Surface Organometallic Chemistry: Synthesis and X-ray Characterization of Novel Silanolate Surface Models $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiR_2R')]$ and of the First Models with Two Homo and Hetero Metal Carbonyl Fragments Linked to Vicinal or Geminal Silanols

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Reaction of $[Re_2(CO)_8(THF)_2]$ with $R_2R'SiOH$ (R = Et, Ph; R′ = Et, Ph, OH, $OSiPh_2OH$) gives the new molecular models $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiR_2R')]$, which mimic a surface $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSi\equiv)]$ species anchored to isolated, geminal, or vicinal silanols. The bridging structure has been confirmed by the X-ray structure of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$. Thermal treatment (70 °C) of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OH)]$ with excess Et_3SiOH is another way to form $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiEt_3)]$, which can be reconverted into the hydroxo complex by addition of excess water at the same temperature. Both $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiEt_3)]$ and $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OH)]$ are readily transformed into $[Re_2(CO)_{10}]$ under 1 atm of CO at 150 °C. These molecular models, which are the only neutral carbonyl rhenium complexes bearing silanolate ligands reported up to now, constitute a new tool to clarify the first step of the surface chemistry of the photochemical interaction of $[Re_2(CO)_{10}]$ with a rather inert support such as silica. Although the free silanol OH of both $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$ and $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$ is much less reactive than the OH of the corresponding noncoordinated silanol, it reacts at 25 °C with excess $[Re_2(CO)_8(THF)_2]$ to give the first bimetallic models $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2O\text{-}\mu)(\mu\text{-}H)Re_2(CO)_8]$ and $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2O\text{-}\mu)(\mu\text{-}H)Re_2(CO)_8]$, respectively. The latter complex, less stable to hydrolysis, is of particular interest because it constitutes the first molecular model of two metal carbonyl fragments linked to geminal surface silanols, thus suggesting that this kind of bimetallic system may occur also on a surface. Remarkably, the reaction of the rather unreactive $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$ cluster with the very reactive $[Re_2(CO)_8(THF)_2]$ affords $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2O\text{-}\mu)(\mu\text{-}H)Os_3(CO)_{10}]$, the first heterobimetallic molecular model whose structure has been determined by X-ray diffraction.

Introduction

Transition-metal carbonyls supported on silica are interesting hybrid materials, which may be convenient precursors of highly dispersed metals with unusual catalytic properties.[1] However, the surface organometallic chemistry involved is not always clear. It can be better understood from the structure and reactivity of molecular organometallic compounds bearing silanolate ligands to mimic the functional groups of the silica surface. These models are an important tool not only to define structural aspects but also to clarify by a molecular approach the chemical behavior of organometallic species bound to silica.[2] Although models of silica-

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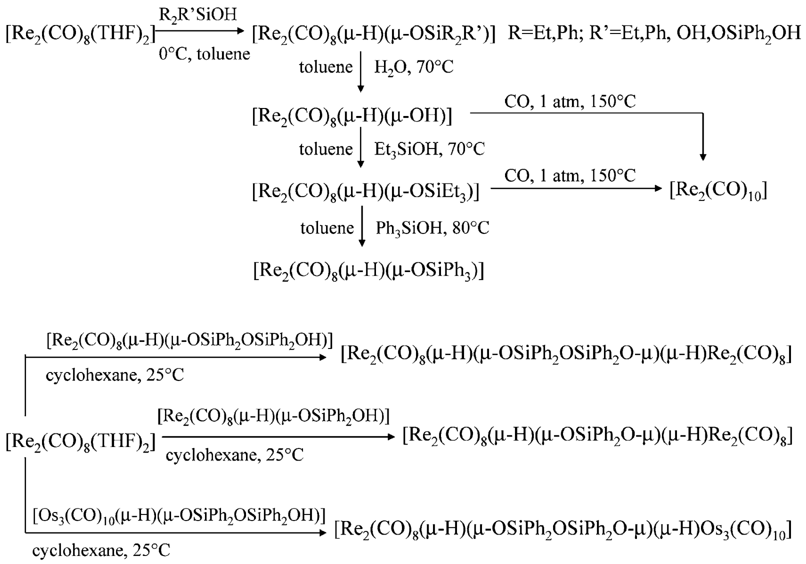
Scheme 1. Synthesis and Reactivity of Novel Silanolate Complexes



anchored carbonyl species of various metals (e.g. Rh,[3] Os,[2,4] Ru[5]) have been prepared and characterized, in the case of Re only recently has the anionic species $[Re_2(CO)_6(\mu\text{-}OH)_{3-x}(\mu\text{-}OSiEt_3)_x]^-$ ($x = 1-3$) been obtained.[6] Yet, there is a need for neutral rhenium carbonyl species bearing silanolate ligands as models to understand and confirm the proposed chemistry of silica-supported rhenium carbonyl species such as $[Re_2(CO)_{10}]$ and $[Re(CO)_3OH]_4$. This specific surface organometallic chemistry is not well-known,[7] particularly with respect to the industrial relevance of Re catalysts supported on inorganic oxides for reactions such as olefin metathesis[8a] and epoxidation,[8b] hydrogenation,[8c] dehydrogenation,[8d] and petroleum refining.[8e] Therefore, to produce a better insight into the organometallic chemistry of Re carbonyl species supported on silica, we studied the preparation of neutral Re carbonyl silanolate complexes such as $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiR_2R')]$ (R = Et, Ph; R′ = Et, Ph, OH, $OSiPh_2OH$), which, by analogy with the known activation of $[Os_3(CO)_{12}]$ by silica to give silica-anchored $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi\equiv)]$,[9a] could be models of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSi\equiv)]$, first formed by thermal interaction of $[Re_2(CO)_{10}]$ with silica. This surface species, never clearly identified, could also be the key intermediate in the formation of $[Re_2(CO)_{10}]$ upon treatment of silica-supported $[Re(CO)_3(OH)]_4$ with CO (1 atm, 150−200 °C)[7c] by analogy with the well-known reductive carbonylation of silica-anchored $[Os(CO)_x(OSi\equiv)_2]_n$ ($x = 2,3$)[9a] or silica-supported $[Os(CO)_3(OH)_2]_n$[9b] to give $[Os_3(CO)_{12}]$ via $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi\equiv)]$.

$[Re_2(CO)_8(THF)_2]$ is a very reactive species derived from $[Re_2(CO)_{10}]$, capable of activating different H−Y bonds (e.g. Y = H, Cl, C≡CPh, CH═CHPh, $CH_2C(O)OEt$, OH) to give the corresponding $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}Y)]$ complexes.[10] Therefore we investigated its reactivity with different 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 (Scheme 1).

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Table 1. Selected ^{1}H and ^{29}Si NMR Signals in Toluene-d_8 of Various Silanolate Complexes

silanolate complex	^{1}H NMR $\delta(\mu$-H) (ppm)	^{29}Si NMR δ (ppm)
$[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_3)]$	−10.87	−2.12
$[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiEt_3)]$	−10.67	+34.38
$[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$	−10.79	−28.77; −37.31
$[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$	−10.81	−22.53
$[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2O\text{-}\mu)(\mu\text{-}H)Re_2(CO)_8]$	−10.79	−29.80
$[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2O\text{-}\mu)(\mu\text{-}H)Re_2(CO)_8)]$	−10.85	−14.86
$[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2O\text{-}\mu)(\mu\text{-}H)Os_3(CO)_{10}]$	−10.83; −11.96	−28.69; −29.60
$[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$[4g]	−12.20	−29.11; −36.78

Results and Discussion

Preparation and Characterization of Molecular Models of the Type $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiR_2R')]$. The activation of H−Y bonds by $[Re_2(CO)_8(THF)_2]$ often proceeds only in solvents other than tetrahydrofuran.[10] No reaction takes place in THF, even in the presence of a 7-fold excess of $R_2R'SiOH$ (R = Et, Ph; R′ = Et, Ph, OH, $OSiPh_2OH$). However, when working in anhydrous toluene instead of tetrahydrofuran, the corresponding dinuclear species $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiR_2R')]$ are readily formed, in a few minutes, even at 0 °C and using a stoichiometric amount of $R_2R'SiOH$, as evidenced by ^{1}H and ^{29}Si NMR spectroscopy. Thus, the addition of $[Re_2(CO)_8(THF)_2]$ to a solution of Ph_3SiOH (molar ratio 1:1) in anhydrous deuterated toluene, working at 0 °C under nitrogen, can be followed by ^{1}H NMR spectroscopy (by the appearance of a signal at δ −10.87 ppm assigned to a hydride bridging two Re atoms)[10a] and by ^{29}Si NMR spectroscopy (by the decrease of the intensity of the signal at δ −14.26 ppm due to free Ph_3SiOH and the parallel formation of a signal at lower field, δ −2.12 ppm, attributable to a silanolate bound to rhenium[6]). Evaporation to dryness followed by recrystallization from dichloromethane/hexane gives $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_3)]$. Similarly, treatment at 0 °C of an anhydrous toluene solution of Et_3SiOH, $HOSiPh_2OSiPh_2OH$, or $Ph_2Si(OH)_2$ with a stoichiometric amount of $[Re_2(CO)_8(THF)_2]$ gives the corresponding dinuclear species $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiEt_3)]$ or $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2R')]$ (R′ = OH, $OSiPh_2OH$), which can be purified by the same process of recrystallization. These new silanolate compounds have been fully characterized by infrared and ^{1}H NMR and ^{29}Si NMR spectroscopy, by elemental analysis, and, in some cases, by mass spectrometry (EI) (see Table 1 and Experimental Section). In the particular case of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$ the molecular structure was established by X-ray crystallography (Figure 1). Crystal data and details of the structure refinement are reported in Table 2, and relevant bond distances and angles are listed in Table 3. The molecule can be seen as being formed by two "Re(CO)$_4$" fragments bridged by a μ-$OSiPh_2OH$ ligand and a μ-H (hydride) atom so that each rhenium atom shows an almost octahedral geometry. The Re−Re bond distance of 3.0226(8) Å is nearly coincident with that found for the precursor compound $[Re_2(CO)_8(THF)_2]$ (3.0224(4) Å)[10a] and is not much different from that of related species such as $[Re_2(CO)_6(\mu\text{-}H)(\mu\text{-}OH)(dppm)]$[11] (dppm = bis(diphenylphosphino)methane) (3.030(1) Å) with a similar "Re(μ-H)(μ-O)Re" core. The structural trend observed in other "M(μ-H)(μ-O)M" cores thus seems confirmed: the lengthening effect, which 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 bridging μ-OR ligand. The equato-

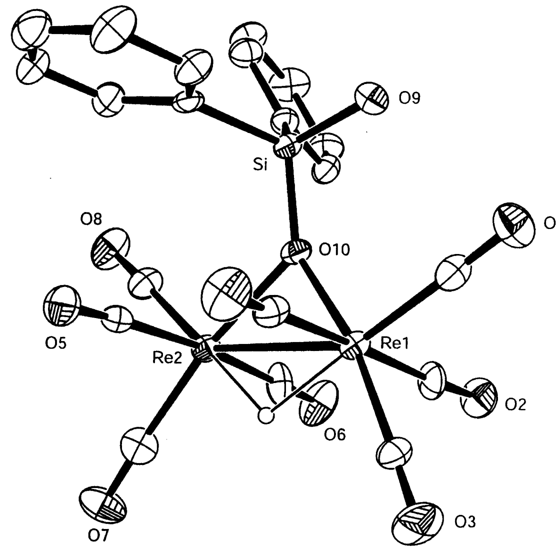

Figure 1. ORTEP diagram of the complex $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$ with a partial labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. The hydrogen atoms of the phenyl groups are omitted for clarity.

Table 2. Summary of Crystal Data and Structure Refinement Parameters for $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$ and $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2O\text{-}\mu)(\mu\text{-}H)Os_3(CO)_{10}]$

	$C_{20}H_{12}O_{10}Re_2Si$	$C_{42}H_{22}O_{21}Os_3Re_2Si_2$
fw	812.79	1861.78
cryst syst	monoclinic	monoclinic
space group (No.)	$P2_1/c$ (14)	$P2_1/c$ (14)
a (Å)	7.624(1)	12.597(1)
b (Å)	35.861(6)	14.044(1)
c (Å)	8.689(2)	28.693(2)
β (deg)	98.68(1)	96.58(1)
V (Å^3)	2348.5(7)	5042.5(6)
Z	4	4
D(calcd), g cm^{-3}	2.299	2.452
abs coeff, mm^{-1}	10.402	12.438
θ range, deg	2−26	2−26
no. of rflns collected	21 515	40 323
no. of indep rflns	4694 (R(int) = 0.0466)	9904 (R(int) = 0.0496)
cryst decay, %	none	none
no. of data/restraints/params	4694/0/298	9904/0/633
goodness of fit on F_o^2	1.360	1.061
R indices ($F_o > 4\sigma(F_o)$)[a,b]	R1, 0.0577; wR2, 0.1149	R1, 0.0282; wR2, 0.0597
R indices (all data)[a,b]	R1, 0.0657; wR2, 0.1173	R1, 0.0429; wR2, 0.0655
largest diff peak and hole, e Å^3	2.095 and −3.086	1.580 and −1.240

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

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Table 3. Selected Bond Lengths (Å) and Angles (deg)

$[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$			
Re(1)−C(3)	1.905(14)	Re(2)−C(8)	1.943(14)
Re(1)−C(4)	1.926(16)	Re(2)−C(6)	1.964(15)
Re(1)−C(2)	1.961(14)	Re(2)−C(5)	2.018(13)
Re(1)−C(1)	2.005(14)	Re(2)−O(10)	2.160(8)
Re(1)−O(10)	2.141(8)	Si−O(10)	1.633(8)
Re(1)−Re(2)	3.0226(8)	Si−O(9)	1.635(9)
Re(2)−C(7)	1.924(16)		
Re(1)−O(10)−Re(2)	89.3(3)	C(8)−Re(2)−C(6)	90.0(6)
C(3)−Re(1)−C(4)	90.8(6)	C(7)−Re(2)−C(5)	88.4(6)
C(3)−Re(1)−C(2)	88.8(6)	C(8)−Re(2)−C(5)	90.2(5)
C(4)−Re(1)−C(2)	89.7(6)	C(6)−Re(2)−C(5)	174.7(6)
C(3)−Re(1)−C(1)	88.3(5)	C(7)−Re(2)−O(10)	169.9(5)
C(4)−Re(1)−C(1)	90.0(6)	C(8)−Re(2)−O(10)	99.9(5)
C(2)−Re(1)−C(1)	177.0(6)	C(6)−Re(2)−O(10)	92.4(5)
C(3)−Re(1)−O(10)	168.2(5)	C(5)−Re(2)−O(10)	92.7(4)
C(4)−Re(1)−O(10)	100.9(5)	O(10)−Si−O(9)	108.5(5)
C(2)−Re(1)−O(10)	89.8(5)	O(10)−Si−C(21)	108.3(5)
C(1)−Re(1)−O(10)	93.2(4)	O(9)−Si−C(21)	111.6(5)
C(7)−Re(2)−C(8)	90.1(6)	O(10)−Si−C(11)	111.8(5)
C(7)−Re(2)−C(6)	86.4(7)	O(9)−Si−C(11)	104.9(5)
$[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2O\text{-}\mu)(\mu\text{-}H)Os_3(CO)_{10}]$			
Os(1)−Os(3)	2.8162(4)	Os(3)−O(21)	2.154(4)
Os(1)−Os(2)	2.8317(4)	Re(1)−C(4)	1.909(8)
Os(2)−Os(3)	2.7863(4)	Re(1)−C(3)	1.927(7)
Re(1)−Re(2)	3.0144(4)	Re(1)−C(1)	1.983(8)
Os(1)−C(12)	1.926(9)	Re(1)−C(2)	1.990(9)
Os(1)−C(11)	1.936(8)	Re(1)−O(20)	2.155(4)
Os(1)−C(9)	1.940(7)	Re(2)−C(8)	1.919(8)
Os(1)−C(10)	1.960(7)	Re(2)−C(7)	1.944(7)
Os(2)−C(17)	1.878(8)	Re(2)−C(5)	1.995(9)
Os(2)−C(14)	1.900(7)	Re(2)−C(6)	1.996(8)
Os(2)−C(16)	1.960(6)	Re(2)−O(20)	2.184(4)
Os(2)−O(21)	2.129(4)	Si(1)−O(19)	1.630(4)
Os(3)−C(18)	1.873(7)	Si(1)−O(21)	1.644(4)
Os(3)−C(15)	1.916(9)	Si(2)−O(20)	1.626(4)
Os(3)−C(13)	1.922(9)	Si(2)−O(19)	1.639(4)
Re(1)−O(20)−Re(2)	88.00(14)	C(1)−Re(1)−C(2)	176.3(3)
Os(2)−O(21)−Os(3)	81.17(13)	C(4)−Re(1)−O(20)	166.0(2)
C(12)−Os(1)−C(11)	101.8(3)	C(3)−Re(1)−O(20)	104.7(2)
C(12)−Os(1)−C(9)	93.4(3)	C(1)−Re(1)−O(20)	90.0(3)
C(11)−Os(1)−C(9)	92.7(3)	C(2)−Re(1)−O(20)	93.7(2)
C(12)−Os(1)−C(10)	93.3(3)	C(8)−Re(2)−C(7)	89.5(3)
C(11)−Os(1)−C(10)	92.8(3)	C(8)−Re(2)−C(5)	85.6(4)
C(9)−Os(1)−C(10)	170.2(3)	C(7)−Re(2)−C(5)	91.0(3)
C(17)−Os(2)−C(14)	91.6(3)	C(8)−Re(2)−C(6)	87.0(3)
C(17)−Os(2)−C(16)	88.4(3)	C(7)−Re(2)−C(6)	89.8(3)
C(14)−Os(2)−C(16)	97.6(3)	C(5)−Re(2)−C(6)	172.5(3)
C(17)−Os(2)−O(21)	167.9(2)	C(8)−Re(2)−O(20)	167.9(3)
C(14)−Os(2)−O(21)	97.9(2)	C(7)−Re(2)−O(20)	102.6(2)
C(16)−Os(2)−O(21)	97.7(2)	C(5)−Re(2)−O(20)	93.7(2)
Os(3)−Os(2)−Os(1)	60.163(10)	C(6)−Re(2)−O(20)	93.4(2)
C(18)−Os(3)−C(15)	91.4(3)	O(19)−Si(1)−O(21)	107.9(2)
C(18)−Os(3)−C(13)	88.9(3)	O(19)−Si(1)−C(121)	111.7(3)
C(15)−Os(3)−C(13)	94.1(4)	O(21)−Si(1)−C(121)	106.5(2)
C(18)−Os(3)−O(21)	165.2(3)	O(19)−Si(1)−C(111)	106.8(2)
C(15)−Os(3)−O(21)	98.0(3)	O(21)−Si(1)−C(111)	111.2(2)
C(13)−Os(3)−O(21)	101.7(3)	O(20)−Si(2)−O(19)	108.2(2)
C(4)−Re(1)−C(3)	89.1(3)	O(20)−Si(2)−C(211)	107.9(2)
C(4)−Re(1)−C(1)	88.1(4)	O(19)−Si(2)−C(211)	107.9(2)
C(3)−Re(1)−C(1)	88.5(3)	O(20)−Si(2)−C(221)	106.6(3)
C(4)−Re(1)−C(2)	88.4(4)	O(19)−Si(2)−C(221)	112.4(2)
C(3)−Re(1)−C(2)	90.2(3)		

rial carbonyls (C8, C7, C4, C3) are coplanar with the two rhenium atoms, the bridging oxygen O10, and hydride atoms with a maximum deviation from the plane not exceeding 0.01 Å. The μ-OSiPh$_2$OH group bridges the two rhenium atoms in an almost symmetric way, the two distances Re1−O10 and Re2−O10 being 2.141(8) and 2.160(8) Å, respectively. The Re1−O10−Re2 angle, 89.3(3)°, is close to that found for $[Re_2(CO)_6(\mu\text{-}H)(\mu\text{-}OH)(dppm)]$, 88.6(2)°, but larger than the Os−O−Os angle reported when the same silanol is bridging two Os atoms as in $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$ (82.65°).[4g] The two "Re(CO)$_4$" fragments adopt an eclipsed conformation, and apart from the −Si(Ph)$_2$OH group the molecule conforms to an idealized C_{2v} point symmetry. Finally, similarly to $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$,[4g] no evidence has been found for inter- or intramolecular hydrogen bonds originated by the free silanol of the μ-OSiPh$_2$OH bridge.

Alternative Synthesis and Reactivity of [Re$_2$(CO)$_8$(μ-H)(μ-OSiR$_2$R′)]. It is known that some complexes or clusters bearing a metal−OH bond react more or less easily with silanol groups of the silica surface to anchor an organometallic species by a metal−OSi≡ bond.[12] With regard to mimicking the reactivity of the silica surface,[12b] it was recently reported by some of us that the OH ligand of the cluster $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ exchanges with silanol molecules such as R$_2$R′SiOH (R = Et, Ph; R′ = Et, Ph, OH, OSiPh$_2$OH), when working in anhydrous *m*-xylene at 138 °C, to afford the related osmium cluster with a silanolate bridge.[4g] This seems to be a quite general reaction.[4h] For instance, some of us have described the reaction of $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_3]$ with excess triethylsilanol to give the related silanolate species $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_{3-x}(\mu\text{-}OSiEt_3)_x]$ (working at 25 °C, $x = 1$; working at 150 °C, $x = 2$, 3 depending on the reaction time).[6] We thus investigated the reactivity with Et$_3$SiOH of the hydroxo complex $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OH)]$, recently prepared by some of us,[10b,c] as another way to produce the bridging rhenium silanolates described above.

The complex $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OH)]$ does not react in the presence of a 10-fold amount of Et$_3$SiOH, working at room temperature in anhydrous deuterated toluene. However, an increase of the temperature to 70 °C leads to the formation of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiEt_3)]$, as evidenced by ^{1}H NMR spectroscopy (see the Experimental Section). After 2 h the reaction is complete. The bridging OH ligand of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OH)]$ exchanges with Et$_3$SiOH at a temperature lower than that for the hydroxo group of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ but at a temperature higher than that for the first bridging hydroxo group of the anionic species $[Re_2(CO)_6(\mu\text{-}OH)_3]^-$. In addition, whereas $[Re_2(CO)_6(\mu\text{-}OH)_{3-x}(\mu\text{-}OSiEt_3)_x]^-$ ($x = 1-3$) species are immediately converted back to $[Re_2(CO)_6(\mu\text{-}OH)_3]^-$ by addition of a few drops of water at room temperature,[6] hydrolysis of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiR_3)]$ (R = Et, Ph) to give $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OH)]$ occurs when working at higher temperature (70 °C for 20 min) only (see the Experimental Section). The reversible exchange reaction between the bridging hydroxo and the bridging silanolate ligand is general: addition of a 10-fold amount of Ph$_3$SiOH to a solution of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiEt_3)]$ in anhydrous toluene, followed by stirring at 80 °C for 1 h, leads to the formation of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_3)]$.

Besides, $[Re_2(CO)_{10}]$ is formed (slowly at 25−80 °C and rapidly at 150 °C) by bubbling CO into an anisole or triethylsilanol solution of either $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiEt_3)]$ or $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OH)]$. After 7 h at 150 °C the conversion is complete. This kind of reductive

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carbonylation gives further evidence to our suggestion that silica-anchored [$Re_2(CO)_8(\mu$-H)(μ-OSi≡)] (or silica-supported [$Re_2(CO)_8(\mu$-H)(μ-OH)] when working with a incompletely dehydrated silica) could be the key intermediate in the reductive carbonylation of silica-supported [$Re(CO)_3(OH)]_4$ to give [$Re_2(CO)_{10}$].[7c]

Molecular Models with Vicinal or Geminal Silanols Connecting Two "$Re_2(CO)_8(\mu$-H)" Moieties: [$Re_2(CO)_8(\mu$-H)(μ-$OSiPh_2OSiPh_2O$-μ)(μ-H)$Re_2(CO)_8$] and [$Re_2(CO)_8(\mu$-H)(μ-$OSiPh_2O$-μ)(μ-H)$Re_2(CO)_8$]. Both silanol groups of either the disilanol $HOSiPh_2OSiPh_2OH$ or the silanediol $Ph_2Si(OH)_2$ are reported to react with various high-oxidation-state early transition metals or main-group metals, affording cyclic metallasiloxanes.[13] For example, reaction of $HOSiPh_2OSiPh_2OH$ with $TiCl_4$ affords the spirocyclic complex [$Ti(OSiPh_2OSiPh_2O)_2$][14] and reaction with [$Zr(CH_2SiMe_3)_4$] leads to the formation of [$Zr(CH_2SiMe_3)_2(OSiPh_2OSiPh_2O)$] with a six-membered ZrO_3Si_2 ring,[13,15] while reaction with chromium trioxide affords [$Cr(=O)_2(OSiPh_2OSiPh_2O)]_2$, where the two disilanolate ligands bind to two chromium dioxo units, generating a unique 12-membered metallacyclic fragment.[16] $Ph_2Si(OH)_2$ reacts with $Ti(OBu)_4$ to yield, by a self-condensation process, the spirocyclic complex [$Ti(OSiPh_2(OSiPh_2)_3O)_2$],[17] but it reacts with R_2GeX_2 (R = Me, Ph; X = Cl, Br) to give [$Ph_2SiO_2GeR_2]_2$, which has a $Ge_2Si_2O_4$ eight-membered-ring core structure.[18] However, with a metal carbonyl species such as [$Os_3(CO)_{10}(\mu$-H)(μ-OH)], various attempts to react both silanol groups in order to prepare even simple bridged dinuclear species such as [$Os_3(CO)_{10}(\mu$-H)(μ-$OSiPh_2OSiPh_2O$-μ)(μ-H)$Os_3(CO)_{10}$] and [$Os_3(CO)_{10}(\mu$-H)(μ-$OSiPh_2O$-μ)(μ-H)$Os_3(CO)_{10}$] by reaction of [$Os_3(CO)_{10}(\mu$-H)(μ-$OSiPh_2OSiPh_2OH$)] and [$Os_3(CO)_{10}(\mu$-H)(μ-$OSiPh_2OH$)] with excess [$Os_3(CO)_{10}(\mu$-H)(μ-OH)] failed. These results suggested that the second silanol group does not react when the disilanol is bound to a metal carbonyl species such as an osmium cluster. It was thus relevant to understand if this latter point is general or is limited to the case of the "$Os_3(CO)_{10}(\mu$-H)" moiety. Therefore, we investigated whether the free silanol groups of [$Re_2(CO)_8(\mu$-H)(μ-$OSiPh_2OSiPh_2OH$)] and [$Re_2(CO)_8(\mu$-H)(μ-$OSiPh_2OH$)] react with excess [$Re_2(CO)_8(THF)_2$].

Addition of an excess of [$Re_2(CO)_8(THF)_2$] to a solution of $HOSiPh_2OSiPh_2OH$ in deuterated toluene (molar ratio 2:1), at 0 or 25 °C, does not lead to the formation of the bridged species [$Re_2(CO)_8(\mu$-H)(μ-$OSiPh_2OSiPh_2O$-μ)(μ-H)$Re_2(CO)_8$]. ^{29}Si NMR spectroscopy indicated that only [$Re_2(CO)_8(\mu$-H)(μ-$OSiPh_2OSiPh_2OH$)] is formed. Equally, $Ph_2Si(OH)_2$ under the same reaction conditions gives [$Re_2(CO)_8(\mu$-H)(μ-$OSiPh_2OH$)] as the only product. These results seem to confirm that the free silanol group in these kinds of silanolate complexes is much less reactive than the free silanol of a disilanol or of a silanediol. However, we were unable to investigate the above reaction for a long period because we found that the excess of [$Re_2(CO)_8(THF)_2$] reacts in parallel with toluene, a reaction which is under investigation in our laboratories.[19] Therefore, to avoid this side reaction, cyclohexane was used as solvent.

Addition of an excess of [$Re_2(CO)_8(THF)_2$] to a solution of [$Re_2(CO)_8(\mu$-H)(μ-$OSiPh_2OSiPh_2OH$)] in anhydrous cyclohexane (molar ratio 2:1), at room temperature, leads after 1.5 h to [$Re_2(CO)_8(\mu$-H)(μ-$OSiPh_2OSiPh_2O$-μ)(μ-H)$Re_2(CO)_8$], as confirmed by isolation of a crude product with the expected ^{29}Si NMR spectrum (only one signal at δ −29.80 ppm in deuterated toluene). The pure compound, obtained by successive recrystallizations (dichloromethane/hexane and then pentane), was fully characterized by infrared and ^1H NMR and ^{29}Si NMR spectroscopy and by elemental analysis (see Table 1 and the Experimental Section). Similarly, [$Re_2(CO)_8(\mu$-H)(μ-$OSiPh_2O$-μ)(μ-H)$Re_2(CO)_8$] is formed by addition of an excess of [$Re_2(CO)_8(THF)_2$] to a solution of [$Re_2(CO)_8(\mu$-H)(μ-$OSiPh_2OH$)] in anhydrous cyclohexane (molar ratio [$Re_2(CO)_8(THF)_2$]:[$Re_2(CO)_8(\mu$-H)(μ-$OSiPh_2OH$)] = (1.5−2):1), at room temperature for 2 h (see Table 1 and Experimental Section), as evidenced by ^{29}Si NMR spectroscopy (one signal at δ −14.86 ppm). However, various attempts to isolate and purify this new complex failed, due to its quick hydrolysis under crystallization conditions to give back [$Re_2(CO)_8(\mu$-H)(μ-$OSiPh_2OH$)]. It appears that [$Re_2(CO)_8(\mu$-H)(μ-$OSiPh_2OSiPh_2O$-μ)(μ-H)$Re_2(CO)_8$] is more stable than [$Re_2(CO)_8(\mu$-H)(μ-$OSiPh_2O$-μ)(μ-H)$Re_2(CO)_8$], probably due to steric effects.

Not only do these new bridged complexes with two homo metal carbonyl fragments linked by a silanediol or a disilanol bridge constitute the first molecular models carrying two metal carbonyl fragments but their synthesis also confirms a large decrease of reactivity of both vicinal and geminal silanol groups, when one of the silanols is bound to a low-oxidation-state metal carbonyl species. They thus produce evidence that on a silica surface two metal fragments could be linked not only to vicinal surface silanols but also to geminal silanols, although in this latter case in a rather unstable way.

Molecular Model with Two Heteronuclear Metal Carbonyl Fragments: [$Re_2(CO)_8(\mu$-H)(μ-$OSiPh_2OSiPh_2O$-μ)(μ-H)$Os_3(CO)_{10}$]. The formation of [$Re_2(CO)_8(\mu$-H)(μ-$OSiPh_2OSiPh_2O$-μ)(μ-H)$Re_2(CO)_8$)] by reaction of [$Re_2(CO)_8(\mu$-H)(μ-$OSiPh_2OSiPh_2OH$)] with [$Re_2(CO)_8(THF)_2$] is remarkable because, as mentioned above, the free silanol group of [$Os_3(CO)_{10}(\mu$-H)(μ-$OSiPh_2OSiPh_2OH$)] does not react with an excess of [$Os_3(CO)_{10}(\mu$-H)(μ-OH)].[4g] Therefore, the high reactivity of [$Re_2(CO)_8(THF)_2$] prompted us to investigate the reaction of [$Os_3(CO)_{10}(\mu$-H)(μ-$OSiPh_2OSiPh_2OH$)] with [$Re_2(CO)_8(THF)_2$]. This reaction occurs in anhydrous cyclohexane, affording [$Re_2(CO)_8(\mu$-H)(μ-$OSiPh_2OSiPh_2O$-μ)(μ-H)$Os_3(CO)_{10}$]. After the mixture is stirred for 3 h at room temperature, evaporation of the solvent to dryness gives a crude product purified by successive recrystallizations (dichloromethane/pentane and then pentane) and characterized by infrared and ^1H NMR and ^{29}Si NMR spectroscopy and by elemental analysis (see Table 1 and the Experimental Section). This is a unique new com-

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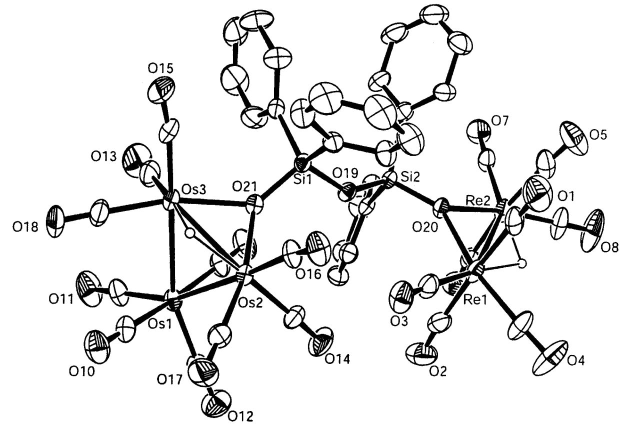

Figure 2. ORTEP diagram of the complex $[Re_2(CO)_8(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{O-}\mu)(\mu\text{-H})Os_3(CO)_{10}]$ with a partial labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. The hydrogen atoms of the phenyl groups are omitted for clarity.

plex because it contains for the first time two very different metal carbonyl fragments linked to the two silanol groups of a vicinal disilanol. Its structure was solved by X-ray diffraction and compared to those of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$[4g] and of $[Re_2(CO)_8(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]$, previously described (Figure 1).

The molecular structure of $[Re_2(CO)_8(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{O-}\mu)(\mu\text{-H})Os_3(CO)_{10}]$ is shown in Figure 2. Crystal data and details of the structure are reported in Table 2, and relevant bond distances and angles are listed in Table 3. The structure can be discussed by analyzing three components: the trinuclear osmium cluster "$Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-O})$", the dimeric rhenium fragment "$Re_2(CO)_8(\mu\text{-H})(\mu\text{-O})$", and the disilanolate ligand "$\mu\text{-OSiPh}_2\text{OPh}_2\text{O-}\mu$", which helds together the two organometallic moieties. The structural features of the two organometallic frameworks resemble those of $[Re_2(CO)_8(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]$ (see above) and $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$.[4g] The osmium cluster shows the expected triangular arrangement of the metal core framework, with two longer (Os1−Os2, 2.8317(4) Å; Os1−Os3, 2.8162(4) Å) and one shorter (Os2−Os3, 2.7863(4) Å) Os−Os edge, the latter bearing the μ-H and μ-OR bridges. The "$Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-O}-)$" core preserves the idealized C_s point symmetry (with the pseudo mirror plane passing through the Os1, H, and O21 atoms), as suggested for $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$. Equally the dinuclear rhenium fragment "$Re_2(CO)_8(\mu\text{-H})(\mu\text{-O})$" preserves the idealized C_{2v} point symmetry previously evidenced for $[Re_2(CO)_8(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OH})]$. The difference between this heterobimetallic species and $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$ is in the conformation of the $-\text{OSiPh}_2\text{OSiPh}_2\text{O}-$ bridge. In $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$ the two silanolate oxygens are "trans" (torsion angle O−Si···Si−O = 177.2°), while in $[Re_2(CO)_8(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{O-}\mu)(\mu\text{-H})Os_3(CO)_{10}]$ the two oxygens are "gauche" (O21−Si1···Si2−O20 = 90.5°), as illustrated in Figure 3.

Conclusion

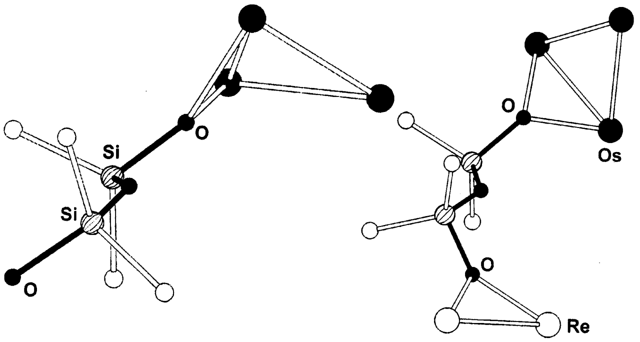

Figure 3. Comparison of the coordination around the Si atoms in $Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{OH})]$ (left) and $[Re_2(CO)_8(\mu\text{-H})(\mu\text{-OSiPh}_2\text{OSiPh}_2\text{O-}\mu)(\mu\text{-H})Os_3(CO)_{10}]$ (right).

The easy reaction of $[Re_2(CO)_8(THF)_2]$ with $R_2R'SiOH$ (R = Et, Ph; R′ = Et, Ph, OH, $OSiPh_2OH$) provides an entry to the novel model complexes $[Re_2(CO)_8(\mu\text{-H})(\mu\text{-OSiR}_2\text{R}')]$, which mimic a $[Re_2(CO)_8(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ species anchored to isolated, geminal, or vicinal silanols of the silica surface, thus confirming, as first evidenced by the reactivity of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$,[4g] that all the different silanol species of the silica surface may interact with metallic fragments. The synthesis of these new rhenium carbonyl complexes with a bridging silanolate ligand constitutes a new approach to the understanding of the surface chemistry which occurs during the photolysis of a solution of $[Re_2(CO)_{10}]$ in THF in the presence of silica. In this specific case the formation of silica-anchored $[Re_2(CO)_8(\mu\text{-OSi}\equiv)_2]$, $[Re(CO)_5OSi\equiv]$, and $[\equiv SiORe(CO)_3(\equiv SiOSi\equiv)_2]$ has been suggested only on the evidence that the carbonyl bands of the surface species are similar to those of known compounds such as $[Re_2(CO)_8(SPh)_2]$, $[Re(CO)_5Cl]$, and $[Re(CO)_3OH]_4$.[7b] However, it has been reported that the photochemical transformation of $[Re_2(CO)_{10}]$ into $[Re(CO)_3OH]_4$, working in wet tetrahydrofuran without the presence of silica, could involve the reactive species $[Re_2(CO)_8(H_2O)_2]$ and $[Re_2(CO)_8(\mu\text{-H})(\mu\text{-OH})]$ as intermediates.[20] Our models now suggest that the silica-anchored species formed during the photolysis of $[Re_2(CO)_{10}]$ in THF in the presence of silica and proposed to be $[Re_2(CO)_8(\mu\text{-OSi}\equiv)_2]$[7b] could be $[Re_2(CO)_8(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ generated directly or generated by reaction of $[Re_2(CO)_8L_2]$ (L = THF, H_2O) or $[Re_2(CO)_8(\mu\text{-H})(\mu\text{-OH})]$ with the surface silanol groups. Its formation, even when working under nonanhydrous conditions,[7b] would be reasonable, since our molecular models $[Re_2(CO)_8(\mu\text{-H})(\mu\text{-OSiR}_3)]$ are not easily hydrolyzed at room temperature and in addition are easily prepared from $[Re_2(CO)_8(\mu\text{-H})(\mu\text{-OH})]$ by exchange with excess silanol ligands, as probably may occur on an incompletely dehydrated silica surface.

In addition, we confirmed some previous observations[4g] on the very low reactivity of the remaining free silanol group of either disilanol or silanediol linked by one silanol to a metal carbonyl fragment. Despite such a low reactivity, the high reactivity of $[Re_2(CO)_8(THF)_2]$ allows the formation of the first molecular models with two homo or hetero metal carbonyl fragments linked to vicinal or even geminal surface silanols, including the first model of a rhenium/osmium bimetallic species. In these new models we also evidenced for the first time the low stability toward hydrolysis when two metal carbonyl fragments are linked to a geminal system.

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Experimental Section

General Comments. $[Re_2(CO)_8(THF)_2]$ was prepared following a reported procedure and was usually contaminated with unreactive $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ (ca. 10%).[10a] $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$[4g] and $HOSiPh_2OSiPh_2OH$[21] were prepared according to the literature, whereas Et_3SiOH, Ph_3SiOH, and $Ph_2Si(OH)_2$ were purchased from Sigma-Aldrich. Ph_3SiOH and $Ph_2Si(OH)_2$ were recrystallized (CH_2Cl_2) before use, whereas Et_3SiOH and the organic solvents were dried over molecular sieves (4 Å). All reactions, carried out under N_2 (dried by flowing over Drierite) in anhydrous conditions, were monitored by ^1H and ^{29}Si NMR spectroscopy. Products were characterized by infrared and ^1H NMR and ^{29}Si NMR spectroscopy, by elemental analysis, and, in some cases, by mass spectrometry (EI). Spectral data were obtained by use of the following spectrometers: Bruker-Vector 22 or Jasco FT-IR 420 (IR), Bruker AC-200 or Bruker DRX-300 (^1H and ^{29}Si NMR; $SiMe_4$ was used as standard), Varian VG9090 (MS). Elemental analyses were carried out at the Università di Milano.

Synthesis of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiR_2R')]$ (R = Et, Ph; R′ = Et, Ph, OH, $OSiPh_2OH$). In a typical synthesis, a solution of $R_2R'SiOH$ (R = Et, Ph; R′ = Et, Ph, OH, $OSiPh_2OH$) (0.027 mmol) in anhydrous toluene (3 mL) was prepared, under N_2 in a 25 mL two-neck round-bottomed flask equipped with a magnetic bar, and cooled to 0 °C with an ice bath. $[Re_2(CO)_8(THF)_2]$ (20 mg; 0.027 mmol) was added and the resulting orange-red solution stirred until it became yellow (ca. 5 min). Evaporation to dryness of toluene, followed by addition of dichloromethane (to dissolve the crude product) and reprecipitation with a few drops of hexane, gave pure $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiR_2R')]$ as a white powder. Crystals, suitable for X-ray diffraction, of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$ were obtained at −20 °C by using the biphasic system CH_2Cl_2/pentane.

$[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_3)]$. IR (in CH_2Cl_2): ν(CO) 2096 (w), 2016 (s), 1992 (m), 1954 (m) cm^{-1}. ^1H NMR (in toluene-d_8): δ (ppm) −10.87 (s, 1 H, bridging hydride), 7.22 (m, 9 H, ortho and para H of the 3 Ph), 7.82 (m, 6 H, meta H of the 3 Ph). ^{29}Si NMR (in toluene-d_8): δ (ppm) −2.12; the ^{29}Si NMR signal of the free ligand $HOSiPh_3$ in toluene-d_8 is at −14.26 ppm. Anal. Calcd: C, 35.78; H, 1.83. Found: C, 35.93; H, 1.60.

$[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiEt_3)]$. IR (in CH_2Cl_2): ν(CO) 2097 (w), 2016 (s), 1990 (m), 1953 (m) cm^{-1}. ^1H NMR (in toluene-d_8): δ (ppm) −10.67 (s, 1 H, bridging hydride), 0.516 (q, 6 H, 3 CH_2), 0.978 (t, 9 H, 3 CH_3). ^{29}Si NMR (in toluene-d_8): δ (ppm) 34.38; the ^{29}Si NMR signal of the free ligand $HOSiEt_3$ in toluene-d_8 is at 17.07 ppm. Anal. Calcd: C, 23.01; H, 2.20. Found: C, 22.92; H, 2.46. Mass spectrum: *m/e* 728 $[M]^+$.

$[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$. IR (in THF): ν(CO) 2096 (w), 2015 (s), 1996 (m, sh), 1955 (m) cm^{-1}. ^1H NMR (in toluene-d_8): δ (ppm) −10.79 (s, 1 H, bridging hydride), 3.57 (s, 1 H, OH), 7.16 (m, 12 H, ortho and para H of the 4 Ph), 7.74 (m, 8 H, meta H of the 4 Ph). ^{29}Si NMR (in toluene-d_8): δ (ppm) −28.77 (ReOSi), −37.31 (HOSi); the ^{29}Si NMR signal of the free ligand $HOSiPh_2OSiPh_2OH$ in toluene-d_8 is at −36.99 ppm. Anal. Calcd: C, 38.02; H, 2.18. Found: C, 38.17; H, 2.34.

$[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$. IR (in pentane): ν(CO) 2097 (w), 2015 (s), 1997 (m, sh), 1965 (s) cm^{-1}. ^1H NMR (in toluene-d_8): δ (ppm) −10.82 (s, 1 H, bridging hydride), 3.39 (s, 1 H, OH), 7.19 (m, 6 H, ortho and para H of the 2 Ph), 7.61 (m, 4 H, meta H of the 2 Ph). ^{29}Si NMR (in toluene-d_8): δ (ppm) = −22.53; the ^{29}Si NMR signal of the free ligand $HOSiPh_2OH$ in toluene-d_8 is at −37.34 ppm. Anal. Calcd: C, 29.56; H, 1.48. Found: C, 29.48; H, 1.57. Mass spectrum: *m/e* 812 $[M]^+$.

Reversible Conversion of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OH)]$ into $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiEt_3)]$. Addition of a 10-fold amount of Et_3SiOH (0.014 mL; 0.09 mmol) to a solution of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OH)]$ (5.5 mg; 0.009 mmol) in anhydrous deuterated toluene (0.5 mL), followed by stirring at 70 °C for 2 h, led to the formation of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiEt_3)]$ in quantitative yield, as evidenced by ^1H NMR monitoring (disappearance of the hydridic signal at δ −11.32 ppm, characteristic of the hydroxo complex, and parallel appearance of an hydridic signal at δ −10.67 ppm, characteristic of the silanolate complex). The reaction is reversible. In fact, when a solution of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiEt_3)]$ (5 mg; 0.007 mmol) in anhydrous deuterated toluene (0.5 mL) with a few drops of water was stirred at 70 °C for 20 min, $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OH)]$ was formed, as confirmed by ^1H NMR and ^{29}Si NMR spectroscopy (in the ^{29}Si NMR spectrum, the signal at δ 34.38 ppm, characteristic of the triethylsilanolate complex, was replaced by a signal at δ 17.07 ppm, characteristic of free $HOSiEt_3$). Under similar conditions, $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_3)]$ was also hydrolyzed.

Conversion of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiEt_3)]$ into $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_3)]$. Addition of a 10-fold amount of Ph_3SiOH (20.5 mg; 0.074 mmol) to a solution of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiEt_3)]$ (5.4 mg; 0.0074 mmol) in anhydrous deuterated toluene (0.5 mL), followed by stirring at 80 °C for 1 h, led to the formation of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_3)]$ in quantitative yield, as evidenced by ^1H NMR spectroscopy with disappearance of the hydridic signal at δ −10.67 ppm, characteristic of the triethylsilanolate complex, and parallel appearance of an hydridic signal at δ −10.87 ppm, characteristic of the triphenylsilanolate complex.

Reductive Carbonylation of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiEt_3)]$ and $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OH)]$. In a typical reaction, CO (1 atm) was bubbled into a solution of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiEt_3)]$ (20 mg; 0.027 mmol) dissolved in either triethylsilanol or anisole (3−5 mL). After 7 h at 150 °C all the starting complex was converted into $[Re_2(CO)_{10}]$, as confirmed by IR and ^1H NMR spectroscopy. By working under similar conditions, $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OH)]$ is also converted to $[Re_2(CO)_{10}]$.

Synthesis of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2O\text{-}\mu)(\mu\text{-}H)Re_2(CO)_8]$ and $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2O\text{-}\mu)(\mu\text{-}H)Re_2(CO)_8]$. In a typical synthesis, a solution of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$ (10 mg; 0.010 mmol) in anhydrous cyclohexane (5 mL) was prepared, under dry N_2 in a 25 mL two-neck round-bottom flask equipped with a magnetic bar. $[Re_2(CO)_8(THF)_2]$ (15 mg; 0.020 mmol) was added, and the resulting solution was stirred for 1.5 h at room temperature. Evaporation to dryness of the solvent afforded $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2O\text{-}\mu)(\mu\text{-}H)Re_2(CO)_8]$ contaminated by some $[Re(CO)_3OH)]_4$[22] and $[HRe_3(CO)_{14}]$,[23] as evidenced by IR and ^1H NMR spectroscopy in deuterated toluene. Addition of dichloromethane (to dissolve the crude product) and reprecipitation with hexane gave traces of $[Re(CO)_3OH)]_4$. Evaporation to dryness of the filtrate followed by dissolution of the residue in pentane and cooling at −20 °C gave pure $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2O\text{-}\mu)(\mu\text{-}H)Re_2(CO)_8]$. Similarly, when a solution of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$ (23 mg; 0.029 mmol) in anhydrous cyclohexane (10 mL) was stirred with $[Re_2(CO)_8(THF)_2]$ (32 mg; 0.043 mmol) for 2 h under dry N_2 in a 25 mL two-neck round-bottom flask equipped with a magnetic bar, $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2O\text{-}\mu)(\mu\text{-}H)Re_2(CO)_8)]$ was formed, as evidenced by infrared and ^1H NMR spectroscopy. However, various attempts to isolate the latter complex failed, due to its facile reconversion back to $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$. In these two syntheses, and in the synthesis of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2O\text{-}\mu)(\mu\text{-}H)Os_3(CO)_{10}]$ reported below, it was convenient to use an excess of $[Re_2(CO)_8(THF)_2]$ because, by working at room temperature, this very reactive reagent produced some side products such as $[Re(CO)_3OH)]_4$[22] and $[HRe_3(CO)_{14}]$.[23]

$[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2O\text{-}\mu)(\mu\text{-}H)Re_2(CO)_8]$. Infrared (in THF): ν(CO) 2096 (w), 2015 (s), 1996 (m, sh), 1955 (m) cm^{-1}. ^1H NMR (in toluene-d_8): δ (ppm) −10.79 (s, 2 H,

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bridging hydrides), 7.12 (m, 12 H, ortho and para H of the 4 Ph), 7.59 (m, 8 H, meta H of the 4 Ph). ^{29}Si NMR (in toluene-d_8): δ (ppm) −29.80; the ^{29}Si NMR signal of the free ligand $HOSiPh_2OSiPh_2OH$ in toluene-d_8 is at −36.99 ppm. Anal. Calcd: C, 29.89; H, 1.37. Found: C, 29.77; H, 1.43.

$[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2O\text{-}\mu)(\mu\text{-}H)Re_2(CO)_8]$. IR (in pentane): ν(CO) 2097 (w), 2015 (s), 1997 (m), 1965 (m) cm^{-1}. ^{1}H NMR (in toluene-d_8): δ (ppm) −10.85 (s, 2 H, bridging hydrides), 7.20 (m, 6 H, ortho and para H of the 2 Ph), 7.89 (m, 4 H, meta H of the 2 Ph). ^{29}Si NMR (in toluene-d_8): δ (ppm) −14.86; the ^{29}Si NMR signal of the free ligand $HOSiPh_2OH$ in toluene-d_8 is at −37.34 ppm.

Synthesis of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2O\text{-}\mu)(\mu\text{-}H)Os_3(CO)_{10}]$. A solution of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$ (33 mg; 0.026 mmol) dissolved in anhydrous cyclohexane (15 mL) was prepared, under dry N_2 in a 50 mL two-neck round-bottom flask equipped with a magnetic bar. $[Re_2(CO)_8(THF)_2]$ (48 mg; 0.064 mmol) was added, and the resulting solution was stirred for 3 h at room temperature. Evaporation to dryness of the solvent, followed by addition of dichloromethane (minimum amount to dissolve the crude product) and then of hexane, leads to the precipitation of some $[Re(CO)_3(OH)]_4$. Evaporation of the filtrate to dryness followed by dissolution of the residue in pentane and cooling at −78 °C for a few hours or −20 °C overnight leads first to the precipitation of unreacted $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$ and then of pure $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2O\text{-}\mu)(\mu\text{-}H)Os_3(CO)_{10}]$. Crystals, suitable for X-ray diffraction, of the latter cluster were obtained at −20 °C from a pentane solution. IR (in pentane): ν(CO) 2097 (w), 2072 (w), 2059 (w), 2017 (s), 1997 (m), 1965 (s) cm^{-1}. ^{1}H NMR (in toluene-d_8): δ (ppm) −11.96 (s, 1 H, hydride bridging Os_2), −10.83 (s, 1 H, hydride bridging Re_2), 7.13 (m, 12 H, ortho and para H of the 4 Ph), 7.63 (m, 8 H, meta H of the 4 Ph). ^{29}Si NMR (in toluene-d_8): δ (ppm) −29.60 (OsOSi); −28.69 (ReOSi); the ^{29}Si NMR signal of the free ligand $HOSiPh_2OSiPh_2OH$ in toluene-d_8 is at −36.99 ppm, whereas $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2OH)]$ shows signals at −29.11 and −36.78 ppm. Anal. Calcd: C, 27.09; H, 1.19. Found: C, 27.20; H, 1.24.

X-ray Structure Determination of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$ and $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2O\text{-}\mu)(\mu\text{-}H)Os_3(CO)_{10}]$. Crystal data and details of the structure refinement are reported in Table 2; selected bond distances and angles are given in Table 3. Suitable platelike crystals of $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OH)]$ (0.36 × 0.26 × 0.12 mm) and $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiPh_2OSiPh_2O\text{-}\mu)(\mu\text{-}H)Os_3(CO)_{10}]$ (0.40 × 0.22 × 0.10 mm) were mounted on a Bruker SMART CCD area detector diffractometer, and the data collections were performed at 293 K (graphite-monochromated Mo Kα, λ = 0.710 73 Å) by the ω-scan method ($\Delta\omega = 0.3°$), with a crystal-to-detector distance of 4 cm. An empirical absorption correction was applied (SADABS).[24] The structures were solved by direct methods (SIR97)[25] and refined by full-matrix least-squares on F_o^2 (SHELX-97).[26] Anisotropic displacement parameters were assigned to all non-hydrogen atoms. Hydride ligands were located in the idealized positions calculated employing the program HYDEX with d_{M-H} = 1.85 Å and fixed. Hydrogen atoms of the phenyl and silanol groups were placed in the idealized positions and refined riding on their parent atoms.

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Note Added after ASAP: In the version published on the web 7/4/03, the last value in column 2 of Table 1 was incorrectly given as +12.20. In the final Web version published 7/17/03, this value is correct as −12.20.

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