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Surface organometallic chemistry: reductive carbonylation of silica-supported $RuCl_3 \cdot 3H_2O$ *

Dominique Roberto [a], Rinaldo Psaro [b] and Renato Ugo [a]

[a] *Dipartimento di Chimica Inorganica, Metallorganica e Analitica and* [b] *Centro C.N.R., Università di Milano, Via Venezian 21, 20133 Milano (Italy)*

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Abstract

The reductive carbonylation of silica-supported $RuCl_3 \cdot 3H_2O$ was investigated. This physisorbed salt reacts with CO at 25–50°C to form the silica-bound species $[Ru(CO)_2Cl_2(HOSi\leqslant)_2]$, which is converted into the silica-bound tricarbonyl species $[Ru(CO)_3Cl_2(HOSi\leqslant)]$ when the temperature is raised to 100°C. The surface species may be extracted with suitable donor solvents at room temperature. With $[Ru(CO)_3Cl_2(HOSi\leqslant)]$, extraction using acetone followed by recrystallization from dichloroethane/pentane affords $[Ru(CO)_3Cl_2]_2$ in high yield. The dimer sublimes directly from the surface upon carbonylation at 180°C. Liberated HCl probably inhibits further reduction. However, starting from physisorbed $[\{Ru(CO)_3Cl_2\}_2]$, the species $[Ru_2(CO)_6Cl_4(H_2O)]$ is formed on the surface in the presence of CO + H_2O at 100°C. Only traces of $[\{Ru(CO)_3Cl_2\}_2]$ and clusters such as $[Ru_3(CO)_{10}Cl_2]$ and $[Ru_3(CO)_{12}]$ sublime under these conditions.

1. Introduction

In the last few years, many aspects of the surface chemistry of organometallic compounds, in particular metal carbonyl complexes supported on inorganic oxides and zeolites, have been studied [1]. This surface chemistry was interpreted in terms of reactions of organometallic complexes with the functional groups of the support [2], the surface sites of the support being regarded as multidentate ligands [3]. A particular area of this kind of research involves a series of surface reactions leading to well-defined surface complexes, comparable to those occurring in solution [2].

For example, the reductive carbonylation of the grafted species $[Rh^I(CO)_2(O\text{–}S)(HO\text{–}S)]$ (S = $Si\leqslant$ or $Al\leqslant$) gives physisorbed $[Rh_6(CO)_{16}]$ [4]. With highly basic oxides, such as MgO, supported mononuclear osmium and ruthenium salts give osmium and ruthenium carbonyl cluster anions in high yields [5]. Recently Puga *et al.* [6] reported the carbonylation of platinum salts on MgO to give $[\{Pt_3(CO)_6\}_n]^{2-}$ (n = 3, 4). The surface aggregation processes to form physisorbed or ionically linked polynuclear clusters from mononuclear species require a good surface mobility of metal fragments, comparable to that occurring in the homogeneous phase.

Metal catalysts are frequently prepared by impregnation of a support with a solution of a simple metal chloride, followed by drying and reduction. In order to investigate these nucleation processes, we have recently studied [7] the reductive carbonylation, under mild conditions, of silica-supported $MCl_3 \cdot 3H_2O$ (M = Rh or Ir). Here we report the surface organometallic chemistry of the reductive carbonylation of silica-supported $RuCl_3 \cdot 3H_2O$.

2. Results and discussion

2.1. The first step of carbonylation of $RuCl_3 \cdot 3H_2O$ supported on SiO_2

When silica-supported $RuCl_3$ is exposed to CO at atmospheric pressure and room temperature, carbonyl species are slowly formed on the surface, as shown by infrared spectra in the ν(CO) region. After 3 days, two strong and one medium bands appear at 2077, 2010 and 2062 cm^{-1}, respectively, and the initial brown powder is slightly lighter (Fig. 1(A)).

Correspondence to: Professor R. Psaro.

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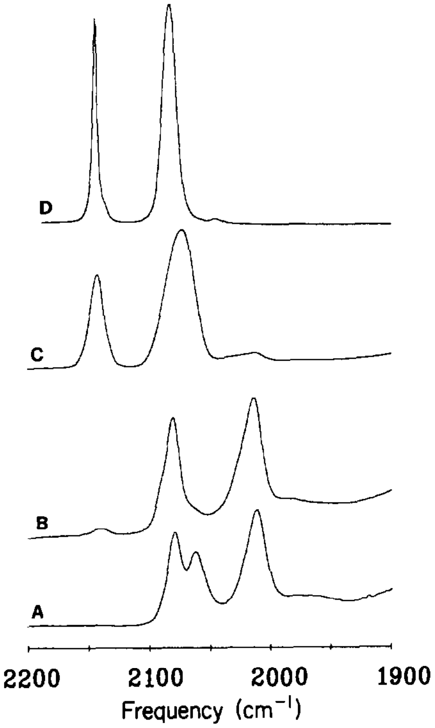


Fig. 1. Infrared spectra in the ν(CO) region. Reactivity of physisorbed $RuCl_3/SiO_2$ under CO: (A) after 3 days at 25°C; (B) a further 4 days at 50°C; (C) a further 2 days at 100°C; (D) recrystallized $[\{Ru(CO)_3Cl_2\}_2]$ in CH_2Cl_2.

The carbonyl surface species can be removed from the silica only by donor solvents; the infrared spectrum of the solution obtained by extraction with ethanol shows absorptions at 2066, 2045 and 1995 cm^{-1} with weak bands at 2057 and 1985 cm^{-1}. The doublet at 2066 and 1995 cm^{-1} is typical of $Ru(CO)_2Cl_2$ with ethanol as ligand [8], while the band at 2045 cm^{-1} may correspond to the species reported to be "$Ru(CO)Cl_3$" [8]. The remaining two weak absorptions indicate the presence of small amounts of $[Ru(CO)_2Cl_4]^{2-}$ [8].

By further treatment of the surface species under CO at 50°C the absorption at 2062 cm^{-1} disappears, with parallel growth of the intensity of the other two major peaks, while a very weak CO band develops at about 2140 cm^{-1} (Fig. 1(B)). The powder at this point is pale yellow.

The first step of the reductive carbonylation of silica-supported $RuCl_3$ is thus formation of physisorbed "$Ru^{III}(CO)Cl_3$" (absorption at 2062 cm^{-1}) which further reacts, affording a "$Ru^{II}(CO)_2Cl_2$" surface species. The last could be a monomer or a dimer bound to the surface silanol groups, as in $[Ru(CO)_2Cl_2(HOSi\leqslant)_2]$ or $[Ru(CO)_2Cl_2(HOSi\leqslant)]_2$, or as in the known polymer $\{Ru(CO)_2Cl_2\}_n$ [9], but physisorbed. The behaviour of this "$Ru^{II}(CO)_2Cl_2$" surface species towards donor solvents was investigated and compared with that of pure $\{Ru(CO)_2Cl_2\}_n$ [9], in order to define its real nature.

2.2. *Reactivity of the surface species "$Ru^{II}(CO)_2Cl_2$" with donor solvents*

The surface species characterized by the doublet at 2077 and 2010 cm^{-1} (Fig. 1(B)) can be totally removed from the silica surface by simple treatment with donor solvents such as pyridine, acetonitrile, ethanol, tetrahydrofuran, and even triethylsilanol. The solutions resulting from these extractions are all yellow and characterized by two intense carbonyl bands at 2070 and 2006 cm^{-1}, 2081 and 2020 cm^{-1}, 2066 and 1995 cm^{-1}, 2060 and 1985 cm^{-1}, 2074 and 2006 cm^{-1}, depending upon the solvent, respectively.

The complex formed by treatment with pyridine is $[Ru(CO)_2Cl_2py_2]$, as shown by its mass spectrum which has a molecular ion peak at 386. In the carbonyl stretching region it absorbs at 2070 and 2006 cm^{-1} (either in pyridine or dichloromethane) in agreement with a *cis*-CO, *cis*-py, *trans*-Cl structure [10,11].

The complex obtained in acetonitrile is not the isomer *cis*-CO, *cis*-CH_3CN, *trans*-Cl $[Ru(CO)_2Cl_2(CH_3CN)_2]$ ($\nu(CO) = 2050$ and 1955 cm^{-1} in Nujol) which can be prepared by carbonylation of $[RuCl_2(NCMe)_4]$ [12]; but the dimer $[\{Ru(CO)_2Cl_2(CH_3CN)\}_2]$, which has been identified by mass spectroscopy and elemental analysis. To our knowledge, this compound has not yet been reported. Its ^1H NMR spectrum shows the presence of at least seven different CH_3CN species (see Experimental section), suggesting a mixture of stereoisomers. As expected for a mixture of closely related isomers, in the infrared spectrum, the carbonyl bands are relatively broad, even in solution. The slight shift in the ^1H NMR spectrum of the resonance of the protons of the coordinated CH_3CN towards lower field ($\Delta\delta = 0.43$–0.64 ppm) and the shift ($\Delta\nu = 47$ and 74 cm^{-1}, see Experimental section) of the CN stretching band towards higher frequencies with respect to the free CH_3CN are in agreement with a coordination of the ligand through the nitrogen lone pair [11,13].

The complexes extracted in EtOH, THF and Et_3SiOH are probably $Ru(CO)_2Cl_2$ fragments linked to the solvent via oxygen. We cannot distinguish between monomers of the type $[Ru(CO)_2Cl_2(solvent)_2]$ and dimers such as $[\{Ru(CO)_2Cl_2(solvent)\}_2]$, since these complexes are stable only in pure solvent. They could not be fully characterized because evaporation of the solvent leads to polymerization to $\{Ru(CO)_2Cl_2\}_n$ as observed by infrared spectroscopy and elemental analysis (see Experimental section).

No $Ru^{II}(CO)_2Cl_2$ species linked to an *O*-donor ligand has yet been well characterized. However, by analogy with the known complexes $[Ru(CO)_2Cl_2(NR_3)_2]$ [10,14] and $[Ru(CO)_2Cl_2(SR_2)_2]$ [10,14,15], we may postulate that the species extracted by pure EtOH, THF and Et_3SiOH are monomers.

2.3. *Comparison between the surface species "$Ru^{II}(CO)_2Cl_2$" and $\{Ru(CO)_2Cl_2\}_n$ with respect to the reactivity with donor solvents*

Consistent with the reactivity of $\{Ru(CO)_2Cl_2\}_n$ with alcohols [14], we observed that the chloro-bridges of this polymer are cleaved in acetonitrile, ethanol, or water, affording solutions of $[\{Ru(CO)_2Cl_2(CH_3CN)\}_2]$, $[Ru(CO)_2Cl_2(EtOH)_2]$, or $[Ru(CO)_2Cl_2(H_2O)_2]$, respectively. This kind of reaction, slow at room temperature, is complete after 5 min under reflux. However, neither THF nor Et_3SiOH cleave the chloro-bridges, at least not after 30 min at reflux. Thus, the behaviour of $\{Ru(CO)_2Cl_2\}_n$ with these weak donor solvents contrasts strongly with that of the "$Ru^{II}(CO)_2Cl_2$" surface species which can be easily extracted from the silica surface with THF and Et_3SiOH at room temperature.

It follows that the carbonylation of silica-supported $RuCl_3$ at 50°C does not lead to a physisorbed polymeric form but to a surface species which can be either $[Ru(CO)_2Cl_2(HOSi\leqslant)_2]$ or physisorbed $[Ru(CO)_2Cl_2(H_2O)_2]$, since under our experimental conditions, physisorbed and chemisorbed water is present on the silica surface.

Further experiments proved that the silica-supported "$Ru^{II}(CO)_2Cl_2$" species is not physisorbed $[Ru(CO)_2Cl_2(H_2O)_2]$, which can be prepared by treatment of silica-supported $[\{Ru(CO)_3Cl_2\}_2]$ with H_2O at room temperature. In fact, physisorbed $[Ru(CO)_2Cl_2(H_2O)_2]$ can be easily extracted from the surface, either with CH_2Cl_2 or CH_3CN, as expected, since $[Ru(CO)_2Cl_2(H_2O)_2]$ is soluble in these solvents (see Experimental section). In contrast, the silica-supported "$Ru^{II}(CO)_2Cl_2$" species obtained by reductive carbonylation of $RuCl_3$ cannot be extracted with a non-donor solvent such as CH_2Cl_2, while extraction with CH_3CN does not afford $[Ru(CO)_2Cl_2(H_2O)_2]$ but $[\{Ru(CO)_2Cl_2(CH_3CN)\}_2]$.

Thus we have evidence that the silica-supported "$Ru^{II}(CO)_2Cl_2$" species obtained by reductive carbonylation of $RuCl_3$, is a $Ru(CO)_2Cl_2$ fragment bound to the silanol groups of silica surface. Most probably it is $[Ru(CO)_2Cl_2(HOSi\leqslant)_2]$ (Scheme 1).

In some preparations of this species, some variation of the CO absorptions was observed in the infrared spectra. The bands at 2077 and 2010 cm^{-1} may be shifted to 2081 and 2016 cm^{-1}, respectively. This may indicate the presence of different isomers or of surface topological effects affecting the properties of the silanol groups.

2.4. *Formation of $[Ru(CO)_2Cl_4]^{2-}$*

As mentioned above, small amounts of $[Ru(CO)_2Cl_4]^{2-}$ are present in the acetonitrile solution obtained by extraction of the powder resulting from treatment of silica-supported $RuCl_3$ with CO at 25–50°C. A question arises: is $[Ru(CO)_2Cl_4]^{2-}$ formed directly on the silica and simply extracted by polar solvents such as acetonitrile, or is it formed later in acetonitrile solution by rapid reaction of the extracted $[\{Ru(CO)_2Cl_2(CH_3CN)\}_2]$ species with HCl, produced during the reductive carbonylation of $RuCl_3$ and therefore physisorbed on the surface of silica?

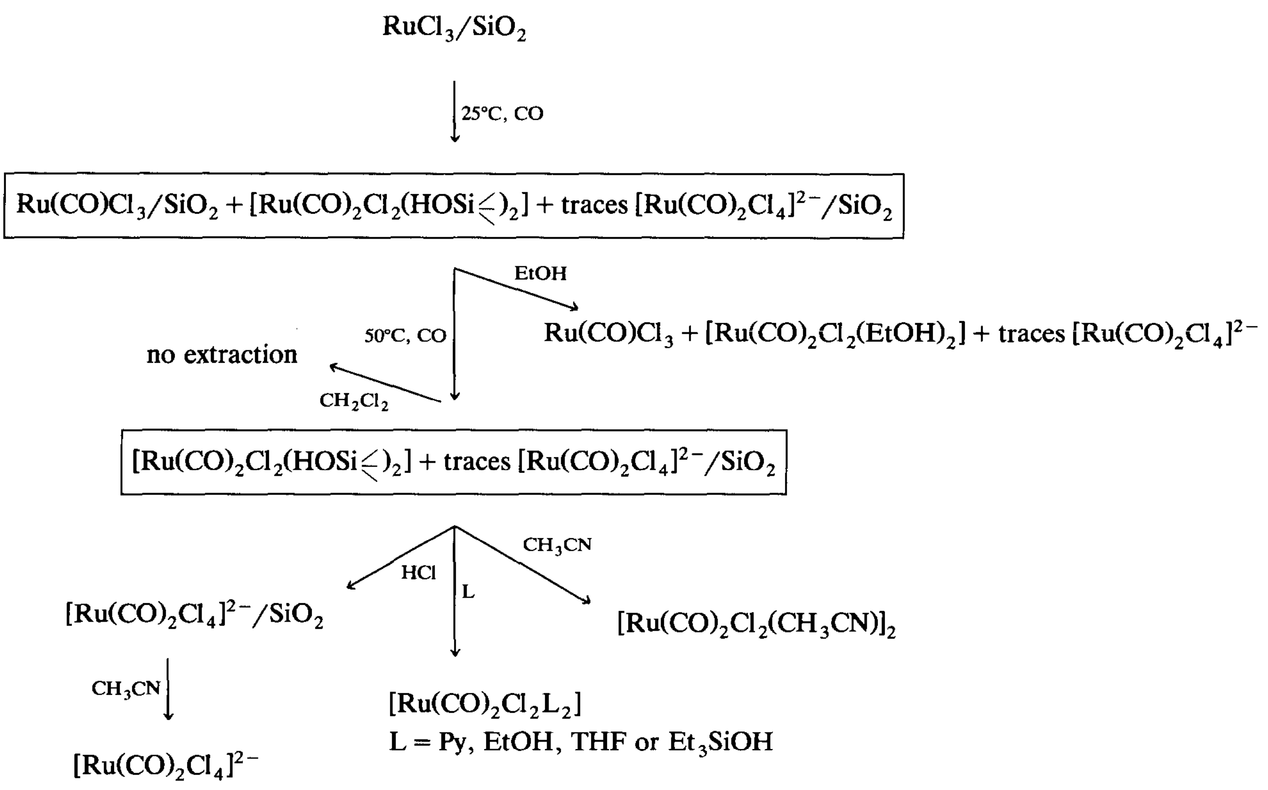
When $[Ru(CO)_2Cl_2(HOSi\leqslant)_2]$ is treated with traces of concentrated HCl for 5 min, the powder changes immediately from pale yellow to orange and the absorptions at 2077 and 2010 cm^{-1} are replaced by two strong bands at 2069 and 2002 cm^{-1}. Extraction with acetonitrile affords pure $[Ru(CO)_2Cl_4]^{2-}$ which is slowly converted to $[\{Ru(CO)_2Cl_2(CH_3CN)\}_2]$. In fact, the bands characteristic of $[Ru(CO)_2Cl_4]^{2-}$ at 2057 and 1986 cm^{-1} decrease with time, being replaced by those typical of $[\{Ru(CO)_2Cl_2(CH_3CN)\}_2]$. The conversion is almost complete after 24 h; at this point, addition of HCl does not regenerate $[Ru(CO)_2Cl_4]^{2-}$.

These data would indicate that traces of $[Ru(CO)_2Cl_4]^{2-}$ can be obtained directly on the surface during the reductive carbonylation of $RuCl_3$ on silica due to the formation of physisorbed HCl, which further reacts (Scheme 1). Its infrared absorptions in the carbonyl region are masked by the intense absorptions of the main surface species $[Ru(CO)_2Cl_2(HOSi\leqslant)_2]$. However, extraction with acetonitrile (or ethanol) reveals it clearly.

2.5. *Carbonylation of $[Ru(CO)_2Cl_2(HOSi\leqslant)_2]$*

The yellow species $[Ru(CO)_2Cl_2(HOSi\leqslant)_2]$ is converted into a white "$Ru^{II}(CO)_3Cl_2$" surface species only when the temperature is raised to 100°C. The carbonyl bands at 2077 and 2010 cm^{-1} are replaced by two carbonyl absorptions at 2140m and 2070s cm^{-1}. After 2 days, the conversion is almost complete (Fig. 1(C)). Only traces of silica-supported "$Ru^{II}(CO)_2Cl_2$" remain, as shown by a weak absorption around 2010 cm^{-1}. The same "$Ru^{II}(CO)_3Cl_2$" species is obtained when silica-supported $RuCl_3$ is exposed to CO directly at 100°C for about 24 h.

The infrared spectrum of this new surface species is slightly different from that of physisorbed $[\{Ru(CO)_3Cl_2\}_2]$ ($\nu(CO) = 2144$m and 2080s cm^{-1}) prepared by impregnation of silica with a dichloromethane solution of $[\{Ru(CO)_3Cl_2\}_2]$. Moreover, whereas freshly physisorbed $[\{Ru(CO)_3Cl_2\}_2]$ can be easily removed from silica with CH_2Cl_2, it is necessary to use solvents such as THF, CH_3CN or acetone in order to extract the



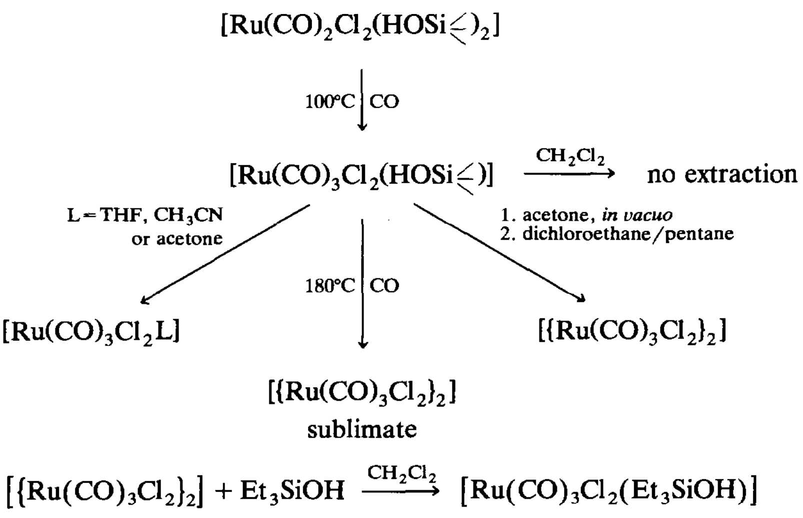
Scheme 1.

surface species "$Ru^{II}(CO)_3Cl_2$" prepared directly from $RuCl_3$.

Obviously, these data indicate that the "$Ru^{II}(CO)_3Cl_2$" surface species interacts with the surface silanol groups and may be written as $[Ru(CO)_3Cl_2(HOSi\leqslant)]$ (Scheme 2). This species has recently been reported by Bergmeister *et al.* [16] who impregnated silica with a solution of $[Ru(CO)_3Cl_2(THF)]$.

We also have evidence that physisorbed $[Ru(CO)_3Cl_2(H_2O)]$ is not formed on the silica surface; in fact, this complex, obtained by reaction of $[\{Ru(CO)_3Cl_2\}_2]$ with H_2O at room temperature (see Experimental section), is soluble in CH_2Cl_2 and therefore it should be extracted from the surface by this solvent.

Extraction of the silica-supported $[Ru(CO)_3Cl_2(HOSi\leqslant)]$ species with THF and CH_3CN affords



Scheme 2.

$[Ru(CO)_3Cl_2(THF)]$ [17] and $[Ru(CO)_3Cl_2(CH_3CN)]$ [11], respectively. Extraction with acetone gives the weak adduct $[Ru(CO)_3Cl_2(acetone)]$ [11] which, after evaporation of the solvent and recrystallization from dichloroethane/pentane affords $[\{Ru(CO)_3Cl_2\}_2]$ (Fig. 1(D)). The dimer can also be recovered directly from the surface by sublimation from the silica-supported $[Ru(CO)_3Cl_2(HOSi\lessgtr)]$ species under CO at 180°C (Scheme 2).

Bridge cleavage reactions of $[\{Ru(CO)_3Cl_2\}_2]$ with donors are well known [14]. This prompted us to prepare in solution the molecular model $[Ru(CO)_3Cl_2(Et_3SiOH)]$ by reaction of $[\{Ru(CO)_3Cl_2\}_2]$ with Et_3SiOH in dichloromethane (see Experimental section, Fig. 2). Its infrared spectrum in CH_2Cl_2 shows two carbonyl bands at 2139m and 2069s cm^{-1} (Fig. 2(D)), very similar to that of the surface species $[Ru(CO)_3Cl_2(HOSi\lessgtr)]$ (2140m and 2070s cm^{-1}).

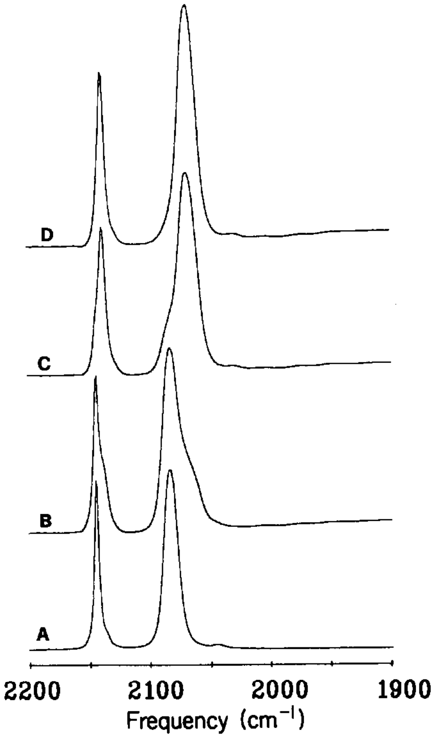
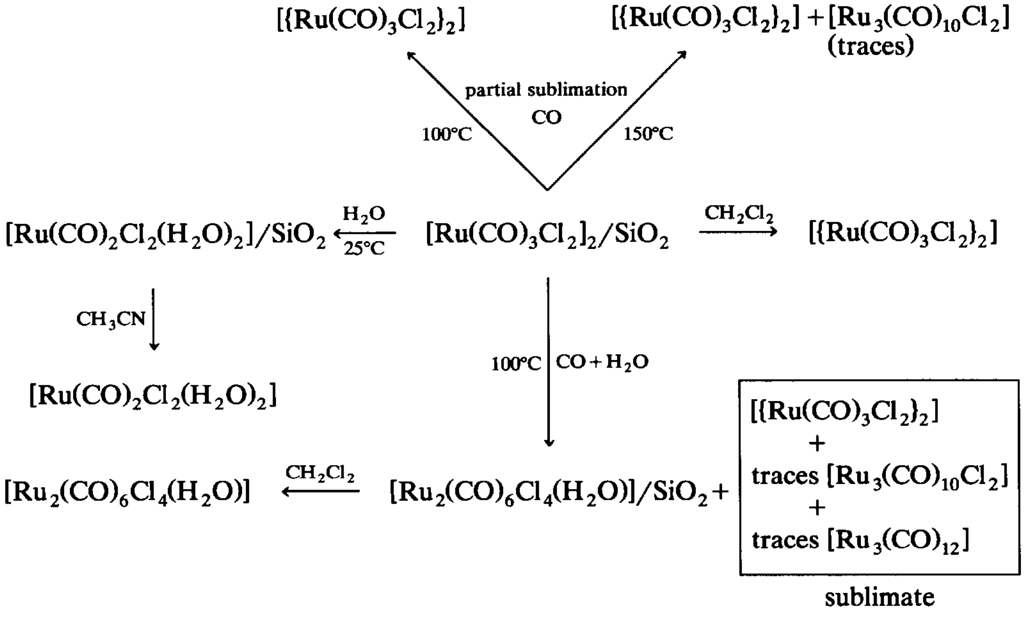


Fig. 2. Infrared spectra in the ν(CO) region. Reaction of $[\{Ru(CO)_3Cl_2\}_2]$ with Et_3SiOH in CH_2Cl_2: (A) $[\{Ru(CO)_3Cl_2\}_2]$ in CH_2Cl_2; (B) 2 min after addition of Et_3SiOH; (C) after a further 30 min; (D) after a further 45 min.

2.6. Surface reactivity of $[\{Ru(CO)_3Cl_2\}_2]$ supported on SiO_2 with CO or with CO + H_2O

Recently we found that silica-supported $RhCl_3 \cdot 3H_2O$ is converted into $[\{Rh(CO)_2Cl\}_2]$ in the presence of CO [7]. The reductive carbonylation does not proceed to give zero-valent carbonyl clusters due to the inhibiting effect on the nucleation process of the HCl evolved. However, we observed that when the pure species $[\{Rh(CO)_2Cl\}_2]$ is used as starting material instead of $RhCl_3 \cdot 3H_2O$, reduction to physisorbed $[Rh_6(CO)_{16}]$ occurs at room temperature under CO + H_2O. The amount of water on the surface plays a significant role, being able to reduce the inhibiting effect of physisorbed HCl [7].

Analogously, the reductive carbonylation of physisorbed $RuCl_3 \cdot 3H_2O$ leads to the surface species



Scheme 3.

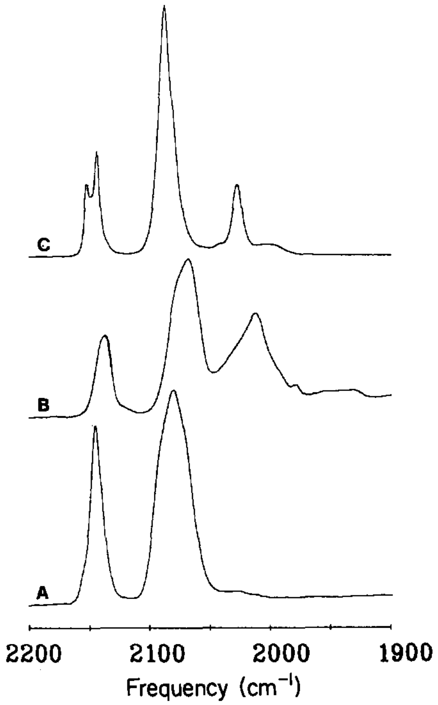


Fig. 3. Infrared spectra in the ν(CO) region. Reactivity of physisorbed $[\{Ru(CO)_3Cl_2\}_2]$ under $CO + H_2O$: (A) physisorbed $[\{Ru(CO)_3Cl_2\}_2]$; (B) after 3 days at 100°C; (C) species extracted with CH_2Cl_2.

$[Ru(CO)_2Cl_2(HOSi\leqslant)_2]$, but a further reduction to physisorbed $[Ru_3(CO)_{12}]$ was unsuccessful. Therefore, we studied the reductive carbonylation of silica-supported $[\{Ru(CO)_3Cl_2\}_2]$.

Some $[\{Ru(CO)_3Cl_2\}_2]$ sublimes when physisorbed $[\{Ru(CO)_3Cl_2\}_2]$ is exposed to CO at 100°C for 4 days (Scheme 3) whereas traces of a new species sublime, together with $[\{Ru(CO)_3Cl_2\}_2]$, when the reaction is carried out at 150°C for 1 day. Its infrared spectrum, obtained after subtraction of the carbonyl bands of the dimer, shows ν(CO) at 2115w, 2088s, 2077s, 2031vs and 1995w cm^{-1} (CH_2Cl_2), in perfect agreement with the spectra reported for the known clusters $[Ru_3(CO)_{10}X_2]$ (X = Br or I) [18]. There is no ^1H NMR spectrum, and consequently it cannot be $[HRu_3(CO)_{10}Cl]$. We believe that this species formed in minute amounts is $[Ru_3(CO)_{10}Cl_2]$, although it was impossible to obtain a better characterization (e.g. by mass spectroscopy) due to its instability.

When physisorbed $[\{Ru(CO)_3Cl_2\}_2]$ (Fig. 3(A)) is heated under CO and H_2O (silica containing 8–41% water by weight) at 100°C for 3 days, $[\{Ru(CO)_3Cl_2\}_2]$ sublimes with traces of $[Ru_3(CO)_{10}Cl_2]$ and $[Ru_3(CO)_{12}]$ (the latter confirmed by mass spectroscopy, thin layer chromatography, and infrared spectroscopy). A new species is left on silica, characterized by three carbonyl bands in the infrared spectrum at 2137m, 2068s and 2012m cm^{-1} (Fig. 3(B)). This can be extracted easily with dichloromethane, affording a yellow solution absorbing at 2152m, 2144m, 2087s and 2027m cm^{-1} (Fig. 3(C)). Evaporation of the solvent gives a yellow powder which was identified as $[Ru_2(CO)_6Cl_4(H_2O)]$ (Scheme 3, see Experimental section). To our knowledge, this species has never been reported.

When the reaction of physisorbed $[\{Ru(CO)_3Cl_2\}_2]$ with CO and H_2O (silica containing 8% water by weight) is carried out at higher temperatures (150°C), only traces of $[Ru_2(CO)_6Cl_4(H_2O)]$ remain on the silica surface after 3 days. A mixture of ruthenium carbonyl complexes sublimes. Addition of degassed dichloromethane to the sublimate affords a solution consisting mainly of $[\{Ru(CO)_3Cl_2\}_2]$ and traces of $[Ru_3(CO)_{10}Cl_2]$.

Thus unlike rhodium carbonyl clusters, $[Ru_3(CO)_{12}]$ cannot be synthesized easily on silica from carbonyl chloride species in the presence of CO (1 atm) and H_2O, due to the greater difficulty of removing completely chloride ligands from ruthenium at room temperature, and the easy sublimation of chlorocarbonylruthenium complexes at higher temperature. This is relevant, because it is known that silica-grafted $[Ru^{II}(CO)_x(OSi\leqslant)_2]$ ($x = 2$ or 3) surface species are easily converted into physisorbed $[Ru_3(CO)_{12}]$ by treatment with CO and H_2O even at 100°C [19].

Our results show that, despite what was previously reported [19], a silica surface is not a hydrogen chloride acceptor in the thermal adsorption of $RuCl_3 \cdot 3H_2O$ and $[\{Ru(CO)_3Cl_2\}_2]$, confirming the observations of Bergmeister *et al.* [16] who reported that it was not possible to separate chloride from $[Ru(CO)_3Cl_2(THF)]$. On the contrary, $[Ru(CO)_3Cl_2(THF)]$ on hydroxylated alumina surfaces yields the chemisorbed species $[Ru(CO)_3(HOAl\leqslant)(OAl\leqslant)_2]$ which is then converted easily into the adsorbed anionic cluster $[HRu_3(CO)_{11}]^-$ by reductive carbonylation [20].

3. Conclusion

Our study on the reductive carbonylation of silica-supported $RuCl_3$ has revealed some new aspects of ruthenium surface organometallic chemistry. After the first step at room temperature of the formation of physisorbed "$Ru^{III}(CO)Cl_3$" species, further reactions take place at 50°C affording silica-bound $[Ru(CO)_2Cl_2(HOSi\leqslant)_2]$, which is then converted successively to $[Ru(CO)_3Cl_2(HOSi\leqslant)]$ at 100°C. We did not observe encapsulation of the "$Ru(CO)_2$" or "$Ru(CO)_3$" moieties in the silica surface to form chemisorbed $[Ru(CO)_x(OSi\leqslant)_2]$ ($x = 2$ or 3) species, because silica, unlike the more basic oxides, Al_2O_3 and MgO, is not as good a hydrogen chloride acceptor, at least with ruthenium species.

$[Ru(CO)_2Cl_2(HOSi\leqslant)_2]$ and $[Ru(CO)_3Cl_2(HOSi\leqslant)]$ are both real surface complexes weakly bonded to the surface silanol groups. They can be extracted from the surface only with donor solvents. Their further reduction to physisorbed ruthenium carbonyl clusters does not occur easily, probably due to the inhibiting effect of physisorbed HCl, the difficulty of removing chloride ligands at relatively low temperatures, and the easy sublimation of $[\{Ru(CO)_3Cl_2\}_2]$ at high temperatures.

We have shown that chemical extraction reactions of these adsorbed species, leading to specific compounds, is a good method for inferring specific surface structures and interactions, even though surface characterization methods might be more appropriate.

4. Experimental details

$RuCl_3 \cdot 3H_2O$ was purchased from Strem Chemicals; the ruthenium content was 40.8%, as determined by atomic absorption. $[\{Ru(CO)_3Cl_2\}_2]$, $\{Ru(CO)_2Cl_2\}_n$ and $[Ru(CO)_2Cl_4]^{2-}$ were prepared according to the literature [9,21].

Silica (Aerosil 200, Degussa) was used as support. It was treated under vacuum (10^{-2} Torr) at 25°C for 3 h prior to use.

4.1. Instrumentation

Infrared spectra were recorded on a Nicolet MX-1 FT spectrometer. ^1H NMR were run at 27°C on a Bruker WP-80 or a Bruker AC 200 spectrometer and are referenced to tetramethylsilane. Mass spectra were carried out on a VG analytical 7070EQ spectrometer while elemental analyses were run on a Perkin-Elmer 2400 spectrometer.

4.2. Preparation of silica-supported ruthenium complexes

4.2.1. $RuCl_3 \cdot 3H_2O$

In a typical experiment, a mixture of silica (11.317 g), $RuCl_3 \cdot 3H_2O$ (0.555 g, 2% by weight Ru/SiO_2) and degassed water (150 ml) was stirred overnight at room temperature under dinitrogen. The resultant slurry was dried at 10^{-2} Torr at 80°C, affording a brown powder.

4.2.2. $[\{Ru(CO)_3Cl_2\}_2]$

A mixture of silica (9.059 g), $[\{Ru(CO)_3Cl_2\}_2]$ (0.459 g, 2% by weight Ru/SiO_2) and CH_2Cl_2 (200 ml, dried over molecular sieves) was stirred for 5 h at room temperature under dinitrogen. The resultant slurry was dried at 10^{-2} Torr affording a white powder which was stored under nitrogen.

4.3. Carbonylation reaction

The sample containing physisorbed complexes were put in a glass cell, equipped with Teflon stop cocks, which can work *in vacuo* or a controlled atmosphere, and treated with CO or with a mixture of CO and H_2O at atmospheric pressure. The carbonylation was carried out between 25 and 180°C.

The surface reactions were monitored by infrared spectroscopy; samples were taken from the glass cell under dinitrogen and studied as Nujol mulls; the infrared spectrum of pure silica in Nujol (reference) was always subtracted.

Silica-supported metal carbonyl species formed in the carbonylation process were quantitatively extracted from the surface with suitable organic solvents.

4.4. Reaction of $\{Ru(CO)_2Cl_2\}_n$ with CH_3CN

A suspension of $\{Ru(CO)_2Cl_2\}_n$ in acetonitrile was heated under reflux for 5 min, affording a yellow solution. Evaporation of the solvent afforded a yellow-orange powder identified as $[\{Ru(CO)_2Cl_2(CH_3CN)\}_2]$ (mixture of isomers). Anal. Found: C, 18.47; H, 1.27; N, 5.09. $C_8Cl_4H_6N_2O_4Ru_2$ calc.: C, 17.86; H, 1.12; N, 5.20%. IR (CH_3CN) ν(CO): 2081s, 2020s cm^{-1}; ($CHCl_3$) ν(CO): 2089s, 2031s cm^{-1}, ν(CN): 2330w, 2300vw cm^{-1}; (Nujol) ν(CO): 2078s,br, 2014s,br cm^{-1}, ν(CN): 2327w, 2300vw cm^{-1}. ^1H NMR ($CDCl_3$, 27°C): δ 2.45, 2.47, 2.48, 2.50, 2.57, 2.62, 2.66. MS, m/e: 540 $[M]^+$, 389 $[Ru_2Cl_3(CH_3CN)_2]^+$, 307 $[Ru_2Cl_3]^+$, 272 $[Ru_2Cl_2]^+$.

4.5. Reaction of $\{Ru(CO)_2Cl_2\}_n$ with EtOH

A suspension of $\{Ru(CO)_2Cl_2\}_n$ in ethanol was heated under reflux for 5 min affording a yellow solution. Its infrared spectrum showed two carbonyl bands at 2066s and 1995s cm^{-1} similar to those reported for $Ru(CO)_2Cl_2$ bound to ethanol [8]. As the solvent was gradually evaporated, we observed that polymerization occurred. When enough EtOH was left (sample still liquid), an infrared spectrum in CH_2Cl_2 showed two bands at 2073 and 2002 cm^{-1}. Gradual evaporation of ethanol afforded a yellow paste, soluble in CH_2Cl_2, with final infrared absorptions at 2083 and 2024 cm^{-1}. Finally, complete removal of EtOH gave a yellow powder, insoluble in CH_2Cl_2, characterized by two bands at 2074 and 2017 cm^{-1} in Nujol, and identified as $\{Ru(CO)_2Cl_2\}_n$ [9] (Anal. Found: C, 10.54; calc.: C, 10.61%). The species initially present in ethanol was probably $[Ru(CO)_2Cl_2(EtOH)_2]$ which transformed stepwise into $[Ru(CO)_2Cl_2(EtOH)_{x \le 1}]_{n \ge 2}$ and finally $\{Ru(CO)_2Cl_2\}_n$.

4.6. Reaction of $\{Ru(CO)_2Cl_2\}_n$ with H_2O

A suspension of $\{Ru(CO)_2Cl_2\}_n$ in water was heated under reflux for 5 min, affording a yellow solution.

Evaporation of almost all the water followed by addition of CH_2Cl_2 gave a yellow solution of $Ru(CO)_2Cl_2$ bound to water, probably $[Ru(CO)_2Cl_2(H_2O)_2]$ (ν(CO) = 2076s and 2007s cm^{-1}). When CH_2Cl_2 was replaced by CH_3CN, the infrared frequencies were at 2077s and 2008s cm^{-1}. Evaporation of more water gave a yellow paste soluble in CH_2Cl_2 and absorbing at 2080s and 2027s cm^{-1}. This was probably $[Ru(CO)_2Cl_2(H_2O)_{x \leq 1}]_{n \geq 2}$ by analogy with $Ru(CO)_2Cl_2$ bound to ethanol.

4.7. Reaction of $[\{Ru(CO)_3Cl_2\}_2]$ with Et_3SiOH

$[\{Ru(CO)_3Cl_2\}_2]$ was dissolved in CH_2Cl_2 at room temperature. Et_3SiOH was added. After 2 min, some $[Ru(CO)_3Cl_2(Et_3SiOH)]$ had been formed, as shown by the presence of shoulders at 2139 and 2069 cm^{-1}, in addition to the carbonyl bands of $[\{Ru(CO)_3Cl_2\}_2]$, at 2144m and 2083s cm^{-1} (Fig. 2(B)). After 45 min, the dimer had been totally converted into $[Ru(CO)_3Cl_2(Et_3SiOH)]$.

Like THF [17], Et_3SiOH cleaves the chloro bridges of $[\{Ru(CO)_3Cl_2\}_2]$, but it is more weakly bonded to ruthenium than THF. In fact, complete evaporation of Et_3SiOH regenerates $[\{Ru(CO)_3Cl_2\}_2]$, whereas $[Ru(CO)_3Cl_2(THF)]$ is converted in the dimer only by sublimation at 140°C (0.1 mmHg) [17].

4.8. Reaction of $[\{Ru(CO)_3Cl_2\}_2]$ with H_2O

$[\{Ru(CO)_3Cl_2\}_2]$ was dissolved in CH_2Cl_2 at room temperature. Addition of water led to the formation of $[Ru(CO)_3Cl_2(H_2O)]$ characterized by two carbonyl bands at 2140m and 2070s cm^{-1}; after about 1 h the conversion was complete. Evaporation of the solvent regenerated $[Ru(CO)_3Cl_2]_2$.

4.9. Conversion of silica-supported $[\{Ru(CO)_3Cl_2\}_2]$ into silica-supported $[Ru_2(CO)_6Cl_4(H_2O)]$

Silica-supported $[\{Ru(CO)_3Cl_2\}_2]$ (2% by weight Ru/SiO_2) was put in a glass cell. Degassed water (8–41% water by weight of silica) was added under dinitrogen. This water was frozen by putting the cell in a CO_2–acetone bath; after evacuation, CO was admitted at room temperature. The cell was heated at 100°C for 3 days. Traces of $[Ru_3(CO)_{12}]$, $[Ru_3(CO)_{10}Cl_2]$, and $[\{Ru(CO)_3Cl_2\}_2]$ sublimed. This mixture was characterized by mass spectroscopy, thin layer chromatography and infrared spectroscopy. A new species was formed on silica, characterized by three carbonyl bands at 2137m, 2068s and 2012m cm^{-1} (Nujol mull). This species was extracted with CH_2Cl_2 and identified as $[Ru_2(CO)_6Cl_4(H_2O)]$. Its mass spectrum showed a molecular ion peak at 532 which first loses H_2O and then fragments, like $[\{Ru(CO)_3Cl_2\}_2]$. Thermogravimetry under dioxygen at a scanning rate of 5°C/min showed that $[Ru_2(CO)_6Cl_4(H_2O)]$ undergoes a weight loss of about 3% from 70 to 130°C while $[Ru_2(CO)_6Cl_4]$ is stable in this range of temperature. This is the change corresponding to a loss of one molecule of water for a molecule of complex. IR (CH_2Cl_2) ν(CO): 2152m, 2144m, 2087s, 2027m cm^{-1}; (KCl) ν(CO): 2146m, 2080sh, 2072s, 2015m, br cm^{-1}, $\nu(H_2O)$: 3389m, br, 1616w, 805w cm^{-1}. MS, *m/e*: 532 $[M]^+$, 514 $[M-H_2O]^+$, 479 $[M-H_2O-Cl]^+$, 458 $[M-H_2O-2CO]^+$, 430 $[M-H_2O-3CO]^+$, 402 $[M-H_2O-4CO]^+$, 374 $[M-H_2O-5CO]^+$, 346 $[M-H_2O-6CO]^+$, 307 $[Ru_2Cl_3]^+$, 272 $[Ru_2Cl_2]^+$.

The related compound $[Ru_2(CO)_6Cl_4]$ has IR (CH_2Cl_2) ν(CO): 2144m, 2083s cm^{-1}; (KCl) ν(CO): 2148m, 2146m, 2095sh, 2087m, 2066s, 2032vw. MS, *m/e*: 514 $[M]^+$, 479 $[M-Cl]^+$, 458 $[M-2CO]^+$, 430 $[M-3CO]^+$, 402 $[M-4CO]^+$, 374 $[M-5CO]^+$, 346 $[M-6CO]^+$, 307 $[Ru_2Cl_3]^+$, 272 $[Ru_2Cl_2]^+$.

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