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Articles

Surface Organometallic Chemistry: A New Synthesis of $[Re_2(CO)_6(\mu\text{-}OH)_3]^-$ from $[Re(CO)_3OH]_4$ Supported on a Silica Surface Added with K_2CO_3; Evidence of Its Thermal Binding to the Surface via Re−O−Si≡ Bonds Confirmed by the Synthesis of the Molecular Models $[Re_2(CO)_6(\mu\text{-}OH)_x(\mu\text{-}OSiEt_3)_{3-x}]^-$ ($x = 0, 1,$ or 2) by Reaction of $[Re_2(CO)_6(\mu\text{-}OH)_3]^-$ with Et_3SiOH

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Reaction at 25 °C of $[Re(CO)_3OH]_4$ on a silica surface added with K_2CO_3 affords physisorbed $K[Re_2(CO)_6(\mu\text{-}OH)_3]$ which is anchored to the silica surface by further treatment at 200 °C. This novel surface chemistry is easily mimicked in solution: reaction of $[Re(CO)_3OH]_4$ with K_2CO_3 or $[NEt_4]OH$ in water represents a new convenient synthesis for $[Re_2(CO)_6(\mu\text{-}OH)_3]^-$ which can be converted into the molecular models $[Re_2(CO)_6(\mu\text{-}OH)_x(\mu\text{-}OSiEt_3)_{3-x}]^-$ ($x = 0$, 1, or 2) by reaction with Et_3SiOH under well-defined conditions.

Introduction

Transition metal carbonyls supported on inorganic oxides are interesting hybrid materials. They may provide a way to heterogenize homogeneous catalytic systems and they are convenient precursors of highly dispersed metals often with unusual catalytic properties.[1] Due to the relevance of rhenium or rhenium−platinum catalysts supported on some inorganic oxides[2] for reactions such as olefin metathesis,[2a] olefin epoxidation,[2b] hydrogenation,[2c] dehydrogenation,[2d] and petroleum refining,[2e] efforts have been devoted to preparing and characterizing rhenium carbonyl species supported on MgO,[3] Al_2O_3,[4] ZrO_2,[5] and TiO_2[5,6] which can be the source of specific heterogeneous catalysts. For example, several methods have been used to prepare on the basic surface of MgO the so-called "rhenium subcarbonyls" proposed to be surface-anchored species such as $Re(CO)_3(HOMg)_x(OMg)_{3-x}$ ($x = 0−3$) on the basis of extended X-ray absorption fine structure and infrared, ultraviolet−visible, Raman, and inelastic electron tunneling spectroscopies.[3] These surface-anchored species may have

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some analogy with molecular species such as $[Re_2(CO)_6(\mu\text{-}OR)_3]^-$ ($R = CH_3$ or Ph).[7] Similar surface species such as $Re(CO)_3(HOAl)_2(OAl)$ were prepared by adsorption on $\gamma\text{-}Al_2O_3$ of $[Re(CO)_5Br]$[4b] or $[H_3Re_3(CO)_{12}]$[4c] followed by thermal treatment. Because of the lower basicity of $\gamma\text{-}Al_2O_3$ with respect to MgO, the oxidative fragmentation of $[H_3Re_3(CO)_{12}]$ deposited on $\gamma\text{-}Al_2O_3$ gives a mixture of alumina-anchored “subcarbonyls” $Re(CO)_3(HOAl)_2(OAl)$ and physisorbed $[Re(CO)_3OH]_4$.[4d] The nature of these surface anchored species, characterized on the basis of spectroscopic evidence, has never been supported by the synthesis of related molecular models. Less work has been done on a less reactive and slightly acidic support such as SiO_2. While stirring of $[Re(CO)_3OH]_4$ with MgO in diethyl ether affords the surface-anchored “rhenium subcarbonyls”,[3e] simple physisorption of $[Re(CO)_3OH]_4$ occurs on the silica surface without any strong interaction with the surface.[8] Recently we reported that the simple addition of a relatively weak base such as an alkali carbonate can give strong basic properties to the silica surface, therefore allowing the easy and selective synthesis of physisorbed anionic ruthenium,[9] osmium,[10] and iridium[11] carbonyl clusters.

These findings prompted us to investigate the formation of silica-supported anionic Re(I) carbonyl species, by reaction of $[Re(CO)_3OH]_4$ with a silica surface added with K_2CO_3. Here we present the results of this investigation together with the synthesis and spectroscopic characterization of new complexes of the type $[Re_2(CO)_6(\mu\text{-}OH)_x(\mu\text{-}OSiEt_3)_{3-x}]^-$ ($x = 0$, 1, or 2), the first molecular models of surface-anchored anionic carbonyl species. These complexes are also of current interest due to the preparation and investigation of various carbonyl Re(I) alkoxide and hydroxide complexes[12] with a potential role as intermediates of some catalytic reactions.[13]

Results and Discussion

Reaction of $[Re(CO)_3OH]_4$ with a Silica Surface Added with K_2CO_3. When a slurry of SiO_2, $[Re(CO)_3OH]_4$ (2 wt % of Re with respect to SiO_2), K_2CO_3 (molar ratio K_2CO_3:Re = 10:1; 15 wt % of K_2CO_3 with respect to SiO_2), and water is stirred at room temperature for 6 h and evaporated to dryness, the final powder shows carbonyl bands at 2007 (s) and 1890 (vs, br) cm^{-1} in Nujol mull, different from those characteristic of silica-supported $[Re(CO)_3OH]_4$ ($\nu_{CO} = 2028$ (s) and 1925 (vs, br) cm^{-1})[8b] but similar to those reported for surface “rhenium subcarbonyls” such as $Re(CO)_3(HOMg)_x(OMg)_{3-x}$ (as wafer, using an hydroxylated MgO surface and $[Re_2(CO)_{10}]$ as precursor, $\nu_{CO} = 2014$ (s), 1894 (vs, br) cm^{-1}).[3c] The same surface species is obtained by stirring for 24 h a solution of $[Re(CO)_3OH]_4$ in dichloromethane with a silica added with K_2CO_3 (15 wt % of K_2CO_3 with respect to SiO_2).

This latter surface rhenium carbonyl species was identified as the anionic rhenium complex $[Re_2(CO)_6(\mu\text{-}OH)_3]^-$ [12d,g,14] simply physisorbed on silica, because it can be quantitatively recovered, as K^+ salt, by easy extraction with anhydrous acetonitrile which is polar enough to solubilize the potassium salt of this anion. Such a salt cannot be extracted with dichloromethane where it is insoluble, in contrast to the starting neutral complex.[8] However, the anion can be extracted with a solution of $[NEt_4]Cl$ in dichloromethane, affording $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_3]$ (in CH_2Cl_2, $\nu_{CO} = 2007$ (s), 1889 (vs) cm^{-1}), a salt soluble enough in dichloromethane. After extraction, no carbonyl species remains on the silica surface as confirmed by infrared spectroscopy. This body of observations confirms that the anionic complex is simply physisorbed and not anchored to the silica surface via $Re{-}OSi{\equiv}$ bonds.[15]

In a few cases complexes or clusters bearing a metal$-$OH bond are reported to react more or less easily with silanol groups of the silica surface to give a metal$-OSi{\equiv}$ bond. For example, stirring a THF solution of $[Cp^*Ir(OH)(Ph)(PMe_3)]$ with SiO_2 at room temperature affords $[Cp^*Ir(OSi{\equiv})(Ph)(PMe_3)]$,[16] while thermal treatment of silica-supported $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ affords silica-anchored $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSi{\equiv})]$.[17] Although negatively charged, also the anionic physisorbed species $[Re_2(CO)_6(\mu\text{-}OH)_3]^-$ can be anchored to the silica surface via thermal condensation of hydroxide ligands with surface silanols, a reaction in accord with exchange reactions, recently reported to occur in solution and studied by electrospray mass spectrometry, involving the bridging hydroxide ligands of this anionic complex with oxygen, sulfur, selenium, phosphorus, and nitrogen donor ligands.[12f,h,18]

Thus, when silica-physisorbed $K[Re_2(CO)_6(\mu\text{-}OH)_3]$, prepared as described above, is heated for 24 h either at 100 °C or at 200 °C under N_2 (1 atm) in the presence of K_2CO_3 (molar ratio K_2CO_3:Re = 10:1) a reaction occurs as evidenced by the shift of the infrared bands from 2007 (s) and 1890 (vs, br) cm^{-1} to 2006 (s) and 1868 (vs, br) cm^{-1}, respectively. Evidence for the condensation

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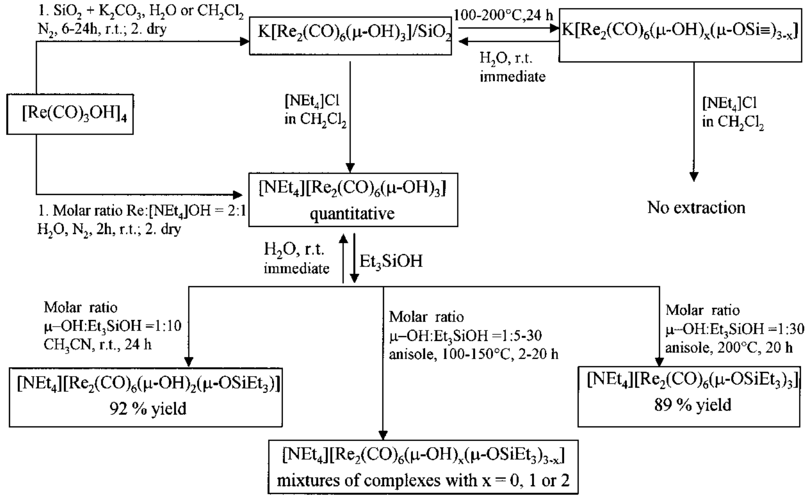
Scheme 1



of at least one bridging hydroxide ligand with a surface silanol via a covalent binding to the surface[15] is given by the lack of extraction with either anhydrous acetonitrile or an anhydrous solution of $[NEt_4]Cl$ in dichloromethane while addition of water to the silica powder regenerates $K[Re_2(CO)_6(\mu\text{-}OH)_3]$ by an easy hydrolysis of surface Re−OSi≡ bonds,[8b] as evidenced by infrared spectroscopy and confirmed by its easy extraction with anhydrous acetonitrile from the silica surface.

Reaction of $[Re(CO)_3OH]_4$ with K_2CO_3 or $[NEt_4]OH$ in Water and Synthesis of the New Model Complexes $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_x(\mu\text{-}OSiEt_3)_{3-x}]$ (x = 0, 1, or 2). Recently we have shown that, in some cases, reactions occurring on the silica surface can take place in a polar solvent with OH groups mimicking surface silanols.[19] Therefore, when a water solution of $[Re(CO)_3OH]_4$ and K_2CO_3 (molar ratio K_2CO_3:Re = 10:1) is stirred at room temperature for 10 min $[Re_2(CO)_6(\mu\text{-}OH)_3]^-$ is formed and can be easily extracted with a dichloromethane solution of $[NEt_4]Cl$. This anionic complex can be directly obtained by reaction in water of $[Re(CO)_3OH]_4$ with $[NEt_4]OH$ (molar ratio Re:OH = 2:1) which gives pure $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_3]$ in quantitative yield. This synthesis, prompted by the reactivity observed on the silica surface, represents a new convenient method for the preparation of this complex, which received much attention recently due to its potential application in radioimmunotherapy and protein labeling[12d−g,20] and which was previously prepared by more complex reactions such as reaction of $[Re(CO)_5Br]$ with KOH in water under reflux[14] or with NaOH in a mixture of THF and water at room temperature[12g] or reaction of an aqueous solution of $AgNO_3$ with $[ReBr_3(CO)_3]^{2-}$ followed by filtration of AgBr and further reaction with NaOH (molar ratio Re:OH = 1:3).[12d]

Mimicking the reactivity of the silica surface, it was reported by some of us that the OH ligand of the complex $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OH)]$ exchanges quite easily with silanol molecules such as R_3SiOH and $R_2Si(OH)_2$ to afford the related metal silanolates.[21] This seems to be a quite general reaction.[22] In fact, by reaction of $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_3]$ with excess triethylsilanol under anhydrous conditions, the silanolate species $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_x(\mu\text{-}OSiEt_3)_{3-x}]$ (x = 0, 1, or 2) are obtained. These complexes can be isolated and identified (when x = 0 or 2) on the basis of elemental analysis, infrared, ^1H NMR, ^{29}Si NMR, and mass spectra (see Experimental Section).

Table 1. Formation of $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_x(\mu\text{-}OSiEt_3)_{3-x}]$ (x = 0, 1, or 2) by Reaction of $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_3]$ with Et_3SiOH in Anisole

			yield, %[a]		
molar ratio μ-OH:Et_3SiOH	T, °C	t, h	$[Re_2(CO)_6(OH)_2(OSiEt_3)]^-$	$[Re_2(CO)_6(OH)(OSiEt_3)_2]^-$	$[Re_2(CO)_6(OSiEt_3)_3]^-$
1:10[b]	25	24	100 (92)[c]	0	0
1:5	100	48	46	47	7
1:30	100	20	37	47	16
1:10	150	4	48	43	9
1:30	150	2	14	60	26
1:10	200	20[d]	0	23	77
1:30	200	20	0	0	100 (89)[c]

[a] ^{29}Si NMR yield. [b] Reaction carried out in CH_3CN. [c] Isolated yield. [d] Yields are similar after 60 h.

Thus, treatment of an anhydrous acetonitrile solution of $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_3]$ with an excess of triethylsilanol (molar ratio μ-OH:Et_3SiOH = 1:10), at room temperature for 24 h, gives $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_2(\mu\text{-}OSiEt_3)]$ (isolated yield = 92%; in $CHCl_3$, ν_{CO} = 2005 (w), 1995 (s), 1881 (vs) cm^{-1}) (Scheme 1). Various attempts to prepare pure $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)(\mu\text{-}OSiEt_3)_2]$ failed, due to the low reactivity of $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_2(\mu\text{-}OSiEt_3)]$ under mild conditions and the fast formation of $[NEt_4][Re_2(CO)_6(\mu\text{-}OSiEt_3)_3]$ under more drastic conditions. By working in anisole at 100−150 °C for 2−20 h (molar ratio μ-OH:Et_3SiOH = 1:5−30), mixtures of $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_2(\mu\text{-}OSiEt_3)]$, $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)(\mu\text{-}OSiEt_3)_2]$, and $[NEt_4][Re_2(CO)_6(\mu\text{-}OSiEt_3)_3]$ are obtained (Table 1), although an increase of the temperature, reaction time, or amount of Et_3SiOH favors the formation of $[NEt_4][Re_2(CO)_6(\mu\text{-}OSiEt_3)_3]$. When the reaction is carried out at 150 °C for 2 h (molar ratio μ-OH:Et_3SiOH = 1:30), fair yields of [NEt$_4$][Re$_2$-

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$(CO)_6(\mu\text{-}OH)(\mu\text{-}OSiEt_3)_2]$ (60%) can be reached but always along with the parallel presence of the singly and triply exchanged complexes (14% and 26% yields, respectively) as evidenced by ^{29}Si NMR spectroscopy. The separation of these anionic complexes cannot be easily accomplished due to the very easy hydrolysis of the Re−O−Si bonds. An increase of the temperature to 200 °C allows the complete substitution of bridging hydroxide ligands in 20 h, $[NEt_4][Re_2(CO)_6(\mu\text{-}OSiEt_3)_3]$ (in $CHCl_3$, $\nu_{CO} = 2006$ (w), 1994 (s), 1879 (vs) cm^{-1}) being isolated in 89% yield. All these silanolate complexes are immediately converted back to $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_3]$ by addition of a few drops of water at room temperature, as confirmed by ^{1}H NMR and ^{29}Si NMR spectroscopies, mimicking the easy hydrolysis of the covalent Re−O−Si≡ bonding of the silica-anchored anionic rhenium carbonyl species described above and confirming that the surface-anchored species is still a dimeric anion.

Conclusion

The facile transformation of $[Re(CO)_3OH]_4$ on the silica surface added with K_2CO_3 into physisorbed $K[Re_2(CO)_6(\mu\text{-}OH)_3]$ is another example of surface-mediated syntheses of anionic metal carbonyl species by this kind of basic surface while the easy reversible covalent binding of this latter metal carbonyl anion to the surface via Re−O−Si≡ bonds by thermal condensation with surface silanol groups is the first clear example of an anionic metal carbonyl species covalently anchored to a slightly acidic inorganic oxide such as silica which is the support most extensively studied in the area of surface organometallic chemistry. This latter result confirms that the reaction of an OH ligand linked to a metal is an easy way to bind covalently a metal complex, or probably even a partially oxidized metal particle surface, to the surface of an inorganic oxide carrying slightly acidic OH groups on its surface such as silica.

Actually we cannot produce evidence for the structure of this anion covalently bound to the silica surface which could involve one, two, or even three Re−O−Si≡ surface bonds, as suggested by the stepwise reaction with excess Et_3SiOH to obtain the molecular models $[Re_2(CO)_6(\mu\text{-}OH)_x(\mu\text{-}OSiEt_3)_{3-x}]^-$ ($x = 0$, 1, or 2). Since detailed spectroscopic properties of these models (for instance ^{29}Si and ^{13}C NMR data or even structures by X-ray diffraction on single crystals) are already known or are underway, we hope in the near future, following the pioneering approach of Ugo, Basset, Markó, Feher, and others,[23] to have enough structural information from the molecular models to be used as references for the characterization of the structure of the covalently bound surface species.

Finally, as in other cases,[19] this novel surface rhenium carbonyl chemistry suggested a new convenient high-yield synthesis in water of the anion $[Re_2(CO)_6(\mu\text{-}OH)_3]^-$ by cleavage of the four μ_3-OH bridges of $[Re(CO)_3OH]_4$ by the OH^- nucleophile. This is an unexpected result because it was reported that very little chemistry has as yet unfolded for this cubane-type complex, due to its perfectly closed structure.[24]

Experimental Section

General Comments. SiO_2 (Aerosil 200 Degussa; 200 m^2/g) was used after treatment in vacuo (10^{-2} Torr) at 25 °C for 3 h. $[Re(CO)_3(OH)]_4$ was prepared according to the literature.[25] The organic solvents were dried over molecular sieves (4 Å) whereas N_2 was dried by flowing over Drierite. Spectral data were obtained by use of the following spectrometers: Bruker-Vector 22 or Jasco FT-IR 420 (IR), Bruker AC-200 or Bruker DRX-300 (^{1}H and ^{29}Si NMR; $SiMe_4$ was used as standard), Varian VG9090 (MS). Elemental analyses were carried out in the analytical laboratory of our department.

Formation of Physisorbed $K[Re_2(CO)_6(\mu\text{-}OH)_3]$ by Reaction of $[Re(CO)_3OH]_4$ Physisorbed on a Silica Surface Added with K_2CO_3. A slurry of SiO_2 (4.86 g), $[Re(CO)_3OH]_4$ (150 mg; 0.131 mmol), K_2CO_3 (724 mg; 5.24 mmol), and water (150 mL) was stirred under N_2 at room temperature for 6 h and evaporated to dryness (at 25 °C and 10^{-2} Torr) affording a white powder. Its infrared spectrum, as Nujol mull, showed the presence of a surface rhenium carbonyl complex (ν(CO) 2007 (s), 1890 (vs, br) cm^{-1}). The same surface species (identified as physisorbed $K[Re_2(CO)_6(\mu\text{-}OH)_3]$, see Results and Discussion) was obtained by stirring for 24 h a solution of $[Re(CO)_3OH]_4$ (150 mg; 0.131 mmol) in CH_2Cl_2 (250 mL) with a powder of K_2CO_3 supported on SiO_2 (prepared by stirring for 2 h K_2CO_3 (724 mg) dissolved in water (150 mL) with SiO_2 (4.86 g) followed by evaporation of the solvent), followed by evaporation of the solvent.

Thermal Treatment of $K[Re_2(CO)_6(\mu\text{-}OH)_3]$ Physisorbed on a Silica Surface Added with K_2CO_3. A sample of $K[Re_2(CO)_6(\mu\text{-}OH)_3]$ physisorbed on a silica surface added with K_2CO_3, prepared as described above, was transferred into a cylindrical Pyrex vessel (diameter 60 mm, length 350 mm) previously described,[26] 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 either 100 or 200 °C. The surface reactivity was monitored by infrared spectroscopy; samples were taken from the glass vessel at room temperature and studied as Nujol mull (see Results and Discussion).

Synthesis of $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_3]$ by Reaction of $[Re(CO)_3OH]_4$ with K_2CO_3 or $[NEt_4]OH$ in Water. When a water solution (50 mL) of $[Re(CO)_3OH]_4$ (80 mg; 0.070 mmol) and K_2CO_3 (386 mg; 2.79 mmol) was stirred at room temperature under N_2 for 10 min, $[Re_2(CO)_6(\mu\text{-}OH)_3]^-$ [12d,g,14] was formed and could be easily extracted with a CH_2Cl_2 solution of $[NEt_4]Cl$. This observation led to direct synthesis with $[NEt_4]OH$.

Aqueous $[NEt_4]OH$ (0.27 mL of a 20 wt % solution in water; 0.366 mmol of $[NEt_4]OH$) was added to a solution of $[Re(CO)_3OH]_4$ (210 mg; 0.183 mmol) in water (60 mL). After stirring for 2 h under N_2, the solution was evaporated to dryness, and the residue was dissolved in CH_2Cl_2. Addition of pentane led to the precipitation of pure $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_3]$ in quantitative yield. The product was characterized by

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elemental analysis (Calcd: C, 23.3; H, 3.20; N, 1.90. Found: C, 23.2; H, 3.30; N, 2.20), infrared spectroscopy (in CH_2Cl_2: ν(CO) 2007 (s), 1889 (vs) cm^{-1}), and ^1H NMR spectroscopy (in acetone-d_6: δ (ppm) $\delta = 1.42$ (t, $J = 7.2$ Hz, 12 H, 4 CH_3), 2.81 (s, 3 H, 3 OH), 3.53 (q, $J = 7.2$ Hz, 8H, 4 CH_2)).

Synthesis of $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_2(\mu\text{-}OSiEt_3)]$. A solution of $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_3]$ (50 mg; 0.069 mmol) and Et_3SiOH (0.32 mL; 2.1 mmol) in anhydrous acetonitrile (1.5 mL) was stirred at room temperature under N_2 in a flask (25 mL) equipped with a closed Pyrex filter funnel (diameter = 30 mm; height = 250 mm) with a fritted disk containing P_2O_5 (2 g; the distance between the reaction solution and the fritted disk is 120 mm).[21] After 24 h, the solution was evaporated to dryness and the residue washed with pentane to give $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_2(\mu\text{-}OSiEt_3)]$ (53 mg; 0.063 mmol; 92% yield) which was characterized by elemental analysis (Calcd: C, 30.80; H, 4.74; N, 1.80. Found: C, 30.35; H, 4.46; N, 1.62), mass spectrometry (in the FAB^- mass spectrum, there is the ion peak corresponding to $[Re_2(CO)_6(\mu\text{-}OH)_2(\mu\text{-}OSiEt_3)]^-$ at $m/e = 705$), infrared spectroscopy (in $CHCl_3$: ν(CO) 2005 (w), 1995 (s), 1881 (vs) cm^{-1}), ^1H NMR (in $CDCl_3$: δ (ppm) = 0.78 (q, $J = 7.7$ Hz, 6 H, 3 $SiCH_2$), 1.04 (t, $J = 7.7$ Hz, 9 H, 3 $SiCH_2CH_3$), 1.25 (s, 2 H, 2 OH), 1.41 (t, $J = 7.2$ Hz, 12 H, 4 NCH_2CH_3), 3.32 (q, $J = 7.2$ Hz, 8H, 4 NCH_2CH_3), and ^{29}Si NMR (in $CDCl_3$: δ (ppm) = 20.88; the ^{29}Si NMR signal of $HOSiEt_3$ in $CDCl_3$ is at 19.0 ppm).

Synthesis of $[NEt_4][Re_2(CO)_6(\mu\text{-}OSiEt_3)_3]$. A solution of $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_3]$ (50 mg; 0.069 mmol) and Et_3SiOH (0.96 mL; 6.3 mmol) in anhydrous anisole (3 mL) was prepared under N_2 in the closed reaction vessel[25] (height = 17 cm; diameter = 3 cm) previously described. The bottom of the vessel (about half of the cylinder) was put in an oven and heated at 200 °C. After 20 h, the solution was evaporated to dryness and washed with pentane, to remove minor amounts of $Et_3SiOSiEt_3$ and traces of $Et_3SiOSiEt_2OSiEt_3$ formed at this temperature,[27] affording $[NEt_4][Re_2(CO)_6(\mu\text{-}OSiEt_3)_3]$ (65 mg; 0.061 mmol; 89% yield). The product was characterized by elemental analysis (Calcd: C, 38.09; H, 6.45; N, 1.40. Found: C, 38.39; H, 6.11; N, 1.18), mass spectrometry (in the FAB^- mass spectrum, there is the ion peak corresponding to $[Re_2(CO)_6(\mu\text{-}OSiEt_3)_3]^-$ at $m/e = 933$), infrared spectroscopy (in $CHCl_3$: ν(CO) 2006 (w), 1994 (s), 1879 (vs) cm^{-1}), ^1H NMR (in $CDCl_3$: δ (ppm) = 0.78 (q, $J = 7.2$ Hz, 18 H, 9 $SiCH_2$), 1.03 (t, $J = 7.2$ Hz, 27 H, 9 $SiCH_2CH_3$), 1.38 (t, $J = 7.3$ Hz, 12 H, 4 NCH_2CH_3), 3.24 (q, $J = 7.3$ Hz, 8H, 4 NCH_2CH_3), and ^{29}Si NMR (in $CDCl_3$: δ = 20.29 ppm; the ^{29}Si NMR signal of $HOSiEt_3$ in $CDCl_3$ is at 19.0 ppm).

Formation of Mixtures of $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_x(\mu\text{-}OSiEt_3)_{3-x}]$ (x = 0, 1, or 2). By working in anisole at 100−150 °C for 2−20 h in the presence of a molar ratio μ-OH:Et_3SiOH = 1:5−30, under N_2 in the closed reaction vessel described above for the synthesis of $[NEt_4][Re_2(CO)_6(\mu\text{-}OSiEt_3)_3]$, mixtures of $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)_2(\mu\text{-}OSiEt_3)]$, $[NEt_4][Re_2(CO)_6(\mu\text{-}OH)(\mu\text{-}OSiEt_3)_2]$, and $[NEt_4][Re_2(CO)_6(\mu\text{-}OSiEt_3)_3]$ were obtained (Table 1) as evidenced by ^{29}Si NMR spectroscopy. All attempts to separate the three species formed step by step failed, due to their instability in the presence of even very small amounts of water. The doubly exchanged complex was characterized by mass spectrometry (in the FAB^- mass spectrum, we found the ion peak corresponding to $[Re_2(CO)_6(\mu\text{-}OH)(\mu\text{-}OSiEt_3)_2]^-$ at $m/e = 819$), infrared spectroscopy (in $CHCl_3$: ν(CO) 2005 (w), 1995 (s), 1881 (vs) cm^{-1}), and ^{29}Si NMR spectroscopy (in $CDCl_3$: δ (ppm) = 23.42; the ^{29}Si NMR signal of $HOSiEt_3$ in $CDCl_3$ is at 19.0 ppm).

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