Surface-Mediated Organometallic Synthesis: High-Yield Syntheses of the Anion [H₃Os₄(CO)₁₂]⁻ from [Os(CO)₃Cl₂]₂ or OsCl₃ on the Silica Surface in the Presence of K₂CO₃

Dominique Roberto,*,[†] Elena Cariati,[†] Rinaldo Psaro,[‡] and Renato Ugo[†]

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

Summary: K[H₃Os₄(CO)₁₂] has been prepared in high yields by reductive carbonylation under rather mild conditions (1 atm and 150 °C) of α-[Os(CO)₃Cl₂]₂ or OsCl₃ supported on SiO₂ in the presence of K₂CO₃ (molar ratio K₂CO₃:Os = 10–15:1); in the latter case a two-step process is required. These surface-mediated syntheses of the anionic cluster are more convenient than the traditional ones in solution (higher yields and selectivity) and do not require clusters such as [H₄Os₄(CO)₁₂] or [Os₃(CO)₁₂] as starting materials.

Introduction

In recent years there has been considerable interest in the use of surfaces of inorganic oxides as a new reaction medium for the preparation of metal carbonyl complexes of various nuclearities.[1–3] It appeared that strongly basic surfaces such as MgO favor the formation of anionic metal carbonyl complexes[1,4] while neutral complexes may be prepared on the surface of rather neutral supports such as SiO₂.[2,3]

In our investigations on the reductive carbonylation of silica-supported MCl₃ (M = Ir, Rh, Ru, Os),[3,5,6] we discovered the negative role of HCl produced during the formation of metal carbonyl chlorides for further reduction to metal carbonyl clusters. In order to introduce some basic properties onto a SiO₂ surface, we added NaHCO₃ to SiO₂ under specific experimental conditions, and we observed a positive effect on the formation of metal carbonyl clusters.[6]

Here we report the high-yield synthesis of the anion [H₃Os₄(CO)₁₂]⁻ from α-[Os(CO)₃Cl₂]₂ or OsCl₃ supported on a SiO₂ surface treated with K₂CO₃.

Results and Discussion

Synthesis of K[H₃Os₄(CO)₁₂] from α-[Os(CO)₃Cl₂]₂. When a slurry of SiO₂, α-[Os(CO)₃Cl₂]₂ (2 wt % Os/SiO₂), K₂CO₃ (molar ratio K₂CO₃:Os = 10:1), and CH₂Cl₂ 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 2121 (m), 2029 (s), and 1923 (m) cm⁻¹ quite different from

those reported for α-[Os(CO)₃Cl₂]₂ physisorbed on SiO₂ (2137 (m), 2048 (s) cm⁻¹).[6] Frequencies and trends of the spectrum are close to those reported for the anchored species [Os(CO)ₓ(OSi◁)₂]ₙ (x = 2,3) obtained by thermal degradation in vacuo or under oxygen of the grafted cluster [HOs₃(CO)₁₀(OSi◁)].[7]

The grafting of the organometallic moiety, which surprisingly occurs at room temperature, is supported also by the failure to extract any osmium species by treatment of the solid with solvents (e.g., acetonitrile, acetone, tetrahydrofuran, alcohols). Furthermore, as expected, washing of the sample with water affords free chloride ions. In the absence of base, the grafting reaction does not occur, at least at room temperature. Thus, as already observed when NaHCO₃ is added to silica,[6] the addition of K₂CO₃ seems to favor removal of chloro ligands from the coordination sphere of osmium carbonyl chloride, with parallel anchoring of the organometallic fragments.

Treatment of these white surface-bound carbonyl species with 1 atm of CO at 150 °C for 24 h in a closed reaction vessel affords a new yellow species, as evidenced by the infrared spectrum of the final sample at ν(CO) = 2080 (w), 2044 (s), 2022 (s), 2002 (s), and 1967 (sh) cm⁻¹.

Extraction of this latter surface species with acetonitrile results in a yellow solution, the infrared spectrum of which is identical with that reported for the anion [H₃Os₄-(CO)₁₂]⁻.[8] This species may also be extracted with acetone. In both cases, evaporation of the solvent affords pure K[H₃-Os₄(CO)₁₂] as confirmed by elemental analysis and thin layer chromatography. The identification of K[H₃Os₄-(CO)₁₂] as the product is further confirmed by ¹H NMR and by fast atom bombardment mass spectroscopy (see Experimental Section). Synthetic yields are 79% and 91% after 5 and 24 h, respectively, with a metal loading of 2 wt % Os/SiO₂ (Table 1).

Interestingly, to our knowledge, the silica-surface-mediated synthesis of [H₃Os₄(CO)₁₂]⁻ reported here represents the first example of preparation of an anionic cluster carbonyl species on silica.

In our surface-mediated synthesis the importance of using a liquid phase for the preparation of the sample must be emphasized. In fact, the reductive carbonylation is slower and less selective when the reagents (viz., SiO₂, α-[Os(CO)₃Cl₂]₂, K₂CO₃) are mixed by grinding without solvent. In this case, treatment with CO at 150 °C for 24 h affords only a 51% yield of K[H₃Os₄(CO)₁₂] along with

† Dipartimento di Chimica Inorganica, Metallorganica e Analitica.
‡ Centro CNR.
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Table 1. Synthesis of K[H₃Os₄(CO)₁₂] from [Os(CO)₃Cl₂]₂ or OsCl₃ on the Silica Surface

starting material[a]	gas	P (atm)	T (°C)	t (h)	yield[b] (%)
[Os(CO)₃Cl₂]₂	CO	1	150	5	79
	CO	1	150	24	91
OsCl₃	CO	1	150	120	17
	CO	10	250	30	49
	CO/H₂	10	150	120	59
	CO/H₂	10	250	15	55[c]
Os(CO)₃Cl₂(HOSi<)[d]	CO	1	150	5	74
	CO	1	150	24	92

[a] Os/SiO₂, 2 wt %. [b] Yields are of analytically pure materials. [c] K₂[Os₁₀C(CO)₂₄] was also isolated in 7% yield. [d] Prepared by reductive carbonylation of silica-supported OsCl₃.

5% of [Os₃(CO)₁₂] contaminated with [H₄Os₄(CO)₁₂]. This different behavior may be due to an inefficient, nonhomogeneous distribution of the reagents on the SiO₂ surface. As described above, the most convenient way to obtain a homogeneous distribution is to stir all reagents together in one step with a solvent such as CH₂Cl₂. However, similar selectivity and yields of K[H₃Os₄(CO)₁₂] are obtained when SiO₂ is treated first with K₂CO₃ and water and dried, and then the resultant powder stirred with α-[Os(CO)₃Cl₂]₂ dissolved in CH₂Cl₂.

An interesting aspect of this new method of synthesis is that yields are not limited very much by the osmium loading. Increasing the metal loading up to 30 wt % Os/SiO₂ (molar ratio K₂CO₃:Os always equal to 10:1) slows down the reductive carbonylation but, differently from other syntheses on SiO₂,[3] does not affect yields very much. For example, with osmium loadings of 10% and 30%, 88% and 76% yields of K[H₃Os₄(CO)₁₂] are obtained after 24 h. After extraction with acetonitrile, some unreacted [Os(CO)ₓ(OSi<)₂]ₙ surface species remain on the SiO₂ surface. These may be converted to the anion by further treatment under CO at 150 °C for 24 h, raising the final yield to 92%. These results imply that the surface reactions may involve not only the process of anchoring Os(II) species to the surface, since, with an osmium loading of 30%, there would not be enough surface silanol groups[3] to convert all α-[Os(CO)₃Cl₂]₂ to [Os(CO)ₓ(OSi<)₂]ₙ. Most probably, other intermediate species such as [Os(CO)ₓ(OH)₂]ₙ, not anchored to the SiO₂ surface, are also formed on the surface.[9]

The surface-mediated synthesis of K[H₃Os₄(CO)₁₂] is really a new and simple way to prepare this compound, directly from α-[Os(CO)₃Cl₂]₂. It represents a rather attractive method from a synthetic point of view because yields are not limited very much by metal loading and because the anion is not entrapped by the SiO₂ matrix and may therefore be easily and quantitatively removed from the silica surface.

It is worth noting that this surface method gives better yields and seems to be more convenient than the established syntheses in solution since reaction conditions are mild and they do not require cluster compounds such as [H₄Os₄(CO)₁₂] or [Os₃(CO)₁₂] as starting materials. Indeed, the best synthetic route in solution is by reaction of the cluster [H₄Os₄(CO)₁₂] with KOH in MeOH (75% yield)[8] or by reaction of [Os₃(CO)₁₂] with KOH in refluxing Bu^iOH (45% yield of [H₃Os₄(CO)₁₂]⁻ is obtained along with other osmium clusters).[10,11] Some [H₃Os₄(CO)₁₂]⁻

has also been produced by reductive carbonylation of H₂-OsCl₆ adsorbed on MgO under more drastic conditions (viz., flowing CO + H₂ (equimolar) at 275 °C and 11 atm), but the yield of the isolated pure anion was not specified.[1] Furthermore, studies on the surface reactivity of [H₄Os₄-(CO)₁₂] showed that this neutral cluster hydride is easily deprotonated on hydroxylated MgO[12] and Al₂O₃,[13] affording [H₃Os₄(CO)₁₂]⁻. On highly dehydroxylated MgO a further deprotonation occurs, leading to the dianion [H₂Os₄(CO)₁₂]²⁻.[14]

Synthesis of K[H₃Os₄(CO)₁₂] from OsCl₃. Since [Os(CO)₃Cl₂]₂ may be synthesized by reductive carbonylation of silica-supported OsCl₃ under mild conditions (100–180 °C, 1 atm of CO),[3] it seemed possible to prepare K[H₃Os₄(CO)₁₂] directly from OsCl₃.

Some bonding of osmium species to the surface occurs when OsCl₃ supported on SiO₂ is treated with a dichloromethane slurry of K₂CO₃ (molar ratio K₂CO₃:Os = 15:1) at room temperature. The color of the silica changes from gray-violet to gray, and contrarily to simply physisorbed OsCl₃, osmium complexes cannot be extracted with acetonitrile or acetone. The new surface osmium species is therefore strongly bound to SiO₂, as confirmed by the fact that washing the sample with water affords chloride ions, suggesting that the presence of K₂CO₃ allows the removal of chloro ligands.

Some K[H₃Os₄(CO)₁₂] is produced by reductive carbonylation under mild conditions (150 °C, 1 atm of CO) of this new surface-bound osmium species. However, after either 5 or 21 days, extraction with acetonitrile affords the anionic cluster in only 17% yield (Table 1).

Similar low yields are obtained when the reaction is carried out at higher temperatures such as 170–200 °C. In this case, small amounts of K₂[Os₁₀C(CO)₂₄] are also formed (IR in acetone: ν(CO) = 2034 (s), 1992 (s) cm⁻¹).[15] After extraction with acetonitrile, the two anions may be separated easily by silica gel column chromatography (see Experimental Section).

Working under 10 atm of CO at 150 °C affords 38% yields of pure K[H₃Os₄(CO)₁₂] after 5 days. At this higher pressure, it is possible to increase the temperature up to 250 °C without formation of [Os₁₀C(CO)₂₄]²⁻; the reaction is faster, but the yield is improved only slightly (32% and 49% after 15 and 30 h, respectively).

Additional experiments were performed in order to examine the influence of the addition of H₂ to the gas phase on the formation of K[H₃Os₄(CO)₁₂].

At 170 °C and under 1 atm of CO + H₂ (equimolar), 29% yields of K[H₃Os₄(CO)₁₂], contaminated with traces of K₂[Os₁₀C(CO)₂₄], are obtained after 6 days.

If the reaction is run at 150 °C and under 10 atm of CO + H₂ (equimolar), 59% yields of pure K[H₃Os₄(CO)₁₂] are obtained after 5 days. As above, at this relatively high pressure, no K₂[Os₁₀C(CO)₂₄] is formed.

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Increasing the temperature to 250 °C accelerates the reaction, but leads always to the formation of some K_2-$[Os_{10}C(CO)_{24}]$. Thus, after 15 h under 10 atm of CO + H_2 (equimolar), 55% yields of $K[H_3Os_4(CO)_{12}]$ are obtained along with 7% of $K_2[Os_{10}C(CO)_{24}]$. The yields are not improved by leaving the reaction for an additional 15 h. Similar results are observed by increasing the pressure to 25 atm of CO + H_2 (equimolar) and working at 250 °C. Thus, as a general trend, higher but not satisfactory yields and a certain decrease of selectivity are observed under a relatively high pressure when a mixture of CO + H_2 (equimolar) is used instead of CO (see Table 1). In all cases, after extraction of the anionic clusters, no carbonyl band is left on the pale gray silica samples.

Although many of the details of the surface chemistry involved remain to be elucidated, it is clear that the osmium species formed by reaction of $OsCl_3$ with K_2CO_3 on the SiO_2 surface is not easily transformed into surface intermediates which would be rapidly and easily converted to $K[H_3Os_4(CO)_{12}]$ under mild conditions. For this reason, an alternative two-step route to $K[H_3Os_4(CO)_{12}]$ starting from silica-supported $OsCl_3$ was investigated.

Synthesis of $K[H_3Os_4(CO)_{12}]$ from $OsCl_3$ via the Intermediate Synthesis of $[Os(CO)_3Cl_2(HOSi<)]$. When anhydrous $OsCl_3$ or $OsCl_3\cdot3H_2O$ supported on SiO_2 is heated at 180 °C under 1 atm of CO in a closed reaction vessel, $[Os(CO)_3Cl_2(HOSi<)]$ and traces of physisorbed *cis*-$[Os(CO)_4Cl_2]$ are formed. The conversion is complete after 2 days, but traces of α-$[Os(CO)_3Cl_2]_2$ and *cis*-$[Os(CO)_4Cl_2]$ sublime in parallel.[3,6] Treatment of the combined resultant SiO_2 powder and sublimate with a slurry of K_2CO_3 in dichloromethane (molar ratio K_2CO_3:Os = 15:1) affords the surface-bound species $[Os(CO)_x$-$(OSi<)_2]_n$ (x = 2, 3). After evaporation of the solvent, further reaction with 1 atm of CO at 150 °C gives $K[H_3$-$Os_4(CO)_{12}]$ in 74% and 92% yields after 5 and 24 h, respectively.

This two-step surface-mediated synthesis is the best method to prepare $K[H_3Os_4(CO)_{12}]$ directly from $OsCl_3$.

Attempted Synthesis of $K[H_3Os_4(CO)_{12}]$ from $[Os(CO)_3Cl_2]_2$ on the MgO Surface and the Role of the Nature of Alkaline Species on the Silica Surface. In agreement with the literature,[16] we observed that surface-bound $[Os(CO)_x(OMg)_2]_n$ (x = 2, 3) species (ν-(CO) = 2114, 2023, and 1935 cm^{-1}) are readily formed when α-$[Os(CO)_3Cl_2]_2$ is stirred with MgO and CH_2Cl_2 at room temperature.

The reductive carbonylation of these MgO-anchored carbonyl species is much more difficult than that of $[Os$-$(CO)_x(OSi<)_2]_n$ (x = 2, 3). In fact, treatment of these surface species with 1 atm of CO at 150 °C does not afford anionic clusters.

As a matter of fact, it is known that these species are reduced to give anionic osmium clusters only at temperatures approaching 275 °C.[1] We confirmed that treatment with 1 atm of CO at 275 °C of the surface-anchored $[Os$-$(CO)_x(OMg)_2]_n$ species prepared from α-$[Os(CO)_3Cl_2]_2$ affords $[Os_{10}C(CO)_{24}]^{2-}$, which may be extracted by cation metathesis with $[N(PPh_3)_2]Cl$ in acetone (33% isolated yield after 24 h under CO).

Thus, the reductive carbonylation of α-$[Os(CO)_3Cl_2]_2$ on an intrinsic strongly basic surface as MgO occurs differently than on a silica surface treated with K_2CO_3,

confirming that surface basicity is not the only condition to produce the anion $[H_3Os_4(CO)_{12}]^-$.

It is worth noting that an attractive feature of the silica surface as reaction medium is that the base may be added at any time of a multistep silica-mediated synthesis. This might be useful, as observed during the synthesis of $K[H_3$-$Os_4(CO)_{12}]$ starting from silica-supported $OsCl_3$, where it was more convenient to add the base after the formation of $[Os(CO)_3Cl_2(HOSi<)]$.

In our silica-mediated syntheses, the role of the potassium carbonate is 2-fold: first, it promotes the easy removal of chloro ligands from the coordination sphere of osmium chlorides to form a reactive osmium surface species; second, it gives the required and well-balanced basicity for the formation of the anion.

Work is in progress to investigate the influence of the nature of the base in directing the reductive carbonylation on the silica surface of α-$[Os(CO)_3Cl_2]_2$ or $OsCl_3$ toward the formation of different osmium cluster compounds. In fact, preliminary results showed that when Na_2CO_3 is used instead of K_2CO_3 in our silica-mediated synthesis, only traces of $Na[H_3Os_4(CO)_{12}]$ and $[H_4Os_4(CO)_{12}]$ are formed, $[Os_3(CO)_{12}]$ being the major product.[9] A very different and much lower surface reactivity is observed when NaOH or KOH is added to silica.[9] It appears that Na_2CO_3 supported on SiO_2 behaves as a weaker base than K_2CO_3. This could be due to the low solvation of the cations by the surface silanol groups, thus producing a stronger ion-pair interaction of the smaller Na$^+$ cation with the CO_3^{2-} anion. This effect is well-known in organic chemistry when a base such as alkali *tert*-butoxide is used in a poorly solvating solvent (the potassium salt is more basic than the sodium salt).[17] We can clearly point out that the selectivity of the reductive carbonylation is regulated by the base strength given to the silica surface. Control of the nature and quantity of the added base is therefore of crucial importance in the design of a given silica surface synthesis by reductive carbonylation.

Experimental Section

General Comments. SiO_2 (Aerosil 200 Degussa, with a nominal surface area of 200 m^2/g) was used as support after treatment in vacuo (10^{-2} Torr) at 25 °C for 3 h. MgO (Carlo Erba, with a surface area of about 150 m^2/g) was treated with water under reflux for 2 h, filtered, calcined by heating to 400 °C in air for 2 h, and finally evacuated (10^{-2} Torr) for 15 h prior to use. $OsCl_3$ and $OsCl_3\cdot3H_2O$ were purchased from Aldrich Chemicals while α-$[Os(CO)_3Cl_2]_2$ was prepared according to the literature.[3,18]

Products were identified, after extraction from the support, by infrared, proton nuclear magnetic resonance, and mass spectroscopies, their spectra being compared to those reported in the literature. Their purity was verified by elemental analysis and by thin layer chromatography.

Spectra data were obtained by use of the following spectrometers: Nicolet MX-1 FT (IR), Bruker AC 200 (^{1}H NMR), VG analytical 7070EQ (MS).

Synthesis of $K[H_3Os_4(CO)_{12}]$ from $[Os(CO)_3Cl_2]_2$ on SiO_2. In a two-necked flask, a suspension of SiO_2 (3.648 g), α-$[Os(CO)_3$-$Cl_2]_2$ (0.132 g; 0.191 mmol), K_2CO_3 (0.529 g; 3.833 mmol), and CH_2Cl_2 (100 mL) was stirred under N_2 for 2 days at room temperature. The solvent was evaporated (10^{-2} Torr), affording silica-bound $[Os(CO)_x(OSi<)_2]_n$ (x = 2, 3), which was transferred into the cylindrical Pyrex vessel previously described for the

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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 150 °C for 24 h. The resulting yellow powder was placed in a Pyrex Büchner filter funnel and extracted with acetonitrile or acetone (100–150 mL). Evaporation of the solvent afforded pure $K[H_3Os_4(CO)_{12}]$ (0.099 g; 0.087 mmol; 91% yield) as confirmed by elemental analysis and TLC (silica plates; eluant hexane:ethanol = 1:1; R_f = 0.70). A similar yield (92%) was obtained on a 3-fold scale. Reactions with higher metal loadings were carried out under similar conditions (see Results and Discussion). IR (CH_3CN): $\nu(CO)$ = 2050 (s), 2024 (s), 2001 (s), 1983 (m), 1948 (vw), 1920 (vw) cm^{-1}. ^1H NMR (CD_3-$COCD_3$; −20 °C): δ −19.41, −19.99, −21.96 ppm; (50 °C) δ −20.12 ppm. MS (FAB$^-$) m/e 1101 [M]$^+$, 1073 [M − CO], 1045 (M − 2CO], 1017 [M − 3CO], 989 [M − 4CO], 961 [M − 5CO], 933 [M − 6CO], 905 [M − 7CO], 877 [M − 8CO], 849 [M − 9CO], 821 [M − 10CO].

Synthesis of $K[H_3Os_4(CO)_{12}]$ from $OsCl_3$ via $Os(CO)_3Cl_2$ (HOSi<) on SiO_2. In the cylindrical Pyrex vessel previously described,[3] a suspension of SiO_2 (4.137 g), anhydrous $OsCl_3$ (0.129 g; 0.436 mmol) and H_2O (80 mL) was stirred under N_2 overnight at room temperature. After evaporation of the solvent, the gray-violet silica-supported $OsCl_3$ 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 (40 mL) and K_2CO_3 (0.903 g; 6.54 mmol) were added, and the suspension was stirred for 2 days under N_2. The solvent was evaporated (10^{-2} Torr), affording silica-bound

$[Os(CO)_x(OSi<)_2]_n$, and the reaction vessel was exposed to CO at atmospheric pressure, closed, and heated at 150 °C for 24 h. Extraction with acetonitrile (150 mL) afforded pure $K[H_3Os_4(CO)_{12}]$ (0.114 g; 0.109 mmol; 92% yield) as confirmed by elemental analysis and TLC. The same yield was obtained on a 3-fold scale.

Synthesis of $K[H_3Os_4(CO)_{12}]$ from $OsCl_3$ on SiO_2 under Pressure. Silica-supported $OsCl_3$ (2 wt % Os/SiO_2), K_2CO_3, and CH_2Cl_2 were stirred at room temperature under N_2 for 2 days. The slurry was dried in vacuo (10^{-2} Torr), affording a silica-bound osmium species. 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 or CO + H_2 (equimolar), and heated at 150 or 250 °C (Table 1). After the mixture cooled to room temperature, the pressure was released slowly and the autoclave was opened. The resulting powder was placed in a Pyrex Büchner filter funnel and extracted first with CH_2Cl_2 to remove [$Os_3(CO)_{12}$] and [H_4-$Os_4(CO)_{12}$], when they were present, and then with CH_3CN to remove the anionic osmium species. When $K[H_3Os_4(CO)_{12}]$ was contaminated with $K_2[Os_{10}C(CO)_{24}]$, purification was achieved by silica gel column chromatography, using 1:1 ethanol/hexane 1:1 as eluant.