ORGANOMETALLICS

Synthesis and Reactivities of Polyhydrido Osmium Arylsilyl Complexes Prepared from OsH₃Cl(PPh₃)₃

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S Supporting Information

ABSTRACT: Reactions of silanes with transition-metal complexes are of interest because their relevance to Si-H bond activation, the structural properties of polyhydrides, and catalytic hydrosilylation reactions. This work presents the results derived from reactions of arylsilanes Ph_2SiH_2 and $PhSiH_3$ with $OsH_3Cl(PPh_3)_3$ (1). Reaction of 1 with 1 equiv or excess Ph_2SiH_2 affords $OsH_3(SiClPh_2)(PPh_3)_3$ (2) or $OsH_4(SiClPh_2)$ -(SiLIPL)(PPL) (2) expectively.



 $(SiHPh_2)(PPh_3)_2$ (3), respectively. These silyl complexes are formed via the oxidative addition of Si-H bonds and H/Cl exchange via silylene intermediates. Similarly, reaction of 1 with excess PhSiH₃ produced the analogous bis(silyl) complex OsH₄(SiClHPh)(SiH₂Ph)(PPh₃)₂ (4). The bis(silyl) complexes are dodecahedral tetrahydride complexes containing weak Si…H interactions. The complex 3 reacts with PPh₃ and CH₃CN to selectively eliminate Ph₂SiH₂. Computational studies show that the preference for reductive eliminations from 3 follows the order Ph₂SiH₂ > Ph₂SiHCl > Ph₂HSi-SiClPh₂.

INTRODUCTION

Reactions of silanes with transition-metal complexes are of interest because their relevance to Si–H bond activation,^{1a–c} the structural properties of polyhydrides,^{1d,e} and catalytic hydrosilylation reactions.^{1a–d} In the area of osmium chemistry, reactions of silanes have been reported with Os(0) mono-nuclear² and cluster complexes,³ Os(II) halo,^{4,5} hydride, and alkyl/aryl complexes,^{6–9} Os(IV) hydride^{10,11} and halohydride¹² complexes, and OsO₄.¹³

The reactions of silanes with osmium complexes can give varied products depending on the structures of silanes as well as the ligands of osmium complexes. The most common products of the reactions are hydridosilyl complexes $L_nOSH_x(SiR_3)$ (e.g., $OsCl(SiEt_3)(H_2)(CO)(PiPr_3)_2$, ^{8b,c} $Cp*OsHBr(SiR_3)-(PiPr_3)_2$, ^{5,6a,11} and $OsH_3(SiR_3)(CO)(PR'_3)_2$, ^{7a,8a,9a}) formed by oxidative addition of R_3Si-H to unsaturated osmium centers and/or silyl complexes $L_nOs-SiR_3$ (e.g., $OsCl(SiR_3)(CO)-(PPh_3)_2$, ^{7c,8a,c,9e-k} $OsH_3(SiR_3)(PPh_3)_3$, ¹⁰ and $Cp*(Me_3P)_2Os-(SiCliPr_2)^{6b}$) formed as a result of metathesis reactions between R_3Si-H and L_nOs-X (X = halide, H, alkyl). Other interesting products include the osmium silylene complexes $L_nOsH(=SiR_2)$ (e.g., $Cp*OsH(=SiHR)(PiPr_3)_6^{6a}$ $OsH_3(=SiPhCl)\{2,6-(CH_2PtBu_2)_2C_6H_3\}$, ¹² and $OsH_2(=SiR_2)(CO)\{PMe-(tBu)_2\}_2^{7a}$) formed by α -H elimination of silyl intermediates $L_nOs(SiHR_2)$ and/or bis(silyl) complexes $L_nOs(SiHR_2)_2$ (e.g., $Os(SiR_3)_2(CO)_4^{3a}$ and $Cp*(Me_3P)OsH(SiMe_2Cl)_2^{6d}$) formed by further reactions of silanes with initially generated mono(silyl) intermediates.

In this work, we report the isolation and characterization of bis(silyl) complexes $OsH_4(SiClR_2)(SiHR_2)(PPh_3)_2$ and mono-

(silyl) complexes $OsH_3(SiClR_2)(PPh_3)_3$ obtained from the reactions of $OsH_3Cl(PPh_3)_3$ with R_2SiH_2 . The reductive elimination reactions of the bis(silyl) complex $OsH_4(SiClPh_2)$ -(SiHPh₂)(PPh₃)₂ are also described.

The results are interesting for the following reasons. (1) The complexes $OsH_4(SiClR_2)(SiHR_2)(PPh_3)_2$ represent a new type of organometallic complexes formed from the reactions of silanes with osmium complexes. The complexes are structurally related to the $bis(\eta^2$ -silane) complexes $RuH_2(\eta^2$ -H-SiR_3)_2(PR'_3)_2, which were known as early as 1997.¹⁴ (2) The SiClR_2 group in the complexes $OsH_3(SiClR_2)(PPh_3)_3$ and $OsH_4(SiClR_2)(SiHR_2)(PPh_3)_2$ is apparently formed via H/Cl exchange of the Si-H/Os-Cl bonds, which has rarely been observed previously in the reactions of silanes with osmium complexes. (3) The reductive elimination reactions of the bis(silyl) complex $OsH_4(SiClPh_2)(SiHPh_2)(PPh_3)_2$ provide an opportunity to compare the relative ease of reductive elimination of H₂, Ph₂ClSiH, Ph₂SiH₂, or Ph₂ClSi-SiHPh₂.

RESULTS AND DISCUSSION

Reactions of OsH₃Cl(PPh₃)₃ with Silanes. This work stems from our interest in comparing the structural properties of OsH₃(SiR₃)(PR'₃)₃ and OsClH₂(SiR₃)(PR'₃)₃. Chloride and hydride are known to have different effects on the structures of polyhydridosilyl complexes. For example, the complex OsH₃(SiHPh₂)(CO)(PiPr₃)₂, which was obtained from the reaction of OsH₂(CH₂=CHEt)(CO)(PiPr₃)₂ with Ph₂SiH₂, is

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a classical trihydride complex,^{8a} while OsCl(SiEt₃)(H₂)(CO)-(P*i*Pr₃)₂, which was obtained from the reaction of OsHCl-(CO)(P*i*Pr₃)₂ with Et₃SiH, is a nonclassical dihydrogen complex.^{8b,c}

The hydridosilyl complexes $OsH_3(SiR_3)(PPh_3)_3$ (R = pyrrolyl, Et, Ph) are known to display interesting weak Si…H interactions.¹⁰ It is therefore of interest to prepare complexes of the formula $OsClH_2(SiR_3)(PPh_3)_3$ in order to further examine the chloride effect on the structure of polyhydridosilyl osmium complexes. The complexes $OsH_3(SiR_3)(PPh_3)_3$ can be prepared from the reactions of $OsH_4(PPh_3)_3$ with R_3SiH .¹⁰ One might anticipate that the complexes $OsClH_2(SiR_3)(PPh_3)_3$ could be similarly prepared from the reactions of $OsH_3(PPh_3)_3$ (1) with R_3SiH .

We first investigated the reaction of $OsH_3Cl(PPh_3)_3$ (1) with Ph_2SiH_2 . To our surprise, the reaction did not produce the expected complex $OsClH_2(SiHPh_2)(PPh_3)_3$ but instead gave the mono(silyl) complex $OsH_3(SiClPh_2)(PPh_3)_3$ (2) and bis(silyl) complex $OsH_4(SiClPh_2)(SiHPh_2)(PPh_3)_2$ (3) with a $SiClPh_2$ group derived from H/Cl exchange of the Si-H/Os-Cl bonds (Scheme 1).

Scheme 1. Reactions of OsH₃Cl(PPh₃)₃ with Silanes



The in situ ${}^{31}P\{{}^{1}H\}$ NMR spectrum indicated that, after a mixture of 1 and 10 equiv of Ph_2SiH_2 in toluene was stirred at room temperature for 2 h, the starting hydride complex was consumed completely and the reaction produced a new species with a singlet ${}^{31}P\{{}^{1}H\}$ signal at 9.5 ppm along with free PPh₃. When only 1 equiv of Ph_2SiH_2 was used, the in situ ${}^{31}P\{{}^{1}H\}$ NMR spectrum indicated that the starting hydride complex partially reacted with Ph_2SiH_2 to give two products with singlet ${}^{31}P\{{}^{1}H\}$ signals at 9.5 and 4.9 ppm, respectively.

We have tried to isolate the reaction products. From the reaction with 3 equiv of Ph_2SiH_2 , the species with the singlet ${}^{31}P{}^{1}H{}$ signal at 9.5 ppm was isolated as a white solid, which was subsequently identified to be the bis(silyl) complex $OsH_4(SiClPh_2)(SiHPh_2)(PPh_3)_2$ (3) (Scheme 1). From the reaction with 1 equiv of Ph_2SiH_2 , a species with a singlet ${}^{31}P{}^{1}H{}$ signal at 4.9 ppm was isolated also as a white solid, which was subsequently identified to be the monosilyl complex $OsH_3(SiClPh_2)(PPh_3)_3$ (2). When $OsH_3Cl(PPh_3)_3$ (1) was replaced by $OsHCl(PPh_3)_3$ (5), the reaction also gave complexes 2 and 3. Further experiments showed that the bis(silyl) complex 3 could also be produced from the reaction of Ph_2SiH_2 with isolated monosilyl complex 2.

Similar reactions occurred between $OsH_3Cl(PPh_3)_3$ and the primary silane PhSiH₃. The bis(silyl) complex

 $OsH_4(SiClHPh)(SiH_2Ph)(PPh_3)_2$ (4) was obtained from the reaction of $OsH_3Cl(PPh_3)_3$ with excess $PhSiH_3$. As monitored by in situ ³¹P{¹H} NMR, the reaction of 1 equiv of $PhSiH_3$ with $OsH_3Cl(PPh_3)_3$ produced the bis(silyl) complex 4 as the major product. The reaction also produced a minor species with a singlet ³¹P{¹H} signal at 5.2 ppm, which could be the trihydride complex $OsH_3(SiClHPh)(PPh_3)_3$ considering that the ³¹P chemical shift is similar to that (4.9 ppm) of $OsH_3(SiClPh_2)$ -(PPh_3)₃. Unfortunately, we have failed to obtain a pure sample of the minor product by either recrystallization or chromatography. Under the same conditions, Ph_3SiH and tBu_2SiH_2 were unreactive.

Characterization of Bis(silyl) Complexes. The presence of four hydride ligands in 3 is indicated by the ¹H NMR spectrum, which shows two broad hydride signals of equal intensity at -6.0 and -9.7 ppm at room temperature (Figure 1). The ¹H NMR spectra of 3 are temperature dependent.



Figure 1. Hydride region of the $^1\mathrm{H}$ NMR spectra of 3 in $\mathrm{C}_6\mathrm{D}_5\mathrm{CD}_3$ at 295–242 K.

Coalescence of the two hydride signals to give a single signal at -7.9 ppm is obtained when the temperature is above 326 K. When the temperature is below 262 K, the hydride signals become sharp. At 252 K, two hydride signals appear at -5.9 and -9.6 ppm as sharp multiplets. At 248 K and 400 MHz, the peaks at -5.9 and -9.6 ppm have rather long T_1 values of 359 and 366 ms, respectively, indicating that the complex does not have an η^2 -H₂ ligand. The ${}^{31}P{}^{1}H{}$ NMR spectrum of the bis(silyl) complex 3 displays a singlet signal at ca. 9.5 ppm in the temperature range of 323–243 K.

The presence of SiHPh₂ and SiClPh₂ groups in 3 is indicated by the ²⁹Si{¹H} NMR spectrum, which displays two triplets at 19.7 (²J_{PSi} = 12.2 Hz) and -16.8 ppm (²J_{PSi} = 6.6 Hz). The ²⁹Si DEPT135 NMR experiment indicates that the signal at 19.7 ppm is due to SiClPh₂ while the other at -16.8 ppm is due to SiHPh₂. In the ²⁹Si NMR spectrum (see Figure S9 in the Supporting Information), the signal of SiHPh₂ appears as a broad doublet ($w_{1/2}$ = 36 Hz) with a ¹J_{HSi} coupling of 204.6 Hz and the signal of SiClPh₂ appears as a broad singlet ($w_{1/2}$ = 40 Hz) with no observable J_{HSi} coupling. As additional Si–H coupling was not resolved, we conclude that the coupling between silicon and the hydrides, if present, should be less than 40 Hz (considering the half-width of the broad peaks). The structure of the bis(silyl) complex **3** has been confirmed by X-ray diffraction. As shown in Figure 2, the complex



Figure 2. ORTEP drawing of $OsH_4(SiClPh_2)(SiHPh_2)(PPh_3)_2$ (3) with thermal ellipsoids at the 50% probability level. The phenyl groups of the phosphines are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os(1)-Si(1) 2.408(3), Os(1)-Si(2) 2.425(15); Si(2)-Cl(2) 2.068(3), Os(1)-P(1) 2.403(2), Os(1)-P(2) 2.414(2); P(1)-Os(1)-P(2) 99.31(8), P(1)-Os(1)-Si(1) 128.99(8), P(1)-Os(1)-Si(2) 106.4(4), P(2)-Os(1)-Si(2) 126.1(6), Si(1)-Os(1)-P(2) 107.25(8), Si(1)-Os(1)-Si(2) 92.0(6).

contains SiHPh₂ and SiClPh₂ groups which are cis to each other with a Si-Os-Si angle of 92.0(6)°. The two phosphine ligands are also cis to each other with a P-Os-P angle of 99.31(8)°. Unfortunately, the positions of the hydride ligands could not be accurately located by the X-ray diffraction study.

Complexes 6 and 7 (see Figure 3 for their structures) are reported examples of complexes having a set of ligands similar



Figure 3. Selected bond angles (deg) of complexes 3, 6, and 7.

to that of **3**. Complex **6** is a bis(η^2 -silane) complex with the silane ligands cis to the phosphine ligands.^{14c} Complex 7 is a bis(stannyl) tetrahydride complex with a dodecahedral structure.¹⁵ As indicated by the structural parameters shown in Figure 3, the P–Os–P, Si–Os–Si, and P–Os–Si angles of **3** are different from those of **6** and 7. When only the P–M–Si angles are considered, the geometry of **3** is closer to that of the dodecahedral tetrahydride complex 7. Considering the structural and NMR data, we propose that the complex **3** has a structure closer to that of 7.

We noted that square-planar complexes of the type $Pt(SiR'_3)_2(PR_3)_2$ with two cis-disposed SiR_3 groups and two cis PR_3 ligands are known.¹⁶ In such complexes, the Si-Pt-Si angles are appreciably smaller. For example, the complex $Pt(SiHPh_2)_2(PPh_3)_2$ has a Si-Pt-Si angle of $80.37(7)^{\circ}$.^{16a}

Support for the proposed structure of 3 comes from our DFT calculations. Figure 4 shows the B3LPY optimized



Figure 4. B3LYP optimized structure of complex 3 that reproduces the X-ray data. Selected bond lengths (Å) and angles (deg): Os-H1 1.674, Os-H2 1.625, Os-H3 1.673, Os-H4 1.632, H1-H2 2.068, H2-H3 2.824, H1-H4 2.706, H3-H4 2.118, H2-H4 2.672, Os-P2 2.530, Os-P1 2.518, Os-Si1 2.488, Os-Si2 2.462, Si1-H1 2.231, Si1-H2 2.453, Si1-H4 2.152, Si2-H2 2.309, Si2-H3 2.165, Si2-H4 2.549; P1-Os-P2 98.28, Si1-Os-Si2 92.87, Si1-Os-P2 106.14, Si1-Os-P1 132.02, Si2-Os-P2 130.32, Si2-Os-P1 101.93, H1-Os-H2 77.61, H1-Os-H3 158.72, H1-Os-H4 109.86, H1-Os-P2 87.39, H1-Os-P1 79.81, H1-Os-Si1 61.18, H1-Os-Si2 140.57, H2-Os-H3 117.79, H2-Os-H4 110.29, H2-Os-P2 164.62, H2-Os-P1 75.91, H2-Os-Si1 69.64, H2-Os-Si2 65.06.

structure of complex 3 that reproduces the X-ray data. Consistent with the solution NMR data, the optimized structure contains two types of hydrides: two of the hydrides are essentially trans to phosphorus atoms (P2–Os–H2, 164.62°; P1–Os–H4, 169.20°), and the other two are approximately trans to each other (H1–Os–H3, 158.72°). The Os–H bonds for the mutually trans hydrides are of similar bond distances and are longer than the Os–H bonds (which are also of similar bond distances) trans to the phosphine ligands. In agreement with a classical hydride structure, the separations between the hydride signals at –5.9 and –9.6 ppm displayed by the low-temperature ¹H NMR spectrum of 3 can be assigned to the hydrides trans and cis to the phosphine ligands, respectively.

A close look at the optimized structure of 3 reveals that there are Si…H contacts which are shorter than the sum (3.3 Å) of the van der Waals radii of H (1.2 Å) and silicon (2.1 Å),¹⁷ indicating the presence of weak secondary Si…H interactions. The Si(1) is in close contact with H(1) and H(4) (Si(1)–H(1), 2.231 Å; Si(1)–H(4), 2.152 Å), while Si(2) is in close contact with H(2) and H(3) (Si(2)–H(2), 2.309 Å; Si(2)–H(3), 2.165 Å) (Figure 4).

The structure of the bis(silyl) complex 4 can be assigned on the basis of its NMR data. The ¹H NMR spectroscopic data of 4 are similar to those of 3 (see the Experimental Section for details). Due to the presence of the chiral Si center in the SiHClPh group, the two phosphorus atoms are magnetically inequivalent. Thus, the ³¹P{¹H} NMR spectrum shows an AB pattern centered at 13.50 ppm with $\Delta \delta_{AB} = 0.13$ ppm and $J_{AB} = 16.2$ Hz.

One of the most interesting aspects of the reactions of $OsH_3(PPh_3)_3$ with Ph_2SiH_2 and $PhSiH_3$ is the Os-Cl/Si-H exchange to give chlorine-substituted silyl complexes. Similar H/X exchange reactions have been observed occasionally for reactions involving $IrX^{18,19}$ and $RuCl^{12,20}$ complexes. In the case of osmium chemistry, the only reported examples are the reactions of PhSiH_3 with $[OsH_2Cl\{CH(C_2H_4PR_2)_2\}]$ (8) and $[OsH_2Cl\{2,6-(CH_2PR_2)_2C_6H_3\}]$ (10, R = t-Bu), which produced $[OsH_5(SiClPh_2)(SiH_2PR_2(CH_2)_5PR_2)]$ (9) and $[OsH_3(=SiPhCl)\{2,6-(CH_2PR_2)_2C_6H_3\}]$ (11, R = t-Bu), respectively (Scheme 2).¹²

Scheme 2. Reactions of Pincer Osmium Hydride Complexes with PhSiH₃



Mechanistic Considerations. Scheme 3 shows plausible pathways for the formation of the monosilyl complex 2 and the

Scheme 3. Proposed Mechanisms for the Formation of 2 and 3



bis(silyl) complex 3. Since complexes 2 and 3 can also be formed from reactions of $OsHCl(PPh_3)_3$ (5) with Ph_2SiH_2 , we assume that the first step of the reaction is the dissociation of one molecule of H_2 from the trihydride complex 1 to give the monohydride $OsHCl(PPh_3)_3$ (5). Si-H oxidative addition of

 Ph_2SiH_2 to 5 would produce the hydridosilyl intermediate 12, which eventually evolves to complexes 2 and 3.

There are two possible routes for the conversion of complex 12 to complex 2: one involves a silylene intermediate (path A), and the other involves reversible reductive elimination and oxidative addition of Ph_2SiCIH (path B).

In path A, the complex 12 first dissociates a PPh₃ ligand to give the 16e species 13, which can then undergo α -H elimination to give the silvlene complex 14. Migratory insertion of the silvlene group into the osmium-chloride bond of 14 can give the unsaturated intermediate 15, which could then react with PPh_3 to give the complex 2. We noted that silvlene intermediates have been suggested previously for the reaction of Ir-X complexes with silanes Ph₂SiH₂ to give Ir-SiXPh₂ complexes. Examples include the reaction of Cp*(PMe₃)Ir- $(CH_3)(OTf)$ with Ph_2SiH_2 to produce $Cp^*(PMe_3)IrH_2$ ${SiPh_2(OTf)}^{18a}$ the reactions of Ph_2SiH_2 with the triflato complexes $Ir(OTf)(TFB)(PR_3)$ (R = *i*-Pr, Cy; OTf = triflate; TFB = tetrafluorobenzobarrelene) to give $(R_3P)(TFB)(H)_2$ Ir- ${Si(OTf)Ph_2}^{18a}$ the reaction of $Ir(OCOCH_3)(TFB)L$ (L = py, PPh₃, PCy₃, PiPr₃) with Ph₂SiH₂ to give IrH₂{Si- $(OCOCH_3)Ph_2$ (TFB) (PR_3) ,^{18b} and the reaction of $Ir(\eta^1$ - $OCOCH_3)(CO)_2(PCy_3)$ with Ph_2SiH_2 to give $IrH_2{Si (OCOCH_3)Ph_2\}(CO)_2(PCy_3).^{18c}$

In path B, the complex 12 first isomerizes via intermediate 13 to 16, which then undergoes reductive elimination involving the chloride and the SiHPh₂ ligands to give Ph₂SiClH and the five-coordinate intermediate $OsH_2(PPh_3)_3$ (17). The complex 2 could then be formed by oxidative addition of the Si-H bond of Ph₂SiClH to 17. A similar reaction sequence has been suggested for the reaction of Cp*RuCl(PiPr₃) with mesitylsilane (MesSiH₃) to give Cp*RuH₂(SiHClMes)(PiPr₃).¹⁹

The complex 3 could be formed by the oxidative addition reaction of Ph_2SiH_2 with the intermediate $OsH_3(SiClPh_2)$ - $(PPh_3)_2$ (15). We have shown experimentally that the complex 3 could also be formed from the reaction of the complex 2 with excess Ph_2SiH_2 , presumably also via the intermediate 15 generated by dissociation of a PPh_3 ligand from the complex 2.

To confirm whether the proposed mechanism shown in Scheme 3 is reasonable or not and to determine which pathway is more likely involved in the formation of 2, we have calculated the energy profiles for the two reaction pathways starting from the reaction of OsHCl(PPh₃)₃ (5) with Ph₂SiH₂.

As shown in Figure 5, the oxidative addition of OsHCl-(PPh₃)₃ (5) with Ph₂SiH₂ to give OsH₂Cl(SiHPh₂)(PPh₃)₃ (12) is almost thermodynamically neutral (or slightly favored by 0.2 kcal/mol) with a barrier of 18.5 kcal/mol. The complex 12 can evolve to complex 2 exothermically (by 15.0 kcal/mol) with reasonably low reaction barriers, in agreement with experimental observation that the complex 2 rather than the complex 12 was isolated from the reaction.

The path for converting 12 to 2 involving a silylene intermediate (path A) has an overall barrier of 22.1 kcal/mol. In this pathway, the complex 12 dissociates a PPh₃ ligand to give the complex 13 in a slightly endothermic process (by 4.4 kcal/mol) with a barrier of 12.7 kcal/mol. The complex 13 then isomerizes to the complex 13A also in a slightly endothermic process (by 2.0 kcal/mol) with a small barrier of 6.5 kcal/mol. α -H elimination in 13A to give the silylene complex 14 occurs slightly endothermically (by 4.1 kcal/mol) with a small barrier of 6.2 kcal/mol. The silylene complex 14 undergoes a migration insertion reaction to give the silyl complex 15A in an exothermic process (by 4.1 kcal/mol) with a barrier of 11.5



Figure 5. Reaction profile for the reaction of $OsH_3Cl(PPh_3)_3$ (1) with Ph_2SiH_2 . The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

kcal/mol. This step is the rate-determining step. Subsequent reaction of the silyl complex 15A with PPh₃ can proceed in an exothermic process (by 21.4 kcal/mol) via intermediate 15 with a very low barrier of ca. 5 kcal/mol.

The path for converting 12 to 2 involving reversible reductive elimination and oxidative addition of Ph_2SiHCl (path B) has an overall barrier of 26.6 kcal/mol. In this pathway, the complex 12, which contains three meridionally bound PPh₃ ligands, first isomerizes to the isomeric complex 16 containing three facially bound PPh₃ ligands via intermediate 13. Reductive elimination of Ph₂SiHCl from 16 to give the complex 16B containing a bound Ph₂SiHCl (through the chloride atom) proceeds in an endothermic process (by 15.2 kcal/mol) with a barrier of 22.7 kcal/mol. This step is the rate-determining step. Dissociation of Ph₂SiHCl from 16B occurs exothermically (by 5.0 kcal/mol) with a barrier of 3.5 kcal/mol to give the dihydride complex 17, which then reacts with PPh₃ to give complex 2 in an exothermic process (by 29.1 kcal/mol) with a very low barrier of 5.1 kcal/mol.

We have also considered conversion of 16 to 2 by a concerted process involving Cl^- side-attacking the Si center and H-shifting to the metal center simultaneously. However, we were unable to locate such a transition state, implying that the concerted process is unlikely.

The calculated reaction barriers for the two pathways suggest that conversion of **12** to **2** most likely proceeds through the path involving a silylene intermediate (path A) rather than the path involving reversible reductive elimination and oxidative addition of Ph₂SiClH (path B). It is noted that silylene intermediates have been suggested previously for the reactions of M–X complexes with R₂SiH₂ to give M–SiXR₂ complexes,^{17,18} but the process has not been studied computationally.

Comments on the Energies and Structures of 2, 12, and 16. Complexes 2, 12, and 16 are structural isomers with the same coordination number. Interestingly, they have different stabilities and the complex 2 is thermodynamically

more stable than complexes **12** and **16** by 15.0 and 18.9 kcal/ mol, respectively.

The complex 2 is more stable than complexes 12 and 16 probably because a Si–Cl bond is stronger than a Si–H bond. For example, the Si–H bond energy in Me₃SiH is 90.3 kcal/ mol, while the Si–Cl bond energy in Me₃SiCl is 113 kcal/ mol.²¹ In addition, the Os–Si bonds in complexes 12 and 16 are weaker than that in complex 2, as reflected by the Os–Si distances in complexes 12 (2.470 Å), 16 (2.480 Å), and 2 (2.380 Å) shown in Figure 6. The complex 12 is more stable than complex 16 probably because the steric interaction of the three facially bound PPh₃ ligands in 16 is larger than that of the three meridionally bound PPh₃ ligands in 12.



Figure 6. Optimized structures and selected structural parameters (Å) of complexes 2, 12, and 16.

At this point, it might be worthwhile to comment on the structures of the trihydrido complex 2 and the chloro dihydrido complexes 12 and 16 in a bit more detail. As shown in Figure 6, the trihydrido complex and the chloro dihydrideo complexes adopt different coordination geometries around osmium. The trihydrido complex 2 can be best viewed as a distorted capped octahedron with the SiClPh₂ group capping one of the triangular faces. The chloro dihydrido complexes 12 and 16, despite their different ligand arrangements, can both be viewed as a distorted pentagonal bipyramid with the SiClPh₂ group lying approximately on the pentagonal plane. Like OsH₃(SiR₃)- $(PPh_3)_3$ (R = pyrrolyl, Et, Ph),¹⁰ there are weak Si…H interactions in trihydrido complex 2 and the chlorodihydrido complexes 12 and 16. It is also noted that the Si atom in complex 12 is in close contact with the chloride ligand with a Si…Cl distance of 3.022 Å, which is less than the sum (3.85 Å) of the van der Waals radii of Si (2.10 Å) and Cl (1.75 Å).¹⁶ The calculated structural parameters of complexes 16 and 2 indicate that the presence of the chloride ligand on osmium does not change the Si---H interaction remarkably.

It has been reported that the complex $OsH_3(SiHPh_2)(CO)$ - $(PiPr_3)_2$ is a classical trihydride complex.^{8a} while the complex $OsCl(H_2)(SiEt_3)(CO)(PiPr_3)_2$ is a dihydrogen complex.^{8b,c} Thus, replacement of a hydride ligand in $OsH_3(SiHPh_2)(CO)$ - $(PR_3)_2$ with a chloride enhances the H···H interaction. In our system, replacement of a hydride ligand in $OsH_3(SiR_3)(PPh_3)_2$ with a chloride does not lead to enhanced H···H or Si···H interaction.

Reactions of $OsH_4(SiClPh_2)(SiHPh_2)(PPh_3)_2$ (3) with PPh₃ and CH₃CN. Complex 3 contains four terminal hydride ligands and two different silyl ligands. Its reductive elimination is interesting, as it provides an opportunity to compare the relative ease of reductive eliminations of H₂, Ph₂ClSiH, Ph₂SiH₂, and Ph₂ClSi-SiHPh₂. We have therefore studied the reactions of 3 with CH₃CN and PPh₃. The complex 3 was found to react with PPh₃ and CH₃CN to give the trihydride complexes OsH₃(SiClPh₂)(PPh₃)₃ (2) and OsH₃(SiClPh₂)-(PPh₃)₂(NCMe) (18), respectively, via elimination of Ph₂SiH₂ (Scheme 4).

Scheme 4. Reactions of $OsH_4(SiClPh_2)(SiHPh_2)(PPh_3)_2$ (3) with PPh₃ and CH₃CN



Complex 2 has been characterized by NMR spectroscopy and elemental analysis. The $^{31}P\{^1H\}$ NMR spectrum in CD₂Cl₂ showed a singlet at 4.9 ppm. The 1H NMR spectrum showed characteristic hydride signal at -10.4 ppm. The IR spectrum showed $\nu(Os-H)$ at 2064 and 2012 cm $^{-1}$. The chemical shift and the IR frequencies of Os-H of 2 are similar to those reported for OsH₃(SiPh₃)(PPh₃)₃.¹⁰

The structure of **18** has been confirmed by X-ray diffraction. As shown in Figure 7, the non-hydrogen donor atoms are arranged in an approximately tetrahedral manner around osmium. The Si–Os–N and P–Os–P angles are $110.78(4)^{\circ}$ and $101.324(15)^{\circ}$, respectively. The two Si–Os–P angles are 124.572(16) and $123.868(16)^{\circ}$. The structural parameters are similar to those observed for OsH₃(SiMe₃)(CO)(PPh₃)₂.^{9f} It is



Figure 7. ORTEP drawing of $OsH_3(SiClPh_2)(NCMe)(PPh_3)_2$ (18) with thermal ellipsoids at the 50% probability level. The phenyl groups of the phosphines are omitted for clarity. Selected bond lengths (Å) and angles (deg): Os1–P1 2.3773(4), Os1–P2 2.3459(4), Os1–Si1 2.3254(5), Os1–N1 2.0885(16), Os1–H1 1.5917(239), Os1–H2 1.6077(255), Os1–H3 1.6003(313); P2–Os1–P1 101.324(15), Si1–Os1–P1 124.572(16), Si1–Os1–P2 123.868(16), N1–Os1–P1 92.19(4), N1–Os1–P2 96.28(4).

noted that the P–Os–P angle 101.324(15)° is much smaller than that (146.06(7)°) in OsH₃(SiHPh₂)(CO)(P*i*Pr₃)₂.^{8a} The three hydride ligands are approximately trans to CH₃CN and the PPh₃ ligands, as reflected by the H–Os–P or H–Os–N angles (H(3)–Os–N(1), 177.59(1.90)°; H(2)–Os–P(2), 179.46(0.90)°; H(1)–Os–P(1), 175.73(0.88)°). Thus, the complex can be viewed as either a distorted tetrahedron with three face-capped hydrides or a distorted octahedron with a face-capped SiClPh₂ group.

The Os–Si bond length in complex **18** is 2.3254(5) Å, which is appreciably shorter than those in OsH₃(SiHPh₂)(CO)-(P*i*Pr₃)₂ (2.448(2) Å)^{8a} and OsH₃(SiMe₃)(CO)(PPh₃)₂ (2.4533(8) Å).^{9f}

The solid-state structure is supported by the solution NMR spectroscopic data. The ³¹P{¹H} NMR spectrum in CD₂Cl₂ showed a singlet at 17.6 ppm in the temperature range of 295–193 K. The IR spectrum showed ν (Os–H) signals at 2070 and 1991 cm⁻¹. Like OsH₃(SiR₃)(CO)(PR'₃)₂, the ¹H NMR spectra of OsH₃(SiClPh₂)(PPh₃)₂(NCMe) (**18**) are temperature dependent (Figure S22 in the Supporting Information). At room temperature, the ¹H NMR spectrum in CD₂Cl₂ shows a broad hydride signal at –11.0 ppm. As expected, the hydride signal is split into two signals in a 2:1 intensity ratio when the temperature was lowered below 233 K. At 193 K, the two hydride signals appeared at –9.1 (dd, ²J_{PH} = 47.6, 22.0 Hz) and –15.1 ppm (t, ²J_{PH} = 19.6 Hz). As in the case of OsH₃(SiR₃)(CO)(PR'₃), the H–H coupling was not resolved for **18**.

Complexes $OsH_3(SiR_3)(PR'_3)_3^{10}$ and $OsH_3(SiR_3)(CO)-(PR'_3)_2^{8a}$ are classical hydride complexes with weak Si…H interaction. Our computational work confirms that such weak Si…H interaction is also present in complexes 2 and 18 (see Figures S23 and S34 in the Supporting Information).

In the reaction of **3** with PPh₃ and CH₃CN, complexes **2** and **18** are apparently formed by elimination of Ph₂SiH₂. In principle, elimination of H₂, Ph₂SiClH, and Ph₂ClSi-SiHPh₂ are also possible. However, we have no evidence for such processes. To understand the selectivity of the reductive elimination reactions, we have calculated the reaction energy changes for the reactions of **3** with CH₃CN. Our computational studies

suggest that the elimination reaction is thermodynamically controlled, as illustrated in Figure 8.²² Consistent with our



Figure 8. Free energy changes for the reactions of **3** with CH_3CN . The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

experimental observation, only the elimination of Ph_2SiH_2 from 3 to give 18 is thermodynamically favored (by 0.9 kcal/mol). Interestingly, the elimination of Ph_2SiHCl to give 19 is significantly thermodynamically unfavorable (by 14.3 kcal/mol). The reaction involving elimination of H_2 to give bis(silyl) complex 20 is thermodynamically slightly unfavored by 1.5 kcal/mol. The reaction involving elimination of $Ph_2ClSiSiHPh_2$ to give the dihydrogen complex 21 is thermodynamically most unfavorable by 17.9 kcal/mol.

A plausible explanation for the selectivity of the elimination reactions is as follows. Formation of **21** is least favorable because the eliminated species ($Ph_2ClSiSiHPh_2$) has a weak Si–Si bond. Formation of **20** is slightly thermodynamically unfavorable probably because complex **20** is sterically very crowded, which weakens the Os–ligand bond. In agreement with this argument, the Os–Si(Cl) (2.590 Å) bond in the optimized structure of **20** is appreciably longer than the corresponding distance (2.370 Å) of **18**. Elimination of Ph_2SiH_2 from **3** to give **18** is preferred over elimination of Ph_2SiHCl from **3** to give **19**, probably because the Os–SiClPh₂ bond is stronger than Os–SiHPh₂. Indeed, in the calculated structure of **3**, the Os–SiClPh₂ (2.462 Å) bond is shorter than the Os–SiHPh₂ bond (2.488 Å) (Figure 4).

CONCLUSION

In summary, we have found that complex $OsH_3Cl(PPh_3)_3$ can react with R_2SiH_2 to give the mono(silyl) complexes $OsH_3(SiClR_2)(PPh_3)_3$ and bis(silyl) complexes $OsH_4(SiClR_2)$ - $(SiHR_2)(PPh_3)_2$. Computational studies reveal that the $SiClR_2$ group was generated through an H/Cl exchange process involving Si-H/Os-Cl bonds via a silylene intermediate. Unlike the $bis(\eta^2$ -silane) ruthenium complexes $RuH_2(\eta^2$ -H- $SiR_3)_2(PR'_3)_2$, the osmium complexes $OsH_4(SiClR_2)(SiHR_2)$ - $(PPh_3)_2$ can be best described as dodecahedral tetrahydride complexes with weak Si···H interactions, suggesting that metals can significantly affect the structures of polyhydridosilyl complexes. The bis(silyl) complex $OsH_4(SiClPh_2)(SiHPh_2)$ - $(PPh_3)_2$ reacts with L (L = PPh_3, CH_3CN) to give $OsH_3(SiClPh_2)(L)(PPh_3)_{2^j}$ as a result of selective elimination of Ph_2SiH_2 . Computational studies show that preference for the possible reductive eliminations from $OsH_4(SiClPh_2)(SiHPh_2)$ - $(PPh_3)_2$ follows the order $Ph_2SiH_2 > H_2 > Ph_2SiHCl > Ph_2HSi SiClPh_2$.

EXPERIMENTAL SECTION

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (hexane, ether), sodium (toluene), or calcium hydride (CH₂Cl₂, CH₃CN). OsH₃Cl-(PPh₃)₃ (1) was prepared according to the procedure reported in the literature.²³ The silanes and other reagents were used as purchased from Aldrich Chemical Co. USA. Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ¹H, ¹³C{¹H}, ³¹P{¹H}, and ²⁹Si{¹H} NMR spectra were collected on a Bruker ARX-400 spectrometer (400 MHz) or Bruker Advance II-300 spectrometer (300 MHz). ¹H and ¹³C NMR shifts are relative to TMS, and ³¹P chemical shifts are relative to 85% H₃PO₄. Infrared (IR) spectra were recorded on a Nicole Avator 360 apparatus (Nicolet, USA).

 $OsH_3(SiClPh_2)(PPh_3)_3$ (2). Method A. To a suspension of $OsH_3Cl(PPh_3)_3$ (1; 200 mg, 0.197 mmol) in toluene (4.0 mL) was added Ph_2SiH_2 (37 μ L, 0.199 mmol). The reaction mixture was stirred for 3 h to give a gray suspension. The solvent was removed under vacuum, and the residue was washed with DCM (0.5 mL × 3) and then with ether (2 mL × 3) to give a white solid, which was dried under vacuum. Yield: 47.0 mg (0.0392 mmol), 19.9%.

Method B. A solution of OsH₄(SiClPh₂)(SiHPh₂)(PPh₃)₂ (3; 35 mg, 0.0313 mmol) and PPh₃ (10 mg, 0.0381 mmol) in C₆D₆ (0.40 mL) was heated at 55 °C for 12 h to give a white precipitate, which was collected by filtration, washed with ether (0.5 mL × 3) and then DCM (0.3 mL × 2), and dried under vacuum. Yield: 30.7 mg (0.0256 mmol), 82.1%. ³¹P{¹H} NMR (161.98 MHz, CD₂Cl₂): δ 4.9 (s). ¹H NMR (400.13 MHz, CD₂Cl₂): δ –10.4 (m, 3H, OsH₃), 6.8–7.1 (m, 42H, *Ph*), 7.18 (t, *J*_{HH} = 7.2 Hz, 9H, *Ph*), 7.30 (d, *J*_{HH} = 6.8 Hz, 4H, *Ph*). IR: *ν* 2064, 2012 cm⁻¹ (Os-H). Anal. Calcd for C₆₆H₅₈ClOsSiP₃: C, 66.18; H, 4.88. Found: C, 66.29; H, 5.08.

OsH₄(SiClPh₂)(SiHPh₂)(PPh₃)₂ (3). A suspension of OsH₃Cl-(PPh₃)₃ (1; 1.0 g, 0.985 mmol) in toluene (10 mL) was added Ph₂SiH₂ (0.55 mL, 2.96 mmol). The reaction mixture was stirred for 2 h to give a pale brown solution. The solvent was removed under vacuum, and the residue was washed with ether $(2 \text{ mL} \times 3)$ then with hexane $(3 \text{ mL} \times 3)$ to give a white solid, which was dried under vacuum. Yield: 0.963 g (0.86 mmol), 87.3%. ³¹P{¹H} NMR (121.49 MHz, C_6D_6): δ 9.5 (s). ¹H NMR (400.13 MHz, $C_6D_5CD_3$): δ -9.7 $(br, 2H, OsH_4), -6.0 (br, 2H, OsH_4), 6.27 (t, 1H, J_{PH} = 6.8 Hz, J_{SiH} =$ 204.0 Hz, SiH), 6.8-7.6 (m, 50H, Ph). ¹³C{¹H} NMR (100.62 MHz, CD₂Cl₂): δ 147.5 (s, Ph), 143.4 (s, Ph), 136.1-135.6 (m, Ph), 135.1 (s, Ph), 134.5-134.4 (m, Ph), 130.3 (s, Ph), 128.5 (s, Ph), 128.2-128.1 (m, Ph), 127.5 (s, Ph), 127.2 (s, Ph). ²⁹Si{¹H} NMR (59.63 MHz, C_6D_6): δ 19.7 (t, J_{PSi} = 12.2 Hz, $OsSiClPh_2$), -16.8 ppm (t, J_{PSi} = 6.6 Hz, OsSiHPh₂). At 400 MHz and 248 K, the hydride signals at -5.8 and -9.6 ppm have T_1 values of 359 and 366 ms, respectively. Anal. Calcd for C₆₀H₅₅ClOsSi₂P₂: C, 64.35; H, 4.95. Found: C, 64.37; H, 5.14.

OsH₄(SiClHPh)(SiH₂Ph)(PPh₃)₂ (4). To a suspension of OsH₃Cl-(PPh₃)₃ (1; 1.0 g, 0.985 mmol) in toluene (10 mL) was added PhSiH₃ (0.32 mL, 2.59 mmol). The reaction mixture was stirred for 1 h to give a pale brown solution. The solvent was removed under vacuum, and the residue was washed with ether (2 mL × 3) then with hexane (3 mL × 3) to give a white solid, which was dried under vacuum. Yield: 0.586 g (0.86 mmol), 61.5%. ³¹P{¹H} NMR (161.98 MHz, C₆D₆): δ 13.50 (ABq, $\Delta \delta_{AB} = 0.13$, $J_{AB} = 16.2$ Hz). ¹H NMR (400.13 MHz, C₆D₆): δ -7.8 (br, 4H, OsH₄), 5.45 (dd, 1H, $J_{HH} = 6.0$ Hz, $J_{PH} = 4.0$ Hz, SiH₂Ph), 5.59 (dd, 1H, $J_{HH} = 6.0$ Hz, $J_{PH} = 4.2$ Hz, SiH₂Ph), 6.7–7.5 (m, 37H, 36H for Ph and 1H for SiHClPh), 7.79 (dd, 2H, $J_{HH} = 7.8$, 1.4 Hz, Ph), 7.84 (dd, 2H, $J_{HH} = 7.8$, 1.4 Hz, Ph). ¹³C{¹H} NMR (100.62 MHz, CD₂Cl₂): δ 146.6 (s, Ph), 141.9 (s, Ph), 136.0–133.7 (m, Ph), 130.4 (s, Ph), 129.0 (s, Ph), 128.5–127.9 (m, Ph). ²⁹Si{¹H} NMR (59.63 MHz, C_6D_6): δ 9.2 (dd, J_{PSi} = 12.3, 9.4 Hz, OsS*i*HClPh), -44.9 ppm (dd, J_{PSi} = 7.2, 5.6 Hz, OsS*i*H₂Ph). The hydride signals at -6.0 and -9.8 ppm have T_1 values of 477 and 400 ms, respectively, at 400 MHz and 233 K. Anal. Calcd for $C_{48}H_{47}ClOsSi_2P_2$: *C*, 59.58; H, 4.90. Found: C, 59.52; H, 5.10.

 $OsH_3(SiClPh_2)(PPh_3)_2(NCCH_3)$ (18). Method A. To a suspension of $OsH_3Cl(PPh_3)_3$ (1; 1.0 g, 0.985 mmol) in toluene (10 mL) was added Ph_2SiH_2 (0.55 mL, 2.96 mmol). After the mixture was stirred for 2 h, 6 mL of CH₃CN was added, and this reaction mixture was further stirred for 6 h to give a white solid, which was collected by filtration, washed with hexane (5 mL × 3), and dried under vacuum. Yield: 0.56 g (0.573 mmol), 58.2%.

Method B. To a solution of $OsH_4(SiClPh_2)(SiHPh_2)(PPh_3)_2$ (3; 100 mg, 0.0893 mmol) in toluene (2 mL) was added CH₃CN (2 mL). The reaction mixture was stirred for 24 h to give a white solid and a light purple solution. The volume of the reaction mixture was reduced to ca. 1 mL. The white solid was then collected by filtration, washed with ether $(2 \text{ mL} \times 3)$ and hexane $(3 \text{ mL} \times 3)$, and dried under vacuum. Yield: 78.0 mg (0.0799 mmol), 89.4%. ³¹P{¹H} NMR (161.98 MHz, C_6D_6): δ 17.6 (s). ¹H NMR (400.13 MHz, C_6D_6): δ -10.2 (br, 3H, OsH₃), 0.59 (s, grease), 0.63 (s, 3H, CH₃CN), 6.8-7.4 (m, 36H, *Ph*), 8.20 (d, $J_{\rm HH}$ = 7.2 Hz, 4H, *Ph*). ¹³C{¹H} NMR (100.62 MHz, CD₂Cl₂): δ 150.4 (s, Ph), 136.0-132.9 (m, Ph), 128.0 (s, Ph), 126.6-126.3 (m, Ph), 125.7 (s, Ph), 119.3 (s, CH₃CN), 2.7 (s, CH₃CN). 29 Si{ 1 H} NMR (79.49 MHz, C₆D₆): δ 19.9 (t, J_{PSi} = 6.8 Hz, OsSiClPh₂). IR: ν 2070, 1991 cm⁻¹ (Os-H). Anal. Calcd for CsoH46ClOsNSiP2: C, 61.49; H, 4.75; N, 1.43. Found: C, 61.39; H, 4.87; N: 1.35.

Crystal Structure Analyses. Crystals of 3 and 18 suitable for Xray diffraction were grown from toluene solution layered with hexane under a hydrogen atmosphere. The crystal was mounted on glass fibers with epoxy glue. The diffraction intensity data of 3 and 18 were collected on a Rigaku Oxford Diffraction SuperNova, Dual, Cu at zero, Atlas diffractometer with monochromated Cu K α radiation (λ = 1.54178 Å) at 100 K. Diffraction data were processed using the CrysAlisPro software (version 1.171.35.19). Empirical absorption corrections were performed using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm in the CrysAlisPro software suite. Structure solution and refinement data for all compounds were obtained using the Olex2²⁴ software package (which embedded ShelXS²⁵ and SHELXTL²⁶). All of the structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least squares on F^2 . All non-hydrogen atoms were refined anisotropically with a riding model for the hydrogen atoms except where noted separately. Further crystallographic details are summarized in Table S1 in the Supporting Information.

Computational Details. All calculations were performed with the Gaussian 09 software package.²⁷ The molecular geometries of all structures presented in this study were fully optimized using the B3LYP method.²⁸ Vibrational frequency calculations were performed at the same level of theory to verify the stationary points with no imaginary frequency for the minima and one imaginary frequency for the transition states. Intrinsic reaction coordinate (IRC) calculations were also performed to identify transition states connecting two relevant minima.²⁹ To consider solvation effects, on the basis of the gas-phase optimized results, single-point energy calculations were performed at the M06³⁰ level of theory in conjunction with the solvation model density (SMD)³¹ continuum method. In the M06-SMD calculations, toluene was used as the solvent. The effective core potentials (ECPs) of Lanl2dz were used to describe Cl, Si, Os, and P atoms,³² with polarization functions for Cl (ζ_d = 0.640), Si (ζ_d = 0.284), Os (ζ_f = 0.886), and P (ζ_d = 0.387) being added.³³ The H atoms, which were related to prototropic, were described by the 6-31G** basis set.³⁴ The 6-31g* basis set was used for CH₃CN reactant and all remaining atoms.³⁵

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.7b00512.

Experimental procedures and spectroscopic data for all new compounds (PDF)

Cartesian coordinates for calculated structures (XYZ)

Accession Codes

CCDC 1550734 and 1550737 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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