Surface organometallic chemistry — Carbonyl complexes of Re(I) with silanolates as models of silica anchored rhenium carbonyl species[1]

Giuseppe D'Alfonso, Claudia Dragonetti, Simona Galli, Elena Lucenti, Piero Macchi, Dominique Roberto, and Renato Ugo

Abstract: Reaction of Me_3SiONa with $[Re(CO)_5Cl]$ affords the new complex $Na[Re_2(CO)_6(\mu\text{-}OSiMe_3)_3]$, which could be generated via formation of $[Re(CO)_5OSiMe_3]$ followed by immediate reaction with Me_3SiO^-. Substitution of some CO ligands by phosphines significantly decreases the electrophilicity of the Re(I) center, and therefore hinders further attack by Me_3SiO^-. Thus, *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)OTf]$ (OTf is the triflate anion) reacts with Me_3SiONa to give *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)OSiMe_3]$, a molecular model of silica anchored $[Re(CO)_5OSi\equiv]$. However, substitution of only one CO by triphenylphosphine is not enough to avoid the formation of $[Re_2(CO)_6(\mu\text{-}OSiMe_3)_3]^-$. While *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)OSiMe_3]$ is stable towards hydrolysis, $[Re_2(CO)_6(\mu\text{-}OSiMe_3)_3]^-$ is readily hydrolyzed to $[Re_2(CO)_6(\mu\text{-}OH)(\mu\text{-}OSiMe_3)_2]^-$, a molecular model of silica anchored $[Re_2(CO)_6(\mu\text{-}OH)(\mu\text{-}OSi\equiv)_2]^-$, whose structure has been determined by single crystal X-ray diffraction.

Key words: surface organometallic chemistry, rhenium, silica, silanolate, molecular model.

Résumé : La réaction de Me_3SiONa avec $[Re(CO)_5Cl]$ fournit le nouveau complexe $Na[Re_2(CO)_6(\mu\text{-}OSiMe_3)_3]$, probablement généré via la formation de $[Re(CO)_5OSiMe_3]$ suivie par une réaction immédiate avec Me_3SiO^-. La substitution de quelques CO par des phosphines diminue fortement l'électrophilicité du centre Re(I) et, par conséquent, empêche toute attaque ultérieure par Me_3SiO^-. Ainsi, *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)OTf]$ (OTf est l'anion triflate) réagit avec Me_3SiONa pour donner *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)OSiMe_3]$, modèle moléculaire de l'espèce ancrée à la silice $[Re(CO)_5OSi\equiv]$. Cependant la substitution d'un seul CO par la triphenylphosphine ne suffit pas à empêcher la formation de $[Re_2(CO)_6(\mu\text{-}OSiMe_3)_3]^-$. Alors que *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)OSiMe_3]$ est stable en présence d'eau, $[Re_2(CO)_6(\mu\text{-}OSiMe_3)_3]^-$ s'hydrolyse rapidement pour donner $[Re_2(CO)_6(\mu\text{-}OH)(\mu\text{-}OSiMe_3)_2]^-$, modèle moléculaire de l'espèce ancrée à la silice $[Re_2(CO)_6(\mu\text{-}OH)(\mu\text{-}OSi\equiv)_2]^-$, dont la structure a été déterminée par diffraction des rayons X.

Mots clés : chimie organométallique de surface, rhénium, silice, silanolate, modèle moléculaire.

Introduction

Transition-metal carbonyls supported on silica are hybrid materials of interest as precursors of highly dispersed metals that may show improved or unusual catalytic properties (1). Although largely investigated in the last two decades (2), the surface organometallic chemistry between molecular metal carbonyl fragments and the surface sites is not always fully established. A recently developed way for a better understanding of the structure and reactivity of molecular metal carbonyl fragments bound to the silica surface is based on the structural and chemical characterization of metal carbonyl compounds bearing various silanolate ligands that mimic the functional groups of the silica surface. These models are a useful tool not only to understand the structural aspects of surface organometallic species, but also to clarify

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the rather complex chemical behavior of metal carbonyl species anchored to silica (2). Many models of silica anchored carbonyl species of various noble metals (e.g., Rh (3), Os (2, 4),[3] and Ru (5)) have been synthesized, structurally characterized, and chemically investigated; however, in the case of the oxophilic metal Re, just anionic $[Re_2(CO)_6(\mu\text{-}OH)_x(\mu\text{-}OSiEt_3)_{3-x}]^-$ (x = 0, 1, or 2) (6) and neutral $[Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}OSiR_2R')]$ (R = Et, Ph; R′ = Et, Ph, OH, or $OSiPh_2OH$) (7) species have been obtained and described only recently. Nevertheless, these few models cannot give a full understanding of the surface organometallic chemistry involving various rhenium carbonyl species anchored to silica. There is still a need for the synthesis and investigation of novel rhenium carbonyl species bearing silanolate ligands to fully clarify the complex surface chemistry occurring when rhenium carbonyl species such as $[Re_2(CO)_{10}]$ or $[Re(CO)_3(OH)]_4$ are chemically interacting with the silica surface. Indeed, this kind of surface organometallic chemistry is not yet well known, despite the industrial relevance of Re catalysts supported on inorganic oxides (8).

Recently, in fact, we reported that silica supported $[Re(CO)_3(OH)]_4$ is easily converted into $[Re_2(CO)_{10}]$ by reductive carbonylation under very mild conditions (1 atm CO, 1 atm = 101.325 kPa). This reaction does not occur in solution, suggesting that the silica surface plays a unique role via the formation of the surface anchored species $[Re(CO)_5OSi\equiv]$, which could also act as the intermediate in the silica mediated conversion under N_2 of $[Re_2(CO)_{10}]$ into $[Re(CO)_3(OH)]_4$ (9). Evidence for an intermediate chemically bound to the silica surface was based on IR studies and on its lack of extraction with solvents, together with its reactivity with HCl and $HReO_4$ to afford $[Re(CO)_5Cl]$ and $[Re(CO)_5OReO_3]$, respectively. This proposed surface species anchored via a Re—OSi bond to the surface is quite peculiar since carbonyl species of the type $[Re(CO)_5OR]$ have so far eluded isolation (9). Therefore, to produce additional evidence for its existence and to enlighthen its chemical behavior, we started an investigation on the synthesis and characterization of molecular models of this unusual silica anchored species.

Results and discussion

Attempts to prepare the molecular model of silica anchored $[Re(CO)_5OSi\equiv]$ by reaction of $[Re(CO)_5Cl]$ with Me_3SiONa invariably failed. The expected compound, $[Re(CO)_5OSiMe_3]$, was not obtained upon addition of Me_3SiONa to a solution of $[Re(CO)_5Cl]$ in dichloromethane (1:1 molar ratio), working under nitrogen at room temperature. Under these conditions, only some $Na[Re_2(CO)_6(\mu\text{-}OSiMe_3)_3]$ (ν(CO) = 2007 (s, br) and 1879 (vs, br) cm^{-1}) is quickly formed. With a 1.5:1 molar ratio Me_3SiONa:$[Re(CO)_5Cl]$, $Na[Re_2(CO)_6(\mu\text{-}OSiMe_3)_3]$ is quantitatively obtained (eq. [1]). Similarly, Et_3SiONa leads to the known anion $[Re_2(CO)_6(\mu\text{-}OSiEt_3)_3]^-$, previously prepared by reaction of an anisole solution of $[Re_2(CO)_6(\mu\text{-}OH)_3]^-$ with an excess of triethylsilanol at 200 °C (6).

$$[1] \qquad 2[Re(CO)_5Cl] + 3Me_3SiO^- \rightarrow [Re_2(CO)_6(\mu\text{-}OSiMe_3)_3]^- + 2Cl^- + 4CO$$

Reaction of $[Re(CO)_5Cl]$ with the anion Me_3SiO^- reasonably generates $[Re(CO)_5OSiMe_3]$ as a very reactive intermediate species, which could not be detected even by working under CO at 0 °C. This intermediate would be so reactive towards nucleophiles to react rapidly with the anion Me_3SiO^- affording, finally, by a double nucleophilic attack, $[Re_2(CO)_6(\mu\text{-}OSiMe_3)_3]^-$. Such an easy dimerization by silanolates bridging and concomitant loss of carbon monoxide, even under a CO atmosphere, suggests that the silanolate anion, as the alkoxide one (10), is an exceptionally good cis-labilizing ligand, which facilitates a further nucleophilic attack: the behavior of Me_3SiO^- towards $[Re(CO)_5Cl]$ is thus parallel to that of the structurally related alkoxide Me_3CO^- (11), despite its lower basicity. The quite high stability of the proposed silica anchored $[Re(CO)_5OSi\equiv]$ intermediate (9) can be due to the much lower nucleophilicity of surface silanols because the lack of dimerization cannot be attributed to the topological arrangement of surface silanols. In fact, we produced evidence for covalent anchoring of the dimer $[Re_2(CO)_6(\mu\text{-}OH)_3]^-$ to surface silanols (6).

It was thus clear that we could follow two strategies to obtain mononuclear Re(I) carbonyl silanolates: to decrease either the nucleophilic power of the silanolate anion or the electrophilic character of the Re(I) center. In this work we report on the results obtained by following the second option.

Substitution of some CO ligands of $[Re(CO)_5Cl]$ by phosphine ligands should decrease the electrophilicity of the Re(I) center and therefore hinder further nucleophilic attacks by Me_3SiO^- with formation of anionic dimeric species. Therefore, we treated *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)Cl]$ with a stoichiometric amount of Me_3SiONa, at room temperature in dichloromethane. No reaction took place because of the large increase of the electronic density on the Re(I) center, as it can be inferred from the IR spectrum. This effect obviously inhibits even the first nucleophilic attack by the trimethylsilanolate anion. However, it is well-known that in Re(I) carbonyl species the triflate anion is a much better leaving group than the chloride one. Thus, we studied the reaction of *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)OTf]$ (OTf is the triflate anion), easily obtained by reaction of AgOTf with *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)Cl]$.

Addition of Me_3SiONa to a dichloromethane solution of *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)OTf]$ slowly affords *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)OSiMe_3]$. The reaction, which can be easily followed by IR and ^{31}P NMR spectroscopies (see the Experimental section), is complete in 2 days. Interestingly, although alkoxide complexes such as *fac*-$[Re(CO)_3(R'_2PCH_2CH_2PR'_2)OR]$ (R = Me, Et, or *i*-Pr; R′ = Et or Ph) were prepared by treatment of the triflate complex with the sodium salt of the appropriate primary or secondary alcohol (10, 12), it was reported that by reaction with the anion Me_3CO^-, structurally related to Me_3SiO^- but of increased nucleophilicity, the corresponding *tert*-butoxide complex was not isolated (10).

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[3] E. Lucenti, F.J. Feher, and J.W. Ziller. Submitted for publication.

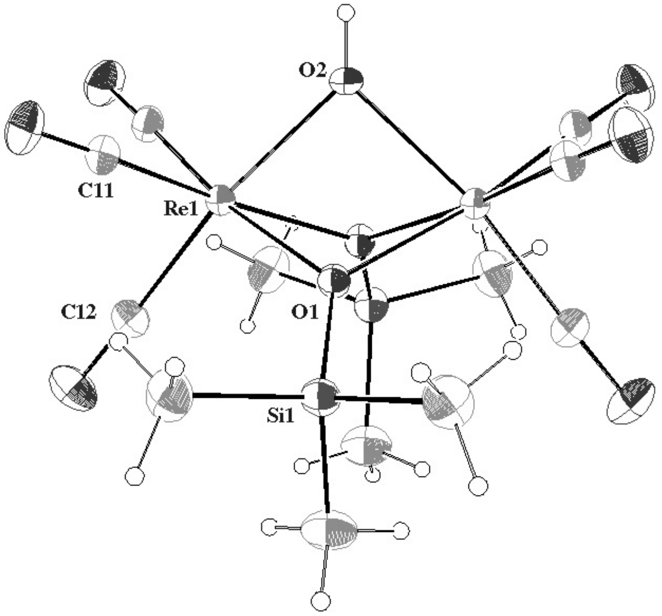
fac-[Re(CO)$_3$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)OSiMe$_3$] reacts readily with HCl(aq) to give *fac*-[Re(CO)$_3$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)Cl], a behavior that mimics the formation of [Re(CO)$_5$Cl] by treatment of the proposed silica anchored [Re(CO)$_5$OSi≡] species with HCl(aq). As a matter of fact, it was already reported that addition of gaseous HCl to the related alkoxide complex *fac*-[Re(CO)$_3$(Et$_2$PCH$_2$CH$_2$PEt$_2$)OEt] results in a similar cleavage of the metal–oxygen bond with formation of the corresponding chloride (13).

It appears that the balance of the electron density on the rhenium atom is of paramount relevance for the stabilization of monomeric silanolate complexes. Indeed, by decreasing the electronic density on the rhenium center, such as when replacing a chelating diphosphine with one triphenylphosphine as in *cis*-[Re(CO)$_4$(PPh$_3$)OTf], reaction with the anion Me$_3$SiO$^-$ still gives [Re$_2$(CO)$_6$(μ-OSiMe$_3$)$_3$]$^-$ with release of CO and even PPh$_3$, as evidenced by ^{29}Si and ^{31}P NMR spectroscopy, also when working at 0 °C (see the Experimental section). This latter result suggests that the coordination to rhenium of only one phosphorous donor atom is not sufficient to avoid aggregation by bridging silanolates when working in the normal range of temperatures between 0 and 25 °C.

It is worth pointing out that the Re-OSiMe$_3$ bond in *fac*-[Re(CO)$_3$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)OSiMe$_3$] is quite stable to hydrolysis in the presence of water at room temperature, as in some other neutral rhenium silanolate models such as [Re$_2$(CO)$_8$(μ-H)(μ-OSiR$_2$R′)] (R = Et, Ph; R′ = Et, Ph, OH, or OSiPh$_2$OH) (7), but in sharp contrast with the fast hydrolysis of anionic species such as [Re$_2$(CO)$_6$(μ-OH)$_x$(μ-OSiEt$_3$)$_{3-x}$]$^-$ (x = 0, 1, or 2) (6). Indeed, addition of a stoichiometric amount of [NEt$_4$]Cl to an acetonitrile solution of Na[Re$_2$(CO)$_6$(μ-OSiMe$_3$)$_3$], followed by evaporation of the solvent and extraction of the organometallic anion with dry dichloromethane, afforded [NEt$_4$][Re$_2$(CO)$_6$(μ-OSiMe$_3$)$_3$]. However, by slow crystallization from dichloromethane–*n*-pentane at –20 °C, only crystals of the product of the first step of the hydrolysis (6), namely [NEt$_4$][Re$_2$(CO)$_6$(μ-OH)(μ-OSiMe$_3$)$_2$], were obtained because a partial hydrolysis arose even from very minor traces of water. The related complex [Re$_2$(CO)$_6$(μ-OH)(μ-OSiEt$_3$)$_2$]$^-$ has already been characterized spectroscopically (6), but has never been structurally investigated, although it is of interest as a model of the silica anchored surface species [Re$_2$(CO)$_6$(μ-OH)(μ-OSi≡)$_2$]$^-$ proposed to be thermally formed by condensation of [Re$_2$(CO)$_6$(μ-OH)$_3$]$^-$ with surface silanols (6).

The crystal structure of [NEt$_4$][Re$_2$(CO)$_6$(μ-OH)(μ-OSiMe$_3$)$_2$] (orthorhombic *Cmcm*) is composed by dimeric [Re$_2$(CO)$_6$(μ-OH)(μ-OSiMe$_3$)$_2$]$^-$ anionic units (Fig. 1), lying about a crystallographic *m2m* position (C_{2v}), counterbalanced by disordered tetraethylamonium cations, lying on a 2/*m* symmetry operator. Crystallographic data as well as data collection and treatment details are gathered in Table 1. A synoptic collection of bond lengths and angles is reported in Table 2. To our knowledge, this is the first example of a [Re$_2$(CO)$_6$(μ-OH)$_x$(μ-OR)$_{3-x}$]$^-$ structure (x = 0, 1, or 2) in which R is a silyl group. Previous characterizations regarding both homo- and hetero-bridged dimers of this kind invariably involved alkoxy or aryloxy bridges (14). Moreover, among the known X-ray structures of hetero-bridged [Re$_2$(CO)$_6$(μ-OH)$_x$(μ-OR)$_{3-x}$]$^-$ complexes, a well-defined structure for the anionic dimer, as in the present case, was obtained only for the anion [Re$_2$(CO)$_6$(μ-OH)(μ-OPh)$_2$]$^-$ (14*f*), heavy disorder affecting the alkoxy groups in all the other cases (14*a*, 14*e*).

Fig. 1. ORTEP representation (at 20% probability) of [Re$_2$(CO)$_6$-(μ-OH)(μ-OSiMe$_3$)$_2$]$^-$. The labels adopted for the structural description are depicted.



Within each [Re$_2$(CO)$_6$(μ-OH)(μ-OSiMe$_3$)$_2$]$^-$ dimer, the metal center, hexa-coordinated in distorted octahedral stereochemistry, is bound by three terminal carbonyl ligands, occupying facial positions, by two bridging -OSiMe$_3$ moieties and a bridging hydroxy group. The metal atom thus satisfies the valence bond electron rule without invoking a bonding metal···metal interaction, whose distance (3.111(1) Å) is anyway only slightly greater than that of 3.02 Å found in [Re$_2$(CO)$_{10}$] (15), as occurs in other RO$^-$ supported Re–Re dimers (see Table 2). Comparable Re—O(H) and Re—O(Si) bond distances (2.142(5) and 2.141(3) Å, respectively) find correspondence in similar Re-O(H)-Re and Re-O(Si)-Re bond angles (93.1(3)° and 93.2(2)°, respectively). Both independent carbonyl groups reveal almost normal features, with Re—C bond distances of 1.888(6) and 1.904(9) Å, C—O bond distances of 1.161(7) and 1.166(11) Å, and Re-C-O angles of 177.3(6)° and 176.9(9)°.

The steric hindrance of the trimethylsilanolate group seems not to induce significant molecular rearrangements: by inspecting Table 2, the major sterical effect seems to occur when PhO$^-$ is acting as the bridge (see, in particular, the Re—O and Re···Re distances).

The dimeric [Re$_2$(CO)$_6$(μ-OH)(μ-OSiMe$_3$)$_2$]$^-$ units pack to generate rows parallel to **a** which stack, staggered, along **b** with minor intermolecular interactions (Fig. 2). Consecutive stacks of rows are separated, along **c**, by the counterions.

Conclusions

Due to (*i*) the high cis-labilizing effect of the silanolate ligand, (*ii*) the lability of CO ligands in "Re(CO)$_5$" and

Table 1. Crystallographic data and structure refinement parameters for compound $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)(\mu\text{-}OSiMe_3)_2]$.

Empirical formula	$C_{20}H_{39}NO_9Re_2Si_2$
Formula weight (g mol^{-1})	865.96
Crystallographic system	Orthorhombic
Space group	*Cmcm*, No. 63
a (Å)	11.062(1)
b (Å)	11.887(2)
c (Å)	23.530(4)
V (Å^3)	3 094.1(8)
Z	4
F(000)	1604
Calculated density (Mg m^{-3})	1.859
Absorption coefficient (mm^{-1})	7.934
Temperature (K)	299
Crystal morphology	Needle
Crystal size (mm^3)	0.12 × 0.14 × 0.22
Integration range (°)	$3.5 \leq 2\theta \leq 61.1$
Indexes range	$-15 \leq h \leq 15$; $-16 \leq k \leq 16$; $-33 \leq l \leq 33$
Measured reflections	26 963
Unique reflections	2 537
Observed reflections for $I > 2\sigma(I)$	2 098
R_{int}, R_σ[a]	0.047, 0.025
Data / Restraints / Parameters	2 537 / 3 / 80
Goodness-of-fit[b]	$S(F^2)$ 1.225
Figures of merit for $I > 2\sigma(I)$[c]	$R(F)$ 0.037, $wR(F^2)$ 0.089
Figures of merit for all data	$R(F)$ 0.050, $wR(F^2)$ 0.092
Largest difference peak and hole (e Å^{-3})	1.24 and –2.36

[a] $R_{int} = \Sigma|F_o^2 - F_{mean}^2|/\Sigma|F_o^2|$; $R_\sigma = \Sigma|\sigma(F_o^2)|/\Sigma|F_o^2|$.

[b] $S(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where *n* is the number of reflections, *p* is the number of parameters, and $w = 1/[\sigma^2(F_o^2) + (0.019P)^2 + 1.88P]$ with $P = (F_o^2 + 2F_c^2)/3$.

[c] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

"$Re(CO)_4$" moieties containing mutually trans carbonyls, and (*iii*) the strong tendency of $OSiR_3$ groups to function as bridging ligands (4*g*), the molecular model $[Re(CO)_5OSiMe_3]$ of the proposed surface species $[Re(CO)_5OSi\equiv]$ can not be obtained by reaction of $[Re(CO)_5Cl]$ with the trimethylsilanolate anion, despite the lower nucleophilicity of this latter compound when compared with alkoxy or aryloxy anions. The reaction product, under different reaction conditions, is invariably the bridged anion $[Re_2(CO)_6(\mu\text{-}OSiMe_3)_3]^-$, as it occurs with alkoxy anions (11).

Only substitution of CO groups with a chelating diphosphine to increase the electron density on the Re(I) complex enhances the stability of CO ligands and thus allows the preparation of neutral rhenium silanolate mononuclear species. Thus, the easy reaction of Me_3SiONa with *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)OTf]$ provides a pathway to the novel complex *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)OSiMe_3]$, characterized by an increased stability towards hydrolysis of a Re—OSi bond in sharp contrast with the easy hydrolysis of anionic species such as $[Re_2(CO)_6(\mu\text{-}OH)_x(\mu\text{-}OSiR_3)_{3-x}]^-$ (x = 0, 1, or 2; R = Me, Et) (6).

The increased stability of carbonyl ligands and the lower electrophilicity of the rhenium center, which is the origin of the stability of the monomeric silanolate complexes towards dimerization by further nucleophilic attack by the trimethylsiloxy anion, are quite dependent on the number of phosphorous donor atoms coordinated to the rhenium center. Whereas the complex *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)OSiMe_3]$ does not react with excess Me_3SiO^-, *cis*-$[Re(CO)_4(PPh_3)OSiMe_3]$, reasonably formed as intermediate species by reaction of *cis*-$[Re(CO)_4(PPh_3)OTf]$ with Me_3SiO^-, still shows a great lability of a cis carbonyl and even a phosphine ligand giving place to $[Re_2(CO)_6(\mu\text{-}OSiMe_3)_3]^-$.

In conclusion, this work has indirectly suggested that the relative stability of the proposed "$Re(CO)_5(OSi\equiv)$" species anchored to the silica surface may be due to the extremely low nucleophilicity of the silanols of the silica surface. Therefore, work is in progress to synthesize $[Re(CO)_5\text{-}OSiR_3]$ species where R_3 better represents the tetrahedral oxygen sphere of silica silanols, which, being quite acidic, display a very low basicity either as such or even as silanolates.

Experimental section

General comments

$[Re(CO)_5Cl]$ and $[Re(CO)_4Cl]_2$ were prepared according to the literature, the first complex by reaction of $[Re_2(CO)_{10}]$ (commercially available from Acros Organics) with Cl_2 (16), the second by heating under reflux a heptane solution of $[Re(CO)_5Cl]$ (17). AgOTf and Me_3SiONa (1 mol/L solution in dichloromethane) were purchased from Sigma-Aldrich. Organic solvents were freshly distilled before use (Et_2O and THF from sodium/benzophenone; CH_2Cl_2 from CaH_2). All reactions were carried out under N_2 (dried by flowing over drierite) in anhydrous conditions. Products were characterized by IR and NMR (^1H, ^{29}Si, ^{31}P) spectroscopies, by mass spectrometry, and by elemental analyses, which were carried out at the Dipartimento di Chimica Inorganica, Metallorganica ed Analitica of the Università di Milano.

Synthesis of $Na[Re_2(CO)_6(\mu\text{-}OSiMe_3)_3]$

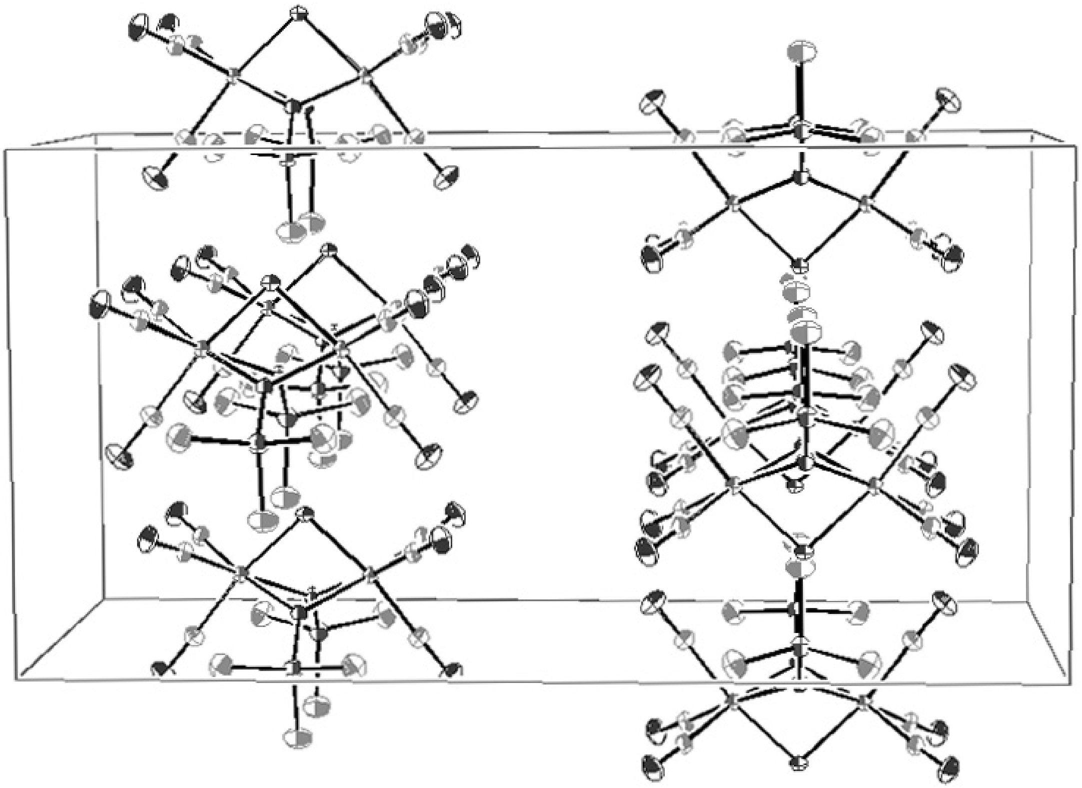
In a typical synthesis, a solution of Me_3SiONa in CH_2Cl_2 (0.65 mL of a 1 mol/L solution) was added to a solution of $[Re(CO)_5Cl]$ (150 mg, 0.415 mmol, molar ratio $[Re(CO)_5Cl]:Me_3SiONa$ = 1:1.6) in freshly distilled anhydr. CH_2Cl_2 (35 mL) under N_2 in a 100 mL two-neck round bottomed flask equipped with a magnetic stirring bar. After 24 h under stirring at room temperature, a white precipitate was present and the reaction was complete as evidenced by IR spectroscopy of the solution, which showed that no $[Re(CO)_5Cl]$ (ν(CO) in CH_2Cl_2 = 2046 (m), 1985 (s) cm^{-1}) was left. Evaporation to dryness of the solvent afforded a white residue that was dissolved in freshly distilled anhydr. THF (5 mL). Anhydr. Et_2O was slowly added to the latter solution, at ca. –5 °C (ice and salt bath), to precipitate the NaCl formed during the reaction. The solution was then separated from the precipitate using a syringe. Evaporation of the solvent followed by washing with a few mL of anhydrous pentane afforded pure $Na[Re_2(CO)_6(\mu\text{-}OSiMe_3)_3]$ as a white powder (162 mg, 0.195 mmol, 94% yield). IR (in

Table 2. Synoptic collection of significant geometrical parameters (distances, Å; angles, °) in the known dimeric anionic $[\mathrm{Re_2(CO)_6(\mu\text{-}OR)_{\mathit{x}}(\mu\text{-}OR')_{\mathit{y}}}]^-$ units ($x + y = 3$).

Dimeric unit	Re···Re (Å)	Re—O(H) (Å)	Re—O (Å)	Re-O(H)-Re (°)	Re-O-Re (°)	Ref.
$[\mathrm{Re_2(CO)_6(\mu\text{-}OSiMe_3)_2(\mu\text{-}OH)}]^-$	3.111	2.141	2.142	93.2	93.1	This work
$[\mathrm{Re_2(CO)_6(\mu\text{-}OMe)_{\mathit{x}}(\mu\text{-}OEt)_{\mathit{y}}}]^-$[a]	3.085	n.a.	2.065	n.a.	95.65	14*a*
$[\mathrm{Re_2(CO)_6(\mu\text{-}OMe)_{\mathit{x}}(\mu\text{-}OEt)_{\mathit{y}}}]^-$[a]	3.117	n.a.	2.123	n.a.	94.51	14*c*
			2.121		94.59	
$[\mathrm{Re_2(CO)_6(\mu\text{-}OPh)_3}]^-$	3.154	n.a.	2.107, 2.149[b,c]	n.a.	95.65	14*b*
			2.133, 2.145[b,c]		94.98	
			2.128, 2.154[b,c]		94.89	
$[\mathrm{Re_2(CO)_6(\mu\text{-}OH)_3}]^-$	3.103	2.063[d]	n.a.	97.55	n.a.	14*d*
		2.130[d]		93.53		
$[\mathrm{Re_2(CO)_6(\mu\text{-}OMe)(\mu\text{-}OEt)_2}]^-$	3.117	n.a.	2.108, 2.109[b,e]	n.a.	95.32	14*e*
			2.145, 2.157[b,f]		92.86	
			2.132, 2.149[b,f]		93.46	
$[\mathrm{Re_2(CO)_6(\mu\text{-}OH)(\mu\text{-}OPh)_2}]^-$	3.152	2.119, 2.138[b]	2.162, 2.163[b,g]	95.51	93.55	14*f*
			2.148, 2.151[b,g]		94.29	

Note: n.a. = not applicable.
[a] Severe disorder affecting the alkoxo groups impeded a definite assessment of stoichiometry.
[b] The two values on each line refer to the two independent Re atoms present.
[c] The values refer to one of the three independent phenoxy ligands.
[d] The values refer to one of the two independent hydroxy ligands.
[e] The values refer to the methoxy ligand.
[f] The values refer to one of the two independent ethoxy ligands.
[g] The values refer to one of the two independent phenoxy ligands present.

Fig. 2. ORTEP representation (at 20% probability) of the packing motif of the dimeric units in $[\mathrm{NEt_4}][\mathrm{Re_2(CO)_6(\mu\text{-}OH)(\mu\text{-}OSiMe_3)_2}]$ viewed down [1 0 0]. Horizontal axis, c; vertical axis, b. Disordered tetraethylammonium cations and hydrogen atoms have been omitted for clarity.



CH_2Cl_2, cm^{-1}): ν(CO) 2007 (s, br), 1879 (vs, br). ^{1}H NMR (in CD_3CN, ppm) δ: 0.02. ^{29}Si NMR (in CD_3CN, ppm) δ: 0.59; the ^{29}Si NMR signal of Me_3SiONa in CD_3CN lies at –13.09 ppm. In the FAB$^-$ mass spectrum, the ion peak corresponding to $[Re_2(CO)_6(\mu\text{-}OSiMe_3)_3]^-$ lies at *m/e* = 807. Elemental anal. calcd.: C 21.67, H 3.25; found: C 21.79, H 3.41.

Synthesis of $Na[Re_2(CO)_6(\mu\text{-}OSiEt_3)_3]$

Synthesis of Et_3SiONa

An excess of metallic Na (3.82 g, 166 mmol, cut in small pieces) was added to a solution of Et_3SiOH (0.98 mmol, 0.15 mL, *d* = 0.846 g/mL) in anhydr. Et_2O (15 mL) under N_2. After stirring at room temperature for ca. 4 h no more gas was evolved, the solution was separated with a syringe and evaporated to dryness affording pure Et_3SiONa. ^{1}H NMR (in CD_3CN, ppm) δ: 0.36 (q, 2H, CH_2), 0.93 (t, 3H, CH_3). ^{29}Si NMR (in CD_3CN, ppm) δ: –3.19.

Synthesis of $Na[Re_2(CO)_6(\mu\text{-}OSiEt_3)_3]$

A solution of Et_3SiONa in anhydr. CH_2Cl_2 (6.5 mL of a 0.0981 mol/L solution) was added to a solution of $[Re(CO)_5Cl]$ (150 mg, 0.415 mmol, molar ratio $[Re(CO)_5Cl]$:Et_3SiONa = 1:1.5) in freshly distilled anhydr. CH_2Cl_2 (35 mL) under N_2 in a 100 mL two-neck round bottomed flask equipped with a magnetic stirring bar. After 24 h under stirring at room temperature, a white precipitate was present and the reaction was complete as evidenced by IR spectroscopy of the solution. Evaporation to dryness of the solvent afforded a white residue that was dissolved in freshly distilled anhydr. THF (5 mL). Anhydr. Et_2O was slowly added to the latter solution, at –5 °C, to precipitate the NaCl formed during the reaction. The solution was then separated from the precipitate using a syringe. Evaporation of the solvent followed by washing with a few mL of anhydrous pentane (to remove traces of $Et_3SiOSiEt_3$ and Et_3SiOH) afforded the known complex $Na[Re_2(CO)_6(\mu\text{-}OSiEt_3)_3]$ (6) as a white powder (188 mg, 0.197 mmol, 95% yield).

Synthesis of *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)OSiMe_3]$

The new complex *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)OSiMe_3]$ was prepared from *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)OTf]$ (12), easily obtained by the reaction of AgOTf with *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)Cl]$ (18) recovered in quantitative yield by refluxing under N_2 for 14 h a $CHCl_3$ solution of $[Re(CO)_4Cl]_2$ (0.154 mmol) with a stoichiometric amount of $PPh_2CH_2CH_2PPh_2$ (0.308 mmol).

Thus, addition of AgOTf (19.8 mg, 0.073 mmol) to a solution of *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)Cl]$ (54 mg, 0.077 mmol, IR (in CH_2Cl_2 cm^{-1}): ν(CO) 2034 (vs), 1954 (s), 1906 (s); ^{31}P NMR (in CD_2Cl_2, ppm) δ: 32.65) in anhydr. CH_2Cl_2 (10 mL) led to the precipitation of AgCl and the formation of *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)OTf]$ as confirmed by IR and ^{31}P NMR spectroscopies (IR (in CH_2Cl_2, cm^{-1}): ν(CO) 2044 (vs), 1966 (s), 1919 (s); ^{31}P NMR (in CD_2Cl_2, ppm) δ: 38.68). After 2.5 h under stirring in the dark at room temperature, the reaction was complete, as evidenced by IR spectroscopy, and the solution containing *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)OTf]$ was transferred with a syringe in a round-bottomed flask. Then Me_3SiONa (1 mol/L solution in CH_2Cl_2, 0.152 mmol, molar ratio Re:Me_3SiONa = 1:2) was added at 0 °C, and the resulting solution was stirred under nitrogen at room temperature for 48 h, evaporated to dryness, and the residue extracted with anhydrous pentane to give, after evaporation to dryness of the solvent, *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)OSiMe_3]$ in 75% yield (43.75 mg, 0.058 mmol). IR (in CH_2Cl_2, cm^{-1}): ν(CO) 2014 (vs), 1927 (s), 1873 (s). ^{1}H NMR (in CD_2Cl_2, ppm) δ: –0.61 (s, 9H, $OSiMe_3$), 2.43 (m, 2H, CH_2), 3.04 (m, 2H, CH_2), 7.21–7.83 (m, 20H, $2PPh_2$). ^{31}P NMR (in CD_2Cl_2, ppm) δ: 31.36. ^{29}Si NMR (in CD_2Cl_2, ppm) δ: 6.05. Mass spectrometry (EI, *m/e*): 758 (M = Molecular ion peak), 730 [M – CO], 702 [M – 2CO], 674 [M – 3CO]. Elemental anal. calcd.: C 50.71, H 4.35; found: C 50.32, H 4.30.

Reactivity of *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)OSiMe_3]$

Addition, at room temperature, of a drop of aq. HCl to *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)OSiMe_3]$ (4 mg) dissolved in CH_2Cl_2 (5 mL) led to the immediate formation of *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)Cl]$ as confirmed by IR and ^{31}P NMR spectroscopies. On the contrary, no reaction occurred upon stirring a CH_2Cl_2 solution of *fac*-$[Re(CO)_3(Ph_2PCH_2CH_2PPh_2)OSiMe_3]$ in the presence of a few drops of water for ca. 48 h at room temperature.

Reactivity of *cis*-$[Re(CO)_4(PPh_3)OTf]$ with Me_3SiONa

Addition of AgOTf (20.6 mg, 0.084 mmol) to a solution of *cis*-$[Re(CO)_4(PPh_3)Cl]$ (19) (40 mg, 0.067 mmol; IR (in CH_2Cl_2, cm^{-1}): ν(CO) 2107 (m), 2005 (vs), 1947 (s); ^{31}P NMR (in CD_2Cl_2, ppm) δ: 4.28) in anhydr. CH_2Cl_2 (8 mL), at room temperature, led to the precipitation of AgCl and the formation of *cis*-$[Re(CO)_4(PPh_3)OTf]$ as confirmed by IR and ^{31}P NMR spectroscopies (IR (in CH_2Cl_2, cm^{-1}): ν(CO) 2117 (m), 2016 (vs), 1961 (s); ^{31}P NMR (in CD_2Cl_2, ppm) δ: 11.60). After 2.5 h under stirring in the dark at room temperature, the reaction was complete, as evidenced by IR spectroscopy, and the solution containing *cis*-$[Re(CO)_4(PPh_3)OTf]$ was filtered on Celite under nitrogen. Then Me_3SiONa (1 mol/L solution in CH_2Cl_2, 0.067 mL, 0.067 mmol, molar ratio Re:Me_3SiONa = 1:1) was added, leading to the precipitation of some product. After 1.5 h, evaporation of the solvent afforded a residue that contained $Na[Re_2(CO)_6(\mu\text{-}OSiMe_3)_3]$ and free PPh_3 as evidenced by ^{29}Si NMR (signal at δ 0.59 ppm) and ^{31}P NMR (signal at δ –4.91 ppm) spectroscopy (in CD_3CN).

Formation of $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)(\mu\text{-}OSiMe_3)_2]$

Addition of $[NEt_4]Cl$ (stoichiometric amount) to a solution of $Na[Re_2(CO)_6(\mu\text{-}OSiMe_3)_3]$ in acetonitrile, followed by evaporation of the solvent to dryness, extraction of the residue with CH_2Cl_2 and filtration, afforded a solution of $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)(\mu\text{-}OSiMe_3)_2]$ because of the presence of traces of water. Addition of pentane to this solution led, at –20 °C, to the formation of colorless crystals of $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)(\mu\text{-}OSiMe_3)_2]$ suitable for X-ray structure determination. IR (in CH_2Cl_2, cm^{-1}): ν(CO) 1995 (s, br), 1876 (vs, br). ^{1}H NMR (in CD_3CN, ppm) δ: 0.22 (s, 18H, $2Si(CH_3)_3$), 1.22 (t, *J* = 7.2 Hz, 12H, $4NCH_2CH_3$), 1.76 (s, 1H, OH), 3.18 (q, *J* = 7.2 Hz, 8H, $4NCH_2CH_3$). ^{29}Si

NMR (in CD_3CN, ppm) δ: 16.61; the ^{29}Si NMR signal of Me_3SiONa in CD_3CN lies at –13.09 ppm.

X-ray crystallography

A suitable colorless needle of $[NEt_4][Re_2(CO)_6(\mu\text{-OH})(\mu\text{-OSiMe}_3)_2]$, obtained by slow crystallization of a CH_2Cl_2–pentane solution of $[NEt_4][Re_2(CO)_6(\mu\text{-OSiMe}_3)_3]$, was mounted in air on the glass fiber tip of a goniometer head. Data collection was performed on a Bruker Axs SMART CCD area-detector equipped with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å), by applying the ω-scan method. 2500 frames were acquired with $\Delta\omega = 0.3°$, t = 25 s per frame, and sample–detector distance fixed at 3.45 cm. Data reduction within the hemisphere with $2\theta < 61.2°$ afforded 26 963 reflections of which 2537 were unique. An empirical absorption correction was applied (20). The structure was solved by direct methods (21) and refined with full-matrix least-squares calculations on F^2 (22). Anisotropic temperature factors were assigned to all atoms but: (*i*) hydrogens, riding their parent atoms with an isotropic temperature factor arbitrarily chosen as 1.2 times that of the parent itself; and (*ii*) the nitrogen and carbon atoms of the tetraethylammonium cation. To properly describe the heavily disordered tetraethylammonium cation: (*i*) some of its carbon atoms have been "splitted" over two positions, with a fixed site occupation factor of 0.5; (*ii*) soft restraints have been imposed on its C—C bond distances (1.55 Å); (*iii*) all its carbon atoms have been given a common isotropic displacement parameter; and (*iv*) hydrogen atoms have not been assigned.[4]

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[4] Supplementary data for this article are available on the Web site or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. DUD 4000. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 256488 contains the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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