Synthesis and Characterization of Osmium-Containing Silsesquioxanes: High-Yield Routes to $\{Os_3(CO)_{10}(\mu\text{-}H)[(\mu\text{-}O)Si_7O_{10}(c\text{-}C_6H_{11})_7]\}$ and the New Clusters $\{Os_3(CO)_{10}(\mu\text{-}H)[(\mu\text{-}O)Si_7O_9(OH)_2(c\text{-}C_6H_{11})_7]\}$, $\{[Os_3(CO)_{10}(\mu\text{-}H)]_2(\mu\text{-}O)_2Si_7O_9(OH)(c\text{-}C_6H_{11})_7\}$, $\{Os_3(CO)_{10}(\mu\text{-}H)[(\mu\text{-}O)Si_8O_{11}(OH)(c\text{-}C_6H_{11})_8]\}$, and $\{[Os_3(CO)_{10}(\mu\text{-}H)]_2(\mu\text{-}O)_2Si_8O_{11}(c\text{-}C_6H_{11})_8\}$

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The reactions of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ (**3**) with the incompletely condensed silsesquioxanes $[(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3]$ (**1**) and $[(c\text{-}C_6H_{11})_8Si_8O_{11}(OH)_2]$ (**2**) afford in high yield $\{Os_3(CO)_{10}(\mu\text{-}H)[(\mu\text{-}O)Si_7O_{10}(c\text{-}C_6H_{11})_7]\}$ (**4**) and the new compounds $\{Os_3(CO)_{10}(\mu\text{-}H)[(\mu\text{-}O)Si_7O_9(OH)_2(c\text{-}C_6H_{11})_7]\}$ (**5**), $\{[Os_3(CO)_{10}(\mu\text{-}H)]_2(\mu\text{-}O)_2Si_7O_9(OH)(c\text{-}C_6H_{11})_7\}$ (**6**), $\{Os_3(CO)_{10}(\mu\text{-}H)[(\mu\text{-}O)Si_8O_{11}(OH)(c\text{-}C_6H_{11})_8]\}$ (**8**), and $\{[Os_3(CO)_{10}(\mu\text{-}H)]_2(\mu\text{-}O)_2Si_8O_{11}(c\text{-}C_6H_{11})_8\}$ (**9**), which are discrete molecular models of silica-anchored $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi\equiv)]$. Compounds **6** and **9** represent the first examples of complexes containing two $[Os_3(CO)_{10}(\mu\text{-}H)]$ cluster cores. The X-ray structures of **5**, **8**, and **9** are reported.

Introduction

Over the past two decades, "surface organometallic chemistry"[1−5] has emerged as an important subdiscipline in the field of heterogeneous catalysis. Numerous systems have been studied in great detail,[6−16] and it is now quite common to view hydroxylated surface sites as ligands in the same way simple alkoxides are used to prepare solution organometallic compounds. Silica is the support most extensively used for modern surface organometallic chemistry because its surface chemistry is relatively simple and well established compared to many other supports (e.g., alumina, metal oxides).

One of the early success stories in surface organometallic chemistry was the reaction of silica with $[Os_3(CO)_{12}]$, which produces a structurally well-defined silica-supported cluster attached to the surface via a single siloxy group.[17−26] A variety of techniques were used to characterize this cluster, and its structure was assigned unambiguously as $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi\equiv)]$ on the basis of IR,[17,18,27] Raman,[22,23] and solid-state NMR[28] spectroscopies, EXAFS,[20,29] and computer model-

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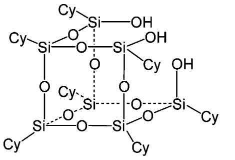
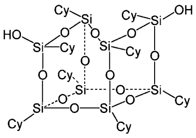
ing[24,30,31] or on the basis of its similarity to structurally analogous homogeneous compounds (e.g., $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiR_3)]$ (R = Et, Ph).[17,18,21,25,32,33] This work convincingly established that (1) silica could indeed be viewed as a ligand, (2) the reaction of silica with an organometallic compound could be highly selective, and (3) the characterization of silica-supported complexes could be achieved with a degree of accuracy and confidence that is approaching the corresponding solution organometallic complexes.

As the field of surface organometallic chemistry advances and a clearer mechanistic understanding of surface chemistry develops, it will become increasingly important to probe subtle effects that are capable of providing low-energy pathways for a variety of well-established surface reactions (e.g., chemisorption of metal carbonyls). One attractive approach for identifying these effects is to study the reactivity of structurally well defined solution complexes that possess the functionality present on a surface. We[34−39] and others[40−53] have been using incompletely condensed silsesquioxanes (e.g., **1** and **2**) for this purpose, and the collective results from this work provide a number of new insights into the chemistry of both silica and silica-supported catalysts.



1 Cy = *c*-C_6H_{11}



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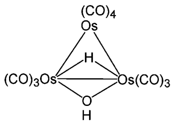
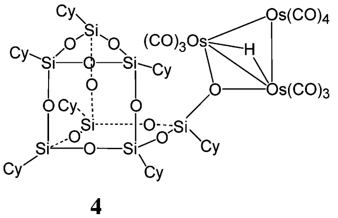


3 $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$

In this paper we present the results from our efforts to prepare osmium-containing clusters with potentially reactive pendent Si−OH groups. The goal of our work was to determine whether Os_3 clusters juxtaposed to potentially reactive Si−OH groups could interact via hydrogen bonding or undergo low-energy reactions not seen with simpler silanols. The springboard for this work was the recent development of a high-yield synthesis of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ (**3**),[54] which is known to react cleanly with silanols—including silanols with more than one SiOH group—to produce osmium carbonyl clusters with the formula $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiR_2R')]$ (R = Et, Ph; R′ = Et, Ph, OH, $OSiPh_2OH$).[55] The results from our studies, as well as their implications for the chemistry of silica-supported complexes, are discussed below.

Results and Discussion

Reaction of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ (3) with $[(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3]$ (1): Synthesis of 4, 5, and 6. Trisilanol **1** does not react significantly with 2 equiv of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ (**3**) in hydrocarbons heated at 80 °C for 6 h. Upon heating to 140 °C in *m*-xylene, both reagents were consumed over a period of 3 h to produce a mixture of Os hydride complexes with ^1H NMR resonances ($CDCl_3$) at δ −12.31, −12.46, and −12.55 with relative intensities of 6:35:59. Small ^1H resonances were also observed at δ −11.48, −12.03, −12.98, −14.94, −20.50, and −21.35; the latter two were observed when pure **3** was heated to 140 °C in *m*-xylene. (Trisilanol **1** is stable in *m*-xylene at 140 °C.) Evaporation of the solvent and elution across silica with CH_2Cl_2/hexanes afforded three compounds. The first to elute with 1:9 CH_2Cl_2/hexane was **4** (^1H δ −12.55), which was identical in all respects to an authentic sample prepared via reaction of trisilanol **1** with $[Os_3(CO)_{12}]$ in refluxing octane.[33] The second compound, which eluted with 1:9 CH_2Cl_2/hexane, was subsequently identified as **6** (^1H δ −12.03). The third compound eluted with 2:1 CH_2Cl_2/hexane. This compound, which crystallizes as a hydrogen-bonded dimer without interactions between SiOH groups and the Os_3 cluster (vide infra), was identified as **5** (^1H δ −12.46). The compound responsible for the ^1H NMR resonance at δ −12.31 in the reaction crude coeluted with several other minor compounds and could not be isolated in pure form; its structure could not be assigned.



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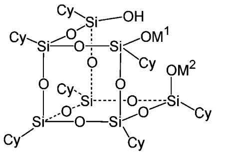

5 $M^1 = H$; $M^2 = \mu\text{-}[Os_3(CO)_{10}(\mu\text{-}H)]$

6 $M^1 = M^2 = \mu\text{-}[Os_3(CO)_{10}(\mu\text{-}H)]$

The combined isolated yield of **4**, **5**, and **6** is typically greater than 70% based on available Os, but the relative amount of each compound depends strongly on the relative amounts of trisilanol **1** and of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ (**3**) used in the

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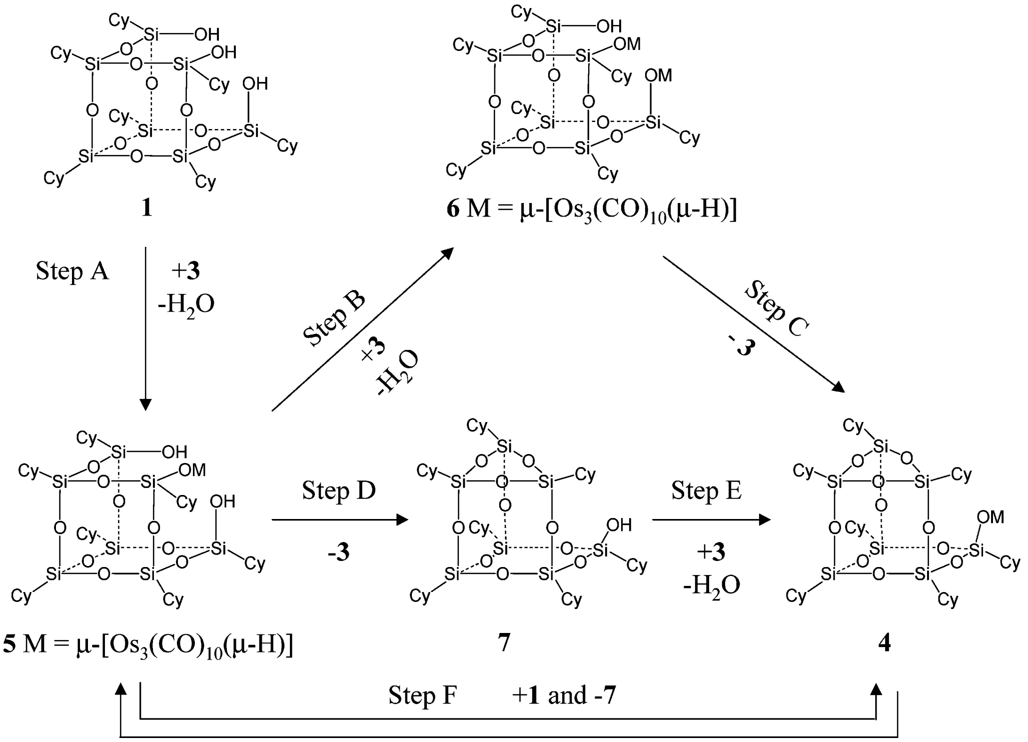
Scheme 1



reaction, as well as the reaction time and temperature. When the reaction was performed at 115 °C for 6 h with a 2:1 mixture of **1** and **3**, approximately two-thirds of the starting Os complex reacted to produce **4** and **5** in a ~1:1 ratio, respectively. After 12 h, the starting Os complex was completely consumed to produce **4** and **5** in a 3:2 ratio. At 140 °C, the reaction of **1** and **3** (2:1) produces **4** and **5** with isolated yields of 35% and 39% after 2.5 h; the corresponding yields of **4** and **5** after 6.5 h are 17% and 73%. Increasing the ratio of **1** to **3** did not improve the selectivity for the formation of **5** versus **4**. In fact, reactions performed at 140 °C (3 h) with 5:1 or 10:1 mixtures of **1** and **3** actually showed a modest increase in selectivity for the formation of **4** (from 1:1 to 3:1).

Somewhat unexpectedly, the reaction of **1** with a 10-fold excess of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ (**3**) did not favor the formation of **6** (or a derivative of **1** with three Os_3 clusters). Instead, **6** formed in trace amounts (along with **5**) and the major product was again **4**. In contrast, the reaction of **5** with a 4-fold excess of **3** (140 °C, 11.5 h) afforded **6** in 55% NMR yield (27% isolated yield), as well as comparable amounts of **4** (24% NMR yield). These results suggest that the formation of **6** competes with the formation of **4** only when **5** is the major silicon-containing species in the reaction mixture.

The mechanisms by which **4**, **5**, and **6** are produced are not known with certainty, but it appears that $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ (**3**) is both a reagent for the formation of **4**−**6** and a catalyst for the cyclodehydration of **1** to **7**. In the absence of **3**, trisilanol **1** is stable in *m*-xylene at 140 °C; no reaction is observed after 2.5 h. Upon addition of a catalytic amount of **3** (5 mol %), trisilanol **1** undergoes clean cyclodehydration to produce **7** with ~70% conversion after 16 h at 140 °C. Base-catalyzed cyclodehydration[35] seems unlikely because $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ (**3**) is poorly Bronsted basic and because the rate of cyclodehydration is similar to the rate for reactions between **3** and other incompletely condensed silsesquioxanes (e.g., **2**, vide infra). The mechanism most consistent with all our observations is shown in Scheme 1. Step A in this mechanism produces **5** via the reaction of trisilanol **1** and **3**. Complex **5** is observed early in our reactions, and it is the major product (48% NMR yield) when **3** is reacted with an excess of trisilanol **1** for short reaction times. The reaction of **5** with a second equivalent of **3** produces **6** (step B), which is the product favored when excess **3** is present and reaction times are relatively short. At longer reaction times, **6** undergoes cycloelimination to produce **3** and **4** (step C). Another route to **4**, which appears to be much more facile under most conditions, involves cycloelimination of **5** to produce **3** and trisilanol **7** (step D), which subsequently condenses with **3** to produce **4** (step E). This route is probably favored because the relative bulk and electron-withdrawing nature of the Os_3 carbonyl cluster combine to produce a good leaving group on silicon. A third route to **4** might involve reversible metathesis of **5** and **7** to produce **4** and **1** (step F), but it seems more likely that this transformation would involve catalysis by traces of water rather than direct reaction of an Os-substituted silsesquioxane with another large silsesquioxane framework.

Reactivity of $\{Os_3(CO)_{10}(\mu\text{-H})[(\mu\text{-O})Si_7O_{10}(c\text{-}C_6H_{11})_7]\}$ (4) with Et_4NOH. The recent discovery that **7** reacts cleanly with aqueous Et_4NOH to afford **1** in high yield[56] suggested that it might be possible to produce **5** via the reaction of Et_4NOH with readily available **4**. Unfortunately, this is not the case. The addition of an equimolar amount of aqueous Et_4NOH (20% or 35 wt %) to a solution of **4** in THF at 25 °C produces an immediate color change from yellow to orange-brown. Neutralization of this solution with a stoichiometric amount of aqueous HCl followed by evaporation of the solvent afforded a brown residue, which exhibited a prominent ^1H NMR resonance for $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ (**3**) and several smaller resonances for other unidentified Os−H hydride species. These results clearly demonstrate that cleavage of the μ-OSi ligand from the osmium

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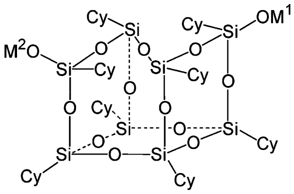
[56] Feher, F. J.; Terroba, R.; Ziller, J. W. *Chem. Commun.* **1999**, 2309.

cluster is comparably facile to base-catalyzed hydrolytic cleave of Si_3O_3 rings.

Reactivity of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ (3) with $[(c\text{-}C_6H_{11})_8Si_8O_{11}(OH)_2]$ (2): Synthesis of 8 and 9. In contrast to reactions of trisilanol **1** with $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ (**3**), the reaction of **3** with disilanol **2** is straightforward. The reaction of **2** with an equimolar amount of **3** occurs cleanly in *m*-xylene at 140 °C to afford a mixture of **8**, **9**, and unreacted **2**. After 1 h, the hydride region of the ^1H NMR spectrum ($CDCl_3$) of the reaction mixture exhibited two new signals at δ −12.31 (16%) and −12.40 (61%), as well as a resonance at δ −12.60 (23%) for unreacted **3**. After 3 h at 140 °C, the resonance for **3** was gone and the hydride region of the ^1H NMR spectrum was dominated by the resonances at δ −12.31 (24%) and −12.40 (71%). Small resonances were also observed at δ −12.35 (4%), −20.48 (<1%), −21.26 (<1%), and −21.36 (<1%)). Evaporation of the reaction mixture and chromatography on silica using CH_2Cl_2/hexanes afforded two compounds in good yield. The first compound to elute (1:4 CH_2Cl_2/hexanes) was **9**, which exhibited a ^1H NMR resonance at δ −12.31. The second compound to elute (1:1 CH_2Cl_2/hexanes) was **8**, which exhibited a ^1H NMR resonance at δ −12.40. Both compounds were unambiguously identified on the basis of multinuclear NMR spectroscopy data and single-crystal X-ray diffraction studies.



8 $M^1 = H$; $M^2 = \mu\text{-}[Os_3(CO)_{10}(\mu\text{-H})]$

9 $M^1 = M^2 = \mu\text{-}[Os_3(CO)_{10}(\mu\text{-H})]$

The combined isolated yield of **8** and **9** is typically greater than 80% based on the amount of **2** available. When the reaction is performed in refluxing xylene (140 °C, 3.5 h) with a 2.5:1 molar ratio of **2** and **3**, an 89:11 mixture of **8** and **9** was obtained, as judged by an ^1H NMR spectrum of the crude product mixture; after chromatography on silica, the isolated yields of **8** and **9** were 74% and 10%, respectively. Higher yields of **9** can be obtained by using larger amounts of **3** and longer reaction times, but not without some decomposition of the Os cluster. For the reaction of **2** with 2.0 molar equiv of **3**, complete consumption of the starting Os cluster requires 18 h at 140 °C and produces a dark black reaction mixture. Evaporation of the solvent and purification by column chromatography on neutral alumina afforded **8** in 11% isolated yield and **9** in 70% isolated yield.

X-ray Structures of 5, 8, and 9. The molecular structures of **5**, **8**, and **9** are shown in Figures 1−3. In each case, the three Os atoms are arranged in a nearly isosceles triangle with two long edges (2.81−2.84 Å) and one short edge (2.78−2.79 Å). The short edge in the triosmium triangle is bridged by the μ-oxygen-bonded silsesquioxane ligand and a hydrogen atom, which was not located or refined. The short edge length is coherent with the average Os−Os distance of 2.68 Å found by EXAFS investigation of the silica-anchored cluster $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$.[17] The average Os−O lengths of 2.08−2.13 Å for the two osmium atoms bridged by μ-oxygen in clusters **5**, **8**, and **9** are in agreement with the Os−O distance of 2.16 Å measured for the alumina-supported cluster $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OAl}<)]$.[29] The interatomic distances and intrabond angles within the Os_3 clusters are not significantly different from those in other crystallographically characterized $Os_3(CO)_{10}$-containing clusters, including $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-Y})]$ with Y= $OSiEt_3$,[21] $OSi_7O_{10}(c\text{-}C_6H_{11})_7$,[33] $OSiPh_2OH$,[55] and $OSiPh_2OSiPh_2OH$.[55]

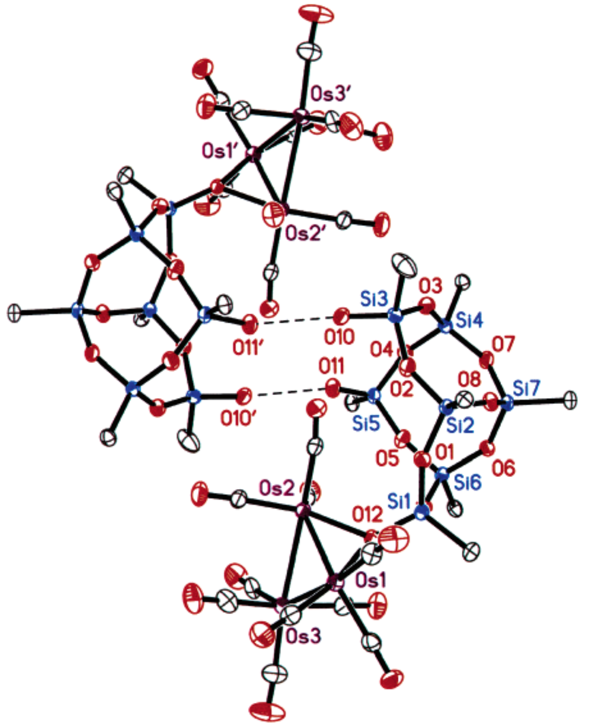


Figure 1. ORTEP plot of **5** with thermal ellipsoids plotted at the 50% probability level. For clarity, only the ipso carbon atoms of the cyclohexyl groups are shown. Selected distances (Å) and angles (deg): Os1−Os2, 2.7955(3); Os1−Os3, 2.8424(3); Os2−Os3, 2.8101(3); Os1−O12, 2.131(3); Os2−O12, 2.125(3); Si1−O1, 1.625(4); Si1−O9, 1.622(3); Si1−O12, 1.632(3); Si3−O10, 1.638(4); Si5−O11, 1.644(3); other Si−O, 1.607−1.634; Os2−Os1−Os3, 59.786(7); Os1−Os2−Os3, 60.936(8); Os2−Os3−Os1, 59.278(7); Si1−O12−Os1, 141.44(19); Si1−O12−Os2, 129.39(19); O1−Si1−O12, 109.35(17); O9−Si1−O12, 106.08(18); Si1−O1−Si2, 153.5(2); Si1−O9−Si6, 143.4(2); other Si−O−Si, 143−166; O−Si−O, 107−111.

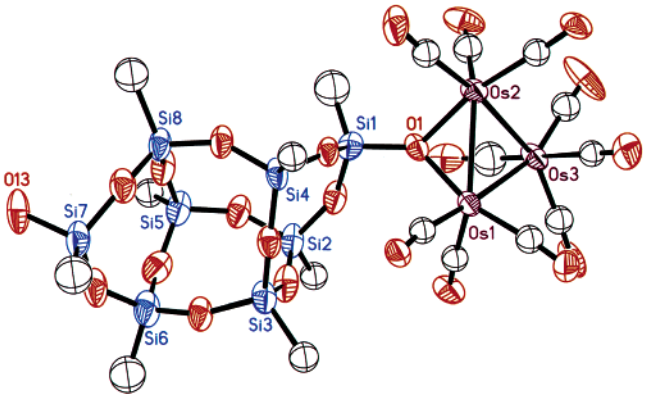


Figure 2. ORTEP plot of **8** with thermal ellipsoids plotted at the 50% probability level. For clarity, only the ipso carbon atoms of the cyclohexyl groups are shown. Selected distances (Å) and angles (deg): Os1−Os2, 2.7841(11); Os1−Os3, 2.8175(11); Os2−Os3, 2.8206(10); Os1−O1, 2.085(13); Os2−O1, 2.095(11); Si1−O1, 1.684(13); Si1−O2, 1.653(14); Si1−O5, 1.603(14); Si7−O13, 1.655(15); other Si−O, 1.58−1.68; Os2−Os1−Os3, 60.47(3); Os1−Os2−Os3, 60.35(3); Os1−Os3−Os2, 59.18(3); Si1−O1−Os1, 128.6(7); Si1−O1−Os2, 132.0(7); O2−Si1−O1, 104.3(6); O5−Si1−O1, 108.0(7); Si1−O2−Si2, 145.0(9); Si1−O5−Si4, 147.3(8); other Si−O−Si, 142−155; O−Si−O, 105−113.

Metrical data for the silsesquioxane framework are also within their generally accepted ranges. In fact, there is no evidence for distortion of the Si/O frameworks due to steric compression

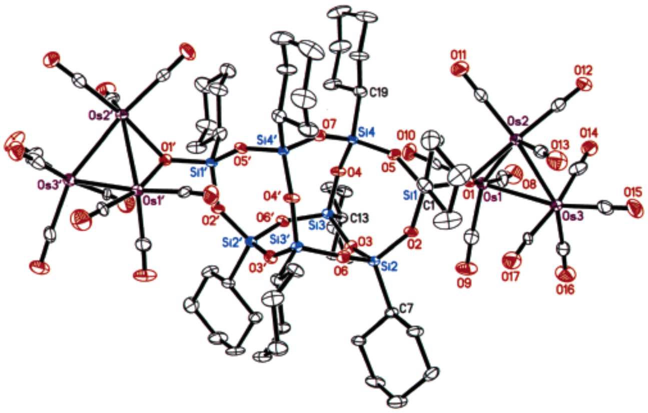


Figure 3. ORTEP plot of **9** with thermal ellipsoids plotted at the 50% probability level. For clarity, only the carbon atoms of the cyclohexyl groups are shown. Selected distances (Å) and angles (deg): Os1−Os2, 2.7830(4); Os1−Os3, 2.8200(5); Os2−Os3, 2.8275(5); Os1−O1, 2.133(5); Os2−O1, 2.125(5); Si1−O1, 1.636(6); Si1−O2, 1.619(5); Si1−O5, 1.611(5); other Si−O, 1.62−1.64; Os2−Os1−Os3, 60.609(11); Os1−Os2−Os3, 60.343(11); Os1−Os3−Os2, 59.048(10); Si1−O1−Os1, 128.3(3); Si1−O1−Os2, 138.8(3); O2−Si1−O1, 104.2(3); O5−Si1−O1, 109.2(3); Si1−O2−Si2, 143.8(4); Si1−O5−Si4, 153.9(4); other Si−O−Si, 142−156; O−Si−O, 107−110.

by the large triosmium cluster. In the case of **8** and **9**, the Si−O distances, as well as O−Si−O and Si−O−Si angles, are comparable to those observed for the bis-triphenyltin derivative of disilanol **2**.[34] In the case of **5**, which possesses two Si−OH groups, the molecule adopts a symmetry-related ($\bar{1}$) dimeric structure with extensive hydrogen bonding. Although the hydrogen atoms for the SiOH groups could not be located in the final difference map, the Si−O distances and intrabond angles for **5** are remarkably similar to those observed for the hydrogen-bonded dimer of $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_2(OSiMe_2Ph)$.[57] Both compounds clearly adopt the same hydrogen-bonded arrangement of SiOH groups, and there is no evidence in the structure of **5** for interaction between SiOH groups and the $Os_3(CO)_{10}$ cluster.

Conclusions

The reactions of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ (**3**) with incompletely condensed silsesquioxanes produce osmium-substituted Si/O frameworks via metathesis of the SiOH for the bridging OH group. In the case of disilanol **2**, which possesses two SiOH groups that are separated by more than 6 Å, reaction with **3** can occur at either or both SiOH groups to produce Si/O frameworks with one or two $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSi}{\equiv})]$ groups. In the case of trisilanol **1**, which possesses three mutually hydrogen-bonded SiOH groups, reaction with **3** is considerably more complicated and the product mixture depends greatly on the reaction stoichiometry and conditions. Three major products have been isolated from the reaction. Two of these products (**5** and **6**) are derived from condensation of **3** with one or two SiOH groups from **1**; the third (**4**) appears to form via Os-catalyzed cyclodehydration of **1** and condensation of the resulting monosilanol (i.e., **7**) with **3**. Both **5** and **6** juxtapose potentially reactive SiOH and $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSi}{\equiv})]$ groups, but there is no evidence for interaction of SiOH groups from either **5** or **6** with neighboring $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSi}{\equiv})]$ groups. As is the case for stoichiometrically analogous silica-supported complexes, the osmium clusters are unperturbed by the presence of neighboring SiOH groups, which clearly prefer to avoid the Os cluster by hydrogen bonding to each other (as well as SiOH groups from a second molecule in the solid state). The stability and unexceptional spectroscopic data for **6** also demonstrate that osmium clusters are unperturbed by the presence of other osmium clusters. Collectively, the results from the work described here parallel the known surface organometallic chemistry of triosmium clusters on silica, and neither the presence of potentially reactive SiOH groups nor neighboring triosmium clusters appear to influence the reactivity or spectroscopic features of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSi}{\equiv})]$ groups. The current description of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSi}{\equiv})]$ on silica as isolated triosmium clusters therefore appears to be accurate regardless of whether the clusters are indeed isolated from each other or additional to surface SiOH groups.

Although the reactions of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ (**3**) with incompletely condensed silsesquioxanes did not uncover any new coordination environments for triosmium clusters, the observation that **3** catalyzes the cyclodehydration of **1** has interesting implications for the surface organometallic chemistry of silica. In particular, it appears that metal complexes chemisorbed via M−O−Si linkages may be susceptible to desorption via reaction with adjacent SiOH groups and that the resulting MOH species may be capable of catalyzing further dehydration of the surface. This pathway is unlikely to be significant on dehydrated surfaces with isolated SiOH groups, but it could become important with more extensively hydroxylated surfaces possessing substantial populations of vicinally hydrogen-bonded SiOH groups.

Experimental Section

General experimental protocols and procedures have been reported earlier.[58] Methods and procedures for the synthesis of $[(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3]$ (**1**), $[(c\text{-}C_6H_{11})_8Si_8O_{11}(OH)_2]$ (**2**), and $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ (**3**) appear elsewhere.[34,54] Unless otherwise noted, reagent-grade chemicals were used without further purification for all work described here; *m*-xylene was dried over activated 4 Å molecular sieves prior to use. The NMR spectra were recorded on General Electric GN-500 (^{1}H, 500.03 MHz; ^{13}C, 125.75 MHz; ^{29}Si, 99.37 MHz) and Omega-500 (^{1}H, 500.22 MHz; ^{13}C, 125.79 MHz; ^{29}Si, 99.34 MHz) spectrometers, infrared spectra were recorded on a Mattson Galaxy Series FTIR 5000 spectrometer, and mass spectra were recorded on a VG Analytical Autospec E double-focusing spectrometer or a Perceptive Biosystems matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) Voyager DE STR spectrometer and a Micromass LCT electrospray ionization-time-of-flight (ESI) spectrometer. Combustion analyses (C, H) were measured at Atlantic Microlab Inc.

General Procedure for Reactions of Incompletely Condensed Silsesquioxanes (i.e., 1, 2, and 5) with $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ (3). Reactions were performed under nitrogen in a small flask (5 mL) fitted with a fritted-glass funnel (diameter = ca. 3 cm; height = ca. 25 cm) containing P_2O_5 (2 g). The distance between the reaction solution and the fritted disk was ca. 12 cm, and the flask was heated by immersion in a thermostated oil bath maintained at 140 °C. In a typical reaction, a solution of **3** (50−100 mg) and the incompletely condensed silsesquioxane in anhydrous *m*-xylene (0.5−1.0 mL; in order to have a concentration of **3** equal to 0.1 M) was heated at 140 °C. Evaporation of the volatiles (25 °C, 0.1 Torr) afforded a residue, which was analyzed by ^{1}H NMR spectroscopy ($CDCl_3$) to determine the relative amounts of compounds containing Os−H bonds. The crude product mixture was usually separated by

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(57) Feher, F. J.; Newman, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 1931.

(58) Feher, F. J.; Schwab, J. J.; Tellers, D. M.; Burstein, A. *Main Group Chem.* **1998**, *2*, 169.

column chromatography on silica using CH_2Cl_2/hexanes as eluent. Evaporation of the eluent typically afforded products that were spectroscopically pure (^1H, ^{13}C, ^{29}Si). Analytically pure samples were obtained as described below.

Reaction of 3 with Trisilanol 1: Synthesis of {$Os_3(CO)_{10}(\mu$-H)[(μ-O)Si_7O_{10}(*c*-$C_6H_{11})_7$]} (4) and {$Os_3(CO)_{10}(\mu$-H)[(μ-O)-$Si_7O_9(OH)_2$(*c*-$C_6H_{11})_7$]} (5). As described above, trisilanol **1** (140.7 mg; 0.144 mmol) and **3** (62.3 mg; 0.072 mmol) were reacted in *m*-xylene for 6.5 h at 140 °C. A ^1H NMR spectrum of the crude product mixture exhibited prominent ^1H NMR resonances ($CDCl_3$) at δ −12.31, −12.46, and −12.55 (4:19:77), as well as small resonances at δ −12.95, −14.92, −20.48, and −21.35. Column chromatography on silica using CH_2Cl_2/hexanes (1:9 then 2:1 v/v) afforded two yellow fractions. The first compound to elute was **4** (94.6 mg; 73% yield); the second was **5** (22.8 mg; 17% yield). When the same reaction was performed at 140 °C for 2.5 h using a 2:1 molar ratio of trisilanol **1** (170.4 mg; 0.175 mmol) and **3** (75.6 mg; 0.087 mmol), the ^1H NMR resonances ($CDCl_3$) at δ −12.31, −12.46, and −12.55 had relative intensities of 9:48:43 and the isolated yields of **4** and **5** were 35% (55.4 mg) and 39% (61.9 mg), respectively. Both **4** and **5** were obtained as spectroscopically pure, yellow microcrystalline powders after evaporation of the eluent. Analytically pure **4** can be obtained by crystallization from CH_2Cl_2/hexane at −10 °C. Analytically pure **5** was obtained by allowing CH_3OH to diffuse into a solution of **5** in CH_2Cl_2 at 25 °C.

For **4**: ^1H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ −12.55 (s, 1 H, HOs), 0.89 (vbr, m, 7 H), 1.26 (vbr, m, 35 H), 1.71 (vbr, m 35 H). $^{13}C\{^1H\}$ NMR (125.03 MHz, $CDCl_3$, 25 °C): δ 182.46, 180.70, 176.41, 175.82, 173.31, 173.25, 170.95 (s, for CO); δ 27.98, 27.72, 27.52, 27.46, 27.42, 27.38, 27.33, 26.86, 26.70, 26.56, 26.43, 26.39, 26.20 (s, for CH_2); δ 24.41, 23.64, 23.49, 22.96, 22.52 (s, 1:2:1:2:1 for CH). $^{29}Si\{^1H\}$ NMR (99.35 MHz, $CDCl_3$, 25 °C): δ −56.02, −56.39, −59.08, −66.73, −68.20 (s, 1:1:2:1:2). IR (C_6H_{12}), ν(CO): 2110 (w), 2072 (vs), 2059 (s), 2019 (vs), 2000 (s), 1986 (m), 1982 (m), 1952 (vw) cm^{-1}. MS (ESI): *m*/*e* 1829 (M + Na^+), 1807 (M + H^+).

For **5**: ^1H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ −12.46 (s, 1 H, HOs), 0.78 (vbr, m, 7 H), 1.26 (vbr, m, 35 H), 1.72 (vbr, m 35 H), 3.65 (s, 2 H, HO). $^{13}C\{^1H\}$ NMR (125.03 MHz, $CDCl_3$, 25 °C): δ 182.58, 180.62, 176.32, 175.59, 173.27, 171.14 (s, for CO); δ 28.02, 27.67, 27.62, 27.55, 27.48, 26.82, 26.77, 26.73, 26.63 (s, for CH_2); δ 24.47, 24.27, 23.97, 23.22 (s, 2:1:1:2:2 for CH). $^{29}Si\{^1H\}$ NMR (99.35 MHz, $CDCl_3$, 25 °C): δ −56.64, −59.35, −67.11, −67.29, −68.98 (s, 1:2:1:1:2). IR (C_6H_{12}), ν(CO): 2111 (w), 2073 (vs), 2059 (s), 2021 (vs), 2000 (s), 1986 (m) cm^{-1}. MS (ESI): *m*/*e* 1847 (M + Na^+), 1825 (M + H^+). Anal. Calcd for $C_{52}H_{80}O_{22}Si_7Os_3$ (found): C, 34.23 (34.44); H, 4.65 (4.53).

Reaction of 3 with 5: Synthesis of {[$Os_3(CO)_{10}(\mu$-H)]$_2$-(μ-O)$_2Si_7O_9$(OH)(*c*-$C_6H_{11})_7$} (6). As described above, **3** (103.3 mg; 0.119 mmol), **5** (52.0 mg; 0.028 mmol), and *m*-xylene (0.55 mL) were reacted at 140 °C under N_2 for 11.5 h. The crude product mixture exhibited prominent ^1H NMR resonances at δ −12.03, −12.31, −12.55, and −12.60 (22:8:10:60), as well as much smaller resonances at δ −12.95, −14.92, −20.48, and −21.35. Chromatography on silica with CH_2Cl_2/hexanes (1:9, v/v) first afforded **4**. Further elution with 1:9 CH_2Cl_2/hexanes afforded spectroscopically pure **6** (20.2 mg; 27% yield), and continued elution with 1:1 CH_2Cl_2/hexanes recovered unreacted **3**.

For **6**: ^1H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ −12.03 (s, 1 H, HOs), 0.75 (vbr, m, 7 H), 1.26 (vbr, m, 35 H), 1.77 (vbr, m 35 H)), 3.55 (s, 1 H, HO). $^{13}C\{^1H\}$ NMR (125.03 MHz, $CDCl_3$, 25 °C): δ 183.42, 180.70, 176.63, 176.46, 175.73, 175.64, 173.39, 173.29, 172.95, 172.63 (s, for CO); δ 27.91, 27.70, 27.60, 27.56, 27.51, 27.46, 27.36, 26.85, 26.72, 26.69, 26.58, 26.47 (s, for CH_2); δ 25.74, 24.62, 24.44, 23.13 (s, 1:3:2:1 for CH). $^{29}Si\{^1H\}$ NMR (99.35 MHz, $CDCl_3$, 25 °C): δ −56.25, −60.96, −66.71, −68.87, −69.50 (s, 2:1:1:1:2). IR (CH_2Cl_2), ν(CO): 2110 (w), 2072 (vs), 2057 (s), 2020 (vs), 1998 (m), 1982 (m, sh) cm^{-1}. MS (ESI): *m*/*e* 2698 (M + Na^+), 2676 (M + H^+).

Reaction of 3 with Disilanol 2: Synthesis of {$Os_3(CO)_{10}(\mu$-H)[(μ-O)Si_8O_{11}(OH)(*c*-$C_6H_{11})_8$]} (8) and {[$Os_3(CO)_{10}(\mu$-H)]$_2$-(μ-O)$_2Si_8O_{11}$(*c*-$C_6H_{11})_8$} (9). As described above, **3** (110.0 mg; 0.126 mmol), disilanol **2** (349.6 mg; 0.318 mmol), and *m*-xylene (1.25 mL) were reacted at 140 °C for 3.5 h. The ^1H NMR spectrum of the crude product mixture exhibited prominent resonances at δ −12.31 and −12.40 (11:89), as well as three smaller signals at δ −11.52, −20.48, and −21.35. Chromatography on silica with CH_2Cl_2/hexanes (1:4, v/v) first afforded **9** (17.6 mg; 10% yield); continued elution with 1:1 CH_2Cl_2/hexanes afforded **8** (182.3 mg; 74% yield). When the same reaction was performed at 140 °C for 18.5 h using a 1:2 molar ratio of disilanol **2** (68.6 mg; 0.062 mmol) and **3** (107.4 mg; 0.124 mmol), the crude mixture exhibited prominent ^1H NMR resonances ($CDCl_3$) at δ −12.31, −12.40, and −12.61 (80:14:6), and the isolated yields of **8** and **9** were 11% (13.8 mg) and 70% (121.3 mg), respectively. Analitically pure **8** was obtained by allowing CH_3OH to diffuse into a CH_2Cl_2 solution of **8** at 25 °C. Pure **9** can be obtained by recrystallization from hot 1,2-dichloroethane.

For **8**: ^1H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ −12.40 (s, 1 H, HOs), 0.78 (vbr, m, 8 H), 1.26 (vbr, m, 40 H), 1.72 (vbr, m, 40 H), 2.11 (s, 1 H, HO). $^{13}C\{^1H\}$ NMR (125.03 MHz, $CDCl_3$, 25 °C): δ 182.48, 180.58, 176.20, 175.63, 173.56, 173.52, 171.26, 171.11 (s, for CO); δ 27.78, 27.61, 27.54, 27.51, 27.47, 27.42, 27.36, 26.86, 26.74, 26.69, 26.61, 26.58, 26.54, 26.49, 26.28 (s, for CH_2); δ 23.98, 23.84, 23.66, 23.52, 23.48, 23.38, 23.20 (s, 1:1:1:1:1:1:2 for CH). $^{29}Si\{^1H\}$ NMR (99.35 MHz, $CDCl_3$, 25 °C): δ −54.75, −57.44, −65.59, −65.84, −67.82, −68.01, −69.05, −69.16 (s, 1:1:1:1:1:1:1:1). IR ($CDCl_3$), ν(CO): 2110 (w), 2070 (vs), 2059 (m), 2021 (vs), 2003 (s), 1983 (m, sh) cm^{-1}. MS (ESI): *m*/*e* 1973 (M + Na^+), 1951 (M + H^+). Anal. Calcd for $C_{58}H_{90}O_{23}Si_8Os_3$ (found): C, 35.71 (36.96); H, 4.65 (4.76).

For **9**: ^1H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ −12.31 (s, 1 H, HOs), 0.76 (vbr, m, 8 H), 1.24 (vbr, m, 40 H), 1.73 (vbr, m 40 H). $^{13}C\{^1H\}$ NMR (125.03 MHz, $CDCl_3$, 25 °C): δ 182.44, 180.50, 176.05, 175.47, 173.62, 171.53, 171.34 (s, for CO); δ 27.70, 27.59, 27.50, 27.43, 27.31, 27.06, 26.80, 26.72, 26.66, 26.57, 26.48, 26.34, 26.00 (s, for CH_2); δ 24.00, 23.92, 23.71, 23.41 (s, 2:2:2:2 for CH). $^{29}Si\{^1H\}$ NMR (99.35 MHz, $CDCl_3$, 25 °C): δ −55.74, −65.84, −67.71, −71.51 (s, 2:2:2:2). IR ($CDCl_3$), ν(CO): 2110 (w), 2069 (vs), 2060 (s), 2017 (vs), 2003 (s), 1983 (m, sh) cm^{-1}. Anal. Calcd for $C_{68}H_{90}O_{33}Si_8Os_6$ (found): C, 29.16 (29.06); H, 3.24 (3.28).

Catalytic Cyclodehydration of 1 to 7 by 3. As described above, a solution of trisilanol **1** (211.5 mg; 0.217 mmol) was heated in *m*-xylene (1.10 mL) for 16 h at 140 °C with 5 wt % of **3** (9.1 mg; 0.010 mmol). Evaporation of the volatiles afforded a 7:3 mixture of **7** and unreacted trisilanol **1** as determined by ^{29}Si NMR spectroscopy.

For **1**: $^{29}Si\{^1H\}$ NMR (99.35 MHz, $CDCl_3$, 25 °C): δ −60.42, −68.18, −69.76 (3:1:3).

For **7**: $^{29}Si\{^1H\}$ NMR (99.35 MHz, $CDCl_3$, 25 °C): δ −56.18, −57.25, −57.66, −67.06 (1:1:2:3). (Note: In the absence of **3**, the cyclodehydration of **1** to **7** does not occur to any significant extent under the same conditions.)

Thermolysis of 5 (NMR Tube Reaction). An NMR tube containing **5** (10.8 mg; 0.006 mmol) in toluene-d_8 (0.4 mL) was progressively heated and periodically monitored by ^1H NMR spectroscopy. After 1 h at 60 °C, no changes were observed in the spectrum. At 90 °C, the Os−H resonance for **3** began to appear at δ −13.30 (versus −12.60 in $CDCl_3$) and grow at the expense of the resonance for **5**. The percentage of **3** relative to total Os−H was 3%, 12%, and 27% after 1, 4, and 12 h, respectively. An electrospray ionization mass spectrum of the crude reaction mixture

Table 1. Details of the X-ray Structure Determinations

	5	8	9
empirical formula	$C_{104}H_{160}O_{44}Os_6Si_{14}\cdot CH_2Cl_2$	$C_{116}H_{180}O_{46}Os_6Si_{16}$	$C_{68}H_{90}O_{33}Os_6Si_8\cdot C_2H_4Cl_2$
fw	3733.71	3901.24	2900.27
temperature, K	158(2)	163(2)	158(2)
wavelength, Å	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*	*C*2/*c*
a, Å	a = 15.8524(7)	a = 51.535(2)	a = 29.3568(18)
b, Å	b = 25.8552(12)	b = 12.9064(5)	b = 13.3023(8)
c, Å	c = 33.6161(15)	c = 24.7552(10)	c = 24.8330(16)
α, deg	α = 90	α = 90	α = 90
β, deg	*β* = 90.6020(10)	*β* = 107.8740(10)	*β* = 106.3810(10)
γ, deg	*γ* = 90	*γ* = 90	*γ* = 90
volume, $Å^3$	13777.4(11)	15670.8(11)	9304.0(10)
Z	4	4	4
density(calc), g/cm^3	1.800	1.654	2.071
absorp coeff, mm^{-1}	5.750	5.041	8.400
F(000)	7312	7696	5520
cryst size, mm^3	0.26 × 0.22 × 0.11	0.25 × 0.12 × 0.05	0.27 × 0.11 × 0.04
θ, deg	1.21 to 28.29	0.83 to 28.31	1.45 to 28.32
index ranges	$-20 \leq h \leq 21$, $-34 \leq k \leq 34$, $-44 \leq l \leq 44$	$-68 \leq h \leq 68$, $-17 \leq k \leq 17$, $-32 \leq l \leq 32$	$-39 \leq h \leq 38$, $-17 \leq k \leq 17$, $-33 \leq l \leq 32$
no. of reflns collected	73 141	83 561	47 919
no. of indep reflns	16 635 [*R*(int) = 0.0433]	19 118 [*R*(int) = 0.1351]	11 206 [*R*(int) = 0.1068]
completeness to *θ* max.	97.2%	98.0%	96.6%
absorp corr	numerical	numerical	numerical
max. and min. transmn	0.5704 and 0.3164	0.7867 and 0.3655	0.7299 and 0.2101
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	16 635/0/765	19 118/336/539	11 206/0/532
goodness-of-fit on F^2 [b]	1.069	1.057	1.041
final *R* indices [$I > 2\sigma(I)$][a]	R1 = 0.0354, wR2 = 0.0779	R1 = 0.0943, wR2 = 0.2741	R1 = 0.0450, wR2 = 0.0876
R indices (all data)[a]	R1 = 0.0509, wR2 = 0.0836	R1 = 0.2209, wR2 = 0.3557	R1 = 0.0907, wR2 = 0.1019
largest diff peak and hole, e·$Å^{-3}$	2.765 and −1.639	3.956 and −2.183	2.284 and −2.461

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum[w(F_o^2 - F_o^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [b] 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 total number of parameters refined.

after 12 h at 90 °C revealed prominent peaks for unreacted **5** (*m*/*e* 997 ($M + Na^+$), 974 ($M + H^+$)) and silanol **7** (*m*/*e* 956 ($M + H^+$)).

Reaction of 4 with 1 (NMR Tube Reaction). An NMR tube containing **4** (42.6 mg; 0.024 mmol) and trisilanol **1** (24.1 mg; 0.024 mmol) in toluene-d_8 (0.4 mL) was progressively heated and periodically monitored by ^1H NMR spectroscopy. No significant changes were observed in the spectrum after 1 h at 60 °C and 1 h at 90 °C. After 1 h at 110 °C, a very small resonance characteristic of **3** appeared at δ −13.30 (versus −12.60 in $CDCl_3$). No further changes in the Os−H region of the spectrum were noted after 4.5 h at 100 °C and 1 h at 140 °C. After 12 h at 140 °C, the Os−H resonance for **3** is nearly gone and the ^1H NMR spectrum exhibits a prominent resonance for **4** (δ −12.65). Small resonances are also observed at δ −9.86, −13.30 (characteristic of **3**), −15.03, and −20.70. The ^{13}C NMR spectrum exhibits methine (Si*C*H) resonances for **4** (δ 25.18, 24.41, 24.32, 23.77, 23.20 (1:2:1:2:1)) and **7** (δ 25.18, 23.93, 23.90, 23.77, 23.13 (1:2:1:2:1)). The characteristic methine resonances for trisilanol **1** (δ 24.79, 24.39, 23.87 (3:3:1)) were not observed.

Reaction of 4 with NEt_4OH. Aqueous 20% Et_4NOH (22 μL) was added to a solution of **4** (57.5 mg; 0.032 mmol) in THF (2 mL) at 25 °C. Within 5 min, the color of the solution changed from yellow to orange-brown. After 15 min, the solution was neutralized with 0.5 N HCl. Evaporation of the volatiles afforded a dark brown residue that exhibited the characteristic ^1H NMR resonance ($CDCl_3$) for **3** (δ −12.60), as well as several smaller resonances for other unidentified compounds containing Os−H. There was no resonance attributable to **5** (δ −12.46).

Collection of X-ray Diffraction Data for 5. Crystals suitable for X-ray diffraction studies were grown by allowing CH_3OH to diffuse into a CH_2Cl_2 solution of **5** at 25 °C. Diffraction data were collected on a Bruker CCD platform diffractometer with Mo Kα radiation and a graphite monochromator. Relevant experimental data are colleted in Table 1. The structure was solved by direct methods (SHELXTL). Hydrogen atoms were included using a riding model. Full-matrix least-squares refinement of positional and thermal parameters (anisotropic for all non-H atoms) led to convergence with R1 = 0.0354, wR2 = 0.0779 and GOF = 1.069 for 765 variables refined against those 13 724 data with $I > 2.0\sigma(I)$. All other details regarding the crystal structure appear in the Supporting Information.

Collection of X-ray Diffraction Data for 8. Well-formed but poorly diffracting crystals were grown by allowing CH_3OH to diffuse into a CH_2Cl_2 solution of **8** at 25 °C. Diffraction data were collected on a Bruker CCD platform diffractometer with Mo Kα radiation and a graphite monochromator. Relevant experimental data are colleted in Table 1. The structure was solved by direct methods (SHELXTL). Seven of eight cyclohexyl groups exhibit large thermal ellipsoids when refined with anisotropic thermal parameters; these were refined as groups without hydrogen atoms. Full-matrix least-squares refinement of positional and thermal parameters (anisotropic for all remaining atoms) led to convergence with R1 = 0.0943, wR2 = 0.2741 and GOF = 1.057 for 539 variables refined against those 7750 data with $I > 2.0\sigma(I)$. All other details regarding the crystal structure appear in the Supporting Information.

Collection of X-ray Diffraction Data for 9. Crystals suitable for X-ray diffraction studies were grown by recrystallization from hot 1,2-dichloroethane. Diffraction data were collected on a Bruker CCD platform diffractometer with Mo Kα radiation and a graphite monochromator. Relevant experimental data are collected in Table 1. The structure was solved by direct methods (SHELXTL). Hydrogen atoms were included using a riding model. Full-matrix least-squares refinement of positional and thermal parameters (anisotropic for all non-H atoms) led to convergence with R1 = 0.0450, wR2 = 0.0876 and GOF = 1.041 for 532 variables refined against those 7652 data with $I > 2.0\sigma(I)$. All other details regarding the crystal structure appear in the Supporting Information.

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Supporting Information Available: Complete details on the X-ray analysis of **5**, **8**, and **9**, including tables of bond distances and angles, thermal parameters, hydrogen atom coordinates, and ORTEP figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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