

Surface-Mediated Organometallic Synthesis: High-Yield Preparations of $\{\text{Ir}(\text{CO})_3\text{Cl}\}_n$, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$, $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$, $[\text{Ir}_4(\text{CO})_{12}]$, and $[\text{Rh}_6(\text{CO})_{16}]$ by Reductive Carbonylation, under Mild Conditions, of Silica-Supported Metal Chlorides

Dominique Roberto,*† Rinaldo Psaro,‡ and Renato Ugo†

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

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$\{\text{Ir}(\text{CO})_3\text{Cl}\}_n$, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$, and $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$ have been synthesized in high yield from the corresponding metal trichloride supported on a silica surface by reductive carbonylation at atmospheric pressure. With $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$, the synthesis can be directed to give selectively $[\text{Ir}_4(\text{CO})_{12}]$ by working at 70 °C in the presence of CO and H_2O . $[\text{Rh}_6(\text{CO})_{16}]$ has also been prepared by reductive carbonylation at room temperature of silica-supported $[\text{Rh}(\text{CO})_2\text{Cl}]_2$. These surface-mediated synthetic methods give yields comparable or often higher than those of the traditional solution syntheses.

Introduction

In recent years there has been considerable interest in the use of the surfaces of inorganic oxides as a new reaction medium for the preparation of various organometallic complexes.^{1,2} The first surface-mediated organometallic synthesis was reported by Fischer et al. 30 years ago; they observed that $\text{MCl}_3 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Ir}, \text{Rh}^4$) adsorbed on silica gel yielded, respectively, $\{\text{Ir}(\text{CO})_3\text{Cl}\}_n$ and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, after successive thermal treatments with a stream of chlorine and then of carbon monoxide. Nevertheless, it was a long time before the potential of this innovative synthetic method was realized.

Inorganic oxide surfaces are attractive replacements for solvent environments in organometallic synthesis owing to the fact that (i) the surface properties can be chosen and controlled to provide the desired acidic, basic, or redox properties, (ii) high temperatures can be used without concern for solvent degradation, and finally, (iii) recovery of the products by solvent extraction is generally easy.^{1,2}

Strongly basic surfaces such as magnesium oxide favor the formation of anionic organometallic products while neutral complexes may be prepared on rather neutral supports such as silica. Thus, high nuclearity osmium and ruthenium carbonyl cluster anions are synthesized in high yield by reductive carbonylation of H_2OsCl_6 and RuCl_3 supported on magnesium oxide.¹ Similarly, the carbonylation of platinum salts on the same support affords $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ ($n = 3, 4$),⁵ this surface chemistry being very similar to that occurring in basic solution. The neutral hydride carbonyl clusters $[\text{H}_2\text{M}_4(\text{CO})_{12}]$ ($\text{M} = \text{Ru}, \text{Os}$) are obtained in high yield by selective hydrogenation, under mild conditions, of silica-supported $[\text{M}_3(\text{CO})_{12}]$.² These

surface aggregation processes are suggestive of a mobility of the surface reaction intermediates as high as occurs in solution.

Earlier research in surface organometallic chemistry has predicted the use of surfaces of inorganic oxides and of zeolite supercages as "solid-solvent" to promote chemical reactions (e.g., the synthesis of $[\text{Rh}_6(\text{CO})_{16}]$ from the grafted surface mononuclear species $[\text{Rh}^I(\text{CO})_2(\text{O}-\text{S})(\text{HO}-\text{S})]$ ($\text{S} = \text{Si}, \text{Al}$)⁶ and the synthesis of some metal carbonyl clusters in the zeolite supercages by means of the so-called "ship-in-bottle" technique⁷). However, in the case of ship-in-bottle synthesis the entrapped products cannot be recovered. Thus, albeit this latter technique shows unique performance in catalyst design, it is useless when applied to the field of surface-mediated organometallic synthesis.

Our recent investigations on the surface organometallic chemistry involved in the reductive carbonylation of silica-supported metal chlorides have shown that selective reactions could be afforded under rather mild conditions.^{8,9} This observation prompted us to develop, from a synthetic point of view, the reductive carbonylation of $\text{MCl}_3 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Ir}, \text{Rh}, \text{Ru}, \text{Os}$) supported on a silica surface.

Results and Discussion

Synthesis of $\{\text{Ir}(\text{CO})_3\text{Cl}\}_n$ and $[\text{Ir}_4(\text{CO})_{12}]$. In order to prepare $\{\text{Ir}(\text{CO})_3\text{Cl}\}_n$ Fischer et al.³ treated $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ supported on silica gel first with a stream of chlorine at 150 °C and then with a stream of CO at 180 °C. $\{\text{Ir}(\text{CO})_3\text{Cl}\}_n$ sublimed, being formed in 47% yield after 3 h. It was necessary to chlorinate at 150 °C the remaining silica-supported species and to carbonylate again at 180 °C to obtain more of the polymeric iridium carbonyl

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* Dipartimento di Chimica Inorganica, Metallorganica e Analitica.
† Centro CNR.

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Table I. Reductive Carbonylation at Atmospheric Pressure of Silica-Supported Metal Chlorides

MCl ₃ ·nH ₂ O	silica	M/SiO ₂ (wt %)	H ₂ O/SiO ₂ (wt %) ^a	T (°C)	t (days)	metal carbonyl chloride (yield %) ^b
IrCl ₃ ·nH ₂ O	Aerosil	2	0	120	1	24
		2	0	120	6	87
		3	10	70	4	0 ^c
		3	0	150	1	83
		5	0	150	1	76
RhCl ₃ ·nH ₂ O	Grace	3	0	150	2	9
		3	0	150	7	20 ^d
RhCl ₃ ·nH ₂ O	Aerosil	1.5	0	25	2	69
		1.5	6	25	2	82
		1.5	6	25	8	84
		5	15	25	1	80
		1.5	6	25	1	83
RuCl ₃ ·nH ₂ O	Aerosil	2	0	100	3	93
		2	0	100	1	69
		5	0	100	3	88
		10	0	100	3	60
OsCl ₃ ·nH ₂ O	Grace	2	0	100	3	84
		2	0	180	2	82
OsCl ₃	Aerosil	2	0	180	1	62
		5	0	180	2	90
OsCl ₃	Grace	5	0	180	2	83

^a This is the amount of water added to the silica-supported metal chloride. ^b Yields are of analytically pure materials. ^c 68% of [Ir₄(CO)₁₂] was extracted from silica. ^d 41% of [Ir₄(CO)₁₂] was extracted from silica.

chloride. After five cycles of chlorination/carbonylation, a 93% yield of {Ir(CO)₃Cl}_n was obtained.³

We found that such a tedious series of treatments with chlorine is not necessary when Aerosil, a nonporous silica, is used. When IrCl₃·nH₂O supported on Aerosil (3–5% by weight Ir/SiO₂) was heated at 150 °C under CO in a closed vessel, the silica powder color changed gradually from pale yellow to blue and finally to white, while brown-violet needles of {Ir(CO)₃Cl}_n sublimed on the walls of the vessel outside the oven. The reaction was complete after 24 h, affording 76–83% yields of {Ir(CO)₃Cl}_n. The silica powder was completely white and contained only some [Ir₄(CO)₁₂] (see Experimental Section; Table I). The reductive carbonylation can also be carried out at 120 °C, but in this case, the formation of {Ir(CO)₃Cl}_n is slower, 6 days being necessary to reach an 87% yield.

The reductive carbonylation can be made to proceed further by controlling the temperature and by increasing the amount of water to 10% by weight, to give selectively [Ir₄(CO)₁₂]. When IrCl₃·nH₂O supported on Aerosil was heated at 70 °C under CO and water (silica containing 10% water by weight), [Ir₄(CO)₁₂] was formed slowly on the silica surface. It could be separated easily from the support by extraction with tetrahydrofuran or dichloroethane (68% yield; Table I). If there is not enough water on silica (e.g., silica containing only 1–6% water by weight), the reaction stops before complete conversion to [Ir₄(CO)₁₂]. In addition, in order to obtain good yields of [Ir₄(CO)₁₂] it is important not only to have the right amount of water on the silica but also to work at a temperature low enough (<100 °C) to avoid sublimation of {Ir(CO)₃Cl}_n.

However, when a porous silica such as Grace SG 121 is used instead of Aerosil, reasonable yields of [Ir₄(CO)₁₂] are obtained even without adding water and working at 150 °C (Table I). Probably, in this case, sublimation of {Ir(CO)₃Cl}_n is partially inhibited by pore diffusion.

Our results show that the reductive carbonylation of silica-supported IrCl₃·nH₂O may be controlled to give

selectively {Ir(CO)₃Cl}_n or [Ir₄(CO)₁₂], subject to the reaction temperature, the amount of added water, and finally the type of silica.

As far as {Ir(CO)₃Cl}_n is concerned, our preparation is by far the best, avoiding the use of chlorine and consuming only a very low amount of CO. Our synthesis of [Ir₄(CO)₁₂] is comparable to conventional synthetic methods in solution.^{10,11}

Synthesis of [Rh(CO)₂Cl]₂, [Rh₄(CO)₁₂], and [Rh₆(CO)₁₆]. Reaction of RhCl₃·nH₂O supported on Aerosil (1.5–5% by weight Rh/SiO₂) with CO at room temperature affords [Rh(CO)₂Cl]₂ which can be easily separated from the support by extraction with dichloromethane at room temperature. Higher yields (80–84%) are obtained in the presence of water (Table I).

The dimer may be prepared in similar yield on the surface of a porous silica such as Grace SG 121 (Table I). However, in this case, it is preferable to use acetone for the extraction because the last traces of [Rh(CO)₂Cl]₂ are removed with greater difficulty from the porous silica when dichloromethane is used as solvent.

Our synthetic method is simpler than that previously reported by Fischer et al.⁴ The experimental conditions are also milder than those of the method reported by McCleverty and Wilkinson for the reductive carbonylation of solid hydrated RhCl₃.¹² In the McCleverty and Wilkinson synthesis, the water released during the reaction was bothersome. Failure to periodically remove it caused decomposition of the dimer, resulting in poor yields and impure product.^{12,13} Surprisingly, water is not troublesome in our surface-mediated synthesis. On the contrary, its presence leads to higher yields of [Rh(CO)₂Cl]₂, probably because it reduces the acidity released during the reductive carbonylation.⁵ The fact that the dimer is not decomposed by water may be due to some stabilizing effect of the silica surface.

While silica-supported IrCl₃·nH₂O may be transformed into [Ir₄(CO)₁₂] under suitable conditions, we could not convert silica-supported RhCl₃·nH₂O directly to [Rh₄(CO)₁₂] or [Rh₆(CO)₁₆]. When the reductive carbonylation is carried out at room temperature, either on Aerosil or Grace silica, the reaction stops at [Rh(CO)₂Cl]₂ even in the presence of water. At higher temperatures, for example 70 °C, complete sublimation of the dimer occurs, preventing further reduction to zerovalent rhodium clusters when Aerosil is used as support. Although this sublimation is inhibited on the porous Grace silica, rhodium carbonyl clusters could not be obtained because the initially formed dimer decomposes already at 70 °C to give supported metallic rhodium.

However, when silica-supported [Rh(CO)₂Cl]₂ (1.5% by weight Rh/SiO₂) is treated at room temperature with carbon monoxide and water (silica containing 11% water by weight), a reduction to physisorbed [Rh₆(CO)₁₆] occurs slowly in 10 days (Table II). The rhodium carbonyl cluster can then be extracted easily with dichloromethane. Yields are sensitive to the amount of water and rhodium loadings (Table II).

In fact, no reaction occurs in the absence of water. When a large amount of water is used (silica containing 89% water), the reductive carbonylation is faster, affording a

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Table II. Reductive Carbonylation of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ Supported on Aerosil^a

Rh/SiO ₂ (wt %)	H ₂ O/SiO ₂ (wt %)	t (days)	$[\text{Rh}_4(\text{CO})_{12}]$ (yield %)	$[\text{Rh}_6(\text{CO})_{16}]$ (yield %)
1.5	0	4	0	0
1.5	11	10	0	46
1.5	89	1	47	21
0.4	11	5	0	73

^a The reaction is carried out at room temperature under 1 atm of carbon monoxide in a closed vessel (see Experimental Section).

mixture of $[\text{Rh}_6(\text{CO})_{16}]$ (21%) and $[\text{Rh}_4(\text{CO})_{12}]$ (47%) after 24 h. Thus, increasing the amount of water accelerates the reaction and favors the formation of $[\text{Rh}_4(\text{CO})_{12}]$ over $[\text{Rh}_6(\text{CO})_{16}]$. It is remarkable that this water effect is similar to that observed during the reductive carbonylation of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in aqueous methanol.¹⁴

Moreover, we obtained higher yields of $[\text{Rh}_6(\text{CO})_{16}]$ with lower rhodium loadings (0.4% instead of 1.5%), probably because less hydrochloric acid is evolved during the reductive carbonylation, since it is known that this acid inhibits the reductive aggregation to rhodium clusters.^{8,14}

Use of silica as a reaction medium for the reductive carbonylation of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ gives a chemistry reminiscent of that in solution.¹⁴ Nevertheless, the yields are not competitive with those of the traditional solution methods to prepare $[\text{Rh}_4(\text{CO})_{12}]$ ¹⁵ and $[\text{Rh}_6(\text{CO})_{16}]$.¹⁴

Synthesis of $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$. We have also studied the surface organometallic chemistry of the reductive carbonylation of silica-supported $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$.⁹

The first step of the carbonylation, at 25–50 °C, is the formation of the silica-bound species $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{HOSi}\langle)_2]$. At 100 °C, one silanol ligand of this surface species is easily replaced by CO, affording good yields of $[\text{Ru}(\text{CO})_3\text{Cl}_2(\text{HOSi}\langle)]$ in 2–3 days.⁹ Treatment of this surface species with CO at 180 °C leads to the sublimation of pure $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ (82% yield after 11 days). However, since this sublimation process is slow, it is more convenient to extract the silica-bound $[\text{Ru}(\text{CO})_3\text{Cl}_2(\text{HOSi}\langle)]$ species with acetone; evaporation of the solvent and recrystallization from dichloroethane/pentane gives $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ in high yields (88–93%; Table I). Similar yields are obtained when the porous Grace silica is used instead of the nonporous Aerosil.

Yields are sensitive to ruthenium loadings. The optimal metal loading is the range between 2 and 5% (Table I). On Aerosil, 88% and 60% yields of $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ were obtained after 3 days with a ruthenium loading of 5 and 10%, respectively. The lower yield of $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ is accompanied by the formation on the silica surface of some oligomers of the type $\{\text{Ru}(\text{CO})_2\text{Cl}_2\}_n$, as shown by infrared spectroscopy (see Experimental Section). These oligomers remain on the support when the dimer is extracted with acetone. They react further but slowly with CO at 100 °C to give $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$. The conversion is not complete even after an additional 3 days.

A possible explanation for the formation of supported $\{\text{Ru}(\text{CO})_2\text{Cl}_2\}_n$ with a loading of 10% ruthenium follows. The surface of Aerosil treated at 100 °C is covered with about 1.19 mmol of hydroxyl groups/g of silica.¹⁶ Assuming that this is approximately the hydroxyl coverage under our experimental conditions (80 °C under 10^{-2} Torr), there

would be about 1.2 hydroxyl groups per ruthenium on the surface with a loading of 10% metal. About 21% of these hydroxyl groups are geminal¹⁷ and are thus less reactive than the "isolated" silanol groups.¹⁸ Also, the hydrogen chloride, formed during the reduction of RuCl_3 , may react with the hydroxyl groups.¹⁹ Thus, it is conceivable that when the ruthenium loading is too high, there are not enough accessible, reactive surface silanol groups to transform all of the $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ to the known intermediate $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{HOSi}\langle)_2]$;⁹ therefore oligomers of the type $\{\text{Ru}(\text{CO})_2\text{Cl}_2\}_n$ are also obtained.

Our surface-mediated synthesis of $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ by reductive carbonylation of silica-supported $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, working at 100 °C and under 1 atm of static CO, is an attractive preparation of this compound. The best synthetic route to $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ has been reported to be by heating $[\text{Ru}_3(\text{CO})_{12}]$ with chloroform under 5 atm of nitrogen (53–60% yield).²⁰ The less expensive, direct carbonylation of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ in methanol at 65 °C affords the dimer (73% yield) but requires 10 atm of CO and the presence of silver metal.²¹

While rhodium carbonyl clusters may be prepared from silica-supported $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, $[\text{Ru}_3(\text{CO})_{12}]$ could not be synthesized in good yield on silica starting from $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ in the presence of CO and water due to the difficulty of removing chloro ligands from ruthenium at low temperature. The use of high temperatures (150–200 °C) was of no avail since chlorocarbonylruthenium complexes sublime easily from Aerosil. On the porous Grace silica, where sublimation is less favored, the dimer is first converted to $[\text{Ru}(\text{CO})_3\text{Cl}_2(\text{HOSi}\langle)]$, at 150 °C, but at 200 °C, it decomposes to metal.

Synthesis of $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$. When anhydrous or hydrated OsCl_3 supported on Aerosil (2–5% by weight Os/SiO_2) is heated at 180 °C under CO (1 atm) in a closed reaction vessel, the silica powder color changes from gray-violet to white due to the formation of $[\text{Os}(\text{CO})_3\text{Cl}_2(\text{HOSi}\langle)]$ and physisorbed *cis*- $[\text{Os}(\text{CO})_4\text{Cl}_2]$.²² The conversion is complete after 2 days. During the reaction some $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$ and *cis*- $[\text{Os}(\text{CO})_4\text{Cl}_2]$ sublime. Extraction of the sublimate and of the silica powder with hot chloroform affords pure $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$ (80–90% yield, Table I), any *cis*- $[\text{Os}(\text{CO})_4\text{Cl}_2]$ being converted to the dimer under reflux. At 100 °C, this reductive carbonylation is much slower. Similar yields are obtained when the porous Grace silica is used (Table I).

It is remarkable that on the silica surface the dimer may be prepared in excellent yield under mild conditions (i.e., relatively low temperature and 1 atm of static CO). Indeed, a way to prepare $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$ is by reaction of $[\text{Os}_3(\text{CO})_{12}]$ with hydrochloric acid at 170 °C for 40 h in cyclohexane in a sealed tube (about 80% yield after purification).²³ The direct carbonylation of solid anhydrous OsCl_3 can be effected only by working at 155 °C under 65 atm of CO, affording *cis*- $[\text{Os}(\text{CO})_4\text{Cl}_2]$ (60% yield).²⁴ Under more drastic conditions (165 °C, 80 atm),

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some $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$ is also produced (10–15%). *cis*- $[\text{Os}(\text{CO})_4\text{Cl}_2]$ may then be converted quantitatively to $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$ by refluxing in chloroform.²⁴

Recently, Herrmann et al.²⁵ reported that when $\text{OsCl}_3 \cdot n\text{H}_2\text{O}$ is treated at 270 °C with a stream of CO containing traces of methanol, $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$ sublimes in high yield (77–92%). The presence of methanol is necessary to avoid the formation of unreactive anhydrous OsCl_3 . In contrast, on a silica surface, anhydrous OsCl_3 may be reductively carbonylated, thus showing the important role played by the support. In fact, when silica is stirred with a suspension of anhydrous OsCl_3 in dichloromethane, its initially white color turns gradually gray, while the brown crystals of anhydrous OsCl_3 disappear. This suggests an interaction with the support, probably with the formation of $\text{OsCl}_3 \cdot n(\text{HOSi}\langle)$ surface species, in which the silanol groups are acting as donor ligands.

Attempts to prepare specifically $[\text{Os}_3(\text{CO})_{12}]$ using Aerosil or Grace silica-supported $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$ as starting material failed. The reductive carbonylation of this latter species in the presence of CO and water, working at 200–250 °C, affords some $[\text{Os}_3(\text{CO})_{12}]$, but always contaminated with various hydrides such as $[\text{HOS}_3(\text{CO})_{10}\text{Cl}]$, $[\text{HOS}_3(\text{CO})_{11}\text{Cl}]$, $[\text{H}_2\text{Os}_3(\text{CO})_{12}]$, and $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$. At lower temperatures (for example, 130 °C) only a slow sublimation of *cis*- $[\text{Os}(\text{CO})_4\text{Cl}_2]$ and $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$ occurs.

Silica Surface: An Unusual Reaction Medium. The reported surface-mediated syntheses involve three steps: (i) impregnation, (ii) reductive carbonylation, (iii) recovery of the products by solvent extraction or sublimation. The reactant is first dispersed on the silica surface and then the reaction proceeds at the gas–solid interface. Consequently, the silica plays the role of a real reaction medium (e.g., the activation of anhydrous OsCl_3 due to the formation of $\text{OsCl}_3 \cdot n(\text{HOSi}\langle)$).

The peculiar property of this solid solvent is that it may act as a “solid donor ligand” due to its surface silanol groups. During the reductive carbonylation, many surface species bound to the silica surface have been identified (e.g., $[\text{Ir}(\text{CO})_2\text{Cl}_3(\text{HOSi}\langle)]$,⁸ $[\text{Rh}(\text{CO})_2\text{Cl}(\text{HOSi}\langle)]$,⁸ $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{HOSi}\langle)_2]$,⁹ $[\text{Ru}(\text{CO})_3\text{Cl}_2(\text{HOSi}\langle)]$,⁹ and $[\text{Os}(\text{CO})_3\text{Cl}_2(\text{HOSi}\langle)]$ ²²). The formation of such intermediate surface species probably is the key step of the remarkable selectivity of these surface-mediated syntheses. The limitation of using metal loadings up to about 5% is probably due to the surface concentration of available donor silanol groups. Too high metal loadings should be avoided because they may lead to side reactions.

Furthermore, because the silanols are not strong ligands, they may be easily replaced by donor solvents, allowing an easy extraction of the reaction products.

Moreover, the type of silica may affect the behavior of the surface species. Sublimation occurs more easily from nonporous Aerosil than from porous Grace silica. Consequently, some surface species which sublime easily from Aerosil are retained by the porous silica and may react further.

Conclusion

The field of preparative organometallic chemistry mediated by surfaces is becoming a new area of synthetic chemistry.

We have shown that, using the silica surface as reaction medium, $\{\text{Ir}(\text{CO})_3\text{Cl}\}_n$, $[\text{Ir}_4(\text{CO})_{12}]$, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, $[\text{Rh}_6(\text{CO})_{18}]$, $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$, and $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$ can be easily prepared in high yields by reductive carbonylation of metal chlorides, working under rather mild conditions (low temperatures and CO atmospheric pressure).

Yields and selectivity are comparable to those reported for reactions carried out classically in solution. Sometimes the method is more convenient as far as reaction conditions and yields are concerned than those reported up to now (e.g., the syntheses of $\{\text{Ir}(\text{CO})_3\text{Cl}\}_n$ and of $[\text{M}(\text{CO})_3\text{Cl}_2]_2$, $\text{M} = \text{Ru}, \text{Os}$). The selectivity of the carbonylation reactions can be controlled by the amount of water, by the temperature, and sometimes by the porosity of silica, so that it is possible to modulate the reaction products. A specific limitation of this synthetic method is given by the metal loadings which cannot be higher than 5% in order to achieve high yields and selectivities.

These surface-mediated reductive carbonylations are carried out at atmospheric pressure in a closed vessel. Thus they might be the best method to synthesize isotopically pure chlorocarbonyl or carbonyl cluster complexes of rhodium, iridium, ruthenium, and osmium, using only the stoichiometric amount of ¹³CO.

Experimental Section

General Comments. Silica (Aerosil 200 Degussa, with a nominal surface area of 200 m²/g, or microporous Grace SG 121 with a surface area of 750–800 m²/g and an average pore diameter of 22 Å) was used as support after treatment in vacuo (10⁻² Torr) at 25 °C for 3 h.

$\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ were purchased from Engelhard SPA and Strem Chemicals; the rhodium and ruthenium contents were respectively 29.8% and 40.8%, as determined by atomic absorption. $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ (54.24% Ir) was bought from Metalli Preziosi SPA, while OsCl_3 and $\text{OsCl}_3 \cdot n\text{H}_2\text{O}$ (54.25% Os) were purchased from Aldrich Chemicals. A pure sample of $\{\text{Ir}(\text{CO})_3\text{Cl}\}_n$ was bought from Strem Chemicals, while pure samples of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$, and $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$ were prepared according to the literature^{12,20,25} and used for comparison.

Products were identified, after extraction from silica, by infrared and mass spectroscopy, comparing their spectra to those of pure samples. Their purity was verified by elemental analysis. Infrared spectra were recorded on a Nicolet MX-1 FT spectrometer, while a VG analytical 7070EQ spectrometer was used for mass spectral determinations. Elemental analyses were carried out in the analytical laboratory of our department.

Preparation of Silica-Supported Starting Materials and the Carbonylation Reaction. The hydrated metal salt ($\text{MCl}_3 \cdot n\text{H}_2\text{O}$, $\text{M} = \text{Rh}, \text{Ir}, \text{Ru}, \text{Os}$), degassed water, and silica were stirred overnight at room temperature under nitrogen. The resulting slurry was dried under vacuo (10⁻² Torr), using a water bath at 80 °C. Similarly, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$, anhydrous OsCl_3 , and $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$ were supported using dichloromethane as solvent instead of water. The powders were stored under nitrogen.

The apparatus for the reductive carbonylation was a cylindrical Pyrex flask (diameter 60 mm, length 150 or 350 mm) fitted with a central neck bearing a side neck equipped with a Rotaflo stopcock (see Figure 1). The end necks were female Rotulex glass spherical joints 19/9. The central neck was usually stopped (metal clamp and O-ring) with the suitable male joint cap. The side neck was connected to a vacuum or gas line, whereas the central neck allowed one to put the samples in or out under controlled atmosphere.

The samples containing physisorbed salts or complexes were placed in the vessel, treated in vacuum (10⁻² Torr) at room temperature, and then exposed to CO or to a well-defined mixture of CO and water at atmospheric pressure. The bottom of the

(25) Herrmann, W. A.; Herdtweck, E.; Schäfer, A. *Chem. Ber.* 1988, 121, 1907.

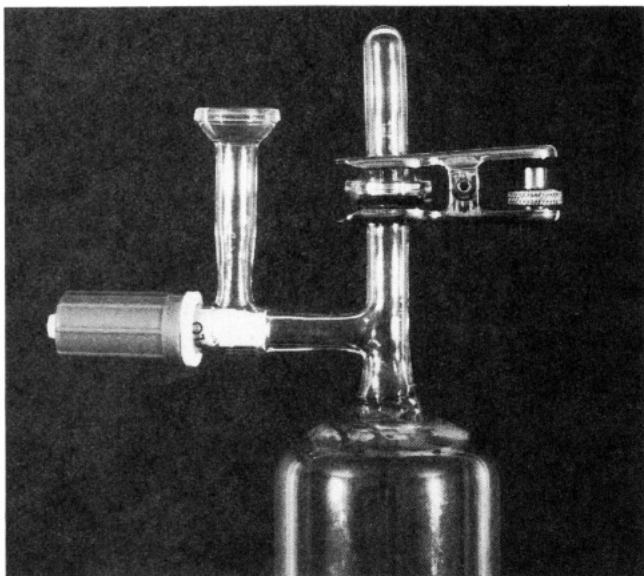


Figure 1. Top of the apparatus for the reductive carbonylation.

vessel (about half of the cylinder) was put in an oven and heated in the range of temperatures between 25 and 250 °C.

The reactions were monitored by infrared spectroscopy; samples were taken from the glass vessel under nitrogen at room temperature and studied as Nujol mulls. Silica-supported metal carbonyl species, formed during the carbonylation process, were quantitatively extracted from the surface with suitable organic solvents through a Pyrex Büchner filter funnel (30-mm-diameter sintered disk, porosity grade 3, overall height 300 mm), while sublimed products were recovered by scratching the walls of the vessel. The extraction process was usually easier when Aerosil was used as the support, the last traces of silica-supported species being removed with greater difficulty from Grace silica. All reported yields are of analytically pure products.

Synthesis of $\{\text{Ir}(\text{CO})_3\text{Cl}\}_n$. In a typical experiment, the yellow Aerosil-supported $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ powder (4.01 g; 3% by weight Ir/SiO_2 ; 0.589 mmol of $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$) was heated at 150 °C under CO (1 atm). $\{\text{Ir}(\text{CO})_3\text{Cl}\}_n$ sublimed, on the walls of the vessel outside the oven, as brown-violet needles having a metallic luster. In order to avoid silica contamination during the recovery of the product by scratching the walls of the vessel, a modified apparatus was used; the cylindrical Pyrex flask was cut at about half and the seal was made by a Rotulex joint system. The reaction was complete after 24 h, affording the product in 83% yield (153 mg; 0.491 mmol). At this point, the silica powder was completely white and contained some physisorbed $[\text{Ir}_4(\text{CO})_{12}]$, as shown by infrared spectroscopy; this cluster was extracted with tetrahydrofuran and identified by mass spectroscopy.

Synthesis of $[\text{Ir}_4(\text{CO})_{12}]$. Aerosil-supported $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ powder (5.97 g; 3% by weight Ir/SiO_2 ; 0.883 mmol of $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$) was placed in the vessel, hydrated with degassed water (0.70 mL; 10% by weight $\text{H}_2\text{O}/\text{SiO}_2$) and heated under CO at 70 °C until completion of the reaction (4 days). The resulting yellow powder was dried for 1 h in vacuum at room temperature and then placed in a Soxhlet apparatus and extracted with tetrahydrofuran or dichloroethane (about 125 mL) under nitrogen. Evaporation of the solvent afforded $[\text{Ir}_4(\text{CO})_{12}]$, contaminated with traces of an unidentified dark brown carbonyliridium species ($\nu(\text{CO}) = 2053 \text{ cm}^{-1}$ in CH_2Cl_2). This latter compound (ca. 5 mg) was removed by washing with some dichloromethane (5 mL). Filtration gave canary-yellow $[\text{Ir}_4(\text{CO})_{12}]$ (165 mg; 0.149 mmol; 68% yield).

Synthesis of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$. Salmon-pink Grace SG 121 silica-supported $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$ (5.38 g; 1.5% by weight Rh/SiO_2 ;

0.747 mmol of $\text{RhCl}_3 \cdot n\text{H}_2\text{O}$) was placed in the vessel, hydrated with degassed water (0.34 mL; silica containing 6% water by weight), and exposed to CO (1 atm) at room temperature. After 24 h, the resulting yellow powder was dried for 1 h in vacuum at room temperature. Extraction with dichloromethane (about 900 mL) or more easily with acetone (100 mL) under nitrogen at room temperature was followed by evaporation of the solvent, affording $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ which was recrystallized from pentane (119 mg; 0.310 mmol; 83% yield).

Synthesis of $[\text{Rh}_4(\text{CO})_{12}]$ and $[\text{Rh}_6(\text{CO})_{16}]$. In a two-necked flask, degassed water (100 mL) was saturated with CO. Aerosil-supported $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (12.22 g; 1.5% by weight Rh/SiO_2 ; 0.882 mmol of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$) was added under a CO stream. The slurry was stirred under static CO (1 atm) for 24 h. Extraction with pentane under CO ($6 \times 25 \text{ mL}$), followed by solvent evaporation, afforded $[\text{Rh}_4(\text{CO})_{12}]$ (154 mg; 0.206 mmol; 47% yield). Further extraction with dichloromethane (200 mL), followed by solvent evaporation, gave $[\text{Rh}_6(\text{CO})_{16}]$ (67 mg; 0.063 mmol; 21% yield).

Only $[\text{Rh}_6(\text{CO})_{16}]$ (15 mg; 0.014 mmol; 73% yield) was recovered when Aerosil-supported $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (2.80 g; 0.4% by weight Rh/SiO_2 ; 0.054 mmol of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$) was placed in a vessel, hydrated with degassed water (0.35 mL; 11% water by weight) and exposed to static CO (1 atm) at room temperature for 5 days. The product was extracted from silica using dichloromethane (100 mL) and recovered by solvent evaporation (73% yield).

Synthesis of $[\text{Ru}(\text{CO})_3\text{Cl}]_2$. Brown Aerosil-supported $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (11.51 g; 5% by weight Ru/SiO_2 ; 5.44 mmol of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$) was placed in the vessel under CO (1 atm) and heated at 100 °C until the silica powder became completely white (2–3 days). Extraction with acetone (150 mL) at room temperature followed by evaporation of the solvent and recrystallization from dichloroethane/pentane gave $[\text{Ru}(\text{CO})_3\text{Cl}]_2$ in 88% yield (1.22 g; 2.38 mmol).

When the metal loading was 10% by weight Ru/SiO_2 , the silica powder was still brown after 3 days. An infrared spectrum showed three carbonyl bands at 2145 (m), 2083 (s), and 2027 (m) cm^{-1} due to the presence on the surface of $[\text{Ru}(\text{CO})_3\text{Cl}]_2$ ($\nu(\text{CO}) = 2145 \text{ (m)}$ and 2083 (s) cm^{-1}) and $\{\text{Ru}(\text{CO})_2\text{Cl}\}_n$ ($\nu(\text{CO}) = 2081 \text{ (s)}$ and 2027 (s) cm^{-1}). Extraction with acetone (150 mL), followed by solvent evaporation, afforded $[\text{Ru}(\text{CO})_3\text{Cl}]_2$ (60% yield), while $\{\text{Ru}(\text{CO})_2\text{Cl}\}_n$ remained on the silica surface. This latter species reacted further slowly with CO at 100 °C to give some additional $[\text{Ru}(\text{CO})_3\text{Cl}]_2$ (after an additional 3 days the conversion is not complete yet).

Synthesis of $[\text{Os}(\text{CO})_3\text{Cl}]_2$. Gray-violet Aerosil-supported anhydrous OsCl_3 (4.65 g; 5% by weight Os/SiO_2 ; 1.13 mmol of OsCl_3) was heated in the vessel at 180 °C under CO (1 atm) until the silica powder became completely white (2 days). During the reaction some *cis*- $[\text{Os}(\text{CO})_4\text{Cl}]_2$ and $[\text{Os}(\text{CO})_3\text{Cl}]_2$ sublimed. The sublimate and the silica powder were combined and extracted with chloroform (150 mL) in a Soxhlet apparatus for 48 h, affording pure $[\text{Os}(\text{CO})_3\text{Cl}]_2$ (0.352 g; 0.510 mmol; 90% yield). A similar yield was obtained on a 3-fold scale. Alternatively, the sublimate and the silica powder were treated with acetone (150 mL) at room temperature. Evaporation of the solvent followed by a 2-h reflux in chloroform (to convert any *cis*- $[\text{Os}(\text{CO})_4\text{Cl}]_2$ in $[\text{Os}(\text{CO})_3\text{Cl}]_2$)²⁴ afforded $[\text{Os}(\text{CO})_3\text{Cl}]_2$ which was recrystallized from dichloromethane/pentane or sublimed (150 °C, 10^{-2} Torr; 83% yield using Grace silica as support).

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