

Chemical and Thermal Behavior of the Molecular Models [Os₃(CO)₁₀(μ-H)(μ-OSiR₂R')] (R = Et, Ph; R' = Et, Ph, OH, OSiPh₂OH): Molecular Approach to the Clarification of the Surface Chemistry of the Silica-Anchored Cluster [Os₃(CO)₁₀(μ-H)(μ-OSi≡)]

Elena Lucenti, Dominique Roberto,* and Renato Ugo

Dipartimento di Chimica Inorganica, Metallorganica e Analitica and Centro CNR "CSSSCMTBSO", Università di Milano, Via G. Venezian, 21, 20133 Milano, Italy

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The reactivity (e.g., toward hydrolysis, alcoholysis, reduction by CO or H₂) of various [Os₃(CO)₁₀(μ-H)(μ-OSiR₂R')] (R' = Ph, OH, OSiPh₂OH) clusters and the thermal behavior of [Os₃(CO)₁₀(μ-H)(μ-OSiEt₃)] have been studied with the aim of clarifying by a molecular approach some aspects of the surface chemistry of silica-anchored [Os₃(CO)₁₀(μ-H)(μ-OSi≡)]. Their easy and selective reduction to [Os₃(CO)₁₂] (under CO) and to [H₄Os₄(CO)₁₂] (under H₂) suggests that [Os₃(CO)₁₀(μ-H)(μ-OSi≡)] does not require, as a reactive intermediate, a previous hydrolysis to the more reactive molecular species [Os₃(CO)₁₀(μ-H)(μ-OH)] in order to generate different osmium carbonyl clusters in their silica-mediated synthesis starting from OsCl₃ or [Os(CO)₃Cl₂]₂. The thermal behavior of [Os₃(CO)₁₀(μ-H)(μ-OSiEt₃)] dissolved in triethylsilanol (to mimic a silica surface with many available surface silanols) or triglyme (to mimic a highly dehydroxylated silica surface) gives an answer to the controversy on the nature of the products formed by thermal degradation on the silica surface of [Os₃(CO)₁₀(μ-H)(μ-OSi≡)]. In triethylsilanol, oxidation occurs to give a Os(II) hydrido carbonyl species which, on the basis of chemical and spectroscopic evidence, we suggest to be [Os(CO)₃(μ-OSiEt₃)₂(OSiEt₃)(H)Os(CO)₂]_n (n = probably 2), whereas in triglyme an aggregation to high-nuclearity clusters such as [H₄Os₁₀(CO)₂₄]²⁻ and [H₅Os₁₀(CO)₂₄]⁻ occurs. Therefore, it is shown for the first time that molecular models not only are a tool to define structural aspects but also may be a springboard to understand and clarify by a molecular approach aspects of the reactivity of organometallic species on the silica surface.

Introduction

Because of the usefulness of molecular models for getting a better insight into surface organometallic species,^{1–9} the synthesis and structural characterization of molecular organometallic compounds bearing silanolate ligands as models of the silica-anchored surface

species [Os₃(CO)₁₀(μ-H)(μ-OSi≡)], the first well-described organometallic carbonyl cluster species covalently bound to silica, has attracted increasing attention.^{1a,2,3,6b,9} However, this approach was limited to the identification of the structural features. Very little is known about the surface chemistry and thermal decomposition of [Os₃(CO)₁₀(μ-H)(μ-OSi≡)], which not only is a catalyst for olefin isomerization¹⁰ and hydrogenation¹¹ but which also seems to be an intermediate in the synthesis of various neutral and anionic osmium carbonyl clusters starting from OsCl₃ or [Os(CO)₃Cl₂]₂

* To whom correspondence should be addressed. FAX: +39-2-2362748. E-mail: dominique.roberto@unimi.it.

(1) (a) Psaro, R.; Ugo, R.; Besson, B.; Smith, A. K.; Basset, J. M. *J. Organomet. Chem.* **1981**, *213*, 215. (b) Smith, A. K.; Besson, B.; Basset, J. M.; Psaro, R.; Fusi, A.; Ugo, R. *J. Organomet. Chem.* **1980**, *192*, C31. (c) Besson, B.; Moraweck, B.; Smith, A. K.; Basset, J. M.; Psaro, R.; Fusi, A.; Ugo, R. *J. Chem. Soc., Chem. Commun.* **1980**, 569. (d) Ugo, R.; Psaro, R.; Zanderighi, G. M.; Basset, J. M.; Theolier, A.; Smith, A. K. In *Fundamental Research in Homogeneous Catalysis*; Tsutsui, M., Ed.; Plenum Press: New York, 1979; Vol. 3.

(2) (a) Evans, J.; Gracey, B. P. *J. Chem. Soc., Dalton Trans.* **1982**, 1123. (b) Calvert, R. B. Ph.D. Thesis, University of Illinois at Urbana-Champaign, 1979.

(3) D'Ornelas, L.; Choplin, A.; Basset, J. M.; Hsu, L. Y.; Shore, S. *Nouv. J. Chim.* **1985**, *9*, 155.

(4) (a) Zucchi, C.; Shchegolikhina, O. I.; Borsari, M.; Cornia, A.; Gavioli, G.; Fabretti, A. C.; Rentschler, E.; Gatteschi, D.; Ugo, R.; Psaro, R.; Pozdniakova, Y. A.; Lindeman, S. V.; Zhdanov, A. A.; Pályi, G. *J. Mol. Catal. A* **1996**, *107*, 313 and references therein. (b) Vizi-Orosz, A.; Ugo, R.; Psaro, R.; Sironi, A.; Moret, M.; Zucchi, C.; Ghelfi, F.; Pályi, G. *Inorg. Chem.* **1994**, *33*, 4600. (c) Pályi, G.; Zucchi, C.; Ugo, R.; Psaro, R.; Sironi, A.; Vizi-Orosz, A. *J. Mol. Catal.* **1992**, *74*, 51.

(5) Puga, J.; Fehlner, T. P.; Gates, B. C.; Braga, D.; Grepioni, F. *Inorg. Chem.* **1990**, *29*, 2376.

(6) (a) Feher, F. J.; Walzer, J. F. *Inorg. Chem.* **1991**, *30*, 1689. (b) Liu, J. C.; Wilson, S. R.; Shapley, J. R.; Feher, F. J. *Inorg. Chem.* **1990**, *29*, 5138. (c) Feher, F. J.; Walzer, J. F. *Inorg. Chem.* **1990**, *29*, 1604. (d) Feher, F. J.; Gonzales, S. L.; Ziller, J. W. *Inorg. Chem.* **1988**, *27*, 3440. (e) Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 3850.

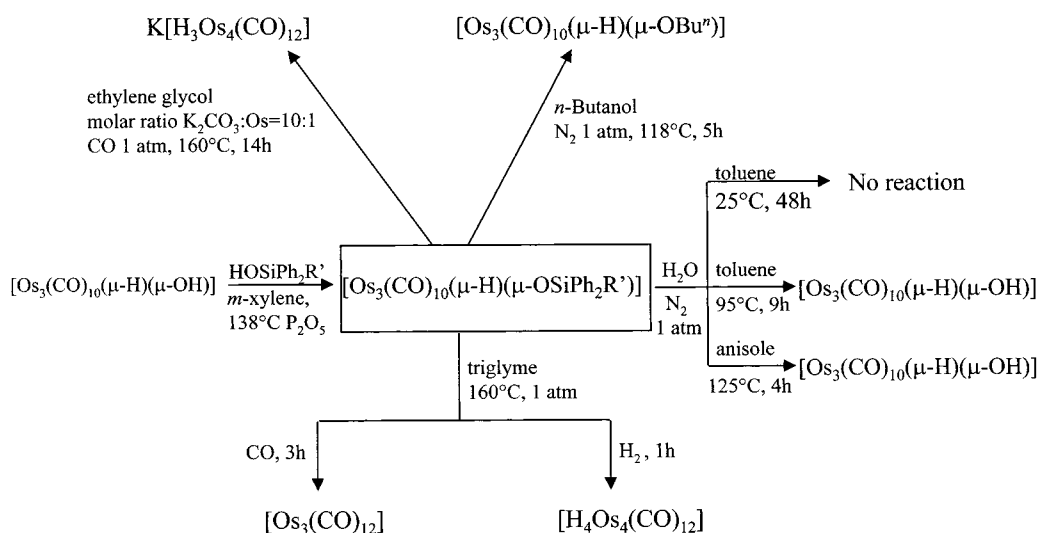
(7) (a) Meyer, T. Y.; Woerpel, K. A.; Novak, B. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 10290. (b) Abbenhuis, H. C. L.; Vorstenbosch, M. L. W.; van Santen, R. A.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1997**, *36*, 6431.

(8) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Rev.* **1996**, *96*, 2205 and references therein.

(9) (a) Lucenti, E.; Roberto, D.; Roveda, C.; Ugo, R.; Sironi, A. *Organometallics* **2000**, *19*, 1051. (b) Lucenti, E.; Feher, F. J.; Ziller, J. W. *Organometallics*, in press.

(10) (a) Barth, R.; Gates, B. C.; Zhao, Y.; Knözinger, J.; Hulse, J. *J. Catal.* **1983**, *82*, 147. (b) Dossi, C.; Fusi, A.; Grilli, E.; Psaro, R.; Ugo, R.; Zanoni, R. *J. Catal.* **1990**, *123*, 181.

(11) Choplin, H.; Besson, B.; D'Ornelas, L.; Sanchez-Delgado, R.; Basset, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 2783.

Scheme 1. Reactivity of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{R}')] (\text{R}' = \text{Ph, OH, OSiPh}_2\text{OH})$ 

supported on silica in the presence of alkali-metal carbonates.^{12,13} In particular, its thermal decomposition has been first reported by one of us to give rise to Os(II) carbonyl¹ or even to Os(II) hydrido carbonyl¹⁴ species anchored to the surface of silica. In contrast, another group suggested the thermal formation on the surface of high-nuclearity osmium carbonyl clusters.¹⁵ Surprisingly, although the investigation of the reactivity of simple molecular silanolate models could be a way to mimic the complex chemical and thermal behavior of silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$, to our knowledge this approach has never been attempted. This lack can be attributed to the difficulty of synthesizing molecular models such as $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiR}_3)]$ ($\text{R} = \text{Et, Ph}$)^{1a,2,3} and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}_7\text{O}_{10}(\text{C}_6\text{H}_{11})_7)]$,^{6b} which were obtained only in rather low yields in one or more steps starting from $[\text{Os}_3(\text{CO})_{12}]$; probably for this reason, the more easily prepared $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OPh})]$ was used as a molecular model in order to obtain mechanistic insight into the olefin hydrogenation catalyzed by silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$.¹¹ However, recently we found that the direct reaction of the easily available reactive cluster $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$ with different silanols (e.g., $\text{HOSiR}_2\text{R}'$, where $\text{R} = \text{Et, Ph}$ and $\text{R}' = \text{Et, Ph, OH, OSiPh}_2\text{OH}$) is a convenient route for a high-yield (79–84%) preparation of molecular models of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ anchored not only to a surface isolated silanol, such as $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiR}_3)]$ (where $\text{R} = \text{Et, Ph}$), but also to a surface geminal silanol, such as $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]$, or vicinal silanol, such as $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$.^{9a} This method was recently confirmed by the synthesis in good yields of models with silsesquioxanes, including for the first time the synthesis of $\{[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})]_2(\mu\text{-O})_2\text{Si}_8\text{O}_{11}\text{Cy}_8\}$ carrying two “ $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})]$ ” moieties.^{9b} The ready availability in good amounts of a series of these molecular models prompted us to study their reactivity and thermal behavior in order to mimic and therefore to clarify by an organometallic approach the still poorly defined chemistry of silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$, which up to now has been interpreted by a rather qualitative and unsatisfactory approach.

In the present work we describe the reactivity of these models toward (i) hydrolysis and alcoholysis in order to

define the strength of the bonding to the silica surface and (ii) reduction by CO or H_2 in order to confirm the possible involvement of silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ as an intermediate in the synthesis of various osmium carbonyl clusters starting from OsCl_3 or $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$ supported on silica in the presence of alkali-metal carbonates^{12,13} and finally the thermal transformation of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$ as a way to clarify the real molecular nature of the species formed on the silica surface by thermal degradation of silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$. By this approach, molecular models not only are a tool to define structural aspects of surface organometallic species but also may be a springboard to better understand their reactivity and thermal behavior, which up to now were interpreted by starting from spectroscopic evidence,^{1–9} from mass balance of gaseous products,^{1,14} or more recently by using a series of methods of extraction of organometallic species from the silica surface.¹⁶

Results and Discussion

1. Hydrolysis, Alcoholysis, and Reduction by CO or H_2 of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{R}')] (\text{R}' = \text{Ph, OH, OSiPh}_2\text{OH})$ (Scheme 1). We investigated first the reactivity of the model compound $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$, because at the temperature (ca. 150–200 °C) of the synthesis of various osmium carbonyl clusters starting from OsCl_3 or $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$ supported on silica in the presence of alkali-metal carbonates,^{12,13} ca. 62% of the total surface silanols are vicinal, whereas ca. 25% and 13% are isolated and geminal silanols, respectively.¹⁷ In a second experiment, to confirm and extend the observed behavior, we investi-

(12) Cariati, E.; Roberto, D.; Ugo, R. *Gazz. Chim. Ital.* **1996**, *126*, 339.

(13) Cariati, E.; Recanati, P.; Roberto, D.; Ugo, R. *Organometallics* **1998**, *17*, 1266.

(14) Basset, J. M.; Besson, B.; Choplin, A.; Hugues, F.; Leconte, M.; Rojas, D.; Smith, A. K.; Theolier, A.; Chauvin, Y.; Commereuc, D.; Psaro, R.; Ugo, R.; Zanderighi, G. M. In *Fundamental Research in Homogeneous Catalysis*; Giongo, M., Graziani, M., Eds.; Plenum: New York, 1984; Vol. 4, p 19.

(15) Collier, G.; Hunt, D. J.; Jackson, S. D.; Moyes, R. B.; Pickering, I. A.; Wells, P. B.; Simpson, A. F.; Whyman, R. *J. Catal.* **1983**, *80*, 154.

(16) Roberto, D.; Cariati, E.; Pizzotti, M.; Psaro, R. *J. Mol. Catal.* **1996**, *111*, 97.

gated the reactivity of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_3)]$, $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]$, and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$.

1.1. Hydrolysis of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{R}')] (\text{R}' = \text{Ph, OH, OSiPh}_2\text{OH})$. When silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ is stirred at 95 °C under nitrogen for ca. 6 h, in the biphasic solvent system water/toluene, $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$ is formed in 94% yield. The rate of hydrolysis is strongly temperature dependent: for instance, at 40 °C only traces of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$ are formed, even after 24 h.¹⁸

The hydrolysis of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$ mimics quite well that of silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$. No reaction occurs when $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$ dissolved in toluene is stirred in the presence of water, at 25 °C under nitrogen for a few days. When the reaction is carried out at 95 °C for 9 h, the hydrolysis is fast, affording $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$ in quantitative yield. As expected, the hydrolysis is even faster at higher temperatures: it is complete in ca. 4 h by working at 125 °C with the biphasic solvent system water/anisole. Similarly, under the latest conditions, $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_3)]$ and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]$ are also readily hydrolyzed, as shown by ¹H NMR spectroscopy.

1.2. Reaction of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{R}')] (\text{R}' = \text{Ph, OH, OSiPh}_2\text{OH})$ with 1-Butanol. When a slurry of silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ in a given alcohol, ROH, is refluxed under nitrogen, the molecular species $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OR})]$ is obtained and easily extracted from the surface, the reaction being faster when high-boiling alcohols are used, due to the higher temperatures.¹⁸ Similarly, when a solution of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$ in anhydrous 1-butanol is stirred under nitrogen at reflux temperature (118 °C) for 5 h, $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OBu}^n)]$ is formed in 80% yield. Under these conditions, $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_3)]$ and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]$ also react to generate $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OBu}^n)]$, as shown by ¹H NMR spectroscopy.

1.3. Reduction of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{R}')] (\text{R}' = \text{Ph, OH, OSiPh}_2\text{OH})$ and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$. Recently some of us reported that both silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ and silica-supported $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$ can be selectively reduced to various carbonyl clusters ($[\text{Os}_3(\text{CO})_{12}]$, $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$, $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$, $[\text{H}_2\text{Os}_4(\text{CO})_{12}]^{2-}$, $[\text{Os}_5\text{C}(\text{CO})_{14}]^{2-}$, and $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$) by reductive carbonylation or hydrogenation, under appropriate conditions, in the presence of alkali-metal carbonates.^{12,13} For a given set of reaction parameters (nature and quantity of alkali-metal carbonate, temperature, gas-phase composition), the selectivity starting from silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ and silica-supported $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$ is similar to that observed starting from silica-supported $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$.^{19,20} This evidence does not allow us to discriminate between silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})$

$(\mu\text{-OSi}\equiv)]$ and silica-supported $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$ as intermediates in the silica-mediated synthesis of different osmium carbonyl clusters starting from $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$.^{12,13} In fact, these two potential intermediates may interconvert under reaction conditions,¹² therefore, due to the presence of surface water, the surface species $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ could first hydrolyze to the more reactive molecular species $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$, which could be the key intermediate also in the surface-mediated synthesis of $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$ by easy hydrogenation of silica physisorbed $[\text{Os}_3(\text{CO})_{12}]$.^{21,22}

To clarify whether silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ could be directly reduced to various carbonyl clusters, without involving the intermediate formation of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$, we studied the reduction in anhydrous triglyme of the molecular models $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$, $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]$, and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_3)]$. For comparison, we also studied the reduction of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$ under similar conditions.

Reduction under CO. When an anhydrous triglyme solution of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$ is heated under a flux of CO (1 atm) at 160 °C for 2.5 h, a yellow material precipitates. Filtration affords $[\text{Os}_3(\text{CO})_{12}]$ in 79% yield. Under the same conditions, yields of $[\text{Os}_3(\text{CO})_{12}]$ are slightly lower starting from $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_3)]$ (71% yield after 3 h) and, in a more significant manner, from $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]$ (59% yield after 3.5 h). However, $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$ is more easily reduced by CO (1 atm) than the related silanolate derivatives: at 160 °C in anhydrous triglyme, $[\text{Os}_3(\text{CO})_{12}]$ is generated in 84% yield after only 2 h.

These results confirm the already observed higher reactivity of silica-supported $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$ and clearly show that silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ could be directly reduced to $[\text{Os}_3(\text{CO})_{12}]$ without involving a preliminary hydrolysis.¹²

In the easy reductive carbonylation (1 atm of CO, 150 °C) of silica-physisorbed $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$ to $\text{K}[\text{H}_3\text{Os}_4(\text{CO})_{12}]$ in the presence of K_2CO_3 (molar ratio $\text{K}_2\text{CO}_3:\text{Os} = 10:1$),¹⁹ silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ and silica-supported $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$ were suggested as possible intermediate species.^{12,13} To confirm the involvement of these species as reactive intermediates, we tried a model homogeneous reaction. When an anhydrous ethylene glycol solution of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$ is heated under a flux of CO (1 atm) at 160 °C for 14 h in the presence of K_2CO_3 (molar ratio $\text{K}_2\text{CO}_3:\text{Os} = 10:1$), $\text{K}[\text{H}_3\text{Os}_4(\text{CO})_{12}]$ is formed selectively, as shown by infrared spectroscopy of the resulting solution. Extraction with a dichloromethane solution of $[\text{NBu}_4]\text{I}$ gives $[\text{NBu}_4][\text{H}_3\text{Os}_4(\text{CO})_{12}]$ in 72% yield. However, the same yields are obtained under similar reaction conditions starting from $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$, because both $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$ and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$ are readily converted to the same species $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OCH}_2\text{-CH}_2\text{OH})]$ prior to reduction, as confirmed by mass spectrometry (molecular ion peak *m/e* 914). Unfortu-

(17) Vansant, E. F.; Van Der Voort, P.; Vrancken, K. C. In *Characterization and Chemical Modification of the Silica Surface in Studies in Surface Science and Catalysis*; Delmon, B., Yates, J. T., Eds.; Elsevier: Amsterdam, 1995; Vol. 93.

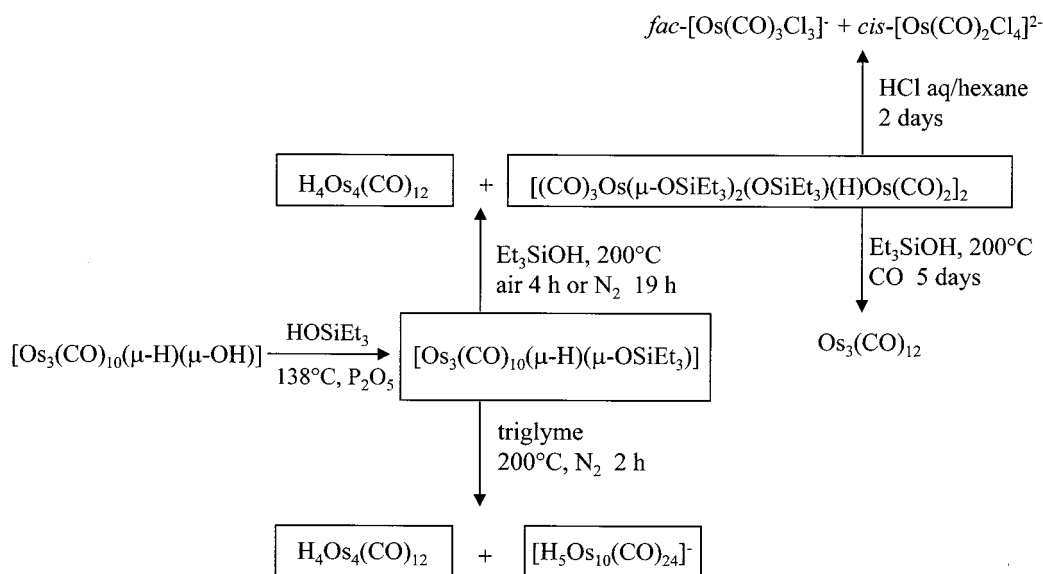
(18) Roberto, D.; Lucenti, E.; Roveda, C.; Ugo, R. *Organometallics* **1997**, *16*, 5974.

(19) Roberto, D.; Cariati, E.; Psaro, R.; Ugo, R. *Organometallics* **1994**, *13*, 734.

(20) Roberto, D.; Cariati, E.; Ugo, R.; Psaro, R. *Inorg. Chem.* **1996**, *35*, 2311.

(21) Dossi, C.; Psaro, R.; Roberto, D.; Ugo, R.; Zanderighi, G. M. *Inorg. Chem.* **1990**, *29*, 4368.

(22) Roberto, D.; Pizzotti, M.; Ugo, R. *Gazz. Chim. Ital.* **1995**, *125*, 133.

Scheme 2. Thermal Degradation of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$ 

nately the reactive ethylene glycol was the only available solvent which could dissolve K_2CO_3 under the reaction conditions, unlike, for instance, triglyme.

Reduction under H_2 . When an anhydrous triglyme solution of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$ is heated under a flux of H_2 (1 atm) at 160°C for 30 min, a yellow material precipitates. Filtration affords $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$ in 61% yield. Under similar conditions, $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]$ and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_3)]$ are also converted to $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$ in similar yields (63–64%). These results give some evidence of a conversion of silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ into $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$ ²² which does not require the intermediate formation of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$, although the latter is also reduced to $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$ in 65% yield, by working in an anhydrous triglyme solution as above.

2. Thermal Behavior of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$ as a Model of the Thermal Degradation of Silica-Anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ (Scheme 2). Metal clusters supported on inorganic oxides constitute an interesting class of hybrid materials, and their use as catalyst precursors may provide activities and selectivities often different from those displayed by the usual supported metallic catalysts.^{23–25} Since a thermal treatment of these materials is generally required to promote their catalytic activity, this aspect cannot be limited to the evidence of thermal rearrangements of surface species,¹⁵ but it may involve a complex surface organometallic chemistry originated by reaction with the OH groups of the support.^{1,23–24,26} With silica-supported $[\text{Os}_3(\text{CO})_{12}]$, it is now well established that thermal treatment (at $100\text{--}150^\circ\text{C}$) causes, as the first step of chemisorption, oxidative addition of a surface

silanol group into an Os–Os bond of the triangular frame with formation of silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$.^{1,23,24} Further thermal treatment (at $150\text{--}250^\circ\text{C}$) leads to new surface species of interest in view of their catalytic activity;^{10b,14,27} however, their nature has been, as already pointed out, the subject of some controversy.^{1,14–15,28–29}

On a hydroxylated or partially dehydroxylated silica surface under vacuum (4–72 h; $150\text{--}250^\circ\text{C}$)^{1,29,31,32} or under oxygen (1–2 h; $150\text{--}200^\circ\text{C}$),^{10b,31} both physisorbed $[\text{Os}_3(\text{CO})_{12}]$ and silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ (2.0 wt % Os with respect to SiO_2) are converted to new surface species characterized by three broad carbonyl bands (for instance, in Nujol, ν_{CO} 2126 (m, br), 2036 (s, br), and 1952 (m, br) cm^{-1}) in their infrared spectrum. The relative intensities of these bands is dependent upon temperature, time of treatment, and further addition of a CO atmosphere.¹ The real nature and structure of these surface species, which are also obtained by refluxing a *n*-decane²⁷ or nonane³⁰ solution of $[\text{Os}_3(\text{CO})_{12}]$ in the presence of silica, is still an open question. The similarities of their infrared spectra with those of known complexes of Os(II) such as $[\text{Os}(\text{CO})_3\text{X}_2]_2$ (X = Cl, Br, I) and $[\text{Os}(\text{CO})_2\text{I}_2]_n$, the K^3 Fourier transform of their EXAFS spectra, which showed the absence of any ordered Os–Os bond, and the observation that an oxygen atmosphere favors this kind of surface transformation first suggested complete rupture of the original cluster cage with formation of mononuclear oxidized Os(II) surface species such as $[\text{Os}(\text{CO})_x(\text{OSi}\equiv)_2]_n$ (x = 2, 3) which were in equilibrium of carbonylation/decarbonylation.¹ An *x* value of about 2.7 was proposed by a temperature-programmed decompo-

(23) Basset, J. M.; Choplin, A. *J. Mol. Catal.* **1983**, *21*, 95.

(24) Psaro, R.; Ugo, R. In *Metal Clusters in Catalysis*; Gates, B. C., Guzzi, L., Knozinger, H., Eds.; Elsevier: Amsterdam, 1986; p 427, and references therein.

(25) (a) Psaro, R.; Recchia, S. *Catal. Today* **1998**, *41*, 139. (b) Knozinger, H.; Zhao, Y. *J. Catal.* **1981**, *71*, 337. (c) Ichikawa, M. *J. Catal.* **1979**, *59*, 67.

(26) (a) Scott, S. L.; Basset, J. M. *J. Mol. Catal.* **1994**, *86*, 5. (b) Basset, J. M.; Candy, J. P.; Choplin, A.; Leconte, M.; Theolier, In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1990; Vol. 7, p 85. (c) Lamb, H. H.; Gates, B. C.; Knozinger, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1127.

(27) Deeba, M.; Gates, B. C. *J. Catal.* **1981**, *67*, 303.

(28) Psaro, R.; Dossi, C.; Fusi, A.; Ugo, R. *Res. Chem. Intermed.* **1991**, *15*, 31.

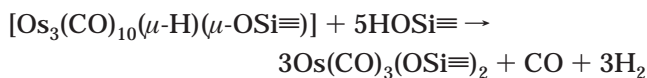
(29) Dossi, C.; Fusi, A.; Grilli, E.; Psaro, R.; Ugo, R.; Zandoni, R. *Catal. Today* **1988**, *2*, 585.

(30) Cook, S. L.; Evans, J.; McNulty, G. S.; Greaves, G. N. *J. Chem. Soc., Dalton Trans.* **1986**, 7.

(31) Dossi, C.; Fusi, A.; Psaro, R.; Ugo, R.; Zandoni, R. In *Structure and Reactivity of Surfaces*; Morterra, C., Zecchina, A., Costa, G., Eds.; Elsevier: Amsterdam, 1989; p 375.

(32) Dossi, C.; Fusi, A.; Psaro, R.; Zanderighi, G. M. *Appl. Catal.* **1989**, *46*, 145.

sition and oxidation study,^{31,32} whereas the formation of Os(II) surface species, by treatment under O_2 at 200 °C of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$, was confirmed by XPS spectroscopy.²⁹ However, a careful investigation of the mass balance showed that the amount of the evolved hydrogen was less than that required (3 mol of H_2 /mol of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$) for the surface reaction



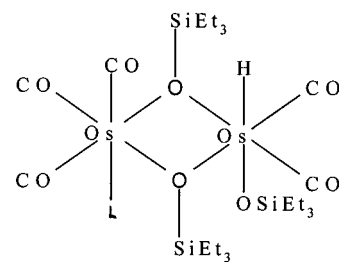
suggesting that the oxidation process could occur with complete breaking of the cluster framework but with parallel formation of some hydridocarbonylosmium(II) species covalently bound to the silica surface such as $[\text{HOS}(\text{CO})_3(\text{OSi}\equiv)(\text{HOSi}\equiv)]$.¹⁴ The latter species could then to some extent, particularly under oxygen, lose H_2 to give the previously proposed $[\text{Os}(\text{CO})_x(\text{OSi}\equiv)_2]_n$ ($x = 2, 3$) species.¹

In addition, it has been reported that, on a highly dehydroxylated silica surface, thermal treatment up to 250 °C of physisorbed $[\text{Os}_3(\text{CO})_{12}]$ (2.0 wt % Os with respect to SiO_2) affords new surface species also characterized by three broad carbonyl bands (in Nujol, ν_{CO} 2122 (m, br), 2030 (s, br), and 1950 (s, br) cm^{-1}) in their infrared spectrum.¹⁵ On the basis of UV/visible reflectance spectra, which evidenced retention of Os–Os bonding, temperature-programmed decomposition, and high-resolution transmission electron microscopy, the authors suggested a thermal process of cluster growth to produce high-nuclearity surface species such as $[\text{Os}_n(\text{CO})_{2.8n}\text{C}_{0.1n}\text{Z}_{0.3n}]$ ($n = \text{ca. } 12$), where Z represents adsorption sites. In this particular study, the formation of high-nuclearity species, instead of carbonylosmium(II) species, was attributed^{15,28} to the use of a high rate of heating, high $[\text{Os}_3(\text{CO})_{12}]$ surface loadings, and highly dehydroxylated silica, which would inhibit an easy interaction of $[\text{Os}_3(\text{CO})_{12}]$ with surface silanols and therefore could lead to its simple well-known pyrolysis to produce high-nuclearity carbonyl species.³³ The conversion of silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ to high-nuclearity species, by thermal treatment under an inert atmosphere, was not experimentally studied under conditions reported in ref 15, but it is well-known that this latter species is easily formed as the first step of chemisorption by heating $[\text{Os}_3(\text{CO})_{12}]$ physisorbed on silica at 150–200 °C.¹

To contribute to this still-open controversy, we investigated the thermal reactivity, in air or under nitrogen, of the molecular model $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$ dissolved in triethylsilanol (to mimic a silica surface with available surface silanols) or triglyme (to mimic a highly dehydroxylated silica surface). This latter cluster was chosen as a molecular model because its reactivity is particularly easy to monitor by ^1H and ^{13}C NMR spectroscopy.

When a solution of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$ in pure anhydrous triethylsilanol is heated in dried air at 200 °C for ca. 4 h in the closed reaction vessel previously described,³⁴ some $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$ (11% isolated yield) is formed, along with a new osmium carbonyl species that

can be purified by column chromatography and that we propose to be $[\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2]_n$ (52% isolated yield) on the basis of elemental analysis and infrared, ^1H NMR, ^{13}C NMR, ^{29}Si NMR, and mass spectra (see Experimental Section). The infrared spectral pattern of this new species (in CH_2Cl_2 , ν_{CO} 2115 (s), 2021 (vs, br), 2008 (s), 1921 (s) cm^{-1} ; in hexane, ν_{CO} 2112 (s), 2020 (sh), 2017 (vs), 1933 (s) cm^{-1}), which is quite similar to that reported for the surface species formed by thermal degradation of silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$, would suggest the presence of both *fac*-($\text{CO})_3\text{Os}^{\text{II}}$ (ν_{CO} in CH_2Cl_2 2115 (s) and 2021 (vs, br) cm^{-1}) and *cis*-($\text{CO})_2\text{Os}^{\text{II}}$ (ν_{CO} in CH_2Cl_2 2008 (s) and 1921 (s) cm^{-1}) moieties,³⁵ as confirmed both by its easy reaction with aqueous HCl to produce equimolar amounts of *fac*- $[\text{Os}(\text{CO})_3\text{Cl}_3]^-$ and *cis*- $[\text{Os}(\text{CO})_2\text{Cl}_4]^{2-}$ (see later) and by the ^{13}C NMR spectrum, carried out in CDCl_3 , which shows three signals in a 2:1:2 ratio, one at δ (ppm) 181.16 attributed to *cis*- $\text{Os}(\text{CO})_2$ and two at 169.99 and 169.63 attributed to *fac*-($\text{CO})_3\text{Os}$, by analogy with the ^{13}C NMR spectrum of *fac*- $[\text{Os}(\text{CO})_3\text{Cl}_2(\text{acetone})]$, which shows two signals at δ (ppm) 167.75 and 166.34. The ^1H NMR spectrum, carried out in CDCl_3 , shows the presence of a hydridic signal ($\text{Os}-\text{H}$, δ -14.68 ppm) characterized by a $^{187}\text{Os}-^1\text{H}$ coupling constant of 94 Hz, a value that is quite high³⁶ but is not too far from the value of the $^{187}\text{Os}-^1\text{H}$ coupling constant of 76.2 Hz reported for the terminal hydrogen in $[(\eta^5\text{-Cp})\text{H}(\text{PMe}_3)_2\text{-Os}]$.³⁷ The hydridic signal is coupled selectively to the C signal of the CO's at 181.16 ppm, as evidenced by heteronuclear multiple quantum correlation (HMQC) spectroscopy with the bilinear rotation decoupling (BIRD) technique, giving evidence for a *cis*- $\text{HOS}(\text{CO})_2$ moiety. The presence of two kinds of "Et₃SiO–" groups, in a 1:2 ratio as expected for one terminal Et₃SiO– and two bridging Et₃SiO– groups, is confirmed by the two signals in the ^{29}Si NMR spectrum (in CDCl_3 , δ 27.57 and 29.71 ppm; see Experimental Section). Finally both the EI and FAB mass spectra show a peak at m/e 916 corresponding to the fragment " $\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2$ ", whereas the ESI+ mass spectrum in CH_3CN evidences peaks at m/e 1914 and 998 corresponding to " $[\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2]_2 \cdot 2\text{CH}_3\text{CN}$ " and " $[\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2] \cdot 2\text{CH}_3\text{CN}$ ", respectively. On the basis of all this spectroscopic evidence, a possible structure can be proposed for this new carbonyl species based on " $\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2$ " units such as



L = OSiEt₃ from another unit

These units may aggregate via OSiEt₃ bridges, in

(33) Braga, D.; Lewis, J.; Johnson, B. F. G.; McPartlin, M.; Nelson, W. J. H.; Vargas, M. D. *J. Chem. Soc., Chem. Commun.* **1983**, 241.

(34) Roberto, D.; Psaro, R.; Ugo, R. *Organometallics* **1993**, *12*, 2292.

(35) (a) Johannsen, F. H.; Preetz, W. *J. Organomet. Chem.* **1976**, *104*, 79. (b) Johannsen, F. H.; Preetz, W.; Scheffler, A. *J. Organomet. Chem.* **1975**, *102*, 527. (c) Preetz, W.; Johannsen, F. H. *J. Organomet. Chem.* **1975**, *86*, 397. (d) Cleare, M. J.; Griffith, W. P. *J. Chem. Soc. A* **1969**, 372.

agreement with the 18-electron rule. The evidence of a dimer, given by the ESI+ mass spectrum, would suggest a cubane structure similar to that of the Os(II) complex $[(\text{CO})_3\text{OsO}]_4$ ³⁸ and common to many complexes with a metal having a low-spin d^6 configuration such as Pt(IV) ($[\text{Me}_3\text{PtCl}]_4$,³⁹ $[\text{Me}_3\text{PtOH}]_4$ ⁴⁰), Mn(I) ($[(\text{CO})_3\text{Mn-SR}]_4$ ⁴¹), and Re(I) ($[(\text{CO})_3\text{ReSR}]_4$,⁴¹ $[(\text{CO})_3\text{ReOH}]_4$ ⁴²).

The same species, which we propose to be $[\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2]_n$, is formed, along with traces of $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$, also by thermal degradation under N_2 of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$ dissolved in triethylsilanol. The reaction is slower than when carried out in air, being incomplete even after 19 h. In both cases, minor amounts of $\text{Et}_3\text{Si}(\text{OSiEt}_2)_n\text{OSiEt}_3$ ($n = 0-2$) species are also formed, as evidenced by mass spectrometry⁴³ and ²⁹Si NMR spectroscopy, due to thermal condensation of triethylsilanol as confirmed by a blank experiment (see Experimental Section).

In pure anhydrous triglyme under N_2 at 200 °C, $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$ is rapidly (less than 2 h) converted to mixtures of $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$ and $[\text{H}_5\text{Os}_{10}(\text{CO})_{24}]^-$ only (identified by infrared and ¹H NMR spectroscopy; see Experimental Section), confirming that the presence of excess silanol groups inhibits the formation of high-nuclearity clusters such as $[\text{H}_5\text{Os}_{10}(\text{CO})_{24}]^-$ which occurs by simple thermal pyrolysis.³³

The above observations prompted us to reinvestigate in great detail the already studied thermal degradation, under N_2 at 200 °C and using the now well-established so-called extraction methodology developed in our laboratory,¹⁶ of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$ (1.7 wt % Os with respect to SiO_2) anchored to a silica surface having enough available surface silanols (Degussa Aerosil 200, number of surface silanols equal ca. 4.9 OH/nm²). After 88 h, the reaction is complete, affording the expected silica surface species characterized by three broad carbonyl bands (in Nujol: ν_{CO} 2121 (m, br), 2035 (s, br), and 1955 (m, br) cm^{-1}) along with small traces of $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$, $[\text{H}_4\text{Os}_{10}(\text{CO})_{24}]^{2-}$, and $[\text{H}_5\text{Os}_{10}(\text{CO})_{24}]^-$, which were easily removed from the silica surface by extraction with dichloromethane (neutral cluster) and acetonitrile (anionic clusters) and then identified by infrared and ¹H NMR spectroscopy (see Experimental Section). The remaining silica-anchored osmium carbonyl species were extracted with aqueous HCl, affording a mixture of *fac*- $[\text{Os}(\text{CO})_3\text{Cl}_3]^-$ and *cis*- $[\text{Os}(\text{CO})_2\text{Cl}_4]^{2-}$, which confirms the presence of Os(II) surface species and the parallel presence of both $(\text{CO})_3\text{Os}^{\text{II}}$ and $(\text{CO})_2\text{Os}^{\text{II}}$ moieties as first proposed.¹ As in the homogeneous models, this thermal degradation is much faster in air than

under nitrogen, being complete in ca. 3 h and affording Os(II) silica-anchored carbonyl species only.

It is remarkable that the species proposed as $[\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2]_n$ perfectly reproduces the behavior toward aqueous HCl of silica-anchored dicarbonyl- and tricarbonylosmium(II) species obtained by thermal degradation of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$. In fact, when this species is dissolved in hexane or CHCl_3 , it reacts with aqueous HCl, affording $\text{Et}_3\text{-SiOSiEt}_3$ and a mixture of *fac*- $[\text{Os}(\text{CO})_3\text{Cl}_3]^-$ and *cis*- $[\text{Os}(\text{CO})_2\text{Cl}_4]^{2-}$ (molar ratio 1:1) which can be easily separated by column chromatography (see Experimental Section). In addition, when a solution of $[\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2]_n$ in triethylsilanol is heated under CO (1 atm) at 200 °C in the closed reaction vessel previously described,³⁴ $[\text{Os}_3(\text{CO})_{12}]$ is slowly formed (yield 50% after 5 days), mimicking the well-known reductive carbonylation of the silica-anchored dicarbonyl- and tricarbonylosmium(II) species to regenerate $[\text{Os}_3(\text{CO})_{12}]$.²⁴

Unfortunately, the proposed $[\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2]_n$ species (where n is probably 2), obtained by thermal degradation of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$ in triethylsilanol, is oily (probably with a low melting point). Therefore, it was impossible to confirm the proposed structure by X-ray crystallography, but the body of spectroscopic evidence produced is in good agreement with the main features of the proposed structural arrangement.

Conclusion

The information obtained in this work (see Schemes 1 and 2), through the study of the reactivity and thermal behavior of surface molecular models such as $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiR}_2\text{R}')]_n$ ($\text{R} = \text{Et, Ph}$; $\text{R}' = \text{Et, Ph, OH, OSiPh}_2\text{-OH}$), led to a clarification of aspects of the surface chemistry of the silica-anchored species $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$ still to be fully defined.

Remarkably, the study of the thermal behavior of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$ dissolved in triethylsilanol (to mimic a silica surface with available surface silanols) or triglyme (to mimic a highly dehydroxylated silica surface) clarifies definitively the controversy on the nature of the products formed by thermal degradation of silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$.²⁸ In the absence of silanol groups only a thermal degradation occurs, to produce by pyrolysis some high-nuclearity clusters, including anionic clusters, confirming that the growth to high-nuclearity osmium species reported to occur on the surface by Wells et al.¹⁵ was due, as also suggested by one of us,²⁸ not only to the high rate of heating but also mainly to the very low concentration on the surface of reactive silanol groups. In addition, we produced direct evidence that on a silica surface having enough reactive silanol groups, the breakdown of the cluster structure occurs easily by oxidative addition of the silanol groups with formation of both $(\text{CO})_3\text{Os}^{\text{II}}$ and $(\text{CO})_2\text{Os}^{\text{II}}$ surface anchored fragments, as one of us proposed for the first time.¹ In fact, the isolation in excellent yields by thermal degradation of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$ in triethylsilanol of a molecular species that, on the basis of an extended spectroscopic and chemical evidence, we propose to be $[\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2]_n$, where n is

(36) Granger, P.; Harris, R. K. Eds. *Multinuclear Magnetic Resonance in Liquids and Solids—Chemical Applications*; NATO ASI Series C: Mathematical and Physical Sciences; Kluwer Academic: Amsterdam, 1990; Vol. 322.

(37) Benn, R.; Brenneke, H.; Joussen, E.; Lehmkuhl, H.; Ortiz, F. L. *Organometallics* **1990**, *9*, 756.

(38) Nyholm, R. S.; Truter, M. R.; Bradford, C. W. *Nature* **1970**, *228*, 648.

(39) Rundle, R. E.; Sturdivant, J. H. *J. Am. Chem. Soc.* **1947**, *69*, 1561.

(40) (a) Spiro, T. G.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1968**, *7*, 2165. (b) Preston, H. S.; Mills, J. C.; Kennard, C. H. L. *J. Organomet. Chem.* **1968**, *14*, 447.

(41) Braterman, P. S. *J. Chem. Soc. A* **1968**, 2907.

(42) Herberhold, M.; Suss, G.; Ellermann, J.; Gabelein, H. *Chem. Ber.* **1978**, *111*, 2931.

(43) Mysov, E. I.; Akhrem, I. S.; Avetisyan, D. V. *Org. Mass Spectrom.* **1976**, *11*, 358.

probably 2, not only confirms the degradation of the original cluster to silica-anchored $(\text{CO})_3\text{Os}^{\text{II}}$ and $(\text{CO})_2\text{-Os}^{\text{II}}$ fragments linked by bridging silanulates, as originally proposed,¹ but also gives additional direct evidence that the process of thermal degradation of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ produces surface hydridic osmium species as suggested by one of us.¹⁴

The presence on the silica surface of stable hydridic species would explain some aspects of the catalytic properties toward olefin isomerization of the Os(II) carbonyl species anchored to silica produced by thermal degradation of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$; this isomerization was reported to increase by working in the presence of hydrogen.^{10b}

Another remarkable observation reached in the course of this work is the evidence that, as reported for $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$,¹ the thermal degradation of the model $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$ occurs more easily under oxygen than under nitrogen, producing a molecular Os(II) carbonyl species with a ratio of CO to Os of 2.5, not too far from the value of 2.7 obtained by a temperature-programmed decomposition and oxidation of the Os(II) carbonyl species generated on the silica surface by thermal degradation of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$.³²

Finally, we produced strong chemical evidence that not only is the silica-anchored species $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ easily attacked by water or alcohols but it can also be the intermediate in the silica-mediated synthesis of different osmium carbonyl clusters, starting from OsCl_3 or $[\text{Os}(\text{CO})_3\text{Cl}_2]$.^{12,13}

In conclusion, for the first time, molecular silanolate models of surface species such as $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ are used not only as tools to define structural aspects but also as springboards to understand their surface chemistry on the silica surface. Work is in progress in our laboratory to prepare and characterize new Os(II) compounds by thermal degradation of silanolate models with more complex silanolate ligands^{9b} that mimic even better the complexity of the silica surface and could give crystalline compounds good for a full X-ray characterization of their structure.

Experimental Section

General Comments. $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]^{18}$ and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]^{10,18}$ were prepared according to the literature. $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{R}')] (R' = \text{Ph, OH, OSiPh}_2\text{OH})$ molecular models were prepared as recently reported^{9a} by heating, at 138 °C under N_2 , an anhydrous *m*-xylene solution of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$ and the corresponding $R'\text{Ph}_2\text{SiOH}$ (molar ratio $(\text{Ph}_3\text{SiOH}$ or $\text{HOSiPh}_2\text{OSiPh}_2\text{OH}):[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})] = 2:1$, reaction time 4 h; molar ratio $\text{Ph}_2\text{-Si}(\text{OH})_2:[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})] = 60:1$, reaction time 50 min), whereas $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$ was prepared by heating, at 138 °C under N_2 for 2.5 h, an anhydrous Et_3SiOH solution of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$ (molar ratio $\text{Et}_3\text{SiOH}:[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})] = 9:1$). Most gases (N_2 , CO , H_2) were dried by flowing over Drierite, whereas air was dried by flowing over molecular sieves (4 Å) at -78 °C and then over P_2O_5 . For some reactions (see below) N_2 was deoxygenated on a copper BASF catalyst. The organic solvents were usually dried over molecular sieves (3 Å). Products were purified by recrystallization or by column chromatography using silica gel 60. Spectroscopic data were obtained by use of the following spectrometers: Bruker-Vector 22 or Jasco FT-IR 420 (IR), Bruker DRX-300 (^1H NMR, ^{13}C NMR, and ^{29}Si NMR), Varian VG9090 (EI and

FAB⁻ MS), Hewlett-Packard 5988 (ESI⁺ MS). Elemental analyses were carried out in the analytical laboratory of our department.

Hydrolysis of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{R}')] (R' = \text{Ph, OH, OSiPh}_2\text{OH})$. $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]^{9a}$ (20 mg, 0.016 mmol) was dissolved in toluene (10 mL) in a two-necked flask, equipped with a magnetic stirrer, a condenser, and a thermometer and stirred under nitrogen in the presence of water (5 mL). After a few days at room temperature, no reaction occurred, as shown by ^1H NMR spectroscopy. When the reaction mixture was heated at reflux temperature (95 °C), the hydrolysis took place, affording $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]^{18}$ in quantitative yield (^1H NMR) after 9 h. The hydrolysis was complete in less than 4 h by working at 125 °C with the biphasic solvent system water (1 mL)/anisole (20 mL). Under these conditions, $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_3)]^{9a}$ and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]^{9a}$ were also readily hydrolyzed, as shown by the appearance of the typical ^1H NMR hydridic signal at $\delta -12.64$ ppm (in CDCl_3).¹⁸

Reaction of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$ with 1-Butanol. A solution of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]^{9a}$ (49.0 mg, 0.039 mmol) in anhydrous 1-butanol (8 mL) was heated under nitrogen at 118 °C in a two-necked flask equipped with a magnetic stirrer, a condenser, and a thermometer. After 5 h, evaporation to dryness of the solution, followed by recrystallization (pentane), afforded pure $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OBu}^n)]^{18}$ (28.6 mg, 0.031 mmol; 80% yield). Under these conditions, $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_3)]^{9a}$ and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]^{9a}$ also reacted to generate $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OBu}^n)]^{18}$, as shown by ^1H NMR spectroscopy.¹⁸

Reduction of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$, $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_3)]$, $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]$, and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$ under CO. (i) Reduction of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$. A solution of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]^{9a}$ (55.6 mg, 0.044 mmol) in anhydrous triglyme (28 mL) was heated under a flux of CO (1 atm) at 160 °C in a three-necked flask equipped with a condenser, a thermometer, and a magnetic stirrer. The reaction was followed by infrared spectroscopy in the carbonyl region by monitoring the appearance of the bands characteristic for $[\text{Os}_3(\text{CO})_{12}]$. After 2.5 h the reaction was complete. The solution was cooled at -20 °C in order to precipitate $[\text{Os}_3(\text{CO})_{12}]$. Filtration followed by washing with pentane (ca. 3 mL), to remove the last drops of triglyme eventually present, afforded pure $[\text{Os}_3(\text{CO})_{12}]$ (31.4 mg, 0.035 mmol; 79% yield). $[\text{Ph}_2\text{SiO}]_4$ was present in the triglyme solution, since the EI mass spectrum showed the molecular ion peak of the tetrameric species at m/e 792 $[\text{M}]^+$. As a consequence, during the reductive carbonylation, the silanolate ligand is converted to the tetrameric species $[\text{Ph}_2\text{SiO}]_4$ and some water is evolved in this condensation process; however, traces of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$ could not be detected by ^1H NMR or by mass spectrometry even in the first stage of the reaction: for example, by stopping the reaction after 30 min. This latter observation confirms that the reduction does not proceed via previous hydrolysis of the silanolate ligand.

Reduction in the Presence of K_2CO_3 . A suspension of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]^{9a}$ (55.6 mg, 0.044 mmol) in anhydrous ethylene glycol (25 mL) added to K_2CO_3 (185 mg, 1.34 mmol; molar ratio $\text{K}_2\text{CO}_3:\text{Os} = 10:1$) was heated under a flux of CO (1 atm) at 160 °C in a three-necked flask equipped with a condenser, a thermometer, and a magnetic stirrer. The reaction was followed by infrared spectroscopy in the carbonyl region by monitoring the appearance of the bands characteristic for $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$. After 14 h the reaction was complete. The solution was extracted with $[\text{NBu}_4]\text{I}$ (35.0 mg, 0.095 mmol) dissolved in CH_2Cl_2 (35 mL). The dichloromethane solution was evaporated to dryness, affording a brown residue which was washed twice with water (2×5 mL), to remove the excess of $[\text{NBu}_4]\text{I}$, and then purified by column chromatography on

silica using CH_2Cl_2 as eluent, to obtain pure $[\text{NBu}_4][\text{H}_3\text{Os}_4(\text{CO})_{12}]$ (31.8 mg, 0.024 mmol; 72% yield).

(ii) Reduction of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]$. A solution of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]^{9a}$ (72.8 mg, 0.068 mmol) in anhydrous triglyme (10 or 14 mL) was heated under a flux of CO (1 atm) at 160 °C in a three-necked flask equipped with a condenser, a thermometer, and a magnetic stirrer. The reaction was followed by infrared spectroscopy in the carbonyl region by monitoring the appearance of the bands characteristic for $[\text{Os}_3(\text{CO})_{12}]$. After 3.5 h, the solution was cooled at -20 °C in order to precipitate $[\text{Os}_3(\text{CO})_{12}]$. Filtration followed by washing with pentane (ca. 3 mL), to remove the last drops of triglyme eventually present, afforded pure $[\text{Os}_3(\text{CO})_{12}]$ (36.7 mg, 0.040 mmol; 59% yield). The triglyme solution was evaporated to dryness, and the residue was analyzed by mass spectrometry; both EI and FAB⁻ mass spectra showed the molecular ion peak of the trimer $[\text{Ph}_2\text{SiO}]_3$ at *m/e* 594.

(iii) Reduction of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_3)]$. A solution of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_3)]^{9a}$ (63.0 mg, 0.056 mmol) in anhydrous triglyme (14 mL) was heated under a flux of CO (1 atm) at 160 °C in a three-necked flask equipped with a condenser, a thermometer, and a magnetic stirrer. The reaction was followed by infrared spectroscopy in the carbonyl region by monitoring the appearance of the bands characteristic for $[\text{Os}_3(\text{CO})_{12}]$. After 3 h, the solution was cooled at -20 °C in order to precipitate $[\text{Os}_3(\text{CO})_{12}]$. Filtration followed by washing with pentane (ca. 3 mL), to remove the last drops of triglyme eventually present, afforded pure $[\text{Os}_3(\text{CO})_{12}]$ (36.2 mg, 0.040 mmol; 71% yield).

(iv) Reduction of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$. A solution of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]^{18}$ (36.0 mg, 0.041 mmol) in anhydrous triglyme (28 mL) was heated under a flux of CO (1 atm) at 160 °C in a three-necked flask equipped with a condenser, a thermometer, and a magnetic stirrer. The reaction was followed by infrared spectroscopy in the carbonyl region by monitoring the appearance of the bands characteristic for $[\text{Os}_3(\text{CO})_{12}]$. After 2 h the reaction was complete. The solution was cooled at -20 °C in order to precipitate $[\text{Os}_3(\text{CO})_{12}]$. Filtration followed by washing with pentane (ca. 3 mL), to remove the last drops of triglyme eventually present, afforded pure $[\text{Os}_3(\text{CO})_{12}]$ (31.4 mg, 0.035 mmol; 84% yield).

Reduction in the Presence of K_2CO_3 . A solution of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]^{18}$ (65.0 mg, 0.075 mmol) in anhydrous ethylene glycol (22 mL) added to K_2CO_3 (310 mg, 2.25 mmol; molar ratio $\text{K}_2\text{CO}_3:\text{Os} = 10:1$) was heated under a flux of CO (1 atm) at 160 °C in a three-necked flask equipped with a condenser, a thermometer, and a magnetic stirrer. The reaction was followed by infrared spectroscopy in the carbonyl region by monitoring the appearance of the bands characteristic for $[\text{H}_4\text{Os}_4(\text{CO})_{12}]^-$. After 14 h the reaction was complete. The solution was extracted with $[\text{NBu}_4]\text{I}$ (46.1 mg, 0.125 mmol) dissolved in CH_2Cl_2 (50 mL). The dichloromethane solution was evaporated to dryness, affording a brown residue which was washed twice with water (2×5 mL), to remove the excess of $[\text{NBu}_4]\text{I}$, and then purified by column chromatography on silica using CH_2Cl_2 as eluent, to obtain pure $[\text{NBu}_4][\text{H}_3\text{Os}_4(\text{CO})_{12}]$ (45.5 mg, 0.034 mmol; 60% yield).

Reduction of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$, $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_3)]$, $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]$, and $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$ under H_2 . **(i) Reduction of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$.** A solution of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]^{9a}$ (60.8 mg, 0.048 mmol) in anhydrous triglyme (10 mL) was heated under a flux of H_2 (1 atm) at 160 °C in a three-necked flask equipped with a condenser, a thermometer, and a magnetic stirrer. The reaction was followed by infrared spectroscopy in the carbonyl region by monitoring the appearance of the bands characteristic for $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$. After 30 min the reaction was complete. The solution was cooled at -20 °C in order to precipitate $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$. Filtration followed by washing with pentane (ca. 3 mL), to remove the last drops of triglyme eventually present,

afforded pure $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$ (24.3 mg, 0.022 mmol; 61% yield). Traces of $[\text{H}_4\text{Os}_{10}(\text{CO})_{24}]^{2-}$ and $[\text{H}_5\text{Os}_{10}(\text{CO})_{24}]^-$ were present in the filtered triglyme solution, as suggested by infrared spectroscopy in the carbonyl region.^{33,44} Even in the first stage of the reaction, traces of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$ could not be detected by ^1H NMR or by mass spectrometry, suggesting that the reduction does not proceed via preliminary hydrolysis of the silanolate ligand.

(ii) Reduction of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]$. A solution of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]^{9a}$ (84.0 mg, 0.079 mmol) in anhydrous triglyme (14 mL) was heated under a flux of H_2 (1 atm) at 160 °C in a three-necked flask equipped with a condenser, a thermometer, and a magnetic stirrer. The reaction was followed by infrared spectroscopy in the carbonyl region by monitoring the appearance of the bands characteristic for $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$. After 1 h the reaction was complete. The solution was cooled at -20 °C in order to precipitate $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$. Filtration followed by washing with pentane (ca. 3 mL), to remove the last drops of triglyme eventually present, afforded pure $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$ (41.3 mg, 0.037 mmol; 64% yield). Minor traces of $[\text{H}_4\text{Os}_{10}(\text{CO})_{24}]^{2-}$ and $[\text{H}_5\text{Os}_{10}(\text{CO})_{24}]^-$ were present in the filtered triglyme solution, as suggested by infrared spectroscopy in the carbonyl region;^{33,44} the presence of $[\text{H}_4\text{Os}_{10}(\text{CO})_{24}]^{2-}$ was confirmed also by ^1H NMR spectroscopy (in CD_3COCD_3 : $\delta -16.4$ ppm).^{33,44}

(iii) Reduction of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_3)]$. A solution of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiPh}_3)]^{9a}$ (44.0 mg, 0.039 mmol) in anhydrous triglyme (14 mL) was heated under a flux of H_2 (1 atm) at 160 °C in a three-necked flask equipped with a condenser, a thermometer, and a magnetic stirrer. The reaction was followed by infrared spectroscopy in the carbonyl region by monitoring the appearance of the bands characteristic for $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$. After 30 min the reaction was complete. The solution was cooled at -20 °C in order to precipitate $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$. Filtration followed by washing with pentane (ca. 3 mL), to remove the last drops of triglyme eventually present, afforded pure $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$ (20.3 mg, 0.018 mmol; 63% yield). Minor traces of $[\text{H}_4\text{Os}_{10}(\text{CO})_{24}]^{2-}$ and $[\text{H}_5\text{Os}_{10}(\text{CO})_{24}]^-$ were present in the filtered triglyme solution, as suggested by infrared spectroscopy in the carbonyl region.^{33,44}

(iv) Reduction of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]$. A solution of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OH})]^{18}$ (35.8 mg, 0.041 mmol) in anhydrous triglyme (20 mL) was heated under a flux of H_2 (1 atm) at 160 °C in a three-necked flask equipped with a condenser, a thermometer, and a magnetic stirrer. The reaction was followed by infrared spectroscopy in the carbonyl region by monitoring the appearance of the bands characteristic for $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$. After 30 min, the reaction was complete. The solution was cooled at -20 °C in order to precipitate $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$. Filtration followed by washing with pentane (ca. 3 mL), to remove the last drops of triglyme eventually present, afforded pure $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$ (22.2 mg, 0.020 mmol; 65% yield). Minor traces of $[\text{H}_4\text{Os}_{10}(\text{CO})_{24}]^{2-}$ and $[\text{H}_5\text{Os}_{10}(\text{CO})_{24}]^-$ were present in the filtered triglyme solution, as suggested by infrared spectroscopy in the carbonyl region.^{33,44}

Thermal Degradation of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$. A solution of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]^{9a}$ (70.2 mg, 0.071 mmol) in anhydrous triethylsilanol (1.8 mL), prepared under N_2 in the closed reaction vessel (height 17 cm; diameter 3 cm) previously described,³⁴ was treated under vacuum (10^{-2} Torr) at 25 °C and then exposed to dried air at atmospheric pressure. The bottom of the vessel (about half of the cylinder) was put in an oven and heated at 200 °C. The reaction was monitored by infrared spectroscopy in the carbonyl region; samples were taken from the glass vessel at room temperature and analyzed after dilution in dichloromethane. After ca. 4 h, the reaction was complete and a black precipitate was present. The triethylsilanol solution was taken from the reaction vessel,

(44) Lucenti, E.; Roberto, D.; Roveda, C.; Ugo, R.; Cariati, E. *J. Cluster Sci.*, in press.

while the precipitate was washed with pentane (ca. 10 mL). Further treatment of the precipitate with dichloromethane (ca. 10 mL) afforded yellow $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$ (6.7 mg, 0.006 mmol; 11% yield), whereas evaporation to dryness of the combined pentane and triethylsilanol solutions gave 64.6 mg of a brown oil. In the last drops of distillate, minor amounts of $\text{Et}_3\text{-SiOSiEt}_3$ (^{29}Si NMR in CDCl_3 , δ (ppm) 8.51; ^1H NMR in CDCl_3 , δ (ppm) 0.56 (q, 12 H, 6 CH_2), 0.96 (t, 18 H, 6 CH_3); MS (EI) m/e 246 $[\text{M}]^+$, 217 $[\text{M} - \text{Et}]^+$) were present together with $\text{Et}_3\text{-SiOH}$ (^{29}Si NMR in CDCl_3 , δ (ppm) 19.28; ^1H NMR in CDCl_3 , δ (ppm) 0.62 (q, 12 H, 6 CH_2), 0.99 (t, 18 H, 6 CH_3); MS (EI) m/e 132 $[\text{M}]^+$, 103 $[\text{M} - \text{Et}]^+$) and small traces of $\text{Et}_3\text{SiOSiEt}_2\text{-OSiEt}_3$ (MS (EI) m/e 319 $[\text{M} - \text{Et}]^+$) and $\text{Et}_3\text{Si}(\text{OSiEt}_2)_2\text{OSiEt}_3$ (MS (EI) m/e 421 $[\text{M} - \text{Et}]^+$).⁴³ These $\text{Et}_3\text{Si}(\text{OSiEt}_2)_n\text{OSiEt}_3$ species ($n = 0\text{--}2$) were also formed by heating in dried air pure triethylsilanol in the closed reaction vessel at 200 °C for 4 h, as confirmed by ^{29}Si NMR spectroscopy and by mass spectrometry.

The crude brown oil was purified by column chromatography on silica using as eluent hexane, to obtain a colorless oil (50.3 mg, 0.028 mmol; 52% yield with respect to starting $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$). It was characterized as $[\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2]_n$ by elemental analysis (Anal. Calcd: C, 30.18; H, 5.03. Found: C, 31.67; H, 4.92), mass spectrometry (in both the EI and the FAB^- mass spectra, there is a peak at m/e 916 which corresponds to the fragment " $\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2$ ", followed by an intense peak at m/e 888 that could correspond to the loss of one CO; in the ESI+ mass spectrum in CH_3CN there are peaks at m/e 1914, 998, and 970 that correspond to $[\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2]_2 \cdot 2\text{CH}_3\text{CN}$, $[\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2] \cdot 2\text{CH}_3\text{CN}$, and $[\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2] \cdot 2\text{CH}_3\text{CN}$ with loss of one CO, respectively), infrared spectroscopy (in CH_2Cl_2 , ν_{CO} 2115 (s), 2021 (vs, br), 2008 (s), 1921 (s) cm^{-1} ; in hexane, ν_{CO} 2112 (s), 2020 (sh), 2017 (vs), 1933 (s) cm^{-1}), ^1H NMR spectroscopy (in CDCl_3 : δ (ppm) 1.098 (t, 9 H, 3 CH_3 , $J = 7.9$ Hz), 1.078 (t, 18 H, 6 CH_3 , $J = 7.6$ Hz), 0.809 (q, 6 H, 3 CH_2 , $J = 7.9$ Hz), 0.800 (q, 12 H, 6 CH_2 , $J = 7.6$ Hz), -14.68 (s, 1 H, H_{Os} , $^1J(^{187}\text{Os}\text{-}^1\text{H}) = 94$ Hz)), ^{29}Si NMR spectroscopy (in CDCl_3 , δ (ppm) 29.71 (2 OSiEt_3), 27.57 (1 OSiEt_3)) and ^{13}C NMR spectroscopy (in CDCl_3 , δ (ppm) 7.67 (9 CH_3), 8.17 (9 CH_2), 181.16 (*cis*- $(\text{CO})_2\text{Os}$); 169.99 and 169.63 (*fac*- $(\text{CO})_3\text{Os}$) by analogy with the ^{13}C NMR spectrum of *fac*- $[\text{Os}(\text{CO})_3\text{Cl}_2\text{-}(\text{acetone})]$, two signals at δ (ppm) 167.75 and 166.34).

Heteronuclear multiple quantum correlation (HMQC) spectroscopy with the bilinear rotation decoupling (BIRD) technique showed that the hydridic signal is coupled selectively to the CO's at 181.16 ppm.

The same species $[\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2]_n$ was also formed, along with traces of $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$, by thermal degradation under deoxygenated N_2 of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$ (15.0 mg, 0.015 mmol) dissolved in triethylsilanol (0.75 mL). However, the reaction was slower than when it was carried out in air, being not complete even after 19 h.

In addition, in pure anhydrous triglyme (12 mL) under deoxygenated N_2 at 200 °C, $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSiEt}_3)]$ (15.7 mg, 0.016 mmol) was rapidly (less than 2 h) converted to mixtures of $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$ and $[\text{H}_5\text{Os}_{10}(\text{CO})_{24}]^-$, as shown by the infrared and ^1H NMR spectra^{20,33} in CD_3CN of the crude residue obtained after evaporation to dryness of the triglyme solution; the two clusters can be easily separated, since the solubility of $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$ in dichloromethane is different from that of $[\text{H}_5\text{Os}_{10}(\text{CO})_{24}]^-$.⁴⁴

Reactivity of the Proposed $[\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2]_n$. (i) **With Aqueous HCl.** In a two-necked flask, $[\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2]_n$ (11.0 mg, 0.006 mmol) was dissolved in hexane (8 mL) and stirred vigorously, at room temperature, with 36% aqueous HCl (8 mL). After 2 days the reaction, which was followed by monitoring the decrease of

the carbonyl bands in the infrared spectrum of the organic phase, was complete. Evaporation of the aqueous phase afforded a mixture of *fac*- $[\text{Os}(\text{CO})_3\text{Cl}_3]^-$ and *cis*- $[\text{Os}(\text{CO})_2\text{Cl}_4]^{2-}$ (molar ratio 1:1) as confirmed by infrared spectroscopy in ethanol.³⁵ Addition of $[\text{NBu}_4]\text{Cl}$ followed by evaporation of the solvent and column chromatography on silica (eluent CH_3OH) afforded first *fac*- $[\text{NBu}_4][\text{Os}(\text{CO})_3\text{Cl}_3]$ (IR in CH_2Cl_2 , ν_{CO} 2115 (m), 2023 (s) cm^{-1}) and then *cis*- $[\text{NBu}_4]_2[\text{Os}(\text{CO})_2\text{Cl}_4]$ (IR in CH_2Cl_2 , ν_{CO} 2012 (s), 1922 (s) cm^{-1}) in the ratio 1:1. The reaction of $[\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2]_n$, dissolved in CDCl_3 , with 36% aqueous HCl was also followed by ^{29}Si NMR spectroscopy: after 2 days the signals at δ 29.7 and 27.5 ppm were replaced by an intense signal at δ 8.51 ppm (due to $\text{Et}_3\text{SiOSiEt}_3$) and a weak signal at δ 36.13 ppm (due to $\text{Et}_3\text{-SiCl}$). A blank experiment showed that Et_3SiOH reacts with 36% aqueous HCl more rapidly (the reaction is complete in ca. 40 min) than $[\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2]_n$, affording Et_3SiCl only.

(ii) **With CO.** A solution of $[\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2]_n$ (62.8 mg, 0.034 mmol) in anhydrous triethylsilanol (2.0 mL) was heated under CO (1 atm) at 200 °C in the closed reaction vessel previously described.³⁴ During the reaction a yellow precipitate was formed whereas, in parallel, a yellow powder sublimed on the cold walls of the vessel. After 5 days the triethylsilanol solution, containing some unreacted $[\text{Os}(\text{CO})_3(\mu\text{-OSiEt}_3)_2(\text{OSiEt}_3)(\text{H})\text{Os}(\text{CO})_2]_n$, was separated, whereas the sublimate and the precipitate were combined and chromatographed on a silica column, affording pure $[\text{Os}_3(\text{CO})_{12}]$ (20.6 mg, 0.023 mmol; 50% yield).

Thermal Degradation of $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$. Silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ ^{10,18} (1.824 g; 1.74 wt % Os with respect to SiO_2) was transferred into the closed reaction vessel (height 17 cm; diameter 3 cm) previously described,³⁴ treated under vacuum (10^{-2} Torr) at 25 °C and then exposed to deoxygenated N_2 at atmospheric pressure. The bottom of the vessel (about half of the cylinder) was put in an oven and heated at 200 °C. The reaction was monitored by infrared spectroscopy in the carbonyl region; samples were taken from the glass vessel at room temperature and analyzed as Nujol mulls. After 88 h, the reaction was complete, affording silica-anchored osmium carbonyl species (in Nujol, ν_{CO} 2121 (m, br), 2035 (s, br) and 1955 (m, br) cm^{-1}) along with traces of $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$, $[\text{H}_4\text{Os}_{10}(\text{CO})_{24}]^{2-}$, and $[\text{H}_5\text{Os}_{10}(\text{CO})_{24}]^-$, which were removed from the silica surface with dichloromethane (neutral cluster) and acetonitrile (anionic clusters) and then identified by infrared and ^1H NMR spectroscopy.^{20,33,44} The remaining silica-anchored osmium carbonyl species were quantitatively extracted from the surface with aqueous HCl, affording, after evaporation of the aqueous solution to dryness, a mixture of *fac*- $[\text{Os}(\text{CO})_3\text{Cl}_3]^-$ and *cis*- $[\text{Os}(\text{CO})_2\text{Cl}_4]^{2-}$, as confirmed by infrared spectroscopy of the solid residue in both ethanol and Nujol.³⁵ The thermal degradation of silica-anchored $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ was much faster in air than under N_2 , being complete in ca. 3 h and affording the same dicarbonyl- and tricarbonylosmium(II) species only.

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