Surface-Mediated Organometallic Synthesis: High-Yield and Selective Syntheses of Neutral and Anionic Ruthenium Carbonyl Clusters by Controlled Reduction of Silica-Supported RuCl$_3$ in the Presence of Na$_2$CO$_3$ or K$_2$CO$_3$

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[Ru$_3$(CO)$_{10}$Cl$_2$], [Ru$_3$(CO)$_{12}$], [H$_4$Ru$_4$(CO)$_{12}$], [H$_3$Ru$_4$(CO)$_{12}$]$^-$, [HRu$_6$(CO)$_{18}$]$^-$, and [Ru$_6$C(CO)$_{16}$]$^{2-}$ have been synthesized in good or high yields by one-step or two-step (with the surface species [Ru(CO)$_3$Cl$_2$(HOSi≡)] as intermediate) *one-pot* controlled reduction of RuCl$_3$ supported on silica in the presence of alkali carbonates. The selectivity of the reaction is controlled by the (i) nature and quantity of the alkali carbonate (Na$_2$CO$_3$ or K$_2$CO$_3$), (ii) manner by which the alkali carbonate is deposited on the silica surface, (iii) gas-phase composition (CO, CO + H$_2$, or CO + H$_2$O), (iv) temperature, and (v) reaction time. The unusual selectivity can be explained by the initial formation of [Ru(CO)$_x$(OH)$_2$]$_n$ (x = 2, 3) which, under CO, aggregates first to [Ru$_3$(CO)$_{12}$], key intermediate for the synthesis *in situ* of various ruthenium carbonyl clusters on the silica surface.

Introduction

Preparative organometallic chemistry mediated by surfaces of inorganic oxides is a new area of synthesis of metal carbonyl complexes and clusters, whereby the surface of an inorganic oxide plays the role of the solvent in conventional syntheses. It is usually characterized by high yields and excellent selectivities.[1] As a general trend, strongly basic surfaces such as MgO favor the formation of anionic metal carbonyl clusters[1a–c] while uncharged carbonyl complexes and clusters are generated on the surface of rather neutral supports such as SiO$_2$.[1d–f] However, we found recently that both neutral and anionic osmium carbonyl clusters can be synthesized by controlled reduction of silica-supported α-[Os(CO)$_3$Cl$_2$]$_2$ or OsCl$_3$ in the presence of alkali carbonates.[1g,h] We have reported that the reductive carbonylation of silica-supported β-[Ru(CO)$_3$Cl$_2$]$_2$ to [Ru$_3$(CO)$_{12}$] does not occur easily due to both the sublimation of the starting material at temperatures higher than 100 °C and the difficulty of removing chloro ligands from the ruthenium coordination sphere when working at relatively low temperatures.[1f] Since in the case of osmium, addition of an alkali carbonate to the silica surface favors removal of chloro ligands,[2] we have extended our investigation to the preparation from RuCl$_3$ of various ruthenium carbonyl clusters (generally best prepared in solution starting from [Ru$_3$(CO)$_{12}$][3]). This

work describes the efficient syntheses on the silica surface of neutral ([Ru$_3$(CO)$_{10}$Cl$_2$], [Ru$_3$(CO)$_{12}$], and [H$_4$Ru$_4$(CO)$_{12}$]) and anionic ([H$_3$Ru$_4$(CO)$_{12}$]$^-$, [HRu$_6$(CO)$_{18}$]$^-$, and [Ru$_6$C(CO)$_{16}$]$^{2-}$) clusters working in the presence of Na$_2$CO$_3$ and K$_2$CO$_3$, respectively, and starting from a simple material such as RuCl$_3$.

Results and Discussion

Synthesis of [Ru$_3$(CO)$_{12}$] and [Ru$_3$(CO)$_{10}$Cl$_2$]. When RuCl$_3$ supported on silica (2 wt % of Ru with respect to SiO$_2$) added with Na$_2$CO$_3$ (molar ratio Na$_2$CO$_3$:Os = 3:1; deposited from a water solution) is heated at 100 °C under 1 atm of CO in the closed cylindrical Pyrex vessel previously described,[1e] an orange material sublimes onto the cold walls of the reaction vessel. Extraction of the sublimate and the silica powder with CH$_2$Cl$_2$ affords [Ru$_3$(CO)$_{12}$] in 38% yield after 96 h. Better yields (56%) are achieved by increasing the temperature (130 °C) and by adding some water (Table 1). In both cases, the gray color of the silica powder, after extraction of [Ru$_3$(CO)$_{12}$], suggests some parallel reduction to metallic ruthenium.

As expected, a slight increase of the CO pressure favors the above reductive carbonylation of RuCl$_3$. By working in an autoclave at 130 °C under 5 atm of CO for 7 h, [Ru$_3$(CO)$_{12}$] is obtained in 69% yield (Table 1). After extraction of [Ru$_3$(CO)$_{12}$], the infrared spectrum of the orange silica powder shows a carbonyl band at 2013 cm^{-1} due to an unidentified carbonyl ruthenium species bound to silica which cannot be converted to [Ru$_3$(CO)$_{12}$] by further treatment under 5 atm of CO at 130 °C. By working with a higher ruthenium loading (15 wt % of Ru with respect to SiO$_2$), the reductive

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Table 1. Synthesis of Neutral Ruthenium Carbonyl Clusters on the Silica Surface in the Presence of Na_2CO_3[a]

starting material	Ru/SiO$_2$, wt %	gas (P, atm)	T°C	t, h	[Ru$_3$(CO)$_{12}$] yield, % (mg)[b]	[H$_4$Ru$_4$(CO)$_{12}$] yield, % (mg)[b]
RuCl$_3$/SiO$_2$	2	CO (1)[c]	130	48	56 (312)	0
RuCl$_3$/SiO$_2$	2	CO (5)	130	7	69 (218)	0
RuCl$_3$/SiO$_2$	15	CO (5)	130	24	55 (100)	0
Ru(CO)$_3$Cl$_2$(HOSi≡)[d]	2	CO (1)	110[e]	48	93 (223)	0
Ru(CO)$_3$Cl$_2$(HOSi≡)[d]	5	CO (1)	110	48	82 (295)[f]	0
Ru(CO)$_3$Cl$_2$(HOSi≡)[d,g,h]	15	CO (1)	110	24	49 (229)	0
Ru(CO)$_3$Cl$_2$(HOSi≡)[d]	2	CO:H$_2$ = 1:3 (1)	110	19	0	88 (162)
Ru(CO)$_3$Cl$_2$(HOSi≡)[d]	2	H$_2$ (1)	110	19	0	39 (134)[i]
Ru(CO)$_3$Cl$_2$(HOSi≡)[d,f,h]	5 or 15	CO:H$_2$ = 1:3 (1)	110[e]	24	0	86 (298)
Ru(CO)$_3$Cl$_2$(HOSi≡)[d,h]	5 or 15	CO:H$_2$ = 1:3 (1)	110	48	0	94 (324)

[a] Molar ratio Na$_2$CO$_3$:Ru = 3:1, deposited from a CH$_2$Cl$_2$ slurry. [b] Actual weight of isolated cluster. [c] In the presence of added water (*ca.* 16 wt % of H$_2$O with respect to SiO$_2$). [d] Prepared on the surface by reductive carbonylation of silica-supported RuCl$_3$.[3] [e] Similar yields are reached at 130 °C. [f] Similar yields are reached starting from pure β-[Ru(CO)$_3$Cl$_2$]$_2$/SiO$_2$. [g] Na$_2$CO$_3$ deposited from water instead of CH$_2$Cl$_2$; when Na$_2$CO$_3$ is deposited from a CH$_2$Cl$_2$ slurry, [Ru$_3$(CO)$_{10}$Cl$_2$] (75%, 332 mg) is formed instead of [Ru$_3$(CO)$_{12}$]. [h] By working with a loading of 15 wt % of Ru with respect to SiO$_2$, a mixture of silica-bound [Ru(CO)$_3$Cl$_2$(HOSi≡)] and silica supported β-[Ru(CO)$_3$Cl$_2$]$_2$ is formed by reductive carbonylation of silica-supported RuCl$_3$. [i] Metallic ruthenium is formed in parallel.

Scheme 1. Best Syntheses, at Atmospheric Pressure, of Various Ruthenium Carbonyl Clusters on SiO$_2$ in the Presence of Na$_2$CO$_3$ or K$_2$CO$_3$ Deposited from a CH$_2$Cl$_2$ Slurry
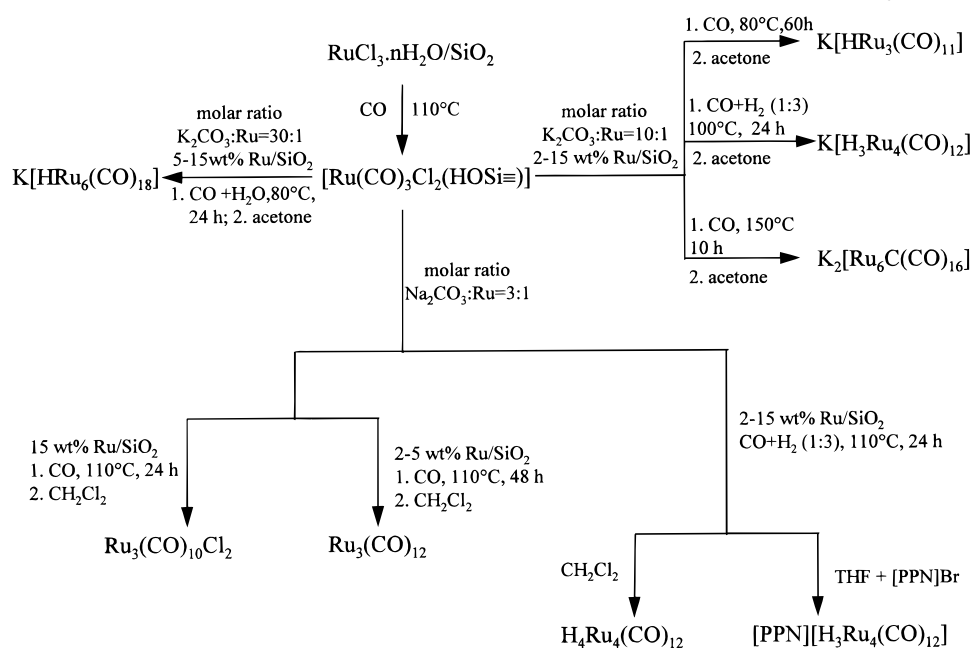
carbonylation (5 atm of CO) gives a lower yield (55%) of [Ru$_3$(CO)$_{12}$] even after 24 h (Table 1).

The direct reductive carbonylation of silica-supported RuCl$_3$ occurs easily, but it does not give high yields of [Ru$_3$(CO)$_{12}$], due to some by-reactions such as reduction to ruthenium metal or to an unreactive ruthenium carbonyl surface species. Therefore, to attain a high yield synthesis of [Ru$_3$(CO)$_{12}$], we investigated a two-step route corresponding to the following: (i) preparation *in situ* of silica-bound [Ru(CO)$_3$Cl$_2$(HOSi≡)] by carbonylation of silica-supported RuCl$_3$ at 110 °C under 1 atm of CO,[1e] and then (ii) addition of a slurry of Na$_2$CO$_3$ in CH$_2$Cl$_2$ (molar ratio Na$_2$CO$_3$:Ru = 3:1), followed by evaporation of the solvent and further reaction with 1 atm of CO at 110 °C. With this two-step approach the reductive carbonylation of RuCl$_3$ (2 wt % of Ru with respect to SiO$_2$) gives 93% yields of [Ru$_3$(CO)$_{12}$] after 48 h (Table 1, Scheme 1).

The possibility of working at high metal loadings is relevant for the production of sizable amounts of reaction products without using large amounts of silica.[1e–h] In a few cases, lower yields and selectivities are reported when too high metal loadings are used. In particular, by working at atmospheric pressure and 100 °C, the formation of [Ru(CO)$_3$Cl$_2$(HOSi≡)] from RuCl$_3$ is sensitive to metal loading, the optimal loading being in the range 2–5 wt % of Ru with respect to SiO$_2$.[1e] At higher loading (10 wt %), yields are lower with parallel formation of poorly reactive [Ru(CO)$_2$Cl$_2$]$_n$, due to the lack of disponible surface silanol groups acting as electron donors.[1e,f] However, we found that high yields of tricarbonylRu(II) surface species (mixture of [Ru(CO)$_3$Cl$_2$(HOSi≡)] and silica-supported β-[Ru(CO)$_3$Cl$_2$]$_2$) can be reached even when the metal loading is high (15 wt % of Ru with respect to SiO$_2$), by working under 1 atm of CO first at 110 °C for 48 h and then at 120 °C for 24 h. Use of a slight CO pressure (5 atm) accelerates the formation of tricarbonylRu(II) species, which is completed in 24 h by working only at 110 °C.

Therefore the metal loading effect on the second step of the silica-mediated synthesis of [Ru$_3$(CO)$_{12}$] was investigated. Treatment of [Ru(CO)$_3$Cl$_2$(HOSi≡)] (5 wt % Ru/SiO$_2$) with a slurry of Na$_2$CO$_3$ (molar ratio Na$_2$CO$_3$:Ru = 3:1) in CH$_2$Cl$_2$, followed by evaporation

of the solvent and reaction with CO (1 atm) at 110 °C, affords pure $[Ru_3(CO)_{12}]$ in 82% yields after 48 h (Table 1). Similar yields are obtained by starting from silica-supported β-$[Ru(CO)_3Cl_2]_2$, prepared by impregnation of silica with β-$[Ru(CO)_3Cl_2]_2$ dissolved in CH_2Cl_2. After extraction of $[Ru_3(CO)_{12}]$, the infrared spectrum of the silica powder shows carbonyl bands at 2049 (w) and 1979 (w) cm^{-1}, similar to those reported for $[Ru(CO)_x$-$(OH)_2]_n$ ($x = 2, 3$).[4] Therefore, an increase of the metal loading from 2 to 5 wt % of Ru with respect to SiO_2 slightly decreases the yields but does not affect selectivity. However, a further increase of the metal loading up to 15 wt % leads to the formation of $[Ru_3(CO)_{10}Cl_2]$ instead of $[Ru_3(CO)_{12}]$ (Scheme 1).

Treatment of a mixture of $[Ru(CO)_3Cl_2(HOSi\equiv)]$ and silica-supported $[Ru(CO)_3Cl_2]_2$ (15 wt % of Ru with respect to SiO_2), obtained by reductive carbonylation of $RuCl_3$, 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 the new compound $[Ru_3(CO)_{10}Cl_2]$, which sublimes in part on the cold walls of the reaction vessel. Extraction of the sublimate and the silica powder with CH_2Cl_2 under N_2 affords this cluster in 75% yield (Table 1). Similar yields are obtained after 48 h, but in this case, some $[Ru_3(CO)_{12}]$ is formed as well (*ca.* 4% yield).

The different selectivity observed by increasing the ruthenium loading (from 2–5 to 15 wt %, Scheme 1) and therefore the alkali carbonate loading (molar ratio Na_2CO_3:Ru = 3:1) could be explained by a nonhomogeneous dispersion of Na_2CO_3 on the silica surface when a slurry in CH_2Cl_2 is used for its deposition. This low homogeneity of the Na_2CO_3 surface dispersion at high loading leads to a lower surface basicity than that expected for a 3:1 molar ratio of Na_2CO_3/Ru and, therefore, to a more difficult removal of chloro ligands from the ruthenium coordination sphere with formation of $[Ru_3(CO)_{10}Cl_2]$ instead of $[Ru_3(CO)_{12}]$. In agreement with this hypothesis, work with a 2-fold amount of Na_2CO_3, reductive carbonylation (1 atm of CO, 110 °C) of a mixture of $[Ru(CO)_3Cl_2(HOSi\equiv)]$ and silica-supported $[Ru(CO)_3Cl_2]_2$ (15 wt % of Ru with respect to SiO_2) gives pure $[Ru_3(CO)_{12}]$ (72% yield after 48 h) instead of $[Ru_3(CO)_{10}Cl_2]$. In addition, when Na_2CO_3 is deposited on the silica surface by using a water solution instead of a CH_2Cl_2 slurry, a better dispersion of the base is reached and only $[Ru_3(CO)_{12}]$ is formed even when the reductive carbonylation is carried out with a 3:1 molar ratio of Na_2CO_3/Ru (Table 1). Clearly, also, the manner by which an alkali carbonate is deposited on the silica surface influences the resulting surface basicity and therefore the selectivity.

To the best of our knowledge, $[Ru_3(CO)_{10}Cl_2]$, which was characterized by elemental analysis, mass spectrometry, and infrared spectroscopy (see Experimental Section), had not been isolated up to now. We simply suggested its formation in traces during the treatment of silica-supported β-$[Ru(CO)_3Cl_2]_2$ with CO + H_2O in the absence of alkali carbonates.[1f] However, the related clusters $[Ru_3(CO)_{10}X_2]$ (X = Br, I), prepared by reaction of 3-X-propene (X = Br, I) with $[HRu_3(CO)_{10}X]$, are well characterized.[5] The infrared spectrum of $[Ru_3(CO)_{10}$-$Cl_2]$ shows ν(CO), in CH_2Cl_2, at 2116 (w), 2088 (s), 2077

(s), 2031 (vs), and 1996 (w) cm^{-1}, in accordance with the infrared spectra of the related clusters $[Ru_3(CO)_{10}X_2]$ (X = Br, I)[5] and $[Os_3(CO)_{10}Cl_2]$[6]. Also Ru–Cl infrared absorptions (ν(Ru–Cl) in polyethylene 288 (m), 272 (m), and 256 (s) cm^{-1}) are similar to those reported for $[Os_3(CO)_{10}Cl_2]$ (ν(Os–Cl) in Nujol 290 (m), 272 (m), and 253 (s) cm^{-1}).[6]

The above-reported synthesis of $[Ru_3(CO)_{12}]$ from $RuCl_3$ by a two-step process is more convenient than the best known syntheses in solution. Yields (93%) are much higher than that obtained by reductive carbonylation at atmospheric pressure of a 2-ethoxyethanolic solution of $RuCl_3$ (45–60% yields)[7] or of a propanolic solution of $[Ru_3O(O_2CCH_3)_6(H_2O)_3](O_2CCH_3)$ (59% yield).[8] They are comparable to yields reached in solution but working under CO pressure (starting from a methanolic solution of $RuCl_3$ under 10–50 atm and from a propanolic solution of $[Ru_3O(O_2CCH_3)_6(H_2O)_3](O_2CCH_3)$ under 3–4 atm, $[Ru_3(CO)_{12}]$ has been obtained in 75–95% yields[9] and 80–85% yields,[8] respectively). In addition, since excellent yields are also reached at relatively high ruthenium loadings of the silica surface, sizable amounts of $[Ru_3(CO)_{12}]$ can be prepared by this surface-mediated synthesis using relatively low amounts of silica (Table 1).

Synthesis of $[H_4Ru_4(CO)_{12}]$. $[H_4Ru_4(CO)_{12}]$ may be synthesized in good yields by reaction of silica-supported $[Ru_3(CO)_{12}]$ with H_2 (1 atm) at 50 °C.[1d] Similarly, treatment of $[Ru_3(CO)_{12}]$ with 1 atm of H_2 in octane under reflux affords $[H_4Ru_4(CO)_{12}]$.[10] This hydridocarbonyl cluster can also be prepared from the less expensive $RuCl_3$ in ethanol, but in low yields (10–30% yields after 3 days at 75–100 °C) and under very high pressures (40 atm of CO + 40 atm of H_2).[11]

When $RuCl_3$ supported on silica (2 wt % of Ru with respect to SiO_2) in the presence of Na_2CO_3 (molar ratio Na_2CO_3:Ru = 3:1) is heated at 130 °C for 48 h under 1 atm of CO + H_2 (molar ratio 1:3), the initially grey-brown silica powder color becomes pale grey, suggesting the formation of metallic ruthenium. Extraction with CH_2Cl_2 affords pure $[H_4Ru_4(CO)_{12}]$ but only in traces. By working at 130 °C but under 10 atm of CO + H_2 (molar ratio 1:3) for 48 h, only $[Ru_3(CO)_{12}]$ is obtained in 12% yield. Under these conditions, the surface species characterized by a carbonyl band at 2013 cm^{-1}, mentioned above, is also formed whereas no $[H_4Ru_4$-$(CO)_{12}]$ is detected, suggesting that its formation is inhibited under CO pressure even in the presence of H_2 in the gas phase.

Such low yields and selectivity and in particular the reduction to metal can be avoided by using a two-step

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Table 2. Synthesis of Anionic Ruthenium Carbonyl Clusters on the Silica Surface from [Ru(CO)$_3$Cl$_2$(HOSi≡)]^a

Ru/SiO$_2$, wt %	M$_2$CO$_3$ (molar ratio M$_2$CO$_3$:Ru)	gas^b	T, °C	t, h	[HRu$_3$(CO)$_{11}$]$^-$ yield, % (mg)^c	[H$_3$Ru$_4$(CO)$_{12}$]$^-$ yield, % (mg)^c	[HRu$_6$(CO)$_{18}$]$^-$ yield, % (mg)^c	[Ru$_6$C(CO)$_{16}$]$^{2-}$ yield, % (mg)^c
2	K$_2$CO$_3$ (10:1)	CO	150	10	0	0	0	95 (246)
5	K$_2$CO$_3$ (20:1)	CO	150	10	0	0	0	85 (298)
15	K$_2$CO$_3$ (20:1)	CO	150	10	0	traces	0	68 (149)
5	K$_2$CO$_3$ (10:1)	CO/H$_2$	100	24	0	60 (288)^d	0	0
5	K$_2$CO$_3$ (20:1)	CO/H$_2$	100	24	0	58 (117)^d	0	0
18	Na$_2$CO$_3$ (3:1)	CO/H$_2$	130	24	0	81 (439)^e	0	0
5	K$_2$CO$_3$ (10:1)	CO	80	60	42 (138)^f	0	0	0
5	K$_2$CO$_3$ (30:1)	CO^g	80	24	0	0	61 (288)^h	0
15	K$_2$CO$_3$ (30:1)	CO^g	80	48	0	0	65 (102)^i	0

^{a} Prepared on the surface by reductive carbonylation of silica-supported RuCl$_3$.[3] ^{b} One atmosphere; molar ratio CO:H$_2$ = 1:3. ^{c} Actual weight of isolated cluster. ^{d} [H$_4$Ru$_4$(CO)$_{12}$] is also obtained in 10% yield (43 mg). ^{e} [H$_4$Ru$_4$(CO)$_{12}$] is formed on the silica surface, but extraction with a THF solution of [PPN]Br affords [PPN][H$_3$Ru$_4$(CO)$_{12}$]; a similar yield is obtained by working at 110 °C. ^{f} [Ru$_3$(CO)$_{12}$] is also obtained in 11% yield (36 mg). ^{g} In the presence of added water (110 wt % of H$_2$O with respect to SiO$_2$). ^{h} [Ru$_3$(CO)$_{12}$] is also obtained in 16% yield (82 mg); similar yields of [Ru$_3$(CO)$_{12}$] and K[HRu$_6$(CO)$_{18}$] by using a 60:1 molar ratio of K$_2$CO$_3$/Ru. ^{i} [Ru$_3$(CO)$_{12}$] is also obtained in 14% yield (24 mg).

route similar to that above described for [Ru$_3$(CO)$_{12}$]. Thus, reductive carbonylation of silica-supported RuCl$_3$ (2 wt % of Ru with respect to SiO$_2$) under 1 atm of CO at 110 °C affords [Ru(CO)$_3$Cl$_2$(HOSi≡)] which by addition of Na$_2$CO$_3$ (molar ratio Na$_2$CO$_3$:Ru = 3:1; deposited from a CH$_2$Cl$_2$ slurry) followed by heating at 110 °C for 19 h under 1 atm of CO + H$_2$ (molar ratio 1:3) affords [H$_4$Ru$_4$(CO)$_{12}$] in 88% total yield (Table 1, Scheme 1). The use of pure H$_2$ as the gas phase affords this hydridocarbonyl cluster in 39% yield only, due to extensive reduction to ruthenium metal.

By working under 1 atm of CO + H$_2$ (molar ratio 1:3) with a higher metal loading (5 or 15 wt % of Ru with respect to SiO$_2$) [H$_4$Ru$_4$(CO)$_{12}$] is obtained in 86 and 94% yields after 24 and 48 h, respectively (Table 1). The same yields are obtained at 130 °C. Similarly, when silica-supported β-[Ru(CO)$_3$Cl$_2$]$_2$ (15 wt % of Ru with respect to SiO$_2$; prepared by impregnation of silica with a CH$_2$Cl$_2$ solution of β-[Ru(CO)$_3$Cl$_2$]$_2$) is heated at 110 °C for 24 h under 1 atm of CO + H$_2$ (molar ratio 1:3) in the presence of Na$_2$CO$_3$ (molar ratio Na$_2$CO$_3$:Ru = 3:1), [H$_4$Ru$_4$(CO)$_{12}$] is obtained in 86% yield (Table 1). The above syntheses are the best known method to convert RuCl$_3$ directly into [H$_4$Ru$_4$(CO)$_{12}$] with excellent yields and under mild conditions (atmospheric pressure); in addition, the possibility of working at high metal loadings allows the production of sizable amounts of this cluster without using too much silica.

Synthesis of [Ru$_6$C(CO)$_{16}$]$^{2-}$. By increasing the basicity of the silica surface by addition of K$_2$CO$_3$ instead of Na$_2$CO$_3$[2] (molar ratio K$_2$CO$_3$:Ru = 10−30:1), [Ru(CO)$_3$Cl$_2$(HOSi≡)] can be converted into anionic ruthenium carbonyl clusters. Treatment of [Ru(CO)$_3$Cl$_2$(HOSi≡)] (2 wt % of Ru with respect to SiO$_2$) with a CH$_2$Cl$_2$ slurry of K$_2$CO$_3$ (molar ratio K$_2$CO$_3$:Ru = 10:1) followed by evaporation of the solvent and further reaction with 1 atm of CO at 150 °C for 10 h affords K$_2$[Ru$_6$C(CO)$_{16}$], easily extracted with acetone under N$_2$, in excellent yield (95%; Table 2; Scheme 1). Working under the same conditions but with a metal loading of 5 wt % of Ru with respect to SiO$_2$, the yields of K$_2$[Ru$_6$C-(CO)$_{16}$] are somewhat lower (80% yield after 10 h) although a slightly better yield (85%) is reached by doubling the K$_2$CO$_3$ amount. Working with a 15 wt % loading of Ru with respect to SiO$_2$, yields of K$_2$[Ru$_6$C-(CO)$_{16}$] are even lower. After 10 h at 150 °C under 1 atm of CO, the latter cluster is obtained in 68% yield only, along with traces of K[H$_3$Ru$_4$(CO)$_{12}$], even in the

presence of a large excess of K$_2$CO$_3$ (molar ratio K$_2$CO$_3$:Ru = 20:1). Therefore, in order to attain excellent yields in this case, it is necessary to avoid too high ruthenium loadings.

Interestingly, when RuCl$_3$ supported on silica (5 wt % of Ru with respect to SiO$_2$) in the presence of K$_2$CO$_3$ (molar ratio K$_2$CO$_3$:Ru = 20:1) was directly heated under 1 atm of CO at either 150 or 200 °C for 24−65 h, we could not observe the formation of K$_2$[Ru$_6$C(CO)$_{16}$], while the infrared spectrum of the resulting silica powder did not show the presence of carbonyl bands. Even by working at 150 °C under 10 atm of CO for 24 h, only very low amounts of K$_2$[Ru$_6$C(CO)$_{16}$] are obtained (*ca.* 2% yield). Therefore, the one-step synthesis of [Ru$_6$C(CO)$_{16}$]$^{2-}$ from silica-supported RuCl$_3$ is not possible although, as shown above, excellent yields can be reached by a two-step route.

[Ru$_6$C(CO)$_{16}$]$^{2-}$ is an interesting compound since it is the key precursor for many carbonylruthenium clusters.[12−14] For example, it is a convenient starting material for the synthesis of clusters bearing the Ru$_6$C core such as [H$_2$Ru$_6$C(CO)$_{16}$],[12] [Ru$_6$C(CO)$_{17}$][13,14] and [Ru$_6$C-(CO)$_{14}$(C$_{14}$H$_{14}$)].[14] Moreover, it has recently been reported that [Ru$_6$C(CO)$_{16}$]$^{2-}$ reacts with [Ru$_3$(CO)$_{12}$] to produce [Ru$_{10}$C(CO)$_{24}$]$^{2-}$, opening a new route to high nuclearity ruthenium clusters.[15] The above-reported two-step silica-mediated synthesis of [Ru$_6$C(CO)$_{16}$]$^{2-}$ from RuCl$_3$ via [Ru(CO)$_3$Cl$_2$(HOSi≡)] is a very attractive method of preparation of this important intermediate. In solution, the best routes to this cluster reported so far require [Ru$_3$(CO)$_{12}$] as starting material (yields 60−90%).[12−14,16] On the surface of MgO, the reduction of RuCl$_3$ (H$_2$, 300 °C, followed by treatment with CO + H$_2$, molar ratio 1:1, 1−10 atm, 225 °C) affords [Ru$_6$C(CO)$_{16}$]$^{2-}$, but yields are not reported.[17]

Synthesis of [H$_3$Ru$_4$(CO)$_{12}$]$^-$. [H$_3$Ru$_4$(CO)$_{12}$]$^-$ may be prepared by deprotonation of [H$_4$Ru$_4$(CO)$_{12}$] both in solution[18] and on the surface of basic inorganic oxides[19] such as Al$_2$O$_3$ and MgO. However, to our knowledge,

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there is no reported synthesis of $[H_3Ru_4(CO)_{12}]^-$ starting directly from $RuCl_3$ or β-$[Ru(CO)_3Cl_2]_2$. We reported that the osmium analogue can be prepared by reduction on the silica surface (1 atm of CO, 150 °C) of $[Os(CO)_3Cl_2]_2$ or $[Os(CO)_3Cl_2(HOSi\equiv)]$ in the presence of K_2CO_3,[1g] but by working under these conditions, $[Ru_6C(CO)_{16}]^{2-}$ is obtained instead of $[H_3Ru_4(CO)_{12}]^-$, as described above. This different reactivity is not surprising since synthetic routes to clusters of ruthenium and osmium often differ widely due to the different balance of M–M and M–CO bond strengths for the two kinds of metal clusters.[20]

However it is known that, on the surface of Al_2O_3 and MgO, $[H_3Ru_4(CO)_{12}]^-$ is converted to $[Ru_6C(CO)_{16}]^{2-}$ by treatment under CO + H_2 (molar ratio 1:1) at 200 °C.[19] Therefore, $[H_3Ru_4(CO)_{12}]^-$ could be an intermediate species in the silica-mediated synthesis of $[Ru_6C(CO)_{16}]^{2-}$ described above. Treatment of $[Ru(CO)_3Cl_2(HOSi\equiv)]$ (5 wt % of Ru with respect to SiO_2) with a slurry of K_2CO_3 (molar ratio K_2CO_3:Ru = 10:1) in CH_2Cl_2, followed by evaporation of the solvent, drying under vacuum (10^{-2} Torr) for 3 h at 100 °C, and reduction for 24 h under 1 atm of CO + H_2 (molar ratio 1:3) at lower temperatures such as 100 °C, affords a mixture of $[H_4Ru_4(CO)_{12}]$ (10% yield) and $K[H_3Ru_4(CO)_{12}]$ (60% yield, Table 2) which can be separated by selective extraction under N_2 from the silica surface with CH_2Cl_2 and acetone, respectively. The treatment under vacuum at 100 °C prior to reduction is necessary to avoid too much physisorbed water, which favors a fast aggregation of $[H_3Ru_4(CO)_{12}]^-$ to $[Ru_6C(CO)_{16}]^{2-}$. Similar selectivities and yields ($[H_4Ru_4(CO)_{12}]$, 10% yield, and $K[H_3Ru_4(CO)_{12}]$, 58% yield) are obtained by using a 2-fold amount of K_2CO_3, whereas both longer reaction time and higher temperatures give some $[Ru_6C(CO)_{16}]^{2-}$ as byproduct. The unavoidable formation of some $[H_4Ru_4(CO)_{12}]$, even by working with a highly basic silica surface, is probably due to its rapid sublimation under reaction conditions. So in order to reach a complete selectivity to $[H_3Ru_4(CO)_{12}]^-$, an alternative method of extraction was investigated.

Treatment of $[H_4Ru_4(CO)_{12}]$ with [PPN]Cl in THF gives $[PPN][H_3Ru_4(CO)_{12}]$ in 100% yield.[18c] Similarly when silica-supported $[H_4Ru_4(CO)_{12}]$ (18 wt % of Ru with respect to SiO_2), prepared by the two-step route from silica-supported $RuCl_3$, is extracted under N_2 with a stoichiometric amount of [PPN]Br in THF, $[PPN][H_3Ru_4(CO)_{12}]$ is obtained in 81% total yield (Table 2, Scheme 1), corresponding to an excellent selectivity to $[H_3Ru_4(CO)_{12}]^-$ starting from a simple material such as $RuCl_3$. Obviously this selective method of extraction can be used also for mixtures of $[H_4Ru_4(CO)_{12}]$ and $[H_3Ru_4(CO)_{12}]^-$ obtained from $[Ru(CO)_3Cl_2(HOSi\equiv)]$ as above described.

Synthesis of $[HRu_3(CO)_{11}]^-$ and $[HRu_6(CO)_{18}]^-$. Adsorption of $[Ru_3(CO)_{12}]$ onto hydroxylated magnesia,[21] zinc oxide,[21] lanthanum oxide,[21] or aluminum oxide[22] yields $[HRu_3(CO)_{11}]^-$, which can be extracted from the surface with [PPN]Cl, whereas reaction of $[Ru_3(CO)_{12}]$

with KOH in methanol/tetrahydrofuran and water/tetrahydrofuran affords $[HRu_3(CO)_{11}]^-$ (100% yield) and $[Ru_6(CO)_{18}]^{2-}$ (80% yield), respectively,[9c] showing a remarkable effect of water on the reaction selectivity. $[HRu_3(CO)_{11}]^-$ has also been prepared by reaction with CO at 25 °C of $[Ru(CO)_3Cl_2(THF)]$ supported on Al_2O_3.[23] Because $[HRu_3(CO)_{11}]^-$ and $[Ru_6(CO)_{18}]^{2-}$ have never been prepared directly from $RuCl_3$, we studied their synthesis from $[Ru(CO)_3Cl_2(HOSi\equiv)]$, easily obtained on silica from $RuCl_3$.[1e]

Treatment of $[Ru(CO)_3Cl_2(HOSi\equiv)]$ (5 wt % of Ru with respect to SiO_2) with K_2CO_3 (molar ratio K_2CO_3:Ru = 10:1) deposited from a CH_2Cl_2 slurry, followed by heating at 80 °C for 60 h under 1 atm of CO, affords a mixture of $[Ru_3(CO)_{12}]$ and $K[HRu_3(CO)_{11}]$ (Table 2). Successive selective extractions with CH_2Cl_2 and acetone under N_2 give the neutral cluster (11% yield) and the anionic cluster (42% yield), respectively. Similar yields are obtained after 96 h. Attempts to obtain only $[HRu_3(CO)_{11}]^-$ failed, because both an increase of the temperature (100 °C) and of the surface basicity (molar ratio K_2CO_3:Ru = 20:1) gave mixtures of $[Ru_3(CO)_{12}]$, $K[HRu_3(CO)_{11}]$, $K[H_3Ru_4(CO)_{12}]$, and $K_2[Ru_6C(CO)_{16}]$ with ratios related to reaction time. Obviously it is more convenient to first prepare $[Ru_3(CO)_{12}]$ from $RuCl_3$ supported on silica as described above and then to convert it into $[HRu_3(CO)_{11}]^-$ in solution[9c] or on the surface of basic inorganic oxides.[21,22]

The effect of water on the reduction (1 atm of CO) at 80 °C of $[Ru(CO)_3Cl_2(HOSi\equiv)]$ (5 wt % of Ru with respect to SiO_2) in the presence of K_2CO_3 (molar ratio K_2CO_3:Ru = 10:1) was investigated. By working with a large amount of water (110 wt % of H_2O with respect to SiO_2), $K[HRu_6(CO)_{18}]$ is formed instead of $K[HRu_3(CO)_{11}]$ (Table 2), but yields of the former anion are low (10–13% after 24 h), the major product being $[Ru_3(CO)_{12}]$. However, use of a 3-fold amount of K_2CO_3 favors the formation of $K[HRu_6(CO)_{18}]$ (61% yield, Scheme 1) at the expense of $[Ru_3(CO)_{12}]$ (16% yield). Further increase of the surface basicity (molar ratio K_2CO_3:Ru = 60:1) does not improve the yield of $K[HRu_6(CO)_{18}]$, $[Ru_3(CO)_{12}]$ still being present (13% yield). The two clusters can be easily separated by successive selective extractions with CH_2Cl_2, which extracts $[Ru_3(CO)_{12}]$, and acetone, which extracts $K[HRu_6(CO)_{18}]$. Yields are not so good when working with higher ruthenium loadings (Table 2). For example, with a 15 wt % loading of Ru with respect to SiO_2, $K[HRu_6(CO)_{18}]$ and $[Ru_3(CO)_{12}]$ are obtained in 40 and 4% yields, respectively, after 24 h, although reaction for a further 24 h increases yields to 65 ($K[HRu_6(CO)_{18}]$) and 14% ($[Ru_3(CO)_{12}]$).

Therefore, under basic conditions, the presence of excess water favors aggregation of trinuclear to hexanuclear clusters on the silica surface as in solution.[9c] However, whereas in solution water favors the formation of $[Ru_6(CO)_{18}]^{2-}$,[9c] on the silica surface a large excess of water favors the formation of $[HRu_6(CO)_{18}]^-$. Since $[HRu_6(CO)_{18}]^-$ is usually prepared in solution by acidification of $[HRu_3(CO)_{11}]^-$ (50% yield) or $[Ru_6(CO)_{18}]^{2-}$ (80% yield),[9c] its direct silica-mediated synthesis from

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$RuCl_3$, although not highly selective, is an attractive way to prepare it under mild conditions and in good yields.

Steps of the Reduction of Silica-Bound [Ru-$(CO)_3Cl_2(HOSi\equiv)$] To Generate Various Neutral and Anionic Carbonyl Clusters. In order to understand the surface organometallic chemistry involved in the above-described syntheses of various ruthenium carbonyl clusters, we investigated the (i) nature of the species initially formed by reaction of silica-supported β-[Ru(CO)$_3$Cl$_2$]$_2$ or [Ru(CO)$_3$Cl$_2$(HOSi$\equiv$)] with alkali carbonates, (ii) evidence for some key intermediates in the nucleation process, and (iii) possible pathways for the generation of the various neutral and anionic ruthenium clusters.

When a slurry of silica, β-[Ru(CO)$_3$Cl$_2$]$_2$, M$_2$CO$_3$ (M = Na or K; molar ratio M:Ru = 6−60:1), and CH$_2$Cl$_2$ is stirred at room temperature, new surface ruthenium carbonyl species are produced. Similar species are obtained by starting from [Ru(CO)$_3$Cl$_2$(HOSi$\equiv$)], formed *in situ* by reductive carbonylation of silica-supported RuCl$_3$.[1e] The infrared spectra of these surface species are characterized by three carbonyl bands (2132−2135 (m), 2062−2065 (s), and 1999−2006 (m) cm^{-1}, in Nujol) which vary slightly, depending on the nature and quantity of the added alkali carbonate. Lower frequencies are observed when K$_2$CO$_3$ is used instead of Na$_2$CO$_3$ and when the molar ratio of M$_2$CO$_3$/Ru increases, that is, by increasing the surface basicity.[2] The carbonyl bands of these surface ruthenium species are at lower frequencies than those of either silica-supported β-[Ru(CO)$_3$Cl$_2$]$_2$ (2144 (m) and 2080 (s) cm^{-1}, in Nujol) or [Ru(CO)$_3$Cl$_2$(HOSi$\equiv$)] (2140 (m) and 2070 (s) cm^{-1}, in Nujol),[1f] but they are similar to those of a mixture of silica-anchored species such as [Ru(CO)$_3$(OSi$\equiv$)$_2$]$_n$ (2138 (m), 2069 (s), 2014 (m) cm^{-1}) and [Ru(CO)$_2$(OSi$\equiv$)$_2$]$_n$ (2069 (s), 2005 (s) cm^{-1}) obtained by thermal treatment of silica-supported [Ru$_3$(CO)$_{12}$].[24] This infrared evidence suggests the removal of chloro ligands from the coordination sphere of ruthenium to afford new species similar or related to [Ru(CO)$_x$(OSi$\equiv$)$_2$]$_n$ (x = 2, 3).

However, from the behavior of some ruthenium silanolate complexes, we know that the Ru−OSi bond generates easily, in the presence of water, the Ru−OH bond.[25] Therefore, any ruthenium silanolate species that could be generated by reaction in the presence of alkali carbonates of the silanol groups of the silica surface with β-[Ru(CO)$_3$Cl$_2$]$_2$ should easily hydrolyze to the known compounds [Ru(CO)$_x$(OH)$_2$]$_n$ (x = 2, 3),[4] because water is present on the surface under our experimental conditions. In any case, by working with high ruthenium loadings (15 wt % of Ru with respect to SiO$_2$), there would not be enough surface silanol groups to convert all β-[Ru(CO)$_3$Cl$_2$]$_2$ to [Ru(CO)$_3$(OSi$\equiv$)$_2$]$_n$.[1e] At least in this latter case, some physisorbed [Ru(CO)$_x$(OH)$_2$]$_n$ (x = 2, 3) should be formed as well.

In agreement with this hypothesis, we found that the surface species obtained by reaction of silica-supported β-[Ru(CO)$_3$Cl$_2$]$_2$ or [Ru(CO)$_3$Cl$_2$(HOSi$\equiv$)] (2 wt % of Ru with respect to SiO$_2$) with Na$_2$CO$_3$ (molar ratio Na$_2$CO$_3$:

Ru = 3:1) can be extracted with acetone. After extraction, only weak carbonyl bands (2047 (w) and 1980 (w) cm^{-1}, in Nujol) remain on the silica surface whereas the infrared spectrum of the acetone solution containing the extracted ruthenium species is similar to that characteristic of [Ru(CO)$_x$(OH)$_2$]$_n$ species (x = 2, 3; ν(CO) = 2048 (s), 1974 (s), and 1944 (w, sh) cm^{-1}).[4,26] Evaporation of this solution affords a powder that does not present Ru−Cl infrared absorption bands, in accordance with complete removal of the chloro ligands. Reaction with HCl(aq) of this powder dissolved in ethanol affords a mixture of [Ru(CO)$_2$Cl$_2$(EtOH)$_2$] and *fac*-[Ru(CO)$_3$-Cl$_3$]$^-$, suggesting the presence of a mixture of dicarbonyl and tricarbonyl species on the silica surface.[4,26]

The above observations would support the formation of species such as [Ru(CO)$_x$(OH)$_2$]$_n$ (x = 2, 3) by reaction of β-[Ru(CO)$_3$Cl$_2$]$_2$ or [Ru(CO)$_3$Cl$_2$(HOSi$\equiv$)] with alkali carbonates on the silica surface under our reaction conditions, as it occurs in the case of the reductive carbonylation of α-[Os(CO)$_3$Cl$_2$]$_2$ physisorbed on silica in the presence alkali carbonates.[2] These ruthenium species are quite reactive, and they are easily converted to [Ru$_3$(CO)$_{12}$] on the silica surface by working under CO (1 atm) at 110 °C (Scheme 1). On the silica surface, it is possible that the aggregation process occurs via [HRu$_3$(CO)$_{10}$(OR)] (R = H, Si$\equiv$), as evidenced by the reduction of the related silica-supported carbonylosmium(II) species to various osmium carbonyl clusters.[27] However, attempts to stop the reduction of [Ru(CO)$_3$-Cl$_2$(HOSi$\equiv$)], when detectable amounts of [HRu$_3$(CO)$_{10}$-(OR)] (R = H, Si$\equiv$) are formed, failed due to the known rapid reaction of the latter clusters with CO at room temperature to give [Ru$_3$(CO)$_{12}$].[24]

In fact, the formation of [Ru$_3$(CO)$_{12}$] was observed at 50 °C under 1 atm of CO or CO + H$_2$ (molar ratio 1:3) in the presence of either a low surface basicity (molar ratio Na$_2$CO$_3$:Ru = 3:1) or a high surface basicity (molar ratio K$_2$CO$_3$:Ru = 10:1). After 24 h under these conditions, a mixture of [Ru$_3$(CO)$_{12}$] and unreacted [Ru-(CO)$_x$(OH)$_2$]$_n$ (x = 2, 3) was present on the silica surface. Therefore, [Ru$_3$(CO)$_{12}$] is the first detectable step of the process of nucleation of surface carbonylruthenium(II) entities to various ruthenium carbonyl clusters. It follows that the observed selectivity (Scheme 1) must be explained by involving [Ru$_3$(CO)$_{12}$] as the key intermediate (Scheme 2).

By working with a low surface basicity (molar ratio Na$_2$CO$_3$:Ru = 3:1), we found that silica-supported [Ru$_3$(CO)$_{12}$] can be easily converted to [H$_4$Ru$_4$(CO)$_{12}$] in the presence of H$_2$ (Scheme 2). In the absence of H$_2$ and on a more basic silica surface, [Ru$_3$(CO)$_{12}$] behaves as on the surface of MgO[19] or in basic solution.[28] Treatment of silica-supported [Ru$_3$(CO)$_{12}$] (2 wt % of Ru with respect to SiO$_2$) with a slurry of K$_2$CO$_3$ in CH$_2$Cl$_2$ (molar ratio K$_2$CO$_3$:Ru = 10:1), followed by evaporation of the solvent and treatment under 1 atm of CO at 80 °C for 24 h, affords pure K[HRu$_3$(CO)$_{11}$], which can be

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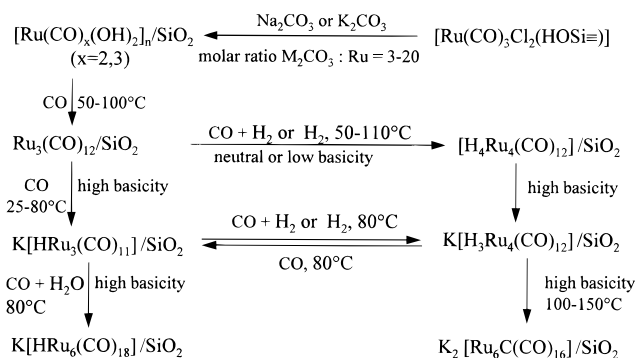(26) Lucenti, E. Doctoral Thesis, Università degli Studi di Milano, Milano, Italy, 1995.

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Scheme 2. Possible Pathways for the Generation of Various Ruthenium Carbonyl Clusters from [Ru(CO)$_3$Cl$_2$(HOSi≡)]

$$[Ru(CO)_x(OH)_2]_n/SiO_2 \xrightarrow[\text{molar ratio } M_2CO_3 : Ru = 3-20]{Na_2CO_3 \text{ or } K_2CO_3} [Ru(CO)_3Cl_2(HOSi≡)]$$
(x=2,3)

CO | 50-100°C ↓

$$Ru_3(CO)_{12}/SiO_2 \xrightarrow[\text{neutral or low basicity}]{CO + H_2 \text{ or } H_2, 50-110°C} [H_4Ru_4(CO)_{12}]/SiO_2$$

CO 25-80°C ↓ high basicity   high basicity ↓

$$K[HRu_3(CO)_{11}]/SiO_2 \underset{CO, 80°C}{\overset{CO + H_2 \text{ or } H_2, 80°C}{\rightleftharpoons}} K[H_3Ru_4(CO)_{12}]/SiO_2$$

CO + H$_2$O | high basicity 80°C ↓   high basicity 100-150°C ↓

$$K[HRu_6(CO)_{18}]/SiO_2 \qquad\qquad K_2[Ru_6C(CO)_{16}]/SiO_2$$

extracted from the silica surface with CH$_3$CN (Scheme 2). However, as on the surface of MgO,[19] the reaction continues when working with a more basic silica surface (molar ratio K$_2$CO$_3$:Ru = 30:1) since [Ru$_3$(CO)$_{12}$] (2 wt % of Ru with respect to SiO$_2$) reacts at 80 °C, under CO (1 atm) and excess water, to give K[HRu$_6$(CO)$_{18}$]. By analogy with the redox condensation in THF of [Ru$_3$(CO)$_{11}$]$^{2-}$ with [Ru$_3$(CO)$_{12}$] to give [Ru$_6$(CO)$_{18}$]$^{2-}$,[13] [HRu$_6$(CO)$_{18}$]$^-$ could be formed on the silica surface by condensation of [HRu$_3$(CO)$_{11}$]$^-$ with some [Ru$_3$(CO)$_{12}$].

On the other hand, when silica-supported [Ru$_3$(CO)$_{12}$] (2 wt % of Ru with respect to SiO$_2$) is treated for 24 h with CO + H$_2$ (molar ratio 1:3, 1 atm) at 80 °C on a basic silica surface (molar ratio K$_2$CO$_3$:Ru = 10:1), K[H$_3$Ru$_4$(CO)$_{12}$] is obtained quantitatively. This latter conversion possibly involves [H$_4$Ru$_4$(CO)$_{12}$] and K[HRu$_3$(CO)$_{11}$] as intermediates. In fact, when [H$_4$Ru$_4$(CO)$_{12}$] does not sublime under reaction conditions, it is easily deprotonated on such a basic silica surface, as confirmed by a blank experiment carried out under N$_2$ (Scheme 2). Besides, treatment at 80 °C for 24 h of K[HRu$_3$(CO)$_{11}$] supported on silica added with K$_2$CO$_3$ (molar ratio K$_2$CO$_3$:Ru = 10:1) with CO + H$_2$ (molar ratio 1:3) affords pure K[H$_3$Ru$_4$(CO)$_{12}$]. The latter transforms back to K[HRu$_3$(CO)$_{11}$] when H$_2$ is removed, the conversion being complete after 24 h at 80 °C under 1 atm of CO. Such a reversible interconversion between [HRu$_3$(CO)$_{11}$]$^-$ and [H$_3$Ru$_4$(CO)$_{12}$]$^-$ can be repeated and mimicks interconversions of these ions in basic solution[29] or on the surface of MgO.[30]

As described above, attempts to prepare selectively [HRu$_3$(CO)$_{11}$]$^-$ by reductive carbonylation (1 atm of CO, molar ratio K$_2$CO$_3$:Ru = 10:1) of [Ru(CO)$_3$Cl$_2$(HOSi≡)] at 100 °C failed, a mixture of [HRu$_3$(CO)$_{11}$]$^-$, [H$_3$Ru$_4$(CO)$_{12}$]$^-$, and some [Ru$_6$C(CO)$_{16}$]$^{2-}$ being obtained. The formation of some [H$_3$Ru$_4$(CO)$_{12}$]$^-$ is linked to the presence in the gas phase of some H$_2$, produced *in situ* by a water gas shift reaction, as confirmed by gas chromatographic analysis which revealed the presence of both H$_2$ and CO$_2$. This reaction is expected since it is known that [HRu$_3$(CO)$_{11}$]$^-$ catalyzes the water gas shift reaction in basic medium.[21,31,32] The presence of some [Ru$_6$C(CO)$_{16}$]$^{2-}$ is explained by a slow thermal conver-

sion of [H$_3$Ru$_4$(CO)$_{12}$]$^-$ because when K[H$_3$Ru$_4$(CO)$_{12}$] supported on silica (2 wt % of Ru with respect to SiO$_2$) added with K$_2$CO$_3$ (molar ratio K$_2$CO$_3$:Ru = 10:1) is heated at 150 °C for 6 h under CO (1 atm), K$_2$[Ru$_6$C(CO)$_{16}$] is obtained quantitatively. This thermal conversion, which also occurs under N$_2$, would explain why K$_2$[Ru$_6$C(CO)$_{16}$] is obtained in quantitative yield when [Ru$_3$(CO)$_{12}$] supported on silica added with excess K$_2$CO$_3$ is treated with CO at 150 °C. At this temperature, H$_2$ is easily produced by the water gas shift reaction, favoring the formation of K[H$_3$Ru$_4$(CO)$_{12}$], which is then thermally converted to K$_2$[Ru$_6$C(CO)$_{16}$], as reported above and as it occurs on Al$_2$O$_3$ and MgO.[19]

In summary, the remarkable selective syntheses of various neutral and anionic ruthenium clusters described in this work can be reasonably explained by the series of organometallic interconversions reported in Scheme 2, where [Ru$_3$(CO)$_{12}$] is the key intermediate and where the selectivity to various clusters is controlled by the basicity of the surface, the composition of the gaseous phase (CO or H$_2$ + CO), and the temperature.

Conclusion

This work is another example of the potential of the silica surface as an efficient, although unusual, reaction medium which allows selective and high-yield syntheses of both neutral and anionic metal carbonyl clusters starting from very simple materials such as metal chlorides. In particular, the observation that the surface basicity is also controlled by the way of deposition of the alkali carbonate suggests that we are in the presence of a basic reagent (the alkali carbonate) deposited on the silica surface and not of a reaction between the silanol groups of the silica surface with the basic reagent. In fact, by impregnation of the alkali carbonate from a water solution instead of a CH$_2$Cl$_2$ slurry, a higher surface basicity is achieved, a result that cannot be explained at all by a reaction with the silanol groups but only by a more homogeneous dispersion of the basic reagent deposited on the surface. The final result is the formation of a new basic phase (the silica surface) characterized by a behavior comparable to that of strong bases dissolved in solution or of strong intrinsically basic surfaces such as MgO.

By working with this new basic medium we achieved quite selective *one-pot* syntheses of various neutral and anionic ruthenium carbonyl clusters, although in the case of [HRu$_3$(CO)$_{11}$]$^-$, both yields and selectivity are not outstanding due to the great tendency of this cluster to condensate with [Ru$_3$(CO)$_{12}$] or to react with H$_2$. In any case, the majority of the syntheses described in this work is the best method to prepare various ruthenium clusters starting from the simple material RuCl$_3$, since generally the best reported syntheses of these clusters involve [Ru$_3$(CO)$_{12}$] as starting material. The possibility of achieving, in the majority of cases, high yields and selectivities even when working with high metal loadings of the silica surface gives to the syntheses described in this work the potentiality of being used for the preparation of good amounts of ruthenium carbonyl clusters (Tables 1 and 2) by using only a few grams of silica which, in any case, can be reused after the reaction.

Experimental Section

General Comments. SiO$_2$ (Aerosil 200 Degussa, with a nominal surface area of 200 m^2/g) was used as the support

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after treatment in vacuo (10^{-2} Torr) at 25 °C for 3 h. $RuCl_3 \cdot nH_2O$ (41.2 wt % Ru) was purchased from Strem Chemicals while β-$[Ru(CO)_3Cl_2]_2$ was prepared according to the literature.[1e] All the reaction products were identified, after extraction from silica, by infrared, ^1H 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. Gas analyses for the detection of H_2 and CO_2 were carried out on a Hewlett Packard 5890 gas chromatograph equipped with a stainless steel Carbosieve SII packed column (outside column diameter $^1/_8$ in.; column length 96 in.; oven program temperature 35 °C isotherm for 7 min and then heated from 35 to 225 °C at a 32 °C/min rate).

Preparation of Silica-Supported RuCl₃ with or without Addition of Alkali Carbonates. A slurry of silica (9.98 g), $RuCl_3 \cdot nH_2O$ (41.2 wt % Ru; correct amount to have the desired Ru loading, 2–15 wt % of Ru with respect to SiO_2), H_2O (200 mL) and, when necessary, Na_2CO_3 or K_2CO_3 (correct amount to have the desired molar ratio of M_2CO_3 to Ru) was stirred overnight under N_2 at 25 °C. The solvent was evaporated under vacuum (10^{-2} Torr) using a water bath at 80 °C. The final powder was stored under N_2.

Preparation of Silica-Supported β-$[Ru(CO)_3Cl_2]_2$, $[Ru_3(CO)_{12}]$, or $[H_4Ru_4(CO)_{12}]$ with Addition of Alkali Carbonates. A slurry of silica (10.0 g), β-$[Ru(CO)_3Cl_2]_2$, $[Ru_3(CO)_{12}]$, or $[H_4Ru_4(CO)_{12}]$ (correct amount to have the desired Ru loading, 2–15 wt % of Ru with respect to SiO_2), Na_2CO_3 or K_2CO_3 (correct amount to have the desired molar ratio of M_2CO_3/Ru), and CH_2Cl_2 (250 mL) was vigorously stirred under N_2 for 24 h at 25 °C. The solvent was evaporated at 25 °C in vacuo (10^{-2} Torr), affording a powder which was stored under N_2.

Preparation of $[Ru(CO)_3Cl_2(HOSi\equiv)]$ with or without Addition of Alkali Carbonates. $[Ru(CO)_3Cl_2(HOSi\equiv)]$ (2–5 wt % of Ru with respect to SiO_2) was prepared by reductive carbonylation (1 atm of CO, 110 °C, *ca.* 48 h) of silica-supported $RuCl_3$.[1e] With a loading of 15 wt % of Ru with respect to SiO_2, it was necessary to carry out the reductive carbonylation (1 atm of CO) first at 110 °C for 48 h and then at 120 °C for 24 h to obtain only tricarbonylRu(II) surface species as evidenced by infrared spectroscopy (mixture of $[Ru(CO)_3Cl_2(HOSi\equiv)]$ and silica-supported β-$[Ru(CO)_3Cl_2]_2$).[1f] By using a slight CO pressure (5 atm), the conversion of $RuCl_3$ (15 wt % of Ru with respect to SiO_2) to tricarbonylRu(II) surface species was complete in 24 h only at 110 °C. The addition of alkali carbonates to $[Ru(CO)_3Cl_2(HOSi\equiv)]$ was made as described above for supported β-$[Ru(CO)_3Cl_2]_2$, but using $[Ru(CO)_3Cl_2(HOSi\equiv)]$ instead of β-$[Ru(CO)_3Cl_2]_2$.

Synthesis of $[Ru_3(CO)_{12}]$ at Atmospheric Pressure. (a) From $[Ru(CO)_3Cl_2(HOSi\equiv)]$. $[Ru(CO)_3Cl_2(HOSi\equiv)]$ (prepared as described above; 3.84 g of powder, 5 wt % of Ru with respect to SiO_2, 0.171 g (1.69 mmol) of Ru) added with Na_2CO_3 (0.501 g; 4.72 mmol; molar ratio Na_2CO_3:Ru = 3:1; deposited from a CH_2Cl_2 slurry as described above) 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.[1e] It was treated in vacuo (10^{-2} Torr) at 25 °C and exposed to CO (1 atm). The bottom of the vessel (half of the cylinder) was put into an oven and heated at 110 °C for 48 h. During the reaction, some $[Ru_3(CO)_{12}]$ sublimed onto the cold part of the reaction vessel. Extraction of the sublimate and the silica powder with CH_2Cl_2 (200 mL), followed by evaporation of the solvent, gave $[Ru_3(CO)_{12}]$ (0.295 g; 0.462 mmol; 82% yield).

(b) From Silica-Supported β-$[Ru(CO)_3Cl_2]_2$. By operating as above but starting from silica-supported β-$[Ru(CO)_3Cl_2]_2$ (5 wt % of Ru with respect to SiO_2) instead of $[Ru(CO)_3Cl_2(HOSi\equiv)]$, $[Ru_3(CO)_{12}]$ was obtained in 83% yield (weight of isolated cluster 0.332 g).

(c) From Silica-Supported $RuCl_3$. Lower yields (38–56%; actual weights of isolated cluster 0.150–0.312 g) of $[Ru_3(CO)_{12}]$ were obtained by operating as above (1 atm of CO; 100–130 °C; 48–96 h; see Table 1) but starting from $RuCl_3$ (2 wt % of Ru with respect to SiO_2) added with Na_2CO_3 (molar ratio Na_2CO_3:Ru = 3:1).

Synthesis of $[Ru_3(CO)_{12}]$ from Silica-Supported $RuCl_3$ under 5 atm of CO. Silica-supported $RuCl_3$ (1.06 g of powder; 15 wt % of Ru with respect to SiO_2; 0.086 g of Ru; 0.850 mmol of Ru) added with Na_2CO_3 (0.270 g; 2.56 mmol; molar ratio Na_2CO_3:Ru = 3:1; deposited from a water solution) was placed in a stainless steel autoclave containing a glass liner. The autoclave was closed, purged twice with N_2, evacuated, pressurized to 5 atm of CO, and heated at 130 °C for 24 h. After the mixture cooled to room temperature, the pressure was released and the autoclave opened. Extraction with CH_2Cl_2 of the final powder afforded pure $[Ru_3(CO)_{12}]$ (0.100 g; 0.158 mmol; 55 % yield).

Synthesis of $[Ru_3(CO)_{10}Cl_2]$ from $[Ru(CO)_3Cl_2(HOSi\equiv)]$. A mixture of $[Ru(CO)_3Cl_2(HOSi\equiv)]$ and silica-supported β-$[Ru(CO)_3Cl_2]_2$ (prepared as described above; 2.06 g of powder; 15 wt % of Ru with respect to SiO_2; 0.222 g of Ru; 2.20 mmol of Ru) added with Na_2CO_3 (0.702 g; 6.60 mmol; molar ratio Na_2CO_3:Ru = 3:1; deposited from a CH_2Cl_2 slurry) was heated in the cylindrical vessel under CO (1 atm) at 110 °C for 24 h. During the reaction, some product sublimed onto the cold part of the reaction vessel. Extraction of the sublimate and the silica powder with CH_2Cl_2 (*ca.* 200 mL) under CO or N_2 afforded pure $[Ru_3(CO)_{10}Cl_2]$ (0.360 g; 0.550 mmol; 75% yield), which was characterized by elemental analysis (Anal. Calcd: C, 18.36; Cl, 10.84. Found: C, 18.38; Cl, 10.76), mass spectrometry (in the EI mass spectrum, there is the molecular ion peak at $m/e = 653$, followed by peaks corresponding to the successive loss of 10 COs), and infrared spectroscopy (in CH_2Cl_2, $\nu(CO)$ 2116 (w), 2088 (s), 2077 (s), 2031 (vs), and 1996 (w) cm^{-1}; in polyethylene, $\nu(Ru-Cl)$ 288 (m), 272 (m), and 256 (s) cm^{-1}). $[Ru_3(CO)_{10}Cl_2]$ decomposes in air and therefore must be stored under CO or N_2. When Na_2CO_3 was deposited from a water solution, under the same reaction conditions, $[Ru_3(CO)_{12}]$ (0.229 g; 0.359 mmol; 49% yield) was obtained instead of $[Ru_3(CO)_{10}Cl_2]$.

Synthesis of $[H_4Ru_4(CO)_{12}]$ from $[Ru(CO)_3Cl_2(HOSi\equiv)]$. A mixture of $[Ru(CO)_3Cl_2(HOSi\equiv)]$ and silica-supported β-$[Ru(CO)_3Cl_2]_2$ (prepared as described above; 1.71 g of powder; 15 wt % of Ru with respect to SiO_2; 0.188 g of Ru; 1.86 mmol of Ru) added with Na_2CO_3 (0.593 g; 5.58 mmol; molar ratio Na_2CO_3:Ru = 3:1; deposited from a CH_2Cl_2 slurry) was heated in the cylindrical vessel at 110 °C for 24 h under CO/H_2 (molar ratio 1:3; 1 atm). During the reaction, some product sublimed onto the cold part of the reaction vessel. Extraction of the sublimate and the silica powder with CH_2Cl_2 (200 mL) under N_2 afforded $[H_4Ru_4(CO)_{12}]$ (0.298 g; 0.400 mmol; 86% yield). When the reaction time is increased to 48 h, $[H_4Ru_4(CO)_{12}]$ is obtained in 94% yield (0.324 g; 0.436 mmol). When pure H_2 is used as the gas phase, $[H_4Ru_4(CO)_{12}]$ is obtained in only 39% yield (0.134 g; 0.181 mmol), after 19 h, due to some reduction to ruthenium metal.

Synthesis of $K_2[Ru_6C(CO)_{16}]$ from $[Ru(CO)_3Cl_2(HOSi\equiv)]$. $[Ru(CO)_3Cl_2(HOSi\equiv)]$ (4.19 g of powder; 5 wt % of Ru with respect to SiO_2; 0.187 g of Ru; 1.85 mmol of Ru) added with K_2CO_3 (5.10 g; 37 mmol; molar ratio K_2CO_3:Ru = 20:1; deposited from a CH_2Cl_2 slurry) was heated in the closed vessel at 150 °C for 10 h under CO (1 atm). Extraction of the final silica powder with acetone (*ca.* 150 mL) under N_2, followed by evaporation of the solvent, afforded $K_2[Ru_6C(CO)_{16}]$ (0.298 g; 0.262 mmol; 85% yield). With higher loadings (15 wt % of Ru with respect to SiO_2), $K_2[Ru_6C(CO)_{16}]$ is isolated after 10 h in only 68% yield (weight of isolated cluster 0.148 g).

Synthesis of $K[H_3Ru_4(CO)_{12}]$ from $[Ru(CO)_3Cl_2(HOSi\equiv)]$. $[Ru(CO)_3Cl_2(HOSi\equiv)]$ (5.50 g of powder; 5 wt % of Ru with respect to SiO_2; 0.246 g of Ru; 2.45 mmol of Ru) added with K_2CO_3 (3.39 g; 24.6 mmol; molar ratio K_2CO_3:Ru = 10:1;

deposited from a CH_2Cl_2 slurry) was transferred into the cylindrical vessel, treated in vacuo (10^{-2} Torr) for 3 h at 100 °C, exposed to CO/H_2 (molar ratio 1:3; 1 atm), and then heated at 100 °C for 24 h. During the reaction, some $[H_4Ru_4(CO)_{12}]$ sublimed onto the cold part of the reaction vessel. Extraction of the sublimate and the silica powder with CH_2Cl_2 (*ca.* 100 mL) under N_2, followed by evaporation of the solvent, afforded pure $[H_4Ru_4(CO)_{12}]$ (0.043 g; 0.060 mmol; 10% yield). Further extraction of the silica powder with acetone (*ca.* 150 mL) under N_2 afforded $K[H_3Ru_4(CO)_{12}]$ (0.288 g; 0.366 mmol; 60% yield).

Synthesis of $K[H_3Ru_4(CO)_{12}]$ from $[Ru(CO)_3Cl_2(HOSi\equiv)]$ via $[H_4Ru_4(CO)_{12}]$. A mixture of $[Ru(CO)_3Cl_2(HOSi\equiv)]$ and silica-supported β-$[Ru(CO)_3Cl_2]_2$ (prepared as described above; 1.355 g of powder; 18 wt % of Ru with respect to SiO_2; 0.172 g of Ru; 1.67 mmol of Ru) added with Na_2CO_3 (0.479 g; 4.52 mmol; molar ratio Na_2CO_3:Ru = 3:1; deposited from a CH_2Cl_2 slurry) was heated as described above in the cylindrical vessel at 110 or 130 °C for 24 h under CO/H_2 (molar ratio 1:3; 1 atm). During the reaction, some $[H_4Ru_4(CO)_{12}]$ sublimed onto the cold part of the reaction vessel. Treatment of the sublimate and the silica powder with a solution of [PPN]Br (0.216 g; 0.350 mmol) in degassed THF (200 mL) under N_2 for 2 h, followed by filtration and evaporation of the solvent, gave [PPN]-$[H_3Ru_4(CO)_{12}]$ (0.439 g; 0.343 mmol; 81% yield).

Synthesis of $K[HRu_3(CO)_{11}]$ from $[Ru(CO)_3Cl_2(HOSi\equiv)]$. $[Ru(CO)_3Cl_2(HOSi\equiv)]$ (3.42 g of powder; 5 wt % of Ru with respect to SiO_2; 0.153 g of Ru; 1.51 mmol of Ru) added with K_2CO_3 (2.09 g; 15.2 mmol; molar ratio K_2CO_3:Ru = 10:1; deposited from a CH_2Cl_2 slurry) was heated in the cylindrical vessel at 80 °C for 60 h under CO (1 atm). Extraction of the silica powder with CH_2Cl_2 (100 mL) under N_2 afforded pure $[Ru_3(CO)_{12}]$ (0.036 g; 0.057 mmol; 11% yield). Further extraction of the silica powder with acetone (150 mL) under N_2 gave $K[HRu_3(CO)_{11}]$ (0.138 g; 0.212 mmol; 42% yield).

Synthesis of $K[HRu_6(CO)_{18}]$ from $[Ru(CO)_3Cl_2(HOSi\equiv)]$. $[Ru(CO)_3Cl_2(HOSi\equiv)]$ (5.592 g of powder; 5 wt % of Ru with respect to SiO_2; 0.248 g of Ru; 2.46 mmol of Ru) added with K_2CO_3 (10.5 g; 75.8 mmol; molar ratio K_2CO_3:Ru = 30:1; deposited from a CH_2Cl_2 slurry) was transferred into the cylindrical vessel. Degassed water (18 mL) was added under N_2. The slurry was rapidly treated in vacuo (10^{-2} Torr) at 25 °C, exposed to CO (1 atm), heated at 80 °C for 24 h, and finally evaporated to dryness. Extraction of the silica powder with CH_2Cl_2 (100 mL) under N_2 afforded $[Ru_3(CO)_{12}]$ (0.082 g; 0.129

mmol; 16% yield). Further extraction of the silica powder with acetone (150 mL) under N_2 afforded $K[HRu_6(CO)_{18}]$ (0.288 g; 0.251 mmol; 61% yield). Under the same conditions but with 15 wt % of Ru with respect to SiO_2 loading, $K[HRu_6(CO)_{18}]$ and $[Ru_3(CO)_{12}]$ were obtained in 65 and 14% yields, respectively, only after 48 h.

Reactivity of β-$[Ru(CO)_3Cl_2]_2$, $[Ru_3(CO)_{12}]$, $[H_4Ru_4$-$(CO)_{12}]$, $K[HRu_3(CO)_{11}]$, or $K[H_3Ru_4(CO)_{12}]$ on the Silica Surface Added with Alkali Carbonates. A sample (4.0 g) of the desired ruthenium carbonyl compound supported on silica (2 wt % of Ru with respect to SiO_2) added with Na_2CO_3 or K_2CO_3 (the correct amount to have the desired molar ratio M_2CO_3:Ru) was prepared as described above. The sample was transferred into the cylindrical vessel, treated in vacuo (10^{-2} Torr) at 25 °C, exposed to N_2, CO, CO + H_2 (molar ratio 1:3), or H_2 at atmospheric pressure, and heated at the desired temperature (50–150 °C). The surface reactions were monitored by infrared spectroscopy: samples were taken from the glass vessel at room temperature and studied as Nujol mulls. Extraction of the reaction products was carried out with CH_2Cl_2 (in the case of neutral products) or with acetone (in the case of anionic products).

Reversible Interconversion between $K[HRu_3(CO)_{11}]$ and $K[H_3Ru_4(CO)_{12}]$ on the Silica Surface Added with K_2CO_3. When $K[HRu_3(CO)_{11}]$ supported on silica added with K_2CO_3 (molar ratio K_2CO_3:Ru = 10:1) was heated at 80 °C for 24 h under CO + H_2 (molar ratio 1:3), pure $K[H_3Ru_4(CO)_{12}]$ was obtained (as shown by infrared spectroscopy of the silica powder and extraction with acetone). Successive treatment under vacuo (10^{-2} Torr) at 25 °C, followed by exposure to CO and heating at 80 °C for 24 h, gave back $K[HRu_3(CO)_{11}]$ (as shown by infrared spectroscopy of the silica powder and extraction with acetone). This reversible process was repeated three times.