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A Re(CO)$_5$ Fragment Bonded to a Polyhedral Oligomeric Hydroxysilsesquioxane as a Model which Gives Further Evidence to the Existence of an Unexpected Re(CO)$_5$ Surface Species

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Most of the significance of surface organometallic chemistry relies on reaction paths rather selective or otherwise forbidden and on the stabilization of species too labile to survive in solution.[1] The origin of such stabilization is one of the key aspects still not completely understood.

Very recently,[2] a notable example was provided by the unexpected detection of a surface-anchored pentacarbonyl rhenium(I) species,[3] during the reductive carbonylation of silica-supported [Re(CO)$_3$OH]$_4$, which finally afforded [Re$_2$(CO)$_{10}$] under mild conditions. This reductive carbonylation does not occur in solution, suggesting that the silica surface plays a unique role "via" the formation of the [Re(CO)$_5$OSi≡] intermediate. In solution, pentacarbonyl rhenium(I) species bearing an OR$^-$ ligand have so far eluded isolation,[4−6] due to the strong *cis*-labilizing power of OR$^-$ groups and to their great tendency to assume a bridging coordination, resulting in the fast formation of dimeric complexes containing Re(CO)$_3$ units joined by three bridging RO$^-$ groups.[7]

This different behavior might be imputable either to the silica surface acting as reaction medium, which may modify (or hinder) the process of condensation reactions with respect to what occurs in solution (although [Re$_2$(CO)$_6$(OH)$_n$(OSi≡)$_{3-n}$]$^-$ (n = 0, 1, or 2) species were observed on the silica surface),[8] or to the different electronic properties of silanolates with respect to alkoxide and aryloxide ligands, for instance, a lower nucleophilicity of the silanolate oxygen nonbonding electrons. To confirm this latter hypothesis, we attempted the synthesis of molecular models bearing a silanolate ligand.

Reaction of [Re(CO)$_5$Cl] with trimethylsilanolate reproduced the known reactivity typical of alkoxides, leading instantaneously to anionic dimers containing bridging Me$_3$SiO$^-$ ligands, such as [Re$_2$(CO)$_6$(μ-OH)$_n$(μ-OR)$_{3-n}$]$^-$ (R = Me$_3$Si),[9] even under CO atmosphere and at low temperature.[10] However, trimethylsilanol could not be a good model of surface silanols which are much more electrophilic than alkyl silanols so that further nucleophilic attacks could be less facile. By reacting the less nucleophilic aryl silanolate (C$_6$H$_5$)$_3$SiO$^-$ and by changing, at the same time, the chloride with the better leaving group triflate (no reaction occurred with [Re(CO)$_5$Cl]), we in fact observed at 253 K the formation of an elusive species with spectroscopic features typical for a rhenium pentacarbonyl complex.[11] Therefore, we investigated the reaction with the anion of a more electron-withdrawing silanol, with an electrophilicity closer to that of the silica silanol sites,[12] such as the hydroxysilsesquioxane (c-C$_6$H$_{11}$)$_7$Si$_8$O$_{12}$OH (Figure 1A), which has been recently developed as an effective homogeneous model for isolated silanols in partially dehydroxylated silica.[13]

Deprotonation of the hydroxy group of (c-C$_6$H$_{11}$)$_7$Si$_8$O$_{12}$OH by a molar amount of n-BuLi affords [(c-C$_6$H$_{11}$)$_7$Si$_8$O$_{12}$O$^-$Li$^+$][14] that reacts with [Re(CO)$_5$(O$_3$SCF$_3$)][15] in CH$_2$Cl$_2$ solution under CO atmosphere at 273 K to give {Re(CO)$_5$[OO$_{12}$Si$_8$(c-C$_6$H$_{11}$)$_7$]} (**1**, Scheme S1 in Supporting Information), characterized by ν_{CO} (CH$_2$Cl$_2$) at 2038(vs) and 1970(m) cm^{-1} and ^{13}C NMR signals (CD$_2$Cl$_2$) at δ 180.3 (4CO) and 179.3 (1CO) ppm, typical of rhenium pentacarbonyl complexes.[16] The ν_{CO} frequencies are slightly shifted to lower frequency with respect to the [Re(CO)$_5$OSi≡] surface species (ν_{CO} in Nujol 2049(vs) and 1991(m) cm^{-1}), probably due to both the higher electrophilicity and the topological effects of the silica surface.[17] Both "surface" and "solution" species show the same reactivity toward HCl, affording easily [Re(CO)$_5$Cl], as expected for a "Re(CO)$_5$" moiety covalently bound to oxygen donor groups of rather low nucleophilicity.

Complex **1** is the first [Re(CO)$_5$OR] species (R = alkyl, aryl, or silyl) stable enough to be characterized, although it is not as stable as the anions [W(CO)$_5$OR]$^-$ (R = Ph, m-CH$_3$C$_6$H$_4$), where the presence of a negative charge decreases the *cis* lability.[7] Actually, complex **1**, which can be stabilized only under CO atmosphere, is unstable above 273 K. At room temperature, IR monitoring (Figure S1 in Supporting Information) shows that **1** slowly loses one carbonyl ligand and dimerizes, affording cleanly the novel bridged dimeric species **2** (Reaction 1 below and Scheme S1).

$$2\,\{\mathrm{Re(CO)_5[OO_{12}Si_8}(c\text{-}\mathrm{C_6H_{11})_7]}\} \rightarrow \{\mathrm{Re(CO)_4[(}\mu\text{-}\mathrm{O)O_{12}Si_8}(c\text{-}\mathrm{C_6H_{11})_7]}\}_2 + 2\,\mathrm{CO} \quad (1)$$

To our knowledge, **2** is the first example of a μ-oxo-bridged dimer of the type [Re$_2$(CO)$_8$(μ-OR)$_2$],[18] although related [Re$_2$(CO)$_8$(μ-SR)$_2$] complexes (R = C$_6$F$_5$ or C$_6$H$_5$,[19] CF$_3$[20]) are known and species of the type [Re$_2$(CO)$_8$(μ-OR)$_2$] (R = Ph,[21] H[22]) have been proposed (but never detected) as possible intermediates in the syntheses of [Re$_3$(μ_3-OMe)(μ-OR)$_3$(CO)$_9$]$^-$. The structure of **2** has been unambiguously established by X-ray diffraction analysis of crystals grown from CH$_2$Cl$_2$ or n-pentane solutions at 253 K (Figure 1B). In both cases, the solvents were co-crystallized, producing two pseudo-polymorphs (though, with the same space group $P2_1$ and two similar cell axes). The structure of **2** is built around the Re$_2$(CO)$_8$ "core" bridged by the two OR groups, and it is comparable to that of other double bridged molecules, such as [Re$_2$(CO)$_8$(μ-Cl)$_2$].[23] No formal Re−Re bond is expected from electron counting, and actually, the Re···Re distance (3.45 Å) is longer than the reference unsupported Re−Re bond in Re$_2$(CO)$_{10}$ (3.04 Å).[24]

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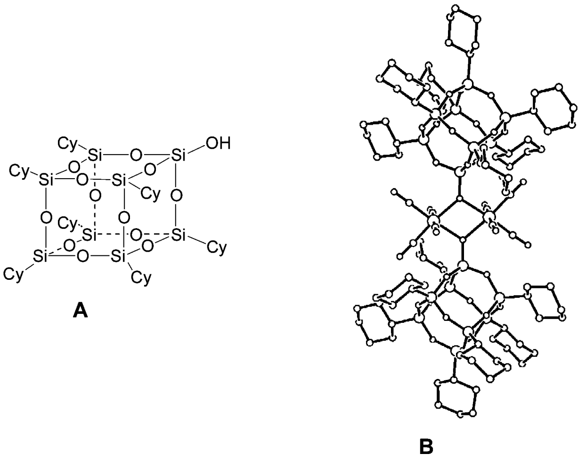

Figure 1. (A) $(c\text{-}C_6H_{11})_7Si_8O_{12}OH$; Cy = $c\text{-}C_6H_{11}$. (B) Molecular structure of $\{Re(CO)_4[(\mu\text{-}O)O_{12}Si_8(c\text{-}C_6H_{11})_7]\}_2$ (**2**).

This distance is shorter than with four-electron donor bridges of the third period or below (3.8−4.0 Å) but is in agreement with the other $Re_2(CO)_{8-n}L_n(OR)_2$ ($n = 1, 2$) species known (L = any non-carbonyl ligand),[25] meaning that the oxo bridge requires a much smaller Re−O−Re angle.[26] The observed stereochemistry around the oxygen bridge is close to a (distorted) trigonal coordination rather than pyramidal as observed for S-bridged dimers[20] (<Re−O−Si> = 126°; <Re−O−Re> = 106°; O, Si, and the two Re atoms lie almost on the same plane). Each $O_{12}Si_8(c\text{-}C_6H_{11})_7$ group can be regarded as a slightly distorted cube, whose vertexes are occupied by Si atoms (Si···Si in the range 3.03−3.17 Å), attached to the μ_2 bridging oxygen along one of its 3-fold axes. The two "cubanes" approximately share the same orientation, and they assume an eclipsed mutual conformation.[27]

Contrary to its pentacarbonyl precursor **1**, complex **2** is stable at room temperature and does not lose CO ligands even after vacuum treatment. It reacts with HCl to give the expected $[Re_2(CO)_8(\mu\text{-}Cl)_2]$ derivative.[28] Interestingly, reaction 1 is not reversible. No evidence for the formation of the pentacarbonyl derivative **1** or of $[Re_2(CO)_{10}]$ was obtained by treating a CH_2Cl_2 solution of **2** under CO (up to 100 atm, either at 273 or 298 K) for 22 h.

In conclusion, this work has shown that hydroxysilsesquioxane, $(c\text{-}C_6H_{11})_7Si_8O_{12}OH$, owing to the very low nucleophilicity of its anion, can stabilize for the first time a $[Re(CO)_5OR]$ species, previously detected on the silica surface only but never isolated in solution. On the other hand, the chemical and thermal stability of the molecular model is lower than that of the corresponding surface pentacarbonyl species, thus confirming the unique role of the silica surface as an unusual reaction medium.

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Supporting Information Available: Figure S1, Scheme S1, full synthetic details, spectroscopic data, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) An analogous behavior was observed for the related zero-valent $[M(CO)_5OR]^-$ anionic complexes (M = Cr, Mo, W), but in that case (at least for M = W and R = Ph), the presence of a negative charge made it possible to avoid easy CO elimination by nucleophilic attack, for a time long enough to grow crystals of $[NEt_4][W(CO)_5OPh]$ (Darensbourg, D. J.; Sanchez, K. M.; Reibenspies, J. H.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 7094).

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(27) The planarity of the $Re_2(OSi)_2$ core and the steric crowding of the axial carbonyls of **2** suggest that dimerization to a structure such as the previously proposed $[Re_2(CO)_8(OSi\equiv)_2]$[18] should not be favored on the silica surface, even in the presence of vicinal silanol sites.

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