Surface Organometallic Chemistry: Easy Reductive Carbonylation of Silica-Supported $[Re(CO)_3(OH)]_4$ to $[Re_2(CO)_{10}]$ via Silica-Anchored $[Re(CO)_5(OSi{\equiv})]$ and the Thermal Behavior of Silica-Supported $[Re_2(CO)_{10}]$

Giuseppe D'Alfonso, 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

Claudia L. Bianchi

Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano, Via Golgi, 19, 20133 Milano, Italy

Angelo Sironi

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

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Silica-supported $[Re(CO)_3(OH)]_4$ is easily converted to $[Re_2(CO)_{10}]$ by reductive carbonylation under very mild conditions (1 atm CO). This reaction does not occur in solution, suggesting that the silica surface plays a unique role via the surface-anchored species $[Re(CO)_5(OSi{\equiv})]$. This latter intermediate, of particular interest since organometallic species of the type $[Re(CO)_5(OR)]$ have so far eluded isolation, reacts with HCl, $HReO_4$, and water to give $[Re(CO)_5Cl]$, $[Re(CO)_5OReO_3]$, and $[Re(CO)_3(OH)]_4$, respectively. No evidence was reached for the previously proposed formation of $[HRe_3(CO)_{14}]$ in the reductive carbonylation of silica-physisorbed $[Re(CO)_3(OH)]_4$. In addition, silica-supported $[Re_2(CO)_{10}]$ can be easily reoxidized to $[Re(CO)_3(OH)]_4$ on the silica surface by thermal treatment at 150−250 °C under nitrogen. Some highly oxidized rhenium species such as $ROReO_3$ ($R = H$, $Si{\equiv}$) are formed in parallel, as suggested by an XPS study and confirmed by further treatment under 1 atm of CO at 200 °C, which affords mixtures containing also $[Re(CO)_5OReO_3]$. The latter was isolated and fully characterized by X-ray diffraction. Obviously these oxidation reactions, in which the silica surface plays an important positive role, are faster in air than under nitrogen.

Introduction

Supported metal catalysts derived from supported metal carbonyls can show interesting catalytic properties.[1] Therefore a large amount of work has been devoted to the investigation of the thermal and chemical behavior of various transition metal carbonyls supported on the silica surface.[2] However, even though the industrial importance of supported rhenium catalysts for reforming of petroleum naphtha and metathesis of alkenes is well established,[3] the study of the behavior of rhenium carbonyls supported on silica has received limited attention and, to our knowledge, only two nonexhaustive investigations appeared.[4,5]

In a photoacoustic infrared study,[4] photolysis (300−360 nm) at room temperature of a THF solution of $[Re_2(CO)_{10}]$ in the presence of silica was reported to produce $[Re_2(CO)_9(H_2O)]$ and a mixture of silica-supported carbonyl species, characterized by a complex infrared spectrum in the carbonyl stretching region ($\nu_{CO} = 2150$(w), 2101(m), 2050(m, sh), 2027(s), 1992(w, sh), 1977(w, sh), 1921(s) cm^{-1}). By comparison with the infrared spectra of known complexes,[6,7] two strong absorptions at 2027 and 1921 cm^{-1} were tentatively assigned to the tricarbonyl surface-anchored species $[Re(CO)_3(OSi{\equiv})({\equiv}SiOSi{\equiv})_2]$, whereas the other bands were associated with minor amounts of the poorly characterized anchored species $[Re(CO)_5(OSi{\equiv})]$ and $[Re(CO)_4(OSi{\equiv})]_2$. When a noncoordinating solvent such as benzene was

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* Corresponding author. Fax: +39-02-2362748. E-mail: dominique.roberto@unimi.it.

[1] Psaro, R.; Recchia, S. *Catal. Today* **1998**, *41*, 139.

[2] Psaro, R.; Ugo, R. In *Metal Clusters in Catalysis*; Gates, B. C., Guczi, L., Knözinger, H., Eds.; Elsevier: Amsterdam, 1986; p 451.

[3] Yermakov, Y. I.; Kuznetsov, B. N.; Zakharov, V. A. *Catalysis by Supported Complexes*; Elsevier: New York, 1981.

[4] McKenna, W. P.; Higgins, B. E.; Eyring, E. M. *J. Mol. Catal.* **1985**, *31*, 199.

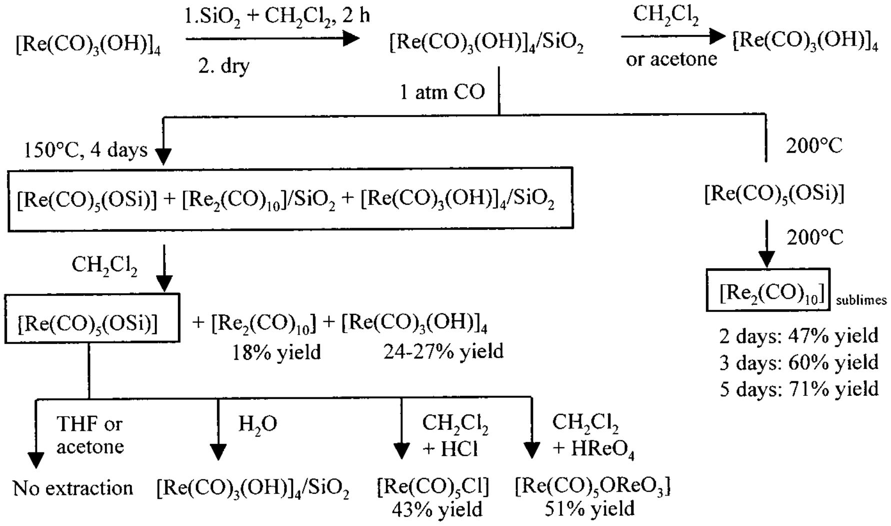
[5] Kirlin, P. S.; Gates, B. C. *Inorg. Chem.* **1985**, *24*, 3914.

[6] Brateman, P. S. *Metal Carbonyl Spectra*; Academic Press: New York, 1975.

[7] Gard, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 6340.

10.1021/om000028j CCC: $19.00

Scheme 1. Reductive Carbonylation of Silica-Supported $[Re(CO)_3(OH)]_4$



All yields are with respect to the starting $[Re(CO)_3(OH)]_4$

used, the photoacoustic infrared spectrum suggested only the presence of the supposed tricarbonyl species.[4]

Also, it has been reported[5] that by refluxing *n*-octane and $[H_4Re_4(CO)_{12}]$ in the presence of hydrated silica, silica-supported $[Re(CO)_3(OH)]_4$ is generated. Exposure of this latter species to CO (1 atm) at 150 °C for 4 h leads to the formation of a surface species characterized by carbonyl bands at 2095(w), 2053(s, br), 1992(m, br), and 1933(w) cm^{-1}, similar to those reported for $[HRe_3(CO)_{14}]$.[8] On the basis of the infrared evidence only, a silica-mediated reductive carbonylation of $[Re(CO)_3(OH)]_4$ to $[HRe_3(CO)_{14}]$ was then proposed,[5] although the lack of fragmentation under CO of the supposed silica-supported Re_3 cluster to $[HRe(CO)_5]$ and $[Re_2(CO)_{10}]$ was unexpected.[8,9]

This relatively easy surface reactivity under CO of $[Re(CO)_3(OH)]_4$[5] was suggestive of a new way to synthesize rhenium carbonyl clusters as it occurs with less oxophilic metals such as Rh, Ir, Ru, or Os.[10] In this area, as a preliminary result, it has only been reported that reductive carbonylation of ammonium perrhenate supported on silica affords $[Re_2(CO)_{10}]$ in ca. 40% yield, but by working under high pressures of CO (ca. 20 atm) and H_2 (ca. 130 atm) at 150 °C.[11] This latter result prompted us to study more deeply the reductive carbonylation of $[Re(CO)_3(OH)]_4$ and to investigate in parallel the thermal stability of $[Re_2(CO)_{10}]$, both supported on the silica surface.

Results

Reductive Carbonylation of Silica-Supported $[Re(CO)_3(OH)]_4$ to $[Re_2(CO)_{10}]$ via $[Re(CO)_5(OSi{\equiv})]$ (Scheme 1). When a slurry of SiO_2, $[Re(CO)_3(OH)]_4$ (2 wt % of Re with respect to SiO_2), and CH_2Cl_2 is stirred at room temperature for 2 h and evaporated to dryness, the final white powder shows two carbonyl bands at 2028(s) and 1925(vs) cm^{-1} in Nujol mull, similar to those of $[Re(CO)_3(OH)]_4$ in CH_2Cl_2 (ν_{CO} = 2031(s) and 1925(vs) cm^{-1}).[12] The quantitative recovery of $[Re(CO)_3(OH)]_4$ by extraction of the silica with dichloromethane or acetone confirms a simple physisorption.[5]

When physisorbed $[Re(CO)_3(OH)]_4$ is heated at 200 °C under 1 atm of CO in the closed cylindrical Pyrex vessel previously described,[10a] some $[Re_2(CO)_{10}]$ sublimes onto the cold walls of the reaction vessel. After 2, 3, and 5 days, extraction of both the sublimate and the silica powder with anhydrous pentane affords $[Re_2(CO)_{10}]$ in 47%, 60%, and 71% yields, respectively. By stopping the reaction after 2 days, the infrared spectrum of the remaining silica powder, as a Nujol mull, shows the presence of some unreacted $[Re(CO)_3(OH)]_4$, a weak carbonyl band at 2089 cm^{-1}, and two carbonyl bands at 2049(s) and 1991(m) cm^{-1}, which we tentatively assign to a surface pentacarbonyl Re(I) species by analogy with the infrared spectrum of $[Re(CO)_5Cl]$ or $[Re(CO)_5Br]$.[13]

Attempts to convert quantitatively $[Re(CO)_3(OH)]_4$ into this latter intermediate surface species, by working under milder conditions, failed due to its relatively easy conversion into $[Re_2(CO)_{10}]$, although it is produced in good amounts by working at 150 °C. After 4 days under CO at this temperature, some $[Re_2(CO)_{10}]$ sublimes, whereas the infrared spectrum of the silica powder, as Nujol mull, shows carbonyl bands at 2089(w), 2069(w), 2049(vs), 2028(m), 2012(m), 1991(m), 1974(w), and 1925(s) cm^{-1} due to a mixture of $[Re_2(CO)_{10}]$ (ν_{CO} =

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(8) Fellmann, W.; Kaesz, H. D. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 63.

(9) Harril, R. W.; Kaesz, H. D. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 69.

(10) (a) Roberto, D.; Psaro, R.; Ugo, R. *Organometallics* **1993**, *12*, 2292. (b) Roberto, D.; Cariati, E.; Psaro, R.; Ugo, R. *Organometallics* **1994**, *13*, 734. (c) Roberto, D.; Cariati, E.; Ugo, R.; Psaro, R. *Inorg. Chem.* **1996**, *35*, 2311. (d) Roberto, D.; Cariati, E.; Lucenti, E.; Respini, M.; Ugo, R. *Organometallics* **1997**, *16*, 4531. (e) Roberto, D.; Lucenti, E.; Roveda, C.; Ugo, R. *Organometallics* **1997**, *16*, 5974. (f) Cariati, E.; Lucenti, E.; Roberto D.; Ugo R. In *Supported Reagents and Catalysts in Chemistry*; Hodnett, B. K., Kybett, A. P., Clark, J. H., Smith, K., Eds.; The Royal Society of Chemistry: London, 1998; pp 214–219. (g) Cariati, E.; Roberto, D.; Ugo, R. *J. Cluster Science* **1998**, *9*, 329. (h) Cariati, E.; Lucenti, E.; Roberto, D.; Ugo, R. In *Metal Clusters in Chemistry*; Braunstein, P., Oro, L., Raithby, P., Eds.; Wiley-VCH Verlag: Weinheim, 1999; pp 860–876.

(11) Marchionna, M.; Lami, M.; Raspolli Galletti, A. M.; Braca, G. *Gazz. Chim. Ital.* **1993**, *123*, 107.

(12) (a) Herberhold, M.; Süss, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 4, 700. (b) Herberhold, M.; Süss, G.; Ellermann, J.; Gabelein, H. *Chem. Ber.* **1978**, *111*, 2931.

(13) Schmidt, S. P.; Trogler, W. C.; Basolo, F. *Inorg. Synth.* **1985**, *23*, 41.

2069(w), 2012(m), and 1974(w) cm^{-1}), $[Re(CO)_3(OH)]_4$ (ν_{CO} = 2028(m) and 1925(s) cm^{-1}), traces of still unidentified rhenium carbonyl species (ν_{CO} = 2089(w) and 1927(w) cm^{-1}), and the supposed surface pentacarbonyl Re(I) species (ν_{CO} = 2049(vs) and 1991(m) cm^{-1}), which appears to be the major component of the mixture. Such assignments are confirmed by extraction of both the sublimate and silica with anhydrous pentane, which affords $[Re_2(CO)_{10}]$ (18% yield), whereas successive extraction with anhydrous CH_2Cl_2 gives $[Re(CO)_3(OH)]_4$ (24−27% yields) and leaves, on the silica surface, the traces of an unidentified carbonyl rhenium species together with the supposed pentacarbonyl Re(I) species as the major component. These latter two species cannot be extracted even by further treatment of the silica powder with donor solvents such as acetone or THF, suggesting that they are strongly interacting with the silica surface. The supposed pentacarbonyl Re(I) species could interact with a surface silanolate either bound covalently (as in $[Re(CO)_5(OSi\equiv)]$) or attached by ion-pairing (as in $[Re(CO)_5(HOR)]^+ \equiv SiO^-$ where R = H or $\equiv$Si).[14] We found that the pentacarbonyl Re(I) species cannot be extracted even by treatment with $[NBu_4]Cl$ dissolved in dichloromethane. This observation allows rejection of a cationic formulation of the carbonyl rhenium species and is in agreement with a covalent bonding to a surface silanolate.

We added further evidence to the proposed formulation $[Re(CO)_5(OSi\equiv)]$ by the well-established method of cleavage of $M-OSi\equiv$ (M = metal) bonds by reaction under mild conditions with an acid such as HCl(aq) followed by solvent extraction.[14] For instance, silica-anchored $[HOs_3(CO)_{10}(OSi\equiv)]$ reacts with HCl(aq) affording $[HOs_3(CO)_{10}Cl]$, which can be easily extracted with CH_2Cl_2.[15] The silica powder, after extractions as above, is then treated with CH_2Cl_2 acidified with a few drops of HCl(aq), producing pure $[Re(CO)_5Cl]$ (43% yield with respect to the initial silica-supported $[Re(CO)_3(OH)]_4$; Scheme 1), which dissolves in CH_2Cl_2. Similarly, use of $HReO_4$ instead of HCl leads to the quantitative conversion of the surface species into $[Re(CO)_5OReO_3]$,[16] which is soluble in dichloromethane (51% yield with respect to the initial silica-supported $[Re(CO)_3(OH)]_4$; Scheme 1). Following the above extraction processes, the combined isolated yields of $[Re_2(CO)_{10}]$, $[Re(CO)_5X]$ (X = Cl or $OReO_3$), and unreacted $[Re(CO)_3(OH)]_4$ are 88−96%, whereas traces of still unidentified surface rhenium carbonyl species (ν_{CO} as Nujol mull = 2089(w) and 1927(w) cm^{-1}) are not extracted even after treatment with CH_2Cl_2 acidified with HCl(aq).

The proposed $[Re(CO)_5(OSi\equiv)]$ species is readily (less than 1 h) converted back to silica-physisorbed $[Re(CO)_3(OH)]_4$ either by addition of a few drops of water at room temperature or by leaving the silica powder in air overnight. This behavior is in agreement with an expected easy hydrolysis of a $Re-OSi\equiv$ bond and could reasonably involve the unknown "$Re(CO)_5(OH)$" species as intermediate, which would be readily converted to $[Re(CO)_3(OH)]_4$:

$$[Re(CO)_5(OSi\equiv)]/SiO_2 \xrightarrow[-\ HOSi\equiv]{+\ H_2O} [Re(CO)_5(OH)]/SiO_2 \xrightarrow[-2CO]{} 1/4[Re(CO)_3(OH)]_4/SiO_2$$

It has been reported[17] that reaction of $[Re(CO)_5FBF_3]$ with aqueous sodium hydroxide results in the precipitation of a product of analytical composition "$Re(CO)_5(OH)$", which was proposed, by infrared spectroscopy only, to be $[(OC)_4(HO)Re-C(OH)O-Re(CO)_5]$, easily converted in organic solvents (e.g., acetone, dichloromethane, or tetrahydrofuran) into $[(OC)_4Re(CO_2)Re(CO)_5]_2$ with μ_3-CO_2 bridges, as evidenced by X-ray structural analysis. However, we could not isolate these species during the hydrolysis of the proposed $[Re(CO)_5(OSi\equiv)]$ species, the final product being always $[Re(CO)_3(OH)]_4$.

Also, during our study on the reductive carbonylation of silica-supported $[Re(CO)_3(OH)]_4$, we could not reach evidence of the formation of $[HRe_3(CO)_{14}]$[5] since extraction with pentane failed to give this cluster, even in traces, although we proved that silica-supported $[HRe_3(CO)_{14}]$ can be easily removed from the silica surface by extraction with pentane.

In fact, when a slurry of SiO_2, $[HRe_3(CO)_{14}]$ (2 wt % of Re with respect to SiO_2), and pentane is stirred at room temperature for 2 h and evaporated to dryness, a pale yellow powder is obtained. Its infrared spectrum, as Nujol mull, shows carbonyl bands at 2146(vw), 2100(w), 2046(vs), 2013(m), 1991(s), 1974(w), 1965(w), 1955(vw), and 1932(w) cm^{-1}, similar to those of $[HRe_3(CO)_{14}]$ dissolved in cyclohexane (ν_{CO} = 2143(vw), 2100(w), 2045(s), 2014(m), 1992(m), 1975(w), 1966(w), 1956(vw), and 1936(w) cm^{-1}).[8] The cluster can be quantitatively recovered by extraction of the silica powder with pentane, as expected for a simple physisorption.

Moreover, we investigated the behavior of silica-supported $[HRe_3(CO)_{14}]$ under CO.

Treatment under CO (1 atm) at room temperature of physisorbed $[HRe_3(CO)_{14}]$ in the closed cylindrical Pyrex vessel previously described[10a] affords, as it occurs in solution,[8] $[Re_2(CO)_{10}]$ and $[HRe(CO)_5]$, which are extracted with $CHCl_3$ and characterized by infrared and ^{1}H NMR spectroscopies. By working under 1 atm of CO at 150 °C for 4 h (i.e., the same conditions used by Kirlin et al.[5] to obtain what they proposed to be $[HRe_3(CO)_{14}]$ physisorbed on the silica surface) the pale yellow silica powder turns white while some $[Re_2(CO)_{10}]$ sublimes onto the cold walls of the reaction vessel. Treatment of the sublimate and silica powder with anhydrous pentane affords pure $[Re_2(CO)_{10}]$, whereas no carbonyl rhenium species remains on the silica surface, as expected due to the known formation of $[Re_2(CO)_{10}]$ by thermal treatment at 100 °C of $[HRe(CO)_5]$.[18] Our obvious conclusion is that $[HRe_3(CO)_{14}]$ is not stable on the silica surface by working under 1 atm of CO at 150 °C; therefore the conclusion of Kirlin et al.[5] is not confirmed by our experimental evidence.

The infrared spectrum of the surface species (ν_{CO} as silica wafer = 2095(w), 2053(s, br), 1992(m, br), 1933-

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[14] Roberto, D.; Cariati, E.; Pizzotti, M.; Psaro, R. *J. Mol. Catal. A* **1996**, *111*, 97, and references therein.

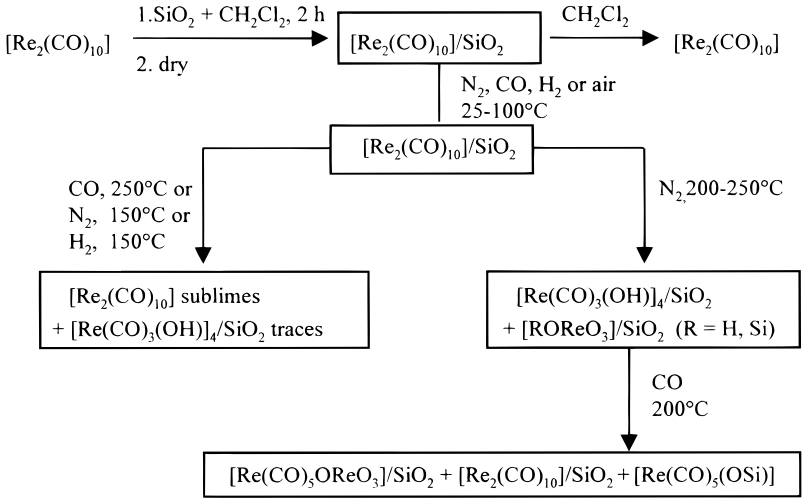
[15] Roberto, D.; Pizzotti, M.; Ugo, R. *Gazz. Chim. Ital.* **1995**, *125*, 133.

[16] Heidrich, J.; Loderer D.; Beck, W. *J. Organomet. Chem.* **1986**, *312*, 329.

[17] Beck, W.; Raab, K.; Nagel, U. Steimann, M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 526. (b) Raab, K.; Beck, W. *Chem. Ber.* **1985**, *118*, 3830.

[18] Beck, V. W.; Hieber, W.; Braun, G. *Z. Anorg. Allg. Chem.* **1961**, *308*, 23.

Scheme 2. Thermal Behavior of Silica-Supported [$Re_2(CO)_{10}$] at Atmospheric Pressure



(w) cm^{-1}) obtained by these authors[5] by reductive carbonylation of silica-supported [$Re(CO)_3(OH)]_4$, and proposed to be [$HRe_3(CO)_{14}$], is much simpler than that of silica-supported [$HRe_3(CO)_{14}$] and is quite similar to that of the sample (ν_{CO} as Nujol mull = 2089(w), 2049(s), 1991(m), and 1927(w) cm^{-1}) obtained in the present work under analogous conditions by treatment of silica-supported [$Re(CO)_3(OH)]_4$ under 1 atm of CO at 150 °C followed by solvent extractions to remove some minor amounts of [$Re_2(CO)_{10}$] and [$Re(CO)_3(OH)]_4$. The slight difference in the carbonyl stretching frequencies (by ca. 4−6 cm^{-1}) is expected on going from silica wafer to Nujol mull,[19] as confirmed by us in the case of silica-supported [$Re(CO)_3(OH)]_4$. Therefore the infrared spectrum of Kirlin et al.[5] could be interpreted as well as a mixture of surface carbonyl species containing as major component the intermediate [$Re(CO)_5(OSi{\equiv})$] (ν_{CO} as silica wafer = 2053(s), 1992(m) cm^{-1}).

The Thermal Behavior of Silica-Supported [$Re_2(CO)_{10}$] (Scheme 2). When a slurry of SiO_2, [$Re_2(CO)_{10}$] (2 wt % of Re with respect to SiO_2), and CH_2Cl_2 is stirred at room temperature for 2 h and evaporated to dryness, the final white powder shows three carbonyl bands, in Nujol mull, at 2070(m), 2013(vs), and 1975(m) cm^{-1}, similar to those of [$Re_2(CO)_{10}$] dissolved in CH_2Cl_2 (ν_{CO} = 2071(m), 2013(vs), and 1967(m) cm^{-1}); [$Re_2(CO)_{10}$] can be quantitatively recovered by extraction with dichloromethane or pentane.

It is known that thermal treatment of many silica-supported metal carbonyls leads to the formation of oxidized silica-anchored carbonyl species.[2] For example, thermal degradation of silica-supported [$Ru_3(CO)_{12}$] and [$Os_3(CO)_{12}$], at ca. 100 and 200 °C, respectively, affords silica-anchored species such as [$M(CO)_x(OSi{\equiv})_2]_n$ (M = Ru, Os; $x = 2$ or 3).[2,20] A similar oxidation process occurs with [$Re_2(CO)_{10}$] dissolved in tetrahydrofuran in the presence of silica under photolytic conditions.[4] These results prompted us to study the possible formation of oxidized species anchored to silica by thermal treatment under nitrogen of silica-supported [$Re_2(CO)_{10}$].

Silica physisorbed [$Re_2(CO)_{10}$] does not react when heated at 100 °C under nitrogen in the closed cylindrical Pyrex vessel previously described[10a] for 16 h; an increase of the temperature to 150 °C leads to the sublimation of some [$Re_2(CO)_{10}$] onto the cold walls of the reaction vessel and to the formation of traces of physisorbed [$Re(CO)_3(OH)]_4$. After 17 h at the same temperature, almost all [$Re_2(CO)_{10}$] sublimes, whereas the infrared spectrum of the remaining silica powder shows the presence of only traces of physisorbed [$Re_2(CO)_{10}$] and [$Re(CO)_3(OH)]_4$, which can be easily separated by selective extraction first with pentane (which gives [$Re_2(CO)_{10}$]) and then with dichloromethane (which gives [$Re(CO)_3(OH)]_4$).

Only a further increase of the temperature to 200 °C leads to a large oxidation of [$Re_2(CO)_{10}$] to physisorbed [$Re(CO)_3(OH)]_4$. After 17 h at this temperature, only 11% of the starting [$Re_2(CO)_{10}$] sublimes, whereas the infrared spectrum, as Nujol mull, of the resulting beige silica powder shows carbonyl bands at 2028(s) and 1925(vs) cm^{-1}, typical of physisorbed [$Re(CO)_3(OH)]_4$. Extraction of this beige silica powder with acetone affords [$Re(CO)_3(OH)]_4$ in 45% yield. After the extraction process, no carbonyl species remains on the silica surface, as evidenced by infrared spectroscopy. However, since rhenium oxides such as $Re_2O_3{\cdot}xH_2O$ and ReO_2 are black and brown, respectively,[21] the beige color of the silica powder suggests the presence on the silica surface of some oxidized rhenium species totally decarbonylated.

The oxidation process is faster at 250 °C: after 30 min only, traces of [$Re_2(CO)_{10}$] sublimes onto the cold walls of the reaction vessel (ca. 1% of the starting complex), whereas the infrared spectrum of the resulting beige silica powder shows the presence of [$Re(CO)_3(OH)]_4$, which can be easily extracted with acetone (63% yield). By heating for a longer time (17 h), further degradation takes place, resulting in a dark gray silica powder showing the presence of only traces of physisorbed [$Re(CO)_3(OH)]_4$.

As expected, the oxidation of silica-supported [$Re_2(CO)_{10}$] is much faster by working in air instead of nitrogen, although it does not take place at temperatures lower than 100 °C. After 10 min at 250 °C, only

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

(20) (a) Psaro, R.; Ugo, R.; Zanderighi, G. M.; Besson, B.; Smith, A. K.; Basset, J. M. *J. Organomet. Chem.* **1981**, *213*, 215. (b) Zanderighi, G. M.; Dossi, C.; Ugo, R.; Psaro, R.; Theolier, A.; Choplin, A.; D'Ornelas, L.; Basset, J. M. *J. Organomet. Chem.* **1985**, *296*, 127.

(21) Pacer, R. A. *J. Inorg. Nucl. Chem.* **1976**, *38*, 817.

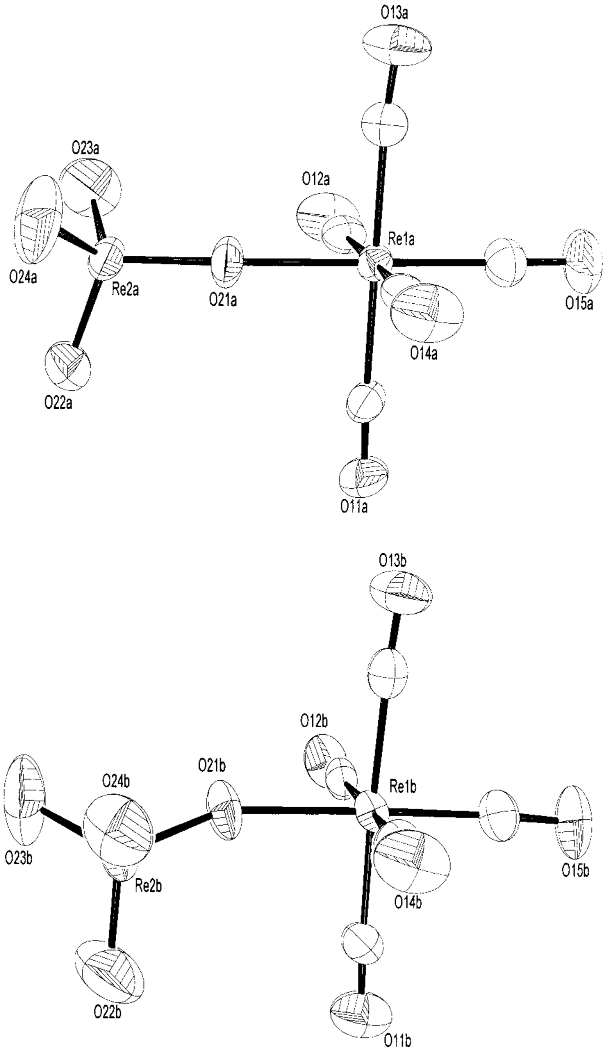

Figure 1. ORTEP diagrams (with thermal ellipsoids drawn at the 50% of probability level) of the two independent molecules in the asymmetric unit of $[(CO)_5Re(\mu\text{-}O)\text{-}ReO_3]$. The C atoms of the CO groups bear the same numbering of the corresponding O atoms.

Table 1. Bond Lengths (Å) and Angles (deg) for $(CO)_5ReOReO_3$

	molecule A	molecule B
Re(1)−C(15)	1.923(7)	1.915(7)
Re(1)−C(14)	1.995(7)	1.994(7)
Re(1)−C(13)	2.003(7)	2.000(7)
Re(1)−C(11)	2.033(7)	2.007(8)
Re(1)−C(12)	2.052(7)	2.034(7)
Re(1)−O(21)	2.135(4)	2.146(4)
C(11)−O(11)	1.118(7)	1.123(7)
C(12)−O(12)	1.117(7)	1.134(7)
C(13)−O(13)	1.132(7)	1.146(8)
C(14)−O(14)	1.133(7)	1.105(7)
C(15)−O(15)	1.140(7)	1.143(7)
Re(2)−O(24)	1.682(5)	1.667(6)
Re(2)−O(23)	1.691(5)	1.682(6)
Re(2)−O(22)	1.704(5)	1.706(5)
Re(2)−O(21)	1.752(4)	1.744(4)
C(15)−Re(1)−C(14)	88.8(3)	92.0(3)
C(15)−Re(1)−C(13)	87.9(3)	89.1(3)
C(14)−Re(1)−C(13)	90.3(3)	90.4(3)
C(15)−Re(1)−C(11)	92.0(3)	88.4(3)
C(14)−Re(1)−C(11)	88.3(3)	89.9(3)
C(13)−Re(1)−C(11)	178.6(3)	177.5(3)
C(15)−Re(1)−C(12)	93.4(3)	92.1(3)
C(14)−Re(1)−C(12)	177.8(3)	175.5(3)
C(13)−Re(1)−C(12)	89.6(3)	91.4(3)
C(11)−Re(1)−C(12)	91.8(3)	88.4(3)
C(15)−Re(1)−O(21)	178.5(2)	178.5(2)
C(14)−Re(1)−O(21)	89.8(2)	88.2(2)
C(13)−Re(1)−O(21)	91.4(2)	89.4(2)
C(11)−Re(1)−O(21)	88.6(2)	93.1(2)
C(12)−Re(1)−O(21)	87.9(2)	87.7(2)
O(11)−C(11)−Re(1)	176.8(6)	176.4(6)
O(12)−C(12)−Re(1)	177.4(6)	179.1(6)
O(13)−C(13)−Re(1)	174.6(6)	176.2(6)
O(14)−C(14)−Re(1)	177.3(6)	177.7(7)
O(15)−C(15)−Re(1)	176.8(7)	176.9(7)
O(24)−Re(2)−O(23)	108.5(3)	107.9(4)
O(24)−Re(2)−O(22)	109.1(3)	107.7(3)
O(23)−Re(2)−O(22)	107.8(3)	110.5(3)
O(24)−Re(2)−O(21)	109.7(2)	110.9(3)
O(23)−Re(2)−O(21)	110.3(3)	109.9(3)
O(22)−Re(2)−O(21)	111.3(2)	109.9(2)
Re(2)−O(21)−Re(1)	161.9(3)	151.2(3)

traces of $[Re(CO)_3(OH)]_4$ are left on the dark gray silica surface. On the contrary, by working under 1 atm of CO at 250 °C for 30 min, only traces of $[Re(CO)_3(OH)]_4$ are formed, but almost all $[Re_2(CO)_{10}]$ sublimes on the cold walls of the reaction vessel (Scheme 2). Finally, some $[Re(CO)_3(OH)]_4$ is obtained also by thermal treatment of silica-supported $[Re_2(CO)_{10}]$ under H_2 at 150−200 °C, although at 150 °C most $[Re_2(CO)_{10}]$ sublimes. Under these latter conditions neither $[H_3Re_3(CO)_{12}]$ nor $[H_4Re_4(CO)_{12}]$ is formed, although these clusters are readily generated by hydrogenation (1 atm) of $[Re_2(CO)_{10}]$ in Decaline or dodecane solution at 150−170 °C.[22]

When an oxidized silica sample containing both $[Re(CO)_3(OH)]_4$ and the decarbonylated oxidized rhenium species (obtained by thermal treatment under nitrogen at 250 °C for 30 min of silica-supported $[Re_2(CO)_{10}]$) is treated under 1 atm of CO at 200 °C for 24−48 h, a mixture of the above-described $[Re(CO)_5(OSi\equiv)]$, $[Re_2(CO)_{10}]$, $[Re(CO)_5OReO_3]$[16] (fully characterized, see below), and traces of a surface species characterized by a carbonyl band at 2087 cm^{-1} is formed (Scheme 2). $[Re_2(CO)_{10}]$ and $[Re(CO)_5OReO_3]$ can be easily removed from the silica surface by selective extraction with pentane and dichloromethane, respectively. Successive extraction with acetone affords traces of a species characterized by a carbonyl band at 2081 cm^{-1}, which could be $[Re(CO)_6][ReO_4]$ by analogy with the known complex $[Re(CO)_6][AlCl_4]$ (ν_{CO} in acetone = 2081 cm^{-1}),[23] whereas only the silica-anchored $[Re(CO)_5(OSi\equiv)]$ species remains on the surface.

We confirmed the formation of $[Re(CO)_5OReO_3]$ both by mass spectrometry (its FAB+ mass spectrum shows the molecular ion peak at 578) and by X-ray diffraction of suitable crystals. $[(CO)_5Re(\mu\text{-}O)ReO_3]$ crystallizes in the monoclinic space group *P*21/*c* with two independent molecules in the asymmetric unit separated by normal van der Waals interactions. The molecular stereochemistry together with the pertinent labeling for the two molecules are shown in Figures 1a and 1b, respectively. Relevant bond distances and angles are listed in Table 1. By comparison of Figures 1a and 1b, it appears that the two independent molecules in the asymmetric unit have a slightly different conformation; that is, they are

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(22) Kaesz, H. D.; Knox, S. A. R.; Koepke, J. W.; Saillant, R. B. *Chem. Commun.* **1971**, 477.

(23) Hieber, V. W.; Kruck, T. *Z. Naturforsch.* **1961**, *166*, 709.

different rotamers about the Re1−O21 and O21−Re2 single bonds.

Although $[Re(CO)_5OReO_3]$ was prepared a few years ago by reacting $[Re(CO)_5Br]$ with $AgReO_4$,[16] to our knowledge the coordination of the perrhenate ion to the $[Re(CO)_5]^+$ moiety was not firmly established up to now.[24] This bonding is easily cleaved by addition of a few drops of 37% aqueous HCl to a solution of $[Re(CO)_5OReO_3]$ in dichloromethane, at room temperature, with formation of $[Re(CO)_5Cl]$ in quantitative yield. The perrhenate anion, which is a relatively strong ligand with respect to $[ClO_4]^-$, $[SO_3CF_3]^-$, and $[BF_4]^-$,[16] can be displaced even by a large excess of acetone, as evidenced by both infrared spectroscopy[25,26] and conductivity measurements of an acetone solution of $[Re(CO)_5OReO_3]$:

$$[Re(CO)_5OReO_3] \underset{+\text{ acetone}}{\overset{-\text{ acetone}}{\rightleftharpoons}} [Re(CO)_5(\text{acetone})][ReO_4]$$

As expected for an equilibrium reaction, evaporation of the acetone solution gives back $[Re(CO)_5OReO_3]$, while, in agreement with the behavior of $[Re(CO)_5O_3SCF_3]$ dissolved in dichloromethane,[27] the addition of a few drops of acetone to a solution of $[Re(CO)_5OReO_3]$ in dichloromethane is not enough to cause the formation of $[Re(CO)_5(\text{acetone})][ReO_4]$, as evidenced by infrared spectroscopy.

The isolation and full characterization of $[Re(CO)_5OReO_3]$ add further evidence to our suggestion that highly oxidized species such as $ROReO_3$ ($R = H$, Si≡) are formed on the silica surface by silica-mediated oxidation at 250 °C of $[Re(CO)_3(OH)]_4$ even working under nitrogen.

Additional evidence for a process of oxidative decomposition of $[Re_2(CO)_{10}]$ or even $[Re(CO)_3(OH)]_4$ with total decarbonylation was given by X-ray photoelectron spectroscopy (XPS) studies. In the case of rhenium species supported on alumina, the reported binding energy (E_b) of the Re $4f_{7/2}$ peak in the different valence states are as follows: (0) 40.6 eV; (+1) 41.0 eV; (+4) 42.9 eV; (+6) 44.4 eV; (+7) 46.5 eV.[28] Similar values are reported for the Re $4f_{7/2}$ peak of silica-supported $[NH_4][ReO_4]$ before (46.0 eV) and after reduction to metal (40.9 eV) under hydrogen at 500 °C.[29] We investigated by XPS the following samples: (i) silica-supported $[Re_2(CO)_{10}]$ (2 wt % of Re with respect to SiO_2); (ii) silica-supported $[Re(CO)_3(OH)]_4$ (2 wt % of Re with respect to SiO_2); (iii) silica sample obtained by thermal oxidative treatment, for 30 min at 250 °C under nitrogen of silica-supported $[Re_2(CO)_{10}]$ (2 wt % of Re with respect to SiO_2). The E_b of the Re $4f_{7/2}$ peaks, the weight percentage of Re with respect to SiO_2, and the percentage of the different rhenium species in a given oxidation state with respect to the total rhenium are reported in Table 3.

XPS quantitative results give a wt % of total Re with respect to SiO_2 (1.38−2.44%), which can be different from the total amount actually supported on silica (ca. 2 wt % of Re with respect to SiO_2). This discrepancy is explained by a nonhomogeneous distribution of rhenium on the silica surface, as shown by a SEM investigation of the various samples.

Table 2. Crystal Data and Structure Refinement for $(CO)_5ReOReO_3$

empirical formula	C5 O9 Re2
fw	576.45
temperature	293(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimens	$a = 11.8801(10)$ Å, $\alpha = 90°$ $b = 13.932(2)$ Å, $\beta = 95.256(5)°$ $c = 12.984(2)$ Å, $\gamma = 90°$
volume	2140.1(5) Å^3
Z	8
density (calcd)	3.578 Mg/m^3
abs coeff	22.635 mm^{-1}
$F(000)$	2016
cryst size	0.35 × 0.20 × 0.20 mm^3
θ range for data collection	1.72−27.86°
index ranges	$-15 \leq h \leq 15$, $-18 \leq k \leq 18$, $-16 \leq l \leq 16$
no. of reflns collected	25 483
no. of ind reflns	4732 [R(int) = 0.0434]
completeness to $\theta = 27.86°$	92.8%
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	4732/0/289
goodness-of-fit on F^2	0.953
final R indices [$I > 2\sigma(I)$]	R1 = 0.0234, wR2 = 0.0444
R indices (all data)	R1 = 0.0397, wR2 = 0.0467
largest diff peak and hole	1.196 and −1.244 e Å^{-3}

A disadvantage of XPS investigations is the requirement of ultrahigh-vacuum conditions, which, in some cases, could change in situ the original nature of the surface organometallic species.[14] We found that, while silica-supported $[Re_2(CO)_{10}]$ is stable under XPS conditions ($P = 10^{-9}$ Torr), silica-supported $[Re(CO)_3(OH)]_4$ turns out to be easily oxidized, affording selectively a Re^{4+} species which could be anchored to the silica surface by analogy with alumina-supported Re^{7+} species, which were proposed to have several ReOAl bonds.[28] The demolition of $[Re(CO)_3(OH)]_4$ to an oxidized non-carbonyl rhenium species was confirmed by infrared spectroscopy of the sample after the XPS measurements. The easy oxidation with formation of Re^{4+} surface species can be attributed to a strong decrease of the amount of physisorbed water due to the high-vacuum conditions, because it is known that refluxing a slurry of octane, $[H_4Re_4(CO)_{12}]$, and uncalcined silica affords $[Re(CO)_3(OH)]_4$, whereas the use of calcined (700 °C for 12 h) silica leads to the selective formation of a Re^{6+} decarbonylated species, showing clearly that a decrease of physisorbed water favors the oxidation and decarbonylation of rhenium carbonyl species on the silica surface.[5]

The XPS analysis of the powder obtained by thermal treatment, at 250 °C under nitrogen for 30 min, of silica-supported $[Re_2(CO)_{10}]$ shows the total absence of Re(0) species and the presence of oxidized rhenium species in the (+1) valence state (corresponding to 6.8% of the total rhenium species), (+4) valence state (corresponding to 56.6% of the total rhenium species), and (+7) valence state (corresponding to 36.6% of the total rhenium species). If the Re^{4+} species is formed in situ under the XPS conditions from silica-supported $[Re(CO)_3(OH)]_4$, the percentage of $[Re(CO)_3(OH)]_4$ sup-

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[24] Chakravorti, M. C. *Coord. Chem. Rev.* **1990**, *106*, 205.

[25] Raab, K.; Olgemoller, B.; Schloter, K.; Beck, W. *J. Organomet. Chem.* **1981**, *214*, 81.

[26] Horn, E.; Snow, M. R. *Aust. J. Chem.* **1984**, *37*, 1375.

[27] Nitschke, J.; Schmidt, S. P.; Trogler, W. C. *Inorg. Chem.* **1985**, *24*, 1972.

[28] Zsoldos, Z.; Beck, A.; Guczi, L. *Stud. Surf. Sci. Catal.* **1988**, *48*, 955.

[29] Shpiro, E. S.; Avaev, V. I.; Antoshin, G. V.; Ryashentseva, M. A.; Minachev, Kh. M. *J. Catal.* **1978**, *55*, 402.

Table 3. XPS Measurements

sample[a]	% Re/SiO_2 (wt %)	E_b Re $4f_{7/2}$ (eV)	% Re in various oxidation states (0)	(+1)	(+4)	(+7)
$[Re_2(CO)_{10}]/SiO_2$	1.38	40.55	100	0	0	0
$[Re(CO)_3(OH)]_4/SiO_2$	2.44	42.26	0	0	100	0
$[Re_2(CO)_{10}]/SiO_2$ after 30 min under N_2 at 250 °C	1.60	41.09; 42.39; 46.50	0	6.8	56.6	36.6

[a] Sample prepared with ca. 2 wt % of Re with respect to SiO_2.

ported on the silica surface before the XPS measurement should be ca. 63.4% (corresponding to 6.8% + 56.6%), in excellent agreement with the amount of $[Re(CO)_3(OH)]_4$ actually extracted with acetone from the silica surface (63%, see above). The XPS analysis confirms the presence, in 36.6% yield, of Re^{7+} species which could be of the type $ROReO_3$ (R = H, $Si\equiv$), as suggested by the formation of $[Re(CO)_5OReO_3)]$ by successive treatment under 1 atm of CO and at 200 °C of the silica powder (Scheme 2).

Discussion and Conclusion

The facile reduction of $[Re(CO)_3(OH)]_4$ to $[Re_2(CO)_{10}]$ on the silica surface and under relatively mild conditions (150−200 °C and 1 atm CO) is a remarkable new observation showing that silica-supported $[Re(CO)_3(OH)]_4$, which does not sublime, could be a useful starting material for the synthesis of Re(0) carbonyl clusters. Surely the silica surface plays a unique role in this easy reduction of $[Re(CO)_3(OH)]_4$ to a Re(0) species because working in *n*-octanol (a high-boiling hydroxylated solvent that could mimic surface silanols) as reaction medium the reduction does not occur at all. Treatment of an *n*-octanol solution of $[Re(CO)_3(OH)]_4$ with a flux of CO (1 atm) at 170 °C does not generate $[Re_2(CO)_{10}]$, which is stable under these reaction conditions, as confirmed by a blank experiment. The treatment leads to the slow formation of a carbonyl rhenium complex characterized by an infrared spectrum (ν_{CO} = 1995(s) and 1882(vs) cm^{-1}) typical of the $[(CO)_3Re(\mu\text{-}OR)_3Re(CO)_3]^-$ (R = alkyl group) anion.[30]

The facile reduction on the silica surface is probably due to a specific stabilization under a CO atmosphere of the $[Re(CO)_5]^+$ moiety by anchoring to the surface. We have produced a large amount of evidence that this moiety can be covalently bound to the silica surface probably via a $Re-OSi\equiv$ bond, which, as expected, can be easily cleaved by H_2O, HCl, or $HReO_4$, as shown by the use of the "extraction method",[14] which allows the chemical characterization of complex mixtures of surface metal carbonyl species, which cannot be easily defined by infrared spectroscopy only.

The proposed species $[Re(CO)_5(OSi\equiv)]$ is of particular interest since complexes of the type $[Re(CO)_5(OR)]$ (R = alkyl or aryl) have never been reported to be stable up to now, therefore its stability on the surface is noteworthy. It could be attributed to the rigidity of the topological arrangement of surface silanols, which prevents the aggregation of $[Re(CO)_5(OSi\equiv)]$ by bridging silanolate or hydroxo bonds and loss of carbon monoxide to give dinuclear surface species of the type $[(CO)_3Re(\mu\text{-}OSi\equiv)_3Re(CO)_3]^-$. In fact the related alkoxy derivatives of the type $[Re(CO)_5(OR)]$ have so far eluded isolation,[30b,31] due to (i) the strong tendency of OR groups to function as bridging ligands, (ii) the relative lability of mutually transoid CO ligands, and (iii) the low steric hindrance of OR ligands against the aggregation of "$Re(CO)_3(OR)$" fragments.[31] Even $[Re(CO)_5(OBu^t)]$ could not be isolated, by reaction of $NaOBu^t$ with $[Re(CO)_5Br]$, due to the easy formation of $Na[(CO)_3Re(\mu\text{-}OBu^t)_3Re(CO)_3]$.[30b]

The reduction with CO (1 atm) of silica-anchored $[Re(CO)_5(OSi\equiv)]$ to give $[Re_2(CO)_{10}]$ is a new example of the known easy reductive carbonylation of silica-anchored oxidized metal carbonyl species such as $[Os(CO)_x(OSi\equiv)_2]_n$ (x = 2, 3), which affords $[Os_3(CO)_{12}]$.[32] Since the original goal of our investigation was that of defining reaction conditions for the silica-mediated synthesis of Re(0) carbonyl clusters, we have shown that a simple Re(0) carbonyl cluster such as $[Re_2(CO)_{10}]$ is relatively stable on silica, unexpectedly even under 1 atm of H_2. Only at 200−250 °C under nitrogen it is transformed into $[Re(CO)_3(OH)]_4$, as occurs when a suspension of $[Re_2(CO)_{10}]$ in water is heated at 200 °C under nitrogen in an autoclave.[12] However, on silica, the relatively high temperature (200−250 °C) necessary to generate silica-supported $[Re(CO)_3(OH)]_4$ with respect to the sublimation of $[Re_2(CO)_{10}]$ produces even under nitrogen some further oxidation up to Re^{7+}, as confirmed by XPS and by treatment of these oxidized surface rhenium species with CO, which affords some $[Re(CO)_5OReO_3]$. Because solid $[Re(CO)_3(OH)]_4$ oxidizes with decomposition in air only at temperatures higher than 360 °C,[5] it appears that the silica surface must play an important role in favoring a more facile oxidation process.

In conclusion, our work clarified and unveiled some new aspects of the surface organometallic chemistry of silica-supported $[Re(CO)_3(OH)]_4$ and $[Re_2(CO)_{10}]$, confirming the importance of the "extraction method" as a tool to fully identify supported organometallic species and their mixtures.[14] We have shown in particular that the silica surface plays quite a relevant role in the increased reactivity of $[Re(CO)_3(OH)]_4$ toward oxidation even under nitrogen or vacuum, when compared to its behavior in solution or in the solid state. In addition its high tendency to be reduced with CO to $[Re_2(CO)_{10}]$, by cleavage of Re−O bonds and formation of a Re−Re

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[30] (a) Ginsberg, A. P.; Hawkes, M. J. *J. Am. Chem. Soc.* **1968**, *90*, 5930. (b) Ioganson, A. A.; Lokshin, B. V.; Kolobova, E. E.; Anisimov, K. N. *J. Gen. Chem.* **1974**, *20*, 20. (Translated from *Zh. Obshch. Khim.* **1974**, *44*, 23). (c) Albano, V. G.; Ciani, G.; Freni, M.; Romiti, P. *J. Organomet. Chem.* **1975**, *96*, 259. (d) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Organomet. Chem.* **1978**, *152*, 85. (e) Ciani, G.; Sironi, A.; Albinati, A. *Gazz. Chim. Ital.* **1979**, *109*, 615. (f) Herrmann, W. A.; Mihalios, D.; Ofele, K.; Kiprof, P.; Belmedjahed, F. *Chem. Ber.* **1992**, *125*, 1795.

[31] Jiang, C.; Wen, Y. S.; Liu, L. K.; Hor, T. S. A.; Yan, Y. K. *Organometallics* **1998**, *17*, 173.

[32] Dossi, C.; Fusi, A.; Grilli, E.; Psaro, R.; Ugo, R.; Zanoni, R. *Catal. Today* **1988**, *2*, 585.

bond, is noteworthy for an oxophilic metal and encouraging in further attempts to investigate the synthesis of rhenium(0) carbonyl clusters from oxidized Re species mediated by the silica surface.

Experimental Section

General Comments. SiO_2 (Aerosil 200 Degussa, with a nominal surface area of 200 m^2/g) was used as the support after treatment in vacuo (10^{-2} Torr) at 25 °C for 3 h. $[Re_2(CO)_{10}]$ and $HReO_4$ were purchased from INALCO and Sigma-Aldrich, respectively. $[Re(CO)_3(OH)]_4$ was prepared according to the literature and characterized by infrared and ^1H NMR spectroscopies[12] and by mass spectrometry (in the FAB−mass spectrum, we observed the molecular ion peak at 1150, never reported before). Organic solvents were dried over molecular sieves (4 Å) prior to use. All the reaction products were identified, after extraction from silica, by mass, infrared, and/or ^1H NMR spectroscopies, their spectra being compared to those of pure samples. Their purity was also controlled by elemental analysis. Spectral data were obtained by use of the following spectrometers: Bruker-Vector 22 (IR), Bruker AC-200 or Bruker DRX-300 (^1H NMR), Varian VG9090 (MS). Elemental analyses were carried out in the analytical laboratory of our department, whereas XPS measurements were performed using M-Probe (SSI) equipment. The source was monochromatic Al Kα radiation (1486.6 eV). The 1s level hydrocarbon-contaminant carbon was taken as the internal reference at 284.6 eV.

Preparation of Silica-Supported $[Re(CO)_3(OH)]_4$. In a typical preparation, a slurry of silica (8.23 g), $[Re(CO)_3(OH)]_4$ (254 mg; 0.221 mmol; 2.0 wt % Re with respect to SiO_2), and CH_2Cl_2 or acetone (300 mL) was stirred under N_2 at 25 °C for 2 h. The solvent was evaporated at 25 °C under vacuum (10^{-2} Torr), affording a white powder, which was stored under N_2.

Preparation of Silica-Supported $[Re_2(CO)_{10}]$. In a typical preparation, a slurry of silica (14.16 g), $[Re_2(CO)_{10}]$ (494 mg; 0.757 mmol; 2.0 wt % Re with respect to SiO_2), and CH_2Cl_2 (300 mL) was stirred under N_2 at 25 °C for 2 h. The solvent was evaporated at 25 °C under vacuum (10^{-2} Torr), affording a white powder, which was stored under N_2.

Preparation of Silica-Supported $[HRe_3(CO)_{14}]$. In a typical preparation, a slurry of silica (1.82 g), $[HRe_3(CO)_{14}]$ (42 mg; 0.625 mmol; 2.0 wt % Re with respect to SiO_2), and pentane (70 mL) was stirred under N_2 at 25 °C for 2 h. The solvent was evaporated at 25 °C under vacuum (10^{-2} Torr), affording a pale yellow powder, which was stored under N_2.

Reductive Carbonylation of Silica-Supported $[Re(CO)_3(OH)]_4$. The silica powder sample containing $[Re(CO)_3(OH)]_4$ (2.0 wt % Re with respect to SiO_2) was transferred into the cylindrical Pyrex vessel (diameter 60 mm, length 350 mm) previously described for the reductive carbonylation of silica-supported metal chlorides at atmospheric pressure,[10a] treated under vacuum (10^{-2} Torr) at 25 °C and then exposed to CO at atmospheric pressure. The bottom of the vessel (about half of the cylinder) was put into an oven and heated at the desired temperature (100−250 °C). The surface reactions were monitored by infrared spectroscopy; samples were taken from the glass vessel at room temperature and studied as Nujol mull (see Results and Discussion sections). Extraction of the supported rhenium species was carried out under N_2 with pentane or dichloromethane (in the case of $[Re_2(CO)_{10}]$) and dichloromethane or acetone (in the case of $[Re(CO)_3(OH)]_4$). $[Re(CO)_5(OSi{\equiv})]$ could not be extracted by treatment with donor solvents such as acetone or THF, as expected for a species anchored to the surface via covalent bonds.[14]

(i) At 100 °C. Silica-supported $[Re(CO)_3(OH)]_4$ reacted very slowly when heated at 100 °C under CO with formation of only traces of the proposed $[Re(CO)_5(OSi{\equiv})]$ species after 2 days.

(ii) At 150 °C. When silica-supported $[Re(CO)_3(OH)]_4$ (5.19 g of powder corresponding to 0.556 mmol Re) was heated under CO at 150 °C for 4 days, some $[Re_2(CO)_{10}]$ sublimed, whereas the infrared spectrum of the silica powder showed carbonyl bands at 2089(w), 2069(w), 2049(vs), 2028(m), 2012(m), 1991(m), 1974(w), and 1925(s) cm^{-1}. Treatment of the sublimate and silica powder with anhydrous pentane afforded $[Re_2(CO)_{10}]$ (33 mg; 0.050 mmol; 18% yield), whereas successive extraction of the silica powder with anhydrous CH_2Cl_2 gave $[Re(CO)_3(OH)]_4$ (44 mg; 0.038 mmol; 27% yield) and left the proposed $[Re(CO)_5(OSi{\equiv})]$ species and traces of unidentified rhenium carbonyl species (ν_{CO} = 2089(w) and 1927(w) cm^{-1}) on the silica surface.

(iii) At 200−250 °C. When silica-supported $[Re(CO)_3(OH)]_4$ (4.28 g of powder corresponding to 0.459 mmol Re) was heated at 200 °C under CO, a white material sublimed onto the cold walls of the reaction vessel. After 2, 3, and 5 days, extraction of both the sublimate and the silica powder with anhydrous pentane afforded $[Re_2(CO)_{10}]$ in 47% (70 mg; 0.107 mmol), 60% (90 mg; 0.138 mmol), and 71% (106 mg; 0.162 mmol) yields, respectively. Similar yields were reached by working at 250 °C.

Reactivity of Silica-Anchored $[Re(CO)_5(OSi{\equiv})]$. As above-reported, a silica powder sample containing silica-anchored $[Re(CO)_5(OSi{\equiv})]$ was obtained by treatment of silica-supported $[Re(CO)_3(OH)]_4$ (5.19 g of powder corresponding to 0.556 mmol Re) under CO at 150 °C for 4 days, followed by successive extraction under N_2 with anhydrous pentane and CH_2Cl_2 to remove $[Re_2(CO)_{10}]$ and $[Re(CO)_3(OH)]_4$. The powder sample was divided into two equal parts, whose reactivity with HCl and $HReO_4$ is reported below.

(i) With HCl. Extraction of silica-anchored $[Re(CO)_5(OSi{\equiv})]$ with dichloromethane (ca. 200 mL) acidified with a few drops of HCl(aq), followed by evaporation of the solution, afforded $[Re(CO)_5Cl]$[13] (43 mg; 0.119 mmol; 43% yield with respect to starting silica-supported $[Re(CO)_3(OH)]_4$). After this extraction process, traces of unidentified rhenium carbonyl species (ν_{CO} = 2089(w) and 1927(w) cm^{-1}) remained on the silica surface, as evidenced by infrared spectroscopy.

(ii) With $HReO_4$. Extraction of silica-anchored $[Re(CO)_5(OSi{\equiv})]$ with dichloromethane (ca. 200 mL) acidified with a few drops of $HReO_4$, followed by evaporation of the solution, afforded crude $[Re(CO)_5OReO_3]$,[16] which was recrystallized from dichloromethane/hexane (82 mg; 0.142 mmol; 51% yield with respect to starting silica-supported $[Re(CO)_3(OH)]_4$). After this extraction process, traces of unidentified rhenium carbonyl species (ν_{CO} = 2089(w) and 1927(w) cm^{-1}) remained on the silica surface, as evidenced by infrared spectroscopy. $[Re(CO)_5OReO_3]$ was characterized by elemental analysis (calcd C, 10.42; found C, 10.55), mass spectrometry (in the FAB+ mass spectrum, never reported before, there is the molecular ion peak at $m/e = 578$ $[M]^+$), and infrared spectroscopy (in CH_2Cl_2: ν_{CO} = 2164(w), 2057(vs), and 2002(m) cm^{-1}).

Carbonylation of Silica-Supported $[HRe_3(CO)_{14}]$. The silica powder sample containing $[HRe_3(CO)_{14}]$ (ca. 200 mg of powder; 2.0 wt % Re with respect to SiO_2) was transferred into the cylindrical Pyrex vessel (diameter 60 mm, length 350 mm) previously described for the reductive carbonylation of silica-supported metal chlorides at atmospheric pressure,[10a] treated under vacuum (10^{-2} Torr) at 25 °C and then exposed to CO at atmospheric pressure.

(i) At Room Temperature. Silica-supported $[HRe_3(CO)_{14}]$ reacted very slowly under CO at room temperature. After 7 days, a mixture of $[HRe_3(CO)_{14}]$, $[Re_2(CO)_{10}]$, and $[HRe(CO)_5]$ was present on the silica surface and could be characterized by infrared and ^1H NMR spectroscopies[8] after extraction with $CDCl_3$.

(ii) At 150 °C. When pale yellow silica-supported $[HRe_3(CO)_{14}]$ was heated under CO at 150 °C for 4 h, the silica powder color became white and some $[Re_2(CO)_{10}]$ sublimed. Treatment of the sublimate and silica powder with anhydrous pentane afforded pure $[Re_2(CO)_{10}]$, whereas no carbonyl rhenium species remained on the silica surface, as evidenced by infrared spectroscopy.

Thermal Behavior of Silica-Supported [$Re_2(CO)_{10}$]. The silica-supported [$Re_2(CO)_{10}$] (2.0 wt % Re with respect to SiO_2) was transferred into the cylindrical Pyrex vessel (diameter 60 mm, length 350 mm) previously described for the reductive carbonylation of silica-supported metal chlorides at atmospheric pressure,[10a] treated under vacuum (10^{-2} Torr) at 25 °C, and then exposed to N_2, CO, H_2, or air at atmospheric pressure. The bottom of the vessel (about half of the cylinder) was put into an oven and heated at the desired temperature (100−250 °C). The surface reactions were monitored by infrared spectroscopy; samples were taken from the glass vessel at room temperature and studied as Nujol mull (see Results section). Extraction of the supported rhenium species was carried out under N_2 with pentane or dichloromethane (in the case of [$Re_2(CO)_{10}$]) and dichloromethane or acetone (in the case of [$Re(CO)_3(OH)]_4$).

Thermal Behavior of Silica-Supported [$Re_2(CO)_{10}$] under N_2 at 250 °C. In a typical preparation, silica-supported [$Re_2(CO)_{10}$] (6.59 g of powder corresponding to 0.704 mmol Re) was heated under N_2 at 250 °C for 30 min. Treatment with pentane of the silica powder and of the sublimate, formed during the reaction onto the cold walls of the vessel, afforded [$Re_2(CO)_{10}$] in ca. 1% yield (ca. 2 mg; ca. 0.003 mmol). Further extraction of the silica powder with acetone, followed by evaporation of the solution to dryness, afforded crude [$Re(CO)_3(OH)]_4$, which was recrystallized from dichloromethane/pentane at −30 °C (128 mg; 0.111 mmol; 63% yield).

Thermal Behavior of Silica-Supported [$Re_2(CO)_{10}$] under N_2 at 250 °C Followed by Carbonylation. The silica powder sample containing [$Re_2(CO)_{10}$] (2.0 wt % Re with respect to SiO_2; 3.02 g of silica powder) was transferred into the cylindrical Pyrex vessel,[10a] treated under vacuum (10^{-2} Torr) at 25 °C, and then exposed to N_2 at atmospheric pressure. The bottom of the vessel (about half of the cylinder) was put into an oven and heated at 250 °C for 30 min. The vessel was cooled to room temperature, treated under vacuum (10^{-2} Torr), exposed to CO at atmospheric pressure, and then heated at 200 °C. After either 24 or 48 h, the infrared spectrum of the silica powder, as Nujol mull, showed carbonyl bands at 2087(w), 2069(w), 2049(vs), 2012(m), 1991(m), and 1974(w) cm^{-1}. The extraction of the supported rhenium species was carried out under N_2. Treatment of the sublimate and silica powder with anhydrous pentane afforded [$Re_2(CO)_{10}$], whereas successive extraction of the silica powder with anhydrous CH_2Cl_2 gave [$Re(CO)_5OReO_3$]. Successive extraction with acetone afforded traces of a species characterized by a carbonyl band at 2081 cm^{-1}, which could be [$Re(CO)_6$][ReO_4] by analogy with the known complex [$Re(CO)_6$][$AlCl_4$] (ν_{CO} in acetone = 2081 cm^{-1}),[23] whereas silica-anchored [$Re(CO)_5(OSi\equiv)$] remained on the gray silica surface, as confirmed by infrared spectroscopy (ν_{CO} as Nujol mull = 2049(vs) and 1991(m) cm^{-1}) of the sample.

Reactivity of [$Re(CO)_5OReO_3$]. (i) With HCl. Addition of a few drops of 37% aqueous HCl to a solution of [$Re(CO)_5OReO_3$] in dichloromethane, at room temperature, afforded [$Re(CO)_5Cl$][13] in quantitative yield. The reaction was complete in less than 5 min, as evidenced by infrared spectroscopy.

(ii) With Acetone. No change occurred in the infrared spectrum of [$Re(CO)_5OReO_3$] in dichloromethane upon addition of a few drops of either acetone or water. However, the carbonyl bands of [$Re(CO)_5OReO_3$] were shifted to lower frequencies by using pure acetone (ν_{CO} = 2043(s) and 1989(m) cm^{-1}) instead of dichloromethane (ν_{CO} = 2164(w), 2057(vs), and 2002(m) cm^{-1}) as solvent due to the formation of [$Re(CO)_5$(acetone)][ReO_4]. This shift is in agreement with that observed going from [$Re(CO)_5FBF_3$] (ν_{CO} in CH_2Cl_2 = 2166(w), 2066(s), and 2008(m) cm^{-1}) to [$Re(CO)_5(H_2O)$][BF_4] (ν_{CO} in CH_2Cl_2 = 2160(w), 2057(s), and 2004(s) cm^{-1}).[25,26] The formation of [$Re(CO)_5$(acetone)][ReO_4] was confirmed by conductive measurements using a Amel 160 conductivity meter. The conductivity of pure acetone was 0.23 μS, whereas that of a solution of [NBu_4]OH (10^{-3} M) and [$Re(CO)_5OReO_3$] (6.2×10^{-4} M) in acetone was 121.5 and 60.11 μS, respectively. A dichloromethane solution of [$Re(CO)_5OReO_3$] (6.2×10^{-4} M) did not conduct.

X-ray Structure Determination of [$(CO)_5Re(\mu\text{-}O)ReO_3$]. A suitable crystal of the title compound was chosen and mounted, in air, on a glass fiber onto a goniometer head and collected at RT on a Siemens SMART CCD area-detector diffractometer. Crystal data are reported in Table 2. Graphite-monochromatized Mo Kα (λ = 0.71073 Å) radiation was used with the generator working at 45 kV and 40 mA. Cell parameters and orientation matrix were obtained from least-squares refinement on reflections measured in three different sets of 15 frames each. The data collection was performed by measuring 2500 frames (15 s per frame; ω scan method, $\Delta\omega = 0.3°$; sample−detector distance fixed at 5.5 cm), which, upon data reduction, afforded almost all reflections belonging to the sphere with $2\theta < 56°$. The first 100 frames were recollected at the end to monitor crystal decay, which was not observed; an absorption correction was applied (SADABS, minimum relative effective transmission factor 0.404).[33]

A total of 25 483 reflections were collected (4732 unique, $R_{int} = 0.0434$; $R_\sigma = 0.0377$).[34] The structure was solved by direct methods (SIR97)[35] and refined with full-matrix-block least-squares (SHELX97);[36] anisotropic temperature factors were assigned to all atoms.

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Supporting Information Available: Refined atoms coordinates (Table S1), anisotropic thermal parameters (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) Sheldrick, G. M. *SADABS*; University of Göttingen: Germany, 1996.

(34) $R_{int} = \sum|F_o^2 - F_{mean}^2|/\sum F_o^2$; $R_\sigma = \sum\sigma(F_o^2)/\sum F_o^2$; $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = (\sum(F_o^2 - F_c^2)^2/\sum wF_o^4)^{1/2}$

(35) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *24*, 435.

(36) Sheldrick, G. M. *SHELX97-Program for the refinement of crystal structure*; University of Göttingen: Germany, 1997.