Novel High-Yield Method for the Synthesis of [$Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiR}_2R')$] Species and X-ray Characterization of [$Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})$] and [$Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})$], First Molecular Models of Osmium Surface Species Anchored to Vicinal and Geminal Surface Silanols

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The easy replacement of the hydroxy ligand in [$Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})$] by siloxy ligands affords a high-yield procedure to model compounds of the type [$Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiR}_2R')$] (R = Et, Ph; R′ = Et, Ph, OH, $OSiPh_2OH$), a springboard to better understand the reactivity of osmium carbonyl species on the silica surface. The new clusters [$Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})$] and [$Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})$], characterized by X-ray crystallography, represent the first molecular models of silica-anchored [$Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)$] having a ligand that mimics surface geminal and vicinal silanols, respectively.

Introduction

Since the pioneering work of Ugo and Basset on the covalent binding of the "$Os_3(CO)_{10}(\mu\text{-H})$" fragment to the silica surface via surface silanol groups,[1−3] a lot of spectroscopic work has been devoted to confirm the nature of the species formed by interaction of [$Os_3(CO)_{12}$] with silica at ca. 150 °C because, based only on infrared evidence, the triosmium core could bind a single surface oxygen, to form [$Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)$], or two surface oxygens to form [$Os_3(CO)_{10}(\mu\text{-OSi}\equiv)_2$].[1−3] Evidence for the binding via a single surface silanol group has been reached by infrared,[1−6] Raman,[4] EXAFS [1b,6,7] and ^{13}C NMR[8] spectroscopies. Computer modeling[9,10] and the reaction of [$Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)$] with HF(aq) and HCl(aq) to give [$Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})$][11] and [$Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-Cl})$],[12] respectively, confirmed the binding of the osmium carbonyl cluster to the silica surface via only one silanol group and its hydridic nature.

Such an organometallic carbonyl cluster species covalently bound to the silica surface not only is a catalyst for olefin isomerization[13] and hydrogenation[14] but also appears to be a possible intermediate in the high-yield synthesis of various neutral and anionic osmium carbonyl clusters starting from $OsCl_3$ or [$Os(CO)_3Cl_2$]$_2$ supported on silica in the presence of alkali carbonates and physisorbed water.[15,16] However heterogeneous systems are more difficult to characterize than homogeneous systems. Therefore, due to the usefulness of specific organometallic molecules as models for getting a better understanding of the nature of surface organometallic species,[17−23] the synthesis of molecular

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models of the surface species $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi\equiv)]$ has attracted increasing attention.[2,17,18,19d] However, models such as $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiR_3)]$ (R = Et, Ph)[2,17,18] and $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi_7O_{10}(c\text{-}C_6H_{11})_7)]$[19d] could be obtained only with rather low yields (ca. 8−28%) in one or more steps starting from $[Os_3(CO)_{12}]$. Probably for this reason, the more easily prepared $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OPh)]$ was used as molecular model in order to obtain mechanistic insight into the olefin hydrogenation catalyzed by silica-anchored $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi\equiv)]$.[14]

Surprisingly, only molecular models with a ligand mimicking surface-isolated silanols had been prepared,[2,17,18,19d] although on the silica surface there are different silanol types that could exhibit different reactivity and whose concentration is a function of the temperature:[24](i) the isolated groups (or free silanols, where the surface silicon atom has three bonds into the bulk structure and the fourth bond attached to a single OH group), which correspond to 25% of the total surface silanols at 200 °C, a temperature similar to that used for the preparation of silica-anchored $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi\equiv)]$;[1−3] (ii) the geminal silanols (where two hydroxyl groups are attached to one silicon atom), which correspond to 13% of the total surface silanols at 200 °C; (iii) the vicinal silanols (where two single silanol groups, attached to different silicon atoms, are close enough to hydrogen bond), which correspond to 62% of the total surface silanols at 200 °C.

Computer modeling has suggested binding of the "$Os_3(CO)_{10}(\mu\text{-}H)$" moiety to vicinal or geminal surface silanols;[9,10] therefore it was an interesting challenge to find an easy route for a simple, high-yield preparation of molecular models of the silica-anchored $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi\equiv)]$ species grafted not only to a surface-isolated silanol but also to a surface vicinal or even geminal silanol.

In the course of our investigation on the multistep process of formation of various osmium carbonyl clusters from silica physisorbed $OsCl_3$ or $[Os(CO)_3Cl_2]_2$,[16] we reached clear evidence for a facile equilibrium on the silica surface between physisorbed $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ and $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi\equiv)]$.[15] Such an observation prompted us to investigate the reaction of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ with different molecular silanols in order to prepare a significant series of molecular models. Our choice was also supported by our recent finding of a high-yield synthesis of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OR)]$ (R = Me, Bu, or Ph) by reaction of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ with ROH.[25] Since the displacement of the hydroxy ligand was favored by an increased acidity of the ROH species (e.g., PhOH better than MeOH), it was expected that molecular silanols should displace rather easily the hydroxy ligand from $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ because their acidity is higher than that of alcohols, although it is lower than that of phenol.[26] To mimic in an extensive way the behavior of a silica surface, we choose three types of molecular silanols: (i) R_3SiOH (R = Et, Ph) to mimic surface-isolated silanols; (ii) $Ph_2Si(OH)_2$ to mimic surface geminal silanols, and (iii) $HOSiPh_2OSiPh_2OH$ to mimic surface vicinal silanols.

In this work we present the results of this investigation which, by reproducing a reaction that occurs on the silica surface, led to a new high-yield method for the preparation, under mild conditions and in excellent yields, of the known models $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiR_3)]$ (R = Et, Ph), obtained up to now in very low yields.[2,17,18] We also report the synthesis and X-ray characterization of the new species $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$ and $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$, which are the first molecular models of silica-anchored $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi\equiv)]$ having a ligand that mimics surface geminal and vicinal silanols, respectively.

Results and Discussion

1. Synthesis of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiR_2R')]$ (R = Et, Ph; R′ = Et, Ph, OH, $OSiPh_2OH$). We have evidence from our investigation on the reactivity of silica physisorbed $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$[15] that the displacement of the hydroxy group by surface silanol groups is an equilibrium reaction:

$$[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)] + {\equiv}SiOH \leftrightarrows [Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi\equiv)] + H_2O$$

Similar evidence has been reached by Bergman et al. with a hydroxo iridium complex.[22] Therefore when extending this kind of reactivity to organic silanols, we had to work with continuous water removal, for example by use of a Markusson apparatus or by working in the presence of a water scavenger such as P_2O_5. This procedure must be carefully defined in order to avoid self-condensation of silanols to siloxanes.[27]

1.1. Synthesis of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_3)]$. The reaction of Ph_3SiOH with $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$, prepared by hydrolysis of silica-anchored $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi\equiv)]$,[25] was first investigated under nitrogen in anhydrous *m*-xylene at reflux temperature (138 °C), using a Markusson apparatus in order to shift the equilibrium by removing water. The reaction was best followed by ^1H NMR spectroscopy, looking at the molar ratio of the H−Os resonance of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ (δ in $CDCl_3$ = −12.64 ppm) and $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_3)]$ (δ in $CDCl_3$ = −11.36 ppm).

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Table 1. Synthesis of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiR}_2\text{R}')]$ (R = Et, Ph; R′ = Et, Ph, $OSiPh_2OH$, OH) from $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$[a]

$R_2R'SiOH$	$[HOs_3(CO)_{10}OH]$mol/L	molar ratio $[HOs_3(CO)_{10}OH]:R_2R'SiOH$	*t* (h)	$[HOs_3(CO)_{10}OSiR_2R']$ yield (%)
Ph_3SiOH[b]	6×10^{-4}	1:30	5	25[c]
Ph_3SiOH[b,d]	6×10^{-4}	1:300	5	50[c]
			24	100[c]
$Ph_3SiOH + HBF_4$[b]	6×10^{-4}	1:300	10	0[c]
Ph_3SiOH[e]	1×10^{-1}	1:2	5	100[c] (84)[f]
Ph_3SiOH[e]	1×10^{-1}	1:1	7	67[c,g]
Et_3SiOH[b]	4×10^{-4}	1:300	24	50[c]
Et_3SiOH[e,h]	6×10^{-1}	1:9	2.5	100[c] (81)[f]
$O(SiPh_2OH)_2$[e]	1×10^{-1}	1:2	4	100[c] (84)[f]
$O(SiPh_2OH)_2$[e]	1×10^{-1}	2:1	11	50[c]
$Ph_2Si(OH)_2$[e]	5×10^{-2}	1:2	3	40[c,i]
$Ph_2Si(OH)_2$[e]	9×10^{-2}	1:10	2.5	69[c,j]
$Ph_2Si(OH)_2$[e]	3×10^{-2}	1:60	0.83	100[c] (79)[f]
			2.5	77[c,k]

[a] Reactions carried out under N_2 in *m*-xylene at 138 °C. [b] Using the Markusson apparatus as water scavenger. [c] ^{1}H NMR yield; obtained from the molar ratio of the H−Os resonance of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ and $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiR}_2\text{R}')]$; the remainder is unreacted $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$. [d] Similar results are obtained using P_2O_5 as water scavenger. [e] Using P_2O_5 as water scavenger. [f] Isolated yields of material after chromatography on silica gel. [g] $[H_2Os_3(CO)_{10}]$ (4% yield) is also formed. [h] Reaction carried out in pure Et_3SiOH. [i] $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$ (20% yield) is also formed. [j] $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$ is also formed (31% yield); similar results are obtained with a concentration of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})] = 3 \times 10^{-2}$ M. [k] $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$ (23% yield) is also formed.

When a dilute solution of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ (6×10^{-4} M) and Ph_3SiOH (molar ratio $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]:Ph_3SiOH = 1:30$) in *m*-xylene is refluxed for 5 h, $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_3)]$ is obtained in 25% yield (^{1}H NMR yield; Table 1), the remainder being unreacted $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$. An increase of the reaction time leads to thermal decomposition of the desired cluster, affording a mixture of $[H_2Os_3(CO)_{10}]$, $[H_4Os_4(CO)_{12}]$, and traces of a still unidentified hydridic carbonyl osmium species (δ in $CDCl_3 = -15.54$ ppm). The thermal decomposition of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_3)]$ to metallic particles and unidentified carbonyl species was previously reported.[18]

However, in agreement with the increased reactivity of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ when working with excess phenol to give $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OPh})]$,[25] the formation of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_3)]$ is favored when the relative amount of Ph_3SiOH is increased. By using a molar ratio $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]:Ph_3SiOH = 1:300$, $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_3)]$ is obtained in 50%, 66%, and 100% yields after 5, 10, and 24 h, respectively. Similar results are obtained by using a small reaction flask equipped with a drying tube containing P_2O_5, instead of the Markusson apparatus (Table 1).

While the formation of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OR})]$ (R = Me, Bu, Ph) from $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ and ROH is acid-catalyzed,[25] the addition of a few drops of $HBF_4 \cdot Et_2O$ inhibits the formation of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_3)]$ due to the known fast condensation of silanols under acidic conditions.[27]

The use of excess silanol, which requires a difficult purification, can be avoided by working with a concentrated solution of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ (1×10^{-1} M instead of 6×10^{-4} M). In this latter case, the formation of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_3)]$ occurs readily, even without an excess of Ph_3SiOH, and is much faster than its thermal decomposition. Treatment of a solution of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ (1×10^{-1} M) and Ph_3SiOH (molar ratio $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]:Ph_3SiOH = 1:2$) in *m*-xylene, at 138 °C under nitrogen and in the presence of P_2O_5 for 5 h, affords $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_3)]$ in quantitative yield, as shown by ^{1}H NMR spectroscopy. Evaporation of the solvent, followed by chromatography, affords the final product in 84% isolated yield.

1.2. Synthesis of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$. When a dilute solution of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ ($(4-6) \times 10^{-4}$ M) and Et_3SiOH (molar ratio $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]:Et_3SiOH = 1:300$) in *m*-xylene is refluxed, under nitrogen using a Markusson apparatus, for 10 and 24 h, $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$ is obtained in 25% and 50% yields only, respectively (^{1}H NMR yield; Table 1), the remainder being unreacted $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$.

However, by working in pure Et_3SiOH (molar ratio $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]:Et_3SiOH = 1:9$), at 138 °C under nitrogen and in the presence of P_2O_5, $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ is rapidly (less than 3 h) converted to $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$ in quantitative yield (Table 1). Evaporation of the excess of Et_3SiOH, followed by chromatography, affords the final product in 81% isolated yield.

1.3. Synthesis of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$. Treatment of a solution of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ (1×10^{-1} M) and $HOSiPh_2OSiPh_2OH$ (molar ratio $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]:HOSiPh_2OSiPh_2OH = 1:2$) in *m*-xylene, for 4 h at 138 °C under nitrogen and in the presence of P_2O_5, affords $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$ in quantitative yield, as shown by ^{1}H NMR spectroscopy (Table 1). Evaporation of the solvent, followed by chromatography, affords the final product in 84% isolated yield.

The structure of the new cluster $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$ was characterized by infrared, ^{1}H NMR, ^{29}Si NMR, and mass spectra (see Experimental Section) and confirmed by X-ray diffraction (Figure 1, see later). This is the first molecular model of silica-anchored $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ having a ligand that better mimics the silica surface. In fact at the temperature (less than 200 °C) used for the formation of silica-anchored $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$,[1−3] most surface silanols are vicinal (more than 62%);[24] in addition computer modeling showed that a good fit can be achieved by placing the "$Os_3(CO)_{10}(\mu\text{-H})$" fragment on a vicinal oxygen of a silica surface siloxane group.[9,10]

1.4. Synthesis of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]$. Computer modeling for the surface sites of hydroxylated

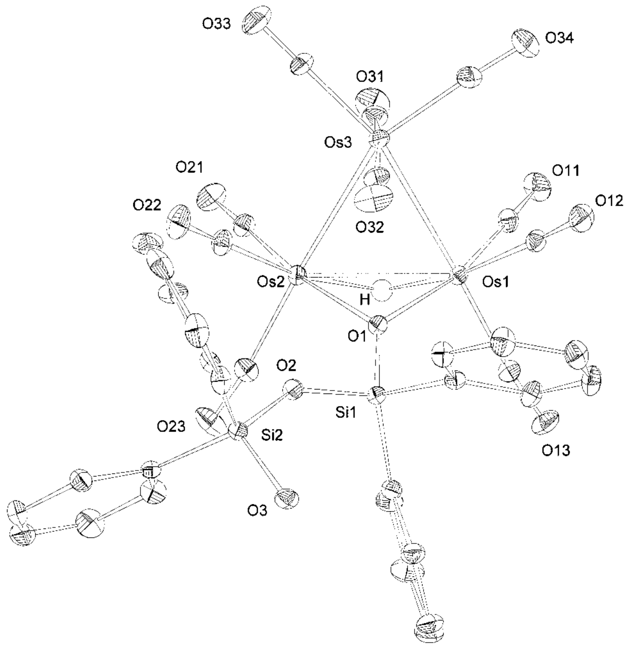

Figure 1. ORTEP diagram of $[\mathrm{Os_3(CO)_{10}}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{-OSiPh}_2\text{OH})]$ showing 50% thermal ellipsoids. C atoms of the CO groups bear the same numbering of the corresponding O atoms. H atoms of the phenyl groups are omitted for clarity.

silica, based on the structure of β-cristobalite, suggested that the "$\mathrm{Os_3(CO)_{10}}(\mu\text{-H})$" fragment cannot be accommodated on a geminal silanol of a fully hydroxylated (100) surface. However, a satisfactory fit can be achieved by placing the cluster on a geminal silanol of a defect site created by the intersection of the (100) face with the (001) face.[9] To confirm that this kind of unusual and more difficult binding to the silica surface could occur, we choose $\mathrm{Ph_2Si(OH)_2}$ as a simple model for geminal silanols of the silica surface. Treatment of a solution of $[\mathrm{Os_3(CO)_{10}}(\mu\text{-H})(\mu\text{-OH})]$ (5×10^{-2} M) and $\mathrm{Ph_2Si(OH)_2}$ (molar ratio $[\mathrm{Os_3(CO)_{10}}(\mu\text{-H})(\mu\text{-OH})]$: $\mathrm{Ph_2Si(OH)_2} = 1{:}2$) in *m*-xylene, for 3 h at 138 °C under nitrogen and in the presence of $\mathrm{P_2O_5}$, affords $[\mathrm{Os_3(CO)_{10}}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{-OH})]$ (40% ^{1}H NMR yield; Table 1) along with some $[\mathrm{Os_3(CO)_{10}}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$ (20% ^{1}H NMR yield), the remainder being unreacted $[\mathrm{Os_3(CO)_{10}}(\mu\text{-H})(\mu\text{-OH})]$.

The reaction is easier in the presence of a higher amount of $\mathrm{Ph_2Si(OH)_2}$ (molar ratio $[\mathrm{Os_3(CO)_{10}}(\mu\text{-H})(\mu\text{-OH})]$:$\mathrm{Ph_2Si(OH)_2} = 1{:}10$; concentration of $[\mathrm{Os_3(CO)_{10}}(\mu\text{-H})(\mu\text{-OH})] = (3-9) \times 10^{-2}$ M). After 2.5 h, the conversion of $[\mathrm{Os_3(CO)_{10}}(\mu\text{-H})(\mu\text{-OH})]$ is complete, but a mixture of $[\mathrm{Os_3(CO)_{10}}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]$ (69% ^{1}H NMR yield) and $[\mathrm{Os_3(CO)_{10}}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$ (31% ^{1}H NMR yield) is obtained, which can be separated by column chromatography.

$[\mathrm{Os_3(CO)_{10}}(\mu\text{-H})(\mu\text{-OH})]$ can be selectively converted to $[\mathrm{Os_3(CO)_{10}}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]$ only by working under well-controlled conditions, with a huge amount of $\mathrm{Ph_2Si(OH)_2}$ (molar ratio $[\mathrm{Os_3(CO)_{10}}(\mu\text{-H})(\mu\text{-OH})]$:$\mathrm{Ph_2Si\text{-}(OH)_2} = 1{:}60$). After 50 min, the desired cluster is formed in 100% ^{1}H NMR yield. Evaporation of the solvent, followed by chromatography, affords the pure cluster in 79% isolated yield. Interestingly, an increase of the reaction time to 2.5 h decreases the selectivity, leading to the formation of some $[\mathrm{Os_3(CO)_{10}}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$ (23% yield), due to further condensation of $[\mathrm{Os_3(CO)_{10}}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]$ with excess $\mathrm{Ph_2Si(OH)_2}$.

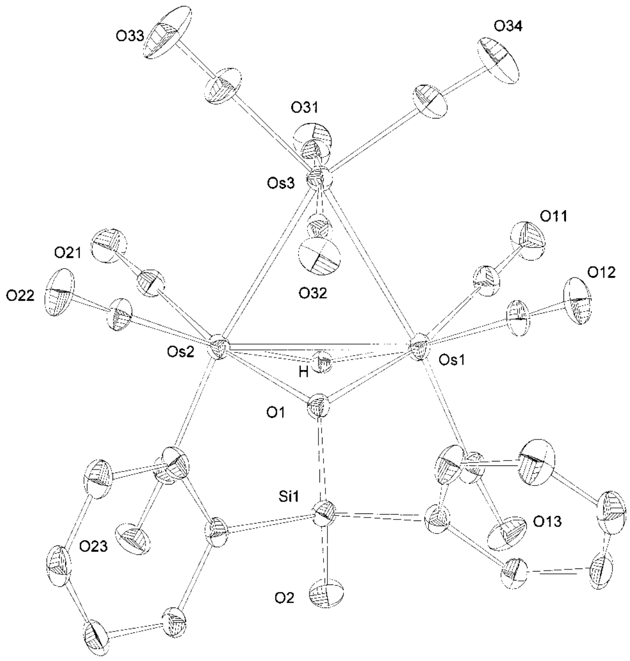

Figure 2. ORTEP diagram of $[\mathrm{Os_3(CO)_{10}}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{-OH})]$ showing 50% thermal ellipsoids. C atoms of the CO groups bear the same numbering of the corresponding O atoms. H atoms of the phenyl groups are omitted for clarity.

The structure of the new cluster $[\mathrm{Os_3(CO)_{10}}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]$ was characterized by infrared, ^{1}H NMR, ^{29}Si NMR, and mass spectra (see Experimental Section) and confirmed by X-ray diffraction (Figure 2, see later). This is the first molecular model of silica-anchored $[\mathrm{Os_3(CO)_{10}}(\mu\text{-H})(\mu\text{-OSi}{\equiv})]$ having a ligand that mimics surface geminal silanols.

1.5. An Investigation of the Reactivity of the Free Silanol Groups of $[\mathrm{Os_3(CO)_{10}}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{-OSiPh}_2\text{OH})]$ and $[\mathrm{Os_3(CO)_{10}}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]$.

Both silanol groups of either the disilanol $\mathrm{HOSiPh_2\text{-}OSiPh_2OH}$ or the silanediol $\mathrm{Ph_2Si(OH)_2}$ can react with various early transition metals and with main group metals, affording cyclic metallasiloxanes.[23] For example reaction of $\mathrm{HOSiPh_2OSiPh_2OH}$ with $\mathrm{TiCl_4}$ affords the spirocyclic complex $[\mathrm{Ti(OSiPh_2OSiPh_2O)_2}]$,[28] while reaction with $[\mathrm{Zr(CH_2SiMe_3)_4}]$ leads to the formation of $[\mathrm{(Me_3SiCH_2)_2Zr(OSiPh_2OSiPh_2O)}]$ with a six-membered $\mathrm{ZrO_3Si_2}$ ring.[23,29] Recently it was reported that the same disilanol reacts with chromium trioxide to give $[\mathrm{Cr({=}O)_2\text{-}(OSiPh_2OSiPh_2O)}]_2$, where the two disilanolate ligands bind to two chromium dioxo units, generating a unique 12-membered metallacyclic fragment.[30] In addition, $\mathrm{Ph_2Si(OH)_2}$ shows a tendency to self-condense. For example, it reacts with $\mathrm{Ti(OBu)_4}$ to yield the spirocyclic complex $[\mathrm{Ti(OSiPh_2(OSiPh_2)_3O)_2}]$,[31] although it reacts with $\mathrm{R_2GeX_2}$ (R = Me, Ph) to give $[\mathrm{Ph_2SiO_2GeR_2}]_2$, which

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has a $Ge_2Si_2O_4$ eight-membered ring core structure.[32] Therefore it was interesting to find whether the remaining free silanol groups of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$ and $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$ could react with an excess of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$.

However, various attempts to prepare bridged dinuclear species such as $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2O\text{-}\mu)(\mu\text{-}H)(CO)_{10}Os_3]$ or $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2O\text{-}\mu)(\mu\text{-}H)(CO)_{10}Os_3]$ failed. Working under standard reaction conditions used for the preparation of mononuclear models starting from $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$, an excess of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$ does not react with $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ (molar ratio $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$:$[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)] = 1:4$; see Experimental Section). The same lack of reactivity was shown by $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$ working under similar conditions.

It appears that, under these conditions, the free silanol groups of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$ and $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$ do not displace easily the hydroxy ligand of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$. The reason for this much lower reactivity is not clear yet. It cannot be attributed to a much lower acidity of the remaining free silanol groups since the ^{29}Si NMR chemical shift of $HOSiPh_2OSiPh_2OH$ ($\delta = -36.37$ ppm in $CDCl_3$) is very similar to that of the free silanol of the complex $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$ ($\delta = -36.41$ ppm in $CDCl_3$), suggesting a similar electron density at silicon in both compounds.[33] The approach of another $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ cluster to the free silanol group of a geminal structure could be difficult due to the proximity of the fragment "$Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2)$" (see Figure 2). However this approach cannot be so hindered in the case of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$, where the silanol group should be pointing, as in the crystal structure (see Figure 1), to the other side with respect to the "$Os_3(CO)_{10}(\mu\text{-}H)$" fragment.

Although we cannot give at the moment a satisfactory explanation, these results are in agreement with the observation that silica-anchored $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi\equiv)]$ can be prepared only with loadings less than 4 wt % Os/SiO_2,[8,25] which corresponds to a grafting on less than 5% of the total surface silanol groups when working with Degussa Aerosil 200 (number of surface silanols equals ca. 4.9 OH/nm^2, corresponding to 1.5 mmol $OH/g\ SiO_2$).[24] The failure to obtain silica-anchored $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi\equiv)]$, with high loadings, could be due to the low reactivity of silanol groups located near surface silanolate groups binding a "$Os_3(CO)_{10}(\mu\text{-}H)$" fragment.

We investigated also another route to $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2O\text{-}\mu)(\mu\text{-}H)(CO)_{10}Os_3]$ since it is known that reaction of the dilithium salt $O(SiPh_2OLi)_2$ with various metal chlorides affords silanolate derivatives (e.g., $CoCl_2$ can be converted to $[Co(OSiPh_2OSiPh_2O)_2][Li(THF)_2]_2$);[34] in addition, $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}Cl)]$ was reported to react with lithium phenylacetylide, at room temperature, to give $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)]$.[35] However both Ph_3SiOLi and $O(SiPh_2OLi)_2$[36] do not react with $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}Cl)]$ and $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}O_2CCF_3]$, by working under nitrogen in benzene in a range of temperatures between 25 and 75 °C.

2. X-ray Structures of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$ and $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$. The structures of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$ and $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$ are of a certain interest, being the first examples of a "$Os_3(CO)_{10}(\mu\text{-}H)$" cluster core carrying a free silanol group. The molecular arrangements are shown with the atomic labeling in Figures 1 and 2. Relevant bond distances and angles are listed in Table 2. The two compounds share the expected presence of a triangular metal atom framework with two "long" (Os1−Os3 and Os2−Os3) and one "short" Os−Os (Os1−Os2) edge. The short edge, in both clusters, is bridged by the μ-$OSiR_2OX$ ligand and by the μ-H (hydride) atom (which has been located in the Fourier map and refined in both cases). As commonly observed for $M(\mu\text{-}H)(\mu\text{-}X)M$ moieties, the lengthening that usually accompanies the formation of a three-center two-electron bond upon H-bridging is counterbalanced by an effect in the opposite direction due to the μ-OX ligand; this eventually results in a shortening of the Os−Os distance. The Os−C bond distances are strictly comparable in the two clusters, and their pattern clearly convey the picture that their relative length depends on the nature of the *trans*-ligand: *trans*-to-O (C11 and C21, av 1.873(2) Å) < *trans*-to-H (C12 and C22, av 1.907(5) Å) ≈ *trans*-to-Os (C33 and C34, av 1.913(4) Å) < *trans*-to-Os (C13 and C23, av 1.934(9) Å) ≈ *trans*-to-CO (C31 and C32, av 1.943(12) Å).

The "$Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}O{-})$" cores, as far as only the bond lengths are taken into account, conform to an idealized C_s symmetry (the pseudo mirror plane passing through the Os3, H, and O atoms). This is no longer true if we consider that the Os2−Os3−C33 angle (average in the two clusters 105.0°) is much larger than the Os1−Os3−C34 one (average in the two clusters 96.1°). However, it is not clear if this behavior is due to the fact that the μ-$OSiR_2OX$ ligands do not conform to C_s symmetry. The different steric requirements of the μ-$OSiR_2OX$ and μ-H ligands are easily quantified by the analysis of the distortion of their environment [the Os1−Os2−C22 and Os2−Os1−C12 (which range from 133.0° to 136.6°) are definitely larger than the Os1−Os2−C21 and Os2−Os1−C11 bond angles (which range from 117.4° to 120.4°)].

These molecular characteristics parallel those of the related $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}Y)]$ models (Y = $OSiEt_3$,[18] $OSi_7O_{10}(c\text{-}C_6H_{11})_7$,[19d] OR[37]), confirming that the other substituents attached to the silicon atom linked to the Os_3 core do not have a significant influence on the dimensions of the "$Os_3(CO)_{10}(\mu\text{-}H)$" moiety and in particular on the "$Os_2(\mu\text{-}H)(\mu\text{-}OSi\equiv)$" bond distances.

Finally in both crystal structures the free silanol groups do not interact via intramolecular or intermolecular hydrogen bonding either with the carbonyl groups of a "$Os_3(CO)_{10}(\mu\text{-}H)$" moiety or with an O atom

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Table 2. Bond Lengths (Å) and Angles (deg) for [$Os_3(CO)_{10}(\mu$-H)(μ-$OSiPh_2OSiPh_2OH$)] and [$Os_3(CO)_{10}(\mu$-H)(μ-$OSiPh_2OH$)]

Os(1)−C(11)	1.875(5)	1.873(5)
Os(1)−C(12)	1.914(5)	1.901(6)
Os(1)−C(13)	1.939(4)	1.934(5)
Os(1)−O(1)	2.127(2)	2.128(3)
Os(1)−H	1.72(3)	1.65(4)
Os(1)−Os(2)	2.7999(2)	2.8090(3
Os(1)−Os(3)	2.8254(2)	2.8233(3
Os(2)−C(21)	1.871(4)	1.872(5)
Os(2)−C(22)	1.905(5)	1.909(6)
Os(2)−C(23)	1.921(5)	1.941(5)
Os(2)−O(1)	2.133(3)	2.126(3)
Os(2)−H	1.83(3)	1.72(4)
Os(2)−Os(3)	2.8400(3)	2.8280(3
Os(3)−C(33)	1.908(5)	1.913(6)
Os(3)−C(34)	1.910(6)	1.917(6)
Os(3)−C(32)	1.948(5)	1.924(6)
Os(3)−C(31)	1.948(5)	1.953(6)
C(11)−O(11)	1.135(5)	1.143(5)
C(12)−O(12)	1.128(5)	1.141(6)
C(13)−O(13)	1.126(5)	1.149(6)
C(21)−O(21)	1.148(5)	1.149(5)
C(22)−O(22)	1.140(5)	1.138(6)
C(23)−O(23)	1.146(6)	1.135(5)
C(31)−O(31)	1.135(6)	1.139(6)
C(32)−O(32)	1.132(6)	1.149(6)
C(33)−O(33)	1.133(6)	1.132(6)
C(34)−O(34)	1.147(6)	1.124(6)
Si(1)−O(2)	1.631(3)	1.654(3)
Si(1)−O(1)	1.638(3)	1.645(3)
Si(1)−C(111)	1.858(4)	1.852(5)
Si(1)−C(121)	1.862(4)	1.857(5)
Si(2)−O(2)	1.631(3)	
Si(2)−O(3)	1.632(3)	
Si(2)−C(221)	1.853(4)	
Si(2)−C(211)	1.862(4)	
C(11)−Os(1)−C(12)	89.1(2)	89.5(2)
C(11)−Os(1)−C(13)	92.61(19)	91.6(2)
C(12)−Os(1)−C(13)	95.83(18)	96.2(2)
C(11)−Os(1)−O(1)	166.31(15)	168.29(18)
C(12)−Os(1)−O(1)	100.39(16)	98.30(16)
C(13)−Os(1)−O(1)	96.14(15)	96.18(16)
C(11)−Os(1)−Os(2)	117.42(14)	120.07(17)
C(12)−Os(1)−Os(2)	134.64(13)	136.58(15)
C(13)−Os(1)−Os(2)	117.16(14)	112.47(15)
O(1)−Os(1)−Os(2)	49.01(7)	48.65(7)
C(11)−Os(1)−Os(3)	87.94(14)	89.38(17)
C(12)−Os(1)−Os(3)	86.44(13)	91.94(17)
C(13)−Os(1)−Os(3)	177.68(14)	171.82(15)
O(1)−Os(1)−Os(3)	82.91(7)	81.69(7)
Os(2)−Os(1)−Os(3)	60.642(7)	60.278(7)
C(21)−Os(2)−C(22)	91.06(19)	88.8(2)
C(21)−Os(2)−C(23)	88.7(2)	92.4(2)
C(22)−Os(2)−C(23)	96.8(2)	97.1(2)
C(21)−Os(2)−O(1)	168.32(16)	168.94(17)
C(22)−Os(2)−O(1)	98.43(15)	99.08(16)
C(23)−Os(2)−O(1)	96.86(16)	94.33(16)
C(21)−Os(2)−Os(1)	119.51(14)	120.43(15)
C(22)−Os(2)−Os(1)	132.98(15)	136.46(14)
C(23)−Os(2)−Os(1)	117.04(15)	111.73(15)
O(1)−Os(2)−Os(1)	48.81(7)	48.70(7)
C(21)−Os(2)−Os(3)	91.40(15)	90.59(14)
C(22)−Os(2)−Os(3)	86.51(16)	90.86(16)
C(23)−Os(2)−Os(3)	176.69(15)	171.59(14)
O(1)−Os(2)−Os(3)	82.44(7)	81.60(7)
Os(1)−Os(2)−Os(3)	60.123(6)	60.110(7)
C(33)−Os(3)−C(34)	100.0(2)	98.9(3)
C(33)−Os(3)−C(32)	90.9(2)	92.8(2)
C(34)−Os(3)−C(32)	93.9(2)	92.4(2)
C(33)−Os(3)−C(31)	93.3(2)	94.0(2)
C(34)−Os(3)−C(31)	94.2(2)	95.7(2)
C(32)−Os(3)−C(31)	170.2(2)	168.6(2)
C(33)−Os(3)−Os(1)	164.14(16)	164.6(2)
C(34)−Os(3)−Os(1)	95.73(15)	96.41(19)
C(32)−Os(3)−Os(1)	85.69(14)	84.23(15)
C(31)−Os(3)−Os(1)	87.86(15)	86.77(15)
C(33)−Os(3)−Os(2)	105.05(16)	105.1(2)
C(34)−Os(3)−Os(2)	154.96(15)	155.98(19)
C(32)−Os(3)−Os(2)	84.55(15)	84.36(14)
C(31)−Os(3)−Os(2)	85.77(15)	84.99(14)
Os(1)−Os(3)−Os(2)	59.235(6)	59.612(7)
O(2)−Si(1)−O(1)	105.77(14)	108.95(17)
O(2)−Si(1)−C(111)	109.96(17)	109.1(2)
O(1)−Si(1)−C(111)	109.33(16)	106.72(19)
O(2)−Si(1)−C(121)	112.40(18)	109.8(2)
O(1)−Si(1)−C(121)	111.01(17)	108.90(19)
C(111)−Si(1)−C(121)	108.33(19)	113.2(2)
O(2)−Si(2)−O(3)	108.72(16)	
O(2)−Si(2)−C(221)	110.97(17)	
O(3)−Si(2)−C(221)	106.54(19)	
O(2)−Si(2)−C(211)	108.38(17)	
O(3)−Si(2)−C(211)	111.09(17)	
C(221)−Si(2)−C(211)	111.13(19)	
O(11)−C(11)−Os(1)	178.5(4)	179.7(5)
O(12)−C(12)−Os(1)	177.6(5)	179.9(6)
O(13)−C(13)−Os(1)	172.8(4)	172.9(5)
O(21)−C(21)−Os(2)	178.1(4)	178.8(4)
O(22)−C(22)−Os(2)	178.8(5)	177.4(5)
O(23)−C(23)−Os(2)	173.8(5)	176.3(5)
O(31)−C(31)−Os(3)	179.9(6)	178.5(5)
O(32)−C(32)−Os(3)	177.3(4)	177.6(5)
O(33)−C(33)−Os(3)	177.4(6)	176.5(6)
O(34)−C(34)−Os(3)	176.9(5)	176.4(6)
Si(1)−O(1)−Os(1)	137.44(15)	125.87(16)
Si(1)−O(1)−Os(2)	135.86(16)	130.60(16)
Os(1)−O(1)−Os(2)	82.18(9)	82.65(10)
Si(2)−O(2)−Si(1)	143.33(19)	
C(112)−C(111)−Si(1)	123.5(3)	123.1(4)
C(116)−C(111)−Si(1)	120.1(3)	120.6(4)
C(126)−C(121)−Si(1)	123.9(3)	124.2(4)
C(122)−C(121)−Si(1)	119.8(3)	120.1(4)
C(216)−C(211)−Si(2)	121.4(3)	
C(212)−C(211)−Si(2)	121.3(3)	
C(226)−C(221)−Si(2)	121.0(4)	
C(222)−C(221)−Si(2)	121.7(3)	

of the organic silicon skeleton (either Os−O−Si or Si−O−Si or SiOH bonds). Therefore, from the X-ray evidence, it appears that intramolecular interactions of the free silanol group with the "$Os_3(CO)_{10}(\mu$-H)" core are not relevant, at least in these new molecular models.

Conclusion

The high-yield synthetic method, described in this paper for making Os−OSi bonds in [$Os_3(CO)_{10}(\mu$-H)(μ-$OSiR_2R'$)] clusters, not only suggests a new way of strong interaction of slightly oxidized metal particles with the silica surface but also may open an easy route for the preparation of new molecular models of osmium carbonyl clusters grafted to surface silanol groups. For instance it seems possible by this new synthetic methodology to achieve the bonding of more than one osmium carbonyl cluster to more sophisticated molecular models of the silica surface carrying many vicinal or geminal silanol groups.[19,20c]

From the chemical behavior and from the X-ray structure of two new molecular models of the silica-anchored [$Os_3(CO)_{10}(\mu$-H)(μ-OSi≡)] species, with ligands mimicking geminal and vicinal surface silanols, we have reached some evidence that the free silanol groups are rather unreactive toward another [$Os_3(CO)_{10}(\mu$-H)(μ-OH)] moiety, despite that there is no evidence of perturbation (for instance by intramolecular hydrogen bonding) of the free silanol groups by the already bonded "$Os_3(CO)_{10}(\mu$-H)" core. This is a new observation, which can be of relevance to the understanding of the process of dispersion of small particles or metal clusters on the silica surface, although it should be confirmed by more sophisticated models of the silica surface carrying many vicinal or geminal silanol groups.[19,20c]

Finally the ready availability of sizable amounts of these molecular models allows now a detailed investigation of their reactivity.[38] Therefore, since homogeneous models can be studied more deeply and more easily than their related surface species, it is now possible to make use of this kind of molecular model not only for the elucidation of the structure of surface species, as was done up to now,[2,17,18,19d] but also for confirming or better defining their rather complex surface behavior, which, up to now, has been suggested from spectroscopic evidence[1−5] or indirectly deduced from mass balance of gaseous products produced by chemical reaction with the surface[1,2] or by oxidation of surface species[39] or even by analogies with the chemical behavior of known related metal carbonyl species.[1]

Experimental Section

General Comments. $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ was prepared according to the literature.[25] Ph_3SiOH and $Ph_2Si(OH)_2$, purchased from Sigma-Aldrich, were recrystallized (CH_2Cl_2) before use. $HOSiPh_2OSiPh_2OH$ was prepared according to the literature[40] by hydrolysis of $ClSiPh_2OSiPh_2Cl$ (purchased from ABCR GmbH & Co), whereas Et_3SiOH was purchased from Sigma-Aldrich and used without further purification. The organic solvents were dried over molecular sieves (3 Å), whereas nitrogen was dried by flowing over drierite. Products were purified by recrystallization or by column chromatography using silica gel 60 (purchased from Fluka). Spectra were obtained by use of the following spectrometers: Bruker-Vector 22 or Jasco FT-IR 420 (IR), Bruker AC-200 or Bruker DRX-300 (^{1}H NMR and ^{29}Si NMR), Varian VG9090 (MS). Elemental analyses were carried out in the analytical laboratory of our department.

1. Syntheses. To reach high yields, we used two strategies to remove water: (i) use of a Markusson apparatus for continuous distillation of water, when working with large (50 mL) amounts of solvent and dilute solutions, and (ii) use of a drying tube containing P_2O_5, particularly when working with small (few mL) amounts of solvent. The second method turned out to be the most convenient also because the best yields were reached by working with concentrated solutions of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ (see Table 1).

Because the infrared spectra in the carbonyl region of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]^{25}$ and of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiR_2R')]$ species (R = Et, Ph; R′ = Et, Ph, OH, $OSiPh_2OH$) are very similar, reactions were best followed by ^{1}H NMR spectroscopy: samples of the reaction mixtures were either analyzed as such or evaporated to dryness and dissolved in $CDCl_3$. ^{1}H NMR yields were obtained by determining the molar ratio from the H−Os resonance of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ (δ in $CDCl_3 = -12.64$ ppm)[25] and of the reaction product $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiR_2R')]$. In some cases, for example by working with dilute solutions of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ (6×10^{-4} M) under not optimized reaction conditions, $[H_2Os_3(CO)_{10}]$ (δ in $CDCl_3 = -11.77$ ppm), $[H_4Os_4(CO)_{12}]$ (δ in $CDCl_3 = -20.45$ ppm), and/or a still unidentified hydride species (δ in $CDCl_3 = -15.54$ ppm) were also formed (see Results and Discussion). The best syntheses for the various $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiR_2R')]$ clusters are described below.

$\mathbf{[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_3)]}$**.** A solution of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]^{25}$ (101 mg; 0.116 mmol) and Ph_3SiOH (66.0 mg; 0.238 mmol; molar ratio $Ph_3SiOH{:}[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)] = 2{:}1$) in anhydrous *m*-xylene (1 mL; $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)] = 1 \times 10^{-1}$ M) was heated (138 °C) under N_2 in a small flask (5 mL) equipped with a closed Pyrex filter funnel (diameter = ca. 30 mm; height = ca. 250 mm) with a fritted disk containing P_2O_5 (2 g; the distance between the reaction solution and the fritted disk is ca. 120 mm). After 5 h, the formation of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_3)]$ was quantitative, as shown by ^{1}H NMR spectroscopy. The solution was evaporated to dryness, pentane was added to dissolve $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_3)]$, and the resulting suspension was filtered in order to remove the excess Ph_3SiOH. The filtrate was evaporated to dryness, and the residue was chromatographed on a silica column using as eluant pentane/CH_2Cl_2 (10:1), to obtain pure $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_3)]$ (111 mg; 0.098 mmol; 84% yield). The product was characterized by elemental analysis (calcd C, 29.82; H, 1.42; found C, 30.16; H, 1.42), mass spectrometry (in the EI mass spectrum, there is the molecular ion peak at *m*/*e* = 1128 $[M]^+$, followed by peaks corresponding to the successive loss of 10 CO's), infrared spectroscopy (in CH_2Cl_2: ν(CO) 2109(w), 2070(vs), 2057(s), 2021(vs), 1999(m), and 1980(w) cm^{-1}), ^{1}H NMR (in $CDCl_3$: $\delta = 7.44$ (m, 15 H, 3 Ph) and -11.36 (s, 1 H, HOs) ppm), and ^{29}Si NMR (in $CDCl_3$: $\delta = 0.26$ ppm; for comparison the ^{29}Si NMR signal of $HOSiPh_3$ in $CDCl_3$ is at $\delta = -12.47$ ppm).

$\mathbf{[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiEt_3)]}$**.** $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ (153 mg; 0.176 mmol) was dissolved in pure Et_3SiOH (0.25 mL; 1.62 mmol; molar ratio $Et_3SiOH{:}[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)] = 9{:}1$; $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)] = 6 \times 10^{-1}$ M) and heated at 138 °C under N_2 in a small flask (5 mL) equipped with a closed Pyrex filter funnel (diameter = ca. 30 mm; height = ca. 250 mm) with a fritted disk containing P_2O_5 (2 g; the distance between the reaction solution and the fritted disk is 120 mm). The reaction was complete after 2.5 h, as shown by ^{1}H NMR spectroscopy. The solution was evaporated to dryness, and the residue was chromatographed on a silica column using as eluant hexane, to obtain pure $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiEt_3)]$ (140 mg; 0.143 mmol; 81% yield). The product was characterized by elemental analysis (calcd C, 19.53; H, 1.63; found C, 19.84; H, 1.88), mass spectrometry (in the EI mass spectrum, there is the molecular ion peak at *m*/*e* = 983 $[M]^+$, followed by peaks corresponding to the successive loss of 10 CO's), infrared spectroscopy (in CH_2Cl_2: ν(CO) 2108(w), 2069(vs), 2056(s), 2019(vs), 1996(m) and 1981(w) cm^{-1}), ^{1}H NMR (in $CDCl_3$: $\delta = 0.99$ (t, 6 H, 3 CH_2), 0.62 (q, 9 H, 3 CH_3), -12.36 (s, 1 H, HOs) ppm), and ^{29}Si NMR (in $CDCl_3$: $\delta = 38.36$ ppm; for comparison, the ^{29}Si NMR signal of $HOSiEt_3$ in $CDCl_3$ is at $\delta = 19$ ppm).

$\mathbf{[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]}$**.** A solution of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ (165 mg; 0.190 mmol) and $HOSiPh_2OSiPh_2OH$ (159 mg; 0.384 mmol; molar ratio $HOSiPh_2OSiPh_2OH{:}[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)] = 2{:}1$) in anhydrous *m*-xylene (1.5 mL; $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)] = 1.2 \times 10^{-1}$ M) was heated under N_2 in a small flask (5 mL) equipped with a closed Pyrex filter funnel (diameter = ca. 30 mm; height = ca. 250 mm) with a fritted disk containing P_2O_5 (2 g; the distance between the reaction solution and the fritted disk is ca. 120 mm). The reaction was complete after 4 h, as shown by ^{1}H NMR spectroscopy. The solution was evaporated to dryness, and the residue was chromatographed on a silica column using as eluant CH_2Cl_2/pentane (10:3), to obtain pure $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$ (203 mg; 0.160 mmol; 84% yield). Crystals, suitable for X-ray diffraction, of this new cluster were obtained by slow addition at room temperature of pentane to its solution in CH_2Cl_2. $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$ was also characterized by elemental analysis (calcd C, 32.25; H, 1.73; found C, 32.51; H, 1.79), mass spectrometry (in the EI mass spectrum, there is the molecular ion peak at *m*/*e* =

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Table 3. Summary of Crystal Data and Structure Refinement Parameters for $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$ and $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$

formula	$C_{34}H_{21}O_{13}Os_3Si_2$	$C_{22}H_{11}O_{12}Os_3Si$
fw	1264.29	1066.00
cryst syst	monoclinic	triclinic
space group	$P2_1/a$	$P\bar{1}$
a, Å	19.555(1)	9.974(1)
b, Å	9.326(1)	10.413(1)
c, Å	22.079(1)	14.305(1)
α, deg	90.00(1)	100.59(1)
β, deg	111.97(1)	104.50(1)
γ, deg	90.00(1)	101.51(1)
V, Å^3	3734.0(3)	1366.01(12)
Z	4	2
F(000)	2340	962
D(calc), g cm^{-3}	2.249	2.592
temp, K	293(2)	293(2)
diffractometer	SMART	SMART
radiation (graph monochr), Å	0.71073	0.71073
abs coeff, mm^{-1}	10.310	14.020
cryst size, mm	0.20 × 0.10 × 0.10	0.15 × 0.15 × 0.10
scan method	ω	ω
frame width, deg	0.3	0.3
max time per frame, s	20	20
θ range, deg	0.99−29.34	1.52−29.23
index ranges	$-25 \le h \le 25, -12 \le k \le 12, -29 \le l \le 29$	$-13 \le h \le 13, -13 \le k \le 14, -19 \le l \le 19$
reflns collected	56 804	16 756
ind reflns	9414 [R(int) = 0.0283]	6636 [R(int) = 0.0277]
cryst decay, %	no	no
refinement method	least-squares on F_o^2	least-squares on F_o^2
no. of data/restraints/params	9414/0/473	6636/0/347
goodness-of-fit on F_o^2	1.104	0.816
rest goodness-of-fit on F_o^2	1.104	0.816
R indices [$F_o > 4\sigma(F_o)$]	R1 0.0242, wR2 0.0569	R1 0.0215, wR2 0.0421
R indices (all data)	R1 0.0349, wR2 0.0591	R1 0.0320, wR2 0.0436
largest diff peak and hole, e Å^{-3}	0.896 and −1.553	0.674 and −1.064
weighting scheme	calc	calc

1266 $[M]^+$, followed by peaks corresponding to the successive loss of 10 CO's), infrared spectroscopy (in CH_2Cl_2: ν(CO) 2110(w), 2072(vs), 2058(s), 2021(vs), 2001(m), and 1981(w) cm^{-1}), ^1H NMR (in $CDCl_3$: $\delta = 7.45$ (m, 20 H, 4 Ph), 2.78 (s, 1 H, OH), −12.02 (s, 1 H, HOs) ppm), and ^{29}Si NMR (in $CDCl_3$: $\delta = -28.72$ ($OsOSiPh_2O$), −36.41 ($OSiPh_2OH$) ppm; for comparison, the ^{29}Si NMR signal of $HOSiPh_2OSiPh_2OH$ in $CDCl_3$ is at $\delta = -36.37$ ppm and in CD_3COCD_3 is at $\delta = -39.66$ ppm).

$[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$. $Ph_2Si(OH)_2$ (1.738 g; 8.04 mmol) was added to a solution of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ (115 mg; 0.133 mmol; molar ratio $Ph_2Si(OH)_2$:$[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)] = 60:1$) in anhydrous *m*-xylene (4.3 mL; $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)] = 3.1 \times 10^{-2}$ M) in a small flask (5 mL) equipped with a closed Pyrex filter funnel (diameter = ca. 30 mm; height = ca. 250 mm) with a fritted disk containing P_2O_5 (2 g; the distance between the reaction mixture and the fritted disk is ca. 120 mm), and the resulting slurry (due to the huge excess of $Ph_2Si(OH)_2$) was heated under N_2 at 138 °C. After about 15 min a homogeneous solution was obtained. ^1H NMR spectroscopy evidenced the formation of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$ in 67% yield. After 50 min, the formation of this new cluster was quantitative. The solution was evaporated to dryness, and the residue was chromatographed on a silica column using as eluant CH_2Cl_2/hexane (3:2), to obtain pure $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$ (112 mg; 0.105 mmol; 79% yield). Interestingly, an increase of the reaction time to 2.5 h leads to the formation of some $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$ (23% yield) due to the condensation of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$ with excess $Ph_2Si(OH)_2$. Crystals, suitable for X-ray diffraction, of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$ were obtained by slow evaporation at room temperature of its solution in CH_2Cl_2. This new cluster was also characterized by elemental analysis (calcd C, 24.75; H, 1.12; found C, 25.05; H, 1.41), mass spectrometry (in the EI mass spectrum, there is the molecular ion peak at $m/e = 1068$ $[M]^+$, followed by peaks corresponding to the successive loss of 10 CO's), infrared spectroscopy (in CH_2Cl_2: ν(CO) 2109(w), 2072(vs), 2058(s), 2019(vs), 2002(m), and 1979(w) cm^{-1}), ^1H NMR (in $CDCl_3$: $\delta = 7.55$ (m, 10 H, 2 Ph), 2.95 (s, 1 H, OH), −12.50 (s, 1 H, HOs) ppm), and ^{29}Si NMR (in $CDCl_3$: $\delta = -20.72$ ppm; for comparison, the ^{29}Si NMR signal of $Ph_2Si(OH)_2$ in CD_3COCD_3 is at $\delta = -33.01$ ppm).

Attempted Synthesis of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2O\text{-}SiPh_2O\text{-}\mu)(\mu\text{-}H)(CO)_{10}Os_3]$. (i) A solution of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ (77.0 mg; 0.089 mmol) and $HOSiPh_2OSiPh_2OH$ (18.7 mg; 0.045 mmol; molar ratio $HOSiPh_2OSiPh_2OH$:$[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)] = 1:2$) in anhydrous *m*-xylene (0.9 mL; $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)] = 0.99 \times 10^{-1}$ M) was heated (138 °C) under N_2 in a small flask (5 mL) equipped with a closed Pyrex filter funnel (diameter = ca. 30 mm; height = ca. 250 mm) with a fritted disk containing P_2O_5 (2 g; the distance between the reaction solution and the fritted disk is ca. 120 mm). The reaction was monitored by ^1H NMR spectroscopy: after 3 and 11 h, $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$ was formed in 25% and 50% yields, respectively, the remainder being unreacted $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$. (ii) A solution of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ (27.7 mg; 0.032 mmol) and $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$ (154 mg; 0.122 mmol; molar ratio $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$:$[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)] = 4:1$) in anhydrous *m*-xylene (0.3 mL; $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)] = 1 \times 10^{-1}$ M) was heated (138 °C) for 3 h under N_2 in a small flask (5 mL) equipped with a closed Pyrex filter funnel (diameter = ca. 30 mm; height = ca. 250 mm) with a fritted disk containing P_2O_5 (2 g; the distance between the reaction solution and the fritted disk is ca. 120 mm). No reaction occurred, as evidenced by ^1H NMR spectroscopy of the reaction mixture. (iii) A solution of $O(SiPh_2OLi)_2$ in anhydrous benzene (prepared by reaction of $HOSiPh_2OSiPh_2OH$ with BuLi;[36] $[O(SiPh_2OLi)_2] = 3.7 \times 10^{-2}$ M; 0.7 mL corresponding to 0.026 mmol of $O(SiPh_2OLi)_2$) was added to a solution of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}O_2CCF_3)]$[25] (50.4 mg; 0.052 mmol; molar ratio $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}O_2CCF_3)]$:$O(SiPh_2OLi)_2 = 2:1$) in anhydrous benzene (20 mL) and stirred under N_2. After 12 h at room temperature or after 6 h under reflux (75 °C), no reaction occurred, as shown by infrared spectroscopy in the carbonyl region where are present only the bands due to unreacted $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}O_2CCF_3)]$.

2. X-ray Structure Determination of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$ and $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$. A suitable crystal of each compound was chosen and mounted, in air, on a glass fiber onto a goniometer head and collected at room temperature on a Siemens SMART CCD area-detector diffractometer. Crystal data are reported in Table 3. Graphite-monochromatized Mo Kα ($\lambda = 0.71073$ Å) radiation was used with the generator working at 45 kV and 40 mA. Cell parameters and orientation matrix were obtained from least-squares refinement on reflections measured in three different sets of 15 frames each, in the range $0° < \theta < 23°$. The data collection was performed by measuring 2100 frames (20 s per frame; ω scan method, $\Delta\omega = 0.3°$; sample−detector distance fixed at 5 cm), which, upon data reduction, afforded almost all reflections belonging to the sphere with $2\theta < 58°$. The first 100 frames were recollected at the end to monitor crystal decay, which was not observed; an absorption correction was applied (SADABS).[41]

For $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$ a total of 56 804 reflections were collected (9414 unique, $R_{int} = 0.0283$; $R_\sigma = 0.0236$),[42] while for $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$ a total of 16 756 reflections were collected (6636 unique, $R_{int} = 0.0277$; $R_\sigma = 0.0431$).[42] The structures were solved by direct methods (SIR97)[43] and refined with full-matrix-block least-squares (SHELX93);[44] anisotropic temperature factors were assigned to all non-hydrogen atoms. All phenyl hydrogens were riding on their carbon atoms with individual isotropic displacement parameters 1.2 times that of the pertinent carbon atom. The hydridic ligand has been located on the Fourier map and refined in both structures.

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Supporting Information Available: Refined atoms coordinates (Tables S1 and S4), anisotropic thermal parameters (Tables S2 and S5), idealized hydrogen atom coordinates (Tables S3 and S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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[42] $R_{int} = \sum|F_o^2 - F_{mean}^2|/\sum F_o^2$; $R_\sigma = \sum\sigma(F_o^2)/\sum F_o^2$; $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = (\sum(F_o^2 - F_c^2)^2/\sum wF_o^4)^{1/2}$.

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