Surface-Mediated Organometallic Synthesis: High-Yield Preparations of Neutral and Anionic Osmium Carbonyl Clusters by Controlled Reduction of Silica-Supported $[Os(CO)_3Cl_2]_2$ and $OsCl_3$ in the Presence of Na_2CO_3 or K_2CO_3

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$[Os_3(CO)_{12}]$, $[H_4Os_4(CO)_{12}]$, $[H_2Os_4(CO)_{12}]^{2-}$, $[Os_5C(CO)_{14}]^{2-}$, and $[Os_{10}C(CO)_{24}]^{2-}$ have been synthesized selectively and in high yields by reductive carbonylation or hydrogenation of $OsCl_3$ or α-$[Os(CO)_3Cl_2]_2$ supported on silica in the presence of alkali carbonates. The selectivity of the reaction is controlled by the choice of (i) the nature and quantity of the alkali carbonate (Na_2CO_3 or K_2CO_3) added to silica, (ii) temperature, (iii) reaction time, and (iv) the gas-phase composition (CO, CO + H_2, or H_2). These surface-mediated syntheses are often more selective and more efficient and usually require less drastic conditions than the best known syntheses in solution, confirming the potential use of the silica surface as a new reaction medium to prepare both neutral and anionic metal carbonyl clusters.

Introduction

The field of preparative organometallic chemistry mediated by surfaces is becoming a new area of synthetic chemistry for specific classes of compounds, such as metal carbonyl complexes, whereby the surface of a solid such as an inorganic oxide plays the role of the solvent in conventional syntheses.[1−6] As a general trend, strongly basic surfaces such as magnesium oxide favor the formation of anionic metal carbonyl complexes[1,5−6] while neutral complexes are generated on the surface of rather neutral supports such as silica.[2,3] However, recently, we found that the anion $[H_3Os_4(CO)_{12}]^-$ is formed in high yields by reductive carbonylation of $OsCl_3$ or α-$[Os(CO)_3Cl_2]_2$ supported on silica in the presence of K_2CO_3.[4] It follows that addition of a specific base, such as K_2CO_3, may change the properties of the surface, thus allowing the synthesis of anionic metal carbonyl clusters even on silica. Later, we found that the formation of $[Os_3(CO)_{12}]$ is favored compared to that of $[H_3Os_4(CO)_{12}]^-$ when Na_2CO_3 is used instead of K_2CO_3. Thus, the nature of the added base can direct the reductive carbonylation on the silica surface toward the formation of different osmium clusters. Since the established syntheses of osmium clusters are often characterized by relatively low yields, drastic conditions, and tedious separations,[1,7] these syntheses were reinvestigated using the controlled reduction of $OsCl_3$ or α-$[Os(CO)_3Cl_2]_2$ supported on silica in the presence of alkali carbonates.

This work describes the results of this investigation which led to efficient and convenient syntheses of $[Os_3(CO)_{12}]$, $[H_4Os_4(CO)_{12}]$, $[H_2Os_4(CO)_{12}]^{2-}$, $[Os_{10}C(CO)_{24}]^{2-}$, and $[Os_5C(CO)_{14}]^{2-}$, using the silica surface as a reaction medium.

Results and Discussion

Synthesis of $[Os_3(CO)_{12}]$. The reductive carbonylation of silica-supported $[Os(CO)_3Cl_2]_2$ to $[Os_3(CO)_{12}]$ does not occur readily due to the easy sublimation of chlorocarbonylosmium clusters at relatively high temperatures and to the difficulty of removing chloro ligands from osmium at lower temperatures.[8] However, the anion $[H_3Os_4(CO)_{12}]^-$ is obtained in high yields on the silica surface in the presence of K_2CO_3,[4] while the use of $NaHCO_3$ appears to favor the formation of $[Os_3(CO)_{12}]$.[8]

We found that when a slurry of SiO_2, α-$[Os(CO)_3Cl_2]_2$ (2 wt % Os/SiO_2), Na_2CO_3 (molar ratio Na_2CO_3:Os = 2:1), and CH_2Cl_2 is stirred at room temperature for 2 days, a surface reaction occurs. The infrared spectrum of the final powder, obtained after evaporation of the solvent, shows three carbonyl bands at 2125 (m), 2036 (s), and 1962 (w) cm^{-1}. These frequencies are lower than those typical of either silica-supported α- or β-$[Os(CO)_3Cl_2]_2$[8] or of the silica-bound species $[Os(CO)_3Cl_2(HOSi\equiv)]$[8] but are rather close to those reported for the so-called silica-anchored species $[Os(CO)_x(OSi\equiv)_2]_n$ ($x = 2, 3$) (2121 (m), 2038 (s), and 1956 (w) cm^{-1}) obtained by thermal treatment of the grafted cluster $[HOs_3(CO)_{10}(OSi\equiv)]$.[9,10] The grafting of the organometallic moiety to the silica surface is suggested also by the failure to extract any osmium carbonyl species by treatment of the solid with solvents which usually extract species either physisorbed (e.g. dichloromethane) or weakly bound to the surface (e.g., acetonitrile or acetone).[3,8]

When this white osmium carbonyl surface species is heated at 200 °C under CO (1 atm) for 3 days in a closed reaction vessel, the silica powder color becomes yellow while some yellow material sublimes onto the cold walls of the reaction vessel (Scheme 1). Extraction of the sublimate and the silica powder with dichloromethane affords $[Os_3(CO)_{12}]$ in high yields

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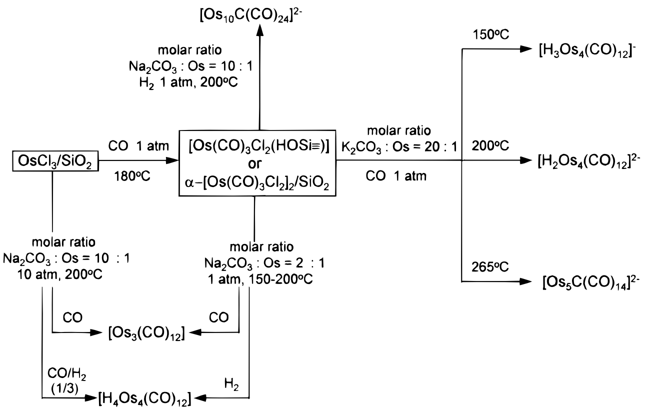
Scheme 1



(82%; Table 1) along with minor amounts of $[H_4Os_4(CO)_{12}]$, which can be easily separated. Further extraction of the silica powder with acetonitrile gives minor traces of $Na_2[Os_{10}C(CO)_{24}]$ (see Experimental Section). If the reaction is stopped after 24 h, $[Os_3(CO)_{12}]$ is obtained in only 39% yield. However, use of 10 atm of CO accelerates the reductive carbonylation, since $[Os_3(CO)_{12}]$ is already formed in 90% yield (Table 1) after 24 h. When the molar ratio Na_2CO_3:Os is increased to 10:1, the formation of $[Os_3(CO)_{12}]$ is slightly less selective. Higher amounts of $[H_4Os_4(CO)_{12}]$ are obtained, probably due to the increased amount of surface water associated with Na_2CO_3, as shown by infrared spectra of the initial silica powder. It has been reported that the presence of water favors the formation of $[H_4Os_4(CO)_{12}]$.[8]

The silica-mediated synthesis of $[Ru(CO)_3Cl_2]_2$ is sensitive to metal loadings[3] while that of $[H_3Os_4(CO)_{12}]^-$ is not.[4] In order to confirm, from a preparative point of view, the flexibility of the surface-mediated synthesis of $[Os_3(CO)_{12}]$ described above, we investigated the metal loading effect. Treatment of silica-supported α-$[Os(CO)_3Cl_2]_2$ (15 wt % Os/SiO_2) with Na_2CO_3 (molar ratio Na_2CO_3:Os = 2:1), followed by reaction with CO (1 atm) at 200 °C for 3 days, affords $[Os_3(CO)_{12}]$ in 76% yield along with minor amounts of the polynuclear hydrides $[H_4Os_4(CO)_{12}]$, $[HOs_3(CO)_{10}Cl]$, and $[HOs_3(CO)_{10}OH]$ (in a ^{1}H NMR molar ratio = 1:1:6) and of the anionic cluster $Na_2[Os_{10}C(CO)_{24}]$ (ca. 2%), which can be easily separated (see Experimental Section). It follows that this method of synthesis can be applied to larger scale preparations.

Since α-$[Os(CO)_3Cl_2]_2$ may be easily synthesized *in situ* by reductive carbonylation of silica-supported $OsCl_3$ under mild conditions (100−180 °C, 1 atm of CO),[3] it seemed possible to prepare $[Os_3(CO)_{12}]$ directly from $OsCl_3$. However, when $OsCl_3$ supported on silica (2 wt % Os/SiO_2) in the presence of Na_2CO_3 (molar ratio Na_2CO_3:Os = 10:1) is heated under CO at 200 °C, $[Os_3(CO)_{12}]$ is formed in much lower yields (not greater than 40%; Table 1), even working under 20 atm of CO for 3 days. Similarly, in the presence of K_2CO_3, much higher yields of $K[H_3Os_4(CO)_{12}]$ were obtained starting with α-$[Os(CO)_3Cl_2]_2$ than with $OsCl_3$.[4] As in this latter case, a two-step route to $[Os_3(CO)_{12}]$ starting from silica-supported $OsCl_3$ was investigated. Treatment of the silica-bound species $[Os(CO)_3Cl_2(HOSi\equiv)]$, obtained by carbonylation of silica-supported $OsCl_3$ (2 wt % Os/SiO_2) at 180 °C under 1 atm of CO for 2 days,[3] with a slurry of Na_2CO_3 in dichloromethane (molar ratio Na_2CO_3:Os = 2:1) affords the surface-grafted osmium carbonyl species described above. After evaporation of the solvent, further reaction with 1 atm of CO at 200 °C for 3 days, followed by extraction with dichloromethane, gives $[Os_3(CO)_{12}]$ in 64% yield (Table 1) along with traces of $[HOs_3(CO)_{10}Cl]$ which can be easily separated (see Experimental Section). This two-step surface-mediated synthesis is a very attractive method to prepare $[Os_3(CO)_{12}]$ directly from $OsCl_3$ under mild conditions.The best synthetic route to this carbonyl cluster reported so far requires highly toxic osmium tetroxide reacting in methanol under CO pressure (75 atm) at 125 °C for 12 h (yields = 70−80%).[11]

Synthesis of $[H_4Os_4(CO)_{12}]$. The cluster $[H_4Os_4(CO)_{12}]$ may be synthesized in good yields by reaction of silica-supported $[Os_3(CO)_{12}]$ with H_2 (1 atm) at 100−150 °C.[2] Here we report improved silica-mediated syntheses using a more convenient starting material such as α-$[Os(CO)_3Cl_2]_2$ or $OsCl_3$.

When silica-supported α-$[Os(CO)_3Cl_2]_2$ (2 wt % Os/SiO_2) is heated at 150 °C under 1 atm of H_2, some sublimation of α-$[Os(CO)_3Cl_2]_2$ occurs, while unreacted α-$[Os(CO)_3Cl_2]_2$ is left on the silica surface. At higher temperatures (200 °C), α-$[Os(CO)_3Cl_2]_2$ sublimes along with traces of $[H_4Os_4(CO)_{12}]$ while the initially white silica powder becomes pale gray and shows a very weak and broad carbonyl band at about 2024 cm^{-1}, similar to that at 2030 cm^{-1} reported for CO adsorbed on metallic osmium supported on silica.[9]

However, treatment of silica-supported α-$[Os(CO)_3Cl_2]_2$ (2 wt % Os/SiO_2) with a slurry of Na_2CO_3 in dichloromethane (molar ratio Na_2CO_3:Os = 2:1) to form the silica-anchored osmium carbonyl species described above, followed by evaporation of the solvent and reaction with 1 atm of H_2 at 150 or 200 °C for 3 days, affords mainly $[H_4Os_4(CO)_{12}]$ along with traces of $[HOs_3(CO)_{10}Cl]$ and minor amounts of $Na_2[Os_{10}C(CO)_{24}]$ (Scheme 1). During the reaction, $[H_4Os_4(CO)_{12}]$ and $[HOs_3(CO)_{10}Cl]$ partially sublime onto the cold part of the walls of the reaction vessel. Extraction of the sublimate and the silica powder with dichloromethane gives $[H_4Os_4(CO)_{12}]$ (isolated yields = 69−70%; Table 1) contaminated by traces of $[HOs_3(CO)_{10}Cl]$ which can be easily removed due to its higher solubility in dichloromethane (see Experimental Section). Further extraction of the silica powder with acetonitrile affords some $Na_2[Os_{10}C(CO)_{24}]$ (17% and 24% yields when the reaction is carried out at 150 and 200 °C, respectively). When the reaction is stopped after 24 h, $[H_4Os_4(CO)_{12}]$ is obtained in only 25% yield, even working at 200 °C. The metal loading effect was investigated. Working at 150 °C under 1 atm of H_2, it turned out that higher yields are obtained with a loading of 15 wt % Os/SiO_2 than with 2 wt % Os/SiO_2 (83% yield compared to 70% yield, respectively; Table 1). With the higher metal loading, only minor amounts of $Na_2[Os_{10}C(CO)_{24}]$ (ca. 4%) are produced, together with traces of $[HOs_3(CO)_{10}Cl]$. After the extraction process, weak carbonyl bands (2114 (vvw), 2016 (w), 1934 (w) cm^{-1}) remain in the infrared spectrum of the beige silica powder.

The synthesis of $[H_4Os_4(CO)_{12}]$ was also investigated starting directly from silica-supported $OsCl_3$. When a slurry of silica-supported $OsCl_3$ (2 wt % Os/SiO_2) in dichloromethane is treated with Na_2CO_3 (molar ratio Na_2CO_3:Os = 10:1) and, after evaporation of the solvent, reacted with 10 atm of a mixture CO + H_2 (1:3) at 200 °C for 24 h, $[H_4Os_4(CO)_{12}]$ is obtained along with some $[Os_3(CO)_{12}]$. During the reaction, $[Os_3(CO)_{12}]$ (ca. 10% yield) and minor amounts of $[H_4Os_4(CO)_{12}]$ sublime on the colder part of the walls of the glass lining of the autoclave, while extraction of the silica powder with dichloromethane affords pure $[H_4Os_4(CO)_{12}]$ (53% yield; Table 1). The cluster $Na_2[Os_{10}C(CO)_{24}]$ is not formed under these conditions, as shown by the failure to extract any anionic cluster with acetonitrile. After extraction, the infrared spectrum of the pale pink silica shows two weak carbonyl bands at about 2021 (w) and 1938 (w) cm^{-1}. The sublimate mixture of $[Os_3(CO)_{12}]$ and $[H_4Os_4(CO)_{12}]$ can be further supported on silica (2 wt %

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Table 1. Synthesis of Neutral Osmium Carbonyl Clusters on the Silica Surface in the Presence of Alkali Carbonates

starting material	M/SiO$_2$ wt %	base	molar ratio M$_2$CO$_3$:Os	gas	P, atm	T, °C	t, h	[Os$_3$(CO)$_{12}$], mg^{a} (yield, %)	[H$_4$Os$_4$(CO)$_{12}$], mg^{a} (yield, %)
α-[Os(CO)$_3$Cl$_2$]$_2$	2	Na$_2$CO$_3$	2:1	CO	1	200	24	245 (39)	traces
	2	Na$_2$CO$_3$	2:1	CO	1	200	72	252 (82)^{b}	traces
	15	Na$_2$CO$_3$	2:1	CO	1	200	72	266 (76)^{b}	traces^{c,d}
	2	Na$_2$CO$_3$	10:1	CO	1	200	72	320 (81)^{b}	traces
	2	Na$_2$CO$_3$	2:1	CO	10	200	24	264 (90)	traces
OsCl$_3$·3H$_2$O	2	Na$_2$CO$_3$	10:1	CO	10	200	24	111 (33)	traces
	2	Na$_2$CO$_3$	10:1	CO	20	200	72	74 (40)	traces
Os(CO)$_3$Cl$_2$(HOSi≡)^{e}	2	Na$_2$CO$_3$	2:1	CO	1	200	72	99 (64)^{d}	0
α-[Os(CO)$_3$Cl$_2$]$_2$	2	Na$_2$CO$_3$	2:1	H$_2$	1	150	72	0	155 (70)^{b,d}
	15	Na$_2$CO$_3$	2:1	H$_2$	1	150	72	0	143 (83)^{b,d}
	2	Na$_2$CO$_3$	2:1	H$_2$	1	200	24	0	137 (25)
	2	Na$_2$CO$_3$	2:1	H$_2$	1	200	72	0	220 (69)^{b,d}
OsCl$_3$·3H$_2$O	2	Na$_2$CO$_3$	10:1	CO/ H$_2$^{f}	10	200	24	14 (ca. 10)^{g}	70 (53)
Os(CO)$_3$Cl$_2$(HOSi≡)^{e}	15	K$_2$CO$_3$	15:1	CO	1	150	24	0	158 (76)^{h}

[a] Actual weight of isolated cluster. [b] Minor amounts of [Os$_{10}$C(CO)$_{24}$]$^{2-}$ are also formed during the reaction. [c] Traces of [HOs$_3$(CO)$_{10}$OH] were also formed during the reaction. [d] Traces of [HOs$_3$(CO)$_{10}$Cl] were also formed during the reaction. [e] Prepared on the surface by reductive carbonylation of silica-supported OsCl$_3$·3H$_2$O. [f] CO/H$_2$ = 1/3. [g] Contaminated by some [H$_4$Os$_4$(CO)$_{12}$]. [h] During the reaction with CO, silica-supported K[H$_3$Os$_4$(CO)$_{12}$] is formed; extraction with CH$_2$Cl$_2$ containing concentrated H$_2$SO$_4$ affords [H$_4$Os$_4$(CO)$_{12}$].

Table 2. Synthesis of Anionic Osmium Carbonyl Clusters on the Silica Surface in the Presence of Alkali Carbonates

starting material^{a}	base	molar ratio M$_2$CO$_3$:Os	gas^{b}	T, °C	t, h	[H$_3$Os$_4$(CO)$_{12}$]$^{-}$, mg^{c} (yield, %)	[H$_2$Os$_4$(CO)$_{12}$]$^{2-}$, mg^{c} (yield, %)	[Os$_5$C(CO)$_{14}$]$^{2-}$, mg^{c} (yield, %)	[Os$_{10}$C(CO)$_{24}$]$^{2-}$, mg^{c} (yield, %)
α-[Os(CO)$_3$Cl$_2$]$_2$	Na$_2$CO$_3$	10:1	H$_2$	200	24	traces	0	0	122 (81)^{d}
	K$_2$CO$_3$	10−20:1	CO	150	24	99 (91)^{e,f}	0	0	0
	K$_2$CO$_3$	20:1	CO	200	48	0	228 (92)^{f}	0	0
	K$_2$CO$_3$	20:1	CO	265	48	0	0	88 (74)	traces

[a] Os/SiO$_2$ = 2 wt %. [b] 1 atm. [c] Actual weight of isolated cluster. [d] [H$_4$Os$_4$(CO)$_{12}$] (4%) was also formed during the reaction; using 15 wt % Os/SiO$_2$, [Os$_{10}$C(CO)$_{24}$]$^{2-}$ and [H$_4$Os$_4$(CO)$_{12}$] were obtained in 39% and 33% yields, respectively. [e] See ref 4. [f] Similar yields are obtained with 15 wt % Os/SiO$_2$.

Os/SiO$_2$) and treated with 1 atm of H$_2$ at 100 °C for 48 h, affording an additional 7% yield of pure [H$_4$Os$_4$(CO)$_{12}$][2] after extraction with dichloromethane. The combined [H$_4$Os$_4$(CO)$_{12}$] yield is therefore 60%. Increasing the amount of CO in the gas mixture (e.g. ratio CO:H$_2$ = 1:1) causes an increase of the quantity of [Os$_3$(CO)$_{12}$], which sublimes.

Yields, reported in Table 1, are comparable to that of the surface-mediated synthesis starting from [Os$_3$(CO)$_{12}$] (68% yield)[2] or to that of the more conventional synthesis in solution,[12] which requires 120 atm of H$_2$ pressure. Both the new surface-mediated syntheses of [H$_4$Os$_4$(CO)$_{12}$] reported here use starting materials such as OsCl$_3$ or α-[Os(CO)$_3$Cl$_2$]$_2$, more easily available than [Os$_3$(CO)$_{12}$].

We studied also a method involving the direct protonation of [H$_3$Os$_4$(CO)$_{12}$]$^{-}$. When silica-supported K[H$_3$Os$_4$(CO)$_{12}$], obtained by a two-step synthesis according to ref 4, is extracted with dichloromethane acidified with a few drops of concentrated H$_2$SO$_4$, the anionic cluster [H$_3$Os$_4$(CO)$_{12}$]$^{-}$ is converted to [H$_4$Os$_4$(CO)$_{12}$] (76% total yield of [H$_4$Os$_4$(CO)$_{12}$] with respect to OsCl$_3$, with a metal loading of 15 wt % Os/SiO$_2$; Table 1). This latter method, which involves three steps in one reactor, is the best way to prepare [H$_4$Os$_4$(CO)$_{12}$] directly from OsCl$_3$, working under mild conditions (atmospheric pressure, relatively low temperatures). Since it can be carried out with high surface loadings, it can be applied for larger scale preparations.

Synthesis of [Os$_{10}$C(CO)$_{24}$]$^{2-}$. A few years ago, Gates et al.[1] reported that treatment of [H$_2$OsCl$_6$] adsorbed on MgO with CO + H$_2$ (1 atm) at 275 °C for 5 h affords [Os$_{10}$C(CO)$_{24}$]$^{2-}$, which can be isolated in 65% yield by cation metathesis with [PPN]Cl in acetone. The yield of [Os$_{10}$C(CO)$_{24}$]$^{2-}$ is equivalent to that obtained in conventional syntheses in solution by reaction of [Os$_3$(CO)$_{12}$] with Na (in tetraglyme, 230 °C, 70 h)[13] or by pyrolysis of [Os$_3$(CO)$_{11}$(C$_5$H$_5$N)] (vacuum, sealed tube, 250 °C, 64 h).[14] However, some [Os$_{10}$C(CO)$_{24}$]$^{2-}$ is always retained by the MgO surface after extraction, perhaps entrapped by the MgO matrix, thus reducing the isolated yield of the anionic cluster.[1] Since we observed that the anionic cluster [H$_3$Os$_4$(CO)$_{12}$]$^{-}$ is not entrapped by the silica matrix, even in the presence of excess K$_2$CO$_3$, we investigated the synthesis of [Os$_{10}$C(CO)$_{24}$]$^{2-}$ on a silica surface treated with alkali carbonates.

We found that treatment of the silica-grafted osmium carbonyl species, prepared as above (2 wt % Os/SiO$_2$; molar ratio Na$_2$CO$_3$:Os = 10:1), with 1 atm of H$_2$ at 200 °C for 24 h affords [Os$_{10}$C(CO)$_{24}$]$^{2-}$ in excellent yield (81% yield; Table 2) along with minor amounts of [H$_4$Os$_4$(CO)$_{12}$] (4% yield) and [H$_3$Os$_4$(CO)$_{12}$]$^{-}$ (traces). The small amounts of [H$_4$Os$_4$(CO)$_{12}$] are easily extracted from silica with dichloromethane. Further extraction with acetonitrile removes both the anionic clusters. During this second extraction process, some acetamide is catalytically formed,[15] which remains with the anionic clusters after evaporation of the acetonitrile. Treatment of the residue with dichloromethane removes the acetamide and the minor amounts of [H$_3$Os$_4$(CO)$_{12}$]$^{-}$ which appears to be more soluble in the presence of the acetamide (see Experimental Section).This is a convenient way to prepare [Os$_{10}$C(CO)$_{24}$]$^{2-}$, since yields are higher and reaction conditions are milder than those previously reported.[1,13,14]

It is worth to point out that only minor amounts of [Os$_{10}$C(CO)$_{24}$]$^{2-}$ were obtained along with [H$_4$Os$_4$(CO)$_{12}$] when the molar ratio Na$_2$CO$_3$:Os was 2:1 instead of 10:1 (Table 1).

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As expected from the positive metal loading effect on the synthesis of $[H_4Os_4(CO)_{12}]$ reported above, increasing the osmium loading favors the formation of $[H_4Os_4(CO)_{12}]$ at the expense of $[Os_{10}C(CO)_{24}]^{2-}$. Treatment of the silica-grafted osmium carbonyl species prepared as above (15 wt % Os/SiO$_2$; molar ratio Na_2CO_3:Os = 10:1) with 1 atm of H_2 at 200°C for 24 h affords $[Os_{10}C(CO)_{24}]^{2-}$ and $[H_4Os_4(CO)_{12}]$ in 39% and 33% yields, respectively.

Synthesis of $[H_2Os_4(CO)_{12}]^{2-}$. It is known that $[H_4Os_4(CO)_{12}]$ is readily deprotonated by KOH in methanol to form the soluble monoanion $[H_3Os_4(CO)_{12}]^-$.[12] However, removal of a second proton by a base is difficult,[16] and there is no report of the preparation of $[H_2Os_4(CO)_{12}]^{2-}$ by this route. This dianionic tetraosmium cluster was prepared for the first time in 39% yield by reduction of $[Os_3(CO)_{12}]$ with sodium borohydride in refluxing dioxane.[17] More recently, Gates et al.[16] reported that deprotonation of $[H_4Os_4(CO)_{12}]$ at room temperature on highly dehydroxylated MgO gives a mixture of the supported clusters $[H_3Os_4(CO)_{12}]^-$ and $[H_2Os_4(CO)_{12}]^{2-}$.

The absence of a high-yield synthesis of $[H_2Os_4(CO)_{12}]^{2-}$ in the literature and the fact that $[H_3Os_4(CO)_{12}]^-$ can be obtained easily under mild conditions on a silica surface treated with K_2CO_3[4] prompted us to investigate a possible route to this dianionic osmium cluster using the silica surface as reaction medium in the presence of an excess of base and working under more drastic conditions. We found that yellow $K_2[H_2Os_4(CO)_{12}]$ is obtained in 92% isolated yield (Table 2) when a mixture of silica, α-$[Os(CO)_3Cl_2]_2$ (2−15 wt % Os/SiO$_2$), K_2CO_3 (molar ratio K_2CO_3:Os = 20:1), and dichloromethane is stirred for 2 days, dried, and then reacted with CO (1 atm) at 200 °C for 48 h. The anion $[H_2Os_4(CO)_{12}]^{2-}$, which is unstable in air,[16,17] must be removed from the silica surface by extraction under anhydrous N_2, using anhydrous acetonitrile as solvent. This rather unstable anionic cluster was characterized by the known infrared and ^{1}H NMR spectra (see Experimental Section) as well as by its reaction with H_2SO_4 which affords pure $[H_4Os_4(CO)_{12}]$. If the reaction is carried out for only 24 h, a mixture of $K[H_3Os_4(CO)_{12}]$ and $K_2[H_2Os_4(CO)_{12}]$ is obtained, confirming that the monoanion is the intermediate species.

This surface-mediated synthesis is by far the best known method to prepare $[H_2Os_4(CO)_{12}]^{2-}$ in excellent yield and with high selectivity (92% yield compared to the 39% yield of the conventional synthesis in solution[17]).

Synthesis of $[Os_5C(CO)_{14}]^{2-}$. The best route to the dianionic cluster $[Os_5C(CO)_{14}]^{2-}$ has been reported by Gates et al. to be by reaction of MgO-supported $[Os_3(CO)_{12}]$ with CO (1 atm) at 275°C for 4 h (isolated yield = 65%).[1] The synthesis is simpler and more efficient than the best method in solution (pyrolysis of $[Os_3(CO)_{12}]$ to give $[Os_5C(CO)_{15}]$ followed by reduction in alcoholic base to give $[Os_5C(CO)_{14}]^{2-}$ in low global yields[18]).

Using the silica surface as a reaction medium, $[Os_5C(CO)_{14}]^{2-}$ can be obtained in relatively high yields starting directly from α-$[Os(CO)_3Cl_2]_2$. Treatment of the silica-anchored osmium carbonyl species, prepared as above (2% wt Os/SiO$_2$; molar ratio K_2CO_3:Os = 20:1), with 1 atm of CO at 265 °C for 2 days affords $[Os_5C(CO)_{14}]^{2-}$ in 74% isolated yield (Table 2).

In order to selectively obtain $[Os_5C(CO)_{14}]^{2-}$, it is important to avoid too much surface water which favors the parallel formation of $[Os_{10}C(CO)_{24}]^{2-}$ (see Experimental Section).

Conclusion

This work gives additional experimental evidence of the potential of the silica surface as a new reaction medium for selective and high-yield syntheses of metal carbonyl complexes and clusters. First of all, the use of a solid as a reaction medium is not limited as in solution by boiling points; therefore, it is possible to work at atmospheric pressure even at relatively high temperatures. In addition, the isolation of the final products is generally easy: neutral and anionic species can be totally extracted with a suitable solvent.

The silica surface behaves usually as a relatively neutral solvent such as an alcohol, favouring the synthesis of neutral carbonyl species. As an alcohol, it may act as a "donor solvent" via surface silanol groups which, by interaction with the coordination sphere of metal atoms, influences both reactivity and selectivity.[3,19] It follows that, in a few cases, very high metal loadings must be avoided as they lead to side reactions, due to the lack of available surface silanol groups,[3] but this limitation is not very often relevant.

We confirmed that the addition of an alkali carbonate to the silica surface may also lead to the synthesis of anionic species, the surface basicity being controlled by the amount and the nature of the alkali carbonate and by the temperature. There is clear evidence that the basicity of the silica surface increases considerably with the amount of base added and going from Na_2CO_3 to K_2CO_3. The role of the cation in controlling the strength of a base is well known in organic chemistry; for instance, potassium alkoxides are much more basic than sodium alkoxides in poorly solvating solvents such as *tert*-butyl alcohol.[20] It is however surprising that super basic properties which, for instance, are necessary to produce $[H_2Os_4(CO)_{12}]^{2-}$ in solution or on the MgO surface, can be reached so easily on the silica surface, although at relatively high temperatures (200 °C).

The nature of the base added to silica is of paramount importance: in the case of the silica-mediated synthesis of $[H_3Os_4(CO)_{12}]^-$, preliminary results showed that the use of NaOH or KOH instead of K_2CO_3 (same K:Os molar ratio) leads to a very low surface reactivity and to a lack of selectivity, affording only low yields of the desired anionic osmium cluster.[4]

From a synthetic point of view, an attractive feature of the silica surface is that the alkali carbonate may be added at any time of a multistep surface synthesis (as starting from $OsCl_3$). This useful tool does not exist with an intrinsic basic surface such as MgO. Syntheses of $[Os_3(CO)_{12}]$, $[H_4Os_4(CO)_{12}]$, $[H_3Os_4(CO)_{12}]^-$, and $[H_2Os_4(CO)_{12}]^{2-}$ are not limited by the osmium loadings. Actually, higher yields of $[H_4Os_4(CO)_{12}]$ are obtained with a loading of 15 wt % Os/SiO$_2$ than with 2 wt % Os/SiO$_2$. However, like some other silica-mediated syntheses previously reported,[3] the synthesis of $[Os_{10}C(CO)_{24}]^{2-}$ is less selective at high metal loadings. It must be pointed out that at high metal loadings (for instance 15 wt % Os/SiO$_2$) there are not enough active surface silanol groups to convert all the physisorbed α-$[Os(CO)_3Cl_2]_2$ into surface-anchored osmium carbonyl species.[3] It follows that the surface organometallic chemistry involved in these surface-mediated syntheses of metal carbonyl clusters in the presence of alkali carbonates is far from being fully understood. We are currently working in order to reach a better knowledge of this surface chemistry.

Finally, the silica-mediated syntheses reported here have some appeal from a synthetic point of view since $OsCl_3$ and even

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α-$[Os(CO)_3Cl_2]_2$ are convenient starting materials for cluster synthesis, particularly when yields and reaction conditions are respectively better and milder than those of the reported syntheses in solution, which often require metal carbonyl clusters as starting materials. In addition, the possibility of working at high metal loadings without affecting yields and selectivities often offers a way to prepare sizable amounts of osmium carbonyl clusters, usually difficult to prepare, without requiring the use of large amounts of silica.

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. $OsCl_3{\cdot}3H_2O$ was purchased from Aldrich Chemicals, while α-$[Os(CO)_3Cl_2]_2$ was prepared according to the literature.[22] All the reaction products were identified, after extraction from the support, by infrared, proton nuclear magnetic resonance (when appropriate), and mass spectroscopies, their spectra being compared to those of pure samples. Infrared spectra were recorded on a Nicolet MX-1 FT spectrometer, while a VG analytical 7070EQ spectrometer was used for mass spectral determinations. ^1H NMR were run at 27 °C on a Bruker AC 200 spectrometer, using tetramethylsilane as reference.

Preparation of Silica-Supported $OsCl_3{\cdot}3H_2O$. In a typical preparation, a suspension of silica (4.14 g), $OsCl_3.3H_2O$ (0.152 g; 0.435 mmol; 2% by weight Os/SiO_2), and H_2O (80 mL) was stirred overnight in a two-necked flask, working under nitrogen and at room temperature. The solvent was evaporated under vacuum (10^{-2} Torr) using a water bath at 80 °C. The resulting silica-supported $OsCl_3{\cdot}3H_2O$ was stored under nitrogen.

Grafting of α-$[Os(CO)_3Cl_2]_2$ to the Silica Surface. In a typical preparation, a suspension of silica (9.32 g), α-$[Os(CO)_3Cl_2]_2$ (the correct amount to have the desired osmium loading, 2 or 15 wt % Os/SiO_2), Na_2CO_3 or K_2CO_3 (the correct amount to have the desired molar ratio M_2CO_3:Os), and degassed CH_2Cl_2 (250 mL) was stirred under nitrogen in a two-necked flask for 2 days working at room temperature. The solvent was evaporated at room temperature in vacuo (10^{-2} Torr) affording a white powder of a surface osmium carbonyl species, which was stored under nitrogen. The grafting to the silica surface is suggested by its infrared spectrum (see Results and Discussion) and by the lack of extraction with different solvents (CH_2Cl_2, EtOH, CH_3CN, etc.).

Synthesis of $[Os_3(CO)_{12}]$ from α-$[Os(CO)_3Cl_2]_2$. In a typical experiment the silica-grafted osmium carbonyl species, obtained from α-$[Os(CO)_3Cl_2]_2$ as described above, using a molar ratio Na_2CO_3:Os = 2:1 (10.31 g of powder; 2 wt % Os/SiO_2; 0.194 g of Os; 1.02 mmol of Os), was transferred into the cylindrical Pyrex vessel (diameter 60 mm, length 350 mm) previously described for the reductive carbonylation of silica-supported metal chlorides at atmospheric pressure.[3] It was treated in vacuo (10^{-2} Torr) at room temperature and then exposed to CO at atmospheric pressure. The bottom of the vessel (about half of the cylinder) was put into an oven and heated at 200 °C for 3 days. During the reaction, most of the $[Os_3(CO)_{12}]$ sublimed onto the cold part of the reaction vessel. Extraction of the sublimate and the silica powder, mixed together, with dichloromethane (150 mL) in a Soxhlet, followed by evaporation of the solvent, afforded $[Os_3(CO)_{12}]$ sometimes contaminated by traces of $[H_4Os_4(CO)_{12}]$ and an unidentified brownish impurity. Traces of $[HOs_3(CO)_{10}X]$ (X = Cl, OH) were also observed using a loading of 15 wt % Os/SiO_2. These impurities are much more soluble in dichloromethane than $[Os_3(CO)_{12}]$ allowing an easy separation. Thus, pure yellow $[Os_3(CO)_{12}]$ (0.252 g; 0.278 mmol; 82% yield) was obtained by washing the residue with a small amount of dichloromethane (ca. 1 mL). Working with a loading of 15 wt % Os/SiO_2 (2.55 g of powder; 0.266 g of Os; 1.40 mmol of Os), a 76% yield of $[Os_3(CO)_{12}]$ (0.321 g; 0.354 mmol) was obtained. The purity of $[Os_3(CO)_{12}]$ was controlled by thin-layer chromatography, mass spectroscopy, and infrared spectroscopy.[11] The polynuclear hydrides obtained as impurities were identified by their infrared (in CH_2Cl_2) and ^1H NMR (in $CDCl_3$) spectra.[2,23−26] Further extraction of the remaining silica powder with acetonitrile afforded traces of $Na_2[Os_{10}C(CO)_{24}]$, characterized by its infrared spectrum in CH_3CN.[1] After the extraction with both CH_2Cl_2 and CH_3CN, weak carbonyl bands at 2120 (vvw) and 2021 cm^{-1} (w) remained on the white silica powder.

Since the reductive carbonylation at atmospheric pressure is carried out under static CO (i.e. in a closed vessel), the cylindrical Pyrex vessel used for the reaction should be big enough (about 1 L in the previously described synthesis) to keep a CO pressure of about 1 atm until the reaction is completed; if the vessel is too small, the CO pressure becomes inferior to 1 atm during the reaction, resulting in lower yields of $[Os_3(CO)_{12}]$ and some unreacted silica-anchored osmium(II) carbonyl species. This point must be taken into account when working at high metal loadings.

The surface synthesis of $[Os_3(CO)_{12}]$ was also investigated under CO pressure. In this latter case, the sample containing the silica-anchored osmium(II) carbonyl species (2 wt % Os/SiO_2) was placed in a stainless steel autoclave containing a glass liner. The autoclave was closed, purged twice with N_2, evacuated, pressurized to 10 atm of CO, and heated at 200 °C for 24 h. After the sample was cooled to room temperature, the pressure was released slowly and the autoclave opened. Purification as above afforded pure $[Os_3(CO)_{12}]$ (0.264 g; 90% yield).

Synthesis of $[Os_3(CO)_{12}]$ from Silica-Supported $OsCl_3{\cdot}3H_2O$. In a typical experiment, silica-supported $OsCl_3{\cdot}3H_2O$ (prepared as described above; 5.65 g of powder; 2 wt % Os/SiO_2; 0.109 g Os; 0.574 mmol Os), Na_2CO_3 (0.603 g; 5.69 mmol; molar ratio Na_2CO_3:Os = 10:1), and CH_2Cl_2 (150 mL) were stirred at room temperature under N_2 for 2 days. The slurry was dried under vacuum (10^{-2} Torr). The resulting powder was placed in a stainless steel autoclave containing a glass liner. The autoclave was closed, purged twice with N_2, evacuated, pressurized to 20 atm of CO, and heated at 200 °C for 3 days. After the mixture cooled to room temperature, the pressure was released slowly and the autoclave opened. Purification as above afforded pure $[Os_3(CO)_{12}]$ (0.074 g; 0.082 mmol; 40% yield). After extraction, two weak carbonyl bands remained on the pale gray silica powder (ν(CO) = 2022 (w), 1938 (w) cm^{-1}).

Synthesis of $[Os_3(CO)_{12}]$ from Silica-Supported $OsCl_3{\cdot}3H_2O$ via Silica-Bound $[Os(CO)_3Cl_2(HOSi{\equiv})]$. In a typical experiment, silica-supported $OsCl_3{\cdot}3H_2O$ (prepared as described above; 5.29 g of powder; 2 wt % Os/SiO_2; 0.103 g Os; 0.542 mmol Os) was heated in the closed vessel at 180 °C under CO (1 atm) until the silica powder became completely white (2 days). After CO evacuation at room temperature, CH_2Cl_2 (100 mL) and Na_2CO_3 (0.115 g; 1.08 mmol; molar ratio Na_2CO_3:Os = 2:1) were added, and the suspension was stirred at room temperature under N_2 for 2 days. The slurry was dried under vacuum (10^{-2} Torr), affording a surface osmium carbonyl species whose infrared spectrum was similar to that of the silica-grafted osmium carbonyl species obtained by direct treatment of physisorbed α-$[Os(CO)_3Cl_2]_2$ as described above. The reaction vessel was exposed to CO at atmospheric pressure, closed, and heated at 200 °C for 3 days. Purification as above afforded pure $[Os_3(CO)_{12}]$ (0.099 g; 0.109 mmol; 64% yield).

Synthesis of $[H_4Os_4(CO)_{12}]$ from α-$[Os(CO)_3Cl_2]_2$. In a typical experiment the silica-grafted osmium carbonyl species, prepared from α-$[Os(CO)_3Cl_2]_2$ as described above with a molar ratio Na_2CO_3:Os = 2:1 (1.14 g of powder; 15 wt % Os/SiO_2; 0.118 g of Os; 0.622 mmol of Os), was transferred into the cylindrical Pyrex vessel described previously and heated under H_2 (1 atm) at 200 °C for 3 days. During the reaction a pale yellow powder sublimed onto the cold part of the reaction vessel. Extraction of the sublimate and the silica powder with dichloromethane (150 mL) in a Soxhlet, followed by evaporation of the solvent, afforded crude $[H_4Os_4(CO)_{12}]$ (0.155 g; 0.140 mmol; 90% crude yield) contaminated with traces of $[HOs_3(CO)_{10}Cl]$, which were

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easily removed by washing the residue with small amounts of dichloromethane (ca. 2 mL). Pure $[H_4Os_4(CO)_{12}]$ (0.143 g; 0.130 mmol; 83% yield) was thus obtained. Its infrared spectrum in CH_2Cl_2 and its ^1H NMR spectrum in $CDCl_3$ were in agreement with that of a pure sample;[2,23] $[HOs_3(CO)_{10}Cl]$ was identified by its infrared spectrum in CH_2Cl_2 and by its ^1H NMR spectrum in $CDCl_3$.[24,25] Further extraction of the silica powder with acetonitrile afforded $Na_2[Os_{10}C(CO)_{24}]$ (0.006 g; 0.002 mmol; ca. 4% yield) characterized by its infrared spectrum in CH_3CN, which was identical to that of a pure sample.[1] After the extraction process, weak carbonyl bands remain on the beige silica powder at 2114 (vvw), 2016 (w), and 1934 (w) cm^{-1}.

Synthesis of $[H_4Os_4(CO)_{12}]$ from Silica-Supported $OsCl_3 \cdot 3H_2O$. In a typical experiment, silica-supported $OsCl_3 \cdot 3H_2O$ (prepared as above described; 4.67 g of powder; 2 wt % Os/SiO_2; 0.091 g Os; 0.476 mmol Os), Na_2CO_3 (0.507 g; 4.78 mmol; molar ratio $Na_2CO_3:Os = 10:1$), and CH_2Cl_2 (150 mL) were stirred at room temperature under N_2 for 2 days. The slurry was dried under vacuum (10^{-2} Torr). The resulting powder was placed in a stainless steel autoclave containing a glass liner. The autoclave was closed, purged twice with N_2, evacuated, pressurized to 10 atm of CO/H_2 (molar ratio 1:3), and heated at 200 °C for 24 h. After cooling of the sample to room temperature, the pressure was released slowly and the autoclave opened. During the reaction all the $[Os_3(CO)_{12}]$ produced (0.014 g; 0.015 mmol; ca. 10% yield) and minor amounts of $[H_4Os_4(CO)_{12}]$ sublimed onto the colder part of the glass liner in the autoclave. Extraction of the silica powder with dichloromethane (100 mL) in a Soxhlet afforded pure $[H_4Os_4(CO)_{12}]$ (0.070 g; 0.064 mmol; 53% yield). After the extraction process, the infrared spectrum of the pale pink silica showed weak carbonyl bands at 2021 (w) and 1938 (w) cm^{-1}.

Synthesis of $[H_4Os_4(CO)_{12}]$ from Silica-Supported $OsCl_3 \cdot 3H_2O$ via Silica-Bound $[Os(CO)_3Cl_2(HOSi\equiv)]$ and Silica-Supported $K[H_3Os_4(CO)_{12}]$. In a typical experiment, silica-supported $OsCl_3 \cdot 3H_2O$ (prepared as above described; 1.23 g of powder; 15 wt % Os/SiO_2; 0.144 g Os; 0.758 mmol Os) was heated in the cylindrical Pyrex vessel at 180 °C under CO (1 atm) until the silica powder became completely white (2 days). After CO evacuation at room temperature, CH_2Cl_2 (100 mL) and K_2CO_3 (1.57 g; 11.4 mmol; molar ratio $K_2CO_3:Os = 15:1$) were added, and the suspension was stirred at room temperature under N_2 for 2 days. The slurry was dried under vacuum (10^{-2} Torr), affording a silica surface osmium carbonyl species whose infrared spectrum was similar to that of the surface osmium carbonyl species obtained by direct treatment of α-$[Os(CO)_3Cl_2]_2$ on the silica surface as described above. The reaction vessel was exposed to CO at atmospheric pressure, closed, and heated at 150 °C for 24 h, affording the species $K[H_3Os_4(CO)_{12}]$.[4] The silica powder was then treated with CH_2Cl_2 (150 mL) and concentrated H_2SO_4 (9 drops), and the suspension was stirred overnight. Then the suspension was transferred into a Soxhlet apparatus and extracted with an additional 50 mL of CH_2Cl_2, affording a solution of $[H_4Os_4(CO)_{12}]$ contaminated with traces of $[HOs_3(CO)_{10}Cl]$. Evaporation of the solvent, followed by washing with dichloromethane (ca. 2 mL, to remove $[HOs_3(CO)_{10}Cl]$) afforded pure $[H_4Os_4(CO)_{12}]$ (0.158 g; 0.143 mmol; 76% yield). Infrared showed that there were no carbonyl bands on the remaining white silica.

Synthesis of $[Os_{10}C(CO)_{24}]^{2-}$ from α-$[Os(CO)_3Cl_2]_2$. In a typical experiment the surface osmium carbonyl species (2 wt % Os/SiO_2), prepared from α-$[Os(CO)_3Cl_2]_2$ as described above with a molar ratio $Na_2CO_3:Os = 10:1$ (6.23 g of powder; 0.108 g of Os; 0.568 mmol of Os), was transferred into the cylindrical Pyrex vessel described previously[3] and heated under H_2 (1 atm) at 200 °C for 24 h. During the reaction a pale yellow powder sublimed onto the cold part of the reaction vessel. Extraction of the sublimate and of the resulting pink silica powder with dichloromethane (150 mL) in a Soxhlet afforded $[H_4Os_4(CO)_{12}]$ (ca. 4% yield). Further extraction with acetonitrile (100 mL), followed by evaporation of the solvent, yielded $Na_2[Os_{10}C(CO)_{24}]$ contaminated with some $Na[H_3Os_4(CO)_{12}]$ and acetamide. Treatment of this mixture with dichloromethane (ca. 5 mL) removed the acetamide and $Na[H_3Os_4(CO)_{12}]$, which seems to be more soluble in the presence of the acetamide. Pure $Na_2[Os_{10}C(CO)_{24}]$ (0.122 g; 0.046 mmol; 81% yield) was thus obtained, its purity being confirmed by thin-layer chromatography. Its infrared spectrum in CH_3CN was identical to that of a pure sample.[1] Moreover, its fast atom bombardment mass spectrum, using nitrobenzyl alcohol as the matrix, clearly showed the molecular ion peak of $[Os_{10}C(CO)_{24}]^{2-}$ at $m/e = 2586$. After the extraction process, the infrared spectrum showed weak carbonyl bands remaining on the white silica powder at 2117 (vvw), 2021 (w) and 1938 (w) cm^{-1}. The selectivity decreases when this synthesis is carried out at high metal loadings, the amount of $[H_4Os_4(CO)_{12}]$ being much higher (see Results and Discussion).

Synthesis of $[H_2Os_4(CO)_{12}]^{2-}$ from α-$[Os(CO)_3Cl_2]_2$. In a typical experiment the surface osmium carbonyl species (2 wt % Os/SiO_2), prepared from α-$[Os(CO)_3Cl_2]_2$ as described above with a molar ratio $K_2CO_3:Os = 20:1$ (10.62 g of powder; 0.160 g of Os; 0.842 mmol of Os), was placed into the cylindrical Pyrex vessel described previously[3] and heated under CO (1 atm) at 200 °C for 2 days. The resulting yellow-orange silica powder was transferred to a Pyrex Buchner filter funnel under nitrogen and extracted with acetonitrile (ca. 200 mL, dried over 4 Å molecular sieves activated in vacuo at 300 °C). Evaporation of the solvent in vacuo (10^{-2} Torr) at room temperature afforded pure $K_2[H_2Os_4(CO)_{12}]$ (0.228 g; 0.194 mmol; 92% yield) which must be kept under nitrogen. Its infrared spectrum in CH_3CN and its ^1H NMR spectrum in CD_3CN were in quite good agreement with the literature data.[17] Moreover, addition of 9 drops of concentrated H_2SO_4 to an acetonitrile solution of this product (100 mL for about 0.228 g) precipitated pure $[H_4Os_4(CO)_{12}]$ (71% yield), as shown by ^1H NMR and IR spectroscopies.[2,23] No carbonyl band was visible in the infrared spectrum of the pale gray silica after the extraction process.

Synthesis of $[Os_5C(CO)_{14}]^{2-}$ from α-$[Os(CO)_3Cl_2]_2$. In a typical experiment the surface osmium carbonyl species (2 wt % Os/SiO_2), prepared from α-$[Os(CO)_3Cl_2]_2$ as described above with a molar ratio $K_2CO_3:Os = 20:1$ (5.27 g of powder; 0.079 g of Os; 0.414 mmol of Os), was transferred into the cylindrical Pyrex vessel described previously,[3] kept under vacuum (10^{-2} Torr) at room temperature for about 6 h, and then heated under CO (1 atm) at 265 °C for 48 h. The resulting silica powder was transferred to a Pyrex Buchner filter funnel under nitrogen and extracted with acetonitrile (ca. 150 mL, dried over 4 Å molecular sieves activated in vacuo at 300 °C). Evaporation of the solvent in vacuo (10^{-2} Torr) at room temperature afforded yellow brown $K_2[Os_5C(CO)_{14}]$ (0.088 g; 0.061 mmol; 74% yield). In some cases traces of $[Os_{10}C(CO)_{24}]^{2-}$ were also formed. The infrared spectrum of the compound in CH_3CN was in agreement with that reported in the literature for $K_2[Os_5C(CO)_{14}]$.[1] Its fast atom bombardment mass spectrum, using nitrobenzyl alcohol as the matrix, clearly showed the molecular peak at m/e 1434 (corresponding to $K_2[Os_5C(CO)_{14}]$) followed by successive losses of 2K and 8CO. It is known that protonation of $[Os_5C(CO)_{14}]^{2-}$ with H_2SO_4 affords $[H_2Os_5C(CO)_{15}]$;[18] extraction of the silica powder after carbonylation with a solution of [PPN]Cl in CH_2Cl_2 followed by addition of concentrated H_2SO_4 (1 drop) afforded this dihydride as shown by its infrared spectrum in CH_2Cl_2, identical to that reported in the literature.[18] Finally, in this silica-mediated synthesis of $[Os_5C(CO)_{14}]^{2-}$, it is important to emphasize that water favors the formation of $[Os_{10}C(CO)_{24}]^{2-}$ (see Results and Discussion). Thus, if the silica powder, containing the silica-grafted osmium carbonyl surface species described above, is weighed and transferred to the reaction vessel in air, as we usually do, it is important to keep it under vacuum (10^{-2} Torr) at room temperature for about 6 h as described above, in order to remove physisorbed water, before introducing CO.

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