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High-yield syntheses, under mild conditions, of various neutral and anionic ruthenium and osmium carbonyl clusters by controlled reduction in ethylene glycol of $[M(CO)_3Cl_2]_2$ or MCl_3 (M=Ru, Os) in the presence of Na_2CO_3 or K_2CO_3☆

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Abstract

$[M_3(CO)_{12}]$, $[H_4M_4(CO)_{12}]$, $[H_3M_4(CO)_{12}]^-$ (M=Ru, Os) and $[Ru_6C(CO)_{16}]^{2-}$ have been synthesized in high yields by *one-pot* controlled reduction at atmospheric pressure of MCl_3 or $[M(CO)_3Cl_2]_2$, dissolved in *t*-amyl alcohol or ethylene glycol, working in the presence of alkali carbonates. The selectivity of the reduction is controlled by the: (i) nature and quantity of the alkali carbonate (Na_2CO_3 or K_2CO_3); (ii) nature of the solvent; (iii) gas-phase composition (CO or CO + H_2); (iv) temperature and (v) reaction time. Yields are so high and reaction conditions so mild that, in most cases, these new syntheses are more convenient than those previously reported either in solution or on the silica surface as reaction medium. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

A few years ago some of us reported that $[M(CO)_3Cl_2]_2$ (M=Ru, Os) can be easily prepared by reductive carbonylation of MCl_3 supported on a silica surface, working under mild conditions (M=Ru, 1 atm CO, 100–120°C, 48 h; M=Os, 1 atm CO, 180°C, 48 h) [1]. Later investigations showed that addition of specific weak bases, such as alkali carbonates, to the silica surface favours removal of chloro ligands [2–6]. In this way, various neutral or anionic osmium [4,5] or ruthenium [6] carbonyl clusters can be synthesized in high yields by controlled reduction at atmospheric pressure of silica-supported $[M(CO)_3Cl_2]_2$ (M = Ru, Os) or silica-bound $[M(CO)_3Cl_2(HOSi\equiv)]$ (generated in situ by controlled reductive carbonylation of silica-supported MCl_3 [1]) in the presence of specific amounts of alkali carbonates. These syntheses appear to be often more convenient than the traditional methods in solution, which usually require more drastic reaction conditions and/or more expensive starting materials such as $[M_3(CO)_{12}]$ or $[H_4M_4(CO)_{12}]$ [4–6]. However, it is not always possible to carry out silica-surface-mediated syntheses without limiting the metal loading of the surface [1,4–6], so that it would be interesting to have related methods of synthesis in solution, characterized by comparable high yields and selectivities and by mild reaction conditions.

A recent detailed investigation has shown that: (i) the role of silica is that of a rather inert solvent but without

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☆ Dedicated to Professor Renato Ugo on the occasion of his 60th birthday.

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boiling point, so that reactions can be easily carried out even at relatively high temperatures (180–275°C) and (ii) the alkali carbonates must be poorly solvated on the silica surface because they behave as strong bases; in particular K_2CO_3 is much more basic than Na_2CO_3 [7]. Therefore it was obvious to try to carry out similar syntheses in solution working with high boiling point solvents carrying non acidic OH groups that could behave like the OH groups of the silica surface.

It is reported that addition of a base in solution favours removal of chloro ligands from the coordination sphere of rhodium [8] and iridium [9] carbonyl complexes or salts. For example, treatment of a methanolic solution of $[Rh(CO)_2Cl]_2$ with 1 atm of CO in the presence of KOH affords $[Rh_6(CO)_{16}]$ [8] whereas $K_2[Ir_6(CO)_{15}]$ has been prepared by reductive carbonylation at atmospheric pressure of K_2IrCl_6 in 2-methoxyethanol containing K_2CO_3 [9]. However, to our knowledge, the reductive carbonylation in solution of MCl_3 (M=Ru, Os) or $[M(CO)_3Cl_2]_2$ has never been studied in the presence of a base. Therefore we investigated the use of ethylene glycol —a high boiling point solvent (b.p. = 196–198°C) with OH functional groups which could mimic the silica surface- as a reaction medium for the synthesis of various ruthenium and osmium clusters, working under conditions quite similar to those required to obtain selectively and in high yields the same clusters using the silica surface as reaction medium. Here we describe the results of this investigation which led to remarkably efficient and selective syntheses of $[M_3(CO)_{12}]$, $[H_4M_4(CO)_{12}]$, $[H_3M_4(CO)_{12}]^-$ (M=Ru, Os) and $[Ru_6C(CO)_{16}]^{2-}$ clusters.

2. Results and discussion

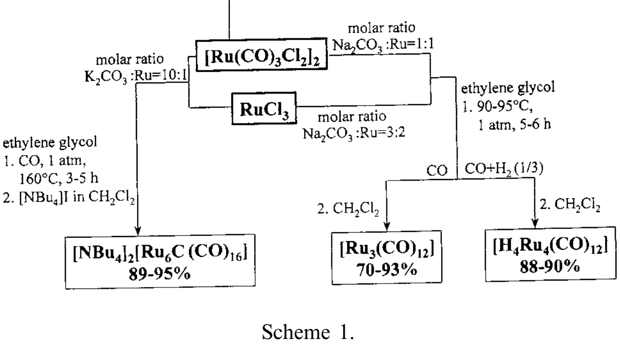
2.1. Synthesis of $[Ru_3(CO)_{12}]$

Recently we reported that controlled reductive carbonylation (1 atm CO, 110°C, 48 h) of silica-supported $[Ru(CO)_3Cl_2]_2$ (2–5 wt% of Ru with respect to SiO_2), in the presence of Na_2CO_3 (molar ratio Na_2CO_3:Ru=3:1) affords $[Ru_3(CO)_{12}]$ in high yields (82–93%), whereas lower yields (38–56%) can be reached by direct reductive carbonylation of $RuCl_3$ on a silica surface added with Na_2CO_3 [6]. In order to prepare $[Ru_3(CO)_{12}]$ in high yields (82–93%) from silica-supported $RuCl_3$ it is necessary to use a two-step process with $[Ru(CO)_3Cl_2(HOSi\equiv)]$ as in situ produced surface intermediate [6]. With this two-step approach high yields of $[Ru_3(CO)_{12}]$ (82–93%) [6] can be achieved. These are much higher than those obtained by reductive carbonylation at atmospheric pressure of a 2-ethoxyethanolic solution of $RuCl_3$ (45–60% yields by a two-step process involving treatment of $RuCl_3$ in 2-ethoxyethanol with CO at 135°C followed by addition of ethanol and zinc and further reaction with CO at 85°C) [10] or of a propanolic solution of $[Ru_3O(O_2CCH_3)_6(H_2O)_3](O_2CCH_3)$ (59% yields by working at 80°C for 30 h in the presence of triethylamine) [11]. Comparable yields can be reached only working under CO pressure (75–95% yields, starting from a methanolic solution of $RuCl_3$ under 10–50 atm [12]; 80–85% yields, starting from a propanolic solution of $[Ru_3O(O_2CCH_3)_6(H_2O)_3](O_2CCH_3)$ under 3–4 atm [11]).

Although methanolic solutions of $[Ru(CO)_3Cl_2]_2$ react with 1 atm of CO in the presence of zinc to give $[Ru_3(CO)_{12}]$ in 36% yield [13], the effect of a base on this reductive carbonylation in solution, to our knowledge, had never been investigated [14].

When an ethylene glycol solution of $[Ru(CO)_3Cl_2]_2$ is heated under a flux of CO (1 atm) at 95°C in the presence of Na_2CO_3 (molar ratio Na_2CO_3:Ru = 1:1), an orange material precipitates in the reaction flask whereas, in parallel, some orange powder sublimes on the cold walls of the condenser (see Experimental). After 5 h, no carbonyl band remains in the ethylene glycol solution. Extraction of the reaction mixture, added with the sublimate, with dichloromethane affords $[Ru_3(CO)_{12}]$ in excellent yield (93%; Table 1 Scheme 1). The use of dichloromethane for the extraction is particularly convenient because it is not miscible with ethylene glycol. Interestingly, $[Ru(CO)_3Cl_2]_2$ appears to be much more reactive in ethylene glycol solution than on the silica surface where 48 h, instead of 5 h in solution, were required to obtain similar yields of $[Ru_3(CO)_{12}]$.

$[Ru_3(CO)_{12}]$ can be also obtained directly from $RuCl_3$ (70% yield after 6 h; Table 1, Scheme 1) working under similar conditions in the presence of Na_2CO_3 (molar ratio Na_2CO_3:Ru = 3:2). After extraction of $[Ru_3(CO)_{12}]$ with dichloromethane, the infrared spectrum of the ethylene glycol solution shows weak carbonyl bands at 2047(w) and 1978(w) cm^{-1}, similar to those reported for $[Ru(CO)_x(OH)_2]_n$ ($x = 2,3$) [15]. Such



Scheme 1.

Table 1
Synthesis of various ruthenium and osmium clusters from MCl_3 or $[M(CO)_3Cl_2]_2$ (M=Ru, Os) in ethylene glycol

Starting material	Molar ratio base:M	Gas[a]	T (°C)	t (h)	$M_3(CO)_{12}$ (M), % yield[b]	$H_4M_4(CO)_{12}$ (M), % yield[b]	$[H_3M_4(CO)_{12}]^-$(M), % yield[b]	$[Ru_6C(CO)_{16}]^{2-}$ % yield[b]
$[Ru(CO)_3Cl_2]_2$	Na_2CO_3:Ru = 1:1	CO	95	5	(Ru), 93	–	–	–
$RuCl_3$	Na_2CO_3:Ru = 3:2	CO	95	6	(Ru), 70	–	–	–
$[Ru(CO)_3Cl_2]_2$	Na_2CO_3:Ru = 1:1	$CO+H_2$[c]	95	6	–	(Ru), 90	–	–
$RuCl_3$	Na_2CO_3:Ru = 3:2	$CO+H_2$[c]	90	12	–	(Ru), 88	–	–
$[Ru(CO)_3Cl_2]_2$	Na_2CO_3:Ru = 3:1	$CO+H_2$[c]	88	12	–	–	(Ru), 93[d]	–
$[Ru(CO)_3Cl_2]_2$	K_2CO_3:Ru = 10:1	CO	160	3	–	–	–	89[e]
$RuCl_3$	K_2CO_3:Ru = 10:1	CO	165	5	–	–	–	95[e]
$[Os(CO)_3Cl_2]_2$	Na_2CO_3:Os = 1:1	CO	160	17	(Os), 65	–	–	–
$OsCl_3$	Na_2CO_3:Os = 3:2	CO	165	15	(Os), 64	–	–	–
$[Os(CO)_3Cl_2]_2$	K_2CO_3:Os = 10:1	CO	160	6	–	–	(Os), 74[e]	–
$OsCl_3$	K_2CO_3:Os = 10:1	CO	165	9	–	–	(Os), 74[e]	–
$OsCl_3$	K_2CO_3:Os = 10:1	CO	165	9	–	(Os), 81[f]	–	–

[a] 1 atm.

[b] Isolated yield.

[c] Molar ratio 1:3.

[d] t-Amyl alcohol used instead of ethylene glycol.

[e] As NBu_4^+ salt.

[f] Obtained in situ by acidification of $[H_3Os_4(CO)_{12}]^-$ formed under these reaction conditions.

yields and selectivities cannot be reached on the silica surface in one step starting from $RuCl_3$ [6].

Interestingly, whereas a small excess of Na_2CO_3 (molar ratio Na:Cl = 2:1) is required to obtain high yields of $[Ru_3(CO)_{12}]$ on the silica surface [6], in ethylene glycol solution the reductive carbonylation *must* be carried out in the presence of the stoichiometric amount of Na_2CO_3 necessary to remove the chloro ligands from the coordination sphere of ruthenium. The presence of a small excess of Na_2CO_3 (e.g. molar ratio Na:Cl = 2:1 instead of 1:1) leads to the parallel formation of anionic byproducts such as $[HRu_3(CO)_{11}]^-$ [14] and $[Ru_6C(CO)_{16}]^{2-}$ [14].

These new syntheses of $[Ru_3(CO)_{12}]$, starting from simple materials such as $RuCl_3$ or $[Ru(CO)_3Cl_2]_2$ dissolved in ethylene glycol in the presence of the stoichiometric amount of Na_2CO_3, are attractive on a preparative point of view because yields are higher than those reported for the best reductive carbonylation at atmospheric pressure of $RuCl_3$ or $[Ru(CO)_3Cl_2]_2$, either in solution [10,13,14] or on the silica surface [6].

2.2. Syntheses of $[H_4Ru_4(CO)_{12}]$ and $[H_3Ru_4(CO)_{12}]^-$

A very convenient method to prepare $[H_4Ru_4(CO)_{12}]$ and $[H_3Ru_4(CO)_{12}]^-$ from $RuCl_3$ is the two-step silica-mediated approach involving reduction (1 atm CO + H_2, 110°C, 19 h) of $[Ru(CO)_3Cl_2(HOSi\equiv)]$ in the presence of Na_2CO_3 [6]. Extraction of the silica powder with dichloromethane affords $[H_4Ru_4(CO)_{12}]$ (86–88% yields) whereas extraction with a solution of [PPN]Br in tetrahydrofuran gives $[PPN][H_3Ru_4(CO)_{12}]$ (81% yield) [6]. $[H_4Ru_4(CO)_{12}]$ can be prepared from $RuCl_3$ in ethanol, but in lower yields (10–30% yields after 3 days at 75–100°C) working under very high pressures of CO + H_2 (molar ratio 1:1; 80 atm) [16]. Up to now the best synthesis in solution of $[H_4Ru_4(CO)_{12}]$ requires treatment of the cluster $[Ru_3(CO)_{12}]$ with 1 atm of H_2 in octane under reflux (88% yield) [17]. Further deprotonation of $[H_4Ru_4(CO)_{12}]$ with KOH or KH in ethanol or addition of [PPN]Cl in tetrahydrofuran gives $[H_3Ru_4(CO)_{12}]^-$ in excellent yields [18].

When an ethylene glycol solution of $[Ru(CO)_3Cl_2]_2$ is heated at 95°C in the presence of Na_2CO_3 (molar ratio Na_2CO_3:Ru = 1:1) under a flux of CO + H_2 (molar ratio = 1:3; 1 atm), a yellow material precipitates whereas, in parallel, some yellow powder sublimes on the cold walls of the condenser. After 6 h, no carbonyl band remains in the ethylene glycol solution. Extraction of the sublimate and the reaction mixture with dichloromethane affords $[H_4Ru_4(CO)_{12}]$ in excellent yield (90%; Table 1, Scheme 1). Like in the case of the $[Ru_3(CO)_{12}]$ synthesis, the reduction *must* be carried out in the presence of the stoichiometric amount of Na_2CO_3 necessary to remove the chloro ligands from the coordination sphere of ruthenium (molar ratio Na:Cl = 1:1). In fact, use of even a small excess of Na_2CO_3 leads to the formation of some $[H_3Ru_4(CO)_{12}]^-$ as byproduct.

While only traces of $[H_4Ru_4(CO)_{12}]$ could be generated by direct reduction with CO + H_2 (molar ratio = 1:3; 1 atm) of $RuCl_3$ supported on silica in the presence of Na_2CO_3 [6], this hydridocarbonyl cluster is obtained in 88% yield (Table 1, Scheme 1) by bubbling, at 90°C and 1 atm for 12 h, the same gas mixture through an ethylene glycol solution of $RuCl_3$ in the presence of Na_2CO_3 (molar ratio Na_2CO_3:Ru = 3:2). This appears to be by far the best known way to convert $RuCl_3$ directly into $[H_4Ru_4(CO)_{12}]$ in excellent yields and under mild conditions.

The selective formation of $[H_3Ru_4(CO)_{12}]^-$ by direct reductive carbonylation in solution of $[Ru(CO)_3Cl_2]_2$ or $RuCl_3$ was also investigated. When a *t*-amyl alcohol solution of $[Ru(CO)_3Cl_2]_2$ is heated at 88°C for 12 h in the presence of excess Na_2CO_3 (molar ratio Na_2CO_3:Ru = 3:1) under a flux of CO + H_2 (molar ratio = 1:3; 1 atm), $Na[H_3Ru_4(CO)_{12}]$ is formed in 93% yield (Table 1Scheme 1). For this particular synthesis, it is more convenient to use *t*-amyl alcohol than ethylene glycol as solvent. Contrarily to *t*-amyl alcohol, ethylene glycol dissolves completely Na_2CO_3 leading to a too high basicity of the reaction medium and therefore to a lower selectivity due to the formation of a mixture of $[H_3Ru_4(CO)_{12}]^-$ and $[Ru_6C(CO)_{16}]^{2-}$.

Various attempts to prepare selectively $[H_3Ru_4(CO)_{12}]^-$ by direct reductive carbonylation of $RuCl_3$ failed, probably due to the low solubility of $RuCl_3$ in *t*-amyl alcohol. For such a reason the reduction was conducted in ethylene glycol. By bubbling CO + H_2 (molar ratio = 1:3, 1 atm) through ethylene glycol solutions containing $RuCl_3$ and excess Na_2CO_3 (molar ratio Na_2CO_3:Ru = 4–9:2), at 88°C, mixtures of $[H_3Ru_4(CO)_{12}]^-$ and $[Ru_6C(CO)_{16}]^{2-}$ were always obtained; $[Ru_6C(CO)_{16}]^{2-}$ is formed as byproduct even when working in the presence of a relatively low excess of Na_2CO_3. For this reason, in order to selectively prepare $[H_3Ru_4(CO)_{12}]^-$ from $RuCl_3$, it is more convenient to synthesize first $[H_4Ru_4(CO)_{12}]$ by direct reductive carbonylation of $RuCl_3$ in ethylene glycol as described above, and then to deprotonate it in situ as previously reported [18].

2.3. Synthesis of $[Ru_6C(CO)_{16}]^{2-}$

In solution, the best routes to $[Ru_6C(CO)_{16}]^{2-}$ reported so far require $[Ru_3(CO)_{12}]$ as starting material (yields = 60–90%) [19]. For example, $[Ru_6C(CO)_{16}]^{2-}$ is obtained in 90% yield by refluxing a diglyme solution of $[Ru_3(CO)_{12}]$ with Na for 12 h [19b]. However, we reported recently that this anionic cluster can be prepared in a more convenient way (95% yield) by controlled reduction (1 atm CO, 150°C, 10 h) of $[Ru(CO)_3Cl_2(HOSi\equiv)]$ in the presence of K_2CO_3 [6].

This remarkable silica-mediated synthesis prompted us to investigate the reductive carbonylation of $[Ru(CO)_3Cl_2]_2$ in ethylene glycol solution in the presence of an alkali carbonate.

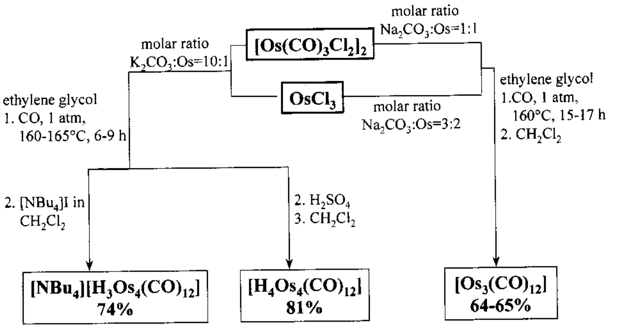
By bubbling CO (1 atm) through an ethylene glycol solution of $[Ru(CO)_3Cl_2]_2$ and excess K_2CO_3 (molar ratio K_2CO_3:Ru = 10:1), at 160°C for 3 h, $K_2[Ru_6C(CO)_{16}]$ is formed. Extraction with a dichloromethane solution of $[NBu_4]I$ gives $[NBu_4]_2[Ru_6C(CO)_{16}]$ in 89% yield (Table 1, Scheme 1). Remarkably, this anionic ruthenium cluster can be also obtained in excellent yields (95%; Table 1, Scheme 1) by direct reductive carbonylation in ethylene glycol (1 atm CO, 160–165°C, 5 h) of $RuCl_3$ in the presence of excess K_2CO_3 (molar ratio K_2CO_3:Ru = 10:1). The latter synthesis is extremely convenient, although unexpected because $K_2[Ru_6C(CO)_{16}]$ was not produced when $RuCl_3$ supported on silica in the presence of excess K_2CO_3 (molar ratio K_2CO_3:Ru = 10–20:1) was heated under 1 atm of CO at either 150 or 200°C for 24–65 h [6].

2.4. Synthesis of $[Os_3(CO)_{12}]$

In solution, $[Os_3(CO)_{12}]$ is usually prepared by reductive carbonylation under high pressure (75 atm CO, 125°C) of OsO_4 dissolved in methanol (yields = 70–80%) [20]. We recently reported that it can be synthesized in similar yields (64–82%) but under milder conditions by silica-mediated reductive carbonylation at atmospheric pressure (CO, 200°C, 3 days) of the more convenient starting materials $[Os(CO)_3Cl_2]_2$ or $[Os(CO)_3Cl_2(HOSi\equiv)]$, obtained in situ by silica-mediated reductive carbonylation of $OsCl_3$ at 180°C under 1 atm of CO for 48 h [1], working in the presence of Na_2CO_3 (molar ratio Na_2CO_3:Os = 2:1) [5].

When an ethylene glycol solution of $[Os(CO)_3Cl_2]_2$ and Na_2CO_3 (molar ratio Na_2CO_3:Os = 1:1) is treated with 1 atm of CO at 160–165°C, a yellow material precipitates whereas, in parallel, some yellow powder sublimes on the cold walls of the condenser. After 17 h, no carbonyl species remains in the ethylene glycol solution as shown by infrared spectroscopy. Extraction of the sublimate and the reaction mixture with dichloromethane affords $[Os_3(CO)_{12}]$ along with traces of $[HOs_3(CO)_{10}Cl]$ and $[HOs_3(CO)_{10}OH]$. Evaporation of the dichloromethane solution followed by washing with pentane, to remove the traces of $[HOs_3(CO)_{10}Cl]$ and $[HOs_3(CO)_{10}OH]$, gives pure $[Os_3(CO)_{12}]$ in 65% yield (Table 1, Scheme 2). Similar yields are obtained by increasing the reaction time (28 h).

It appears that $[Os(CO)_3Cl_2]_2$, like its ruthenium analogue, is much more reactive in ethylene glycol solution than on the silica surface where 72 h at 200°C, instead of 17 h at 160–165°C in solution, were required in order to obtain similar yields of $[Os_3(CO)_{12}]$.



Scheme 2.

Differently from the silica-mediated synthesis in the presence of alkali carbonates [5], $[Os_3(CO)_{12}]$ can be obtained in good yields (64%; Table 1, Scheme 2) by bubbling CO (1 atm) for 15 h at 160–165°C directly through an ethylene glycol solution of $OsCl_3$ in the presence of Na_2CO_3 (molar ratio Na_2CO_3:Os = 3:2). After extraction of the carbonyl cluster with dichloromethane, the infrared spectrum of the yellow ethylene glycol solution shows weak carbonyl bands (2120(m), 2032(s), 2022(s), 2000(m) cm^{-1}) due to some unidentified carbonyl osmium species which cannot be converted to $[Os_3(CO)_{12}]$ by further treatment under CO at 165°C.

This new synthesis of $[Os_3(CO)_{12}]$ by direct reductive carbonylation at atmospheric pressure of $OsCl_3$ dissolved in ethylene glycol added with Na_2CO_3 is very attractive on a preparative point of view. Yields are similar to those reached starting from silica-supported $OsCl_3$ *via* $[Os(CO)_3Cl_2(HOSi\equiv)]$ (64% yields) [5]. However, the synthesis in ethylene glycol is a *one-step* process and it is much more rapid than the silica-mediated synthesis (15 h at 160–165°C instead of 5 days at 180–200°C).

2.5. Syntheses of $[H_4Os_4(CO)_{12}]$ and $[H_3Os_4(CO)_{12}]^-$

In solution, $[H_4Os_4(CO)_{12}]$ is usually prepared (70% yield) by hydrogenation under pressure (120 atm of H_2, 100°C) of $[Os_3(CO)_{12}]$ in octane [21]. The related anionic cluster $[H_3Os_4(CO)_{12}]^-$ can be synthesized by deprotonation of $[H_4Os_4(CO)_{12}]$ with KOH in methanol (75% yield) [21] or by refluxing a butanolic solution of $[Os_3(CO)_{12}]$ with KOH (45% yield) [22]. Both $[H_4Os_4(CO)_{12}]$ and $[H_3Os_4(CO)_{12}]^-$ can be more conveniently prepared on the silica surface by controlled reduction (1 atm CO, 150°C, 24 h) of $[Os(CO)_3Cl_2]_2$ or $[Os(CO)_3Cl_2(HOSi\equiv)]$, obtained in situ by silica-mediated reductive carbonylation of $OsCl_3$ at 180°C under 1 atm of CO for 48 h [1], working in the presence of K_2CO_3 (molar ratio K_2CO_3:Os = 10:1) [4,5]. Extraction of the resulting silica-powder with acetonitrile affords $K[H_3Os_4(CO)_{12}]$ (92% yield) [4], whereas extraction with dichloromethane acidified with a few drops of H_2SO_4 gives $[H_4Os_4(CO)_{12}]$ (76% yield) [5].

By bubbling CO (1 atm) through an ethylene glycol solution of $[Os(CO)_3Cl_2]_2$ and excess K_2CO_3 (molar ratio K_2CO_3:Os = 10:1), at 160–165°C for 6 h, $K[H_3Os_4(CO)_{12}]$ is formed as shown by infrared spectroscopy of the resulting solution ($\nu_{CO} = 2048$(s), 2023(s), 2000(s), 1981(m), 1946(w) cm^{-1}). Extraction with a dichloromethane solution of $[NBu_4]I$ gives $[NBu_4][H_3Os_4(CO)_{12}]$ in 74% yield (Table 1, Scheme 2). Similar yields are obtained by increasing the reaction time (12 h). After extraction of the product, no carbonyl species remains in the ethylene glycol solution.

Remarkably, $K[H_3Os_4(CO)_{12}]$ is also selectively generated by direct reductive carbonylation in ethylene glycol (1 atm CO, 160–165°C, 9 h) of $OsCl_3$ in the presence of excess K_2CO_3 (molar ratio K_2CO_3:Os = 10:1). Depending on the work-up of the reaction mixture, either $[H_4Os_4(CO)_{12}]$ or $[H_3Os_4(CO)_{12}]^-$ can be obtained in excellent yield (Scheme 2). Extraction with a dichloromethane solution of $[NBu_4]I$ gives $[NBu_4][H_3Os_4(CO)_{12}]$ in mixture with some degradation products of ethylene glycol (e.g. salts of various carboxylic organic acids) [23] which can be removed by chromatography on silica (see Experimental; yield of pure $[NBu_4][H_3Os_4(CO)_{12}] = 74\%$, Table 1). On the other hand, acidification of the ethylene glycol reaction mixture with H_2SO_4 leads to the precipitation of yellow $[H_4Os_4(CO)_{12}]$. Successive extraction with dichloromethane gives the latter neutral cluster in 81% yield (Table 1).

These new *one-pot* preparations of $[H_4Os_4(CO)_{12}]$ and $[H_3Os_4(CO)_{12}]^-$ by controlled reductive carbonylation of $OsCl_3$ are by far more advantageous than those previously described either in solution, which require the more expensive $[Os_3(CO)_{12}]$ or $[H_4Os_4(CO)_{12}]$ as starting material [21,22], or on the silica surface, which require a two- step process (formation of $[Os(CO)_3Cl_2(HOSi\equiv)]$ followed by further controlled reduction in the presence of K_2CO_3) and longer reaction time (3 days instead of 9 h in solution) [4,5]. In the case of the synthesis of $[H_3Os_4(CO)_{12}]^-$, the only inconvenience is that the product must be purified by chromatography due to the degradation of ethylene glycol when working at relatively high temperatures and under strongly basic conditions [23].

2.6. A comparison between ethylene glycol and the silica surface as a reaction medium for the synthesis of various ruthenium and osmium clusters by controlled reduction of $[M(CO)_3Cl_2]_2$ or MCl_3 (M=Ru, Os) in the presence of Na_2CO_3 or K_2CO_3

The new syntheses in solution of $[M_3(CO)_{12}]$, $[H_4M_4(CO)_{12}]$, $[H_3M_4(CO)_{12}]^-$ (M=Ru, Os) and $[Ru_6C(CO)_{16}]^{2-}$ described above show how, in some cases, silica-mediated syntheses can be a spring of inspiration for more traditional syntheses in solution.

Some of us reported that various ruthenium [6] and osmium [4,5] carbonyl clusters can be selectively prepared, in high yields by controlled reduction of silica-supported $[M(CO)_3Cl_2]_2$ or silica-bound $[M(CO)_3Cl_2(HOSi\equiv)]$ (M=Ru, Os) in the presence of alkali carbonates. However, these surface-mediated synthetic methods have the disadvantage of requiring a relatively long reaction time. In addition, it is often necessary to involve a pluri-step process in order to reach high yields when starting from silica-supported MCl_3 (M=Ru, Os). Recently we pointed out clearly that the role of the silica surface is that of a polar solvent without boiling point. As a simple extrapolation of this role, by using a solvent like ethylene glycol (or *t*-amyl alcohol in the case of $[H_3Ru_4(CO)_{12}]^-$) the defects of the silica surface can be removed, while maintaining yields and selectivities in the particular cases of the synthesis of $[M_3(CO)_{12}]$, $[H_4M_4(CO)_{12}]$, $[H_3M_4(CO)_{12}]^-$ (M=Ru, Os) and $[Ru_6C(CO)_{16}]^{2-}$. Remarkably, high yields of these ruthenium and osmium clusters can be achieved by *one-step* reductive carbonylation of MCl_3 (M=Ru, Os) under very mild conditions.

This selective and facile direct reductive carbonylation of MCl_3 (M=Ru, Os) is quite unexpected because silica-supported MCl_3 gives a low selectivity and very low yields when reduced under similar conditions in the presence of alkali carbonates [4–6]. An explanation could be the formation on the surface, during the deposition of MCl_3 and the alkali carbonate, of hydroxo or oxo species difficult to reduce [14,24]. These hydroxo or oxo species would not be formed in ethylene glycol solution under our reaction conditions.

In agreement with this picture, no black precipitate, characteristic of Ru(III) hydroxide [24], was detected during the reductive carbonylation of $RuCl_3$ in ethylene glycol containing alkali carbonates. In addition, by bubbling CO at 100–110°C in an ethylene glycol solution of $RuCl_3$, carbonyl species are rapidly formed, as shown by infrared spectroscopy. After 2 h, one weak and two strong bands appear at 2136(w), 2067(s) and 1999(s) cm^{-1}, respectively, and the initial brown solution becomes yellow. By further treatment under CO for 1 h, the absorption at 1999(w) cm^{-1} decreases with parallel growth of the intensity of peaks at 2136(m) and 2065(s) cm^{-1}. This infrared evidence suggests the rapid formation of dichlorodicarbonyl Ru(II) species ($\nu_{CO} =$ 2067(s) and 1999(s) cm^{-1}) and, later, of dichlorotricarbonyl Ru(II) species ($\nu_{CO} = 2136$(m) and 2065(s) cm^{-1}) [2]. Clearly the reduction of Ru(III) to Ru(II) is much more rapid in ethylene glycol (less than 3 h) than on the silica surface (ca. 48 h) [1]. In the presence of alkali carbonates, the dichlorocarbonyl M(II) species would be rapidly converted to reactive intermediates of the type $[M(CO)_x(OH)_2)]_n$ (M=Ru, $x = 2, 3$; M=Os, $x = 3$)

[15], similar to those obtained by reaction of silica-supported $[M(CO)_3Cl_2]_2$ or silica-bound $[M(CO)_3Cl_2(HOSi\equiv)]$ with alkali carbonates [5–7]. As above reported, we have infrared evidence of the formation of $[Ru(CO)_x(OH)_2]_n$ ($x = 2,3$) species during the synthesis of $[Ru_3(CO)_{12}]$ by reductive carbonylation (CO, 95°C) of an ethylene glycol solution of $RuCl_3$ in the presence of Na_2CO_3 (molar ratio Na_2CO_3:Ru = 3:2).

Obviously the reductive carbonylation of $[M(CO)_3Cl_2]_2$ (M=Ru, Os) to carbonyl clusters occurs much more rapidly in ethylene glycol than on the silica surface due to a higher mobility of reagents and intermediate species in solution than on a solid surface. However, in specific cases, this low mobility on the surface can be used in order to allow the selective synthesis of some carbonyl clusters. For example, treatment of silica-supported $[Ru(CO)_3Cl_2]_2$ (15 wt% of Ru with respect to SiO_2) with a slurry of Na_2CO_3 (molar ratio Na_2CO_3:Ru = 3:1) in CH_2Cl_2, followed by evaporation of the solvent and reaction with CO (1 atm) at 110°C for 24 h, affords $[Ru_3(CO)_{10}Cl_2]$ (75% yield) [6]. Due to both the high solubility of alkali carbonates in ethylene glycol and to the high mobility of species in solution, attempts to prepare $[Ru_3(CO)_{10}Cl_2]$ by controlled reductive carbonylation of $RuCl_3$ or $[Ru(CO)_3Cl_2]_2$ dissolved in ethylene glycol failed. Even by working with a defect of base, under 1 atm of CO at 95°C, a mixture of $[Ru_3(CO)_{12}]$ and $[Ru(CO)_{4-x}Cl_2L]$ ($x = 1$ or 2; L=$HOCH_2CH_2OH$) is formed.

Another difference with the behaviour of the silica surface is given by the necessity of carrying out the reductive carbonylation in ethylene glycol solution in the presence of the stoichiometric amount of Na_2CO_3 (molar ratio Na:Cl = 1:1) in order to obtain selectively neutral carbonyl clusters. Otherwise, anionic clusters are formed in parallel as byproducts. On the contrary, on the silica surface, some excess of Na_2CO_3 (e.g. molar ratio Na:Cl = 2–3:1) is always required to obtain high yields of neutral carbonyl clusters [4–6]. This could be due to a lower mobility, and therefore to a lower reactivity, of ruthenium or osmium carbonyl species when physisorbed on the silica surface, a behaviour which allows the selective formation and isolation of intermediates (such as $[HRu_3(CO)_{11}]^-$ or $[HRu_6(CO)_{18}]^-$) [6] which cannot be seen when working in ethylene glycol solution.

It is known that treatment of glycols with bases at high temperatures (ca. 200°C) leads to degradation with exothermic reactions proceeding rapidly and uncontrollably [23,25]. Therefore glycols cannot be used as a safe reaction medium for the syntheses of carbonyl cluster anions which require both high temperatures and strong basic conditions. Obviously this inconvenience does not exist with the silica surface as a reaction medium. Therefore when high temperatures and basic conditions are required, as in the case of the synthesis of $[Os_{10}C(CO)_{24}]^{2-}$ and $[Os_5C(CO)_{14}]^{2-}$ by reductive carbonylation of $[Os(CO)_3Cl_2]_2$ in the presence of excess alkali carbonates (200–275°C; molar ratio Na_2CO_3 or K_2CO_3: Os = 10–20: 1) [5], the role of the silica surface as a convenient reaction medium is unique and compulsory.

3. Conclusion

By a spring of inspiration from the role of the silica surface in the surface-mediated syntheses of various clusters [6,7], $[M_3(CO)_{12}]$, $[H_4M_4(CO)_{12}]$, $[H_3M_4(CO)_{12}]^-$ (M=Ru, Os) and $[Ru_6C(CO)_{16}]^{2-}$ can be rapidly prepared, in excellent yields and under mild conditions, by controlled reduction of simple starting materials such as MCl_3 or $[M(CO)_3Cl_2]_2$ (M=Ru, Os) dissolved in ethylene glycol containing alkali carbonates.

Ethylene glycol was chosen as a particularly suitable solvent for the following reasons:

(i) it can reproduce in a certain way the polarity and the coordinating power of the silanol groups of the silica surface;

(ii) it has a high boiling point (196–198°C) and a stability good enough to allow the use of relatively high temperatures (up to 160°C), required for the synthesis of various osmium carbonyl clusters [4,5];

(iii) it dissolves well the reagents ($RuCl_3$, $OsCl_3$, $[Ru(CO)_3Cl_2]_2$, $[Os(CO)_3Cl_2]_2$, Na_2CO_3, K_2CO_3) and the reaction intermediates, allowing a fast reaction in a completely homogeneous phase;

(iv) it does not dissolve neutral clusters such as $[Ru_3(CO)_{12}]$, $[H_4Ru_4(CO)_{12}]$, $[Os_3(CO)_{12}]$ and $[H_4Os_4(CO)_{12}]$ which can be easily recovered at the end of the reaction by filtration or by extraction with a non-miscible solvent like dichloromethane;

(v) it dissolves the anionic carbonyl clusters as Na^+ or K^+ salts but it does not dissolve well their NBu_4^+ salts which, therefore, can be easily recovered by extraction with dichloromethane. All these properties allow new synthetic methods which are by far the best known for $[M_3(CO)_{12}]$, $[H_4M_4(CO)_{12}]$, $[H_3M_4(CO)_{12}]^-$ (M=Ru, Os) and $[Ru_6C(CO)_{16}]^{2-}$ clusters.

We have confirmed that the behaviour of ethylene glycol is quite unique. For instance, attempts to prepare $[Ru_6C(CO)_{16}]^{2-}$ by reductive carbonylation (1 atm CO) of $RuCl_3$ dissolved in triethylene glycol dimethyl ether failed. By working in the presence of K_2CO_3 (molar ratio K_2CO_3:Ru = 10:1) at 165°C for 6 h, only dichlorotricarbonyl ruthenium(II) species are formed. The lack of further reduction to some carbonyl cluster can be possibly attributed to the lack of solubility of K_2CO_3 in this specific solvent. However in one case we found that *t*-amyl alcohol is more convenient as solvent than ethylene glycol.

In conclusion, a high boiling point solvent with OH functional groups which could mimic the silica surface, such as ethylene glycol, is a convenient reaction medium for the selective and high-yield synthesis of various neutral and anionic metal carbonyl clusters starting from simple materials such as metal chlorides. However, ethylene glycol cannot be used safely for the syntheses of carbonyl clusters which require both high temperatures (ca. 200°C) and strong basic conditions, while this inconvenience does not exist with the silica surface as a reaction medium.

4. Experimental

4.1. General comments

$RuCl_3 \cdot nH_2O$ (41.2 wt% Ru) and $OsCl_3 \cdot 3H_2O$ were purchased from Strem Chemicals and Sigma–Aldrich, respectively, while $[Ru(CO)_3Cl_2]_2$ and $[Os(CO)_3Cl_2]_2$ were prepared according to the literature [1]. All the reactions were monitored by infrared spectroscopy in the carbonyl region. Reaction products were identified by infrared, ^{1}H-NMR (when appropriate), and mass spectroscopies, their spectra being compared to those of pure samples. Their purity was controlled by thin-layer chromatography (when possible) and by elemental analysis.

4.2. Synthesis of $[Ru_3(CO)_{12}]$

4.2.1. From $[Ru(CO)_3Cl_2]_2$

$[Ru(CO)_3Cl_2]_2$ (151 mg; 0.295 mmol) was dissolved in ethylene glycol (60 ml) in a three-necked flask containing a magnetic stirring bar and equipped with a condenser and a thermometer. Na_2CO_3 (62 mg; 0.585 mmol; molar ratio Na_2CO_3:Ru = 1:1) was added and CO was bubbled through the resulting solution at 95°C and 1 atm for 5 h. During the reaction an orange precipitate was formed in the flask whereas, in parallel, an orange powder sublimed on the cold walls of the condenser. Extraction of the sublimate and the reaction mixture with CH_2Cl_2 (150 ml) at room temperature, followed by evaporation to dryness of the CH_2Cl_2 phase, gave an orange solid residue which was washed twice with water (2 × 5 ml), in order to eliminate traces of ethylene glycol, affording pure $[Ru_3(CO)_{12}]$ (117 mg; 0.183 mmol; 93% yield).

4.2.2. From $RuCl_3$

$RuCl_3 \cdot nH_2O$ (180 mg; 0.734 mmol of Ru) was dissolved in ethylene glycol (60 ml) in a three-necked flask containing a magnetic stirring bar and equipped with a condenser and a thermometer. Na_2CO_3 (117 mg; 1.10 mmol; molar ratio Na_2CO_3:Ru = 3:2) was added and CO was bubbled through the resulting solution at 95°C and 1 atm for 6 h. During the reaction an orange precipitate was formed in the flask whereas, in parallel, an orange powder sublimed on the cold walls of the condenser. Extraction of the sublimate and the reaction mixture with CH_2Cl_2 (150 ml) at room temperature, followed by evaporation to dryness of the CH_2Cl_2 phase, gave an orange solid residue which was washed twice with water (2 × 5 ml), in order to eliminate traces of ethylene glycol, affording pure $[Ru_3(CO)_{12}]$ (110 mg; 0.172 mmol; 70% yield).

4.3. Synthesis of $[H_4Ru_4(CO)_{12}]$

4.3.1. From $[Ru(CO)_3Cl_2]_2$

$[Ru(CO)_3Cl_2]_2$ (179 mg; 0.350 mmol) was dissolved in ethylene glycol (60 ml) in a three-necked flask containing a magnetic stirring bar and equipped with a condenser and a thermometer. Na_2CO_3 (74 mg; 0.698 mmol; molar ratio Na_2CO_3:Ru = 1:1) was added and $CO + H_2$ (molar ratio = 1:3) was bubbled through the resulting solution at 95°C and 1 atm for 6 h. During the reaction a yellow precipitate was formed in the flask whereas, in parallel, a yellow powder sublimed on the cold walls of the condenser. Extraction of the sublimate and the reaction mixture with CH_2Cl_2 (150 ml) at room temperature, followed by evaporation to dryness of the CH_2Cl_2 phase, gave a yellow solid residue which was washed twice with water (2 × 5 ml), in order to eliminate traces of ethylene glycol, affording pure $[H_4Ru_4(CO)_{12}]$ (117 mg; 0.157 mmol; 90% yield).

4.3.2. From $RuCl_3$

$RuCl_3 \cdot nH_2O$ (180 mg; 0.734 mmol of Ru) was dissolved in ethylene glycol (60 ml) in a three-necked flask containing a magnetic stirring bar and equipped with a condenser and a thermometer. Na_2CO_3 (117 mg; 1.10 mmol; molar ratio Na_2CO_3:Ru = 3:2) was added and $CO + H_2$ (molar ratio = 1:3) was bubbled through the resulting brown-red solution at 90°C and 1 atm for 12 h. During the reaction a yellow precipitate was formed in the flask whereas, in parallel, a yellow powder sublimed on the cold walls of the condenser. Extraction of the sublimate and the reaction mixture with CH_2Cl_2 (200 ml) at room temperature, followed by evaporation to dryness of the CH_2Cl_2 phase, gave a yellow solid residue which was washed twice with water (2 × 5 ml), in order to eliminate traces of ethylene glycol, affording pure $[H_4Ru_4(CO)_{12}]$ (120 mg; 0.161 mmol; 88% yield).

4.4. Synthesis of $[H_3Ru_4(CO)_{12}]^-$

$[Ru(CO)_3Cl_2]_2$ (100 mg; 0.195 mmol) was dissolved in *t*-amyl alcohol (70 ml) in a three-necked flask containing a magnetic stirring bar and equipped with a condenser and a thermometer. Na_2CO_3 (124 mg; 1.17 mmol; molar ratio Na_2CO_3:Ru = 3:1) was added and $CO + H_2$ (molar ratio = 1:3) was bubbled through the resulting solution at 88°C and 1 atm for 12 h. The solution was evaporated to dryness and the resulting solid residue was treated with acetone and filtered, in order to remove the excess of Na_2CO_3 and the NaCl formed during the reaction. Evaporation to dryness of the acetone solution afforded pure $Na[H_3Ru_4(CO)_{12}]$ (70 mg; 0.091 mmol; 93% yield).

4.5. Synthesis of $[Ru_6C(CO)_{16}]^{2-}$

4.5.1. From $[Ru(CO)_3Cl_2]_2$

$[Ru(CO)_3Cl_2]_2$ (150 mg; 0.293 mmol) was dissolved in ethylene glycol (60 ml) in a three-necked flask containing a magnetic stirring bar and equipped with a condenser and a thermometer. K_2CO_3 (809 mg; 5.85 mmol; molar ratio K_2CO_3:Ru = 10:1) was added and CO was bubbled through the resulting pale-yellow solution at 160°C and 1 atm. After 3 h the reaction was complete, as shown by infrared spectroscopy in the carbonyl region, and the solution was red. Extraction, at room temperature under N_2, of the reaction mixture with a dichloromethane solution (3 × 30 ml) of $[NBu_4]I$ (total amount = 144 mg; 0.390 mmol; molar ratio $[NBu_4]^+$:$[Ru_6C(CO)_{16}]^{2-}$ = 4:1), followed by evaporation to dryness of the CH_2Cl_2 phase, gave a dark-red solid residue which was washed twice with water (2 × 10 ml), in order to eliminate the excess of $[NBu_4]I$ and traces of ethylene glycol, affording pure $[NBu_4]_2[Ru_6C(CO)_{16}]$ (135 mg; 0.087 mmol; 89% yield).

4.5.2. From $RuCl_3$

$RuCl_3 \cdot nH_2O$ (200 mg; 0.815 mmol of Ru) was dissolved in ethylene glycol (70 ml) in a three-necked flask containing a magnetic stirring bar and equipped with a condenser and a thermometer. K_2CO_3 (1.13 g; 8.15 mmol; molar ratio K_2CO_3:Ru = 10:1) was added and CO was bubbled through the resulting brown-red solution at 165°C and 1 atm. After 5 h the reaction was complete, as shown by infrared spectroscopy in the carbonyl region, and the solution was red. Extraction, at room temperature under N_2, of the reaction mixture with a dichloromethane solution (3 × 30 ml) of $[NBu_4]I$ (total amount = 201 mg; 0.544 mmol; molar ratio $[NBu_4]^+$:$[Ru_6C(CO)_{16}]^{2-}$ = 4:1), followed by evaporation to dryness of the CH_2Cl_2 phase, gave a dark-red solid residue which was washed twice with water (2 × 10 ml), in order to eliminate the excess of $[NBu_4]I$ and traces of ethylene glycol, affording pure $[NBu_4]_2[Ru_6C(CO)_{16}]$ (200 mg; 0.129 mmol; 95% yield).

4.6. Synthesis of $[Os_3(CO)_{12}]$

4.6.1. From $[Os(CO)_3Cl_2]_2$

$[Os(CO)_3Cl_2]_2$ (180 mg; 0.261 mmol) was dissolved in ethylene glycol (60 ml) in a three-necked flask containing a magnetic stirring bar and equipped with a condenser and a thermometer. Na_2CO_3 (55 mg; 0.518 mmol; molar ratio Na_2CO_3:Os = 1:1) was added and CO was bubbled through the resulting solution at 160–165°C and 1 atm. After 17 h the reaction was essentially complete as shown by the complete disappearance of carbonyl bands in the infrared spectrum of the ethylene glycol solution. During the reaction a yellow precipitate was formed in the flask whereas, in parallel, a yellow powder sublimed on the cold walls of the condenser. Extraction of the sublimate and the reaction mixture with CH_2Cl_2 (150 ml), followed by evaporation to dryness of the CH_2Cl_2 phase, afforded $[Os_3(CO)_{12}]$ contaminated with traces of $[HOs_3(CO)_{10}OH]$ and $[HOs_3(CO)_{10}Cl]$ (as detected by thin layer chromatography and by ^{1}H-NMR) which were removed by washing with pentane (15 ml). The resulting solid was then washed twice with water (2 × 5 ml), in order to eliminate traces of ethylene glycol, affording pure $[Os_3(CO)_{12}]$ (102 mg; 0.112 mmol; 65% yield).

4.6.2. From $OsCl_3$

$OsCl_3 \cdot 3H_2O$ (182 mg; 0.519 mmol) was dissolved in ethylene glycol (60 ml) in a three-necked flask containing a magnetic stirring bar and equipped with a condenser and a thermometer. Na_2CO_3 (82 mg; 0.774 mmol; molar ratio Na_2CO_3:Os = 3:2) was added and CO was bubbled through the resulting solution at 160–165°C and 1 atm. After 15 h the reaction was essentially complete and the infrared spectrum of the yellow ethylene glycol solution showed very weak carbonyl bands (2120(m), 2032(s), 2022(s), 2000(m) cm^{-1}) due to some unidentified carbonyl osmium species which could not be converted to $[Os_3(CO)_{12}]$ by further treatment under CO at 165°C. During the reaction a yellow precipitate was formed in the flask whereas, in parallel, a yellow powder sublimed on the cold walls of the condenser. Extraction of the sublimate and the reaction mixture with CH_2Cl_2 (150 ml), followed by evaporation to dryness of the CH_2Cl_2 phase, afforded a yellow solid residue which was washed twice with water (2 × 5 ml), in order to eliminate traces of ethylene glycol, giving pure $[Os_3(CO)_{12}]$ (100 mg; 0.110 mmol; 64% yield).

4.7. Syntheses of $[H_4Os_4(CO)_{12}]$ and $[H_3Os_4(CO)_{12}]^-$

4.7.1. $[H_3Os_4(CO)_{12}]^-$ from $[Os(CO)_3Cl_2]_2$

$[Os(CO)_3Cl_2]_2$ (150 mg; 0.217 mmol) was dissolved in ethylene glycol (60 ml) in a three-necked flask containing a magnetic stirring bar and equipped with a condenser and a thermometer. K_2CO_3 (600 mg; 4.34 mmol; molar ratio K_2CO_3:Os = 10:1) was added and CO was bubbled through the solution at 160–165°C and 1 atm. After 6 h the reaction was complete as shown by infrared spectroscopy of the resulting orange solution. Extraction, at room temperature under N_2, of the reaction mixture with a dichloromethane solution (3 × 30 ml) of $[NBu_4]I$ (80 mg; 0.217 mmol; molar ratio $[NBu_4]:[H_3Os_4(CO)_{12}]^- = 2:1$), followed by evaporation to dryness of the CH_2Cl_2 phase, gave a yellow solid residue which was washed twice with water (2 × 10 ml), in order to eliminate the excess of $[NBu_4]I$ and traces of ethylene glycol, affording pure $[NBu_4][H_3Os_4(CO)_{12}]$ (108 mg; 0.080 mmol; 74% yield). Similar yields were obtained by increasing the reaction time (12 h). After extraction of the product, no carbonyl species remained in the ethylene glycol solution.

4.7.2. $[H_3Os_4(CO)_{12}]^-$ from $OsCl_3$

$OsCl_3 \cdot 3H_2O$ (180 mg; 0.513 mmol) was dissolved in ethylene glycol (60 ml) in a three-necked flask containing a magnetic stirring bar and equipped with a condenser and a thermometer. K_2CO_3 (710 mg; 5.14 mmol; molar ratio K_2CO_3:Os = 10:1) was added and CO was bubbled through the resulting solution at 160–165°C and 1 atm for 9 h. Extraction, at room temperature under N_2, of the orange reaction solution with a dichloromethane solution (3 × 30 ml) of $[NBu_4]I$ (94 mg; 0.254 mmol; molar ratio $[NBu_4]:[H_3Os_4(CO)_{12}]^- = 2:1$), followed by evaporation to dryness of the CH_2Cl_2 phase, afforded $[NBu_4][H_3Os_4(CO)_{12}]$ along with some degradation products of ethylene glycol (salts of various carboxylic organic acids). Pure $[NBu_4][H_3Os_4(CO)_{12}]$ (128 mg; 0.095 mmol; 74% yield) was then isolated by column chromatography (silica) with 7:3 CH_2Cl_2/pentane as eluant.

4.7.3. $[H_4Os_4(CO)_{12}]$ from $OsCl_3$

$OsCl_3 \cdot 3H_2O$ (180 mg; 0.513 mmol) was dissolved in ethylene glycol (60 ml) in a three-necked flask containing a magnetic stirring bar and equipped with a condenser and a thermometer. K_2CO_3 (710 mg; 5.14 mmol; molar ratio K_2CO_3:Os = 10:1) was added and CO was bubbled through the resulting solution at 160–165°C and 1 atm for 9 h. Acidification of the ethylene glycol reaction solution with H_2SO_4 conc. (2 ml; pH 1) led to the disappearance of the carbonyl bands of $K[H_3Os_4(CO)_{12}]$ in the infrared spectrum of the ethylene glycol solution and to the precipitation of yellow $[H_4Os_4(CO)_{12}]$. Extraction with CH_2Cl_2 (150 ml), followed by evaporation to dryness of the CH_2Cl_2 phase, afforded a yellow solid residue which was washed twice with water (2 × 10 ml), in order to eliminate traces of ethylene glycol, giving pure $[H_4Os_4(CO)_{12}]$ (114 mg; 0.103 mmol; 81% yield).

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