1266 *Organometallics* **1998,** *17,* 1266−1277

Surface Organometallic Chemistry: Understanding the Multistep Process of Silica-Mediated Synthesis of Various Osmium Carbonyl Clusters from Supported α-$[Os(CO)_3Cl_2]_2$

Elena Cariati, Paola Recanati, Dominique Roberto,* and Renato Ugo

Dipartimento di Chimica Inorganica, Metallorganica e Analitica and Centro CNR,
Università di Milano, Via G. Venezian 21, 20133 Milano, Italy

Received July 11, 1997

Reaction of silica-supported α-$[Os(CO)_3Cl_2]_2$ in the presence of alkali-metal carbonates affords reactive surface osmium(II) species. The nature of the latter depends on the basicity given to the silica surface, with K_2CO_3 behaving as a stronger base than Na_2CO_3 when supported on silica. Infrared evidence suggests that with a low basicity (for instance, molar ratio Na_2CO_3:Os = 2:1), surface species such as $[Os(CO)_3(OR)_2]_n$ (R = H, $\mathrm{Si}\!\in$) are initially formed; an increase of the surface basicity (molar ratio (Na_2CO_3 or K_2CO_3):Os = (10−20):1) leads to the formation of probably anionic $\{[Os(CO)_3(OR)_2]_m(OR)\}^-$ (R = H, $\mathrm{Si}\!\in$; $m > 1$) entities up to the less reactive species $[Os(CO)_3(OH)_3]^-$. The high reactivity of these surface species is confirmed by the controlled reduction by CO or H_2 of silica-supported $[Os(CO)_3(OH)_2]_n$ in the presence of alkali-metal carbonates, which leads selectively to either neutral ($[Os_3(CO)_{12}]$, $[H_4Os_4(CO)_{12}]$) or anionic ($[H_3Os_4(CO)_{12}]^-$, $[Os_{10}C(CO)_{24}]^{2-}$) clusters, in accord with results obtained with supported α-$[Os(CO)_3Cl_2]_2$. There is direct and indirect evidence that the aggregation process occurs via silica-anchored $[HOs_3(CO)_{10}(O\mathrm{Si}\!\in)]$ or silica-supported $[HOs_3(CO)_{10}(OH)]$ species, followed by further condensation to $[H_4Os_4(CO)_{12}]$ or $[H_3Os_4(CO)_{12}]^-$ according to the basicity of the surface. The nature and the quantity of added alkali carbonate (Na_2CO_3 or K_2CO_3), together with the temperature, influence the formation of either $[H_3Os_4(CO)_{12}]^-$ or $[H_2Os_4(CO)_{12}]^{2-}$, which can act as intermediates for further condensation to cluster anions of higher nuclearity. In addition to these reaction parameters, the amount of H_2 in the gas phase is also crucial in defining the relative stability and the reactivity of the surface species $[H_3Os_4(CO)_{12}]^-$ and $[H_2Os_4(CO)_{12}]^{2-}$ and their further condensation to specific carbonyl cluster anions.

Introduction

The reductive carbonylation of metal salts or complexes supported on inorganic oxides to achieve the selective synthesis of metal carbonyl complexes or clusters is a new subject of investigation.[1−9] In general, strongly basic surfaces such as magnesium oxide favor the formation of anionic metal carbonyl clusters,[1,4,5] while uncharged carbonyl complexes and clusters are generated on the surface of a rather neutral support such as silica.[2,3,6]

We recently reported that both neutral (i.e. $[Os_3(CO)_{12}]$ and $[H_4Os_4(CO)_{12}]$) and anionic (i.e. $[H_3Os_4(CO)_{12}]^-$, $[H_2Os_4(CO)_{12}]^{2-}$, $[Os_5C(CO)_{14}]^{2-}$ and $[Os_{10}C(CO)_{24}]^{2-}$) clusters can be synthesized in high yields by controlled reduction of silica-supported α-$[Os(CO)_3Cl_2]_2$ or $OsCl_3$ in the presence of specific amounts of alkali-metal carbonates.[7,8] The selectivity of the synthesis is controlled by the choice of the (i) nature and amount of the alkali carbonate (Na_2CO_3 or K_2CO_3) added to the silica surface, (ii) temperature, (iii) reaction time, and (iv) gas-phase composition (CO, H_2, or mixtures of CO and H_2).[8] In particular, the nature of the added alkali carbonate largely governs the selectivity toward the synthesis of different osmium clusters. For instance, under similar reaction conditions, the formation of $[Os_3(CO)_{12}]$ is favored with respect to that of $[H_3Os_4(CO)_{12}]^-$ when Na_2CO_3 is used instead of K_2CO_3.[8] In contrast, the addition of a strong base such as an alkali-metal hydroxide leads to very low reactivity.[7] Although little is known concerning the surface organometallic chemistry involved, it appears that a delicate control of the surface basicity is necessary in order to produce the right reactive osmium carbonyl surface intermediates.

Recently, we briefly reported that the initial process of aggregation can involve surface trimeric osmium

---

[1] Lamb, H. H.; Fung, A. S.; Tooley, P. A.; Puga, J.; Krause, R.; Kelley, M. J.; Gates, B. C. *J. Am. Chem. Soc.* **1989,** *111,* 8367.

[2] Roberto, D.; Psaro, R.; Ugo, R. *Organometallics* **1993**, *12*, 2292.

[3] Roberto, D.; Psaro, R.; Ugo, R. *J. Organomet. Chem.* **1993**, *451*, 123.

[4] Gates, B. C. *J. Mol. Catal.* **1994**, *86*, 95.

[5] Kawi, S.; Xu, Z.; Gates, B. C. *Inorg. Chem.* **1994**, *33*, 503.

[6] Roberto, D.; Psaro, R.; Ugo, R. *J. Mol. Catal.* **1994**, *86*, 109.

[7] Roberto, D.; Cariati, E.; Psaro, R.; Ugo, R. *Organometallics* **1994**, *13*, 734.

[8] Roberto, D.; Cariati, E.; Ugo, R.; Psaro, R. *Inorg. Chem.* **1996**, *35*, 2311.

[9] Roberto, D.; Cariati, E.; Lucenti, E.; Respini, M.; Ugo, R. *Organometallics* **1997**, *16*, 4531.

[10] Cariati, E.; Roberto, D.; Ugo, R. *Gazz. Chim. Ital.* **1996**, *126*, 339.

S0276-7333(97)00590-6 CCC: $15.00

carbonyl clusters.[10] Now, we present a detailed investigation on a series of reactions occurring on the silica surface and on the factors controlling their role in the selectivity of the synthetic processes.

Results and Discussion

1. Characterization of the Silica Surface before and after Addition of Alkali-Metal Carbonates. The silica used in the synthesis of various osmium carbonyl clusters from α-$[Os(CO)_3Cl_2]_2$,[7,8] Aerosil 200, is prepared by burning at high temperatures $SiCl_4$ with H_2 and O_2.[11,12] In this process HCl is formed, which is mostly evacuated from the system.[12] However, the resulting silica shows a pH value (in 4% aqueous dispersion) of 3.6−4.3, which cannot be explained by the acidity of surface silanol groups but which is largely due to some residual HCl (ca. 0.025 wt % HCl with respect to SiO_2, corresponding to ca. 6.8 μmol of HCl/g of SiO_2).[11] This acidity can affect the reactivity of supported species, particularly when one works with low loadings. For example, with a low osmium loading such as 2 wt % Os with respect to SiO_2, this surface acidity is enough to convert appreciable amounts (up to 27%) of $[H_3Os_4(CO)_{12}]^-$ to $[H_4Os_4(CO)_{12}]$. Impregnation of silica with an acetonitrile solution of $K[H_3Os_4(CO)_{12}]$, followed by evaporation of the solvent, affords mixtures of $[H_3Os_4(CO)_{12}]^-$ and $[H_4Os_4(CO)_{12}]$. Obviously, in work with a silica surface added with an adequate amount of alkali carbonate (e.g. 2 wt % Os/SiO_2; molar ratio K_2CO_3:Os = 10:1 corresponding to 1.0 mmol of K_2CO_3/g of SiO_2), no protonation of $[H_3Os_4(CO)_{12}]^-$ to $[H_4Os_4(CO)_{12}]$ occurs, surface HCl being neutralized by the large excess of K_2CO_3.

In the silica-mediated synthesis of various osmium carbonyl clusters from α-$[Os(CO)_3Cl_2]_2$ in the presence of Na_2CO_3 or K_2CO_3, a dichloromethane slurry was used for the deposition of both α-$[Os(CO)_3Cl_2]_2$, which is soluble, and the alkali carbonate, which is insoluble in this solvent.[7,8] Therefore, a rather nonhomogeneous dispersion of the alkali carbonate on the silica surface would be expected, particularly at high alkali carbonate loadings, also because the amount of physisorbed water, which could partially dissolve the alkali carbonate, is relatively low (about 1.5 wt % H_2O/SiO_2).[11] The nonhomogeneous dispersion was confirmed by scanning electron microscopy (SEM), from a study of the relative intensity of the peaks corresponding to K and Si in the energy-dispersive spectrum collected at various points of the silica surface added with K_2CO_3 deposited from dichloromethane. With a low K_2CO_3 loading such as 2.90 wt % K_2CO_3/SiO_2 (corresponding to a 2 wt % Os/SiO_2 osmium loading and a 2:1 K_2CO_3:Os molar ratio)[8] the ratio "*peak corresponding to K*"/"*peak corresponding to Si*" varied significantly at various points of the silica surface (e.g. ratios going from almost 0 to 0.04 were observed). Similarly, with a high K_2CO_3 loading such as 14.5 wt % K_2CO_3/SiO_2 (corresponding to a 2 wt % Os/SiO_2 osmium loading and a 10:1 K_2CO_3:Os molar ratio)[8] ratios going from 0.15 to 0.51 were observed. However, as expected, a homogeneous dispersion (same ratio "*peak corresponding to K*"/"*peak corresponding to Si*" at various points of the silica surface for a given K_2CO_3 loading) is obtained by using a water solution instead of a dichloromethane slurry for the deposition of K_2CO_3.[9]

In the Aerosil 200 type of silica, the silica microspheres (primary particles, with an average size of 12 nm)[11] are linked into linear chains, affording a nonporous structure with no interior surface.[12] The deposition of alkali-metal carbonates on these chainlike agglomerations of primary particles[12] could reasonably decrease the specific surface area of silica. To obtain a quantitative analysis of this effect, we determined by the Brunauer−Emmet−Teller method[12] (see Experimental Section) the specific surface area of untreated silica (Aerosil 200), of silica treated with dichloromethane only, and of silica treated with a slurry of dichloromethane and K_2CO_3. We found that the specific surface area of untreated Aerosil 200 (200 ± 5% m^2/g) decreases slightly by treatment with dichloromethane followed by evaporation of the solvent (193 ± 5% m^2/g). Treatment with a slurry of K_2CO_3 in dichloromethane, followed by evaporation of the solvent, causes a much higher diminution of the specific surface area, related to the loading of the alkali carbonate: when the K_2CO_3 loading is increased from 2.90 to 14.5 wt % K_2CO_3/SiO_2, the specific surface area decreases from 180 to 140 m^2/g.

It follows that with our standard experimental methodology of alkali carbonate deposition (addition of a dichloromethane slurry of alkali carbonate to silica, followed by evaporation of the solvent at room temperature)[7,8] the surface basicity is probably not due to an intrinsic property of the modified oxide surface, in the way usually considered in surface science (e.g. formation of surface silanolate anions)[12,13] but more properly is due to a nonhomogeneous supported alkali carbonate phase, physisorbed on the silica surface. Alkali-metal carbonates can react with bulk silica to give a mixture of alkali-metal silicates and CO_2 at very high temperatures (ca. 1300 °C) only.[14] Similarly, the formation of alkali-metal oxide and CO_2 by thermal treatment of Na_2CO_3 or K_2CO_3 occurs at very high temperatures (higher than 1000 °C),[14] although when a water solution of Na_2CO_3 is heated under pressure (e.g. 1000 psig) at temperatures in the range 147−312 °C, some NaOH is formed along with CO_2 by an equilibrium reaction.[16,17] Therefore, some thermal decomposition of the alkali carbonate (Na_2CO_3 or K_2CO_3) to produce the correspondingly more basic alkali-metal hydroxide could occur on the silica surface, due to the presence of physisorbed water (about 1.5 wt % H_2O/SiO_2),[11] but only under the extreme reaction conditions (150−275 °C) which are used for the synthesis of specific osmium carbonyl clusters from α-$[Os(CO)_3Cl_2]_2$.[7,8]

When silica-supported Na_2CO_3 (deposited from a dichloromethane slurry, 11.1 wt % Na_2CO_3/SiO_2, corresponding to a 2 wt % Os/SiO_2 osmium loading and a

---

[11] Technical data from Degussa.

[12] Vansant, E. F.; Van Der Voort, P.; Vrancken, K. C. *Characterization and Chemical Modification of the Silica Surface;* Studies in Surface Science and Catalysis 93; Elsevier: Amsterdam, 1997.

[13] Lamb, H.; Gates, B. C.; Knozinger, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1127.

[14] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Interscience: New York, 1988.

[15] *Handbook of Chemistry and Physics*, Lide, D. R. Ed.; CRC Press: Cleveland, OH, 1990.

[16] Straub, F. G.; Larson, R. F. *Ind. Eng. Chem.* **1932**, *24*, 1416.

[17] Thomas, A. M. *J. Chem. Eng. Data* **1963**, *8*, 51.

10:1 Na_2CO_3:Os molar ratio)[8] is heated under N_2 or CO at 275 °C for 24 h, in the closed reaction vessel used for silica-mediated syntheses,[2,7,8] no CO_2 is generated, as evidenced by gas chromatographic analysis of the gaseous phase at the end of the thermal treatment. Therefore, no thermal decomposition of Na_2CO_3 to NaOH occurs on the silica surface at temperatures up to 275 °C.

In contrast, when silica-supported K_2CO_3 (deposited from a dichloromethane slurry, 14.5 wt % K_2CO_3/SiO_2; corresponding to a 2 wt % Os/SiO_2 osmium loading and a 10:1 K_2CO_3:Os molar ratio)[8] is heated under N_2 at 275 °C for 24 h, in the closed reaction vessel used for silica-mediated syntheses,[2,7,8] CO_2 is generated, as evidenced by gas chromatographic analysis of the gaseous phase at the end of the thermal treatment. The amount of CO_2 evolved (0.27 mmol of CO_2 for 1.73 mmol of K_2CO_3 deposited on the silica surface) corresponds to a 16% conversion of K_2CO_3 to KOH. Under the same conditions but with CO instead of N_2, a higher amount of CO_2 is evolved (0.41 mmol CO_2) along with some H_2, suggesting that silica-supported K_2CO_3 can act as a water-gas shift catalyst. This is an interesting observation, because it has been reported that the addition of potassium to copper-based catalysts can significantly enhance the rate of the water-gas shift reaction.[18] However, when the thermal treatment of silica-supported K_2CO_3 is carried out at 150 °C for 24 h, under CO or N_2, no CO_2 is evolved.

Clearly some decomposition of K_2CO_3 to KOH occurs on the silica surface during the silica-mediated syntheses of various osmium clusters carried out at relatively high temperatures (e.g. 275 °C).[7,8] The formation in situ of easily hydrolyzed surface $KOSi\lessdot$ groups is unlikely due to the presence of water, initially physisorbed on the silica surface, which cannot be thermally removed from the system since the controlled reductive carbonylations of α-$[Os(CO)_3Cl_2]_2$ are carried out in a closed reaction vessel.[7,8] These results can explain the much higher basicity reached by starting from K_2CO_3 rather than from Na_2CO_3 on the silica surface at relatively high temperatures (see later). In any case a different surface basicity is observed already at relatively low temperatures, probably due to a stronger ion-pair interaction of CO_3^{2-} with Na^+ than with K^+ cations due to an unexpected low solvation by the silica surface.[7]

2. Evidence of Different Basicities of K_2CO_3 and Na_2CO_3 when Supported on Silica and of the Role of "the Method of Alkali-Metal Deposition" in Controlling the Surface Basicity. To obtain a different basicity of silica-supported Na_2CO_3 or K_2CO_3, we used as reference reaction the deprotonation of $[H_4Os_4(CO)_{12}]$ to generate $[H_3Os_4(CO)_{12}]^-$.[19,20]

When a slurry of silica-supported $[H_4Os_4(CO)_{12}]$, K_2CO_3 (molar ratio K_2CO_3: Os = 10:1) and CH_2Cl_2 is stirred at room temperature for 3 days and then evaporated to dryness, some deprotonation to $[H_3Os_4(CO)_{12}]^-$ occurs, as shown by extraction of silica with CH_3CN, which affords a mixture of $[H_4Os_4(CO)_{12}]$ and $K[H_3Os_4(CO)_{12}]$. When the same silica is heated for 3 h under CO at 150 °C, the deprotonation is complete; extraction affords only $K[H_3Os_4(CO)_{12}]$. On the other hand, when a slurry of silica-supported $[H_4Os_4(CO)_{12}]$, Na_2CO_3 (molar ratio Na_2CO_3:Os = 10:1), and CH_2Cl_2 is stirred at room temperature for 3 days, evaporated to dryness, and heated at 150 °C under CO for 24 h, the deprotonation reaction proceeds to a very limited extent. Extraction with CH_2Cl_2 affords $[H_4Os_4(CO)_{12}]$ (92% yield), whereas further extraction with CH_3CN gives some $Na[H_3Os_4(CO)_{12}]$ (8% yield).

Therefore, there is a clear evidence that silica-supported K_2CO_3 behaves as a stronger base than silica-supported Na_2CO_3. The basicity of the former with respect to $[H_4Os_4(CO)_{12}]$ is quite comparable, even with relatively low loadings, to that of the surface of decarbonated MgO.[20] The lower basicity of silica-supported Na_2CO_3 can be due to a lower solvation of the Na^+ cation and therefore to a stronger ion-pair interaction of this cation with the basic CO_3^{2-} anion, as pointed out above. As a matter of fact, this kind of effect is well-established in organic chemistry. For instance, with a base such as alkali-metal *tert*-butoxide, which is poorly solvated in a solvent such as *tert*-butyl alcohol, the potassium salt is much more basic than the sodium salt, due to stronger ion pairing by the latter.[21] Such a suggestion is in agreement with the observation that an increase of the temperature (e.g. up to 150 °C) increases the surface basicity, as expected for a decrease of the amount of physisorbed water, which should solvate a certain amount of the added alkali carbonate. Therefore, a thermal dehydration of the surface would produce more free CO_3^{2-} anions, leading to an increase of the surface basicity. Besides, at relatively high temperatures such as 275 °C, added K_2CO_3 could show a much higher basicity than Na_2CO_3, due to some thermal decomposition to KOH as described above. Obviously, the basicity increases also by increasing the loading of the alkali carbonate, as suggested by our previous studies on the reductive carbonylation of silica-supported osmium(II) carbonyl species.[7,8]

As far as the loading effect is concerned, we have produced SEM evidence that a high alkali carbonate loading leads to a rather nonhomogeneous dispersion on the silica surface when a slurry in CH_2Cl_2 is used for the deposition of Na_2CO_3. Use of a water solution of Na_2CO_3 instead of a CH_2Cl_2 slurry for the impregnation leads to a more homogeneous dispersion of the base and consequently to an increased surface basicity for a given molar ratio of Na_2CO_3 to M (M = Ru, Os).[8,9] The nonhomogeneous dispersion of the alkali carbonate can account for the osmium loading effect reported for the silica-mediated syntheses of $[H_4Os_4(CO)_{12}]$ or $[Os_{10}C(CO)_{24}]^{2-}$ when CH_2Cl_2 is used as solvent for the impregnation of silica.[8] In fact, an increase of the osmium loading (for example, from 2 to 15 wt % Os/SiO_2), and consequently of the loading of Na_2CO_3, favors the formation of $[H_4Os_4(CO)_{12}]$ at the expense of $[Os_{10}C(CO)_{24}]^{2-}$, in agreement with a lower surface basicity due to the low homogeneity of the Na_2CO_3 dispersion on the surface.

---

(18) (a) Millar, G. J.; Rochester, C. H.; Waugh, K. C. *J. Chem. Soc., Faraday Trans. 1* **1992**, *88*, 1477. (b) Millar, G. J.; Rochester, C. H.; Waugh, K. C. *J. Catal.* **1993**, *142*, 263.

(19) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Sheldrick, E. M.; Wong, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1978**, 673.

(20) Lamb, H. H.; Hasselbring, L. C.; Dybowski, C.; Gates, B. C. *J. Mol. Catal.* **1989**, *56*, 36.

(21) Bethell, D.; Cockerill, A. F. *J. Chem. Soc. B* **1966**, 913.

As expected for a higher surface basicity, when K_2CO_3 (molar ratio K_2CO_3:Os = 10:1; 2 wt % Os/SiO_2) is deposited on the silica surface using a water solution, the reductive carbonylation (1 atm of CO, 150 °C, 24 h) of silica-supported α-$[Os(CO)_3Cl_2]_2$ easily affords pure $[H_3Os_4(CO)_{12}]^-$ in quantitative yield.[7] When Na_2CO_3 is used under similar conditions (molar ratio Na_2CO_3:Os = 10:1), after 24 h the infrared spectrum of the resulting silica powder still shows the presence of some unreacted Os(II) carbonyl surface species (ν(CO) in Nujol 2115 (w), 2017 (s), 1931 (m) cm^{-1}). Extraction with CH_2Cl_2 affords $[Os_3(CO)_{12}]$ (30% yield) and traces of $[H_4Os_4(CO)_{12}]$, whereas further extraction with CH_3CN gives $Na[H_3Os_4(CO)_{12}]$ in 13% yield only. However, since the only reaction product is $[Os_3(CO)_{12}]$ when the same amount of Na_2CO_3 is deposited using a CH_2Cl_2 slurry,[8] the formation of some $[H_3Os_4(CO)_{12}]^-$ is in agreement with an increased surface basicity due to a more homogeneous dispersion of the base. Therefore, the basicity of the surface and, consequently, the selectivity are appreciably affected not only by the nature and amount of the alkali carbonate but also by the manner in which the base is deposited on silica. Interestingly, even when the alkali carbonate is deposited from a water solution, K_2CO_3 behaves as a stronger base than Na_2CO_3. Therefore, its higher basicity, when it is deposited on the silica surface using a CH_2Cl_2 slurry, cannot be attributed to a more homogeneous dispersion due to its higher solubility with respect to Na_2CO_3[15] in the layer of physisorbed water.

Table 1. Infrared Spectra in the Carbonyl Region of the Species Formed by Reaction of Silica-Supported Os(II) Carbonyl Compounds with Bases[a]

Os(II) compd	base	molar ratio M:Os (M = Na, K)	ν(CO) (cm^{-1}; in Nujol)
α-$[Os(CO)_3Cl_2]_2$	K_2CO_3	4:1	2124 (m), 2031 (s), 1939 (m)
α-$[Os(CO)_3Cl_2]_2$	K_2CO_3	20:1	2121 (m), 2028 (s), 1932 (m)[b]
α-$[Os(CO)_3Cl_2]_2$	K_2CO_3	40:1	2118 (m), 2025 (s), 1931 (m)
α-$[Os(CO)_3Cl_2]_2$	K_2CO_3	120:1	2113 (vw), 2006 (s), 1903 (s)
α-$[Os(CO)_3Cl_2]_2$	Na_2CO_3	4:1	2125 (m), 2036 (s), 1962 (w)[c]
α-$[Os(CO)_3Cl_2]_2$	Na_2CO_3	20:1	2122 (m), 2029 (s), 1945 (m)[d,e]
α-$[Os(CO)_3Cl_2]_2$	Na_2CO_3	40:1	2119 (m), 2027 (s), 1936 (m)
α-$[Os(CO)_3Cl_2]_2$	KOH	20:1	2006 (s), 1923 (s)
α-$[Os(CO)_3Cl_2]_2$	NaOH	20:1	2007 (s), 1925 (s)
$[Os(CO)_x(OSi\leqslant)_2]_n$ ($x = 2.7$)	K_2CO_3	20:1	2114 (vw), 2014 (s), 1929 (s)
$[Os(CO)_x(OSi\leqslant)_2]_n$ ($x = 2.7$)	Na_2CO_3	2:1	2121 (m), 2038 (s), 1956 (w)
$[Os(CO)_3(OH)_2]_n$	K_2CO_3	20:1	2120 (m), 2024 (s), 1927 (s)[f]
$[Os(CO)_3(OH)_2]_n$	Na_2CO_3	2:1	2126 (m), 2037 (s), 1958 (m)[f]
$[Os(CO)_3(OH)_3]^-$	K_2CO_3	20:1	2113 (w), 2009 (s), 1922 (s)[f]

[a] Conditions: 2 wt % Os with respect to SiO_2; a CH_2Cl_2 slurry is used for the deposition of the base on silica. [b] When an H_2O solution is used for the deposition of the base, ν(CO) bands are at 2115 (w), 2016 (s), and 1924 (s) cm^{-1}. [c] With 15 wt % Os/SiO_2, ν(CO) bands are at 2125 (m), 2035 (s), and 1958 (w) cm^{-1}. [d] With 15 wt % Os/SiO_2, ν(CO) bands are at 2125 (m), 2033 (s), and 1950 (w) cm^{-1}. [e] When an H_2O solution is used for the deposition of the base, ν(CO) bands are at 2118 (w), 2022 (s), and 1936 (s) cm^{-1}. [f] Deposited from an H_2O solution.

Table 2. Infrared Spectra in the Carbonyl Region of Osmium Carbonyl Complexes

Os(II) compd	medium	ν(CO) (cm^{-1})
α-$[Os(CO)_3Cl_2]_2$	$CHCl_3$	2137 (m), 2064(s)
α-$[Os(CO)_3Cl_2]_2/SiO_2$[a]	Nujol	2137 (m), 2048 (s)
β-$[Os(CO)_3Cl_2]_2$	$CHCl_3$	2129 (m), 2048 (s), 2035(s)
β-$[Os(CO)_3Cl_2]_2/SiO_2$[a]	Nujol	2132 (m), 2050 (s), 2040 (s)
$[Os(CO)_3Cl_2(HOSi\leqslant)]/SiO_2$[a]	Nujol	2131 (m), 2043 (s)
$[Os(CO)_x(OSi\leqslant)_2]_n/SiO_2$ ($x = 2.7$)[a,b]	Nujol	2121 (m), 2038 (s), 1956 (w)
$[Os(CO)_3(OH)_2]_n$	KBr	2123 (m), 2024 (vs), 1933 (m)
$[Os(CO)_3(OH)_2]_n/SiO_2$[a]	Nujol	2126 (m), 2039 (s), 1957 (m)
$[Os(CO)_3(OH)_3]^-$ [c]	KBr	2022 (sh), 2005 (s), 1935 (sh), 1905 (s)
	Nujol	2017 (w,sh), 2003 (s), 1932 (vw, sh), 1903 (s)
$[Os(CO)_3(OH)_3]^-/SiO_2$[a,d]	Nujol	2120 (w), 2028 (s), 1940 (m)
$[Os(CO)_3(OH)_3]^-/SiO_2$[d,e]	Nujol	2121 (w), 2018 (s), 1934 (s)

[a] 2 wt % Os with respect to SiO_2. [b] Prepared by treatment of $[HOs_3(CO)_{10}(OSi\leqslant)]$ in air at 200 °C.[16] [c] Prepared by reaction of α-$[Os(CO)_3Cl_2]_2$ with NaOH in water (molar ratio Na:Os = 3:1).[19] [d] Species obtained using a H_2O solution of $[Os(CO)_3(OH)_3]^-$ for the deposition on untreated slightly acidic silica. [e] 30 wt % Os with respect to SiO_2.

3. Nature of the Osmium Species Formed by Reaction of Silica-Supported α-$[Os(CO)_3Cl_2]_2$ or Silica-Bound $[Os(CO)_3Cl_2(HOSi\leqslant)]$ with Alkali-Metal Carbonates. When a slurry of silica, α-$[Os(CO)_3Cl_2]_2$, M_2CO_3 (M = Na, K; molar ratio M:Os = (4−40):1), and CH_2Cl_2 is stirred at room temperature, reactive surface osmium carbonyl species are produced.[8] Similar surface species are obtained by starting from $[Os(CO)_3Cl_2(HOSi\leqslant)]$, formed in situ by reductive carbonylation of silica-supported $OsCl_3$.[2] The infrared spectra of these surface species are characterized by three carbonyl bands (2118−2125 (m), 2025−2036 (s), 1931−1962 (m-vw) cm^{-1}, in Nujol; Table 1), which vary depending on the nature and quantity of the added alkali carbonate. Lower frequencies are observed when K_2CO_3 is used instead of Na_2CO_3 and when the molar ratio M_2CO_3:Os is increased. In addition, for the same type and with the same quantity of alkali carbonate, the infrared bands shift to lower frequencies when a water solution is used instead of a CH_2Cl_2 slurry for the deposition of the base on the silica surface. Therefore, any increase of the surface basicity causes a decrease of the carbonyl stretching frequencies of the surface osmium(II) carbonyl species. Even when the surface basicity is relatively low (for example using a 2:1 molar ratio of Na_2CO_3:Os), these frequencies are lower than those typical of either silica-supported α- or β-$[Os(CO)_3Cl_2]_2$ or silica-bound $[Os(CO)_3Cl_2(HOSi\leqslant)]$ (Table 2) but they are quite similar to those of silica-anchored $[Os(CO)_x(OSi\leqslant)_2]_n$ (x = 2, 3) obtained by treatment of $[HOs_3(CO)_{10}(OSi\leqslant)]$ in air at 200 °C (Table 2).[22] This observation would suggest the removal of chloro ligands from the coordination sphere of osmium to afford new surface species related to $[Os(CO)_x$-

---

(22) (a) Psaro, R.; Ugo, R.; Zanderighi, G. M.; Besson, B.; Smith, A. K., Basset, J. M. *J. Organomet. Chem.* **1981**, *213*, 215. (b) Dossi, C.; Fusi, A.; Psaro, R.; Ugo, R..; Zanoni, R. In *Structure and Reactivity of Surfaces*; Morterra, C., Zecchina, A., Costa, G., Eds.; Elsevier: Amsterdam, 1989; p 375.

$(OSi\leqslant)_2]_n$ ($x = 2, 3$). The new surface species cannot be extracted with nondonor solvents such as CH_2Cl_2 (in contrast with silica-supported α-$[Os(CO)_3Cl_2]_2$)[6] or with donor solvents such as acetone and CH_3CN (in contrast with $[Os(CO)_3Cl_2(HOSi\leqslant)]$).[6] Extraction of the resulting silica powder with H_2O affords the expected amount of free chloride ions, as revealed by titration with $AgNO_3$. Complete removal of the chloro ligands is also supported by the absence of traces of chloro carbonyl compounds among the various products obtained by reductive carbonylation.

The surface-anchored species $[Os(CO)_x(OSi\leqslant)_2]_n$ has an x value of about 2.7, as determined by the temperature programmed decomposition technique,[23] suggesting a mixture of dicarbonyl and tricarbonyl surface species. In agreement with this suggestion, we found that its reaction with HCl(aq) affords both *cis*-$[Os(CO)_2Cl_4]^{2-}$ and *fac*-$[Os(CO)_3Cl_3]^-$. In contrast, the surface species generated by reaction of silica-supported α-$[Os(CO)_3Cl_2]_2$ or $[Os(CO)_3Cl_2(HOSi\leqslant)]$ with alkali-metal carbonates remain tricarbonylosmium(II) species, as confirmed by their reaction with HCl(aq), which affords only *fac*-$[Os(CO)_3Cl_3]^-$.

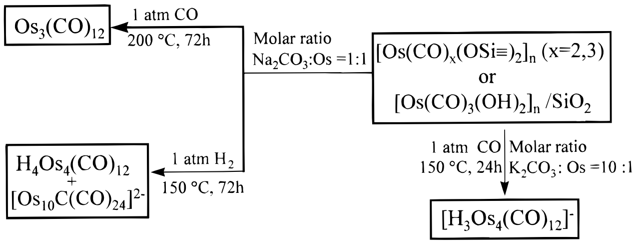
We have evidence, from the behavior of some osmium silanolate carbonyl complexes, that the Os−OSi bond is very weak toward hydrolysis,[24] an observation confirmed by the facile hydrolysis of silica-anchored $[HOs_3(CO)_{10}(OSi\leqslant)]$ to $[HOs_3(CO)_{10}(OH)]$.[10] Therefore, any surface silanolate species generated by reaction of the silanol groups of the silica surface with α-$[Os(CO)_3Cl_2]_2$ should easily hydrolyze to generate, on the surface, the known compound $[Os(CO)_3(OH)_2]_n$,[25] because surface water is present under our experimental conditions. In addition, with high osmium loadings (15 wt % Os/SiO_2) there would not be enough surface silanol groups to convert all α-$[Os(CO)_3Cl_2]_2$ to $[Os(CO)_3(OSi\leqslant)_2]_n$.[2]

Unfortunately, one cannot easily distinguish between $[Os(CO)_3(OSi\leqslant)_2]_n$ and physisorbed $[Os(CO)_3(OH)_2]_n$ on the basis of either infrared spectra, which are very similar (Table 2), or extraction experiments, which must be carried out in the absence of water or of protonic solvents in order to avoid hydrolysis. Unfortunately, silica-supported $[Os(CO)_3(OH)_2]_n$ cannot be extracted from the silica surface by donor solvents such as acetone and acetonitrile.[25]

In summary, addition of an alkali carbonate to silica-supported α-$[Os(CO)_3Cl_2]_2$ produces dehalogenated surface Os(II) carbonyl species such as $[Os(CO)_3(OSi\leqslant)_2]_n$ and physisorbed $[Os(CO)_3(OH)_2]_n$. The formation of (bicarbonato)- or (carbonato)carbonylosmium(II) species can be excluded on the evidence that α-$[Os(CO)_3Cl_2]_2$ dissolved in CH_2Cl_2 reacts slowly in the presence of Na_2CO_3 (molar ratio Na_2CO_3:Os = 4:1), affording only $[Os(CO)_3(OH)_2]_n$.[25]

As shown above, an increase in the surface basicity causes a decrease in the carbonyl stretching frequencies of the surface osmium(II) carbonyl species (Table 1). According to the trends of the infrared spectra of the known compounds $[Os(CO)_3(OH)_2]_n$ and $[Os(CO)_3(OH)_3]^-$,[25] a reasonable explanation would be the progressive formation of surface polymeric anionic species such as $\{[Os(CO)_3(OR)_2]_m(OR)\}^-$ (R = H and/or $Si\leqslant$; $m \geq 1$) when the surface basicity becomes sufficiently high.In fact, when the surface basicity is low (for example using a 2:1 molar ratio of Na_2CO_3 to Os), the infrared spectrum of the surface species is similar to that of $[Os(CO)_x(OSi\leqslant)_2]_n$ ($x = 2.7$) or silica-supported $[Os(CO)_3(OH)_2]_n$, while when a large amount of K_2CO_3 (molar ratio K_2CO_3:Os = 120:1) or a strong base such as an alkali-metal hydroxide (molar ratio (NaOH or KOH):Os = 20:1) is added, the carbonyl stretching frequencies of the surface carbonyl species are similar to those of the anion $[Os(CO)_3(OH)_3]^-$ (Tables 1 and 2).

Scheme 1. Reduction in the Presence of Alkali-Metal Carbonates of $[Os(CO)_x(OSi\leqslant)_2]_n$ (x = 2, 3) and $[Os(CO)_3(OH)_2]_n/SiO_2$



However, when $Na[Os(CO)_3(OH)_3]$ was supported on silica from a freshly prepared water solution, with a high osmium loading (30 wt % Os/SiO_2), the silica powder, after water evaporation, showed carbonyl stretching frequencies at 2121 (w), 2018 (s), and 1934 (s) cm^{-1}, quite low but higher than those of pure $[Os(CO)_3(OH)_3]^-$ (Table 2). With a lower osmium loading (2 wt % Os/SiO_2) the carbonyl frequencies (2120 (w), 2028 (s), and 1940 (m) cm^{-1}) were higher and similar to those of the surface species obtained by reaction of silica-supported α-$[Os(CO)_3Cl_2]_2$ with a large excess of Na_2CO_3 (molar ratio Na_2CO_3:Os = (10−20):1) as a slurry in CH_2Cl_2 (Tables 1 and 2). Probably, $[Os(CO)_3(OH)_3]^-$ is partially neutralized by the acidity of the silica surface (the pH of Aerosil is about 4 due to some residual HCl,[11] as mentioned above). In agreement with a process of partial neutralization by the surface acidity, further addition of K_2CO_3 (molar ratio K_2CO_3:Os = 10:1) caused a decrease of the carbonyl stretching frequencies (2113 (w), 2009 (s), and 1922 (s) cm^{-1}), which finally became similar to those of pure $[Os(CO)_3(OH)_3]^-$.

Interestingly, surface anionic carbonylosmium(II) species are also generated by the addition of alkali-metal carbonates to both $[Os(CO)_x(OSi\leqslant)_2]_n$ ($x = 2.7$), prepared by oxidative degradation of $[HOs_3(CO)_{10}(OSi\leqslant)]$,[22] and silica-supported $[Os(CO)_3(OH)_2]_n$, as suggested by the shift of their carbonyl bands to lower frequencies (Table 1).

4. Reduction in the Presence of Alkali-Metal Carbonates of both Silica-Anchored $[Os(CO)_x(OSi\leqslant)_2]_n$ (x = 2, 3) and Silica-Supported $[Os(CO)_3(OH)_2]_n$. To add some experimental evidence to the suggestion that $[Os(CO)_3(OSi\leqslant)_2]_n$ and/or silica-supported $[Os(CO)_3(OH)_2]_n$ are the active surface species generated in situ, we studied (Scheme 1) the reduction by CO or H_2 of both $[Os(CO)_x(OSi\leqslant)_2]_n$ ($x = 2.7$; 2 wt % Os/SiO_2; prepared by thermal treatment in air of $[HOs_3(CO)_{10}(OSi\leqslant)]$[22]) and silica-supported $[Os(CO)_3(OH)_2]_n$

---

[23] Dossi, C.; Fusi, A.; Psaro, R.; Zanderighi, G. M. *Appl. Catal.* **1989**, *46*, 145.

[24] Riva, L. Doctoral Thesis, Università degli Studi di Milano, Milano, Italy, 1993.

[25] Cariati, E.; Lucenti, E.; Pizzotti, M.; Roberto, D.; Ugo, R. *Organometallics* **1996**, *15*, 4122.

(2 wt % Os/SiO_2; prepared by impregnation of silica with a water solution of $[Os(CO)_3(OH)_2]_n$[25]) in the presence of alkali-metal carbonates (deposited from a CH_2Cl_2 slurry). Also, the reaction of silica-supported $Na[Os(CO)_3(OH)_3]$[25] (2 wt % Os/SiO_2, prepared by impregnation of silica with a water solution of $Na[Os(CO)_3(OH)_3]$) with CO was studied in the presence of alkali-metal carbonates. The results were compared with those reached in the controlled reduction of α-$[Os(CO)_3Cl_2]_2$ supported on silica in the presence of alkali-metal carbonates.[7,8]

4.1. Reactivity with CO. (a) Synthesis of $[Os_3(CO)_{12}]$. It is known that $[Os(CO)_x(OSi\leqslant)_2]_n$ ($x = 2.7$) can be converted into $[Os_3(CO)_{12}]$ by treatment with CO (1 atm) at 200−250 °C, the reaction being faster in the presence of water;[22] equally silica-supported $[Os(CO)_3(OH)_2]_n$ generates $[Os_3(CO)_{12}]$, under 1 atm of CO at 200 °C, the reaction being faster in the presence of added water.

When a small amount of Na_2CO_3 (molar ratio Na_2CO_3:Os = 1:1) is added to $[Os(CO)_x(OSi\leqslant)_2]_n$ or to silica-supported $[Os(CO)_3(OH)_2]_n$, their infrared spectra in the carbonyl region do not change (Tables 1 and 2). Only $[Os_3(CO)_{12}]$ was obtained (91% yield) by treating both powders under CO (1 atm) at 200 °C for 3 days (Scheme 1). Therefore, the presence of a small excess of Na_2CO_3 does not change either the selectivity of the reductive carbonylation or the similar behavior of both $[Os(CO)_x(OSi\leqslant)_2]_n$ and silica-supported $[Os(CO)_3(OH)_2]_n$. Under the same conditions, silica-supported α-$[Os(CO)_3Cl_2]_2$ and $[Os(CO)_3Cl_2(HOSi\leqslant)]$ are also converted into $[Os_3(CO)_{12}]$.[7,8]

(b) Synthesis of $[H_3Os_4(CO)_{12}]^-$. Addition of a large excess of K_2CO_3 to either $[Os(CO)_x(OSi\leqslant)_2]_n$ ($x = 2.7$) or silica-supported $[Os(CO)_3(OH)_2]_n$ (molar ratio K_2CO_3:Os = 10:1) causes a slight shift of their carbonyl bands to lower frequencies (Table 1). Reaction of the resulting powders with CO (1 atm) at 150 °C for 24 h affords only $K[H_3Os_4(CO)_{12}]$ (70−80% yields) in both cases (Scheme 1). Under the same conditions silica-supported α-$[Os(CO)_3Cl_2]_2$ and $[Os(CO)_3Cl_2(HOSi\leqslant)]$ are also converted into $K[H_3Os_4(CO)_{12}]$.[7,8]

(c) Behavior of $[Os(CO)_3(OH)_3]^-$. When silica-supported $Na[Os(CO)_3(OH)_3]$ is treated with CO for 24 h at 150 °C in the presence of a large excess of K_2CO_3 (molar ratio K_2CO_3:Os = 10:1), $[H_3Os_4(CO)_{12}]^-$ is obtained in 48% yield only. After extraction of this cluster with CH_3CN, the resulting silica powder still shows the carbonyl bands characteristic of physisorbed $[Os(CO)_3(OH)_3]^-$. Therefore, the latter anionic species is characterized by a relatively low reactivity toward CO. These observations can account for the low conversion of silica-supported α-$[Os(CO)_3Cl_2]_2$ into $[H_3Os_4(CO)_{12}]^-$ using strong bases such as KOH and NaOH instead of K_2CO_3 (same molar ratio (K or Na):Os).[7] Under these very basic conditions, $[Os(CO)_3(OH)_3]^-$ is probably formed on the silica surface, as evidenced also from the infrared investigation described above.

4.2. Reactivity with H_2. Reaction of $[Os(CO)_x(OSi\leqslant)_2]_n$ ($x = 2.7$) with H_2 (1 atm) at 150 °C in the presence of Na_2CO_3 (molar ratio Na_2CO_3:Os = 1:1) for 3 days affords $[H_4Os_4(CO)_{12}]$ (4% yield) and $Na_2[Os_{10}C(CO)_{24}]$ (3% yield), which can be easily extracted with CH_2Cl_2 and CH_3CN, respectively. The resulting silica is gray and shows infrared bands at 2118 (vw), 2022 (s), and 1957 (s) cm^{-1} (see Experimental Section). Under similar reaction conditions, silica-supported $[Os(CO)_3(OH)_2]_n$ is also converted into $[H_4Os_4(CO)_{12}]$ and $Na_2[Os_{10}C(CO)_{24}]$, but in higher yields (20% and 24% yields, respectively), whereas on the gray silica surface remain the same carbonyl bands as found above, which could be due to an anionic carbonyl Os(II) species of very low reactivity (see Experimental Section).

The above results show clearly that the reaction with H_2 is more sensitive to the nature of the surface carbonyl osmium(II) species than is the reaction with CO. Both silica-supported $[Os(CO)_3(OH)_2]_n$ and the species generated in situ by reaction of silica-supported α-$[Os(CO)_3Cl_2]_2$ with Na_2CO_3 (molar ratio Na_2CO_3:Os = 2:1)[8] are more reactive than $[Os(CO)_x(OSi\leqslant)_2]_n$ ($x = 2.7$). This observation suggests that, under H_2, the presence of three carbonyl ligands in the osmium(II) coordination sphere is a necessary condition to obtain carbonyl clusters in good yields, similar to those reached by starting from α-$[Os(CO)_3Cl_2]_2$.[8]

5. Process of Nucleation of Surface Osmium(II) Carbonyl Species to Metal Carbonyl Clusters. 5.1. Evidence for the Role of $[HOs_3(CO)_{10}(OR)]$ (R = H, Si$\leqslant$) Clusters in the First Step of Nucleation on the Surface. In the reduction of carbonylosmium(II) species, chemisorbed on the surface of MgO, by CO (1 atm) at 275 °C,[1] it was suggested that reductive carbonylation was initiated by nucleophilic attack of adsorbed water on $[Os(CO)_x(OMg)_2]_n$ ($x = 2, 3$) to generate $[HOs(CO)_4]^-$, which could then condense to $[Os_{10}C(CO)_{24}]^{2-}$. It is known that in protic solution (H_2O, 25 °C or H_2O, ethoxyethanol, KOH, 100 °C) the anion $[HOs(CO)_4]^-$ can produce $[HOs_3(CO)_{11}]^-$,[26] which can be converted into $[HOs_3(CO)_{10}(OBu^i)]$ and $[H_3Os_4(CO)_{12}]^-$ by refluxing in 2-methylpropanol.[27] In addition, in the conversion of the silica surface species $[Os(CO)_x(OSi\leqslant)_2]_n$ ($x = 2.7$) into $[Os_3(CO)_{12}]$ by treatment with CO (1 atm) in the presence of water at 250 °C, the aggregation process is reported to occur via $[HOs_3(CO)_{10}(OSi\leqslant)]$.[22]

Therefore, it is conceivable that the reactive Os(II) carbonyl species, generated in situ by reaction of silica-supported α-$[Os(CO)_3Cl_2]_2$ with alkali-metal carbonates, is initially converted to $[HOs(CO)_4]^-$. As suggested in the case of the MgO surface, cluster growth could result from redox condensation of this anion with unreacted $[Os(CO)_3(OR)_2]_n$ (R = H and/or Si$\leqslant$), also by analogy with the suggested condensation of $[Rh(CO)_4]^-$ and $[Rh(CO)_2(OAl)(HOAl)]$ to give $[Rh_6(CO)_{16}]$ on the surface of Al_2O_3.[28] The condensation product would be the cluster $[HOs_3(CO)_{10}(OR)]$ (R = H and/or Si$\leqslant$) which is known to give, by further reaction, various neutral or anionic osmium carbonyl clusters.[10,29] The behavior of $[HOs(CO)_4]^-$ in protic solution[26] cannot exclude the intermediate formation in this condensation process of $[HOs_3(CO)_{11}]^-$, especially in the presence of a high surface basicity, and also because there is clear evidence that

---

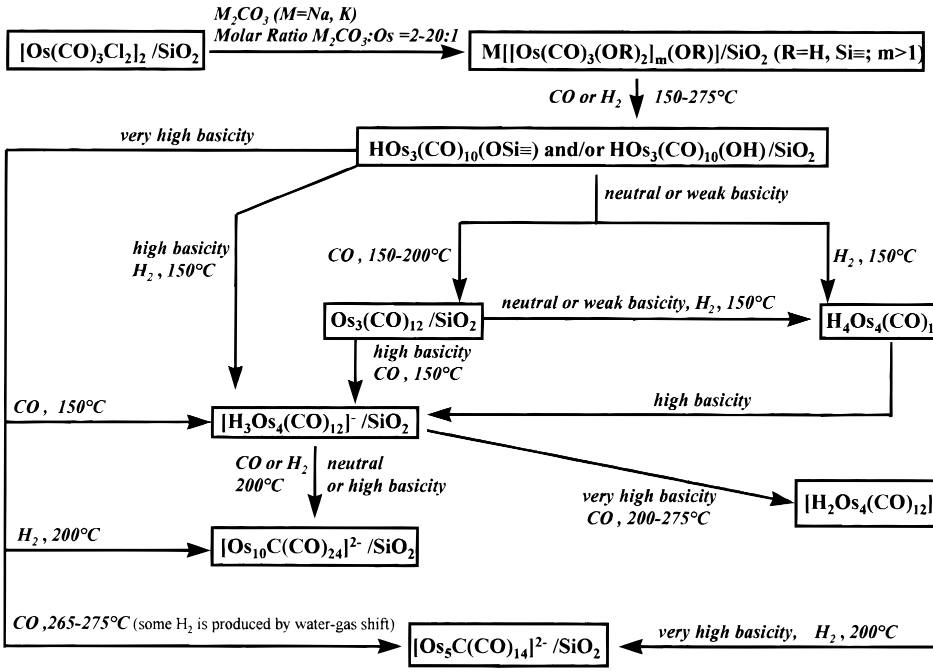
(26) Bricker, J. C.; Bhattacharyya, N.; Shore, S. G. *Organometallics* **1984**, *3*, 201.

(27) Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Vargas, M. D.; Braga, D.; Henrick, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1984**, 2151.

(28) Basset, J. M.; Theolier, A.; Commereuc, D.; Chauvin, Y. *J. Organomet. Chem.* **1985**, *279*, 147.

(29) Roberto, D.; Pizzotti, M.; Ugo, R. *Gazz. Chim. Ital.* **1995**, *125*, 133.

Scheme 2. Process of Nucleation of Surface Osmium(II) Carbonyl Species to Metal Carbonyl Clusters



$[HRu_3(CO)_{11}]^-$ is an intermediate in the silica-mediated synthesis of various ruthenium carbonyl clusters from $RuCl_3$ in the presence of alkali-metal carbonates.[9] However, any $[HOs_3(CO)_{11}]^-$ would be rapidly converted to $[HOs_3(CO)_{10}(OR)]$ (R = H and/or Si<) on the silica surface, because when a red dichloromethane solution of $[PPN][HOs_3(CO)_{11}]$ is stirred with silica (2 wt % Os/SiO_2) at room temperature, the solution and the silica powder immediately turn yellow due to the formation of both $[HOs_3(CO)_{10}(OH)]$ (41% yield) and $[HOs_3(CO)_{10}(OSi<)]$ (see Experimental Section). This conversion is slower (ca. 10 h) in the presence of K_2CO_3 (molar ratio K_2CO_3:Os = 10:1). Unfortunately, the facile equilibrium between $[HOs_3(CO)_{10}(OSi<)]$ and $[HOs_3(CO)_{10}(OH)]$ on the silica surface[10] does not allow us to discriminate between them as the active intermediate to generate clusters of higher nuclearity. In any case, both species are converted, with similar selectivities, to $[Os_3(CO)_{12}]$, $[H_4Os_4(CO)_{12}]$, $[H_3Os_4(CO)_{12}]^-$, $[Os_5C(CO)_{14}]^{2-}$, and $[Os_{10}C(CO)_{24}]^{2-}$ by reduction with CO or H_2 under specific conditions in the presence of alkali-metal carbonates,[10] indirect evidence that $[HOs_3(CO)_{10}(OSi<)]$ or physisorbed $[HOs_3(CO)_{10}(OH)]$ or both could act as intermediates in the silica-mediated synthesis of various osmium carbonyl clusters by starting from α-$[Os(CO)_3Cl_2]_2$ in the presence of alkali-metal carbonates, as suggested also by the detection of traces of both trimeric clusters during the silica-mediated syntheses of $[Os_3(CO)_{12}]$ and $[H_3Os_4(CO)_{12}]^-$.[8]

In addition, when the reaction of silica-supported α-$[Os(CO)_3Cl_2]_2$ is carried out with CO (1 atm) for 24 h under milder conditions (100 °C instead of 150 °C) in the presence of K_2CO_3 (molar ratio K_2CO_3:Os = 10:1), a fair amount of $[HOs_3(CO)_{10}(OH)]$ (15% yield) is obtained together with some $K[H_3Os_4(CO)_{12}]$ (9% yield).

The involvement of $[HOs_3(CO)_{10}(OR)]$ (R = H, Si<) species as the first step of aggregation of the Os(II) carbonyl surface species, generated in situ by addition of alkali-metal carbonates, could be related to an aggregation process on some specific silanol groups of the silica surface, thus implicating the nature and topology of the surface sites as the origin of the selective control of the synthesis of various carbonyl osmium clusters.[7,8]

5.2. Physisorbed $[H_3Os_4(CO)_{12}]^-$ and $[H_2Os_4(CO)_{12}]^{2-}$ as Key Intermediates in the Further Condensation to Higher Nuclearity Clusters. It is known that, at 150−200 °C in the absence or in the presence of minor amounts of Na_2CO_3 (molar ratio Na_2CO_3:Os = 2:1), carbonylation of either supported $[HOs_3(CO)_{10}(OH)]$ or $[HOs_3(CO)_{10}(OSi<)]$ gives $[Os_3(CO)_{12}]$, while reaction with H_2 affords $[H_4Os_4(CO)_{12}]$ (Scheme 2).[10] However when the surface basicity is increased by using K_2CO_3 in large amounts (molar ratio K_2CO_3:Os = 10:1) at 150 °C, the product of carbonylation is $[H_3Os_4(CO)_{12}]^-$.[10] In solution, anionic hydrido carbonyl osmium clusters are obtained from $[Os_3(CO)_{12}]$ under very basic conditions (KOH in *n*-butyl alcohol).[27] Probably when the basicity of the silica surface is high enough, the cluster $[Os_3(CO)_{12}]$, initially formed on the surface by carbonylation of $[HOs_3(CO)_{10}(OR)]$ (R = H or Si<), is easily converted into $[H_3Os_4(CO)_{12}]^-$ (Scheme 2). In agreement with this suggestion, when silica-supported $[Os_3(CO)_{12}]$ is treated with CO (1 atm) for 24 h at 150 °C in the presence of K_2CO_3 (molar ratio K_2CO_3:Os = 10:1), $K[H_3Os_4(CO)_{12}]$ is obtained in high yields (95−100%), while when Na_2CO_3 is used instead of K_2CO_3, most $[Os_3(CO)_{12}]$ does not react and only traces of $[H_4Os_4(CO)_{12}]$ are formed.

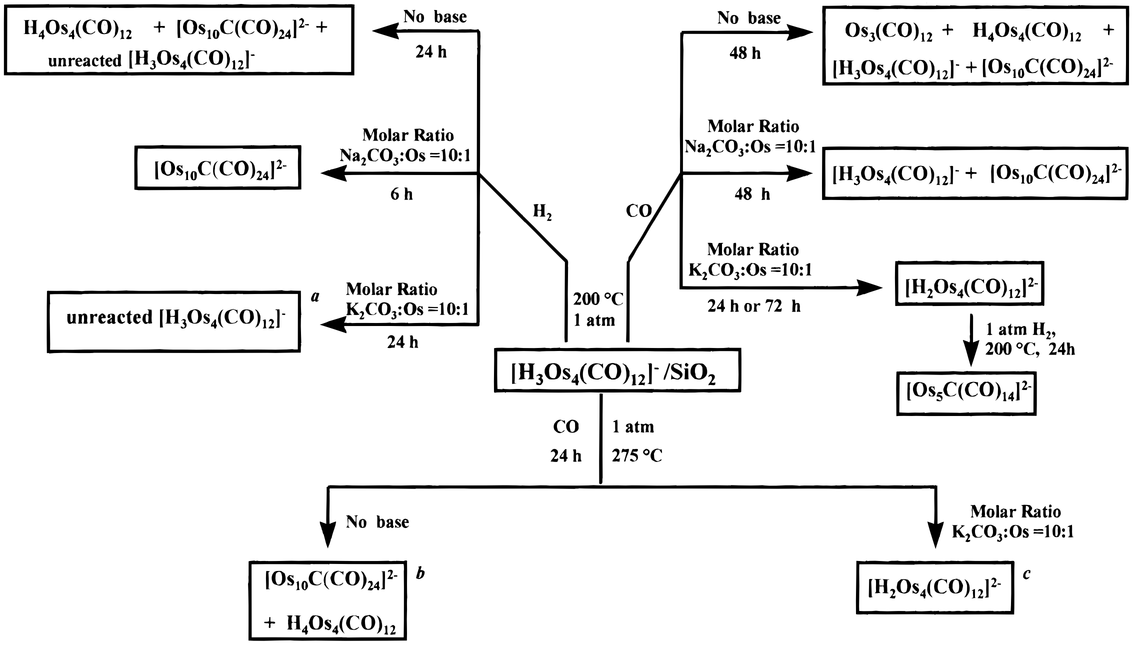
In the presence of H_2, $[Os_3(CO)_{12}]$ initially formed on the surface could also react to produce $[H_4Os_4(CO)_{12}]$,[29,30] which in any case is easily converted into $[H_3Os_4(CO)_{12}]^-$ in the presence of strong surface basicity (Scheme 2).

On the surface of MgO, $[H_3Os_4(CO)_{12}]^-$ is converted to $[Os_5C(CO)_{14}]^{2-}$ and $[Os_{10}C(CO)_{24}]^{2-}$, at high temperatures (275 °C) under CO and CO/H_2, respectively.[1] These results suggest that $[H_3Os_4(CO)_{12}]^-$ could act as the intermediate species in the selective synthesis of

---

(30) Dossi, C.; Psaro, R.; Roberto, D.; Ugo, R.; Zanderighi, G. *Inorg. Chem.* **1990**, *29*, 4368.

Scheme 3. Reactivity, under CO and under H_2, of $[H_3Os_4(CO)_{12}]^-$ on the Silica Surface



[a] Traces of $[Os_{10}C(CO)_{24}]^{3-}$ are formed in parallel. [b] Traces of $Os_3(CO)_{12}$ are formed in parallel. [c] Traces of $[Os_5C(CO)_{14}]^{2-}$ are formed in parallel.

$[Os_5C(CO)_{14}]^{2-}$ or $[Os_{10}C(CO)_{24}]^{2-}$ from α-$[Os(CO)_3Cl_2]_2$ or $[Os(CO)_3Cl_2(HOSi{\leqslant})]$ on a silica surface of sufficiently high basicity. To verify this hypothesis, we investigated the surface reactivity, both under CO and under H_2, of silica-supported $K[H_3Os_4(CO)_{12}]$ in the absence and in the presence of alkali-metal carbonates (Na_2CO_3 or K_2CO_3; Scheme 3).

When silica-supported $[H_3Os_4(CO)_{12}]^-$ is heated under CO (1 atm) at 200 °C, in the absence of alkali carbonate, a slow reaction occurs, as shown by the gradual color change from yellow to violet of the silica powder and by the sublimation of a yellow material on the cold walls of the reaction vessel. After 48 h, extraction of both the sublimate and the silica powder with CH_2Cl_2 affords a mixture of $[Os_3(CO)_{12}]$ and $[H_4Os_4(CO)_{12}]$, whereas further extraction of the silica powder with CH_3CN affords a mixture of $[Os_{10}C(CO)_{24}]^{2-}$ and unreacted $[H_3Os_4(CO)_{12}]^-$. At 275 °C, after 24 h, the conversion of silica-supported $[H_3Os_4(CO)_{12}]^-$ is complete, and extraction with CH_2Cl_2 affords mainly $[H_4Os_4(CO)_{12}]$ along with traces of $[Os_3(CO)_{12}]$, whereas further extraction with CH_3CN gives pure $[Os_{10}C(CO)_{24}]^{2-}$ (Scheme 3).

Formation of some $[H_4Os_4(CO)_{12}]$ could be attributed to protonation at 200−275 °C of $[H_3Os_4(CO)_{12}]^-$, since the pH of the silica (Aerosil 200) is about 4;[11] as mentioned above, this neutralization reaction proceeds already to a limited extent at 20 °C under N_2.

Formation of $[Os_3(CO)_{12}]$ cannot be attributed to further reaction with CO of silica-supported $[H_4Os_4(CO)_{12}]$; the latter does not react when exposed to CO at 200 °C. Probably some $[H_3Os_4(CO)_{12}]^-$ is thermally degraded, by oxidative addition of surface silanol groups, affording silica-anchored oxidized species such as $[HOs_3(CO)_{10}(OSi{\leqslant})]$ and $[Os(CO)_x(OSi{\leqslant})_2]_n$ ($x = 2, 3$), which are known to be further reduced to $[Os_3(CO)_{12}]$ under CO at 200 °C.[22] The observation that only traces of $[Os_3(CO)_{12}]$ are formed at higher temperature, such as 275 °C, is probably due to rapid sublimation of $[H_4Os_4(CO)_{12}]$.

When silica-supported $[H_3Os_4(CO)_{12}]^-$ is heated under CO at 200 °C in the presence of Na_2CO_3 (10:1 Na_2CO_3:Os molar ratio), a mixture of $[Os_{10}C(CO)_{24}]^{2-}$ and unreacted $[H_3Os_4(CO)_{12}]^-$ is obtained after 48 h (Scheme 3). The presence of a base on the silica surface is sufficient, as expected, to prevent the formation of $[H_4Os_4(CO)_{12}]$. The lack of formation of $[Os_3(CO)_{12}]$ can be interpreted by the inability, under basic conditions, of slightly electrophilic surface silanol groups to add oxidatively to $[H_3Os_4(CO)_{12}]^-$ (Scheme 3).

By using K_2CO_3 instead of Na_2CO_3 at 200 °C under CO, deprotonation in 24 h of silica-supported $[H_3Os_4(CO)_{12}]^-$ to $[H_2Os_4(CO)_{12}]^{2-}$ (100% yield) occurs (Scheme 3). In contrast to $[H_3Os_4(CO)_{12}]^-$, $[H_2Os_4(CO)_{12}]^{2-}$ is stable under CO and does not condense to $[Os_{10}C(CO)_{24}]^{2-}$ at either 200 or 275 °C, although it is quantitatively converted after 24 h into $[Os_5C(CO)_{14}]^{2-}$ by reaction under H_2 at 200 °C (Scheme 3).

Silica-supported $[H_3Os_4(CO)_{12}]^-$, when heated at 200 °C for 24 h under H_2 (1 atm) in the absence of alkali carbonate, produces some $[H_4Os_4(CO)_{12}]$, which sublimes on the cold walls of the reaction vessel, whereas $[Os_{10}C(CO)_{24}]^{2-}$ is formed on the surface and minor amounts of $[H_3Os_4(CO)_{12}]^-$ are left (Scheme 3). $[Os_3(CO)_{12}]$ is not observed, as expected because of its easy conversion to $[H_4Os_4(CO)_{12}]$ under such reaction conditions.[29,30]

When silica-supported $[H_3Os_4(CO)_{12}]^-$ is heated under H_2 (1 atm) at 200 °C in the presence of Na_2CO_3 (molar ratio Na_2CO_3:Os = 10:1), the yellow silica gradually turns violet. After ca. 6 h, extraction with CH_3CN affords $[Os_{10}C(CO)_{24}]^{2-}$ in 75−80% yields (Scheme 3); an increase of the reaction time to 24 h causes further reduction to $[Os_{10}C(CO)_{24}]^{3-}$. As expected, neutral clusters such as $[H_4Os_4(CO)_{12}]$ and $[Os_3(CO)_{12}]$ are not formed under these basic conditions. The conversion of $[Os_{10}C(CO)_{24}]^{2-}$ to $[Os_{10}C(CO)_{24}]^{3-}$ on the silica surface is remarkable. In fact, it usually occurs in tetrahydrofuran solution by addition of sodium benzophenone ketyl[31] or on a very basic surface such as activated MgO.[32]

Surprisingly, silica-supported $[H_3Os_4(CO)_{12}]^-$ becomes stabilized under H_2 by a relatively strong surface basicity (molar ratio K_2CO_3:Os = 10:1). This latter observation is quite difficult to rationalize. After 24 h at 200 °C under H_2 (1 atm), only traces of $[Os_{10}C(CO)_{24}]^{3-}$ are formed, whereas most $[H_3Os_4(CO)_{12}]^-$ does not react (Scheme 3). Also, deprotonation of $[H_3Os_4(CO)_{12}]^-$ to $[H_2Os_4(CO)_{12}]^{2-}$ appears to be inhibited, otherwise some $[Os_5C(CO)_{14}]^{2-}$ should be produced in the presence of K_2CO_3 and H_2.

In summary, the reactivity of $[H_3Os_4(CO)_{12}]^-$ suggests that it can be a key intermediate in the silica-mediated syntheses of $[Os_{10}C(CO)_{24}]^{2-}$ and $[Os_5C(CO)_{14}]^{2-}$ starting from α-$[Os(CO)_3Cl_2]_2$ or $[Os(CO)_3Cl_2(HOSi\lessdot)]$.[8] In fact, its intermediate formation can rationalize the high yield (81%) synthesis of $[Os_{10}C(CO)_{24}]^{2-}$ under specific conditions (1 atm, H_2, 200 °C, 24 h) in the presence of a large excess of Na_2CO_3 (molar ratio Na_2CO_3:Os = 10:1) whereas, as expected, $[H_4Os_4(CO)_{12}]$ is the major product (83%) when the surface basicity is very low (molar ratio Na_2CO_3:Os = 2:1).[8] It appears that only when the surface basicity is sufficiently high to allow deprotonation of $[H_4Os_4(CO)_{12}]$ is $[H_3Os_4(CO)_{12}]^-$ generated in situ; it can further condense to $[Os_{10}C(CO)_{24}]^{2-}$ (Scheme 2), as shown above. On the other hand, $[Os_5C(CO)_{14}]^{2-}$ is generated in high yield (74%) by reductive carbonylation (1 atm of CO) of silica-supported α-$[Os(CO)_3Cl_2]_2$ at 275 °C in the presence of excess K_2CO_3 (molar ratio K_2CO_3:Os = 10:1).[8] Under these conditions, both H_2 and CO_2 are produced in parallel by the water-gas shift reaction, as confirmed by gas chromatographic analysis of the gaseous phase at the end of the reaction. The quantity of H_2 produced is probably low enough to allow further deprotonation of the intermediate $[H_3Os_4(CO)_{12}]^-$ to $[H_2Os_4(CO)_{12}]^{2-}$, but it is high enough to favor further thermal condensation of this latter intermediate to $[Os_5C(CO)_{14}]^{2-}$ (Scheme 2).

Similarly, the production of some H_2 via the water-gas shift reaction, confirmed by gas chromatography, would explain the traces of $[Os_5C(CO)_{14}]^{2-}$ formed by treatment under CO at 275 °C of silica-supported $[H_3Os_4(CO)_{12}]^-$ in the presence of excess K_2CO_3 (Scheme 3). In the absence of K_2CO_3, H_2 was not detected in the gas phase, in agreement with the absence of traces of $[Os_5C(CO)_{14}]^{2-}$ among the reaction products (Scheme 3). The catalytic activity for the water-gas shift of α-$[Os(CO)_3Cl_2]_2$ or $[H_3Os_4(CO)_{12}]^-$ supported on silica in the presence of K_2CO_3 is not surprising, since silica-anchored $[Os(CO)_x(OSi\lessdot)_2]_n$ (x = 2.7),[33] zeolite-trapped $[H_3Os_4(CO)_{12}]^-$ under basic conditions,[34] and even silica-supported K_2CO_3 (see above) can catalyze the water-gas shift reaction.

Interestingly, this body of observations can also help interpret the results of Lamb et al., who reported[1] that, at 275 °C on the surface of MgO, $[H_3Os_4(CO)_{12}]^-$ is rapidly converted to $[Os_5C(CO)_{14}]^{2-}$ under CO (1 atm), whereas a very slow condensation to $[Os_{10}C(CO)_{24}]^{2-}$ occurs under a mixture of CO and H_2 (1:3 molar ratio, 10 atm). Our findings would suggest that the facile condensation to $[Os_5C(CO)_{14}]^{2-}$ could be due to the positive role of some H_2, produced by the water-gas shift reaction catalyzed by $[H_3Os_4(CO)_{12}]^-$,[34] on the deprotonated species $[H_2Os_4(CO)_{12}]^{2-}$ generated in situ on the very basic surface of MgO. However, under an excess of H_2 (for example with a mixture of CO and H_2, 1:3 molar ratio), $[H_3Os_4(CO)_{12}]^-$ is stabilized; therefore, it is slowly thermally converted into $[Os_{10}C(CO)_{24}]^{2-}$ but not into $[Os_5C(CO)_{14}]^{2-}$. In fact, the quantity of H_2 in the gas phase is probably too high and therefore deprotonation of $[H_3Os_4(CO)_{12}]^-$ to $[H_2Os_4(CO)_{12}]^{2-}$, the intermediate species for further condensation to $[Os_5C(CO)_{14}]^{2-}$, is hindered, as we have shown.

In summary, the basicity of the silica surface plays an important role in the formation of specific intermediates such as $[H_3Os_4(CO)_{12}]^-$ and $[H_2Os_4(CO)_{12}]^{2-}$, which are characterized by rather different surface reactivities. In particular, their stability and further condensation to $[Os_{10}C(CO)_{24}]^{2-}$ or $[Os_5C(CO)_{14}]^{2-}$ are controlled not only by surface basicity and reaction conditions but also by the amount of H_2 in the gas phase.

Conclusion

It is known that supported inorganic reagents can allow in particular cases highly selective and mild organic chemical reactions.[35] Many attempts have been made to increase the basicity of solid surfaces by adding an inorganic reagent, including the addition of sodium metal to metal oxides such as MgO and Al_2O_3 and even SiO_2.[36] Powerful bases such as metal alkoxides[37] and the fluoride anion[38] have been also added to oxides such as SiO_2 and Al_2O_3, respectively. The two approaches are quite different: in the first case the aim is that of acting on the surface structures by the creation of very basic O^{2-} centers; in the second case a reagent is dispersed on an inert surface in order to increase its specific reactivity. One of the most fascinating aspects of the latter approach to supported inorganic reagents is that the final active solid material has a chemical behavior and a reactivity which rarely can be determined as the simple sum of the properties of the two components. This probably implies some interaction between the reagent and the surface. From our investigations[6–8] on the addition of alkali-metal carbonates to silica as a way to modulate the selectivity of the reduction of physisorbed metal salts or metal carbonyl

---

(31) Drake, S. R.; Barley, M. H.; Johnson, B. F. G.; Lewis, J. *Organometallics* **1988**, *7*, 806.

(32) Lamb, H. H.; Gates, B. C. *J. Phys. Chem.* **1992**, *96*, 1099.

(33) Dossi, C.; Fusi, A.; Psaro, R.; Zanderighi, G. M. *Appl. Catal.* **1989**, *46*, 145.

(34) Lenarda, M.; Ganzerla, R.; Graziani, M.; Spogliarich, R. *J. Organomet. Chem.* **1985**, *290*, 213.

(35) Clark, J. H. *Catalysis of Organic Reaction by Supported Inorganic Reagents*; VCH: New York, 1994.

(36) Malinowski, S.; Kijenski, J. In *Catalysis*; Royal Society of Chemistry: Cambridge, U.K., 1981; Vol. 8, Chapter 4, and Vol. 4, Chapter 5.

(37) Keinan, E.; Mazury, J. *J. Am. Chem. Soc.* **1977**, *99*, 3861.

(38) (a) Yamawaki, J.; Kawate, T.; Ando, T.; Hanafusa, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1885. (b) Villemin, D. *J. Chem. Soc., Chem. Commun.* **1985**, 870. (c) Ando, T.; Brown, S. J.; Clark, J. H.; Cork, D. G.; Hanafusa, T.; Ichihara, J.; Miller, J. M.; Robertson, M. S. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1133.

complexes, we have evidence, confirmed in this work, of an unexpectedly large increase of the intrinsic basicity of the surface itself.

Unfortunately the silica surface has been less studied than other surfaces, such as that of alumina, for the preparation of a strong basic solid by the addition of a basic reagent to an inorganic oxide.[35] In the few known studies, after saturation of the surface with an aqueous solution of an alkali-metal hydroxide, acetate, or carbonate, the supported reagents are thermally treated at temperatures between 300 and 650 °C to leave a silica with strong basic surface sites such as alkali-metal silanolates.[18,36] It is also known that silica gel can be made more basic simply by treatment with aqueous sodium hydroxide, followed by drying at 120 °C.[39] Surprisingly, we have shown that even the addition of a relatively weak base such as an alkali carbonate produces a highly basic silica surface with a basicity dependent upon the nature of the alkali-metal cation, even without particularly strong thermal treatment. As in other cases of supported inorganic reagents, the surface basicity is controlled by loading, method of preparation, and in particular efficiency of reagent dispersion and level of thermal treatment or activation.[35] However, due to (i) the relatively low temperatures reached either in the drying process of preparation of the solid material (less than 80 °C) or during the reactions (only up to 275 °C) and (ii) the presence of water under the reaction conditions of the silica-mediated syntheses of osmium clusters (closed reaction vessel which forbids removal of water),[7,8] we cannot propose any strong interaction of the alkali-metal carbonates with the surface silanol groups to generate for instance highly basic centers such as surface silanolates, which are usually produced in the absence of water and at much higher temperatures.[36] It follows that the basic silica used in our investigation can be better described as a nonhomogeneously supported inorganic base (the alkali-metal carbonates) on the surface of an inert support (the silica). As a matter of fact, the addition of an alkali carbonate decreases slightly the surface area of our silica (Aerosil 200) and a more homogeneous dispersion of the deposited alkali carbonate can be obtained by starting from a water solution instead of a dichloromethane slurry. Of course a more homogeneous dispersion produces a higher basicity. We have evidence that only at relatively high temperatures (e.g. 275 °C) can some thermal decomposition of K_2CO_3 to KOH occur, due to the presence of layers of physisorbed water. Therefore, the unexpectedly strong basic properties of K_2CO_3 and even Na_2CO_3, when supported on silica, suggest a low solvation of the CO_3^{2-} anion on the silica surface. Although no quantitative value has been obtained for the basicity of the alkali-metal carbonates when they are dispersed on the silica surface under our experimental conditions, in agreement with a strong surface basicity many reactions which occur quite easily on silica added with K_2CO_3, such as deprotonation of $[H_4Os_4(CO)_{12}]$ to $[H_3Os_4(CO)_{12}]^-$ or even to $[H_2Os_4(CO)_{12}]^{2-}$ or transformation of $[Os_3(CO)_{12}]$ into $[H_3Os_4(CO)_{12}]^-$, $[H_2Os_4(CO)_{12}]^{2-}$, or $[Os_{10}C(CO)_{24}]^{2-}$, when carried out in solution require strong basic reagents such as alkali-metal hydroxides,[19,27] sodium borohydride,[40] and even metallic sodium.[41] The behavior of our basic silica is quite similar to that reported for the very basic surface of MgO.[1]

The first activation process of a species such as physisorbed α-$[Os(CO)_3Cl_2]_2$ seems to involve simple substitution of the chloride by hydroxide ligands to generate dispersed osmium(II) hydroxo carbonyl complexes which, according to the surface basicity, can be also negatively charged. A covalent interaction of the osmium atoms with surface silanolate groups is less probable, due to the known easy hydrolysis of Os−OSi bonds which can occur in the presence of water layers of the surface.[24] Also both the low reactivity toward H_2 of osmium(II) carbonyl species covalently anchored to silanolate groups of the silica surface and the lack of a strong loading effect on both selectivity and reactivity[8] are in agreement with the above suggestion. Only in subsequent steps of condensation to produce cluster structures is there some evidence that specific surface silanol groups[29] may play a role in the aggregation to intermediate surface trimeric carbonyl hydride clusters (Scheme 2).

The strong effect of some reaction parameters (in particular, the nature of the alkali-metal carbonates and the ratio of alkali carbonate to osmium, but also the temperature and presence of H_2 in the gas phase) on the selectivity toward the formation of specific osmium carbonyl cluster anions[7,8] is explained by the formation of either $[H_3Os_4(CO)_{12}]^-$ or $[H_2Os_4(CO)_{12}]^{2-}$ as the key intermediates for condensation to cluster anions of higher nuclearity (Scheme 2). The first anion is favored by a relatively mild surface basicity and, strangely enough, by the presence of a large amount of H_2 in the gas phase and the second by a strong surface basicity and by temperatures above 200 °C. These two anions show different reactivities which lead to specific pathways of condensation: $[H_3Os_4(CO)_{12}]^-$ increases its nuclearity to form $[Os_{10}C(CO)_{24}]^{2-}$ by raising the temperature under CO or H_2, while $[H_2Os_4(CO)_{12}]^{2-}$, which is stable under CO even at high temperatures, increases its nuclearity at 200 °C to form $[Os_5C(CO)_{14}]^{2-}$ under relatively low amounts of H_2. In summary, we obtained evidence for a step-by-step process (Scheme 2) which explains fairly well the origin of the good selectivities observed in the controlled reduction of silica-supported α-$[Os(CO)_3Cl_2]_2$ to generate different neutral or anionic osmium carbonyl clusters.[7,8]

Although much needs to be learned about the physicochemical characterization of supported inorganic basic reagents such as alkali-metal carbonates, in particular from the point of view of surface science, we have reported herein clear chemical evidence that, on a silica surface added with alkali-metal carbonates, basicities are attained which cannot be easily obtained in solution. In conclusion, we have added evidence that molecular organometallic species can react cleanly on a surface by a multistep process without the involvement of strong solvation effects, thus reaching reactivities and selectivities quite unexpected in comparison with related processes carried out in solution.

---

(39) (a) Malinowski, S.; Basinski, S. *J. Catal.* **1963**, *2*, 203. (b) Malinowski, S.; Szczepanska, S. *J. Catal.* **1963**, *2*, 310.

(40) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Sheldrick, G. M.; Suss, G. *J. Organomet. Chem.* **1978**, *162*, 179.

(41) Hayward, C. M. T.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3816.

Experimental Section

Materials and Instrumentation. 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. α-$[Os(CO)_3Cl_2]_2$, $[Os_3(CO)_{12}]$, $[H_4Os_4(CO)_{12}]$, $[PPN][HOs_3(CO)_{11}]$, and $K[H_3Os_4(CO)_{12}]$ were prepared according to the literature.[8,42,43] $[HOs_3(CO)_{10}(OSi{\leqslant})]$ (2 wt % Os) was prepared by refluxing under N_2 an *n*-octane solution of $[Os_3(CO)_{12}]$ with silica until the solvent was decolorized (10 h); after filtration, a pale yellow powder of $[HOs_3(CO)_{10}(OSi{\leqslant})]$ was obtained and kept under N_2.[44] $[HOs_3(CO)_{10}(OH)]$ was prepared by heating at 95 °C $[HOs_3(CO)_{10}(OSi{\leqslant})]$ in the biphasic system water/toluene until the silica powder was decolorized (5 h); evaporation of the toluene phase afforded $[HOs_3(CO)_{10}(OH)]$.[45]

All the reaction products were identified, after extraction from the support with suitable solvents,[8] by infrared, proton nuclear magnetic resonance (when appropriate), and mass spectroscopy, their spectra being compared to those of pure samples.[8,27,46] Gas analyses for the detection of H_2 and CO_2 were carried out on a Hewlett-Packard 5890 gas chromatograph equipped with a stainless steel carbosieve SII packed column (outside column diameter $^1/_8$ in.; column length 96 in.; oven program temperature 35 °C isotherm for 7 min, then heated from 35 °C to 225 °C at a 32 °C/min rate). The specific surface area of silica samples, with or without addition of K_2CO_3, was determined by the BET (Brunauer-Emmet-Teller) method,[12] from the nitrogen adsorption isotherm at 77K, by using a Sorptomatic 1900 instrument. A Hitachi S 2400 scanning electron microscope was used for SEM measurements: the surface morphology was determined, and energy-dispersive X-ray analysis (EDX) data were obtained by using a Kevex unit.

Preparation of Silica-Supported α-$[Os(CO)_3Cl_2]_2$ Added with Base. In a typical preparation, a suspension of silica (15.0 g), α-$[Os(CO)_3Cl_2]_2$ (correct amount to have the desired osmium loading, from 2 to 15 wt % Os with respect to SiO_2), M_2CO_3 or MOH (M = Na, K; correct amount to have the desired molar ratio M:Os) and CH_2Cl_2 (250 mL) were stirred under N_2 in a two-necked flask (500 mL) for 2 days, at 25 °C. The solvent was evaporated (25 °C, 10^{-2} Torr), affording a powder which was stored under N_2.

In some cases the samples were prepared in two steps: (i) a water solution (200 mL) of the alkali carbonate (correct amount to have the desired molar ratio alkali carbonate:Os) was stirred with silica (15.0 g) for 24 h under N_2 and the solvent was evaporated (80 °C, 10^{-2} Torr), affording silica-supported alkali carbonate; (ii) a slurry of silica-supported alkali carbonate (15.0 g), α-$[Os(CO)_3Cl_2]_2$ (correct amount to have the desired osmium loading, from 2 to 15 wt % Os with respect to SiO_2), and CH_2Cl_2 (250 mL) were stirred for 24 h under N_2. Evaporation of the solvent (25 °C, 10^{-2} Torr) afforded a powder which was stored under N_2.

Preparation of $[Os(CO)_x(OSi{\leqslant})_2]_n$ ($x = 2.7$) with or without Addition of Alkali-Metal Carbonates. $[Os(CO)_x(OSi{\leqslant})_2]_n$ ($x = 2.7$) was prepared according to the literature, by treatment of $[HOs_3(CO)_{10}(OSi{\leqslant})]$ (2 wt % Os with respect to SiO_2) in air at 200 °C.[22] In a typical preparation, $[Os(CO)_x(OSi{\leqslant})_2]_n$ ($x = 2.7$) (15.0 g), M_2CO_3 (M = Na, K; correct amount to have the desired molar ratio M:Os) and CH_2Cl_2 (250 mL) were stirred under N_2 in a two-necked flask (500 mL) for 2 days, at room temperature. The solvent was evaporated (25 °C, 10^{-2} Torr), affording a pale gray powder which was stored under N_2.

Preparation of Silica-Supported $[Os(CO)_3(OH)_2]_n$ with or without Addition of Alkali-Metal Carbonates. $[Os(CO)_3(OH)_2]_n$ was prepared in situ[25] by stirring for 3 h a CH_2Cl_2 solution of α-$[Os(CO)_3Cl_2]_2$ (170 mL; 0.620 g of α-$[Os(CO)_3Cl_2]_2$; 0.898 mmol of α-$[Os(CO)_3Cl_2]_2$) with a water solution of NaOH (10 mL; 0.143 g of NaOH; 3.57 mmol of NaOH). Acetone (200 mL) and silica (17.23 g; 2 wt % Os with respect to SiO_2) were added to the resulting water phase containing $[Os(CO)_3(OH)_2]_n$, affording a slurry which was stirred for 1 h and evaporated to dryness (60 °C, 10^{-2} Torr). In a typical preparation, the alkali carbonate was added by stirring the resulting silica-supported $[Os(CO)_3(OH)_2]_n$ (10.0 g), M_2CO_3 (M = Na, K; correct amount to have the desired molar ratio M:Os), and CH_2Cl_2 (250 mL) under N_2 in a two-necked flask (500 mL) for 2 days, at room temperature. Then the solvent was evaporated (25 °C, 10^{-2} Torr), affording a white powder which was stored under N_2.

Preparation of Silica-Supported $Na[Os(CO)_3(OH)_3]$ with or without Addition of K_2CO_3. $Na[Os(CO)_3(OH)_3]$ was prepared in situ,[25] by stirring for 1 h a CH_2Cl_2 solution of α-$[Os(CO)_3Cl_2]_2$ (100 mL; 0.341 g of α-$[Os(CO)_3Cl_2]_2$; 0.494 mmol of α-$[Os(CO)_3Cl_2]_2$) with a water solution of NaOH (105 mL; 0.118 g of NaOH; 2.95 mmol of NaOH). Silica (correct amount to have the desired osmium loading, from 2 to 15 wt % Os with respect to SiO_2) and more water (100 mL) were added to the water phase containing $Na[Os(CO)_3(OH)_3]$, affording a slurry which was stirred for 1 h and evaporated to dryness (ca. 80 °C, 10^{-2} Torr). In a typical preparation, the alkali carbonate was added by stirring the resulting silica-supported $Na[Os(CO)_3(OH)_3]$ (10.0 g), K_2CO_3 (correct amount to have the desired molar ratio K:Os), and CH_2Cl_2 (250 mL) under N_2 in a two-necked flask (500 mL) for 2 days, at room temperature. Then the solvent was evaporated (25 °C, 10^{-2} Torr) affording a white powder which was stored under N_2.

Preparation of $[HOs_3(CO)_{10}(OSi{\leqslant})]$ or Silica-Supported $[HOs_3(CO)_{10}(OH)]$ with or without Addition of Alkali-Metal Carbonates. In a typical preparation, a suspension of $[HOs_3(CO)_{10}(OSi{\leqslant})]$ (2.00 g; 2 wt % Os with respect to SiO_2), M_2CO_3 (M = Na, K; correct amount to have the desired molar ratio M_2CO_3:Os), and CH_2Cl_2 (about 100 mL) was stirred for 24 h under N_2 in a two-necked flask (200 mL). The solvent was evaporated (25 °C, 10^{-2} Torr), affording a pale yellow powder which was stored under N_2. Silica-supported $[HOs_3(CO)_{10}(OH)]$ added with M_2CO_3 (M = Na, K) was prepared as above using a slurry of silica, M_2CO_3, and $[HOs_3(CO)_{10}(OH)]$ (2 wt % Os with respect to SiO_2) dissolved in CH_2Cl_2.

Preparation of Silica-Supported $[Os_3(CO)_{12}]$, $[H_4Os_4(CO)_{12}]$, or $K[H_3Os_4(CO)_{12}]$ with or without Addition of Alkali-Metal Carbonates. A suspension of silica (10.0 g), $[Os_3(CO)_{12}]$ or $[H_4Os_4(CO)_{12}]$ (correct amount to have 2 wt % Os with respect to SiO_2), CH_2Cl_2 (250 mL), and, when required, M_2CO_3 (M = Na, K; correct amount to have the desired molar ratio M_2CO_3:Os) was stirred for 24 h under N_2 in a two-necked flask (500 mL). Evaporation of the solvent afforded the silica-supported carbonyl osmium cluster with or without added alkali-metal carbonates. Silica-supported $K[H_3Os_4(CO)_{12}]$ with or without added M_2CO_3 (M = Na, K) was prepared as above, but using CH_3CN as solvent instead of CH_2Cl_2.

Preparation of Silica-Supported Na_2CO_3 or K_2CO_3. A suspension of silica (10.0 g), CH_2Cl_2 (250 mL), and M_2CO_3 (M = Na, K; correct amount to have the desired M_2CO_3 loading) was stirred for 24 h under N_2 in a two-necked flask (500 mL). Evaporation of the solvent (25 °C, 10^{-2} Torr) afforded the silica-supported alkali carbonate. In some preparations, water was used instead of CH_2Cl_2 for the deposition of the alkali carbonate.

Reaction with HCl(aq) To Determine the Number of CO Ligands in Silica Surface Osmium(II) Carbonyl Species. The sample containing a silica surface osmium(II) carbonyl species (1.0 g) was stirred overnight with water (100

---

(42) Hermann, W. A.; Herdtweck. E.; Schofer, A. *Chem. Ber.* **1988**, *121*, 1907.

(43) Eady, C. R.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C. *J. Chem. Soc., Dalton Trans.* **1978**, 1358.

(44) Barth, R.; Gates, B. C.; Knozinger, H.; Hulse, J. *J. Catal.* **1983**, *82*, 147.

(45) Roberto, D.; Lucenti, E.; Roveda, C.; Ugo, R. *Organometallics* **1997**, *16*, 5974.

(46) Cleare, M. J.; Griffith, W. P. *J. Chem. Soc. A* **1969**, 372.

mL) and 37% aqueous HCl (2 mL) at room temperature. No carbonyl bands remained on silica after this treatment. The aqueous solution was filtered and evaporated to dryness. The infrared spectrum of the residue taken in ethanol showed the presence of either *fac*-$[Os(CO)_3Cl_3]^-$ or *cis*-$[Os(CO)_2Cl_4]^{2-}$ or both, depending on the number of CO ligands of the starting surface osmium(II) species. Treatment with HCl(aq) of $[Os(CO)_x(OSi\leqslant)_2]_n$ ($x = 2, 3$)[22] afforded a mixture of both *fac*-$[Os(CO)_3Cl_3]^-$ and *cis*-$[Os(CO)_2Cl_4]^{2-}$. On the other hand, the surface species obtained by reaction of α-$[Os(CO)_3Cl_2]_2$ with alkali-metal carbonates afforded by reaction with HCl(aq) only *fac*-$[Os(CO)_3Cl_3]^-$.

Reactivity of [PPN]$[HOs_3(CO)_{11}]$ on the Silica Surface with or without Addition of K_2CO_3. When a red dichloromethane (150 mL) solution of [PPN]$[HOs_3(CO)_{11}]$[43] (0.261 g) was added to silica (5.22 g; 2 wt % Os/SiO_2) at room temperature, the solution and the silica powder turned immediately yellow. The dichloromethane solution was filtered and evaporated to dryness, and the resulting yellow residue was extracted with pentane, affording pure $[HOs_3(CO)_{10}(OH)]$ (0.066 g; 41% yield). On the other hand, $[HOs_3(CO)_{10}(OSi\leqslant)]$ was present on the yellow silica surface, as shown by infrared spectroscopy. This conversion of [PPN]$[HOs_3(CO)_{11}]$ to $[HOs_3(CO)_{10}(OR)]$ (R = H and/or $Si\leqslant$) was slower (ca. 10 h) in the presence of K_2CO_3 (molar ratio K_2CO_3:Os = 10:1).

Carbonylation and Hydrogenation Reactions. The desired silica powder sample was transferred into a cylindrical Pyrex vessel previously described for the reductive carbonylation of silica-supported metal chlorides at atmospheric pressure.[2] The sample was treated under vacuum (10^{-2} Torr) at room temperature and then exposed to CO or H_2 at atmospheric pressure. The bottom of the vessel (about half of the cylinder) was put into an oven and heated at the desired temperature (100−275 °C). The surface reactions were monitored by infrared spectroscopy; silica powder samples were taken from the glass vessel at room temperature and studied as Nujol mulls. Extraction of the reaction products was carried out with CH_2Cl_2 (in the case of neutral products) or with CH_3CN (in the case of anionic products) as previously described.[2,7,8] In some cases, the gaseous phase at the end of the reaction was analyzed by gas chromatography, after the reaction vessel was cooled at room temperature.

Reactivity with H_2 of $[Os(CO)_x(OSi\leqslant)_2]_n$ ($x = 2, 3$) and Silica-Supported $[Os(CO)_3(OH)_2]_n$ in the Presence of Na_2CO_3. Reaction of both $[Os(CO)_x(OSi\leqslant)_2]_n$ ($x = 2.7$) and silica-supported $[Os(CO)_3(OH)_2]_n$ with H_2 (1 atm) at 150 °C in the presence of Na_2CO_3 (molar ratio Na_2CO_3:Os = 1:1) for 3 days afforded a mixture of $[H_4Os_4(CO)_{12}]$ and $Na_2[Os_{10}C(CO)_{24}]$, which were extracted with CH_2Cl_2 and CH_3CN, respectively (see Results and Discussion). The resulting silica was gray and showed infrared bands at 2118 (vw), 2022 (s), and 1957 (s) cm^{-1}, which could be due to an anionic carbonyl Os(II) species of very low reactivity. In fact, by further treatment for 24 h under H_2 at 150 °C, only traces of $[H_4Os_4(CO)_{12}]$ were generated, while the surface species was converted into another poorly reactive species characterized by infrared bands at 2016 (m) and 1934 (m) cm^{-1}. Interestingly, this latter species, poorly reactive under H_2, was quite reactive under CO. After 3 days under CO (1 atm) at 200 °C, it afforded $[Os_3(CO)_{12}]$ along with traces of $[H_4Os_4(CO)_{12}]$ and $[Os_{10}C(CO)_{24}]^{2-}$ while on the silica surface there still remained weak carbonyl bands in the region 2120−1900 cm^{-1}.

Acknowledgment. We wish to thank deeply Professor Howard Alper (University of Ottawa) for constructive suggestions during the preparation of the paper. We are also grateful to Dr. Daniele Delledonne (EniChem SpA, San Donato Milanese) for gas analyses, to Dr. Laura Meda (EniChem-Centro Ricerche Novara) for BET measurements, and to Dr. Paola Fermo (University of Milan) for SEM measurements. E.C. thanks the University of Milan for a postdoctoral fellowship. This work was supported by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica and by the Consiglio Nazionale delle Ricerche (CNR, Rome).

OM970590I