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The Surface of Inorganic Oxides or Zeolites as a Nonconventional Reaction Medium for the Selective Synthesis of Metal Carbonyl Complexes and Clusters

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Contents

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1. Introduction

The practice of carrying out reactions in solution may reflect tradition,[1] but it appeared in the last two decades that one can carry out many organic reactions on solids[1−6] (alumina,[1−4] silica,[2−4] zeolites,[5] clays,[5,6] and polymers[2,3]), generating faster reactions and higher yields than via the traditional solution methods.[1] Recently the surface of inorganic oxides also proved to be a useful reaction medium for the easy high-yield preparation of various metal carbonyl complexes and clusters[7−9a] which are of interest as catalysts or catalysts precursors.[9b−g]

The first surface-mediated synthesis of metal carbonyl complexes was reported by Fischer et al. 40 years ago; they observed that $MCl_3{\cdot}nH_2O$ ($M = Ir$,[10] Rh[11]) supported on silica yielded, respectively, [$Ir(CO)_3Cl]_n$ and [$Rh(CO)_2Cl]_2$, after successive thermal treatments with a stream of Cl_2 and then of CO. Although it was a long time before the potential of this innovative synthetic method was realized, in recent years there has been considerable interest in the use of surfaces of inorganic oxides as a nonconventional reaction medium for the synthesis of metal carbonyl compounds. Typically surface-mediated syntheses involve three simple steps: (i) impregnation of the inorganic oxide with the metal salt or organometallic precursor dissolved in a solvent followed by evaporation to dryness; (ii) treatment of the supported reagent under well-defined reaction conditions; (iii) recovery of the product. Both supported reagent and product can be often fully characterized by various surface methods (e.g., IR, NMR, EXAFS, XPS, extraction, and chemical reactivity methodologies, comparison with molecular models).[12] In many cases, selectivities and yields are so high and reaction conditions so mild that surface-mediated organometallic syntheses (on silica, Table 1; on MgO or Al_2O_3, Table 2) can be recommended over traditional syntheses in solution (Table 3), which often require high pressures, high temperatures, and strongly reducing conditions.[7−9]

Surface-mediated syntheses of metal carbonyl compounds are controlled by the (i) nature and loading of the metal salt or organometallic precursor adsorbed on the inorganic oxide, (ii) nature of the inorganic oxide, (iii) physical and chemical properties of the surface as such or after addition of specific reactants (e.g., alkali or acids), (iv) nature and composition of the gaseous phase, and (v) temperature, pressure, and reaction time. Neutral metal carbonyl species synthesized on the surface, either physisorped or chemisorped, are usually recovered simply by sublimation or by extraction with an adequate solvent. Only in few cases, the organometallic compounds are covalently linked to surface oxy groups, requiring selective cleavage of the covalent bond (e.g., M-OS, S = Si, Al or Mg) with the support at the end of the reaction. Anionic carbonyl com-

Elena Cariati was born in Tradate, Italy, in 1968. She completed her Ph.D. degree in 1995 at the University of Milano. Her doctoral research, performed under the supervision of Professor Renato Ugo, was concerned with the use of silica as a reaction medium for the high-yield synthesis of various metal carbonyl compounds. In 1997 she spent one year as a Fullbright Fellow with Professor Peter C. Ford's group at the University of California, Santa Barbara. During this year she studied the nonlinear optical (NLO) and luminescence properties of different Cu(I) complexes. Since 1998 she has been working as a researcher at the University of Milano. Her current research interests include the study of the photophysical and NLO properties of organometallic and coordination compounds and the surface chemistry of metal carbonyl clusters and complexes.

Dominique Roberto was born in Marseille (France) in 1961. She received the B.S. (in 1984) and the Ph.D. (in 1989) in Chemistry from the University of Ottawa (Canada), where she did research mainly in the synthesis of nitrogen heterocyclic compounds, catalyzed by transition metals, under the guidance of Professor Howard Alper. Since 1989 she has collaborated with Professor Renato Ugo at the University of Milano (Italy), where she became Associate Professor for General and Inorganic Chemistry in 1998. Her current scientific interests include (1) synthesis of organometallic compounds with electric or nonlinear optical properties and (2) surface organometallic chemistry, in particular, (i) reactivity and characterization of metal carbonyl complexes or clusters supported on silica, (ii) synthesis of organometallic compounds as models of surface species, and (iii) use of the silica surface as reaction medium for the selective and high-yield synthesis, working under mild conditions, of various metal carbonyl complexes and clusters.

Renato Ugo, born in Palermo (Italy) in 1938, earned his degree in Industrial Chemistry in 1961 from the University of Milano, where he performed his entire academic activity. In 1973 he became Full Professor of Analytical Chemistry and since 1981 has been Full Professor of General and Inorganic Chemistry. In 1974 he was visiting Professor at the University of Western Ontario (Canada). In 1988, he received a doctor degree honoris causa from Clarkson College—Postdam, NY. He was Editor in Chief up to 1998 of two series of International Advances, i.e., *Aspects of Homogeneous Catalysis* and *Homogeneous Catalysis in Inorganic and Organic Chemistry,* this latter in association with Professor Brian James. He was a member of the Editorial Board of *Journal of Molecular Catalysis*, *Gazzetta Chimica Italiana*, *and Advances in Catalysis and Nouveau Journal de Chimie.* Recognition of the scientific achievements of Renato Ugo appears in a series of lectureship and awards. He received the Bracco-Salata prize (1963) and the Stampacchia prize (1965) for his scientific activities as young researcher. He was then awarded the Miolati prize (1987) and the gold metal of the President of the Italian Republic for advancement in science (2000). Since 1984 he has been a member of the “Accademia Nazionale dei Lincei”. His main research topics include (1) inorganic, coordination, and organometallic chemistry, (2) homogeneous and heterogeneous catalysis, (3) surface organometallic chemistry and surface mediated organometallic synthesis, and (4) photophysical, nonlinear optical, and electric properties of organometallic and coordination compounds.

Elena Lucenti was born in Crema, Italy, in 1969. In 1998 she completed her Ph.D. in Industrial Chemistry at the University of Milano, working under the supervision of Professor Renato Ugo on the synthesis of organometallic complexes as models for silica surface species. In 1999 she was awarded a “NATO-CNR Advanced Fellowship”, which allowed her to spend one year at the University of California at Irvine working with Professor Frank J. Feher on the reactivity of oligosilsesquioxanes with metal carbonyls. In 2000 she joined the CNR-ISTM Research Center of Milano as Researcher. Her current research interests include the use of silica as an unusal medium for the high yield synthesis in mild conditions of metal carbonyl clusters and the synthesis and characterization of organometallic compounds as models for grafting processes on the silica surface.

pounds synthesized on a basic silica surface are simply physisorped and can be easily extracted with an adequate polar solvent, whereas on the surface of MgO or Al_2O_3 they strongly interact with Al^{3+} or Mg^{2+} and therefore must be extracted from the surface by ion exchange (e.g., with $[(Ph_3P)_2N]Cl$ dissolved in CH_2Cl_2).[12−13]

As a general trend, uncharged carbonyl complexes and clusters are generated on the surface of rather neutral supports such as silica[8,9] or in the cages of some zeolites such as NaY.[7] On the other hand, the synthesis of anionic carbonyl clusters from metal salts, neutral carbonyl complexes, or clusters requires an adequate surface basicity. Up to now, the latter has been reached by three different approaches. The first is the use of an intrinsically strongly basic surface such as MgO.[7,13] The basicity strength of this surface can be easily varied by the temperature of treatment: an increase of the temperature leads to gradual decarbonatation and dehydroxylation of the surface with increase of strongly basic O^{2-} centers and therefore to a relevant increase of the surface basicity.[13] A similar behavior occurs on the less basic surface of Al_2O_3.[13] In the second approach, rather, basic zeolites such as NaX can produce in their basic cages anionic metal carbonyl species.[7] The third approach involves an increased basicity of silica by dispersion on the surface of an alkali carbonate.[8,9] In this latter case, the basicity is controlled by (i) the nature and amount of the alkali carbonate, (ii) temperature, and (iii) the manner by which the alkali carbonate is deposited on silica. The surface basicity is affected not only by the amount of the added alkali carbonate but also by its nature. There is clear evidence that silica-supported K_2CO_3 behaves as a stronger basic medium than silica-supported Na_2CO_3, probably due to a low solvation on the silica surface of the alkali carbonates and therefore to a stronger ion-pair interaction of the basic center CO_3^{2-}, which thus decreases its basicity, with the Na^+ cation than with the larger K^+ cation.[14] In agreement with such an hypothesis, due to a decrease of physisorped water which can solvate the alkali carbonate, an increase of the temperature (e.g., up to 150 °C) increases the surface basicity. Finally, a high alkali carbonate loading (e.g., 36 wt % Na_2CO_3 with respect to silica)[15] can lead more to a real solid mixture than to a dispersion on the silica surface. The alkali carbonate is deposited from a slurry in CH_2Cl_2 or a water solution. This latter method leads to a more homogeneous dispersion of the base on the surface and consequently to an increased basicity for a given surface loading.[14−15]

This review covers what is known about this innovative and promising area of syntheses of metal carbonyl complexes and clusters mediated by the surface of inorganic oxides. Emphasis is placed on syntheses which allow comparison of yields and reaction conditions with respect to traditional syntheses in solution, but many interesting surface-mediated syntheses without reported yields are also mentioned. The use of the silica surface will be described first, followed by MgO, Al_2O_3, ZnO, and La_2O_3. Also, brief mention will be made of the synthesis of metal carbonyl clusters in the cages of zeolites, although this chemistry is not of synthetic value because the resultant clusters remain usually

Table 1. Synthesis of Metal Carbonyl Complexes and Clusters on the Silica Surface[a]

product	starting material	reaction conditions	yield (%)	ref
$[Rh(CO)_2Cl]_2$	$RhCl_3 \cdot nH_2O$	CO, 25 °C, 24h[b]	80−84	20
$[Rh_6(CO)_{16}]$	$RhCl_3 \cdot nH_2O$	molar ratio $CH_3CO_2Na/Rh = 20/1$, CO, 50 °C, 48 h[b]	89	24
$[Rh_6(CO)_{16}]$	$[Rh(CO)_2Cl]_2$	molar ratio $Na_2CO_3/Rh = 10/1$, CO, 25 °C, 24 h[b]	83	24
$[Rh_4(CO)_{12}]$	$[Rh(CO)_2Cl]_2$	molar ratio $CH_3CO_2Na/ Rh = 20/1$, $CO + H_2O$, 25 °C, 24 h[c]	85	24
$[Rh_{12}(CO)_{30}]^{2-}$	$[Rh(CO)_2Cl]_2$	molar ratio $K_2CO_3/Rh = 10:1$, CO, 25 °C, 24 h[d,e]	71	24
$[Rh_5(CO)_{15}]^{-}$	$[Rh(CO)_2Cl]_2$	molar ratio $K_2CO_3/Rh = 10:1$, CO, 25 °C, 24 h[d,f]	80	24
$[Ir(CO)_3Cl]_n$	$IrCl_3 \cdot nH_2O$	CO, 150 °C, 24 h; product sublimes during the reaction	76−83	20
$[Ir_4(CO)_{12}]$	$IrCl_3 \cdot nH_2O$	molar ratio $Na_2CO_3/Ir = 1.5/1$, $CO + H_2O$, 90 °C, 48 h[d]	84	32
$[Ir_4(CO)_{12}]$	$[Ir(COT)_2Cl]_2$[g]	molar ratio $Na_2CO_3/Ir = 1/1$, $CO + H_2O$, 90 °C, 6 h[d]	82	32
$[Ir_6(CO)_{15}]^{2-}$	$[Ir(COT)_2Cl]_2$[g]	molar ratio $K_2CO_3/Ir = 5/1$, CO, 120 °C, 22 h[h]	87	32
$[Ir_8(CO)_{22}]^{2-}$	$[Ir(COT)_2Cl]_2$[g]	molar ratio $K_2CO_3/Ir = 5/1$, $CO + H_2O$, 100 °C, 18 h[h]	71	32
$[Ru(CO)_3Cl_2]_2$	$RuCl_3 \cdot nH_2O$	CO, 100 °C, 48 h[i]	88−93	20
$[H_4Ru_4(CO)_{12}]$	$RuCl_3 \cdot nH_2O$	(i) CO, 100 °C, 48 h to give $[Ru(CO)_3Cl_2(HOSi\equiv)]$; (ii) molar ratio $Na_2CO_3/Ru = 3/1$, CO/H_2 (1/3), 110 °C, 19 h[b]	86	15
$[Ru_3(CO)_{12}]$	$RuCl_3 \cdot nH_2O$[j]	(i) CO, 100 °C, 48 h to give $[Ru(CO)_3Cl_2(HOSi\equiv)]$; (ii) molar ratio $Na_2CO_3/Ru = 3/1$, CO, 110 °C, 48 h[b]	82−93	15
$[Ru_3(CO)_{10}Cl_2]$	$RuCl_3 \cdot nH_2O$[k]	(i) CO, 100 °C, 48 h to give $[Ru(CO)_3Cl_2(HOSi\equiv)]$; (ii) molar ratio $Na_2CO_3/Ru = 3/1$, CO, 110 °C, 24 h[b]	75	15
$[Ru_6C(CO)_{16}]^{2-}$	$RuCl_3 \cdot nH_2O$	(i) CO, 100 °C, 48 h to give $[Ru(CO)_3Cl_2(HOSi\equiv)]$; (ii) molar ratio $K_2CO_3/Ru = 10/1$, CO, 150 °C, 10 h[i]	95	15
$[H_3Ru_4(CO)_{12}]^{-}$	$RuCl_3 \cdot nH_2O$	(i) CO, 100 °C, 48 h to give $[Ru(CO)_3Cl_2(HOSi\equiv)]$; (ii) molar ratio $Na_2CO_3/Ru = 3/1$, CO/H_2 (1/3), 110 °C, 19 h[l]	81	15
$[HRu_3(CO)_{11}]^{-}$	$RuCl_3 \cdot nH_2O$	(i) CO, 100 °C, 48 h to give $[Ru(CO)_3Cl_2(HOSi\equiv)]$; (ii) molar ratio $K_2CO_3/Ru = 10/1$, CO, 80 °C, 60 h[h]	42	15
$[HRu_6(CO)_{18}]^{-}$	$RuCl_3 \cdot nH_2O$	(i) CO, 100 °C, 48 h to give $[Ru(CO)_3Cl_2(HOSi\equiv)]$; (ii) molar ratio $K_2CO_3/Ru = 30/1$, $CO + H_2O$, 80 °C, 60 h[i]	61	15
$[Os(CO)_3Cl_2]_2$	$OsCl_3.nH_2O$	CO, 180 °C, 48 h[m]	80−90	20
$[H_4Os_4(CO)_{12}]$	$OsCl_3.nH_2O$	(i) CO, 180 °C, 48 h to give $[Os(CO)_3Cl_2(HOSi\equiv)]$; (ii) molar ratio $Na_2CO_3/Os = 2/1$, H_2, 150 °C, 72 h[b]	70−83	41a
$[H_4Os_4(CO)_{12}]$	$[Os_3(CO)_{12}]$	(i) octane, reflux, 8 h and filtration to give $[HOs_3(CO)_{10}OSi\equiv]$; (ii) H_2, 150 °C, 24 h[b]	94	67a
$[Os_3(CO)_{12}]$	$OsCl_3.nH_2O$	(i) CO, 180 °C, 48 h to give $[Os(CO)_3Cl_2(HOSi\equiv)]$; (ii) molar ratio $Na_2CO_3/Os = 2/1$, CO, 200 °C, 72 h[b]	76−82	41a
$[HOs_3(CO)_{10}OH]$	$[Os_3(CO)_{12}]$	(i) octane, reflux, 8 h and filtration to give $[HOs_3(CO)_{10}OSi\equiv]$; (ii) H_2O/toluene, N_2, 95 °C, 5 h[n]	91	67
$[HOs_3(CO)_{10}OBu]$	$[Os_3(CO)_{12}]$	(i) octane, reflux, 8 h and filtration to give $[HOs_3(CO)_{10}OSi\equiv]$; (ii) *n*-Butanol, N_2, 118 °C, 20 h[n]	87	67a
$[HOs_3(CO)_{10}OMe]$	$[Os_3(CO)_{12}]$	(i) octane, reflux, 8 h and filtration to give $[HOs_3(CO)_{10}OSi\equiv]$; (ii) MeOH, drop $HBF_4.Et_2O$, N_2, 65 °C, 24 h[n]	54	67a
$[HOs_3(CO)_{10}OPh]$	$[Os_3(CO)_{12}]$	(i) octane, reflux, 8 h and filtration to give $[HOs_3(CO)_{10}OSi\equiv]$; (ii) molar ratio $PhOH/Os_3 = 100/1$, heptane, N_2, 98 °C, 5 h[n]	66	67a
$[HOs_3(CO)_{10}X]$, $X = Cl, Br$	$[Os_3(CO)_{12}]$	(i) octane, reflux, 8 h and filtration to give $[HOs_3(CO)_{10}OSi\equiv]$; (ii) HX aq./$CH_2Cl_2$, N_2, 40 °C, 7 h[n]	87−89	67a
$[HOs_3(CO)_{10}O_2CR]$, $R = CH_3, CF_3$	$[Os_3(CO)_{12}]$	(i) octane, reflux, 8 h and filtration to give $[HOs_3(CO)_{10}OSi\equiv]$; (ii) RCO_2H/toluene, N_2, 90 °C, 6 h[n]	56−72	67a
$[H_3Os_4(CO)_{12}]^{-}$	$OsCl_3.nH_2O$	(i) CO, 180 °C, 48 h to give $[Os(CO)_3Cl_2(HOSi\equiv)]$; (ii) molar ratio $K_2CO_3/Os = 10-20/1$, CO, 150 °C, 24 h[h]	91	40
$[H_2Os_4(CO)_{12}]^{2-}$	$OsCl_3.nH_2O$	(i) CO, 180 °C, 48 h to give $[Os(CO)_3Cl_2(HOSi\equiv)]$; (ii) molar ratio $K_2CO_3/Os = 10-20/1$, CO, 200 °C, 48 h[h]	92	41
$[Os_{10}C(CO)_{24}]^{2-}$	$OsCl_3.nH_2O$	(i) CO, 180 °C, 48 h to give $[Os(CO)_3Cl_2(HOSi\equiv)]$; (ii) molar ratio $Na_2CO_3/Os = 10/1$, H_2, 200 °C, 24 h[h]	81	41
$[Os_5C(CO)_{14}]^{2-}$	$OsCl_3.nH_2O$	(i) CO, 180 °C, 48 h to give $[Os(CO)_3Cl_2(HOSi\equiv)]$; (ii) molar ratio $K_2CO_3/Os = 20/1$, CO, 265 °C, 24 h[h]	74	41a
$[H_5Os_{10}(CO)_{24}]^{-}$	$[Os(CO)_3(OH)_2]_n$[o]	H_2, 200 °C, 72 h[h]	65	91
$[Re_2(CO)_{10}]$	$NH_4[ReO_4]$	CO(20 atm) + H_2(130 atm), 150 °C, 24 h	40	99
$[Re_2(CO)_{10}]$	$[Re(CO)_3(OH)]_4$	CO, 200 °C, 72 h[c]	60	100
$[Re(CO)_3(OH)]_4$	$[Re_2(CO)_{10}]$	N_2, 250 °C, 30 min[i]	63	100

[a] Aerosil is used as silica, metal loadings can be in the range 2−15% (w/w) of metal relative to SiO_2, and reactions are carried out under 1 atm in a closed reaction vessel unless otherwise specified; the alkali carbonate is deposited from a CH_2Cl_2 slurry; when different synthetic paths are available, the best methods are reported. [b] Product recovery by extraction with CH_2Cl_2. [c] Product recovery by extraction with pentane. [d] Product recovery by extraction with THF. [e] Extraction under N_2. [f] Extraction under CO. [g] COT = cyclooctene. [h] Product recovery by extraction with CH_3CN. [i] Product recovery by extraction with acetone. [j] Working with 2−5% (w/w) Ru/SiO_2. [k] Working with 15% (w/w) Ru/SiO_2. [l] Product recovery by extraction with [PPN]Br in THF. [m] Product recovery by extraction with hot $CHCl_3$ in a Soxhlet. [n] Both steps are carried out in a three-necked flask; in step i the silica powder containing $[HOs_3(CO)_{10}OSi\equiv]$ is filtered and treated according to step ii, affording the product which goes in the organic phase and is then recrystallized to give the reported yield. [o] Generated in situ by reaction of $[Os(CO)_3Cl_2]_2$ with NaOH.[64]

trapped in the cages (ship-in-bottle synthesis) and cannot be isolated.[7] Finally the role of the syntheses mediated by the surface of inorganic oxides as a spring of inspiration for syntheses of metal carbonyl clusters in solution is outlined (Table 4).

2. Synthesis on the Surface of Silica

Various carbonyl complexes and clusters from groups 7, 8, and 9 have been prepared on silica. As a general trend, neutral compounds are generated on

Table 2. Synthesis of Metal Carbonyl Clusters on the Surface of MgO or Al_2O_3[a]

product	starting material	reaction conditions	yield (%)	ref
$[Pt_{15}(CO)_{30}]^{2-}$	$Na_2[PtCl_6]$	(i) MgO_{400}, MeOH, CO, 25 °C, 8 h; evaporation to dryness (ii) extraction under CO with $[(Ph_3P)_2N]Cl$ in THF	73	107
$[PtRh_5(CO)_{15}]^-$	$Na_2[PtCl_6]$ and $RhCl_3 \cdot nH_2O$, molar ratio Pt/Rh = 1/5	(i) MgO_{25}, MeOH, CO, 25 °C, 48 h; evaporation to dryness (ii) extraction under CO with $[(Ph_3P)_2N]Cl$ in THF	84	108
$[Rh_6(CO)_{15}]^{2-}$	$[Rh_6(CO)_{16}]$	(i) $MgO_{25or200}$, CH_2Cl_2, 25 °C; evaporation to dryness (ii) extraction with $[(Ph_3P)_2N]Cl$ in CH_2Cl_2	40	111
$[Rh_5(CO)_{15}]^-$	$[Rh(CO)_2(acac)]$	(i) MgO, hydrated hexane; evaporation to dryness (ii) CO, 25 °C, 5 days; extraction with CH_3CO_2K in MeOH under CO	47	113
$[HFe_3(CO)_{11}]^-$	$[Fe_3(CO)_{12}]$ or $[Fe(CO)_5]$	(i) MgO_{25}, hexane, 25 °C; evaporation to dryness (ii) extraction with $[Et_4N]Cl$ in CH_2Cl_2	60	115
$[HFe_3(CO)_{11}]^-$	$[Fe_3(CO)_{12}]$ or $[Fe(CO)_5]$	(i) Al_2O_3, hexane, 25 °C, 1 h; evaporation to dryness (ii) extraction with $[Et_4N]Cl$ in CH_2Cl_2	70	115
$[Os_{10}C(CO)_{24}]^{2-}$	H_2OsCl_6	(i) MgO_{400}, H_2O, 25 °C; evaporation to dryness (ii) $CO/H_2(1/1)$, 275 °C, 5 h; extraction with $[(Ph_3P)_2N]Cl$ in acetone	65	95, 118
$[Os_5C(CO)_{14}]^{2-}$	$[Os_3(CO)_{12}]$	(i) MgO_{400}, hexane, 25 °C; evaporation to dryness (ii) CO, 275 °C, 4 h; extraction with $[(Ph_3P)_2N]Cl$ in acetone	65	7, 95, 121

[a] Metal loadings are in the range 1−2.5% (w/w) of metal relative to MgO or Al_2O_3; reactions are carried out under 1 atm.

such a neutral inorganic oxide, but addition of a base allows the formation of anionic species. The basicity of the silica surface can be controlled by the nature and amount of the alkali carbonate, the temperature, and the manner by which the alkali carbonate is deposited on silica. This easy modulation allows an excellent control of the reaction conditions necessary to obtain with high selectivity a specific cluster. In this review, unless otherwise stated, the silica used as reaction medium is Aerosil, a nonporous silica, the metal loading is in the range 2−15% (w/w) of metal with respect to SiO_2, and the reaction is carried out at 1 atm in a closed reaction vessel. An interesting aspect of silica-mediated syntheses is that when a mixture of neutral and anionic species are formed on the surface, as evidenced by infrared spectroscopy, they can be selectively recovered by an adequate choice of the solvents used for extraction. Thus, neutral complexes and clusters simply physisorped on the silica surface can be extracted with a solvent such as pentane or dichloromethane whereas anionic species require a solvent such as acetone or acetonitrile. The recovery of species linked to the surface via silanols such as $[M(CO)_3Cl_2(HOSi\equiv)]$ (M = Ru, Os) needs a solvent able of displacing silanols such as acetone. All yields reported in this section are those of the product obtained after extraction from the silica surface or sublimation (Table 1).

2.1. Cobalt. Neutral and Anionic Clusters: $[Co_4(CO)_{12}]$ and $[RuCo_3(CO)_{12}]^-$

Although, up to now, the reaction of Co clusters on the silica surface has been investigated only from the point of view of the surface organometallic reactivity, the results are promising for synthetic purposes. Thus, physisorped $[Co_2(CO)_8]$ is converted to physisorped $[Co_4(CO)_{12}]$ on the surface of silica gel by a mild thermal treatment (40 °C)[16] like in petroleum ether solution.[17] Besides, it appeared that chemisorped $[Ru(CO)_3Cl_2(HOSi\equiv)]$, prepared by adsorption of $[Ru(CO)_3Cl_2(THF)]$ on silica (Davison), reacts with $[Co(CO)_4]^-$ to give physisorped $[RuCo_3(CO)_{12}]^-$, which can be extracted as the $[(Ph_3P)_2N]^+$ salt by treatment with a solution of $[(Ph_3P)_2N]Cl$ in THF,[18] a reaction that mimics that of $[Ru(CO)_3Cl_2(THF)]$ with $[Co(CO)_4]^-$ in THF solution.[19]

2.2. Rhodium

2.2.1. Neutral Complexes and Clusters: $[Rh(CO)_2Cl]_2$, $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$

$[Rh(CO)_2Cl]_2$. As already pointed out, 40 years ago, Fischer et al. reported that treatment of $RhCl_3 \cdot nH_2O$ physisorped on silica gel first with a stream of Cl_2 at 160°C and then with a stream of CO at 140 °C affords physisorped $[Rh(CO)_2Cl]_2$ (97% yield), which sublimes (Scheme 1).[11] Later, it appeared that such drastic conditions and chlorination are not necessary when Aerosil, a nonporous silica, is used. When $RhCl_3 \cdot nH_2O$ physisorped on Aerosil is treated with CO at 25 °C in a closed vessel, physisorped $[Rh(CO)_2Cl]_2$ is formed on the silica surface from which it can be separated by extraction with CH_2Cl_2 (80−84% yields).[20] This synthesis is very attractive when compared to the traditional synthesis in solution (Table 3),[21a] and the conditions are milder than those of the reductive carbonylation of solid $RhCl_3 \cdot nH_2O$.[21b] Whereas in the latter synthesis failure to periodically remove water caused decomposition of $[Rh(CO)_2Cl]_2$ to metal, water is not troublesome in the silica-mediated synthesis.[20]

$[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$. The formation of physisorped $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$ by treatment with CO and H_2O of chemisorped $[Rh(CO)_2(OSi\equiv)(XOSi\equiv)]$ (X = H or Si≡; formed by oxidation with O_2 of $[Rh_4(CO)_{12}]$ or $[Rh_6(CO)_{16}]$ physisorped on silica) was the first evidence for a high mobility of surface rhodium carbonyls[22] and provided a hint for the study of the silica-mediated synthesis of Rh carbonyl clusters from Rh(I) species,[20] or even from

Table 3. Best Traditional Synthesis of Metal Carbonyl Complexes and Clusters in Solution[a]

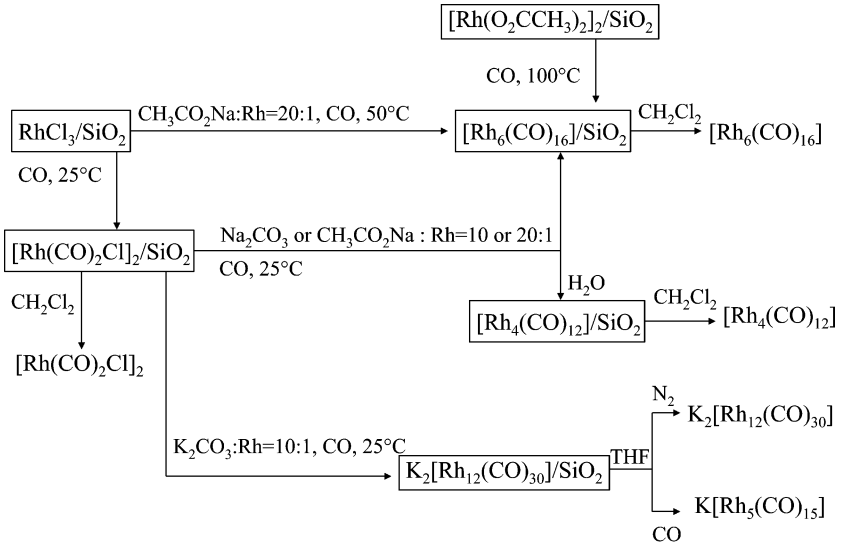
product	starting material	reaction conditions	yield (%)	ref
$[Rh(CO)_2Cl]_2$	$RhCl_3\cdot nH_2O$	(i) $MeOH/H_2O$, ethylene, RT, 7 h (ii) Et_2O, CO, 25 °C, 1 h	40	21a
$[Rh_6(CO)_{16}]$	$[Rh(CO)_2Cl]_2$	MeOH, CH_3CO_2Li, CO, RT, 24 h	78	25
$[Rh_4(CO)_{12}]$	$[Rh(CO)_2Cl]_2$	*n*-hexane, $NaHCO_3$, CO, RT, 24 h	83	25
	$RhCl_3\cdot 3H_2O$	(i) Cu, NaCl, H_2O, CO, RT, 2 h (ii) disodium citrate, CO, RT, 20 h	85	27
$[Rh_{12}(CO)_{30}]^{2-}$	$[Rh(CO)_2Cl]_2$	THF, CH_3CO_2Na, CO, RT, 5 h	88	29
$[Rh_5(CO)_{15}]^-$	$[Rh_4(CO)_{12}]$	THF, $[Rh(CO)_4]^-$, CO, RT	80	30
$[Ir_4(CO)_{12}]$	$IrCl_3\cdot nH_2O$	(i) EtOH, H_2O, CO, reflux, 6 h (ii) disodium citrate, CO, RT, 24 h	65	33
	$IrCl_3\cdot nH_2O$	HCOOH, sealed tube, 100 °C, 12 h	100	34
$[Ir_6(CO)_{15}]^{2-}$	K_2IrCl_6	(i) 2-methoxyethanol, CO, 110 °C, 18 h (ii) K_2CO_3, CO, 90 °C, 5 h	70−75	36
$[Ir_8(CO)_{22}]^{2-}$	$[Ir_4(CO)_{12}]$	THF, Na, CO, RT	42	37
$[Ru(CO)_3Cl_2]_2$	$[Ru_3(CO)_{12}]$	$CHCl_3$, N_2 (5atm), 110 °C, 6 h	53−60	46
	$RuCl_3\cdot nH_2O$	MeOH, Ag; CO(10atm), 65 °C, 30 h	73	47
$[H_4Ru_4(CO)_{12}]$	$[Ru_3(CO)_{12}]$	octane, H_2, reflux, 1 h	88	49
	$RuCl_3\cdot nH_2O$	EtOH, Ag, CO(40 atm)/H_2(80 atm), 75 °C, 72 h	10−30	50b
$[Ru_3(CO)_{12}]$	$RuCl_3\cdot nH_2O$	MeOH, CO(50atm),125 °C, 8h	85−95	53
	$RuCl_3\cdot nH_2O$	(i) 2-ethoxyethanol, CO, 135 °C, 6 h (ii) ethanol, Zn, CO, 85 °C, 6−7 h	45−60	51
	$[Ru_3O(O_2CCH_3)_6(H_2O)_3](O_2CCH_3)$	propanol, NEt_3, CO, 80 °C, 30 h	59	52
	$RuCl_3\cdot nH_2O$	(i) 2-methoxyethanol, CO, 125 °C, 2 h; (ii) 2-methoxyethanol, molar ratio KOH/Ru = 1/1, CO, 85 °C, 20 min	80−90	55d, 55e
$[Ru_6C(CO)_{16}]^{2-}$	$[Ru_3(CO)_{12}]$	diglyme, Na, reflux, 12 h	90	57b
$[H_3Ru_4(CO)_{12}]^-$	$[H_4Ru_4(CO)_{12}]$	THF, [PPN]Cl, RT, 15 min	100	60c
$[HRu_3(CO)_{11}]^-$	$[Ru_3(CO)_{12}]$	THF/MeOH, KOH, RT, 6 h	100	61
$[HRu_6(CO)_{18}]^-$	$[HRu_3(CO)_{11}]^-$	THF, H_2SO_4, RT	50	61
$[Os(CO)_3Cl_2]_2$	$[Os_3(CO)_{12}]$	cyclohexane, HCl, 170 °C, 40 h	80	68
$[H_4Os_4(CO)_{12}]$	$[Os_3(CO)_{12}]$	octane, H_2(120 atm), 100 °C, 24 h	70	70
$[Os_3(CO)_{12}]$	OsO_4	MeOH, CO(75 atm), 125 °C, 12 h	70−80	74
$[HOs_3(CO)_{10}OH]$	$[Os_3(CO)_{12}]$	THF, $NaBH_4$, N_2, 40 °C followed by acidification	27	79a
	$[Os_3(CO)_{12}]$	(i) octane, H_2, reflux, 1.5 h to give $[H_2Os_3(CO)_{10}]$ (ii) hexane, Me_2NCN, reflux, 10 min to give $[HOs_3(CO_{10}(NCHNMe_2)]$ (iii) CH_2Cl_2/H_2O, $HBF_4.Me_2O$, RT, 15 min	33	77
$[HOs_3(CO)_{10}OMe]$	$[Os_3(CO)_{12}]$	MeOH, autoclave, 160−170 °C, 19 h	10	79b
	$[Os_3(CO)_{12}]$	(i) octane, H_2, reflux, 1.5 h to give $[H_2Os_3(CO)_{10}]$ (ii) hexane, Me_2NCN, reflux, 10 min to give $[HOs_3(CO_{10}(NCHNMe_2)]$ (iii) CH_2Cl_2/MeOH, $HBF_4.Me_2O$, RT, 30 min	41	77
$[HOs_3(CO)_{10}OPh]$	$[Os_3(CO)_{12}]$	xylene, PhOH, reflux, 10 h	48	79b
	$[Os_3(CO)_{12}]$	(i) octane, H_2, reflux, 1.5 h to give $[H_2Os_3(CO)_{10}]$; (ii) hexane, cyclohexadiene, N_2, reflux, 4 h to give $[Os_3(CO)_{10}$(cyclohexa-1,3-diene)] (iii) cyclohexane, PhOH, N_2, reflux, ca. 3 h	35	76
$[HOs_3(CO)_{10}X]$ X = Cl, Br	$[Os_3(CO)_{12}]$	(i) octane, H_2, reflux, 1.5 h to give $[H_2Os_3(CO)_{10}]$ (ii) CH_2Cl_2, vinylene carbonate, RT, 28 h to give $[HOs_3(CO)_{10}(OCH{=}CH_2)]$ (iii) CH_2Cl_2, $HBF_4.Me_2O$, Ar, −78 °C, $[NEt_4]X$ 1.5 h	30−36	75
	$[Os_3(CO)_{12}]$	(i) octane, H_2, reflux, 1.5 h to give $[H_2Os_3(CO)_{10}]$ (ii) hexane, cyclohexadiene, N_2, reflux, 4 h to give $[Os_3(CO)_{10}$(cyclohexa-1,3-diene)] (iii) cyclohexane, HX, reflux, 3 h (X=Cl) or 10 min (X=Br)	35	76
	$[Os_3(CO)_{12}]$	(i) octane, H_2, reflux, 1.5 h to give $[H_2Os_3(CO)_{10}]$ (ii) hexane, Me_2NCN, reflux, 10 min to give $[HOs_3(CO_{10}(NCHNMe_2)]$ (iii) CH_2Cl_2, HCl, RT, 0.5 min	55	77
$[HOs_3(CO)_{10}O_2CR]$ R = CH_3, CF_3	$[Os_3(CO)_{12}]$	(i) octane, H_2, reflux, 1.5 h to give $[H_2Os_3(CO)_{10}]$ (ii) hexane, cyclohexadiene, N_2, reflux, 4 h to give $[Os_3(CO)_{10}$(cyclohexa-1,3-diene)] (iii) cyclohexane, RCO_2H, reflux, 1−2 h	40	76
	$[Os_3(CO)_{12}]$	(i) octane, H_2, reflux, 1.5 h to give $[H_2Os_3(CO)_{10}]$ (ii) hexane, Me_2NCN, reflux, 10 min to give $[HOs_3(CO_{10}(NCHNMe_2)]$ (iii) CH_2Cl_2, CF_3CO_2H, RT, 1.5 min	52	77
$[H_3Os_4(CO)_{12}]^-$	$[Os_3(CO)_{12}]$	BuOH, KOH, reflux, 48 h	45	85
	$[H_4Os_4(CO)_{12}]$	MeOH, KOH, RT	75	70
$[H_2Os_4(CO)_{12}]^{2-}$	$[Os_3(CO)_{12}]$	dioxane, $NaBH_4$, reflux	39	86
$[Os_{10}C(CO)_{24}]^{2-}$	$[Os_3(CO)_{12}]$	tetraglyme, Na, 230 °C, 70 h	63	88
$[Os_5C(CO)_{14}]^{2-}$	$[Os_3(CO)_{12}]$	(i) sealed tube, 210 °C, 12 h to give $Os_5C(CO)_{15}$; (ii) CO(50 atm), 165 °C, 16 h; (iii) MeOH, Na_2CO_3, N_2, RT, 2.5 h	37	90
$[H_5Os_{10}(CO)_{24}]^-$	$[Os_3(CO)_{12}]$	(i) BuOH, reflux to give very low yields of $[H_4Os_{10}(CO)_{24}]^{2-}$ (ii) acidification with H_2SO_4 or CF_3CO_2H, RT	very low	92

[a] Carried out at atmospheric pressure unless otherwise specified.

Table 4. Solution Syntheses, Working at Atmospheric Pressure, Inspired by Silica-Mediated Ones

product	starting material	reaction conditions	yield (%)	ref
$[H_4Ru_4(CO)_{12}]$	$RuCl_3 \cdot nH_2O$	(i) ethylene glycol, CO, 110 °C, 3h (ii) Na_2CO_3 (molar ratio base/Ru = 3/2), CO/H_2 (1/3), 95 °C, 12 h	82	55b,55c
$[Ru_3(CO)_{12}]$	$RuCl_3 \cdot nH_2O$	(i) ethylene glycol, CO, 110 °C, 3h (ii) Na_2CO_3 (molar ratio base/ Ru = 3/2), CO, 95 °C, 7 h	80−85	55b,55c
$[Ru_6C(CO)_{16}]^{2-}$	$RuCl_3 \cdot nH_2O$	(i) ethylene glycol, CO, 110 °C, 3h (ii) K_2CO_3 (molar ratio base/ Ru = 10/1), CO, 160 °C, 8 h	80−84	55b,55c
$[H_3Ru_4(CO)_{12}]^-$	$[Ru(CO)_3Cl_2]_2$	*t*-amyl alcohol, Na_2CO_3 (molar ratio base/Ru = 3/1), CO/H_2 (1/3), 88 °C, 12 h	93	55a
$[Os_3(CO)_{12}]$	$OsCl_3 \cdot nH_2O$	ethylene glycol, Na_2CO_3 (molar ratio base/Os = 3/2), CO, 160−165 °C, 15 h	64−70	55b,55c
$[H_4Os_4(CO)_{12}]$	$OsCl_3 \cdot nH_2O$	(i) ethylene glycol, K_2CO_3 (molar ratio base/Os = 10/1), CO, 160−165 °C, 9 h (ii) H_2SO_4; extraction with CH_2Cl_2	74−81	55a
$[H_3Os_4(CO)_{12}]^-$	$OsCl_3 \cdot nH_2O$	ethylene glycol, K_2CO_3 (molar ratio base/Os = 10/1), CO, 160−165 °C, 9 h; extraction with $[NaBu_4]I/CH_2Cl_2$	74−81	55a
$[H_4Os_{10}(CO)_{24}]^{2-}$	$[Os(CO)_3Cl_2]_2$	ethylene glycol, Na_2CO_3 (molar ratio base/Os = 2:1), H_2, 160 °C, 6 h	79−81	55b,91

Scheme 1. Best Syntheses of Various Rhodium Carbonyl Compounds on the Surface of Silica (1 atm)



$RhCl_3 \cdot nH_2O$ since the intermediate chemisorped $[Rh(CO)_2Cl(HOSi\equiv)]$ is easily generated.[23]

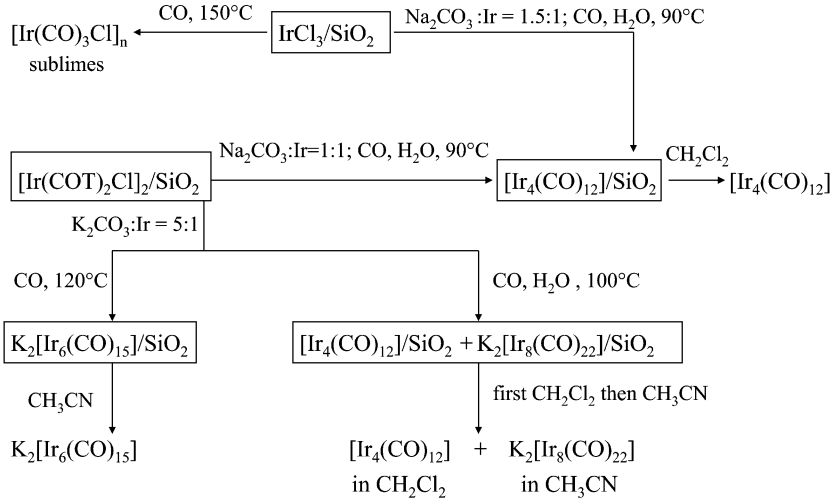
The reductive carbonylation of $RhCl_3 \cdot nH_2O$ and $[Rh(CO)_2Cl]_2$ physisorped on silica has been investigated working under CO either in the absence[20] or in the presence[24] of a base. Physisorped $RhCl_3 \cdot nH_2O$ cannot be converted to $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$ by working under mild conditions in the absence of a base because the reaction stops at $[Rh(CO)_2Cl]_2$. Most probably the amount of HCl liberated during the reaction inhibits at relatively low temperatures aggregation to Rh clusters. At higher temperatures (70 °C), sublimation of the dimer occurs, preventing further reduction.[20] However, treatment at 25 °C of physisorped $[Rh(CO)_2Cl]_2$ (prepared by stirring $[Rh(CO)_2Cl]_2$, pentane, and silica followed by evaporation of the solvent) with CO and water affords slowly mixtures of physisorped $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$.[20] A large amount of water favors the formation of $[Rh_4(CO)_{12}]$, a behavior similar to that reported for the reductive carbonylation of $[Rh(CO)_2Cl]_2$ in methanol.[25]

Addition of a base to the silica surface favors removal of the chloro ligands from the Rh coordination sphere and therefore formation of neutral or even anionic carbonyl clusters.[24] Thus, when the reductive carbonylation of physisorped $RhCl_3 \cdot nH_2O$ is carried out at 50 °C in the presence of CH_3CO_2Na, $[Rh_6(CO)_{16}]$ is obtained in 89% yield. By working under the same conditions but at 25 °C, $RhCl_3 \cdot nH_2O$ does not afford carbonyl species even after 1 month, whereas $[Rh(CO)_2Cl]_2$ can be selectively converted to $[Rh_6(CO)_{16}]$ (83% yield) or $[Rh_4(CO)_{12}]$ (85% yield, when working in the presence of added water). $[Rh_6(CO)_{16}]$ can also be prepared in 83% yield by reductive carbonylation of physisorped $[Rh(CO)_2Cl]_2$ in the presence of Na_2CO_3.[24] The yields and reaction conditions of these silica-mediated syntheses are comparable with those of conventional syntheses in solution of $[Rh_4(CO)_{12}]$[25−27] and $[Rh_6(CO)_{16}]$.[25−26] Besides, $[Rh_6(CO)_{16}]$ can also be prepared by reduction (100 °C, CO) of physisorped $[Rh(O_2CCH_3)_2]_2$,[23] reaction conditions and yield (82%) being similar to those reported for the traditional synthesis from $[Rh(O_2CCH_3)_2]_2$ in propanol.[28]

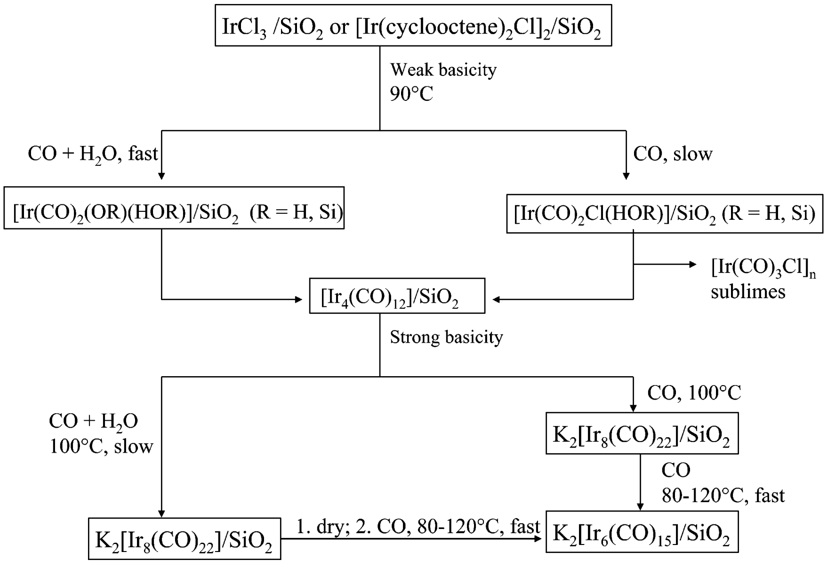
2.2.2. Anionic Clusters: $[Rh_{12}(CO)_{30}]^{2-}$ and $[Rh_5(CO)_{15}]^-$

When $[Rh(CO)_2Cl]_2$ physisorped on silica in the presence of excess K_2CO_3 is treated at 25 °C with CO, reduction to physisorped $K_2[Rh_{12}(CO)_{30}]$ occurs. The cluster can be extracted under N_2 with THF (71% yield), whereas by carrying out the extraction under CO, $K[Rh_5(CO)_{15}]$ is obtained (80% yield), in agreement with the interconversion of these two clusters

Scheme 2. Best Syntheses of Various Iridium Carbonyl Compounds on the Surface of Silica (1 atm)



Scheme 3. Possible Pathways for the Generation of Various Iridium Carbonyl Clusters on the Surface of Silica



in solution.[29,30] The yields and reaction conditions of these silica-mediated syntheses are comparable with those of conventional syntheses in solution.[29−30] Interestingly, a new anionic rhodium carbonyl cluster of high nuclearity, never observed in solution, was isolated in excellent yields by reductive carbonylation (CO, 50−100 °C) of $RhCl_3{\cdot}nH_2O$ or $[Rh(CO)_2Cl]_2$ physisorped on silica in the presence of excess Na_2CO_3 and water (50 wt % of water with respect to the silica powder).[24] The structural characterization and the reactivity of this new cluster are underway.

2.3. Iridium

2.3.1. Neutral Complexes and Clusters: $[Ir(CO)_3Cl]_n$ and $[Ir_4(CO)_{12}]$

$[Ir(CO)_3Cl]_n$. Treatment of $IrCl_3{\cdot}nH_2O$ physisorped on silica gel first with a stream of Cl_2 at 150 °C and then with a stream of CO at 180 °C affords $[Ir(CO)_3Cl]_n$, which sublimes (93% yield after five cycles of chlorination/carbonylation) (Schemes 2 and 3).[10] This surface-mediated synthesis, which 40 years ago was a very convenient way to obtain this complex previously formed in low yields by treatment of finely divided $IrCl_3{\cdot}nH_2O$ with CO at 150 °C,[31a] was reproposed 17 years later working on chromatographic-grade silica gel.[31b] After chlorination and carbonylation for 12 h, 15−43% yields of $[Ir(CO)_3Cl]_n$ were reached but $[Ir_4(CO)_{12}]$ was obtained as byproduct.[31b] More recently, it appeared that such a tedious treatment with Cl_2 is not necessary when Aerosil, a nonporous silica, is used. When $IrCl_3{\cdot}nH_2O$ supported on Aerosil is heated at 150 °C under CO for 24 h in a closed vessel, $[Ir(CO)_3Cl]_n$ sublimes on the cold walls of the vessel outside the oven (76−83% yields).[20]

$[Ir_4(CO)_{12}]$. When silica physisorped $IrCl_3{\cdot}nH_2O$ is heated under CO at 90 °C for 48 h in the presence of water, physisorped $[Ir_4(CO)_{12}]$ is formed and can be easily recovered from the silica surface by extraction with tetrahydrofuran (58% yield).[20,32] Higher yields (79−84%) are reached by working in the presence of a low amount of Na_2CO_3. Similarly, treatment at 90 °C with CO of $[Ir(cyclooctene)_2Cl]_2$ physisorped on silica in the presence of Na_2CO_3 and H_2O (16% (w/w) of H_2O relative to the silica powder) gives physisorped $[Ir_4(CO)_{12}]$ (82% yield after 6 h only).[32]

These silica-mediated syntheses represent an alternative to traditional methods in solution.[33,34]It is interesting to point out that silica physisorped [$Ir_6(CO)_{16}$] is converted to [$Ir_4(CO)_{12}$] by treatment at 100 °C under argon,[35a] an unexpected conversion because an increase in cluster nuclearity on thermal treatment is usually expected. The same decrease of cluster nuclearity upon heating was then reported to occur also by heating [$Ir_6(CO)_{16}$] in dichloroethane at 80 °C under nitrogen.[35b]

2.3.2. Anionic Clusters: [$Ir_6(CO)_{15}$]$^{2-}$ and [$Ir_8(CO)_{22}$]$^{2-}$

When [Ir(cyclooctene)$_2$Cl]$_2$ physisorped on silica in the presence of excess K_2CO_3 is heated at 120 °C under CO, physisorped K_2[$Ir_6(CO)_{15}$] is obtained (87% yield).[32] The amount of water has a strong influence on the selectivity of the reductive carbonylation. With a large excess of H_2O (200% (w/w) of H_2O relative to the silica powder) at 100 °C, a mixture containing K_2[$Ir_8(CO)_{22}$] and [$Ir_4(CO)_{12}$] is formed. Extraction with CH_2Cl_2 affords [$Ir_4(CO)_{12}$] (27% yield), whereas further extraction with CH_3CN gives K_2[$Ir_8(CO)_{22}$] (71%).[32] The silica-mediated synthesis of K_2[$Ir_6(CO)_{15}$] is comparable to the traditional one in solution[36] whereas the silica-mediated route to [$Ir_8(CO)_{22}$]$^{2-}$ is much more attractive (better yields, more convenient starting material) than the synthesis in solution.[37,38] Interestingly, on the silica surface the use of high temperatures (150−200 °C) leads to a new anionic high-nuclearity iridium carbonyl cluster which had never been observed when working in solution.[32] Work is in progress to define its structural characterization.

2.3.3. The Understanding of the Process of Nucleation of Surface Ir(I) Carbonyl Species to Various Iridium Carbonyl Clusters

By working with a low surface basicity (molar ratio Na_2CO_3:Ir = 1−1.5:1), both silica physisorped [Ir(cyclooctene)$_2$Cl]$_2$ and $IrCl_3$ generate [$Ir_4(CO)_{12}$] by treatment with CO (Scheme 2). This process could proceed via some surface Ir(I) species such as [Ir(CO)$_2$(OR)(HOR)] (R = H, Si≡), similar to the suggested [Ir(CO)$_2$(OMg)(HOMg)] species obtained by chemisorption of [Ir(CO)$_2$(acac)] on MgO (see section 3.3).[39] This assumption is in line with the reaction of silica physisorped [$M(CO)_3Cl_2$]$_2$ (M = Os, Ru) in the presence of alkali carbonates to give reactive species of the type [$M(CO)_x(OR)_2$]$_n$ (x = 2, 3; R = H, Si≡) characterized mainly by infrared spectroscopy.[14−15,40−41] However, attempts to obtain infrared evidence of [Ir(CO)$_2$(OR)(HOR)] (R = H, Si≡) failed probably due to its very high reactivity with CO to give [$Ir_4(CO)_{12}$] already at room temperature.

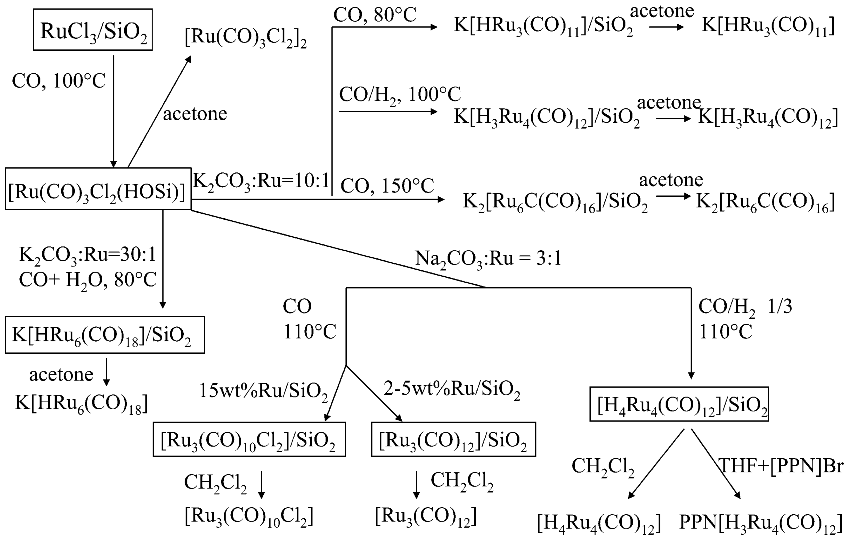
Also, the related surface species [Ir(CO)$_2$Cl(HOSi≡)], formed by carbonylation of silica physisorped [Ir(cyclooctene)$_2$Cl]$_2$, reacts quickly at room temperature and in the absence of alkali carbonate to give [$Ir_4(CO)_{12}$] if an excess of physisorped water is present. In fact, this latter Ir(I) species is stable only on very dry silica (pretreated at 500 °C under 10^{-5} Torr).[42] We have strong evidence that the silica surface must play a role in favoring the process of aggregation under CO of [Ir(CO)$_2$Cl(HOSi≡)], and probably also of the proposed intermediate [Ir(CO)$_2$(OR)(HOR)] (R = H, Si≡), to give [$Ir_4(CO)_{12}$] since the related Ir(I) species [Ir(CO)$_2$Cl]$_2$ is stable under CO at room temperature in donor solvents such as acetonitrile.[42]

On silica added with an excess of K_2CO_3, like in strongly basic solution[37] or on the MgO surface[39] (see section 3.3), the silica-supported [$Ir_4(CO)_{12}$] initially formed gives sequentially [$Ir_8(CO)_{22}$]$^{2-}$ and [$Ir_6(CO)_{15}$]$^{2-}$. By analogy with the iridium chemistry occurring in basic solution[37] or on the MgO surface[39] (see section 3.3), the first anionic iridium cluster formed on the silica surface added with alkali carbonates is probably [$HIr_4(CO)_{11}$]$^-$. However, attempts to define the reaction conditions necessary to detect this cluster, failed. In fact, treatment of silica-physisorped [$Ir_4(CO)_{12}$] at 80 °C for 6 h in the presence of CO and K_2CO_3 (molar ratio K_2CO_3: Ir = 5:1) gives minor amounts of K_2[$Ir_6(CO)_{15}$], but no K[$HIr_4(CO)_{11}$], while most [$Ir_4(CO)_{12}$] does not react. When the reductive carbonylation is carried out at 120 °C for 5 h, [$Ir_4(CO)_{12}$] is totally converted to K_2[$Ir_6(CO)_{15}$]. Probably [$HIr_4(CO)_{11}$]$^-$ is formed already at about 60−80 °C, but it immediately aggregates first to [$Ir_8(CO)_{22}$]$^{2-}$, like it occurs on hydrated MgO[39] (see section 3.3), and then to [$Ir_6(CO)_{15}$]$^{2-}$. To support a sequence of transformation, we found that silica-supported K_2[$Ir_8(CO)_{22}$] is rapidly (ca. 2 h) converted to K_2[$Ir_6(CO)_{15}$] by thermal treatment (80−120 °C) under CO in the presence of K_2CO_3 (molar ratio K_2CO_3:Ir = 5:1).[32]

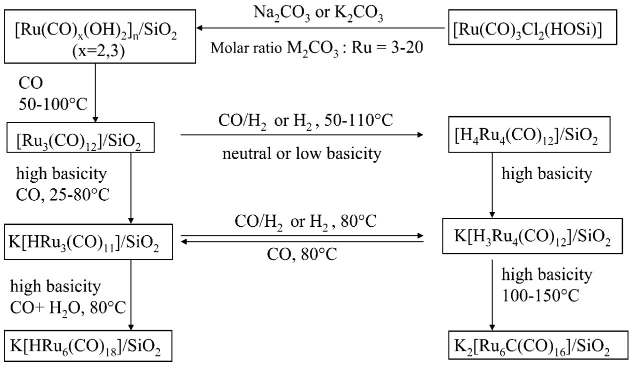
In conclusion the chemistry of "Ir(I)(CO)$_2$" species generated in situ on the silica surface added with alkali carbonates (Scheme 3) parallels the chemistry of similar "Ir(I)(CO)$_2$" species on the hydrated MgO surface[39] (see section 3.3) or of [$Ir_4(CO)_{12}$] in basic solution.[37] The main difference is due to the lower basicity of the silica surface added with small amounts of alkali carbonates when working at temperatures below 50 °C because under these conditions [$HIr_4(CO)_{11}$]$^-$ is not generated from [$Ir_4(CO)_{12}$]. However, on the silica surface added with excess alkali carbonates, this latter anion is probably generated, but it reacts much more quickly than in solution or than on the MgO surface, where probably it is more tightly interacting with Mg^{2+} centers of high polarizing power. In the presence of a huge amount of water, the [$HIr_4(CO)_{11}$]$^-$ produced is transformed via a controlled reaction into [$Ir_8(CO)_{22}$]$^{2-}$ only (as it occurs starting from physisorped [Ir(cyclooctene)$_2$Cl]$_2$ in the presence of excess K_2CO_3). This reaction proceeds to selectively generate [$Ir_6(CO)_{15}$]$^{2-}$ when working in the absence of added water. Since the basicity of a silica surface added with alkali carbonates increases when the amount of physisorped water decreases,[14] it follows that on the silica surface added with K_2CO_3 in absence of excess water, like in strongly alkaline solution[37] or on the surface of MgO[39] (see section 3.3) or inside neutralized basic zeolite cages[43] (see section 6.3) the high basicity favors the direct formation of [$Ir_6(CO)_{15}$]$^{2-}$.[32]

Whereas [$Ir_4(CO)_{12}$] is obtained in excellent yield by direct reduction of $IrCl_3$ working with a low surface basicity or in the absence of any surface

Scheme 4. Best Syntheses of Various Ruthenium Carbonyl Compounds on the Surface of Silica (1 atm)



Scheme 5. Possible Pathways for the Generation of Various Ruthenium Carbonyl Clusters on the Surface of Silica



basicity,[20,32] neither $[Ir_8(CO)_{22}]^{2-}$ nor $[Ir_6(CO)_{15}]^{2-}$ can be prepared in high yields by direct reduction of $IrCl_3$ on a silica surface of high basicity (molar ratio K_2CO_3:Ir = 5−15:1). An explanation of this lack of reactivity could be the formation of hydroxo species (e.g., $Ir(OH)_3$, $[Ir(OH)_6]^{3-}$, or $[Ir(OH)_5(H_2O)]^{2-}$)[44,45] during the impregnation of silica with a water solution of $IrCl_3 \cdot nH_2O$ in the presence of excess K_2CO_3. These hydroxo species, which are not formed when starting from $[Ir(cyclooctene)_2Cl]_2$ (which is rapidly converted into reactive "$Ir(I)(CO)_2$" surface species such as $[Ir(CO)_2(OR)(HOR)]$ (R = H, Si≡)), can be much more difficult to reduce than Ir(I) surface carbonyl species. This suggestion is supported by a similar evidence for the reaction in solution where a two-step process is required to obtain $[Ir_6(CO)_{15}]^{2-}$ from K_2IrCl_6: first reduction of K_2IrCl_6 under CO at 110 °C to generate Ir(I) carbonyl species and then successive reduction under CO at 90 °C in the presence of K_2CO_3 to give $K_2[Ir_6(CO)_{15}]$.[36]

2.4. Ruthenium

2.4.1. Neutral Complexes and Clusters: $[Ru(CO)_3Cl_2]_2$, $[Ru_3(CO)_{12}]$, $[H_4Ru_4(CO)_{12}]$, and $[Ru_3(CO)_{10}Cl_2]$

$[Ru(CO)_3Cl_2]_2$. $RuCl_3 \cdot nH_2O$ physisorped on silica, when heated at 100 °C under CO, generates chemisorped $[Ru(CO)_3Cl_2(HOSi\equiv)]$ (Schemes 4 and 5). Extraction with a donor solvent such as acetone gives $[Ru(CO)_3Cl_2]_2$ in 88−93% yields.[20] This silica-mediated synthesis is attractive when compared to the best traditional synthetic routes in solution which require more drastic conditions and afford lower yields of $[Ru(CO)_3Cl_2]_2$ (Table 3).[46−47]

$[Ru_3(CO)_{12}]$, $[H_4Ru_4(CO)_{12}]$, and $[Ru_3(CO)_{10}Cl_2]$. It appeared that silica physisorped $[Ru_3(CO)_{12}]$ reacts with H_2 at 50 °C to give physisorped $[H_4Ru_4(CO)_{12}]$,[48] a reaction slower (due to the relatively low temperature) but similar to that observed in refluxing octane.[49] This surface reactivity and the easy recovery of $[H_4Ru_4(CO)_{12}]$ by extraction with CH_2Cl_2 hinted the development of a convenient silica-mediated synthesis of $[H_4Ru_4(CO)_{12}]$ directly from $RuCl_3 \cdot nH_2O$, a less expensive material than $[Ru_3(CO)_{12}]$. In ethanol, under very high pressures (40 atm of CO + 40 atm of H_2),[50] $[H_4Ru_4(CO)_{12}]$ can be formed from $RuCl_3 \cdot nH_2O$, but in low yields (10−30% yields after 3 days at 75−100 °C). It turned out that high yields of this cluster can be reached by using a two-step silica-mediated route via the intermediate synthesis of chemisorped $[Ru(CO)_3Cl_2(HOSi\equiv)]$. Thus, treatment of the latter species with a low amount of Na_2CO_3 (Na_2CO_3:Ru = 3:1; deposited from a CH_2Cl_2 slurry) followed by heating at 110 °C under CO + H_2 (molar ratio 1:3) affords $[H_4Ru_4(CO)_{12}]$ in 88% yield. Similar yields are obtained starting from $[Ru(CO)_3Cl_2]_2$.[15] By working with the same reaction parameters but using pure CO as gas phase, both chemisorped $[Ru(CO)_3Cl_2(HOSi\equiv)]$ and physisorped $[Ru(CO)_3Cl_2]_2$ are readily converted to physisorped $[Ru_3(CO)_{12}]$ (82−93% yields) with a loading of 2−5% (w/w) of Ru relative to SiO_2.[15] These yields are higher than those reported in the past working in solution by reductive carbonylation at atmospheric pressure of $RuCl_3 \cdot nH_2O$[51] or $[Ru_3O(O_2CCH_3)_6(H_2O)_3](O_2CCH_3)$[52] and comparable to those reached under pressure.[47,52−53]

Interestingly it was observed that when physisorped $[Ru(CO)_3Cl_2]_2$ (15% (w/w) of Ru relative to SiO_2) is treated with Na_2CO_3 (molar ratio Na_2CO_3:Ru = 3:1; deposited from a CH_2Cl_2 slurry) and heated at 110 °C under CO, no $[Ru_3(CO)_{12}]$ is formed, the product being physisorped $[Ru_3(CO)_{10}Cl_2]$ (75% yield),[15] a new cluster never synthesized in solution although $[Ru_3(CO)_{10}X_2]$ (X = Br, I) is known.[54] The different selectivity observed by increasing the Ru loading from 5% to 15% has been 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.[15] This limited homogeneity leads to a lower surface basicity than that expected for a 3:1 molar ratio of Na_2CO_3:Ru. Therefore it is more difficult to remove all the chloro ligands from the Ru coordination sphere, so that $[Ru_3(CO)_{10}Cl_2]$ is generated instead of $[Ru_3(CO)_{12}]$. In agreement with this hypothesis, when Na_2CO_3 is deposited on silica starting from a water solution instead of a CH_2Cl_2 slurry, thus producing a far better dispersion, only $[Ru_3(CO)_{12}]$ is formed even at high loading. This is a clear example of how much the manner by which an alkali carbonate is deposited on silica can influence the surface basicity and therefore the selectivity. Due to the solubility of alkali carbonates in ethylene glycol, this effect cannot be used in solution for controlling the selectivity. In fact, attempts to prepare $[Ru_3(CO)_{10}Cl_2]$ by controlled reductive carbonylation of $RuCl_3 \cdot nH_2O$ or $[Ru(CO)_3Cl_2]_2$ in ethylene glycol failed, even by working with a defect of base.[55a]

The above silica-mediated syntheses of $[H_4Ru_4(CO)_{12}]$ and $[Ru_3(CO)_{12}]$ were the springboard of new convenient syntheses working in ethylene glycol solution, a high boiling solvent carrying non acidic OH groups that could mimic the OH groups of the silica surface. In particular, although only traces of $[H_4Ru_4(CO)_{12}]$ are generated by reduction with a mixture of $CO + H_2$ (molar ratio = 1:3) of $RuCl_3 \cdot nH_2O$ supported on silica treated with Na_2CO_3,[15] this latter cluster could be obtained in 66−88% yields by bubbling at 90 °C the same gas mixture through an ethylene glycol solution of $RuCl_3 \cdot nH_2O$ in the presence of Na_2CO_3 (molar ratio Na_2CO_3:Ru = 3:2). By working under similar conditions but under pure CO, $[Ru_3(CO)_{12}]$ is formed (70% yield).[55a,55b,55c] Better and well-reproducible yields (80−85%) are obtained by a modified two-step methodology, inspired by the two-step route to convert silica-supported $RuCl_3 \cdot nH_2O$ into Ru carbonyl clusters via $[Ru(CO)_3Cl_2(HOSi{\equiv})]$,[15] involving (i) preparation of $[Ru(CO)_xCl_2$(ethylene glycol)] (x = 2, 3) species by carbonylation of $RuCl_3 \cdot nH_2O$ at 110 °C in ethylene glycol and (ii) addition of Na_2CO_3 (molar ratio Na_2CO_3:Ru = 3:2) and further reduction with $CO + H_2$ (to obtain $[H_4Ru_4(CO)_{12}]$) or pure CO (to obtain $[Ru_3(CO)_{12}]$) at 95 °C. This latter method appears to be a very convenient way to convert $RuCl_3 \cdot nH_2O$ into these neutral carbonyl clusters in excellent yields and under mild conditions.[55b,55c] In the latter preparation of $[Ru_3(CO)_{12}]$, it is worth pointing out that if the second step is carried out in the presence of a molar ratio Na:Cl inferior to 1, a mixture of $[Ru_3(CO)_{12}]$ and unreacted tri- and dicarbonyl Ru(II) species is obtained. This result is in contrast with a recently reported similar two-step preparation of $[Ru_3(CO)_{12}]$ involving (i) reductive carbonylation of $RuCl_3 \cdot nH_2O$ in 2-methoxyethanol at 125 °C followed by addition of ca. 1 equiv of KOH per Ru and successive reductive carbonylation at 85 °C,[55d,55e] but it was then observed that it is better to use a higher amount of KOH (ca. 2 equiv per Ru) in this latter synthesis.[55f]

2.4.2. Anionic Clusters: $[Ru_6C(CO)_{16}]^{2-}$, $[H_3Ru_4(CO)_{12}]^-$, $[HRu_3(CO)_{11}]^-$, and $[HRu_6(CO)_{18}]^-$

$[Ru_6C(CO)_{16}]^{2-}$. When $[Ru_3(CO)_{12}]$ or $K[H_3Ru_4(CO)_{12}]$ physisorped on silica added with excess K_2CO_3 is heated at 150 °C under CO, physisorped $K_2[Ru_6C(CO)_{16}]$ is formed in quantitative yield and can be recovered by extraction with acetone.[15] The same kind of reaction takes place on the surface of MgO.[56] Excellent yields of $K_2[Ru_6C(CO)_{16}]$ (95%) can also be reached starting from $RuCl_3 \cdot nH_2O$ by a one-pot two-step process involving first preparation of chemisorped $[Ru(CO)_3Cl_2(HOSi{\equiv})]$ and then reductive carbonylation in the presence of excess K_2CO_3 (CO, 150 °C).[15] The latter silica-mediated synthesis, of particular interest because the traditional syntheses in solution of $[Ru_6C(CO)_{16}]^{2-}$ require $[Ru_3(CO)_{12}]$ as starting material (Table 3),[57a−d] was the inspiration for new syntheses in solution. Thus $K_2[Ru_6C(CO)_{16}]$ is obtained in 89% yield by bubbling CO through an ethylene glycol solution of $[Ru(CO)_3Cl_2]_2$ and excess K_2CO_3 at 160 °C. Excellent yields (80−84%) are also reached by a methodology, inspired by the two-step route to convert physisorped $RuCl_3 \cdot nH_2O$ into Ru clusters via $[Ru(CO)_3Cl_2(HOSi{\equiv})]$,[15] involving (i) preparation of $[Ru(CO)_xCl_2$(ethylene glycol)] (x=2,3) by carbonylation of $RuCl_3 \cdot nH_2O$ at 110 °C in ethylene glycol and (ii) addition of K_2CO_3 and further reduction with CO at 160 °C. This is the best way to convert $RuCl_3 \cdot nH_2O$ into $[Ru_6C(CO)_{16}]^{2-}$.[55b,55c]

$[H_3Ru_4(CO)_{12}]^-$. When physisorped $[Ru_3(CO)_{12}]$ or $K[HRu_3(CO)_{11}]$ is treated with $CO + H_2$ (molar ratio 1:3) at 80 °C on a silica surface treated with excess K_2CO_3, $K[H_3Ru_4(CO)_{12}]$ is obtained quantitatively.[15] This surface reaction, which is reversible, mimics that reported to occur in solution[58] or on the surface of MgO[59] (see section 3.5). More interestingly, treatment of chemisorped $[Ru(CO)_3Cl_2(HOSi{\equiv})]$ with $CO + H_2$ (molar ratio 1:3) at 100 °C in the presence of K_2CO_3 affords mixtures of physisorped $[H_4Ru_4(CO)_{12}]$ (10% yield) and $K[H_3Ru_4(CO)_{12}]$ (60% yield). Higher yields (81%) of $[H_3Ru_4(CO)_{12}]^-$ can be reached by extraction of silica-physisorped $[H_4Ru_4(CO)_{12}]$, prepared from $RuCl_3 \cdot nH_2O$ (as described in section 2.4.1), with a solution of [PPN]Br in THF.[15] Besides, it appeared that when a *t*-amyl alcohol solution of $[Ru(CO)_3Cl_2]_2$ is heated at 88 °C in the presence of excess Na_2CO_3 under $CO + H_2$ (molar ratio = 1:3), $Na[H_3Ru_4(CO)_{12}]$ is formed in 93% yield.[55a] This new synthesis, inspired from silica-mediated syntheses, is particularly convenient when compared with the traditional syntheses in solution which involve $[H_4Ru_4(CO)_{12}]$ as starting material.[60]

$[HRu_3(CO)_{11}]^-$ and $[HRu_6(CO)_{18}]^-$. Treatment under CO at 80 °C of $[Ru_3(CO)_{12}]$ (or $K[H_3Ru_4(CO)_{12}]$) physisorped on silica in the presence of excess K_2CO_3 affords $K[HRu_3(CO)_{11}]$ in quantitative yield.[15] However, this reaction occurs at much lower temperature (e.g., 25 °C) when working in basic solution,[58,61] on the surface of MgO (see section 3.5),[59,62] of ZnO and La_2O_3 (see section 5.1)[62] and of Al_2O_3 (see section 4.4).[63] Besides, treatment of chemisorped [Ru-

$(CO)_3Cl_2(HOSi\equiv)]$ with CO, working with excess K_2CO_3 at 80 °C, affords a mixture of physisorped $[Ru_3(CO)_{12}]$ (11% yield) and $K[HRu_3(CO)_{11}]$ (42% yield).[15] By working under the same conditions but in the presence of a huge amount of water (110% (w/w) of H_2O relative to SiO_2), a mixture of physisorped $[Ru_3(CO)_{12}]$ (16% yield) and $K[HRu_6(CO)_{18}]$ (61% yield) is obtained.[15] Since $[HRu_6(CO)_{18}]^-$ is usually prepared in solution by acidification of $[HRu_3(CO)_{11}]^-$ (50% yield) or of $[Ru_6(CO)_{18}]^{2-}$ (80% yield),[61] its easy silica-mediated synthesis from $RuCl_3 \cdot nH_2O$ via $[Ru(CO)_3Cl_2(HOSi\equiv)]$ is attractive from a preparative point of view.

2.4.3. The Process of Nucleation of Surface Ru(II) Carbonyl Species to Various Ruthenium Carbonyl Clusters

Evidence has been reached for a step-by-step process (see Scheme 5) which explains the origin of the good selectivities obtained in the controlled reduction of silica-supported $[Ru(CO)_3Cl_2]_2$ or $[Ru(CO)_3Cl_2(HOSi\equiv)]$ to give, in the presence of alkali carbonates, various neutral or anionic ruthenium carbonyl clusters.[15] The first step is probably the formation of hydroxo species such as $[Ru(CO)_x(OH)_2]_n$ ($x = 2, 3$)[64] by reaction of $[Ru(CO)_3Cl_2]_2$ or $[Ru(CO)_3Cl_2(HOSi\equiv)]$ with alkali carbonates on the silica surface. These hydroxo Ru(II) carbonyl species are then converted to $[Ru_3(CO)_{12}]$ under CO, probably via $[HRu_3(CO)_{10}(OR)]$ (R = H, Si≡), as it occurs in the process of aggregation of related Os(II) carbonyl species to various Os carbonyl clusters.[14] Attempts to stop the reduction of Ru(II) carbonyl species when detectable amounts of $[HRu_3(CO)_{10}(OR)]$ (R = H, Si≡) are formed, failed due to the quick reaction of this latter silica-bound cluster with CO to give $[Ru_3(CO)_{12}]$.[65] The role of $[Ru_3(CO)_{12}]$ as key intermediate of the aggregation process was confirmed by the formation of a mixture of $[Ru_3(CO)_{12}]$ and $[Ru(CO)_x(OH)_2]_n$ ($x = 2, 3$) after treatment of $[Ru(CO)_3Cl_2(HOSi\equiv)]$ for 24 h at 50 °C under CO or CO + H_2 (molar ratio 1:3) when working either with a low surface basicity (molar ratio Na_2CO_3:Ru = 3:1) or with a high surface basicity (molar ratio K_2CO_3:Ru = 10:1).

With a low surface basicity, silica-supported $[Ru_3(CO)_{12}]$ is then easily converted to $[H_4Ru_4(CO)_{12}]$ by reaction with H_2 at 50−110 °C. In the absence of H_2 and working with a more basic silica surface (molar ratio K_2CO_3:Ru = 10:1), $[Ru_3(CO)_{12}]$ affords first $K[HRu_3(CO)_{11}]$ (at 25−80 °C), which is quickly transformed into $K[HRu_6(CO)_{18}]$ when working with an even more basic silica surface (molar ratio K_2CO_3:Ru = 30:1) and in the presence of excess water. By analogy with the known redox condensation in THF of $[Ru_3(CO)_{11}]^{2-}$ with $[Ru_3(CO)_{12}]$ to give $[Ru_6(CO)_{18}]^{2-}$,[57b] $[HRu_6(CO)_{18}]^-$ is probably formed on the silica surface by condensation of $[Ru_3(CO)_{12}]$ with the anionic species $[HRu_3(CO)_{11}]^-$, which is first generated from $[Ru_3(CO)_{12}]$ under basic conditions.

On the other hand, $[Ru_3(CO)_{12}]$, supported on a basic silica surface (molar ratio K_2CO_3:Ru = 10:1), reacts with CO + H_2 at 80 °C to give $K[H_3Ru_4(CO)_{12}]$. This process could involve either $[H_4Ru_4(CO)_{12}]$ or $K[HRu_3(CO)_{11}]$ as intermediate. In fact, on such a basic silica surface, $[H_4Ru_4(CO)_{12}]$ is easily deprotonated to give $K[H_3Ru_4(CO)_{12}]$; however, this latter is also obtained by reaction of $K[HRu_3(CO)_{11}]$, formed under alkaline conditions from $[Ru_3(CO)_{12}]$, with a mixture of CO + H_2 at 80 °C. On the silica surface, like in solution,[58] $K[H_3Ru_4(CO)_{12}]$ is reconverted to $K[HRu_3(CO)_{11}]$ when H_2 is removed. Evidence that thermal treatment at 100−150 °C of $K[H_3Ru_4(CO)_{12}]$ supported on a silica surface treated with excess K_2CO_3 gives $K_2[Ru_6C(CO)_{16}]$ suggests that $K[H_3Ru_4(CO)_{12}]$ could act as intermediate in the synthesis of $K_2[Ru_6C(CO)_{16}]$ from silica-supported $[Ru_3(CO)_{12}]$ working with CO at 150 °C and with a high surface basicity. Under these conditions some H_2 is generated by the water gas shift reaction, so that the amount necessary to produce $[H_4Ru_4(CO)_{12}]$ and then $[H_3Ru_4(CO)_{12}]^-$ or to react with $[HRu_3(CO)_{11}]^-$ could be available.

In conclusion, the remarkable selective surface-mediated syntheses of various neutral and anionic Ru clusters starting from $RuCl_3 \cdot nH_2O$ or $[Ru(CO)_3Cl_2]_2$ involves the in situ formation of $[Ru_3(CO)_{12}]$ as the key intermediate. The significant selectivity toward the synthesis of various neutral or anionic clusters is then controlled by the basicity of the surface, the composition of the gaseous phase (CO or CO + H_2), and the temperature.[15]

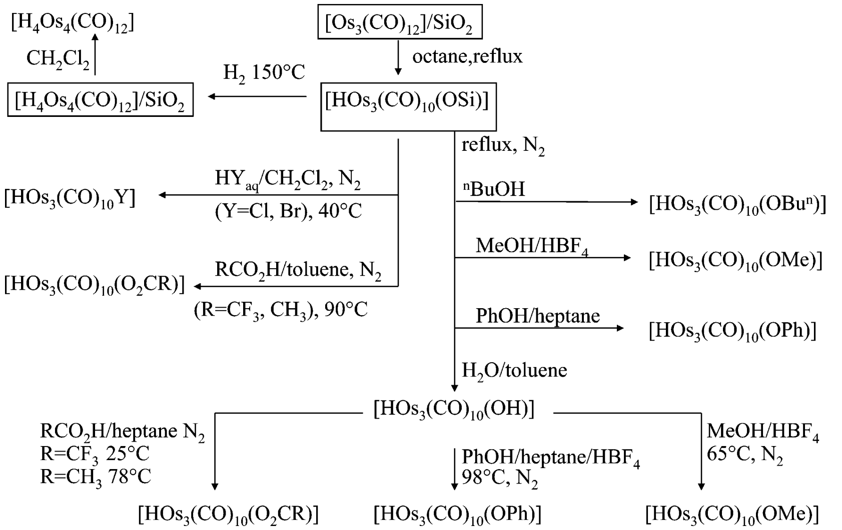
2.5. Osmium

2.5.1. Neutral Complexes and Clusters: α-$[Os(CO)_3Cl_2]_2$, $[Os_3(CO)_{12}]$, $[H_4Os_4(CO)_{12}]$, and $[HOs_3(CO)_{10}Y]$ (Y = OH, OR, Cl, Br, O_2CR)

About 20 years ago, it was shown that reductive carbonylation at 200 °C of chemisorped $[HOs_3(CO)_{10}(OSi\equiv)]$ and $[Os(CO)_x(OSi\equiv)_2]_n$ (x=2,3) gives $[Os_3(CO)_{12}]$,[66] showing an unexpected mobility of Os carbonyl species even if anchored to the silica surface. Starting from this observation, more recently, α-$[Os(CO)_3Cl_2]_2$ and various neutral Os carbonyl clusters have been generated from $OsCl_3$ or $[Os_3(CO)_{12}]$, in high yields and under mild conditions, on the surface of silica added[41] or not[48,67] with an alkali carbonate.[9]

$[Os(CO)_3Cl_2]_2$. Anhydrous or hydrated $OsCl_3$ physisorped on silica, when heated at 180 °C under CO, gives chemisorped $[Os(CO)_3Cl_2(HOSi\equiv)]$ with parallel sublimation of $[Os(CO)_3Cl_2]_2$ and *cis*-$[Os(CO)_4Cl_2]$ on the cold walls of the reactor. Extraction of the sublimate and of the silica powder with hot $CHCl_3$ affords only α-$[Os(CO)_3Cl_2]_2$ (80−90% yield) because any *cis*-$[Os(CO)_4Cl_2]$ is thermally converted to α-$[Os(CO)_3Cl_2]_2$.[20] The excellent yield and the mild conditions are remarkable when compared to the traditional methods in solution.[68] The carbonylation of solid anhydrous $OsCl_3$ can be effected only by working at 155 °C under 65 atm of CO, affording *cis*-$[Os(CO)_4Cl_2]$ (60% yield), which can be converted to α-$[Os(CO)_3Cl_2]_2$ by refluxing in $CHCl_3$.[69a] Since, on a silica surface, anhydrous $OsCl_3$ may be reductively carbonylated at atmospheric pressure, silica must play an important role.[20] In fact the silica surface can behave as a donor system via the surface silanol groups, as suggested by the traces of methanol required to avoid the formation of unreactive anhy-

Scheme 6. Best Syntheses of Various Osmium Carbonyl Compounds, from $[Os_3(CO)_{12}]$, on the Surface of Silica (1 atm)



drous $OsCl_3$ in the synthesis of $[Os(CO)_3Cl_2]_2$ by treatment of $OsCl_3 \cdot nH_2O$ at 270 °C with CO.[69b]

$[H_4Os_4(CO)_{12}]$. Treatment of silica physisorped $[Os_3(CO)_{12}]$ with H_2 at 100 °C affords physisorped $[H_4Os_4(CO)_{12}]$ (68% yield).[48] The particularly mild pressure of H_2 (1 atm) required for this synthesis, compared to the high pressure (120 atm) needed when working in inert solvents such as octane in order to obtain similar yields,[70] was later explained by the activation of $[Os_3(CO)_{12}]$ by interaction with surface silanols to give chemisorped $[HOs_3(CO)_{10}OSi\equiv]$, a reactive and labile intermediate.[71] This synthesis has the disadvantage of requiring a long reaction time due to the necessity of working at low temperatures (100 °C) to avoid parallel sublimation of $[Os_3(CO)_{12}]$.[48] This observation led to a better silica-mediated synthesis involving a one-pot two-step process: (i) formation of $[HOs_3(CO)_{10}OSi\equiv]$ (98% yield) by refluxing an octane solution of $[Os_3(CO)_{12}]$ with silica;[72] (ii) treatment of $[HOs_3(CO)_{10}OSi\equiv]$ with H_2 at 150 °C to give $[H_4Os_4(CO)_{12}]$ in 94% total yield.[67a]

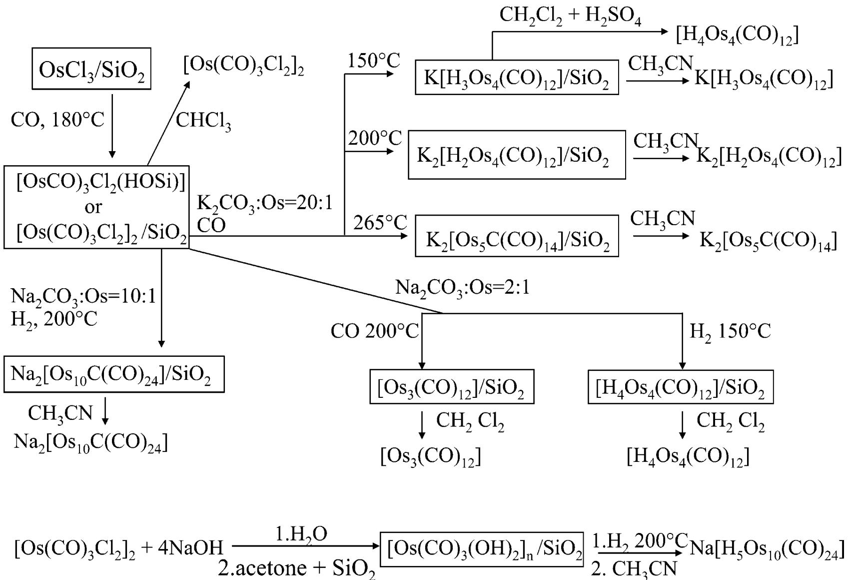
The direct reaction of $OsCl_3 \cdot nH_2O$ or α-$[Os(CO)_3Cl_2]_2$ is a way to synthesize $[H_4Os_4(CO)_{12}]$ from a less expensive species than $[Os_3(CO)_{12}]$. Reaction of silica physisorped α-$[Os(CO)_3Cl_2]_2$ with H_2 (100−200 °C) does not afford $[H_4Os_4(CO)_{12}]$ due to the easy sublimation of the starting dimer at temperatures higher than 100 °C and the difficulty of removing chloro ligands from the Os coordination sphere when working at relatively low temperatures.[73] Only after addition of bases, such as alkali carbonates, chloro ligands are easily removed.[40−41,73] Thus, $[H_4Os_4(CO)_{12}]$ is obtained in 70−83% yields when chemisorped $[Os(CO)_3Cl_2(HOSi\equiv)]$ (obtained in situ by reductive carbonylation of silica physisorped $OsCl_3$)[20] or α-$[Os(CO)_3Cl_2]_2$ physisorped on a silica surface is heated in the presence of Na_2CO_3 (molar ratio $Na_2CO_3{:}Os = 2{:}1$) under H_2 at 150 °C.[41a]

An alternative convenient way to prepare $[H_4Os_4(CO)_{12}]$ (76% yield) directly from $OsCl_3 \cdot nH_2O$ involves three steps:[41a] (i) synthesis of $[Os(CO)_3Cl_2(HOSi\equiv)]$;[20] (ii) addition of K_2CO_3 and reductive carbonylation (CO, 150 °C) to give physisorped $K[H_3Os_4(CO)_{12}]$; (iii) extraction with CH_2Cl_2 acidified with H_2SO_4.[41a]

$[Os_3(CO)_{12}]$. The reductive carbonylation of silica physisorped α-$[Os(CO)_3Cl_2]_2$ to generate $[Os_3(CO)_{12}]$ does not occur easily due to sublimation of chlorocarbonyl Os compounds when working at high temperatures (130−250 °C) and to the difficulty of removing chloro ligands at lower temperatures.[73] However, when chemisorped $[Os(CO)_3Cl_2(HOSi\equiv)]$ (obtained in situ by reductive carbonylation of silica physisorped $OsCl_3$)[20] or α-$[Os(CO)_3Cl_2]_2$ physisorped on silica is heated in the presence of a low amount of Na_2CO_3, $[Os_3(CO)_{12}]$ is obtained in 76−82% yields.[41a] The discovery of the latter synthesis is of particular interest because, in solution, the best route to synthesize $[Os_3(CO)_{12}]$ is the reductive carbonylation under high pressure of OsO_4.[74] This easy surface-mediated synthesis was the springboard for a new convenient synthesis in solution. Thus, treatment of an ethylene glycol solution of α-$[Os(CO)_3Cl_2]_2$ added with a stoichiometric amount of Na_2CO_3 with CO at 160 °C gives $[Os_3(CO)_{12}]$ (65% yield).[55a] In addition, while $[Os_3(CO)_{12}]$ cannot be obtained by direct carbonylation of silica supported $OsCl_3 \cdot nH_2O$ in the presence of alkali carbonates,[41] excellent yields (64−70%) are obtained by bubbling CO at 160−165 °C into an ethylene glycol solution of $OsCl_3 \cdot nH_2O$ and Na_2CO_3.[55a]

$[HOs_3(CO)_{10}Y]$ ($Y = OH, OR, Cl, Br, O_2CR$). The facile activation of $[Os_3(CO)_{12}]$ by the surface, via reaction with surface silanols to give chemisorped $[HOs_3(CO)_{10}OSi\equiv]$, provides a convenient route to the synthesis of $[HOs_3(CO)_{10}Y]$ (Y = a three-electron donor like OH, OR, Cl, Br, O_2CR). These syntheses compare favorably with traditional syntheses in solution (Table 3)[75−79] which require intermediates (e.g., $[HOs_3(CO)_{10}(OCH{=}CH_2)]$,[75] $[Os_3(CO)_{10}$(cyclohexa-1,3-diene)$]$,[76] $[HOs_3(CO)_{10}(NCHNMe_2)]$,[77] $[Os_3(CO)_{10}$(cyclooctene)$_2]$,[78] $[Os_3(CO)_{10}(CH_3CN)_2]$[78]) usually obtained in many steps with low global yields starting from $[Os_3(CO)_{12}]$. Chemisorped $[HOs_3(CO)_{10}OSi\equiv]$ is obtained in one step and in nearly quantitative yield by activation of physisorped $[Os_3(CO)_{12}]$,[72] and its conversion in $[HOs_3(CO)_{10}Y]$ occurs in high yields and under mild conditions (Scheme 6).[67]

Scheme 7. Best Syntheses of Various Osmium Carbonyl Compounds, from $OsCl_3$, on the Surface of Silica (1 atm)



$[HOs_3(CO)_{10}OH]$. $[HOs_3(CO)_{10}OH]$ is obtained in fair yields (56% yield starting from $[Os_3(CO)_{12}]$) by treatment of $[HOs_3(CO)_{10}OSi{\equiv}]$ with aqueous HF which dissolves silica.[80] Better yields are reached under milder hydrolysis conditions. Thus, when $[HOs_3(CO)_{10}OSi{\equiv}]$ is stirred at 95 °C under N_2, in a biphasic system water/toluene, $[HOs_3(CO)_{10}OH]$ is obtained in almost quantitative yield (total yield from $[Os_3(CO)_{12}] = 91\%$, compared with 9−33% yields in solution).[67] This is a relevant synthesis because $[HOs_3(CO)_{10}OH]$ is a convenient intermediate for the synthesis of many related $[HOs_3(CO)_{10}Y]$ clusters (Scheme 6).[67]

$[HOs_3(CO)_{10}OR]$ (R = Bu, Me, Ph). By stirring under N_2 a slurry of $[HOs_3(CO)_{10}OSi{\equiv}]$ in refluxing *n*-butanol, $[HOs_3(CO)_{10}OBu]$ is obtained in 87% yield.[67a] On the contrary, $[HOs_3(CO)_{10}OSi{\equiv}]$ is quite unreactive in refluxing methanol due to the rather low temperature, but addition of $HBF_4{\cdot}Et_2O$ catalyzes the exchange reaction affording $[HOs_3(CO)_{10}OMe]$ in 54% yield.[67a] Besides, when a slurry of $[HOs_3(CO)_{10}OSi{\equiv}]$, excess phenol, and heptane is stirred at 98 °C under N_2, $[HOs_3(CO)_{10}OPh]$ is obtained (66% yield).[67a] $[HOs_3(CO)_{10}OMe]$ and $[HOs_3(CO)_{10}OPh]$ can be prepared in better total yields (82−87%, much higher than those of traditional syntheses in solution which are in the range 10−48%) by using a one-pot three-step process from $[Os_3(CO)_{12}]$: (i) formation of $[HOs_3(CO)_{10}OSi{\equiv}]$, (ii) hydrolysis to $[HOs_3(CO)_{10}OH]$, and (iii) reaction of $[HOs_3(CO)_{10}OH]$ with methanol (at 65 °C) or phenol (at 98 °C) dissolved in heptane in the presence of a few drops of $HBF_4{\cdot}Et_2O$.[67a]

$[HOs_3(CO)_{10}Y]$ (Y = Cl, Br, O_2CR). Treatment of $[HOs_3(CO)_{10}OSi{\equiv}]$ with a mixture of aqueous HY (Y = Cl, Br) and CH_2Cl_2, under N_2 at 40 °C, affords $[HOs_3(CO)_{10}Y]$ in excellent yields (87−89%). Similarly, $[HOs_3(CO)_{10}OSi{\equiv}]$ reacts with CF_3CO_2H or CH_3CO_2H in toluene, under N_2 at 90 °C, affording $[HOs_3(CO)_{10}(O_2CR)]$ (56−72%).[67a] In addition, $[HOs_3(CO)_{10}OH]$, easily prepared by hydrolysis of $[HOs_3(CO)_{10}OSi{\equiv}]$, reacts with CF_3CO_2H or CH_3CO_2H in heptane (at 25 and 78 °C respectively) to give $[HOs_3(CO)_{10}(O_2CR)]$ in excellent total yields with respect to $[Os_3(CO)_{12}]$ (82−91%).[67a] The above yields are much higher than those reported by traditional syntheses in solution starting from $[Os_3(CO)_{12}]$ (30−55%).[75−77,81−82]

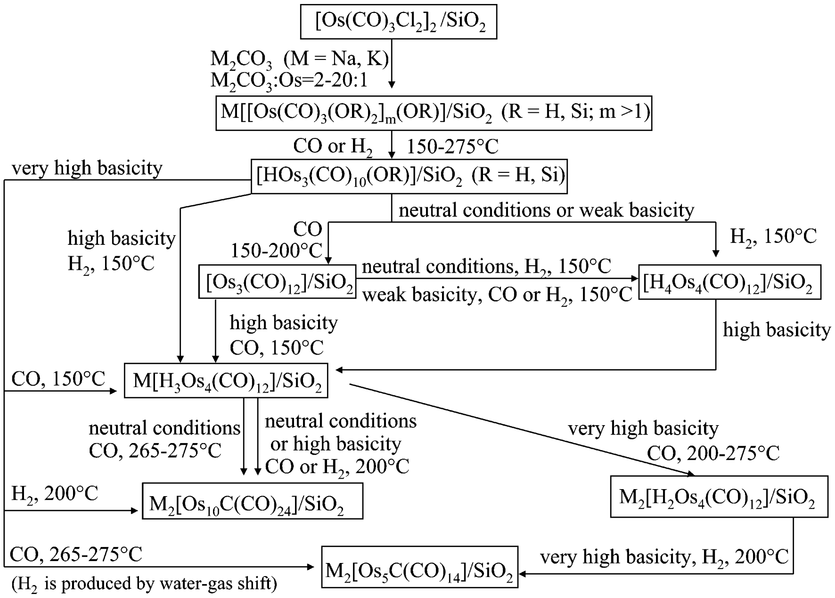
These silica-mediated syntheses are limited by the maximum surface concentration of the intermediate $[HOs_3(CO)_{10}OSi{\equiv}]$, which is controlled by the number of available silanols on the surface.[83] Only loadings up to 4 wt % Os/SiO_2 can be used.[84] Despite this limitation, amounts of ca. 300 mg of cluster can be obtained in a single reaction using ca. 10 g of silica, which can be recycled after workup and completion of the reaction.[67]

2.5.2. Anionic Clusters: $[H_3Os_4(CO)_{12}]^-$, $[H_2Os_4(CO)_{12}]^{2-}$, $[Os_{10}C(CO)_{24}]^{2-}$, $[Os_5C(CO)_{14}]^{2-}$, and $[H_5Os_{10}(CO)_{24}]^-$

$[H_3Os_4(CO)_{12}]^-$ and $[H_2Os_4(CO)_{12}]^{2-}$. When $[H_4Os_4(CO)_{12}]$, $[Os_3(CO)_{12}]$, or α-$[Os(CO)_3Cl_2]_2$ physisorped on silica is treated with CO at 150 °C in the presence of excess K_2CO_3, physisorped $K[H_3Os_4(CO)_{12}]$ is obtained (91−100% yields) (Scheme 7).[14,40] Similar yields are reached starting from chemisorped $[Os(CO)_3Cl_2(HOSi{\equiv})]$, prepared in situ by reductive carbonylation of silica-supported $OsCl_3$.[20] By working at 200 °C, with the same reaction parameters, both α-$[Os(CO)_3Cl_2]_2$ and $[Os(CO)_3Cl_2(HOSi{\equiv})]$ are converted to $K_2[H_2Os_4(CO)_{12}]$ (92% yield).[41]

The silica-mediated syntheses of $K[H_3Os_4(CO)_{12}]$ and $K_2[H_2Os_4(CO)_{12}]$ starting from $OsCl_3$ are more convenient than the traditional syntheses in solution,[70,85−86] which start from the expensive $[H_4Os_4(CO)_{12}]$[70] or $[Os_3(CO)_{12}]$[85,86] clusters and afford, usually under more drastic conditions, lower yields (Table 3). Recently, the silica-mediated synthesis of $K[H_3Os_4(CO)_{12}]$ was the springboard for a convenient one-pot synthesis in solution of both $K[H_3Os_4(CO)_{12}]$ and $[H_4Os_4(CO)_{12}]$.[55a] By bubbling CO through an ethylene glycol solution of $OsCl_3{\cdot}nH_2O$ and K_2CO_3 at 160

Scheme 8. Possible Pathways for the Generation of Various Osmium Carbonyl Clusters on the Surface of Silica



°C, $K[H_3Os_4(CO)_{12}]$ is formed. According to the work-up of the reaction mixture, either $[H_3Os_4(CO)_{12}]^-$ (extracted with a CH_2Cl_2 solution of $[NBu_4]I$) or $[H_4Os_4(CO)_{12}]$ (obtained by acidification of the reaction mixture with H_2SO_4 and then extraction with CH_2Cl_2) is obtained in 74−81% yields. However, ethylene glycol cannot be used as a safe reaction medium for the synthesis of $[H_2Os_4(CO)_{12}]^{2-}$ or high nuclearity clusters such as $[Os_{10}C(CO)_{24}]^{2-}$ and $[Os_5C(CO)_{14}]^{2-}$, which require high temperatures and strong basic conditions. In fact treatment of glycols with strong bases at above 200 °C leads to degradation with exothermic reactions which can proceed uncontrollably,[87] an inconvenience that does not exist when the silica surface is used as reaction medium.

$[Os_{10}C(CO)_{24}]^{2-}$ or $[Os_5C(CO)_{14}]^{2-}$. When chemisorped $[Os(CO)_3Cl_2(HOSi\equiv)]$, prepared in situ by reductive carbonylation of silica-supported $OsCl_3$,[20] or α-$[Os(CO)_3Cl_2]_2$ physisorped on silica is reacted in the presence of excess Na_2CO_3 with H_2 at 200 °C, physisorped $Na_2[Os_{10}C(CO)_{24}]$ is obtained (81% yield), whereas physisorped $K_2[Os_5C(CO)_{14}]$ (74% yield) is formed by working under CO at 265 °C with K_2CO_3.[41] These syntheses are highly attractive when compared with the traditional syntheses in solution from $[Os_3(CO)_{12}]$, or one of its derivative, which usually need more drastic reaction conditions and afford much lower yields of product.[88−90]

$[H_5Os_{10}(CO)_{24}]^-$. Reaction for 3 days of silica physisorped $[Os(CO)_3(OH)_2]_n$, generated in situ from α-$[Os(CO)_3Cl_2]_2$, with H_2 at 200 °C gives some physisorped $[H_4Os_4(CO)_{12}]$ (20% yield) and physisorped $Na[H_5Os_{10}(CO)_{24}]$ (65% yield).[91] This surface-mediated high-yield route to $[H_5Os_{10}(CO)_{24}]^-$ is of interest since this cluster was usually prepared by acidification of $[H_4Os_{10}(CO)_{24}]^{2-}$, obtained in very low yields along with other high nuclearity clusters, by heating under reflux a solution of $[Os_3(CO)_{12}]$ in *iso*-butanol.[92] In addition it was the springboard for a one-pot synthesis in solution of $[H_4Os_{10}(CO)_{24}]^{2-}$ and therefore of $[H_5Os_{10}(CO)_{24}]^-$.[41b,91] In fact $[H_4Os_{10}(CO)_{24}]^{2-}$ has been prepared in 79−81% yields by bubbling H_2 at 160 °C in an ethylene glycol solution of $[Os(CO)_3(OH)_2]_n$[64] or of a mixture of α-$[Os(CO)_3Cl_2]_2$ and Na_2CO_3.[41b,91] However, the latter route is not well reproducible, lower yields (ca. 50%) in $[H_4Os_{10}(CO)_{24}]^{2-}$ have been obtained in some cases due to the parallel formation of $[H_3Os_4(CO)_{12}]^-$ and $[Os_{10}C(CO)_{24}]^{2-}$.[41b] This lack of reproducibility, not yet understood, seems to be related to various factors such as acidity of commercial ethylene glycol. Therefore silica-mediated syntheses may be preferred due to the easier reproducibility of the final products and yields.

2.5.3. The Process of Nucleation of Surface Osmium(II) Carbonyl Species to Various Osmium Carbonyl Clusters

A step-by-step process which explains the origin of the good selectivities of the controlled reduction of silica physisorped α-$[Os(CO)_3Cl_2]_2$ to generate different osmium carbonyl clusters, when working in the presence of alkali carbonates, is reported in Scheme 8. First of all the addition of an alkali carbonate to silica-supported α-$[Os(CO)_3Cl_2]_2$ or $[Os(CO)_3Cl_2(HOSi\equiv)]$ generates on the surface reactive hydroxo or silanolate Os(II) carbonyl species which nature depends on the basicity given to the silica surface. With a low basicity (molar ratio Na_2CO_3:Os = 2:1), neutral surface species such as $[Os(CO)_3(OR)_2]_n$ (R = H or Si≡) are formed. An increase of the surface basicity (molar ratio Na_2CO_3 or K_2CO_3:Os = 10−20:1) leads to anionic $\{[Os(CO)_3(OR)_2]_m(OR)\}^-$ (R = H or Si≡; $m > 1$) entities up to the less reactive anion $[Os(CO)_3(OH)_3]^-$. The low reactivity of this latter species explains why very low yields of carbonyl clusters are obtained in the surface-mediated synthesis when adding a stronger base such as an alkali hydroxide instead of an alkali carbonate.[14,40]

In agreement with the above picture, the selectivity of the reduction (CO or H_2) in the presence of alkali carbonates of both chemisorped $[Os(CO)_x(OSi\equiv)_2]_n$ (x = 2 or 3)[66,94] and physisorped $[Os(CO)_3(OH)_2]_n$[64] is, under similar reaction conditions, the same as that of physisorped α-$[Os(CO)_3Cl_2]_2$ in the presence of alkali carbonates.[40,41] Unfortunately, one cannot distinguish between chemisorped $[Os(CO)_3(OSi{\equiv})_2]_n$ and physisorped $[Os(CO)_3(OH)_2]_n$ on the basis of either infrared spectra, which are very similar, or of extraction experiments. In fact, physisorped $[Os(CO)_3(OH)_2]_n$ cannot be extracted with solvents such as acetone or CH_3CN due to its polymeric nature and therefore to its low solubility. However, as preliminary results, we found that the Os−OSi bond of structurally related Os(II) silanolate carbonyl complexes is easily hydrolyzed. Therefore, any Os(II) surface silanolate species, if generated under strongly alkaline conditions, should easily hydrolyze as well, due to the presence of surface water under usual reaction conditions, to generate $[Os(CO)_3(OH)_2]_n$. Besides, with high Os loadings (15% (w/w) of Os relative to SiO_2) the formation of some $[Os(CO)_3(OH)_2]_n$ is compulsory since there would not be enough surface silanols to convert all physisorped α-$[Os(CO)_3Cl_2]_2$ into $[Os(CO)_3(OSi{\equiv})_2]_n$.

As suggested in the case of MgO (see section 3.6.2),[95] it is conceivable that the reactive silica-supported dehalogenated Os(II) carbonyl species initially formed are first converted to $[HOs(CO)_4]^-$. Cluster growth would then result from redox condensation of this anion with unreacted $[Os(CO)_3(OR)_2]_n$ (R = H and/or Si≡), by analogy with the condensation of $[Rh(CO)_4]^-$ and $[Rh(CO)_2(OAl)(HOAl)]$ to give $[Rh_6(CO)_{16}]$ on the surface of Al_2O_3 (see section 4.1).[96] The first condensation product seems to be $[HOs_3(CO)_{10}(OR)]$ (R = H and/or Si≡). The facile equilibrium between $[HOs_3(CO)_{10}(OSi{\equiv})]$ and $[HOs_3(CO)_{10}(OH)]$ on silica[97] does not allow to discriminate between them. In any case both surface species are converted, with similar selectivities, to $[Os_3(CO)_{12}]$, $[H_4Os_4(CO)_{12}]$, $[H_3Os_4(CO)_{12}]^-$, $[Os_5C(CO)_{14}]^{2-}$, or $[Os_{10}C(CO)_{24}]^{2-}$ by reduction under specific conditions,[97] thus producing an indirect evidence that either chemisorped $[HOs_3(CO)_{10}(OSi{\equiv})]$ or physisorped $[HOs_3(CO)_{10}(OH)]$ or both could act as intermediates in the silica-mediated synthesis in the presence of alkali carbonates of various Os carbonyl clusters starting from α-$[Os(CO)_3Cl_2]_2$. This hypothesis is supported by the detection of traces of both clusters during the silica-mediated syntheses of $[Os_3(CO)_{12}]$ and $[H_3Os_4(CO)_{12}]^-$ from α-$[Os(CO)_3Cl_2]_2$.[40−41a]

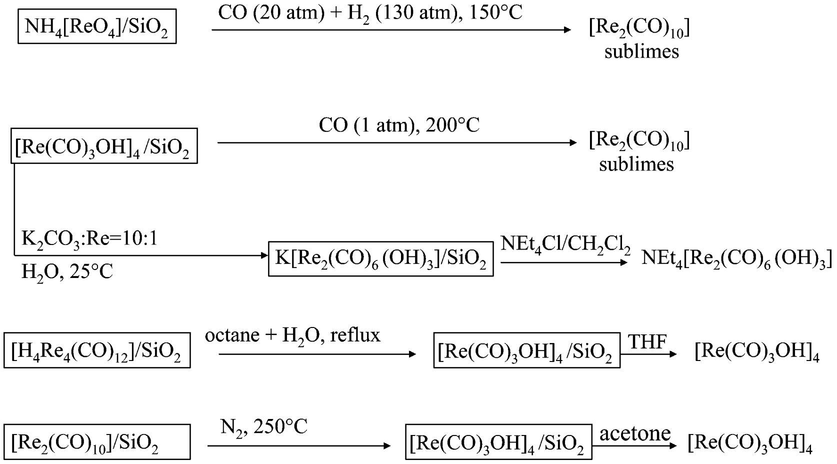
Chemisorped or physisorped $[HOs_3(CO)_{10}(OR)]$ (R = H and/or Si≡) species are converted to silica physisorped $[Os_3(CO)_{12}]$ or $[H_4Os_4(CO)_{12}]$ by working under CO or H_2, respectively, when the surface basicity is low.[97] By increasing the surface basicity, further transformation of $[Os_3(CO)_{12}]$ into $[H_3Os_4(CO)_{12}]^-$ or deprotonation of $[H_4Os_4(CO)_{12}]$ to $[H_3Os_4(CO)_{12}]^-$ or $[H_2Os_4(CO)_{12}]^{2-}$ can occur, according to the basicity and to the reaction conditions. The latter anion is favored by a strong surface basicity (molar ratio K_2CO_3:Os = 10:1) and temperatures above 200 °C; the former by a relatively mild surface basicity (molar ratio Na_2CO_3:Os = 10:1). Strangely enough, in the presence of a large amount of H_2 in the gas phase, $[H_3Os_4(CO)_{12}]^-$ does not deprotonate to $[H_2Os_4(CO)_{12}]^{2-}$, for instance, when working at 200 °C under H_2 with a high basicity of the silica surface (10:1 molar ratio K_2CO_3:Os).[14] These two anions show different reactivities which lead to two specific pathways of condensation: $[H_3Os_4(CO)_{12}]^-$ increases its nuclearity to generate $[Os_{10}C(CO)_{24}]^{2-}$ by raising the temperature under either CO or H_2, while $[H_2Os_4(CO)_{12}]^{2-}$, which is stable under CO even at high temperatures, increases its nuclearity at 200 °C to generate $[Os_5C(CO)_{14}]^{2-}$ under relatively low amounts of H_2.[14] Therefore $[H_3Os_4(CO)_{12}]^-$ can be the key intermediate in the silica-mediated syntheses of $[Os_{10}C(CO)_{24}]^{2-}$ starting from α-$[Os(CO)_3Cl_2]_2$[14,41] (Scheme 6). In agreement with this hypothesis, by working at 200 °C under H_2 in the presence of a low surface basicity (molar ratio Na_2CO_3:Os = 2:1), $[H_4Os_4(CO)_{12}]$ is the major product, but when the reduction is carried out in the presence of a higher basicity (molar ratio Na_2CO_3:Os = 10:1), deprotonation of $[H_4Os_4(CO)_{12}]$ to $[H_3Os_4(CO)_{12}]^-$ occurs, followed by its thermal condensation to $[Os_{10}C(CO)_{24}]^{2-}$. When the reductive carbonylation (1 atm CO) of silica-supported α-$[Os(CO)_3Cl_2]_2$ is carried out at 275 °C in the presence of K_2CO_3 (molar ratio K_2CO_3:Os = 10:1), both H_2 and CO_2 are produced by water gas shift reaction, as confirmed by gas chromatographic analysis. The quantity of H_2 produced is probably low enough to allow deprotonation of the intermediate $[H_3Os_4(CO)_{12}]^-$ to $[H_2Os_4(CO)_{12}]^{2-}$, favored by the high basicity, but it is high enough to favor further thermal condensation of this latter intermediate to $[Os_5C(CO)_{14}]^{2-}$.[14] In summary, the basicity of the surface of silica stabilizes the key intermediates $[H_3Os_4(CO)_{12}]^-$ and $[H_2Os_4(CO)_{12}]^{2-}$, which are characterized by different surface reactivities because their stability and further condensation to $[Os_{10}C(CO)_{24}]^{2-}$ or $[Os_5C(CO)_{14}]^{2-}$ are controlled not only by surface basicity, but also by the temperature and by the amount of H_2 in the gas phase.

2.6. Rhenium. Neutral and Anionic Complexes: $[Re_2(CO)_{10}]$, $[Re(CO)_3OH]_4$, and $[Re_2(CO)_6(\mu\text{-}OH)_3]^-$

The silica-mediated synthesis of Re carbonyl complexes has been investigated only recently[98−101] because the formation of low oxidation Re carbonyl complexes or clusters on the silica surface is quite a challenge, being Re a rather oxophilic metal (Scheme 9).

$[Re_2(CO)_{10}]$. It has been reported that reductive carbonylation of ammonium perrhenate physisorped on silica affords $[Re_2(CO)_{10}]$ in 40% yield, by working under pressure of CO (20 atm) and H_2 (130 atm) at 150 °C. The silica surface plays an important role in this reduction because, by working under similar conditions but using a solvent such as THF instead of the inorganic oxide as reaction medium, yields are much lower.[99] $[Re_2(CO)_{10}]$ can also be prepared in high yields (71%) by treatment of physisorped $[Re(CO)_3(OH)]_4$ with CO at 200 °C.[100] This reduction under relatively mild conditions is relevant because $[Re(CO)_3(OH)]_4$ was reported to be highly unreactive.[102] Surely the silica surface plays a unique role in this easy reduction of $[Re(CO)_3(OH)]_4$ to a Re(0) species because, working under similar conditions in *n*-octanol (a high boiling hydroxylated solvent which could mimic surface silanols) as reaction medium, the

Scheme 9. Best Syntheses of Various Rhenium Carbonyl Compounds on the Surface of Silica



reduction does not occur. There is evidence that this facile reduction on the silica surface proceeds via a reactive surface anchored species $[Re(CO)_5(OSi{\equiv})]$.[100] Its facile reduction with CO to $[Re_2(CO)_{10}]$, by cleavage of Re−O bonds and formation of a Re−Re bond, is noteworthy for an oxophilic metal and encouraging in further attempts to study the silica-mediated synthesis of other Re carbonyl clusters.

$[Re(CO)_3OH]_4$. $[Re(CO)_3(OH)]_4$ has been prepared in 93% yield by heating a suspension of $[H_4Re_4(CO)_{12}]$, silica (Carbosil), octane, and traces of water. Both water and the silica surface play important roles in this chemistry because water not only acts as a reagent, but its presence is necessary to prevent further oxidation of the Re carbonyl by the silanols of the silica surface.[98] $[Re(CO)_3(OH)]_4$ can also be prepared (63% yield) by treatment of silica physisorped $[Re_2(CO)_{10}]$ at 250 °C under N_2.[100] This reactivity is similar to that observed when a suspension of $[Re_2(CO)_{10}]$ in water is heated at 200 °C under N_2 in an autoclave.[103]

$[Re_2(CO)_6(\mu\text{-}OH)_3]^-$. When a slurry of SiO_2, $[Re(CO)_3OH]_4$, excess K_2CO_3, and water is stirred at room temperature and evaporated to dryness, $K[Re_2(CO)_6(\mu\text{-}OH)_3]$ is quantitatively formed.[101] However, the silica surface does not play a significant role in this conversion because it was successively observed that the same complex can be obtained quantitatively by reaction in water of $[Re(CO)_3OH]_4$ with K_2CO_3 or with $[NEt_4]OH$.[101] In any case, the investigation of this silica-mediated synthesis was a springboard for new facile syntheses in solution of $[Re_2(CO)_6(\mu\text{-}OH)_3]^-$, a complex with potential application in radioimmunotherapy and protein labeling[104] and which was usually prepared by more complex reactions.[104]

3. Synthesis on the Surface of Magnesia

Various Pt, Rh, Ir, Fe, Ru, Os, and Re anionic carbonyl clusters can be prepared working on the surface of MgO_x (where x is the temperature of the pretreatment of MgO) and removed from the surface by cation metathesis with a solution of $[(Ph_3P)_2N]Cl$ or $[Bu^t_4N]Br$ in an adequate solvent, but yields are seldom reported. In Table 2 are presented only the surface-mediated syntheses with known yields of isolated product.

3.1. Platinum. Anionic Clusters: $[Pt_6(CO)_{12}]^{2-}$, $[Pt_9(CO)_{18}]^{2-}$, $[Pt_{12}(CO)_{24}]^{2-}$, $[Pt_{15}(CO)_{30}]^{2-}$, and $[PtRh_5(CO)_{15}]^-$

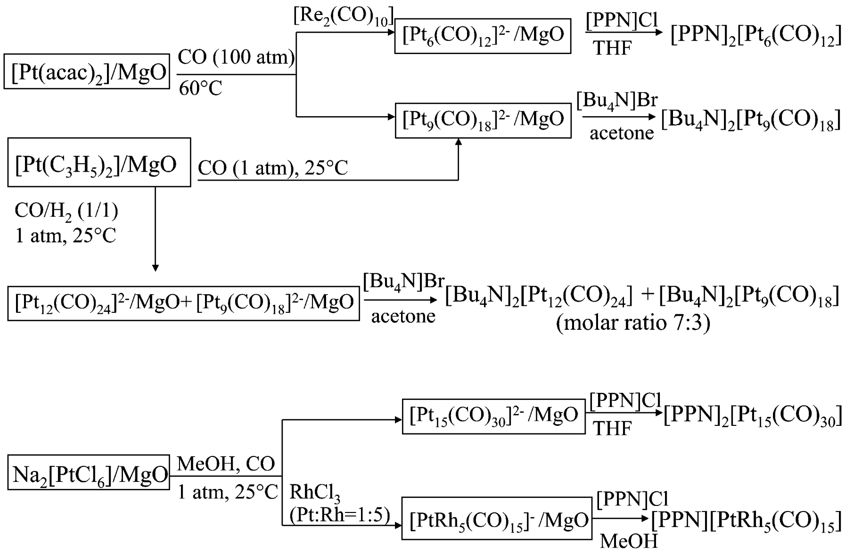
$[Pt_6(CO)_{12}]^{2-}$, $[Pt_9(CO)_{18}]^{2-}$, and $[Pt_{12}(CO)_{24}]^{2-}$. Pt clusters such as $[Pt_3(CO)_6]_n^{2-}$ are traditionally synthesized by reductive carbonylation in basic solutions of $Na_2[PtCl_6]$ (Scheme 10).[105] However, it appeared that $[Pt_6(CO)_{12}]^{2-}$ can be obtained from $[Pt(acac)_2]$ supported on MgO_{400} in the presence of $[Re_2(CO)_{10}]$, under 100 atm of CO and at 60 °C.[7] This synthesis is unusual in that it requires $[Re_2(CO)_{10}]$, because without this Re carbonyl complex, $[Pt_9(CO)_{18}]^{2-}$ is formed.[7] Alternatively, $[Pt_9(CO)_{18}]^{2-}$ is formed by treating $[Pt(C_3H_5)_2]$ supported on MgO_{450} with CO (1 atm) at room temperature.[106] By working under the latter conditions but using CO + H_2 (1:1 molar ratio, 1 atm) as the gas phase, $[Pt(C_3H_5)_2]$ is converted to a mixture of $[Pt_{12}(CO)_{24}]^{2-}$ and $[Pt_9(CO)_{18}]^{2-}$.[106] Yields of these anionic clusters have not been reported.[7,106]

$[Pt_{15}(CO)_{30}]^{2-}$ and $[PtRh_5(CO)_{15}]^-$. $[Pt_{15}(CO)_{30}]^{2-}$ is formed by stirring a slurry of $Na_2[PtCl_6]$, MgO_{400} and methanol under CO (1 atm) at room temperature. Evaporation of the solvent followed by extraction under CO with a solution of $[(Ph_3P)_2N]Cl$ in THF affords the cluster in 73% yield, as estimated by ultraviolet−visible spectroscopy of the extracted solution.[107] When the reaction is carried out in the presence of $RhCl_3{\cdot}nH_2O$ (molar ratio Pt:Rh = 1:5), $[PtRh_5(CO)_{15}]^-$ is formed and can be extracted under CO with a solution of $[(Ph_3P)_2N]Cl$ in methanol or THF.[108] The isolated yield (84%) is comparable to that obtained by working under similar conditions but in the presence of NaOH instead of MgO,[109] suggesting that the high basicity of the surface of MgO plays a role analogous to that of NaOH in solution, also because this synthesis does not occur on the less basic $\gamma\text{-}Al_2O_3$ surface.[108]

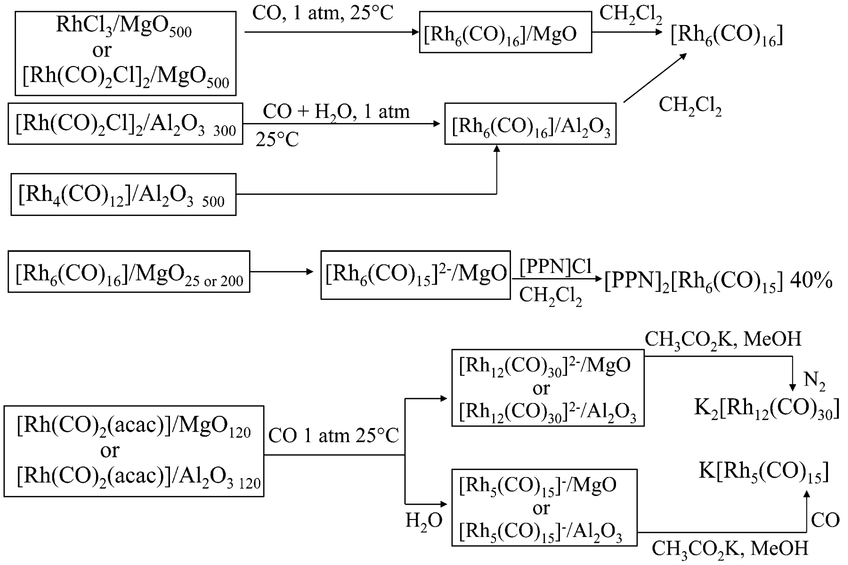
3.2. Rhodium. Neutral and Anionic Clusters: $[Rh_6(CO)_{16}]$, $[Rh_6(CO)_{15}]^{2-}$, $[Rh_{12}(CO)_{30}]^{2-}$, and $[Rh_5(CO)_{15}]^-$

$[Rh_6(CO)_{16}]$. When either $RhCl_3{\cdot}nH_2O$ or $[Rh(CO)_2Cl]_2$ supported on MgO is treated with CO (1 atm) at

Scheme 10. Best Syntheses of Various Platinum Carbonyl Compounds on the Surface of Magnesia (Pretreated at 400−450 °C)



Scheme 11. Best Syntheses of Various Rhodium Carbonyl Compounds on the Surface of Magnesia or Alumina (the Subscript Refers to the Pretreatment of MgO or Al$_2$O$_3$ in °C)

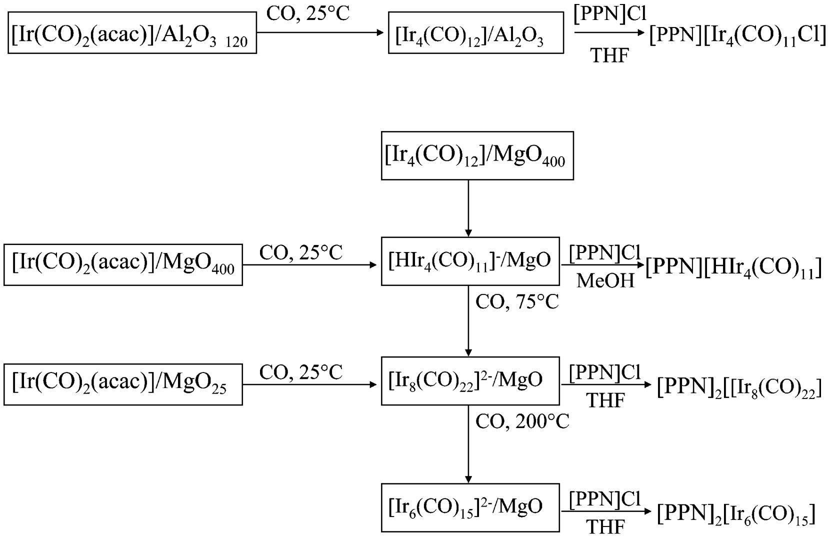


room temperature, [Rh$_6$(CO)$_{16}$] is formed and can be extracted with CH$_2$Cl$_2$ (yields not reported) (Scheme 11). The unusual stability of a neutral cluster on the highly basic MgO surface was attributed to the formation of surface chloride ions which modify the strong basic character of surface sites close to the Rh atoms through formation of acidic Mg−Cl sites.[110]

[Rh$_6$(CO)$_{15}$]^2. When a CH$_2$Cl$_2$ solution of [Rh$_6$(CO)$_{16}$] is brought into contact at 25 °C with MgO$_{25\text{or}200}$, chemisorped [Rh$_6$(CO)$_{15}$]$^{2-}$ is formed, as confirmed by extraction with a solution of [(Ph$_3$P)$_2$N]Cl in CH$_2$Cl$_2$ (ca. 40% yield, as estimated from the analysis of Rh remaining on the surface after extraction).[111] It has been suggested that [Rh$_6$(CO)$_{16}$] undergoes on the basic surface a nucleophilic attack at coordinated CO, leading to [HRh$_6$(CO)$_{15}$]$^-$, which would undergo deprotonation by the high basicity of MgO.[111] The formation of a species covalently bound to MgO such as [Rh$_6$(CO)$_{15}$(COOMg)]$^-$ as intermediate has also been proposed.[112]

[Rh$_{12}$(CO)$_{30}$]$^{2-}$ and [Rh$_5$(CO)$_{15}$]$^-$. Reductive carbonylation at 25 °C and 1 atm of CO of the surface Rh species formed from [Rh(CO)$_2$(acac)] adsorbed on MgO (proposed to be [Rh(CO)$_2${OMg}$_2$]) gives supported [Rh$_{12}$(CO)$_{30}$]$^{2-}$ or supported [Rh$_5$(CO)$_{15}$]$^-$, depending on the degree of hydroxylation of the surface.[113] [Rh$_{12}$(CO)$_{30}$]$^{2-}$ is formed when the adsorption of [Rh(CO)$_2$(acac)] is carried out in the presence of dehydrated hexane whereas [Rh$_5$(CO)$_{15}$]$^-$ is formed when hexane contains some water. Either cluster anion can be extracted with potassium acetate in methanol solution by cation metathesis. [Rh$_{12}$(CO)$_{30}$]$^{2-}$ is easily extracted under N$_2$, but [Rh$_5$(CO)$_{15}$]$^-$ has to be extracted under CO to avoid its known[29,30]-conversion in solution to [Rh$_{12}$(CO)$_{30}$]$^{2-}$. The surface-mediated synthesis was recommended as an efficient method for preparation of [Rh$_5$(CO)$_{15}$]$^-$ (isolated yield is about 47%). There is a quite clear correlation between this surface chemistry[113] and that occurring in basic solutions.[29,30]

Scheme 12. Best Syntheses of Various Iridium Carbonyl Compounds on the Surface of Magnesia or Alumina (the Subscript Refers to the Pretreatment of MgO, or Al_2O_3 in °C)



3.3. Iridium. Anionic Clusters: $[HIr_4(CO)_{11}]^-$, $[Ir_8(CO)_{22}]^{2-}$, and $[Ir_6(CO)_{15}]^{2-}$

$[HIr_4(CO)_{11}]^-$. When a slurry of $[Ir_4(CO)_{12}]$ in hexane is brought in contact with MgO_{400}, $[HIr_4(CO)_{11}]^-$ is formed (Scheme 12).[114] This cluster is also generated by reductive carbonylation (1 atm CO, room temperature) of $[Ir(CO)_2(acac)]$ adsorbed on MgO_{400}.[39] Yields are not reported.

$[Ir_8(CO)_{22}]^{2-}$ and $[Ir_6(CO)_{15}]^{2-}$. Reductive carbonylation (1 atm CO at 25 °C) of $[Ir(CO)_2(acac)]$ on hydrated MgO_{25} affords $[Ir_8(CO)_{22}]^{2-}$, which is converted to $[Ir_6(CO)_{15}]^{2-}$ by further treatment under CO at 200 °C for 2 h.[39] It was suggested that reactive surface species such as $[Ir(CO)_2(OMg)(HOMg)]$ are initially formed by chemisorption of $[Ir(CO)_2(acac)]$ on MgO.[39] Reductive carbonylation of these species gives sequentially $[HIr_4(CO)_{11}]^-$, $[Ir_8(CO)_{22}]^{2-}$, and $[Ir_6(CO)_{15}]^{2-}$, by working at an adequate temperature and in the presence of different amounts of surface hydroxo groups, as expected for different surface basicities.[39] In agreement with this latter point, on the surface of partially dehydroxylated MgO_{400}, treatment of $[HIr_4(CO)_{11}]^-$ with CO (1 atm) for 2 h gives selectively $[Ir_8(CO)_{22}]^{2-}$ and $[Ir_6(CO)_{15}]^{2-}$, working at 75 and 200 °C, respectively.[39,114] Yields have not been reported.

The organometallic chemistry of Ir carbonyl clusters on the surface of MgO clearly mimics that occurring in basic solution[37] or on the silica surface added with alkali carbonates (section 2.3.2).[32] In fact, treatment of $[Ir_4(CO)_{12}]$ in methanol under CO at room temperature with the relatively weak base K_2CO_3 gives $[HIr_4(CO)_{11}]^-$, whereas treatment with Na in tetrahydrofuran gives sequentially $[Ir_8(CO)_{22}]^{2-}$ and $[Ir_6(CO)_{15}]^{2-}$.[37] It is worth pointing out that the use as starting material of $IrCl_3 \cdot nH_2O$ (in the synthesis of $[Ir_4(CO)_{12}]$) or $[Ir(cyclooctene)_2Cl]_2$ (in the synthesis of $[Ir_8(CO)_{22}]^{2-}$ and $[Ir_6(CO)_{15}]^{2-}$) makes the silica surface-added with alkali carbonates[32] slightly more attractive than the MgO surface,[39] where the more exotic $[Ir(CO)_2(acac)]$ is the starting material and which requires more drastic conditions (200 °C instead of 100−120 °C) to generate $[Ir_6(CO)_{15}]^{2-}$.

3.4. Iron. Anionic Cluster: $[HFe_3(CO)_{11}]^-$

When a hexane solution of $[Fe_3(CO)_{12}]$ is stirred at room temperature with MgO_{25} (2.7% (w/w) of Fe relative to MgO), chemisorped $[HFe_3(CO)_{11}]^-$ is formed and can be extracted from the surface with a solution of $[Et_4N]Cl$ in dichloromethane (60% yield) (Scheme 13). The maximum amount of cluster that can be chemisorped corresponds to 2.7% Fe, further adsorption of $[Fe_3(CO)_{12}]$ onto MgO being reversible. The formation of $[HFe_3(CO)_{11}]^-$ reasonably involves a nucleophilic attack[115] at the coordinated CO as it occurs in basic solution.[116] This reaction is very fast on the MgO surface due to its particularly high basicity.[115] By working with low Fe loadings, $[Fe(CO)_5]$ is also readily converted to $[HFe_3(CO)_{11}]^-$ on the MgO surface.[115]

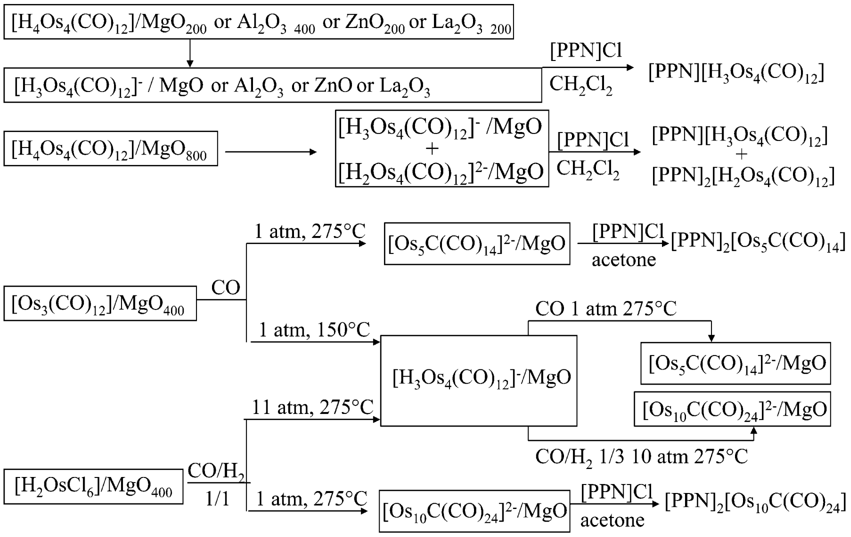
3.5. Ruthenium. Anionic Clusters: $[HRu_3(CO)_{11}]^-$, $[Ru_6(CO)_{18}]^{2-}$, $[H_3Ru_4(CO)_{12}]^-$, and $[Ru_6C(CO)_{16}]^{2-}$

$[HRu_3(CO)_{11}]^-$ and $[Ru_6(CO)_{18}]^{2-}$. The reaction between a CH_2Cl_2 solution of $[Ru_3(CO)_{12}]$ and $MgO_{25,\ 200\ \mathrm{or}\ 500}$ is instantaneous at 25 °C, affording $[HRu_3(CO)_{11}]^-$.[62] This anionic cluster is probably the result of the nucleophilic attack[62] of the basic surface of MgO at coordinated CO, a well-known reaction in solution under basic conditions.[58,61] Besides mixtures of $[HRu_3(CO)_{11}]^-$ and $[Ru_6(CO)_{18}]^{2-}$ are formed by adsorption of $[Ru_3(CO)_{12}]$ on MgO_{200},[56] a reactivity consistent with the growth of anionic ruthenium clusters in very basic solution.[58,61]

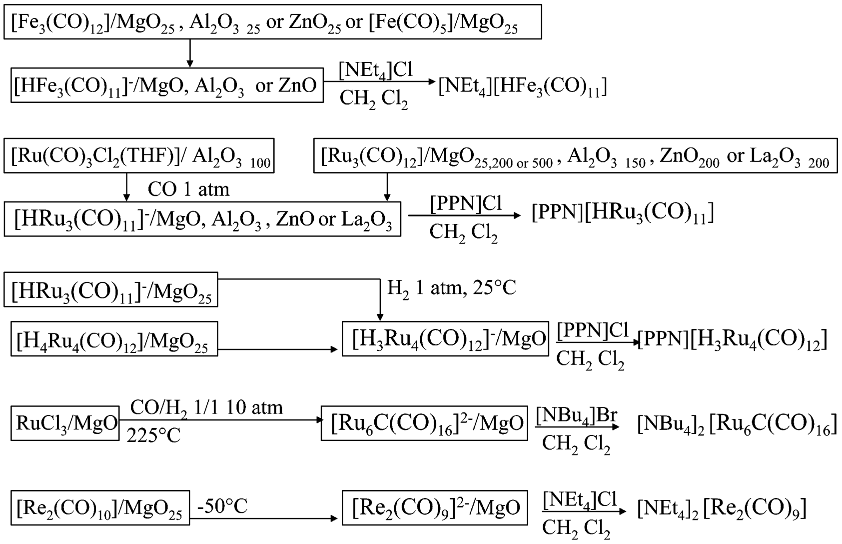
$[H_3Ru_4(CO)_{12}]^-$. $[Ru_3(CO)_{12}]$ impregnated on hydroxylated MgO from a CH_2Cl_2 solution is converted to $[HRu_3(CO)_{11}]^-$, which further reacts, in the presence of H_2 at room temperature, to give $[H_3Ru_4(CO)_{12}]^-$.[59] This latter cluster is also obtained by deprotonation of $[H_4Ru_4(CO)_{12}]$ on hydroxylated MgO.[56,59,117]

$[Ru_6C(CO)_{16}]^{2-}$. Exposure to CO + H_2 (molar ratio 1:1, 10 atm) of $RuCl_3 \cdot nH_2O$ adsorbed on MgO, at 225 °C for 24 h, affords $[Ru_6C(CO)_{16}]^{2-}$.[118]

Scheme 13. Best Syntheses of Various Iron, Ruthenium, and Rhenium Carbonyl Compounds on the Surface of Magnesia, Alumina, Zinc or Lanthanum Oxides (the Subscript Refers to the Pretreatment of MgO, Al_2O_3, ZnO, or La_2O_3, in °C)



Scheme 14. Best Syntheses of Various Osmium Carbonyl Compounds on the Surface of Magnesia, Alumina, Zinc or Lanthanum Oxides (the Subscript Refers to the Pretreatment of MgO, Al_2O_3, ZnO, or La_2O_3, in °C)



3.6. Osmium

3.6.1. Anionic Clusters: $[H_3Os_4(CO)_{12}]^-$, $[H_2Os_4(CO)_{12}]^{2-}$, $[Os_{10}C(CO)_{24}]^{2-}$, and $[Os_5C(CO)_{14}]^{2-}$

$[H_3Os_4(CO)_{12}]^-$ and $[H_2Os_4(CO)_{12}]^{2-}$. $[H_3Os_4(CO)_{12}]^-$ is formed by adding MgO_{200} to a solution of $[H_4Os_4(CO)_{12}]$ in CH_2Cl_2[119] whereas by working with highly dehydroxylated MgO_{800} a mixture of $[H_3Os_4(CO)_{12}]^-$ and $[H_2Os_4(CO)_{12}]^{2-}$ is obtained in agreement with the stronger surface basicity (Scheme 14).[13,120] Besides, adsorption of $[Os_3(CO)_{12}]$ on MgO_{400} followed by heating at 150 °C under CO (1 atm) gives $[H_3Os_4(CO)_{12}]^-$ along with a small amount of $[Os_5C(CO)_{14}]^{2-}$.[95] Finally, treatment of H_2OsCl_6 adsorbed on MgO_{400} with flowing CO + H_2 (equimolar) at 275 °C and under 11 atm affords $[H_3Os_4(CO)_{12}]^-$.[7,95]

$[Os_{10}C(CO)_{24}]^{2-}$ and $[Os_5C(CO)_{14}]^{2-}$. By working at atmospheric pressure and at 275 °C on MgO_{400}, H_2OsCl_6 is easily converted to $[Os_{10}C(CO)_{24}]^{2-}$ under CO + H_2 (equimolar)[95,118], whereas $[Os_3(CO)_{12}]$ affords $[Os_5C(CO)_{14}]^{2-}$ under CO.[7,95,121] Both anionic clusters can be isolated by extraction with $[(Ph_3P)_2N]Cl$ dissolved in acetone but in 65% yield only because they are partially retained by the surface of MgO.[7,95,118,121]

3.6.2. The Understanding of the Process of Nucleation of Surface Osmium(II) Carbonyl Species to Osmium Carbonyl Clusters on the Surface of Magnesia

The process of nucleation to high nuclearity anionic osmium carbonyl clusters can be indirectly inferred from the same process on the surface of silica added with alkali carbonates (section 2.5.3). The first step of the reductive carbonylation (1 atm CO or CO + H_2) of H_2OsCl_6 supported on MgO, carried out at 200−250 °C, produces probably Os(II) subcarbonyl species such as $[Os(CO)_x\{OMg\}_2]$ ($x = 2$ or 3) which are quite stable under CO or CO + H_2 and are reduced to give anionic clusters only at temperatures approaching 275 °C. The reduction of the Os(II) subcarbonyl species and the initiation of cluster growth are coincident with the loss of physisorbed water from the MgO surface, which becomes significant above 250 °C. Therefore, it was suggested that the reduction of Os(II) subcarbonyl species on MgO in the presence of CO alone is initiated by nucleophilic attack of strongly basic surface hydroxyl groups to generate by reductive carbonylation the reactive species $[HOs(CO)_4]^-$. This latter anion could also be obtained by reduction of $[Os(CO)_3\{OMg\}_2]$ at 275 °C working with a mixture of CO + H_2.The cluster growth to high nuclearity initially occurs via attack of the nucleophile $[HOs(CO)_4]^-$ species on the Os(II) subcarbonyl surface species to generate first $[H_3Os_4(CO)_{12}]^-$ as reactive intermediate species.[95]

As above-mentioned (section 2.5.3), working on a silica surface treated with excess alkali carbonates, there is evidence that cluster growth of $[H_3Os_4(CO)_{12}]^-$ or $[H_2Os_4(CO)_{12}]^{2-}$ leads then to the formation of $[Os_{10}C(CO)_{24}]^{2-}$ and $[Os_5C(CO)_{14}]^{2-}$, respectively. The control of the selectivity of the nucleation is related to (i) a relatively mild basicity and the presence of large amounts of H_2 which favor the formation of $[H_3Os_4(CO)_{12}]^-$ and then of $[Os_{10}C(CO)_{24}]^{2-}$ and (ii) the fact that $[H_2Os_4(CO)_{12}]^{2-}$, generated with a high surface basicity, is stable under CO and gives selectively $[Os_5C(CO)_{14}]^{2-}$ only in the presence of small amounts of H_2.[14] This body of observations can be of some help in order to interpret the reported cluster growth of Os carbonyl species on the surface of MgO.[95] In fact, as expected for this strongly basic surface, at 275 °C $[H_3Os_4(CO)_{12}]^-$ is easily converted to $[Os_5C(CO)_{14}]^{2-}$ under CO (1 atm), whereas a very slow condensation to $[Os_{10}C(CO)_{24}]^{2-}$ occurs under a mixture of CO and H_2 (1:3 molar ratio, 10 atm) (Scheme 14).[95] The facile condensation to $[Os_5C(CO)_{14}]^{2-}$ could be due to the positive role of small amounts of H_2, produced by the water−gas shift reaction catalyzed by the osmium anionic carbonyl clusters,[122] on the deprotonated species $[H_2Os_4(CO)_{12}]^{2-}$ generated in situ by the very basic surface of MgO. As expected, under an excess of H_2 (for example with 10 atm of a mixture of CO and H_2, 1:3 molar ratio), $[H_3Os_4(CO)_{12}]^-$ is stabilized; therefore, it is slowly thermally converted into $[Os_{10}C(CO)_{24}]^{2-}$ but not into $[Os_5C(CO)_{14}]^{2-}$. Under these latter reaction conditions, the amount of H_2 in the gas phase is too high to allow conversion of $[H_3Os_4(CO)_{12}]^-$ to $[H_2Os_4(CO)_{12}]^{2-}$.

3.7. Rhenium. Anionic Clusters: $[H_2Re_3(CO)_{12}]^-$ and $[Re_2(CO)_9]^{2-}$

$[H_3Re_3(CO)_{12}]$ is readily deprotonated on MgO_{700} to give $[H_2Re_3(CO)_{12}]^-$.[123] In addition, when a slurry of $[Re_2(CO)_{10}]$, hexane, and hydroxylated MgO is stirred at temperatures exceeding about −50 °C, $[Re_2(CO)_9]^{2-}$ is formed.[124] In this surface-mediated synthesis, it is crucial to use an hydroxylated MgO surface because as the degree of surface dehydroxylation increases, the formation of this anion is reduced and the principal adsorbate is $[Re_2(CO)_{10}]$.[124] By comparison with the related solution chemistry,[125] the chemisorption on MgO is inferred to involve nucleophilic attack of surface OH groups on $[Re_2(CO)_{10}]$ to give first $[HRe_2(CO)_9]^-$, which is then deprotonated by the very basic surface to give $[Re_2(CO)_9]^{2-}$.[124] This selective second step occurring on the surface of hydroxylated MgO is of some interest because, in a contrasting manner, in strongly basic solution there is further nucleophilic attack of OH^- on another CO ligand of $[HRe_2(CO)_9]^-$ to give $[H_2Re_2(CO)_8]^{2-}$.[125] The synthesis in solution of $[Re_2(CO)_9]^{2-}$ involves reaction of $[Re_2(CO)_{10}]$ with the exotic base K(*sec*-$C_4H_9)_3BH$ in tetrahydrofuran at 25 °C.[126]

4. Synthesis on the Surface of Alumina

4.1. Rhodium. Neutral and Anionic Clusters: $[Rh_6(CO)_{16}]$, $[Rh_{12}(CO)_{30}]^{2-}$, and $[Rh_5(CO)_{15}]^-$

$[Rh_6(CO)_{16}]$. $[Rh_6(CO)_{16}]$ is obtained by adsorption of $[Rh(CO)_2Cl]_2$ in $CHCl_3$ solution on the surface of γ- or η-Al_2O_3, followed by treatment at room temperature with 1 atm of a mixture of CO + H_2O.[22a,96,127] The neutral cluster can be easily extracted with CH_2Cl_2[96] or $CHCl_3$,[127] but yields have not been reported. Cluster growth could result from condensation of $[Rh(CO)_4]^-$, generated in situ, on chemisorped $[Rh(CO)_2(OAl)(HOAl)]$.[96] The same cluster is also generated by simple adsorption of $[Rh_4(CO)_{12}]$ in hexane solution on γ- or η-Al_2O_3.[22b,127] Although yields have not been reported, the reaction seems to be quantitative, and in addition the selectivity and the very mild conditions evidence a high surface mobility of rhodium carbonyl species on the surface of Al_2O_3.[22,96,127]

$[Rh_{12}(CO)_{30}]^{2-}$ and $[Rh_5(CO)_{15}]^-$. Like on MgO (see section 3.2.3), reductive carbonylation at 25 °C and 1 atm of CO of chemisorped $[Rh(CO)_2\{OAl\}_2]$, generated by adsorption of $[Rh(CO)_2(acac)]$ on γ−Al_2O_3, gives $[Rh_{12}(CO)_{30}]^{2-}$ or $[Rh_5(CO)_{15}]^-$ depending on the degree of hydroxylation of the surface. $[Rh_{12}(CO)_{30}]^{2-}$ is formed when the adsorption of $[Rh(CO)_2(acac)]$ is carried out in the presence of dehydrated hexane whereas $[Rh_5(CO)_{15}]^-$ is formed when the hexane contains some water.[113] Both clusters can be extracted with potassium acetate in methanol solution by cation metathesis but yields were not reported; $[Rh_{12}(CO)_{30}]^{2-}$ is extracted under N_2, but $[Rh_5(CO)_{15}]^-$ has to be extracted under CO to avoid its conversion to $[Rh_{12}(CO)_{30}]^{2-}$.[29−30]

4.2. Iridium. Anionic Cluster: $[Ir_4(CO)_{11}Cl]^-$

Reductive carbonylation, under 1 atm of CO at room temperature, of $[Ir(CO)_2(acac)]$ chemisorped on γ-Al_2O_3 affords strongly physisorbed $[Ir_4(CO)_{12}]$, which cannot be extracted with tetrahydrofuran; however, treatment with a tetrahydrofuran solution of $[(Ph_3P)_2N]Cl$ generates $[(Ph_3P)_2N][Ir_4(CO)_{11}Cl]$, which is easily extracted. The cluster's yield was not determined.[128]

4.3. Iron. Anionic Cluster: $[HFe_3(CO)_{11}]^-$

When a hexane solution of $[Fe_3(CO)_{12}]$ is stirred at room temperature with Al_2O_3 (η or γ), chemisorped $[HFe_3(CO)_{11}]^-$ is formed. The maximum quantity of cluster that can be chemisorped onto Al_2O_3 varies with the nature of the alumina used. For example, with γ-Al_2O_3 (100 m^2g^{-1} surface area) and η-Al_2O_3 (315 m^2g^{-1} surface area), the maximum amounts correspond to 2.0% and 2.5% Fe, respectively; further adsorption of $[Fe_3(CO)_{12}]$ leads to reversible physisorption of this cluster. When only chemisorption takes place, extraction with a solution of $[Et_4N]Cl$ in CH_2Cl_2 affords $[HFe_3(CO)_{11}]^-$ in 70% yield. Similarly, $[Fe(CO)_5]$ is converted to $[HFe_3(CO)_{11}]^-$ on Al_2O_3, but the yield was not determined. The formation of $[HFe_3(CO)_{11}]^-$ is much slower on Al_2O_3 than on the more basic surface of MgO (see section 3.4),[115] in agreement with the role of the surface basicity in the reduction process.

4.4. Ruthenium. Anionic Cluster: $[HRu_3(CO)_{11}]^-$

$[Ru(CO)_3Cl_2(THF)]$ is adsorbed on γ-Al_2O_3, from a tetrahydrofuran solution at room temperature, affording surface species such as $[Ru(CO)_3(HOAl)(OAl)_2]$ (HOAl and OAl represent surface hydroxyl and oxy groups, respectively). These surface carbonyl species react rapidly with CO (1 atm) to give $[HRu_3(CO)_{11}]^-$, which can be easily extracted from the surface as its $(Ph_3P)_2N^+$ salt in CH_2Cl_2 but the yield was not determined.[129] This anionic cluster is also formed by stirring a hexane solution of $[Ru_3(CO)_{12}]$ with amorphous Al_2O_3.[63]

4.5. Osmium. Anionic Cluster: $[H_3Os_4(CO)_{12}]^-$

When $[H_4Os_4(CO)_{12}]$ is adsorbed from refluxing its hexane suspension onto γ-Al_2O_3 pretreated at 400 °C, $[H_3Os_4(CO)_{12}]^-$ is formed and can be extracted from the surface by ion metathesis with $[(Ph_3P)_2N]Cl$ dissolved in CH_2Cl_2, but the yield was not determined.[13,130]

5. Synthesis on the Surface of Zinc Oxide and Lanthanum Oxide

5.1. Iron and Ruthenium. Anionic Clusters: $[HM_3(CO)_{11}]^-$

The behavior of ZnO[62,115] and La_2O_3[62] surfaces toward $[Ru_3(CO)_{12}]$[62] and $[Fe_3(CO)_{12}]$[115] is very similar to that of the surface of MgO or Al_2O_3 (sections 3.4, 3.5 and 4.3). The rather basic surface OH groups behave as good nucleophiles toward coordinated CO generating the anion $[HM_3(CO)_{11}]^-$ (M = Fe, Ru), which can be extracted from the surface with $[(Ph_3P)_2N]Cl$ dissolved in CH_2Cl_2. However, yields of isolated products were not reported.

5.2. Osmium. Anionic Cluster: $[H_3Os_4(CO)_{12}]^-$

When a solution of $[H_4Os_4(CO)_{12}]$ in CH_2Cl_2 is stirred with ZnO or La_2O_3, deprotonation occurs such as on MgO (section 3.6.1). Extraction with $[(Ph_3P)_2N]Cl$ dissolved in CH_2Cl_2 produces excellent yields (the exact yield is not reported) of $[H_3Os_4(CO)_{12}]^-$.[119]

6. Synthesis in the Cages of Zeolites

Only a brief mention is made of the reported examples of syntheses of metal carbonyl clusters in the cages of zeolites with a limited porosity because this chemistry, although significant in the field of heterogenized homogeneous catalysis, is useless for synthetic purposes since the resultant clusters remain trapped in the cages (ship-in-a-bottle synthesis) and cannot be extracted and isolated.[7,43,122,131−140]

6.1. Palladium and Platinum. Neutral and Anionic Clusters: $Pd_{13}(CO)_x$ and $[Pt_3(CO)_6]_n^{2-}$ (n = 3–5)

6.1.1. $Pd_{13}(CO)_x$

It has been suggested, but on the basis of IR spectroscopy only, that neutral $[Pd_{13}(CO)_x]$ clusters are formed when $[Pd(NH_3)_4]^{2+}$-exchanged NaY zeolite is calcined (O_2, 500 °C), reduced (H_2, 200 °C), and then treated with 1 atm of CO at room temperature.[131]

6.1.2. $[Pt_3(CO)_6]_n^{2-}$

The formation of anionic platinum clusters in basic zeolites has been reported.[132] For example, treatment under CO at 100 °C of $[Pt(NH_3)_4]^{2+}$-exchanged NaY zeolite (Si/Al molar ratio = 5.6) affords $[Pt_9(CO)_{18}]^{2-}$, as suggested by IR spectroscopy and EXAFS.[132b] When the $[Pt(NH_3)_4]^{2+}$-exchanged NaY zeolite is calcined (O_2, 300 °C, 2h) prior to reductive carbonylation, $[Pt_{12}(CO)_{24}]^{2-}$ is formed, whereas under similar conditions but using a more basic zeolite NaX (Si/Al molar ratio = 2.3), $[Pt_{15}(CO)_{30}]^{2-}$ is generated, showing that the size of the platinum cluster dianions is related to the interior basicity of the zeolite cages.[132b]

6.2. Rhodium. Neutral and Anionic Clusters: $[Rh_6(CO)_{16}]$, $[Rh_6(CO)_{15}]^{2-}$ and $[PtRh_5(CO)_{15}]^-$

6.2.1. $[Rh_6(CO)_{16}]$

When $[Rh(NH_3)_6]^{3+}$-exchanged NaY zeolite is heated at 120−130 °C under 80 atm of CO + H_2 (molar ratio 1:1)[133a] or under 2 atm of CO in the presence of water[133b], $[Rh_6(CO)_{16}]$ is generated. The same cluster is formed by treatment of $[Rh(NH_3)_5Cl]^{2+}$ or $[Rh(H_2O)_6]^{3+}$-exchanged NaY zeolite with 1 atm of CO and water or with 1 atm of CO + H_2 at 70−120 °C.[133c−133d] Similarly, when $[Rh(CO)_2Cl]_2$ is introduced in the cages of NaY or even acidic HY zeolites and treated at room temperature with 1 atm of CO in the presence of water, $[Rh_6(CO)_{16}]$ is formed, like on the surface of Al_2O_3.[96]

6.2.2. $[Rh_6(CO)_{15}]^{2-}$ and $[PtRh_5(CO)_{15}]^-$

When $[Rh(NH_3)_5Cl]^{2+}$-exchanged NaX zeolite (a quite basic zeolite having an Si/Al molar ratio of ca. 1.5) is heated at 75 °C under 1 atm of CO in the presence of water, $[Rh_6(CO)_{15}]^{2-}$ is formed, as evidenced by IR spectroscopy.[133d] Under similar conditions but using an exchanged mixture of $[Rh(NH_3)_5Cl]^{2+}$ and $[Pt(NH_3)_4]^{2+}$ (molar ratio 1:5), the bimetallic anionic species $[PtRh_5(CO)_{15}]^-$ is generated.[133e]

6.3. Iridium. Neutral and Anionic Complex and Clusters: $[Ir(CO)_3Cl]$, $[Ir_4(CO)_{12}]$, $[Ir_6(CO)_{16}]$, $[HIr_4(CO)_{11}]^-$, and $[Ir_6(CO)_{15}]^{2-}$

Neutral iridium carbonyl compounds are generated in the less basic NaY cages, whereas anionic clusters are formed in the more basic NaX cages.[43,134−138]

6.3.1. $[Ir(CO)_3Cl]$

$[Ir(NH_3)_5Cl]^{2+}$-exchanged NaY zeolite upon thermal decomposition (O_2, 250 °C) is converted into a species proposed to be "$Ir(OH)_2Cl$", which may undergo reductive carbonylation (1 atm of CO, 170 °C) to generate, inside the zeolite cage, $[Ir(CO)_3Cl]$.[134]

6.3.2. $[Ir_4(CO)_{12}]$, $[Ir_6(CO)_{16}]$, $[HIr_4(CO)_{11}]^-$, and $[Ir_6(CO)_{15}]^{2-}$

Some mononuclear iridium(I) carbonyl species can thermally migrate through the porous network of zeolites and can be further reduced under 1 atm of CO to give $[Ir_4(CO)_{12}]$ [135,136] or $[Ir_6(CO)_{16}]$ [137,138]-entrapped in the zeolite cages. For example, $[Ir(CO)_2(acac)]$ deposited in the pores of NaY zeolite (Si/Al molar ratio about 4.74) is converted into $[Ir_4(CO)_{12}]$ by working under 1 atm of CO at 40 °C;[136] under 1 atm of CO at 125 °C, it is converted into $[Ir_6(CO)_{16}]$.[138]

When a more basic zeolite, NaX, having an Si/Al molar ratio of about 2.5, is used instead of NaY, $[Ir(CO)_2(acac)]$ is converted into $[HIr_4(CO)_{11}]^-$, entrapped in the zeolite cage, by working under 1 atm of CO at 70 °C. Further treatment under CO at 175 °C gives $[Ir_6(CO)_{15}]^{2-}$.[43] This chemistry parallels the chemistry of the synthesis of these anions in basic solution,[37] on the silica surface added with alkali carbonates[32] (see section 2.3.2) or on the magnesia surface[39] (see section 3.3). However, the intermediate formation of $[Ir_8(CO)_{22}]^{2-}$ has never been observed in the zeolite cages perhaps because this cluster is too large to fit.[43]

6.4. Iron. Anionic Clusters: $[HFe_3(CO)_{11}]^-$ and $[Fe_2Rh_4(CO)_{16}]^{2-}$

$[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$ deposited in the pores of the hydrated NaY zeolite yield $[HFe_3(CO)_{11}]^-$, but this anion is not formed using a dehydrated NaY zeolite, as expected if the role of water or zeolite hydroxyl group is that of the nucleophile necessary for reduction.[139] Further reaction of $[HFe_3(CO)_{11}]^-$, generated inside the zeolite cages, with $[Rh_4(CO)_{12}]$ at 70 °C affords $[Fe_2Rh_4(CO)_{16}]^{2-}$, characterized by EXAFS and FTIR spectroscopy.[140]

6.5. Osmium. Anionic Cluster: $[H_3Os_4(CO)_{12}]^-$

$[Os_3(CO)_{12}]$, supported on an acidic zeolite, reacts at high temperature (180 °C) with the hydroxylic groups of the support to give an anchored species supposed to be $[HOs_3(CO)_{10}OAl{=}]$. A suspension of the latter in diglyme or ethoxyethanol in the presence of a base (aliphatic amines or NaOH) and an excess of water reacts under 1 atm of CO at 130 °C to give the anion $[H_3Os_4(CO)_{12}]^-$ trapped in the zeolite framework.[122]

7. Conclusion

The rationalization of the methods of synthesis of high nuclearity metal carbonyl clusters was initiated in the 1960 by Chini[141] and Lewis and Johnson.[89−92,142] Growth of nuclearity was achieved by nucleophilic attack of metal carbonyl species[141] or by thermal condensation,[89−92,142] so that the synthesis and structural characterization of many metal carbonyl clusters was reported. Roughly during the same period, the investigation of the behavior of carbonyl clusters supported on inorganic oxides, carried out by Basset, Ugo, and Psaro[143] and Gates and Knözinger,[13] as prototypes of highly dispersed supported metal catalysts or as precursors of them uniquely suited to making them well defined structurally, was the origin of the so-called surface organometallic chemistry. The understanding that surface metal carbonyl fragments, covalently linked to the surface or weakly chemisorped or physisorped, can be highly mobile was the springboard, particularly in the group of Ugo and Roberto and in that of Gates, of the idea of considering the surface of an inorganic oxide as a reaction medium for organometallic reactions.

From the increasing knowledge of the surface organometallic chemistry of mononuclear metal carbonyl compounds supported on inorganic oxides, it was clear that these species easily move on the surface and can react with the surface itself, where they can loose CO and can aggregate under reductive conditions to generate selectively clusters. In parallel, supported carbonyl clusters under more drastic conditions or by oxidation can disaggregate to regenerate monomeric metal carbonyl fragments, usually covalently bound to the surface.[143] Because surface reactions take place under mild conditions, in particular often at atmospheric pressure, it was obvious to investigate the potentiality of the surface of inorganic oxides as reaction medium for the synthesis from metal salts of metal carbonyl complexes and clusters which often require for their synthesis drastic temperatures or very high pressures. This approach has allowed, as shown in this review, the synthesis of many metal carbonyl complexes and clusters working at atmospheric pressure with selectivities and yields often never achieved before when working in solution.

Although the high selectivity of reactions carried out on the surface of inorganic oxides can be predicted from the known surface organometallic chemistry of metal carbonyl species, the synthetic value of this new approach, in terms of yields and amount of reaction product for 1 g of support, was unexpected. Reactions carried out on the surface of inorganic oxides allow high-yield and selective syntheses of various metal carbonyl complexes and clusters, starting from easily available materials and at atmospheric pressure, often also at relatively low temperatures. The synthetic procedures are simple and straightforward and the recovery of products is easy. Since the use of a solid as reaction medium is not limited as in solution by boiling points and by the thermal instability of some solvents, it is possible to work at atmospheric pressure even at rather high temperatures. Therefore, in many cases, yields and pressure are better and lower, respectively, than those of the syntheses in solution.

As a general trend, neutral compounds are prepared on the surface of silica or in the cages of neutral or acidic zeolites whereas the formation of anionic clusters requires an adequate basicity such as that of the surface of MgO, Al_2O_3, ZnO, La_2O_3 oxide or of silica treated with alkali carbonates. The basicity can be controlled by the nature and amount of alkali carbonate added to the silica surface or by the ratio

Si/Al of neutralized zeolites. Even the high basicity of the MgO surface can be modulated by controlling its carbonatation, the amount of water or of hydroxyl surface groups and by introducing specific Mg−Cl sites on the surface. This easy modulation of the nature of the surface has allowed an excellent definition of the reaction conditions necessary to control the selectivity of a synthesis, in particular of anionic clusters.

Remarkably, the potentiality of easily carrying out reactions at temperatures above 200−250 °C not only has allowed the high-yield synthesis of high nuclearity clusters usually obtained in low yields and with low selectivity but also opens the investigation of the synthesis of new high nuclearity metal carbonyl clusters, for instance, with Rh and Ir, whose cluster chemistry has been investigated, but never working at such high temperatures. For instance, we have isolated, working on silica treated with K_2CO_3 at 150−200 °C, new and unknown high nuclearity anionic carbonyl clusters of Rh and Ir, evidencing that the investigation of selective high-temperature syntheses of high nuclearity clusters can be renewed via the surface-mediated synthetic methodology.

It is worth pointing out that when surface-mediated syntheses are carried out in the absence of solvent, reactions must occur on the surface of the inorganic oxide. However, when surface-mediated syntheses are carried out in the presence of a solvent, the reactions leading to the product can really occur in solution, influenced by the surface. For example, in the synthesis of $[Pt_{15}(CO)_{30}]^{2-}$ by using MgO and methanol as reaction medium, the surface of MgO behaves only as a solid base, working as a slurry.

The understanding of the chemistry involved in the syntheses mediated by the surface of silica has shown that in a few cases, like the conversion of $[Ir_6(CO)_{16}]$ in $[Ir_4(CO)_{12}]$, silica serves as a dispersion medium only and the same reaction can be carried out in an inert solvent of adequate boiling point like dichloroethane. However, in most surface syntheses, the particularly mild reaction conditions are due to activation of some metal carbonyl fragments by reactive surface groups such as silanols, as in the case of reactive intermediates such as $[HOs_3(CO)_{10}\text{-}OSi{\equiv}]$ and $[Re(CO)_5OSi{\equiv}]$. In some cases, by a spring of inspiration derived from the possible role of the silanol groups of the silica surface, a high boiling point solvent with OH groups, which mimic surface silanols, was used as a convenient reaction medium for the high-yield and selective synthesis in solution of various carbonyl clusters starting from simple metal salts.[55] For instance, by using ethylene glycol, the synthesis of many carbonyl clusters from $MCl_3\cdot nH_2O$ (M = Ru, Os), although very delicate when a controlled low basicity is necessary, was achieved at atmospheric pressure and with yields and selectivities very seldom obtained in the previous reported syntheses in solution.[55a,55b] These new syntheses in solution are sometimes faster, and therefore more convenient, than the parent surface-mediated syntheses 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 such as $[Ru_3(CO)_{10}Cl_2]$. Besides, because treatment of glycols with bases at high temperatures (ca. 200 °C) leads to degradation with exothermic reactions proceeding rapidly and uncontrollably, glycols cannot be used as a safe reaction medium for the syntheses of high nuclearity carbonyl cluster anions which require high temperatures and strong basic conditions. Obviously this inconvenience does not exist with a basic 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 $[Os_5C(CO)_{14}]^{2-}$ from $[Os(CO)_3Cl_2]_2$, the role of the silica surface treated with alkali carbonates as a convenient reaction medium is unique and compulsory.[55a,55b] In addition, the selectivity of reactions carried out on surfaces such as silica treated with alkali carbonates can be more easily controlled than when working in solution as in the case of $[H_5Os_{10}(CO)_{24}]^-$.[93]

In conclusion, surface mediated syntheses of metal carbonyl compounds, in particular using the silica surface, is now a well-established useful synthetic methodology, characterized by mild pressure conditions, possibility of working at rather high temperatures, excellent yields and selectivities, convenient starting materials as metal salts, easy and straightforward synthetic procedure in a closed vessel, and easy recovery of products by selective extraction processes. Also, when working at high metal loadings, excellent amounts of products can be obtained using a few grams of inorganic support, which in the case of silica can be recycled after workup and completion of the reaction. This is a new and still open area of research: inorganic oxides such as Al_2O_3, ZnO, or La_2O_3 have been poorly studied; the work with MgO as reaction medium is excellent but often qualitative; the extension of the methodology for the synthesis from metal salts or from metal oxides of metal carbonyl compounds of non noble metals such as Fe, Ni and Co or of oxophilic metals, e.g., Re, is still poorly studied; the surface-mediated synthesis of bimetallic carbonyl clusters is limited to few examples; the use of new zeolites with very large pores opens also the use of these materials as unusual and very flexible reaction medium for synthetic purposes; the surface-mediated synthesis of metal compounds without carbonyl ligands just started with the silica-mediated synthesis of $[RhH_2(PMe_3)_4]^+$ by treatment of bis(allyl)rhodium with PMe_3 followed by H_2.[144]

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