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# SURFACE SUPPORTED METAL CLUSTER CARBONYLS. CHEMISORPTION, REACTIVITY, AND DECOMPOSITION OF $Ru_3(CO)_{12}$ ON SILICA *

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## Summary

$Ru_3(CO)_{12}$ supported on silica is oxidised by surface Si–OH groups in presence of water and/or dioxygen to form oxidised species, probably incorporated into the silica surface, such as $Ru^{II}(CO)_n(OSi\leqslant)_2$ ($n = 2, 3$). The presence of air (involving both water and dioxygen) greatly accelerates this oxidative process. When supported in total absence of dioxygen, $Ru_3(CO)_{12}$ reacts with surface silanol groups to produce the grafted cluster $HRu_3(CO)_{10}(OSi\leqslant)$, which has been characterized by chemical methods and by infrared and Raman spectroscopies. The grafted cluster is not very stable; it is an intermediate in the formation, by controlled thermal decomposition, of both small metallic particles and some $Ru^{II}(CO)_n(OSi\leqslant)_2$ ($n = 2, 3$) carbonyl surface species (this oxidation by surface protons is also evidenced by the formation of molecular hydrogen). The formation of metallic ruthenium accounts for the production of hydrocarbons during the thermal decomposition.

## Introduction

There is a growing interest in the chemical behaviour of mononuclear [1] or cluster carbonyl complexes [2] supported on inorganic oxides. Attention has been

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* Dedicated to Professor Lamberto Malatesta in recognition of his important contributions to organometallic chemistry.

given to the behaviour of $Ru_3(CO)_{12}$ supported on silica [3–5], on alumina [3,4,6] and on magnesia [7], but the information obtained in these investigations, mainly by infrared studies, is not as satisfactory as that for the electronically-related cluster $Os_3(CO)_{12}$ supported on similar oxides [2]. In particular $Ru_3(CO)_{12}$ is kinetically more reactive than $Os_3(CO)_{12}$ and so it is difficult to deal with the real surface chemistry of the former cluster when the samples are prepared in the presence of air. This is not a problem with the less reactive $Os_3(CO)_{12}$ but with $Ru_3(CO)_{12}$ it is necessary to work under well controlled conditions in order to ensure that one is dealing with the real surface organometallic chemistry.

Working under well defined standard experimental conditions, as in our previous work on the surface chemistry of metal carbonyl clusters such as $Rh_6(CO)_{16}$ [8], $Rh_4(CO)_{12}$ [9], $Os_3(CO)_{12}$ [10,11] supported on various inorganic oxides, has allowed us to investigate the adsorption in complete absence of dioxygen and/or water of $Ru_3(CO)_{12}$ on an inorganic oxide, which if necessary can be pretreated under high vacuum at temperatures as high as 770 K for many hours, including progressive heating in high vacuum.

The present study involves a detailed analysis of the surface chemistry of $Ru_3(CO)_{12}$ supported on silica. Part of this work has already been reported in a preliminary communication [12].

## Experimental

### *Materials*

The compounds $Ru_3(CO)_{12}$ [26], $Ru_6C(CO)_{17}$ [17] and $[Ru(CO)_3Cl_2]_2$ [29] were prepared by literature methods.

The $Ru_3(^{13}CO)_{12}$ was prepared by a modification of a published method [27]; in this crude $[Ru_3O(O_2CCH_3)_6(H_2O)_3]O_2CCH_3$ [31] was treated with 90% enriched $^{13}CO$ in a 75 ml glass autoclave at 350 K and $4 \times 10^5$ Pa for 16 h. The yield was 60%.

The various gases, with purities > 99.99%, were supplied by SIO and were used as such. The 90% enriched $^{13}CO$ was supplied by MSD Isotopes IC Chemikalien GMBH. The solvents (n-pentane, $CH_2Cl_2$) were Merck spectroscopic grade, and were degassed with liquid $N_2$ and stored in argon over 5Å molecular sieves. Silica was the non porous "Aerosil 0" Degussa with 200 $m^2/g$ surface area.

### *Equipment and procedures*

For infrared studies, disks were obtained by subjecting 4–20 $mg/cm^2$ of powder to a 10 Ton pressure.

The disks were inserted into a glass unit, previously described [32], equipped for introduction of the cluster solution in a controlled atmosphere and for thermal treatment under various gases and in high vacuum. The upper side of the unit was provided with $CaF_2$ windows. The spectra were recorded with a Fourier transform spectrophotometer (Nicolet MX-1) in the absorbance mode, with a 2 $cm^{-1}$ resolution. The standard pretreatment of the silica pellets before sample adsorption involved either 16 h at $10^{-3}$ Pa and 300 K ($SiO_2$ 300 K) or 16 h at $10^{-3}$ Pa and 770 K ($SiO_2$ 770 K).

Sample introduction was by two different methods:

(a) a deaerated solution of metal carbonyl cluster was dripped on to the pellet under an argon flow from a gas-tight syringe, through a high vacuum Rotulex joint on the side of the glass unit [33].

(b) a sample deaerated solution was poured directly on to the pellet in vacuum by breaking the break-seals, as described elsewhere [32].

Method (a) allows a more homogeneous distribution of the solution on the pellet, with total loading control; method (b) may involve some flash evaporation of the solvent, with possible formation of high local loading, giving rise to an inhomogeneous distribution of the cluster on the pellet.

When not otherwise specified, method (a) was used, with a total cluster loading of 0.5–2%.

*Method of recovery of ruthenium species from the silica surface*

Reactions on silica intended to lead to sample extraction were performed with a 500 mg portion of powder pretreated at 300 K in a Schlenk-like tube. The deaerated pentane cluster solution was introduced under an argon flow to a 2–4% cluster total loading. After 1 h adsorption with stirring, the solvent was taken off by vacuum evaporation. To monitor the reaction of the sample, a portion of the silica-cluster mixture was withdrawn, always under an argon flow, and immediately examined by IR as a Nujol mull. Extraction of physisorbed species was carried out by repeated washing with pentane in argon. Thin layer chromatography of the extracted solution involved silica plates with cyclohexane as eluent.

*Gas evolution*

Gas evolution measurements were performed as described elsewhere [10].

## Results and discussion

We have investigated the adsorption and the surface chemistry of $Ru_3(CO)_{12}$ on silica pretreated in various ways and in the presence of various gases or even in vacuum. We used an approximately 0.5–2% cluster loading; different and more complex surface behaviour of $Ru_3(CO)_{12}$ is sometimes observed at higher loading (see later).

*Impregnation in presence of air*

This area has been investigated to some extent by other workers [3–5], but we report here our more detailed and complete observations.

When the impregnation is carried out in the presence of air at room temperature, a specific reaction occurs to produce well defined surface species, characterized by two strong and sharp carbonyl adsorption bands at about 2070 and 2005 $cm^{-1}$. In addition there is always a weak adsorption band at 2139 $cm^{-1}$; when the sample is kept in vacuo at 470 K for few hours this last band disappears (Fig. 1).

These surface species are quite stable at room temperature even under oxygen; only upon drastic thermal treatment under high vacuum (for instance 470–570 K at $10^{-3}$ Pa) does decarbonylation occur, in about one hour, while the sample turns from pale-yellow to brown. (Under a partial pressure of carbon monoxide a slow recarbonylation process takes place, and this point is discussed later).

Treatment of the carbonyl surface species with a partial pressure of oxygen at 470 K for 2 h produces a strong and broad band at 1875 $cm^{-1}$ while all the bands in the

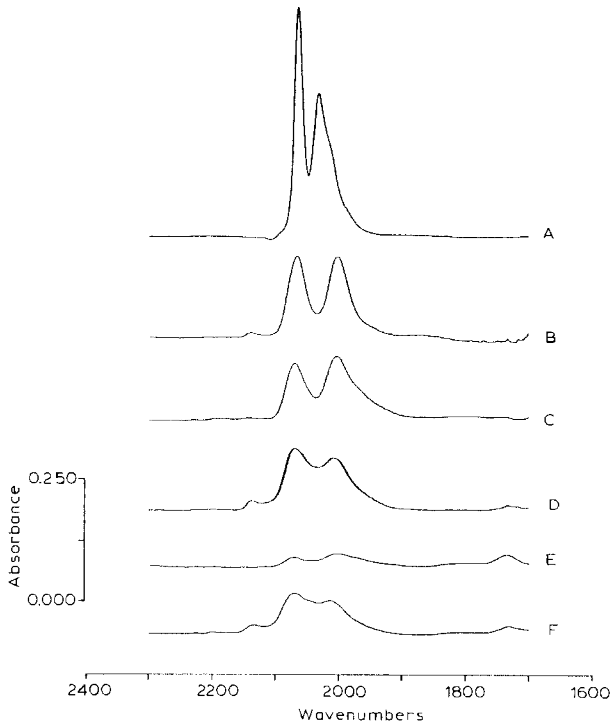


Fig. 1. Infrared spectra in the $\nu$(CO) region after the following treatments: (A) $Ru_3(CO)_{12}$ on $SiO_2$ (300 K); (B) in air at 310 K for 16 h; (C) in vacuum ($10^{-3}$ Pa), 420 K, 2 h; (D) CO ($5 \times 10^4$ Pa), 370 K, 3 h; (E) in vacuum ($10^{-3}$ Pa), 470 K, 16 h; (F) CO ($5 \times 10^4$ Pa), 370 K, 5 h.

linear carbonyl region disappear. Upon increasing the temperature up to 570 K even the strong band at low wavelength disappears, and a grey sample is formed (Fig. 2).

Upon treatment with CO ($8 \times 10^4$ Pa) at 370 K for few hours the strong band at 1875 $cm^{-1}$ disappears, and strong and sharp absorption bands again appear at 2140 and 2075 $cm^{-1}$ (Fig. 2).

The above results can be interpreted in terms of an initial decomposition of $Ru_3(CO)_{12}$ on the silica surface, with complete breakdown of the cluster cage, probably to form monomeric ruthenium(II) carbonylated species, as for the $Ru_3(CO)_{12}$ interaction with an alumina surface [3,4,6].

The positions and relative intensities of the carbonyl bands formed in the adsorption process (Fig. 1 and Table 1) suggest the presence of both $Ru^{II}(CO)_3$ (2140, 2075 $cm^{-1}$) and $Ru^{II}(CO)_2$ (2070 and 2005 $cm^{-1}$) surface species, with the ruthenium ion incorporated into the structure of the silica surface. In contrast to the results with alumina, we could not detect the presence of $Ru^{II}(CO)_4$ surface species [6].

Under our conditions $Ru^{II}(CO)_2$ predominates, because $Ru^{II}(CO)_3$ is easily decarbonylated to $Ru^{II}(CO)_2$ surface species. The assignment of the carbonyl bands to this kind of surface ruthenium(II) carbonyl species is based on the strong analogies (in shape and position) between their infrared spectra and those of some related molecular ruthenium(II) carbonyl complexes (Table 1). This assignment is substantiated by an experiment similar to that described in our investigation of the

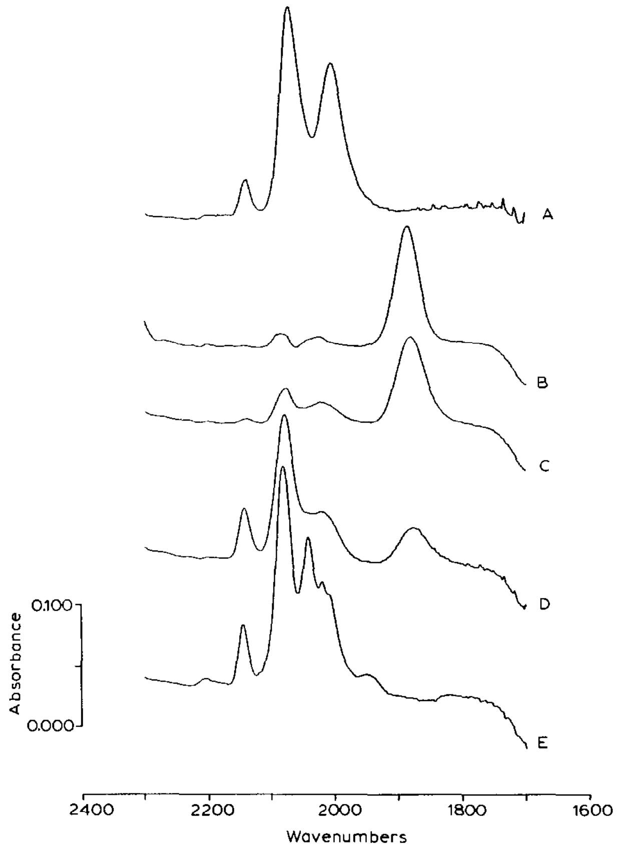


Fig. 2. Infrared spectra in the $\nu$(CO) region after the following treatments: (A) $Ru_3(CO)_{12}$ on $SiO_2$ (300 K) heated in $O_2$ ($5\times10^4$ Pa), at 370 K for 2 h; (B) $O_2$ ($5\times10^4$ Pa), 470 K, 16 h; (C) CO ($5\times10^4$ Pa), 290 K, 8 h; (D) CO ($5\times10^4$ Pa), 370 K, 16 h; (E) CO ($5\times10^4$ Pa), 470 K, 8 h.

TABLE 1

INFRARED STRETCHING FREQUENCIES OF METAL CARBONYL COMPLEXES

| Compound | $\nu$(CO) ($cm^{-1}$) | Reference |
|---|---|---|
| $Ru(CO)_4Cl_2$ | 2182w, 2132s, 2113ms, 2080s [a] | 29 |
| $Ru(CO)_3Cl_2Py$ | 2136s, 2075s, 2051s [b] | 29 |
| $Ru(CO)_2Cl_2Py_2$ | 2070s, 2006s [b] | 29 |
| $[Ru(CO)_3Cl_2]_2$ | 2143s, 2082s [b] | 29 |
|  | 2148s, 2086s [c] | This work |
|  | 2140s, 2092s, 2066s, 2045w, 2026w [d] | 13b |
| $[Ru(CO)_2Cl_2]_n$ | 2063s, 1989s [b] | 13a |
|  | 2076vs, 2018vs [d] | 13b |
| $[Ru(CO)_3(OSi\leqslant)_2]_n$ | 2148s, 2085vs [e] | This work |
|  | 2138m, 2069s, 2014m, br [f] | This work |
| $[Ru(CO)_2(OSi\leqslant)_2]_n$ | 2083s, 2026s [e] | This work |
|  | 2069s, 2005s [f] | This work |
| $[Ru(^{13}CO)_3(OSi\leqslant)_2]_n$ | 2091m, 2029s, 1969m, br [g] | This work |
| $[Ru(^{13}CO)_2(OSi\leqslant)_2]_n$ | 2020s, 1960s [g] | This work |

[a] $CH_2Br_2$. [b] $CH_2Cl_2$. [c] on $SiO_2$ (770 K). [d] Nujol mull. [e] From $[Ru(CO)_3Cl_2]_2$ on $SiO_2$ (770 K). [f] From $Ru_3(CO)_{12}$ on $SiO_2$ (770 K). [g] From $Ru_3(^{13}CO)_{12}$ on $SiO_2$ (770 K).

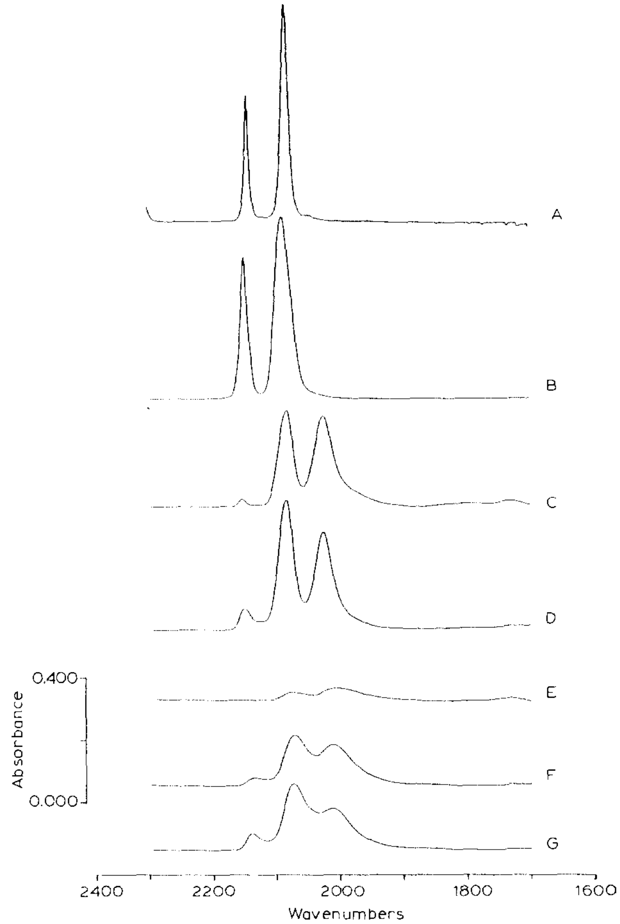


Fig. 3. Infrared spectra in the $\nu$(CO) region after the following treatments: (A) $CH_2Cl_2$ solution of $[Ru(CO)_3Cl_2]_2$; (B) the same on $SiO_2$ (300 K) after solvent removal; (C) in vacuum ($10^{-3}$ Pa), at 470 K for 2 h; (D) CO ($5\times10^4$ Pa), 290 K, 24 h; (E) in vacuum ($10^{-3}$ Pa), 570 K, 1 h; (F) CO ($5\times10^4$ Pa), 290 K, 16 h; (G) CO ($5\times10^4$ Pa), 370 K, 2 h.

surface chemistry of osmium supported on silica [10], involving the formation of surface species by the facile chemisorption on silica of a preformed ruthenium(II) carbonyl complex such as $[Ru(CO)_3Cl_2]_2$. The IR spectrum of the sample thus obtained is similar to that formed by decomposition of $Ru_3(CO)_{12}$ and suggested to be $Ru^{II}(CO)_3$ surface species (Fig. 3). Upon heating this sample under high vacuum, the band at 2148 $cm^{-1}$ disappears, giving place to a strong doublet at 2083 and 2026 $cm^{-1}$, corresponding to the surface decarbonylation previously reported to lead to $Ru^{II}(CO)_2$ surface species. Therefore we can conclude that, starting from well characterized ruthenium(II) carbonyl complexes, we have produced ruthenium(II) surface species similar to those formed by oxidative decomposition of $Ru_3(CO)_{12}$. The small differences in wavelengths are probably due to topological differences of the local surface arrangements of ruthenium(II) ions when starting from clusters or mononuclear complexes, a possibility which is supported by some slight reactivity differences, as noted later.

In seeking to obtain a deeper knowledge of this process of thermal decarbonylation we noted that admission of CO partial pressure leads to a slow transformation at room temperature: the intensity of the band at about 2026 $cm^{-1}$ decreases at higher temperatures (Fig. 3), while a band appears at high wavelengths suggesting some reversible carbonylation forming some $Ru^{II}(CO)_3$ from $Ru^{II}(CO)_2$ surface species. In contrast to the behaviour of the related osmium(II) carbonyl surface species, the $Ru^{II}(CO)_2$ could not be completely recarbonylated to the $Ru^{II}(CO)_3$ surface species.

It seems that the decarbonylation/carbonylation process involved in the surface equilibrium (eq. 1) is strongly shifted towards the dicarbonyl species.

$$Ru(CO)_3(OSi\leqslant)_2 \underset{\Delta}{\overset{CO}{\leftrightarrows}} Ru(CO)_2(OSi\leqslant)_2 + CO \qquad (1)$$

This result is not unexpected, because it is known that the complex $[Ru(CO)_3I_2]_2$ is easily transformed into $[Ru(CO)_2I_2]_n$ [13], whereas the corresponding reaction requires high temperatures in the case of $[Os(CO)_3I_2]_2$ [14].

When the $Ru^{II}(CO)_2$ surface species, formed by breakdown of $Ru_3(CO)_{12}$, is carbonylated at above 370 K, some $Ru_3(CO)_{12}$ is produced, together with $Ru^{II}(CO)_3(OSi\leqslant)_2$ (Fig. 5F). The amount of $Ru_3(CO)_{12}$ is related to the amount of water present. The formation of $Ru_3(CO)_{12}$ is not only suggested by infrared spectroscopy, but also confirmed by its extraction from the silica surface with pentane. When the initial samples were prepared by adsorption of preformed ruthenium(II) carbonyl species, such as $[Ru(CO)_3Cl_2]_2$, the formation of $Ru_3(CO)_{12}$ is much more difficult, since it takes place only to a very small extent even after a long period. Differences in the behaviour of samples of $Ru^{II}(CO)_n$ surface species prepared by different routes are not observed in other transformations: samples prepared by chemisorption of a preformed ruthenium(II) carbonyl complex, give a strong infrared band at 1890 $cm^{-1}$ upon treatment at 470 K with dioxygen ($3 \times 10^4$ Pa) for less than 10 h, with disappearance of all linear carbonyl absorptions. This behaviour is completely similar to that of samples obtained by decomposition of $Ru_3(CO)_{12}$.

We have investigated the origin and assignment of this band at low wavelength, which might reasonably be attributed as a first possibility to an unknown carbonyl compound. Starting from $Ru_3(CO)_{12}$, enriched with $^{13}CO$ (90%), the final sample obtained via the standard thermal treatment with oxygen did not show a shift of the band at about 1875 $cm^{-1}$ at lower frequencies, suggesting that this band does not come from carbonyl ligands (Fig. 4).

During the recarbonylation with $^{13}CO$ to reform $Ru^{II}(CO)_3$ surface species at room temperature, generation of $^{13}CO_2$ is observed, suggesting that this surface species can oxidise CO to $CO_2$, and therefore may possess Ru=O bonds or at least involve a high oxidation state of ruthenium. We cannot at present satisfactorily assign the band at low wavelength; it is obviously related to the new surface ruthenium entity formed by oxidation with molecular oxygen, because it disappears upon reduction with CO. Its high intensity does not favour an assignment as a combination of a Ru=O stretching band.

We now discuss the drastic thermal treatment under vacuum of the ruthenium(II) carbonyl surface species, which has been briefly described. Drastic thermal treatment (570 K for about 1 h under a vacuum of $10^{-3}$ Pa) of any sample (produced

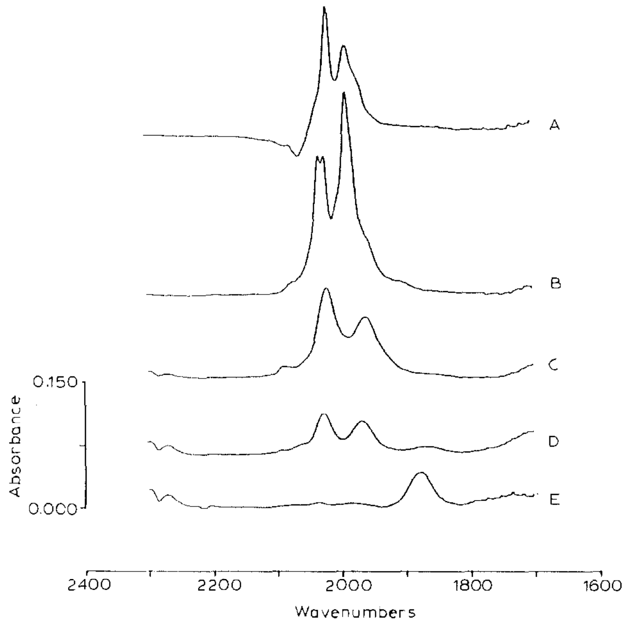


Fig. 4. Infrared spectra in the $\nu$(CO) region after the following treatments: (A) $Ru_3(^{13}CO)_{12}$ on $SiO_2$ (670 K); (B) in vacuum ($10^{-3}$ Pa) at 340 K for 1 h; (C) $O_2$ ($5\times10^4$ Pa), 350 K, 1 h; (D) $O_2$ ($5\times10^4$ Pa), 420 K, 1 h; (E) $O_2$ ($5\times10^4$ Pa), 470 K, 1 h.

from $Ru_3(CO)_{12}$ or $[Ru(CO)_3Cl_2]_2$) leads to total decarbonylation. A quick carbonylation occurs when CO ($6 \times 10^4$ Pa) is admitted at room temperature, finally leading to a broad infrared spectrum (Fig. 1 and 3) which can be interpreted as due to some $Ru^{II}(CO)_3$ surface species (absorption bands at 2140 and 2070 $cm^{-1}$) together with ruthenium metallic particles covered with CO (broad band centered at about 2035 $cm^{-1}$). The shape and other features of this spectrum are quite different when the original material is $Ru_3(CO)_{12}$ than when it is $[Ru(CO)_3Cl_2]_2$; in the case of the cluster, metallic particles are clearly present (Fig. 1F) but there are very few of these when the original material is $[Ru(CO)_3Cl_2]_2$ (Fig. 3F). This observation again indicates some topological surface effect in the mechanism of aggregation of the incorporated oxidised ions, as already noted in the recarbonylation of the $Ru^{II}(CO)_n(OSi\leq)_2$ species to form $Ru_3(CO)_{12}$. These observations are not unexpected, because similar topological effects have been reported in the reduction with CO and $H_2O$ of $Rh^I(CO)_2$ surface species to $Rh_4(CO)_{12}$ or $Rh_6(CO)_{16}$ [8,9].

*Impregnation in presence of dry dioxygen*

Impregnation in the presence of air involves the presence of both surface water and molecular oxygen. In order to avoid the effects due to the presence of surface water we also studied the impregnation of $Ru_3(CO)_{12}$ on a partially dehydroxylated silica surface (treatment under high vacuum at 770 K for 16 h) in presence of dry dioxygen (Fig. 5). Under these conditions a simple physisorption of $Ru_3(CO)_{12}$ occurs; its oxidative decomposition at room temperature to form a mixture of $Ru^{II}(CO)_3$ and $Ru^{II}(CO)_2$ surface species occurs very slowly (it takes about 10 days for complete decomposition of the original cluster). On the other hand surface water accelerates the $Ru_3(CO)_{12}$ oxidative decomposition process. Thus when silica is

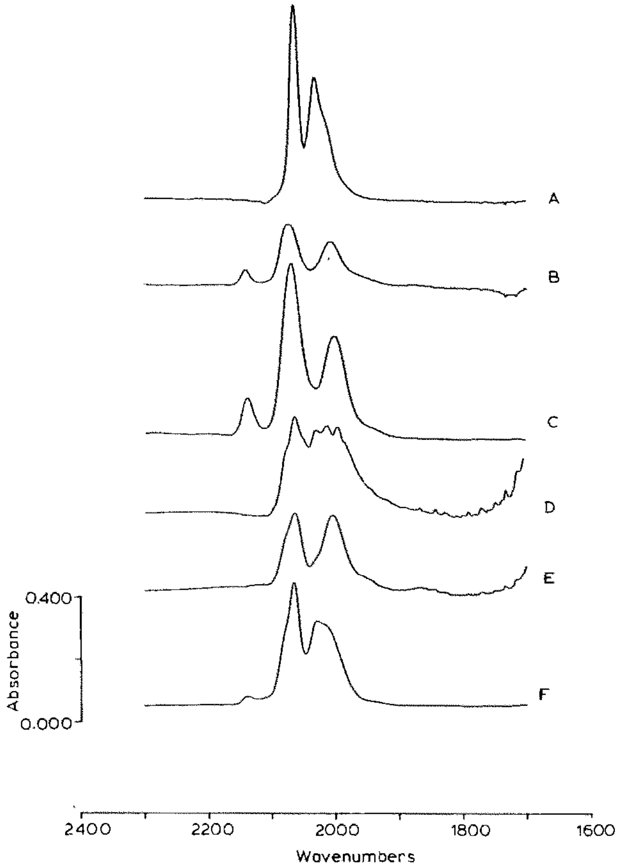


Fig. 5. Infrared spectra in the $\nu$(CO) region after the following treatments: (A) $Ru_3(CO)_{12}$ on $SiO_2$ (300 K); (B) $O_2$ ($5\times10^4$ Pa) at 290 K for 10 days; (C) the same initial sample in CO ($5\times10^4$ Pa), 290 K 10 days; (D) the same initial sample in Ar ($10^5$ Pa) saturated with $H_2O$, 290 K, 16 h; (E) sample (D) in Ar ($10^5$ Pa) saturated with $H_2O$, 310 K, 20 h; (F) sample obtained as (B), (C) or (E) after treatment in CO ($5\times10^4$ Pa) saturated with $H_2O$, 390 K, 24 h.

treated under vacuum at room temperature (which leaves many layers of adsorbed water on the surface) the same process is complete within 5 days. The oxidised species formed respond to various treatments (high vacuum at 570 K, dioxygen at 470 K, high vacuum at room temperature etc.) in the way previously described for the oxidised samples prepared by impregnation of $Ru_3(CO)_{12}$ in the presence of air.

It is evident that the presence of surface water may play a relevant role in the oxidative decomposition of $Ru_3(CO)_{12}$ on the silica surface.

*Impregnation under argon in presence of water*

In order to avoid effects due to dioxygen, we investigated the impregnation under argon of silica saturated with a partial pressure of water ($2.2\times10^3$ Pa). Under these conditions physisorption occurs first but after 16 h a significant and selective transformation into $Ru^{II}(CO)_2$ surface species is observed (Fig. 5). The position of the two strong infrared bands is dependent upon the amount of surface water and upon simple evacuation at room temperature the frequencies shift from 2061–1995 $cm^{-1}$ to 2067–2005 $cm^{-1}$.

As already pointed out, upon treatment with a partial pressure of CO ($10^5$ Pa) some reduction occurs, particularly at temperatures of about 330–350 K, to form some $Ru_3(CO)_{12}$ within 2 h (Fig. 5).

The presence of a significant amount of surface water is a necessary condition for the reformation of the original cluster. A similar effect of water has been observed upon treatment of $Rh^I(CO)_2$ surface species with CO to produce $Rh_6(CO)_{16}$ [9]. If the carbonylated sample is left at room temperature, even under CO, oxidation of $Ru_3(CO)_{12}$ occurs very slowly to reform $Ru^{II}(CO)_n$ ($n$ = 2, 3) surface species. It is evident that oxidative decomposition of $Ru_3(CO)_{12}$ brought about by surface water; however the presence of both surface water and dioxygen is a condition for easy oxidation.

*Impregnation under argon or in vacuo*

We have entered into an area not examined in previous investigations. Use of our standard conditions (see Experimental section) allows us to study the adsorption of $Ru_3(CO)_{12}$ on partially dehydroxylated silica (treated for instance at 770 K for 16–20 hours under high vacuum) in absence of both surface water and dioxygen. Thus the infrared, the Raman spectra and the analysis of the gas phase were always carried out in situ without transfer of the sample in air.

When $Ru_3(CO)_{12}$ is adsorbed on such silica under vacuum (or under argon) the resulting sample exhibits infrared bands at 2063(s), 2032(m), 2018(m,sh) $cm^{-1}$ which are similar in frequency and intensity to those of $Ru_3(CO)_{12}$ after simple physisorption. Upon treatment of this sample under vacuum at 350 K for 1 h or at 300 K for 16 h progressive change of the spectrum is observed, with new carbonyl bands appearing at 2112(w), 2078(m), 2068(m), 2033(s,br) and 1995(m,sh) $cm^{-1}$ (Fig. 6). The new spectrum is fairly similar in intensity and frequencies to that of the well characterized osmium cluster $(H)Os_3(CO)_{10}(OSi\equiv)$ grafted on to a silica surface (Table 2); moreover, similar spectra are reported for molecular clusters with similar structures such as $(H)Ru_3(CO)_{10}X$ ($X = SC_2H_5$, Cl, Br, I) (Table 2).

Evidence for the persistence of metal–metal bonds is also provided by Raman spectroscopy, which was used to confirm the presence of metal–metal bonds in the analogous osmium cluster grafted on an alumina surface [15].

The Raman spectrum of the sample obtained by adsorption of $Ru_3(CO)_{12}$ under argon followed by controlled decarbonylation at 320 K under high vacuum, exhibits several bands in the low frequency region which are typical of $Ru_3(CO)_{12}$, but also two additional bands at 200 and 162 $cm^{-1}$ which can be tentatively assigned to metal–metal stretching vibrations of the grafted cluster (the analogous osmium cluster also exhibits two bands at 159 and 118 $cm^{-1}$, respectively [15]). The stoichiometry of the surface reaction, (eq. 2), was confirmed by an investigation of the gas evolved during the thermal treatment (Fig. 7).

$$Ru_3(CO)_{12} + HOSi\equiv \leftrightarrows (H)Ru_3(CO)_{10}(OSi\equiv) + 2CO \qquad (2)$$

The gas evolved from physisorbed $Ru_3(CO)_{12}$ as the temperature is raised proved to be CO 1.7 ± 0.2 moles per mole of cluster in the 340 to 370 K temperature range. No significant evolution of $H_2$ or $CO_2$ was observed in this range (Fig. 7). These

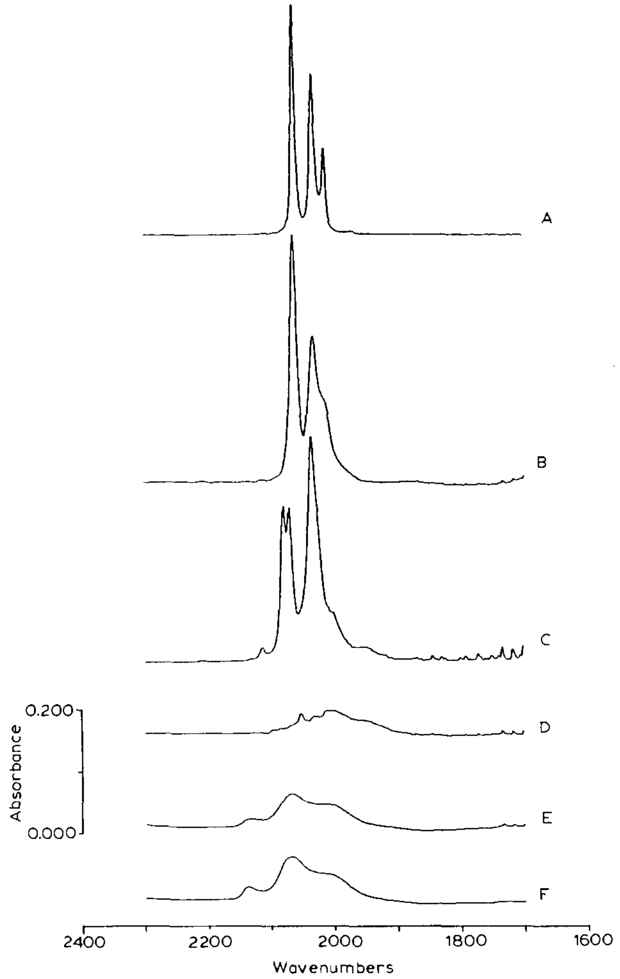


Fig. 6. Infrared spectra in the $\nu$(CO) region after the following treatments: (A) pentane solution of $Ru_3(CO)_{12}$; (B) $Ru_3(CO)_{12}$ on $SiO_2$ (770 K); (C) in vacuum ($10^{-3}$ Pa) at 350 K for 2 h; (D) in vacuum ($10^{-3}$ Pa), 520 K, 3 h; (E) CO ($5\times10^4$ Pa), 290 K, 24 h; (F) CO ($5\times10^4$ Pa), 390 K, 2 h.

results are in agreement with the stoichiometry of the proposed surface reaction (eq. 2), and consistent with a grafted structure for the resulting ruthenium species.

We can conclude that under our well controlled conditions, the first species obtained upon thermal decomposition of physisorbed $Ru_3(CO)_{12}$ is a grafted molecular cluster resulting from the oxidative addition of a surface silanol group to a metal–metal bond of the original $Ru_3(CO)_{12}$.

The grafting process is not facilitated by presence of surface water; thus, when silica is treated under high vacuum for 16 h at 300 K, to form a surface with many layers of water, the controlled decarbonylation of physisorbed $Ru_3(CO)_{12}$ occurs slowly (few days) at room temperature, whereas under the same conditions it occurs in only a day if the silica is pretreated under high vacuum at 770 K, leading to a partially dehydroxylated surface. The grafting process is inhibited, as for $Os_3(CO)_{12}$ [10], by a CO atmosphere. Under these conditions $Ru_3(CO)_{12}$, physisorbed on a partially dehydroxylated silica (treatment at 770 K for 16 h at $10^{-3}$ Pa), is stable up

(*Continued on p. 140*)

TABLE 2

INFRARED STRETCHING FREQUENCIES OF METAL CARBONYL COMPLEXES

| Compound | $\nu$(CO) (cm$^{-1}$) | Reference |
|---|---|---|
| $Ru_3(CO)_{12}$ | 2060vs, 2030s, 2011m [a] | This work |
|  | 2063vs, 2032s, 2018m, sh [b] | This work |
| $Ru_3(^{13}CO)_{12}$ | 2030w, 2011vs, 1998w, 1985s, 1967s [a] | This work |
|  | 2014vs, 1985s, 1975m, sh | This work |
| $HRu_3(CO)_{10}(OSi\equiv)$ | 2112w, 2078s, 2068s, 2033vs, 1995m, sh [c] | This work |
| $HRu_3(^{13}CO)_{10}(OSi\equiv)$ | 2071w, 2029s, 2021s, 1986vs, 1964m, sh [d] | This work |
| $HRu_3(CO)_{10}(SC_2H_5)$ | 2105m, 2064s, 2056s, 2025vs, 2012m, 2008s, 1994m [a] | 35 |
| $HRu_3(CO)_{10}Cl$ | 2113vw, 2077s, 2070s, 2034sh, 2030vs, 1997w [a] | 36 |
| $HRu_3(CO)_{10}Br$ | 2112vw, 2076s, 2069s, 2030vs, 2024sh, 1996w [a] | 36 |
| $HRu_3(CO)_{10}I$ | 2109vw, 2072s, 2066s, 2028vs, 2021sh, 1995w [a] | 36 |
| $HOs_3(CO)_{10}(OSi\equiv)$ | 2114w, 2079s, 2068s, 2032vs, 2012s, sh, 1995m | 10 |
| $HOs_3(CO)_{10}(OSiEt_3)$ | 2110w, 2070vs, 2057s, 2020vs, 1995m, 1982w [e] | 34 |
| $HOs_3(CO)_{10}(OSiPh_3)$ | 2110w, 2070vs, 2057s, 2020vs, 1997s, 1980m [f] | 34 |
| $HOs_3(CO)_{10}(OPh)$ | 2113w, 2075vs, 2065s, 2025vs, 2008s, 1991m, 1987m [g] | 30 |
| CO/Ru metal | $\theta$ [h] = 1  2037br<br>$\theta$ = 0.1  1985br | This work |

[a] Hexane. [b] on $SiO_2$ (770 K). [c] From $Ru_3(CO)_{12}$ on $SiO_2$ (770 K). [d] From $Ru_3(^{13}CO)_{12}$ on $SiO_2$ (770 K). [e] Benzene. [f] $CH_2Cl_2$. [g] Cyclohexane. [h] $\theta$ = surface coverage.

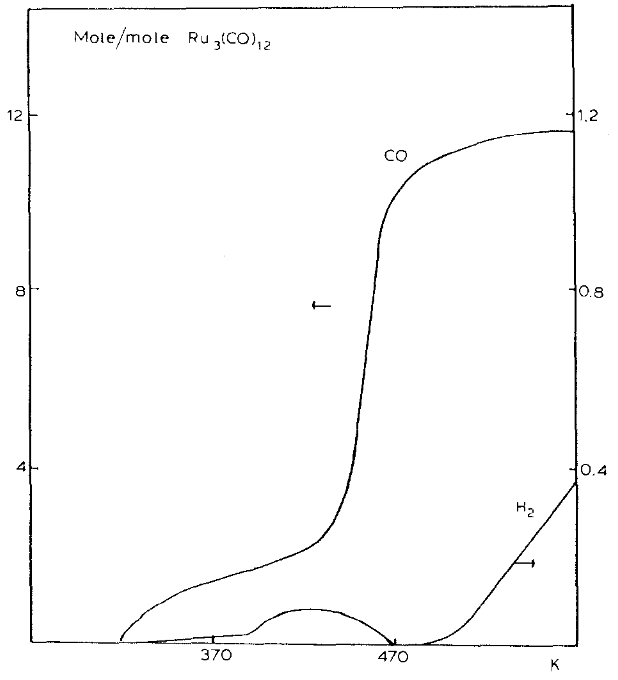


Fig. 7. CO and $H_2$ evolution in the thermal decarbonylation of $Ru_3(CO)_{12}$ adsorbed on $SiO_2$ (770 K).

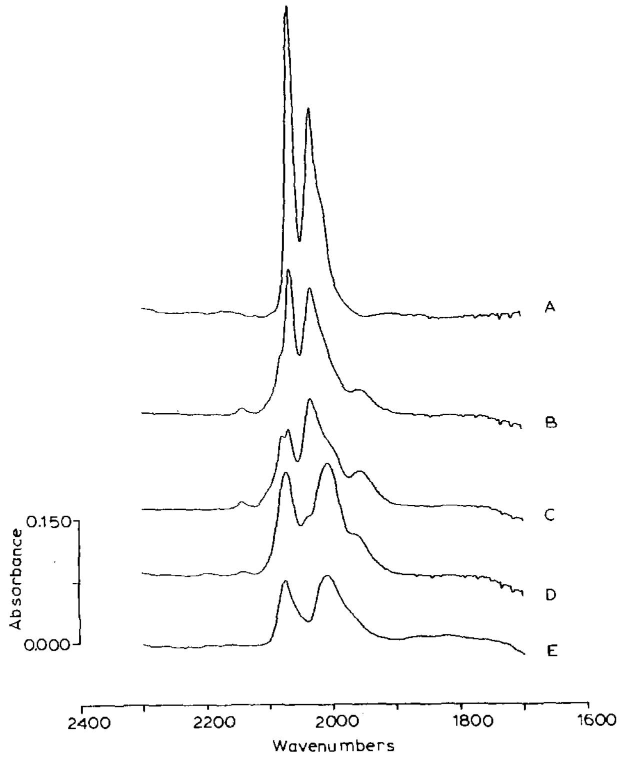


Fig. 8. Infrared spectra in the $\nu$(CO) region after the following treatments: (A) $Ru_3(CO)_{12}$ on $SiO_2$ (300 K); (B) Ar ($10^5$ Pa) at 290 K for 48 h; (C) Ar ($10^5$ Pa), 340 K, 1 h; (D) Ar ($10^5$ Pa), 370 K, 48 h; (E) Ar ($10^5$ Pa), 520 K, 3 h.

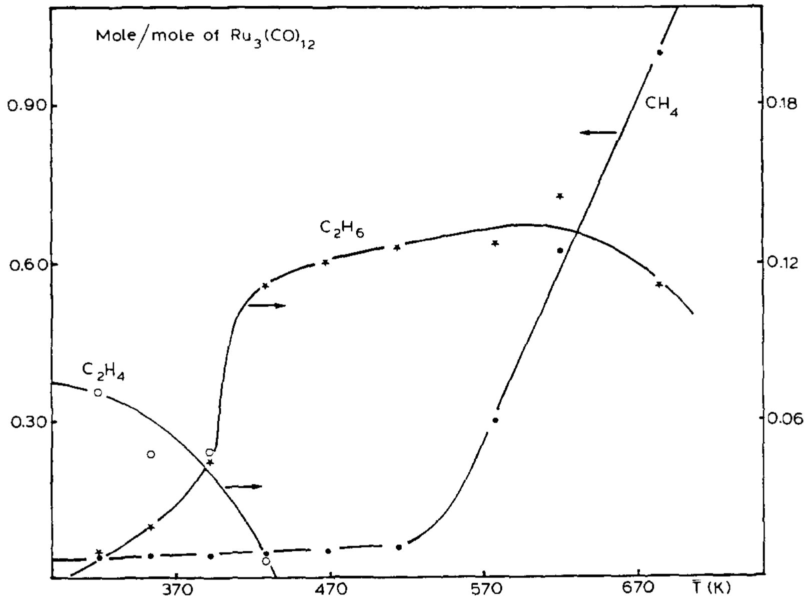


Fig. 9. Hydrocarbon evolution in the thermal decarbonylation of $Ru_3(CO)_{12}$ adsorbed on $SiO_2$ (770 K).

to 470 K and only some sublimation occurs. However a very slow oxidation to $Ru(CO)_n(OSi\leqslant)_2$ ($n = 2, 3$) species occurs even under carbon monoxide pressure at room temperature (Fig. 5C).

The surface grafted ruthenium cluster is less stable toward oxidation with oxygen or simple thermal decomposition than the related osmium species. Upon heating above 390 K (up to about 520 K) progressive transformations occur involving about 10 CO moles per mole of cluster. As some of $H_2$ is concurrently formed, we can identify the process as a partial oxidation of zerovalent ruthenium by surface OH groups with formation of surface oxidised species such as $Ru^{II}(CO)_n(OSi\leqslant)_2$ ($n = 2, 3$) (Fig. 7 and 8). The relative amount of $H_2$ is dependent upon the surface loading, being higher at a relatively low surface loading. Formation of hydrocarbons ($C_2H_4$, $C_2H_6$ and $CH_4$) is also observed above 343 K (Fig. 9).

After thermal decarbonylation of the grafted cluster under high vacuum (16 h and $10^{-3}$ Pa) and above 390 K, the resulting infrared spectrum exhibits a broad peak centered at about 2035 $cm^{-1}$, together with narrow peaks at 2130, 2071 and 2005 $cm^{-1}$. The relative intensities of the two classes of peaks are dependent upon the surface loading and the method of preparation of the samples. At relatively low loading (0.1–1% of $Ru_3(CO)_{12}$) the narrow peaks are predominant, but they become less important at higher loading (3–12% of $Ru_3(CO)_{12}$) (Fig. 10). The broad band also appears at relatively low loading when the sample is prepared by technique (b) described in the experimental section. Upon increasing the temperature under high vacuum the frequency of the broad carbonyl band shifts from 2037 ($\theta = 1$) to 1985 $cm^{-1}$ ($\theta = 0.1$). It is well known that this behaviour is related to release of CO adsorbed on metallic particles, and this is reversible, as shown by the frequency and intensity of the carbonyl absorption after recarbonylation at 290 K (Fig. 11).

These results can be interpreted in terms of thermal decomposition of the grafted cluster to form a mixture of metallic particles and oxidised $Ru(CO)_n(OSi\leqslant)_2$ ($n = 2, 3$) species on the surface. The relative proportions of the two processes are governed

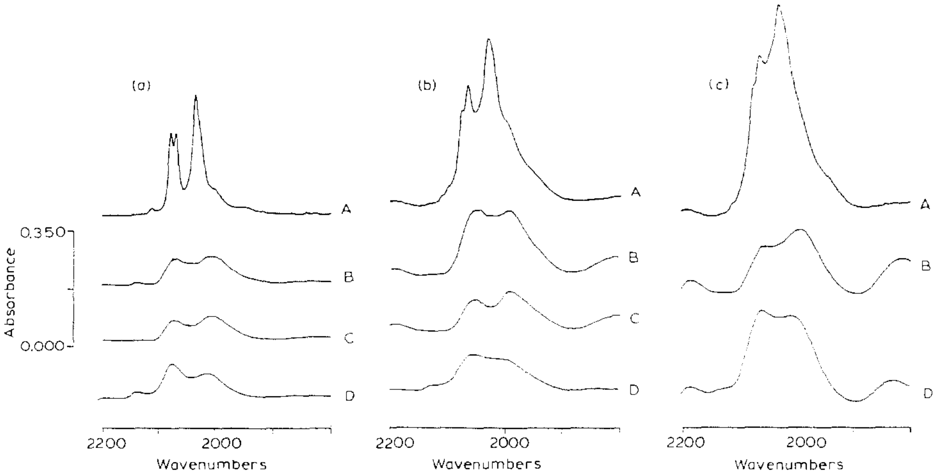


Fig. 10. Infrared spectra in the $\nu$(CO) region after the following treatments: (A) $Ru_3(CO)_{12}$ on $SiO_2$ (770 K) in vacuum ($10^{-3}$ Pa) at 340 K for 3 h; (B) in vacuum ($10^{-3}$ Pa), 370 K, 16 h; (C) in vacuum ($10^{-5}$ Pa), 420 K, 12 h; (D) CO ($5\times10^4$ Pa), 390 K, 24 h. (a), (b), and (c) are referred, respectively, to a 0.5, 5 and 12% total cluster loading.

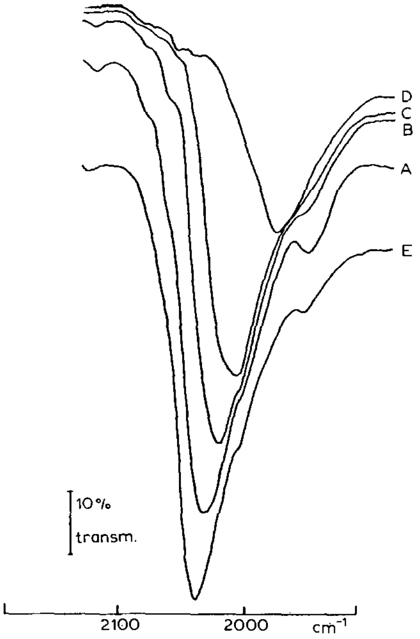


Fig. 11. Infrared spectra in the $\nu$(CO) region after the following treatments: (A) $Ru_3(CO)_{12}$ on $SiO_2$ (770 K) in vacuum ($10^{-3}$ Pa) at 350 K for 1 h followed by heating at 410 K for 5 h; (B) in vacuum ($10^{-3}$ Pa), 440 K, 16 h; (C) in vacuum ($10^{-3}$ Pa), 470 K, 5 h; (D) in vacuum ($10^{-3}$ Pa), 530 K, 5 h. (E) CO adsorption ($4 \times 10^4$ Pa) at 320 K for 5 h followed by vacuum )$10^{-3}$ Pa) at 300 K for 4 h. The spectra recorded in the transmittance mode, were runned on a Perkin-Elmer 225 spectrophotometer.

by the surface loading, and in particular by the local loading of the surface (see Experimental). The presence of metallic particles is confirmed by electron microscopy; there is a very narrow distribution of particle sizes at around 14 Å; similar sizes have been noted by other authors [16].

If the decomposition of the grafted cluster is carried out in the presence of air (involving the presence of dioxygen and water), an oxidised species is formed characterized by two strong IR bands at 2066 and 2002 cm$^{-1}$, corresponding to the formation of $Ru^{II}(CO)_2$ surface species. This process occurs at room temperature in about 36 h. In an atmosphere of dioxygen it requires 5 days (in this case a weak infrared band at 2135 cm$^{-1}$ also appears, consistent with the presence of some $Ru^{II}(CO)_3$ surface species). The transformation is faster at higher temperatures and is complete in about one hour at 340 K.

On the other hand the addition to the grafted cluster of a partial pressure of water alone ($2\text{–}3 \times 10^3$ Pa) under argon does not produce significant effects at room temperature and after 12 h the original infrared spectrum is unchanged. However, admission of some dioxygen leads to a rapid decomposition to oxidised ruthenium(II) surface species.

We conclude that the grafted cluster is unstable toward dioxygen even at room temperature, and is transformed into a complete oxidation to $Ru(CO)_2(OSi\lessgtr)_2$ surface species; the concurrent presence of water favours this oxidation (as observed with physisorbed $Ru_3(CO)_{12}$).

The grafted cluster $(H)Ru_3(CO)_{10}(OSi\lessgtr)$ can be recarbonylated to $Ru_3(CO)_{12}$ at room temperature, more easily in the presence of water (a similar effect was reported for the corresponding carbonylation process with $(H)Os_3(CO)_{10}(OSi\equiv)$ [10]). On silica treated under vacuum at 300 K (presence of water on the surface) the grafted cluster is quickly recarbonylated to $Ru_3(CO)_{12}$ under CO partial pressure, the colour of the sample turning from yellow-orange to yellow. With partially dehydroxylated silica (treated at $10^{-3}$ Pa and at 770 K for 16 h) the same process requires temperatures of about 350–370 K.

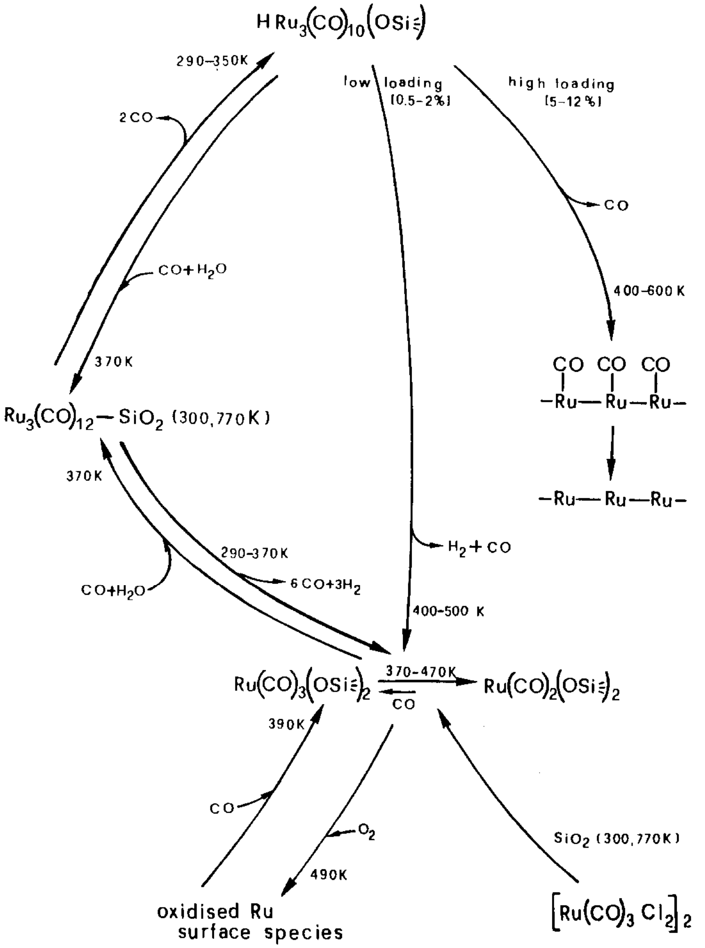
The formation of $Ru_3(CO)_{12}$ is supported not only by infrared evidence, but also by the isolation of the $Ru_3(CO)_{12}$ so formed; thus extraction of the silica with anhydrous pentane leads to recovery of the physisorbed $Ru_3(CO)_{12}$. If the original grafted cluster is generated under vacuum (and not under argon) the $Ru_3(CO)_{12}$ so obtained is always contamined with small amounts of $Ru_6C(CO)_{17}$, characterized by infrared bands in pentane solution at 2045 and 2061 $cm^{-1}$. The presence of this product is confirmed by chromatographic separation of the mixture of $Ru_3(CO)_{12}$ and $Ru_6C(CO)_{17}$ obtained by pentane extraction of the silica sample. The formation even at 340 K of a higher nuclearity cluster containing a carbidic carbon is noteworthy, because this $Ru_6$ cluster is usually thermally obtained from $Ru_3(CO)_{12}$ in relatively low yields either by simple pyrolysis or by treatment of its solution at temperatures of at least 420 K [17]. It seems that the silica surface both facilitates the formation of carbidic atom by CO deoxygenation at relatively low temperatures and increases the cluster nuclearity. The latter effect, which requires a high mobility of molecular metal fragments on the surfaces of an inorganic oxide such as silica, was previously noted in the rapid transformation of physisorbed $Rh_4(CO)_{12}$ into physisorbed $Rh_6(CO)_{16}$ [9].

Similar formation of the above $Ru_6$ carbidic cluster probably occurs during the thermal carbonylation of $Ru^{II}(CO)_2$ to $Ru^{II}(CO)_3$ surface species at temperatures of about 370 K, particularly when the oxidised ruthenium surface carbonyl species is produced by decomposition of $Ru_3(CO)_{12}$. Under these conditions a strong band at about 2040–2045 $cm^{-1}$ appears, together with the carbonyl bands due to $Ru^{II}(CO)_2$ and $Ru^{II}(CO)_3$ surface species (Fig. 2E). This band can be attributed to $Ru_6C(CO)_{17}$, but in this case we have not confirmed the presence of this cluster by extraction from the support. The formation of $Ru_6C(CO)_{17}$ may take place via the intermediate reduction to $Ru_3(CO)_{12}$, which on the surface at the temperature involved, can undergo pyrolysis to the $Ru_6$ carbidic cluster.

## Conclusions

When adsorbed on silica, $Ru_3(CO)_{12}$ behaves quite differently from $Fe_3(CO)_{12}$; its surface chemistry finally resembles that of $Os_3(CO)_{12}$ in some aspects. In particular while with $Fe_3(CO)_{12}$, oxidised carbonyl species on the surface are not sufficiently stable to be characterized [18], the progressive interaction of $Ru_3(CO)_{12}$ with the silanol groups of the silica surface (see Scheme 1) is fairly similar to that of $Os_3(CO)_{12}$ [10], leading to quite stable surface oxidised carbonyl species of formula $M(CO)_n(OSi\equiv)_2$ ($n = 2, 3$; M = Ru, Os). In particular, the first step of interaction in both cases is an oxidative addition of a silanol group to a metal–metal bond of the original metal cage, to form an oxidised carbonyl cluster covalently grafted to the silica surface, and this can be characterized. However the reactivity of this grafted ruthenium surface species is quite different from that of the corresponding osmium species [10]: in contrast to the osmium grafted cluster it is unstable at room temperature in presence of dioxygen. It decomposes thermally at relatively low temperatures between 350 and 370 K (as against the minimum of 420 K required for the osmium analogue); it reacts readily with CO in the presence of water to regenerate physisorbed $Ru_3(CO)_{12}$ (such a reversible carbonylation to the original physisorbed cluster is very slow and difficult with the osmium analogue [10]). In consequence the various steps leading to surface grafting and then to formation of metallic particles and/or of surface ruthenium(II) carbonyl species (see Scheme 1) require well defined and closely controlled conditions, which is not the case with $Os_3(CO)_{12}$. Some of the ruthenium species reported in Scheme 1 cannot be identified if the experiments are not carried out under appropriate conditions, which accounts for some of the previous observations [3–5]. In making these general observations, some processes taking place on the silica surface merit further discussion.

During the thermal decomposition, formation of some ruthenium metal particles



SCHEME 1

occurs even at 390 K, so that these particles are covered with absorbed CO even if the decarbonylation process is carried out under vacuum.

The tendency to generate small metallic particles under well controlled conditions and rather low temperatures is one of the few aspects of similarity with the behaviour of $Fe_3(CO)_{12}$ [18]; with $Os_3(CO)_{12}$ metallic particles are formed with great difficulty and only at high temperatures (over 573 K), so that complete dissociation of adsorbed CO concurrently occurs [10]. With $Fe_3(CO)_{12}$ the thermally generated iron particles are not covered by CO only because CO dissociation occurs from the surface of small iron particles even at low temperatures [18].

With both $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ two parallel thermal processes occur: decomposition to metal particles and oxidation to surface ruthenium(II) or iron(II) species, with hydrogen evolution, by the silanol surface groups. Both hydrogen and carbon monoxide coming from the decomposition of $Ru_3(CO)_{12}$ are responsible for the formation of hydrocarbons (Fig. 9) at a certain stage of the thermal decarbonylation. The hydrocarbons are very likely to be formed on the surface of the very small metallic particles, because they appear at temperatures which are quite close to the typical temperatures of metal particle formation by cluster thermal decomposition.

In addition the two parallel processes (decomposition and aggregation to metal particles and oxidation with parallel hydrogen evolution to form ruthenium(II) carbonyl surface species) occur to different extents depending on the surface loading, and in particular on the local surface loading. For such reason formation of ruthenium metal particles is dependent not only upon the amount of added cluster, but also on the method of its addition (see Experimental section). This effect of the surface loading is probably related to the fact that only specific Si–OH surface groups can chemically interact with the physisorbed cluster. When these groups are fully saturated, the remaining physisorbed cluster decomposes only by a simple thermal process (not by a surface chemical process) to generate metallic particles pyrolytically (Fig. 10).

Such a thermal process, which obviously occurs at high surface loadings, could also account for the contradictory results and conclusions reached by different groups in the study of thermal decomposition of $Os_3(CO)_{12}$ supported on silica [10,19]. It is known that thermal pyrolysis of $Os_3(CO)_{12}$ does produces not only metallic particles but also some polynuclear carbonyl clusters [20], and this has been recognized by some authors [19] as an important step of the thermal decomposition of $Os_3(CO)_{12}$ physisorbed on silica at high loading. As these polynuclear carbonyl clusters are not generated with low surface loadings [10] they obviously would not be detected by investigations using these conditions.

In presence of surface water and/or dioxygen, ruthenium metal particles are not formed at all, but only ruthenium(II) carbonyl surface species, produced independently by both surface loading and temperature (Fig. 8). This effect is consistent with the facile formation of similar oxidised surface carbonyl species under a partial pressure of dioxygen [10] starting from $Os_3(CO)_{12}$ physisorbed on silica (although a temperature of at least 370 K is required with this metal).

It is relevant to note that relatively stable surface hydridocarbonyl species of osmium (probably osmium(III)) have been proposed as the first step in the oxidative decomposition of the grafted osmium cluster; hydrogen evolution is not detected during the surface oxidation by silanol groups [21].

Similar hydridocarbonyl intermediates can not be formed in the case of $Ru_3(CO)_{12}$

because the expected hydrogen evolution is observed. This observation, along with the previous ones, suggests, that the similarities between the behaviour of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$, when adsorbed on silica, are often only apparent rather than real. In agreement with this, while a complete and reversible thermal decarbonylation occurs with $Os^{II}(CO)_n$ surface species (as it does with $Rh^I(CO)_2$ surface species [8]), such a process takes place only partially with the related $Ru^{II}(CO)_n$ surface species, and is accompanied in this case by some reduction and aggregation to form metallic particles. However, the chemistry of the intermediate step of reversible partial decarbonylation, shown in equation 1, is typical of both ruthenium(II) and osmium(II) carbonyl surface species, although this process is cleaner and more reversible with osmium than with ruthenium.

The behaviour of oxidised ruthenium carbonyl surface species is quite different when they are generated from $Ru_3(CO)_{12}$ or $[Ru(CO)_3Cl_2]_2$. Both thermal aggregation to metal particles and reductive carbonylation to regenerate physisorbed $Ru_3(CO)_{12}$ are much easier when the original starting material is $Ru_3(CO)_{12}$. These observations support the view that different starting materials lead to oxidised carbonyl surface species with different structural and topological surface arrangements (these to some extent reflecting the original structure of starting material). This view is also supported by the easy reductive carbonylation of $Rh^I(CO)_2$ surface species (formed from $Rh_4(CO)_{12}$ or $Rh_6(CO)_{16}$) to regenerate the original cluster, compared with the slow process observed when the original material is $[Rh(CO)_2Cl]_2$ [8]. When the original material is a cluster, the oxidised species can be ordered on the surface in close arrangements of carbonyl units similar to those observed in the cubane like molecular structures of $[Os(CO)_3O]_4$ [22], $[Re(CO)_3OH]_4$ [23] or $[M(CO)_3(OH)]_4$ (M = Mo, W) [24]. Such an hypothesis is supported by direct characterization by electron microscopy of ordered and compact surface structures corresponding to the oxidised carbonyl species obtained by decomposition of osmium carbonyl clusters on alumina [25]; in this study the existence of small metal aggregates was observed, and the absence of direct osmium–osmium bonds, already inferred from EXAFS studied [10] was confirmed. Our work indirectly provides further confirmation of the existence of such well ordered structures of metal ions on the surface.

In contrast to $Rh_6(CO)_{16}$ or $Rh_4(CO)_{12}$, synthesis of $Ru_3(CO)_{12}$ from oxidised ruthenium complexes takes place in solution, only under rather drastic conditions [26,27], so it is likely that it occurs readily when starting from well compact and ordered surface structures of oxidised ruthenium(II) species which probably facilitate the triangular metallic arrangement. The analogous reduction does not occur with osmium, probably because of the low reactivity of the osmium atoms or ions on the silica surface, in keeping with the well known kinetic inertness characteristic of this kind of osmium chemistry. Finally following treatment at high temperatures with dioxygen we have obtained evidence for surface species of ruthenium which oxidise CO to $CO_2$ and which probably correspond to ruthenium surface species in high oxidation states (although they are far from being well characterised).

Our work has shown that $Ru_3(CO)_{12}$ on silica displays a complex behaviour which can be interpreted in terms of the known organometallic chemistry of ruthenium. Such an approach, which has been only recently developed [2,28], is likely to lead to rationalisation of the rather empirical approach towards the preparation of heterogeneous supported metallic catalysts and to understanding of their behaviour under different reaction conditions.

## References

1 D.C. Bailey, S.H. Langer, Chem. Rev., 81 (1981) 109; J. Phillips and J.A. Dumesic, Appl. Catal., 9 (1984) 1.
2 R. Psaro and R. Ugo, in H. Knözinger, B.C. Gates and L. Guczi (Eds.), Metal Clusters in Catalysis, Elsevier, Amsterdam, 1985, in press.
3 J. Goodwin and C. Naccache, J. Mol. Catal., 14 (1982) 259.
4 V.L. Kuznetsov, A.T. Bell and Y.I. Yermakov, J. Catal., 65 (1980) 374; J. Evans and G.S. McNulty, J. Chem. Soc., Dalton Trans., (1984) 1123.
5 Z. Schay, K. Lázár, J. Mink and L. Guczi, J. Catal., 87 (1984) 179.
6 A. Zecchina, E. Guglielminotti, A. Bossi and M. Camia, J. Catal., 74 (1982) 225; H. Knözinger, Y. Zhao, B. Tesche, R. Barth, R. Epstein, B.C. Gates and J.P. Scott, Faraday Disc. Chem. Soc., 72 (1982) 53; S. Dobos, I. Böszörmenyi, V. Silberer, L. Guczi and J. Mink, Inorg. Chim. Acta, 96 (1985) L13.
7 R. Pierantozzi, E.G. Valagene, A.F. Norguist and P.N. Dyer, J. Mol. Catal., 21 (1983) 189.
8 J.L. Bilhou, V. Bilhou-Bougnol, W.F. Graydon, J.M. Basset, A.K. Smith, G.M. Zanderighi and R. Ugo, J. Organomet. Chem., 153 (1978) 73; A.K. Smith, F. Hugues, A. Theolier, J.M. Basset, R. Ugo, G.M. Zanderighi, J.L. Bilhou, V. Bilhou-Bougnol and W.F. Graydon, Inorg. Chem., 18 (1979) 3104.
9 A. Theolier, A.K. Smith, M, Leconte, J.M. Basset, G.M. Zanderighi, R. Psaro and R. Ugo, J. Organomet. Chem., 191 (1980) 415.
10 R. Psaro, R. Ugo, G.M. Zanderighi, B. Besson, A.K. Smith and J.M. Basset, J. Organomet. Chem., 213 (1981) 215.
11 R. Psaro, C. Dossi and R. Ugo, J. Mol. Catal., 21 (1983) 331.
12 A. Theolier, A. Choplin, L. D'Ornelas, J.M. Basset, C. Sourisseau, G.M. Zanderighi, R. Ugo and R. Psaro, Polyhedron, 2 (1983) 119.
13 (a) B.F.G. Johnson, R.D. Johnston and J. Lewis, J. Chem. Soc. A, (1969) 792; (b) M.J. Cleare and W.P. Griffith, ibid., (1969) 372.
14 L.A.W. Hales and R.J. Irwing, J. Chem. Soc. A, (1967) 1932.
15 M. Deeba, B.J. Strensand, G.L. Schroder and B.C. Gates, J. Catal., 71 (1981) 373.
16 A.F. Simpson and R. Whyman, J. Organomet. Chem., 213 (1981) 157.
17 B.F.G. Johnson, J. Lewis, I.G. Williams, J. Chem. Soc. A, (1970) 901; G.R. Eady, B.F.G. Johnson and J. Lewis, J. Chem. Soc. Dalton Trans., (1975) 2606.
18 F. Hugues, J.M. Basset, Y. Been Taarit, A. Choplin, M. Primet, D. Rojas and A.K. Smith, J. Am. Chem. Soc., 104 (1982) 7020.
19 G. Collier, D.J. Hunt, S.D. Jackson, R.B. Moyes, I.A. Pickering, R.B. Wells, A.F. Simpson and R. Whyman, J. Catal., 80 (1983) 154.
20 C.R. Eady, B.F.G. Johnson, J. Lewis and P.R. Raithby, J. Chem. Soc. Dalton Trans., (1981) 2250.
21 J.M. Basset, B. Besson, A. Choplin, F. Hugues, M. Leconte, D. Rojas, A.K. Smith, A. Theolier, Y. Chauvin, D. Commereuc, R. Psaro, R. Ugo and G.M. Zanderighi, in M. Giongo and M. Graziani (Eds.), Fundamental Research in Homogeneous Catalysis, Vol. 4, Plenum Press, New York and London, 1984, p. 19.
22 W. Van Bronswik and R.J. Clark, Spectrochim. Acta A, 28 (1972) 1429.
23 M. Herberhold, G. Suss, J. Ellermann and H. Sabalein, Chem. Ber., 111 (1978) 2931.
24 U. Sartorelli, L. Garlaschelli, G. Ciani and G. Bonora, Inorg. Chim. Acta, 5 (1971) 191.
25 J. Schwank, L.F. Allard, M. Deeba and B.C. Gates, J. Catal., 84 (1983) 27.
26 C.R. Eady, P.F. Jackson, B.F.G. Johnson, M.C. Malatesta, J. Chem. Soc. Dalton Trans., (1980) 383.
27 B.R. James, G.L. Rempel, W.K. Teo, Inorg. Synt., 16 (1976) 45.
28 J.M. Basset and A. Choplin, J. Mol. Catal., 21 (1983) 95.
29 E. Benedetti, G. Braca, G. Sbrana, F. Salvetti and B. Grassi, J. Organomet. Chem., 37 (1972) 361.
30 K.A. Azami, A.J. Deeming, R.E. Kimber and P.R. Shukla, J. Chem. Soc. Dalton, (1976) 1853.
31 P. Legzdins, R.W. Mitchell, G.L. Rempel, J.D. Ruddik and G. Wilkinson, J. Chem. Soc. A, (1970) 3322.
32 J.M. Basset, A. Theolier, D. Commereuc and Y. Chauvin, J. Organomet. Chem., 279 (1985) 147.
33 See, for example, R. Di Felice, Thesis, Milano, (1979–80).
34 L. D'Ornelas, A. Choplin, J.M. Basset, L.Y. Hsu and S. Shore, Nouv. J. Chim., 9 (1985) 155.
35 G.R. Crooks, B.F.G. Johnson, J. Lewis and I.G. Williams, J. Chem. Soc. A, (1969) 797.
36 C.E. Kampe, N.M. Boag, C.B. Knobler and H.D. Kaesz, Inorg. Chem., 23 (1984) 1390.