and germyl complexes **3** (10.6 ± 0.2 kcal mol^{-1}) and **9** (11 ± 0.4 kcal mol^{-1}) are higher than the enthalpy estimated for the stannyl derivative **10** (about 6 kcal mol^{-1}).

Concluding Remarks

This study has revealed that the dihydrido−olefin complex $\mathrm{OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2}$ reacts with $\mathrm{R_3E{-}H}$ to give the corresponding $\mathrm{OsH_3(ER_3)(CO)(P^iPr_3)_2}$ (E = Si, Ge, Sn), which can be formulated as derivatives of osmium (IV) with a weak H−E agostic interaction.

For the three types of compound the arrangement of the ligands around the osmium atom is the same. In the solid state and in solution at very low temperatures the coordination polyhedra can be described as a very distorted pentagonal bipyramid with a hydrido ligand and the carbonyl group in the axial positions. The other two hydrido ligands lie in the equatorial plane, one between the phosphine ligands and the other between the $\mathrm{R_3E}$ group and one of the phosphine ligands. In solution at room temperature all compounds are fluxional.

In conclusion, we report the synthesis and characterization of the first trihydrido−silyl, trihydrido−germyl, and trihydrido−stannyl derivatives of osmium(IV). The trihydrido−germyl complexes also are the first examples of compounds of this type for the iron triad.

Experimental Section

General Considerations. All reactions were carried out under an argon atmosphere by using Schlenk techniques. Solvents were dried and purified by known procedures and distilled under argon prior to use. The starting complexes $\mathrm{OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2}$ (**2**)[7] and $\mathrm{OsH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2}$ (**4**)[30] were prepared by a published method.

Physical Measurements. NMR spectra were recorded on a Varian UNITY 300 or on a Bruker AXR 300 spectrometer at room temperature unless stated. Chemical shifts are expresed in parts per million, upfield from $\mathrm{Si(CH_3)_4}$ (^{1}H) and 85% $\mathrm{H_3PO_4}$ (^{31}P{^{1}H} NMR spectra). Coupling constants J and N ($N = J(\mathrm{HP}) + J(\mathrm{HP'})$) are given in Hertz. The T_1 experiments were performed on a Varian UNITY 300 spectrometer with a standard $180°-\tau-90°$ pulse sequence. T_1 values are given in milliseconds (ms). Infrared spectra were recorded on a Perkin-Elmer 783 spectrometer using Nujol mulls on polyethylene sheets. C and H analyses were carried out on a Perkin-Elmer 240C microanalyzer.

Preparation of $\mathbf{OsH_3(SiHPh_2)(CO)(P^iPr_3)_2}$ (3). The complex can be prepared by using two different procedures.

(a) A solution of $\mathrm{OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2}$ (ca. 200 mg, 0.35 mmol) in 5 mL of hexane was treated with $\mathrm{H_2SiPh_2}$ (135.6 μL, 0.70 mmol). The mixture was stirred for 1 h at room temperature and concentrated in vacuo to dryness. Addition of methanol to the resulting residue gave a white solid. The mixture was decanted and the resulting white solid was washed with methanol and dried in vacuo: yield 190.3 mg (75%).

(b) A suspension of $\mathrm{OsH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2}$ (100 mg, 0.18 mmol) in 5 mL of methanol was treated with $\mathrm{H_2SiPh_2}$ (70 μL, 0.36 mmol) and the mixture stirred for 1 h at room temperature. A white solid was formed. The solvent was decanted and the solid washed with methanol and dried in vacuo: yield 91.4 mg (70%). Anal. Calcd for $\mathrm{C_{31}H_{56}OOsP_2Si}$: C, 51.36; H, 7.78. Found: C, 51.21; H, 8.29. IR (Nujol, cm^{-1}): ν(Si−H) 2075, ν(Os−H) 1995, ν(CO) 1890 (s). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 8.07 (d, 4H, $J_{\mathrm{H-H}} = 6.9$ Hz, *o*-$\mathrm{C_6H_5}$); 7.38 (dd, 4H, $J_{\mathrm{H-H}} = J_{\mathrm{H-H'}} = 9.1$ Hz, *m*-$\mathrm{C_6H_5}$); 7.15 (overlapped with the signal of benzene-d_6, *p*-$\mathrm{C_6H_5}$); 6.52 (t, 1H, $J_{\mathrm{P-H}} = 12.1$ Hz, Si−H); 2.21 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$); 1.12 (dvt, 36H, $N = 14.1$ Hz, $J_{\mathrm{P-H}} = 7.2$ Hz, $\mathrm{PCHC}H_3$); −9.65 (br, 3H, $\mathrm{Os}H_3$). ^{31}P{^{1}H} NMR (121.421 MHz, $\mathrm{C_6D_6}$): δ 37.3 (s).

^{1}H NMR (toluene-d_8, 193 K) in the hydride region: δ −11.18 (t, 1H, $J_{\mathrm{P-H}} = 15.0$ Hz); −9.11 (2H, AB part of a second order ABXY spin system).

Preparation of $\mathbf{OsH_3(SiPh_3)(CO)(P^iPr_3)_2}$ (5). A suspension of $\mathrm{OsH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2}$ (120 mg, 0.22 mmol) in 5 mL of methanol was treated with $\mathrm{HSiPh_3}$ (172 mg, 0.66 mmol). After the mixture was stirred for 20 min at room temperature, a white solid precipitated. The mixture was decanted and the resulting white solid repeatedly washed with methanol and dried in vacuo: yield 140 mg (75%). Anal. Calcd for $\mathrm{C_{37}H_{60}OOsP_2Si}$: C, 55.47; H, 7.55. Found: C, 55.53; H, 8.03. IR (Nujol, cm^{-1}): ν(Os−H) 2000, ν(CO) 1890. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 8.03 (d, 6H, $J_{\mathrm{H-H}} = 6.6$ Hz, *o*-$\mathrm{C_6H_5}$); 7.02 (m, 6H, *m*-$\mathrm{C_6H_5}$); 7.27 (t, 3H, $J_{\mathrm{H-H}} = 7.1$ Hz; *p*-$\mathrm{C_6H_5}$); 1.88 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$); 1.01 (dvt, 36H, $N = 12.9$ Hz, $J_{\mathrm{P-H}} = 6.9$ Hz, $\mathrm{PCHC}H_3$); −9.76 (br, 3H, $\mathrm{Os}H_3$). ^{31}P{^{1}H} NMR (121.421 MHz, $\mathrm{C_6D_6}$): δ 24.6 (s).

^{1}H NMR (toluene-d_8, 193 K) in the hydride region: δ −9.92 (2H, AB part of a second order ABXY spin system); −9.39 (t, 1H, $J_{\mathrm{P-H}} = 20.5$ Hz).

Preparation of $\mathbf{OsH_3\{Si(OCH_3)_2Ph\}(CO)(P^iPr_3)_2}$ (6). A suspension of $\mathrm{OsH(\eta^2\text{-}H_2BH_2)(CO)(P^iPr_3)_2}$ (120 mg, 0.22 mmol) in 4 mL of methanol was treated with $\mathrm{H_3SiPh}$ (166 mg, 0.3 mmol) and the mixture stirred for 1 h at room temperature. The solution was stored at −78 °C for 24 h . A white solid was formed. The mixture was decanted and the resulting white solid was washed with methanol and dried in vacuo: yield 137 mg (65%). Anal. Calcd for $\mathrm{C_{27}H_{56}O_3OsP_2Si}$: C, 45.7; H, 7.96. Found: C, 45.86; H, 9.06. IR (Nujol, cm^{-1}): ν(Os−H) 2000, ν(CO) 1900, ν(Si−O) 1075 (s). ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 8.05 (d, 2H, $J_{\mathrm{H-H}} = 6.6$ Hz, *o*-$\mathrm{C_6H_5}$); 7.35 (dd, 2H, $J_{\mathrm{H-H}} = 6.6$ Hz, $J_{\mathrm{H-H'}} = 7.5$ Hz, *m*-$\mathrm{C_6H_5}$); 7.19 (t, 1H, $J_{\mathrm{H-H}} = 7.5$ Hz, *p*-$\mathrm{C_6H_5}$); 3.66 (s, 6H, $\mathrm{Si{-}OC}H_3$); 1.99 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$); 1.08 (dvt, 36H, $N = 13.1$ Hz, $J_{\mathrm{P-H}} = 7.1$ Hz, $\mathrm{PCHC}H_3$); −10.89 (t, 3H, $J_{\mathrm{P-H}} = 8.8$ Hz, $\mathrm{Os}H_3$). ^{31}P{^{1}H} NMR (121.421 MHz, $\mathrm{C_6D_6}$): δ 30.0 (s).

^{1}H NMR (toluene-d_8, 193 K) in the hydride region: δ −10.95 (2H, AB part of a second order ABXY spin system); −10.04 (t, 1H, $J_{\mathrm{P-H}} = 20.0$ Hz).

Preparation of $\mathbf{OsH_3(GeHPh_2)(CO)(P^iPr_3)_2}$ (7). A solution of $\mathrm{OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2}$ (ca. 200 mg, 0.35 mmol) in 5 mL of hexane was treated with $\mathrm{H_2GePh_2}$ (159.6 μL, 0.70 mmol). The mixture was stirred for 6 h at room temperature and concentrated in vacuo to dryness, leaving a yellow oil. ^{1}H NMR (300 MHz, $\mathrm{C_6D_6}$): δ 8.02 (dd, 4H, $J_{\mathrm{H-H}} = 6.6$ Hz, $J_{\mathrm{H-H'}} = 1.0$ Hz, *o*-$\mathrm{C_6H_5}$); 7.31 (t, 4H, $J_{\mathrm{H-H}} = 6.6$ Hz, $J_{\mathrm{H-H'}} = 7.2$ Hz, *m*-$\mathrm{C_6H_5}$); 7.18 (m, 2H, *p*-$\mathrm{C_6H_5}$); 5.89 (t, 1H, $J_{\mathrm{P-H}} = 11.5$ Hz, Ge−*H*); 2.19 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$); 1.04 (dvt, 36H, $N = 14.1$ Hz, $J_{\mathrm{P-H}} = 7.1$ Hz, $\mathrm{PCHC}H_3$); −9.72 (t, 3H, $J_{\mathrm{P-H}} = 14.9$ Hz, $\mathrm{Os}H_3$). ^{31}P{^{1}H} NMR (121.421 MHz, $\mathrm{C_6D_6}$): δ 38.9 (s).

^{1}H NMR (toluene-d_8, 193 K) in the hydride region: δ −9.72 (br, 3H).

Preparation of $\mathbf{OsH_3(GePh_3)(CO)(P^iPr_3)_2}$ (8). A solution of $\mathrm{OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2}$ (ca. 150 mg, 0.261 mmol) in 5 mL of hexane was treated with $\mathrm{HGePh_3}$ (159 mg, 0.522 mmol). The mixture was stirred for 6 h at room temperature, and a white solid was formed. The solvent was decanted and the solid washed with hexane and dried in vacuo: yield 137 mg (62%). Anal. Calcd for $\mathrm{C_{37}H_{60}GeOOsP_2}$: C, 52.55; H, 7.15. Found: C, 53.05; H, 7.40. IR (Nujol, cm^{-1}): ν(Os−H) 1966, ν(CO) 1867. ^{1}H NMR (300 MHz, $\mathrm{C_7D_8}$): δ 8.03 (d, 6H, $J_{\mathrm{H-H}} = 7.5$ Hz, *o*-$\mathrm{C_6H_5}$); 7.56 (m, 6H, *m*-$\mathrm{C_6H_5}$); 7.23 (t, 3H, $J_{\mathrm{H-H}} = 6.9$ Hz, *p*-$\mathrm{C_6H_5}$); 1.94 (m, 6H, $\mathrm{PC}H\mathrm{CH_3}$); 0.96 (dvt, 36H, $N = 12.3$ Hz, $J_{\mathrm{P-H}} = 7.2$ Hz, $\mathrm{PCHC}H_3$); −9.63 (t, 3H, $J_{\mathrm{P-H}} = 15$ Hz, $\mathrm{Os}H_3$). ^{31}P{^{1}H} NMR (121.421 MHz, $\mathrm{C_6D_6}$): δ 35.6 (s).

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(28) Because the chemical shift of the triplets is more dependent upon the nature of the $\mathrm{ER_3}$ groups than the chemical shift of the ABXY systems, we assign the triplets to the corresponding H(3) hydrido ligands.

(29) (a) Jackson, R. A. *J. Organomet. Chem.* **1979**, *166*, 17. (b) Woo, H. G.; Freeman, W. P.; Tilley, T. D. *Organometallics* **1992**, *11*, 2198.

(30) Werner, H.; Esteruelas, M. A.; Meyer, U.; Wrackmeyer, B. *Chem. Ber.* **1987**, *120*, 11.

Table 3. Crystal Data and Data Refinement for $OsH_3(CO)(SiHPh_2)(P^iPr_3)_2$ (**3**)

formula: $C_{31}H_{56}OP_2SiOs$
$a = 16.375(2)$ Å
$b = 11.670(1)$ Å
$c = 18.806(2)$ Å
$\beta = 107.67(1)°$
$Z = 4$
fw = 725.02
space group: $P2_1/c$ (No. 14)

temp = 20 °C
$\lambda = 0.710\ 73$ Å
ρ (calcd) = 1.406 g cm^{-1}
$\mu = 3.87$ mm^{-1}
$R^a = 0.0452$
$R_w{}^b = 0.0489$
$S^c = 1.603$

^{a} $R = \Sigma|[F_o - F_c]|/\Sigma F_o$. ^{b} $R_w = \Sigma(w^{1/2}|[F_o - F_c]|)/(\Sigma w^{1/2}F_o)$. ^{c} $S = \{\Sigma(w|[F_o - F_c]|^2)/(M - N)\}^{1/2}$, where M is the number of observed reflections and N is the number of data.

^{1}H NMR (toluene-d_8, 193 K) in the hydride region: δ −9.63 (br, 3H).

Preparation of $OsH_3(GeEt_3)(CO)(P^iPr_3)_2$ (9). A solution of $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$ (ca. 150 mg, 0.261 mmol) in 5 mL of hexane was treated with $HGeEt_3$ (126 μL, 0.783 mmol). The mixture was stirred for 1 h at room temperature and concentrated in vacuo to dryness. Addition of methanol to the resulting residue gave a solid. The mixture was decanted and the resulting orange solid washed with methanol and dried in vacuo: yield 109.8 mg (60%). Anal. Calcd for $C_{25}H_{60}GeOOsP_2$: C, 42.8; H, 8.62. Found: C, 42.93; H, 8.56 IR (Nujol, cm^{-1}): ν(Os−H) 1957, ν(CO) 1870. ^{1}H NMR (300 MHz, C_6D_6): δ 2.01 (m, 6H, $PCHCH_3$); 1.15 (dvt, 36H, N = 13.8 Hz, J_{P-H} = 6.9 Hz, $PCHCH_3$); 0.99 (t, 9H, J_{H-H} = 7.5 Hz, CH_3); 0.72 (q, 6H, J_{H-H} = 8 Hz, CH_2); −10.41 (br, 3H, OsH_3). $^{31}P\{^1H\}$ NMR (121.421 MHz, C_6D_6): δ 27.7 (s).

^{1}H NMR (toluene-d_8, 193 K) in the hydride region: δ −11.20 (t, 1H, J_{P-H} = 21 Hz); −9.90 (t, 1H, AB part of a second order ABXY spin system).

Preparation of $OsH_3(SnPh_3)(CO)(P^iPr_3)_2$ (10). A solution of $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$ (ca. 200 mg, 0.35 mmol) in 5 mL of hexane was treated with $HSnPh_3$ (244.1 mg, 0.70 mmol). The mixture was stirred for half an hour at room temperature and concentrated in vacuo to dryness. Addition of methanol to the resulting residue gave a solid. The mixture was decanted, and the resulting white solid was washed with methanol and dried in vacuo: yield 233.6 mg (75%). Anal. Calcd for $C_{37}H_{60}OOsP_2Sn$: C, 49.84 H, 6.78. Found: C, 50.07; H, 6.70. IR (Nujol, cm^{-1}): ν(Os−H) 2080, ν(CO) 1966, ν(Sn−C) 247. ^{1}H NMR (300 MHz, C_6D_6): δ 8.11 (d, 6H, J_{H-H} = 6.6 Hz, $J_{^{117}Sn-H}$ = 32.9 Hz, $J_{^{119}Sn-H}$ = 47 Hz, $o\text{-}C_6H_5$); 7.32 (dd, 6H, J_{H-H} = 6.6 Hz, $J_{H-H'}$ = 7.1 Hz, $m\text{-}C_6H_5$); 7.19 (t, 3H, J_{H-H} = 7.1 Hz, $p\text{-}C_6H_5$); 2.05 (m, 6H, $PCHCH_3$); 1.03 (dvt, 36H, N = 14.0 Hz, J_{P-H} = 6.9 Hz, $PCHCH_3$); −9.90 (t, 3H, J_{P-H} = 15.1 Hz, $J_{^{117/119}Sn-H}$ = 52.2 Hz, OsH_3). $^{31}P\{^1H\}$ NMR (121.421 MHz, C_6D_6): δ 39.3 ((s), $J_{^{117/119}Sn-P}$ = 69.5 Hz).

^{1}H NMR (toluene-d_8, 193 K) in the hydride region: δ −10.0 (br, 1H); −10.99 (br, 2H).

Preparation of $OsH_3(Sn^nBu_3)(CO)(P^iPr_3)_2$ (11). A solution of $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P^iPr_3)_2$ (ca. 200 mg, 0.35 mmol) in 5 mL of hexane was treated with HSn^nBu_3 (118 μL, 0.70 mmol). The mixture was stirred for 1 h at room temperature and concentrated in vacuo to dryness, leaving an orange oil. ^{1}H NMR (300 MHz, C_6D_6): δ 2.1−1.0 (the signals for P^iPr_3 and Sn^nBu_3 are buried under resonance for HSn^nBu_3 and hexane); −10.72 (t, 3H, J_{P-H} = 13.5 Hz, $J_{^{117/119}Sn-H}$ = 68.1 Hz, OsH_3). $^{31}P\{^1H\}$ NMR (121.421 MHz, C_6D_6): δ 34.0 (s, $J_{^{117/119}Sn-P}$ = 33.4 Hz).

X-ray Structure Analysis of $OsH_3(CO)(SiHPh_2)(PiPr_3)_2$ (3). Crystals suitable for a single-crystal X-ray analysis were obtained for a concentrated solution of **3** in methanol at −18 °C. A summary of crystal data, intensity collection procedures, and refinement data is reported in Table 3. The prismatic crystal studied was glued on a glass fiber and mounted on a Siemens-Stoe AED-2 diffractometer. Cell constants were obtained from the least-squares fit of the setting angles of 62 reflections in the range $20 \leq 2\theta \leq 40°$. The 7953 recorded reflections were corrected for Lorentz and polarization effects. Three orientation and intensity standards were monitored every 55 min of measuring time; no variation was observed. Reflections were also corrected for absorption by an empirical method.[31]

The structure was solved by Patterson (Os atom) and conventional Fourier techniques. Refinement was carried out by full-matrix least-squares methods with initial isotropic thermal parameters. Anisotropic thermal parameters were used in the last cycles of refinement for all non-hydrogen atoms. Hydride ligands were not located or refined appropriately. Hydrogen atoms were observed or calculated (C−H = 0.97 Å), and included in the refinement riding on carbon atoms with a common isotropic thermal parameter. Atomic scattering factors, corrected for anomalous dispersion for Os and P, were taken from ref 32. Final R and R_w values were 0.0452 and 0.0489. All calculations were performed by use of the SHELXTL-PLUS system of computer programs.[33]

Computational Details. All calculations were performed with the GAUSSIAN 92 program.[34] A molecular orbital ab initio method with introduction of correlation energy through the second level of the Møeller−Plesset (MP2) perturbational approach was applied.[35] Excitations concerning the lowest energy electrons were excluded in the MP2 calculations (frozen core approach). Effective core potentials (ECP) were used to represent the 60 innermost electrons (up to the 4d shell) of the osmium atom,[36] as well as the 10-electron core of the phosphorus and silicon atoms.[37] The basis set used for the osmium atom was that associated to the pseudopotential,[35] with the valence double-ζ (341/321/21) contraction included in the program (LANL2DZ basis set).[34] For the phosphorus and silicon atoms, a valence double-ζ basis set36 with a (21/21) contraction was used, supplemented with a polarization d shell for each atom.[38] The hydrogen atoms directly attached to the metal were described also with a valence double-ζ basis set supplemented with a polarization shell (6-31G**).[39] Finally, the remaining atoms, carbon, oxygen, and the hydrogen atoms attached to the phosphorus and silicon atoms, were described with the 6-31G basis set.[40]

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray study, bond distances and angles, and interatomic distances (12 pages). Ordering information is given on any current masthead page.

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