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SURFACE-SUPPORTED METAL CLUSTER CARBONYLS. CHEMISORPTION, DECOMPOSITION AND REACTIVITY OF $Os_3(CO)_{12}$, $H_2Os_3(CO)_{10}$ AND $Os_6(CO)_{18}$ SUPPORTED ON SILICA AND ALUMINA AND THE INVESTIGATION OF THE FISCHER-TROPSCH CATALYSIS WITH THESE SYSTEMS *

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Summary

On silica and alumina, $Os_3(CO)_{12}$, $H_2Os_3(CO)_{10}$ and $Os_6(CO)_{18}$ are physisorbed (or weakly adsorbed) at room temperature. When the physisorbed cluster $Os_3(CO)_{12}$ is thermally decomposed at ca. 150°C, there is an oxidative addition of a surface M—OH group ($M = Al{<}$, $Si{\leqslant}$) to the Os—Os bond of $Os_3(CO)_{12}$ with formation of the surface species $Os_3(H)(CO)_{10}(OM)$ ($M = Al{<}$, $Si{\leqslant}$) in which the cluster is covalently bonded to the surface by $M—O—Os_3$ bonds. Such a grafted cluster was also obtained by bringing $Os_3(CO)_{10}(CH_3CN)_2$ or $H_2Os_3(CO)_{10}$ into reaction with the surface of silica and alumina. On silica the grafted cluster, when treated with $CO + H_2O$, can regenerate the starting $Os_3(CO)_{12}$ cluster. The structure of the covalently bonded cluster was also confirmed by the synthesis of the model compound $Os_3(H)(CO)_{10}(OSi(Ph)_3)$. Such covalent attachment of a cluster to a surface can be regarded as a model for the metal—support interaction which is frequently involved in heterogeneous catalysis.

When the physisorbed clusters $Os_3(CO)_{12}$, $H_2Os_3(CO)_{10}$, $Os_6(CO)_{18}$ or the chemisorbed cluster $Os_3(H)(CO)_{10}(OM)$, ($M = Al{<}$, $Si{\leqslant}$), are heated at about 200°C, there is a breakdown of the cluster cage with simultaneous oxidation of the osmium to two osmium(II) carbonyl species by the surface proton with simultaneous release of hydrogen. The $[Os^{II}(CO)_3X_2]_2$ and $[Os^{II}(CO)_2X_2]_n$ surface species in which X is a surface oxygen atom can be interconverted by a reversible carbonylation-decarbonylation process at 200°C. These two species

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* Dedicated to the memory of Professor Paolo Chini.

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can be also obtained by decomposition of $[Os(CO)_3X_2]_2$, (X = Cl, Br) onto silica or alumina surface or by CO reduction at 200°C of OsX_3 adsorbed on silica or alumina. The structure of one of these surface compounds was confirmed by synthesis of the model compound $[Os(CO)_3(OSiPh_3)_2]_m$. These surface osmium carbonyl species exhibit a rather high thermal and chemical stability. They appear to be reduced by H_2 to metallic osmium only at 400°C.

The thermal decomposition of the supported clusters is followed by a stoichiometric water gas shift reaction as well as a stoichiometric formation of methane. Under CO + H_2, a Fischer-Tropsch catalyst, which exhibits a high selectivity for methane, is obtained. From the range of temperatures over which those stoichiometric and catalytic reactions are observed it seems reasonable to assume that they involve the Os^{II} carbonyl species rather than metallic osmium.

Introduction

In recent years studies have been carried out in our and other laboratories on the behaviour of metal carbonyl clusters of various metals and varying nuclearity supported on highly divided inorganic oxides. A large amount of work has been devoted to rhodium carbonyl clusters [1—5], owing to their high reactivity with the support and to the catalytic activity of such systems for the selective reduction of carbon monoxide [6—8]. Other investigations have been confined mainly to iron [9—10] and nickel [11] carbonyl clusters.

Very little has been reported on the behaviour of carbonyl clusters of the third transition metal row [12,13], although theoretically these metals could give a variety of quite stable surface species, because, from the kinetic point of view, the third row transition metal carbonyls are rather inert and exhibit strong metal—metal bonds. In brief, while supported metal cluster carbonyls of the first and second transition metal row are more attractive from the catalytic point of view, those of the third row are promising as sources of stable surface organometallic species.

We have previously published a preliminary report of our investigation on the chemistry of various osmium cluster carbonyls supported on silica and alumina [5,14,15]. More recently similar works on these particular systems have appeared [16,17], and we now describe our results fully.

Experimental

The clusters $Os_3(CO)_{12}$ [18], $H_2Os_3(CO)_{10}$, $H_4Os_4(CO)_{12}$ [19] and $Os_6(CO)_{18}$ [20] were prepared by literature methods. $[Os(CO)_3Cl_2]_2$ was also prepared by literature methods, such as the direct carbonylation of commercial hydrated $OsCl_3$ (purchased from Pierce, Rotterdam) [21].

$[Os(CO)_3X_2]_2$ (X = Br, I) were prepared by exchange between $[Os(CO)_3Cl_2]_2$ and LiX in acetone. This reaction is carried out as follows: 140 mg (2×10^{-1} mmol) of $[Os(CO)_3Cl_2]_2$ are dissolved under nitrogen in acetone (200 ml) and 227 mg (1.7 mmol) of LiI are added with stirring. After 48 hours the solvent is evaporated under vacuum and the liberated iodine is extracted with CCl_4. The residue is purified by sublimation at 125°C under 10^{-1} mmHg to give pure $[Os(CO)_3I_2]_2$.

The same procedure can be used for the reaction with LiBr, but no bromine is produced in this case and so the extraction is not required.

$[Os(CO)_2I_2]_n$ is prepared by heating 40 mg of $[Os(CO)_3I_2]_2$ in a Carius tube (sealed under vacuum) at 300°C for 2 hours. The residue is washed with $CHCl_3$. The very insoluble yellow-green material has an IR spectrum in agreement with that reported for $[Os(CO)_2I_2]_n$ [21].

The various gases were supplied by Air-Liquide or SIO. They had purity higher than 99.99%. In all cases they were stored over activated 5 Å molecular sieves. Dichloromethane was purchased from Merck, distilled over P_2O_5, and stored under argon over 5 Å molecular sieves.

The η-Al_2O_3 had a surface area of about 300 m^2/g and an average pore size of 30 Å. The SiO_2 was a non porous silica "Aerosil O" with a surface area of about 200 m^2/g.

Infrared spectra were recorded on a Perkin-Elmer 225 or 621 or a Beckmann 4010 spectrophotometer. The technique of impregnation used to obtain infrared spectra of supported clusters in the complete absence of air has been

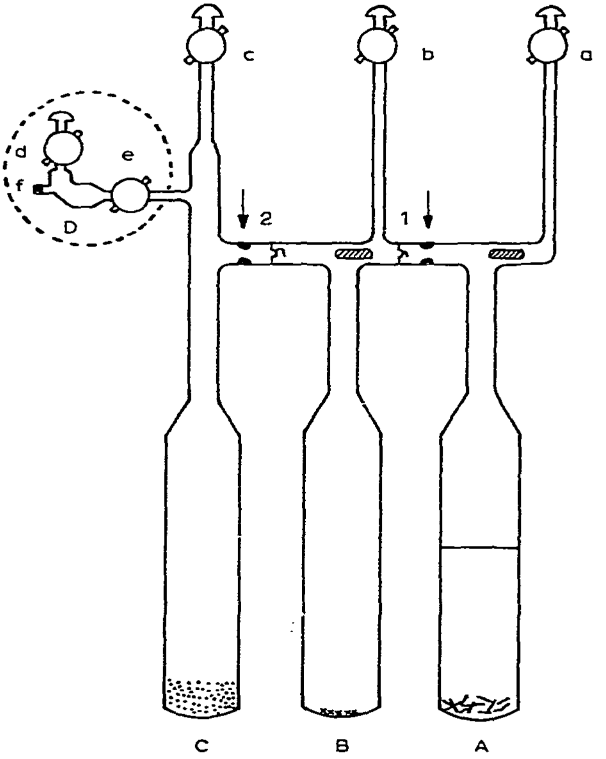


Fig. 1. Diagram of the reactor used in the experiments of gas analysis and in the catalytic tests. A: tube in which dried zeolites and distilled CH_2Cl_2 are stored. B: tube in which the cluster is stored. C: tube in which the support undergoes pretreatment and impregnation. The thermal activation occurs also in this tube. D: Volume used to take samples of gas contained in C. a, b, c, and d: stopcocks used to admit gas or to evacuate tubes A, B, C and D, respectively. e: stopcock used to communicate volume D and tube C. f: septum through which a gastight syringe can take sample of gas in D. 1, 2: break-seals. Arrows: sealing point. In the dashed circle, the part of the reactor devoted to gas phase analysis.

described elsewhere [22]. The technique used to obtain infrared spectra by preparation of the disc of the supported clusters in the air was similar to that originally reported by Watters et al. [1].

The thermal decomposition studies were carried out in the equipment depicted in Figure 1. The solvent was first carefully dehydrated, over zeolite previously treated at 250°C under vacuum, and then degassed by repeated freezing (tube A). The solvent was condensed, through a break seal, into tube B, which contained a known amount of cluster. The solution of the cluster was then introduced into the tube C through a break seal; the solid in tube C having been previously degassed or thermally treated at a given temperature. After stirring for about one hour the solvent was removed under vacuum and the tube C was isolated from tube B by sealing under vacuum. The gas phase was then analysed by removing a sample from vessel F, which was isolated from tube V by a stopcock so as to avoid any contamination by traces of air which might be present in the gas syringe. The analysis of the gas phase was carried out by gas chromatography. The total analysis of CO, CO_2 and CH_4 was obtained on a Porapak R column at 50°C with H_2 as carrier. An oven of methanation (Ni/MgO at 350°C) was located before the flame ionisation detector. The total analysis of C_1 to C_7 hydrocarbons was achieved on a Fracnotrile column at room temperature with N_2 as carrier. Finally, H_2, CO and CH_4 were determined on a molecular sieves column at 60°C with argon as carrier. Two types of desorption experiment were carried out: (a) a static procedure where the gas phase was kept over the supported cluster during the thermal decomposition and (b) the semi-dynamic procedure for which the temperature is raised by increments of

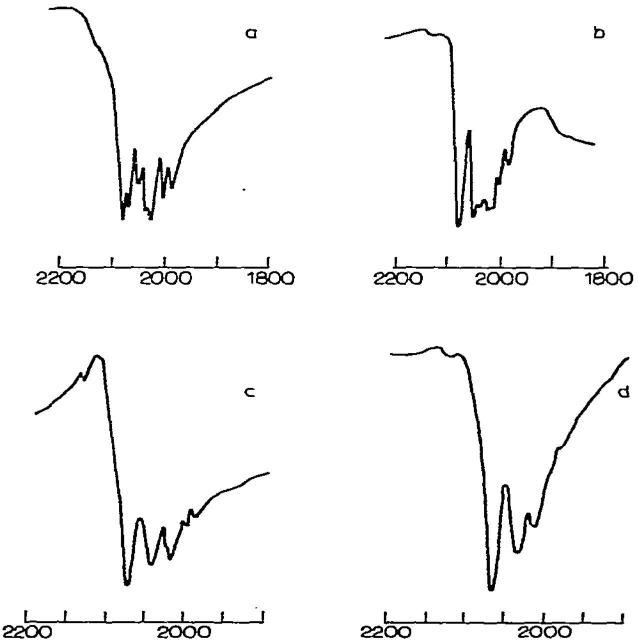


Fig. 2. IR spectra in the ν(CO) region (cm^{-1}). a) $Os_3(CO)_{12}$ in Nujol mull. b) $Os_3(CO)_{12}$ after impregnation on a silica disc pretreated at 25°C under vacuum for 16 hours. c) $Os_3(CO)_{12}$ after impregnation on a silica disc pretreated at 500°C under vacuum for 16 hours. d) $Os_3(CO)_{12}$ after impregnation on a silica disc in air.

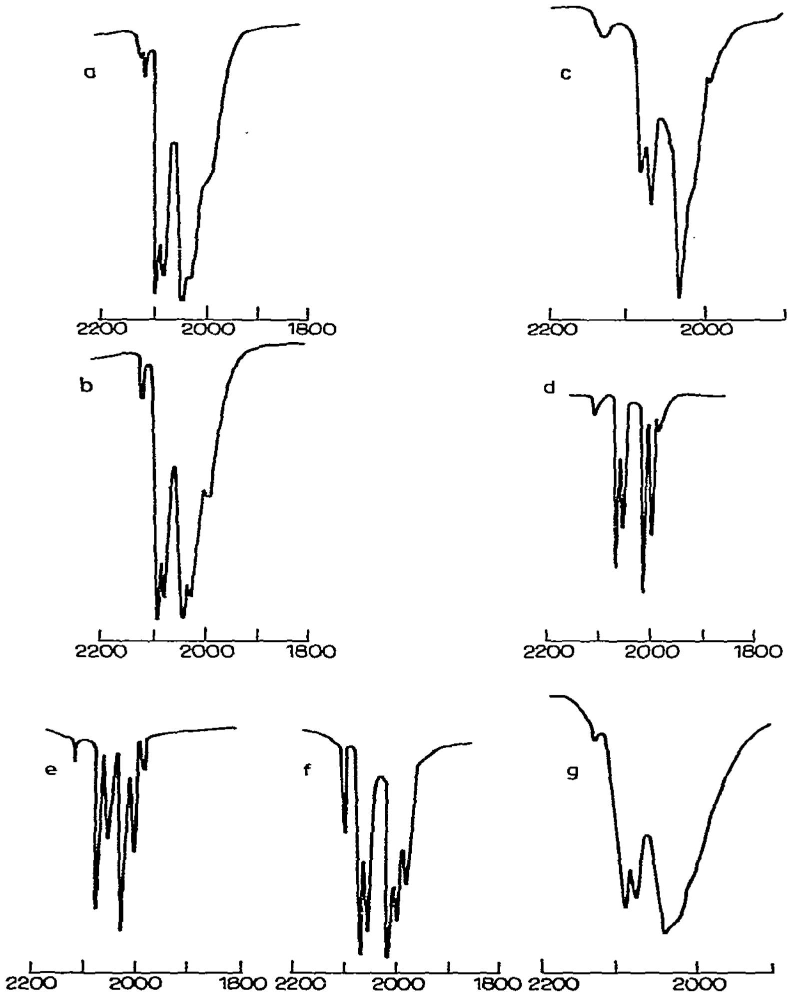


Fig. 3. IR spectra in the ν(CO) region (cm^{-1}). a) $Os_3(CO)_{12}$ on silica$_{25}$ after heating 150°C for 4 hours under argon (800 mmHg). b) $Os_3(CO)_{12}$ on silica$_{350}$ after heating at 150°C for 4 hours under argon (800 mmHg). c) $Os_3(CO)_{12}$ on silica$_{500}$ after heating at 100°C for 3 hours in vacuum. d) $HOs_3(CO)_{10}(OPh)$ in cyclohexane solution. e) $Os_3(CO)_{10}(OPh)_2$ in cyclohexane solution. f) $HOs_3(CO)_{10}(OSiPh_3)$ in cyclohexane solution. g) $Os_3(CO)_{10}(CH_3CN)_2$ after impregnation on silica$_{25}$ at room temperature.

50°C, the gas phase being removed under vacuum after each increment so as to avoid any secondary reaction of evolved gases with the surface. These procedures differ from the TPOE method of Brenner [23].

Results and discussion

In this work we have investigated in detail the adsorption of $Os_3(CO)_{12}$, $H_2Os_3(CO)_{10}$ and $Os_6(CO)_{18}$ on silica and η-alumina as well as the surface organometallic chemistry resulting from the thermal treatment up to 300°C of the supported clusters. Above 300°C a series of very complex transformations of the surface osmium species takes place. We report here only the main experimental features of these high temperature transformations since we do not yet have enough information to interpret in detail the complex chemistry occurring above 300°C.

1. *Behaviour of $Os_3(CO)_{12}$, $H_2Os_3(CO)_{10}$ and $Os_6(CO)_{18}$ on silica*

The major amount of work was devoted to $Os_3(CO)_{12}$. Two types of impregnations were carried out: one in the presence of air and the other in the complete absence of air (argon and (or) vacuum). In the latter case the silica sample was previously treated thermally under vacuum (10^{-5} mmHg) at 25°C or 500°C (silica$_{25}$ and silica$_{500}$) in order to investigate two extreme cases of water content and surface structure of the silica [24]. With both techniques of impregnation, and whatever the pretreatment of the silica (silica$_{25}$ and silica$_{500}$), we found evidence for a simple physisorption of $Os_3(CO)_{12}$ on the silica surface, since the IR spectrum of the final sample was similar to that of $Os_3(CO)_{12}$ in Nujol (Fig. 2). Furthermore we could not detect even traces of CO, CO_2, CH_4 or H_2 in the gas phase. We were also able to extract the physisorbed $Os_3(CO)_{12}$ readily with CH_2Cl_2.

It should be pointed out that the IR spectra of the physisorbed $Os_3(CO)_{12}$ in the carbonyl stretching region are less resolved than those for Nujol mulls (see Fig. 2); besides, the sample on silica$_{500}$, in which there is a strong dehydration of the surface, has a better resolution than that on silica$_{25}$, in which the surface is covered by many monolayers of water.

As for rhodium carbonyl clusters [1—5], the presence of adsorbed water on the surface plays a significant role in the thermal transformations of physisorbed $Os_3(CO)_{12}$. We found that the rates of these transformations are highly dependent upon both the impregnation technique and the thermal treatment of the silica, which control the amount of water on the surface. The sample prepared in the air is converted smoothly during one hour at 150°C under argon into a surface species (A) which has a defined and well reproducible IR spectrum in the ν(CO) region (Fig. 3a). Similar results are obtained after impregnation under argon or vacuum, although great care must be taken to adsorb only a small amount of cluster (<2%) so as to avoid sublimation of physisorbed $Os_3(CO)_{12}$. Such sublimation occurs appreciably when the support has been pretreated at 500°C (Fig. 3c).

The presence on the surface of a relevant amount of water, in equilibrium with the gas phase, favours the selective formation of the well defined surface osmium carbonyl species, characterised by the IR spectrum reported in Figure 3a. This was confirmed by the fact that this species is more easily obtained when $Os_3(CO)_{12}$, physisorbed under vacuum on silica$_{25}$, was treated for 16 hours at 100°C not in vacuum but under a partial pressure of about 18 mmHg of water. In this case we observed no sublimation of $Os_3(CO)_{12}$, but only its smooth transformation into the intermediate surface species A (Fig. 4a).

In reactions of species A under an atmosphere of CO (300 mmHg) we observe no reversion to $Os_3(CO)_{12}$ when the reaction was carried out at about 100°C in the absence of water. In contrast, in the presence of surface water (by introduction of a partial pressure of H_2O) we observed a very slow (200 hours) appearance of an infrared spectrum which could be attributed to physisorbed $Os_3(CO)_{12}$ (Fig. 4b). Conversely, this physisorbed $Os_3(CO)_{12}$ is transformed again into species A at 150°C under vacuum for one hour.

Fig. 4. IR spectra in the ν(CO) region (cm^{-1}). a) $Os_3(CO)_{12}$ physisorbed on silica$_{25}$ after treatment under H_2O (18 mmHg) for 15 hours at 100° C. b) Same sample after treatment with CO (400 mmHg) for 200 hours at 100° C.

Fig. 5. IR spectra in the ν(CO) region (cm^{-1}). a) $H_4Os_4(CO)_{12}$ in Nujol mull. b) $H_4Os_4(CO)_{12}$ after impregnation on silica 25° C.

We investigated by various approaches the molecular nature of species A. The positive effect of the presence of water might suggest a simple surface transformation of $Os_3(CO)_{12}$ into the osmium carbonyl hydride $H_4Os_4(CO)_{12}$, which is reported to be the major product of the high temperature pyrolysis of $Os_3(CO)_{12}$ [25]. We therefore supported $H_4Os_4(CO)_{12}$ on both silica$_{25}$ and silica$_{500}$, but the IR spectra in the carbonyl stretching region (Figure 5b) were quite different from that of species A.

The infrared spectrum of species A is also not very different from that of $H_2Os_3(CO)_{10}$ physisorbed on silica$_{25}$ (see Fig. 8), but that these species are not the same is shown by the fact that the sample containing species A is yellow, in contrast with the red colour of the silica impregnated with $H_2Os_3(CO)_{10}$. Moreover, the failure to extract any carbonyl species by treatment with chlorinated solvents suggests the formation of a species which is strongly bound to the silica surface and not simply physisorbed. This latter observation also rules out the possibility of formation on the surface of physisorbed $Os_3(H)(OH)(CO)_{10}$, which has been reported [25] to have an IR spectrum fairly similar to that of species A (see Table 1).

The general pattern of the IR spectrum of species A is very similar to that of $Os_3(H)(OPh)(CO)_{10}$ and related compounds [26] (Fig. 3d). Moreover, such a pattern is not too different from that of $Os_3(OPh)_2(CO)_{10}$ and related compounds [27] (Fig. 3e). The close similarity between the IR spectra of these

TABLE 1

Compound	ν(CO) (cm^{-1})	Reference
$Os_3(CC)_{12}$ [a]	2127vw, 2070s, 2041s, 2028s, 2016s, 1996s, 1985s	This work
$Os_3(CC)_{12}/SiO_2$ [b] (25°C)	2127vw, 2071vs, 2038s, 2016s, 1995(sh)m, 1981m	This work
$Os_3(CO)_{12}/SiO_2$ [b] (500°C)	2129vw, 2072vs, 2039s, 1017s, 1993m, 1981m	This work
$Os_3(CO)_{12}/\eta$-Al_2O_3 [c] (25°C)	2082w, 2066s, 2032s, 2020s, 2010—1998s(br), 1980s, 1960(sh)	15
$Os_3(CO)_{12}/\eta$-Al_2O_3 [c] (400°C)	2109vw, 2067s, 2033s, 2020s(sh), 2011s(sh), 2000sh(br)	This work
$Os_6(CO)_{18}$ [a]	2109w, 2081s, 2061s, 2039s, 2022s(br), 1996(sh)	This work
$Os_6(CO)_{18}/SiO_2$ [b] (25°C)	2116w, 2087s, 2072s, 2045s(br)	15
$Os_6(CO)_{18}/\eta$-Al_2O_3 [c] (25°C)	2107w, 2080s, 2068s, 2047s, 2020s(br), 1970(sh)	This work
$H_2Os_3(CO)_{10}$ [a]	2066s, 2020s(br), 2002(sh), 1975m	This work
$H_2Os_3(CO)_{10}/SiO_2$ [b] (25°C)	2081s, 2067s, 2041—2032s(br)	This work
$H_2Os_3(CO)_{11}$	2134m, 2090s, 2065vs, 2057m(sh), 2027m, 2001m, 1980m	This work
$H_2Os_3(CO)_{11}/SiO_2$ [b] (25°C)	2092s, 2067s(br), 2020s(br)	This work
$H_2Os_3(CO)_{10}/SiO_2$ [b] (500°C)	2112w, 2078s, 2064s, 2029s, 2012s,	This work
$H_4Os_4(CO)_{12}$ [a]	2115w, 2082s(sh), 2070vs, 2034s(sh), 2022(br), 2001s, 1978m	This work
$H_4Os_4(CO)_{12}/SiO_2$ [b] (25°C)	2111w, 2085s, 2066vs, 2018s(br), 1980s	This work
$HOs_3(CO)_{10}(O—Si)$ [b] (25°C)	2114w, 2079vs, 2066s, 2031vs, 2011s(sh), 1993m(sh)	This work
$HOs_3(CO)_{10}(O—Si)$ [b] (500°C)	2114w, 2079s, 2068s, 2032vs, 2012s(sh), 1995m	This work
$HOs_3(CO)_{10}(OH)$	2110vw, 2072s, 2060m, 2027vs, 2025(sh), 2006m, 1989w	26
$HOs_3(CO)_{10}(O—Ph)$ [d]	2113w, 2075vs, 2065s, 2025vs, 2008s, 1991m, 1987m	26
$Os_3(CO)_{10}(O—Ph)_2$ [d]	2108w, 2076vs, 2058s, 2018vs, 1999s, 1986m	27
$HOs_3(CO)_{10}(O—SiPh_3)$ [d]	2108w, 2069vs, 2056s, 2021vs, 2004s, 1995w, 1988m	This work
$HOs_3(CO)_{10}(O—SiEt_3)$ [d]	2108w, 2069s, 2058m, 2021vs, 1998s, 1990m	32
$Os_3(CO)_{10}(CH_3CN)_2/SiO_2$ [b] (25°C)	2107w, 2080s, 2065s, 2030vs, 2020s(sh), 1983m(sh)	This work
$Os_3(CO)_{10}(CH_3CN)_2/SiO_2$ [b] (500°C)	2109w, 2079s, 2068s, 2028vs, 2010s(sh), 1987s(sh)	This work
$HOs_3(CO)_{10}(O—Al)$ [c] (25°C)	2107w, 2067s, 2055s, 2027vs, 2012s(br)	This work
$HOs_3(CO)_{10}(O—Al)$ [c] (400°C)	2109w, 2070s, 2058s, 2030vs, 2012s(br)	This work
$HOs_3(CO)_{10}(OC_2H_5)$ [d]	2110m, 2071s, 2061s, 2026vs, 2014vs, 1989m, 1981m	26
$Os_3(CO)_{10}(C_6H_8)/Al_2O_3$	2108m, 2067s, 2052s, 2024—2011s(br), 1985(sh), 1941(sh)	16
$Os_3(CO)_{10}(CH_3CN)_2/\eta$-$Al_2O_3$ (500°C)	2107vw, 2066s, 2052s, 2022s(br), 1985s(sh)	This work

[a] Nujol mull. [b] Silica disc. [c] Alumina disc. [d] Cyclohexane.

molecular species and species A suggests an interaction of physosorbed $Os_3(CO)_{12}$ with one or two surface Si—OH groups, leading to a strong interaction by an oxidative addition without cleavage of the original trinuclear cluster cage. The existence on the surface of a cluster cage is confirmed by an EXAFS investigation [14], since this surface species is sufficiently stable at room temperature, even in the air, to permit characterisation by extended X-ray absorption fine structure. The K^3 Fourier transforms of the EXAFS of the surface intermediate

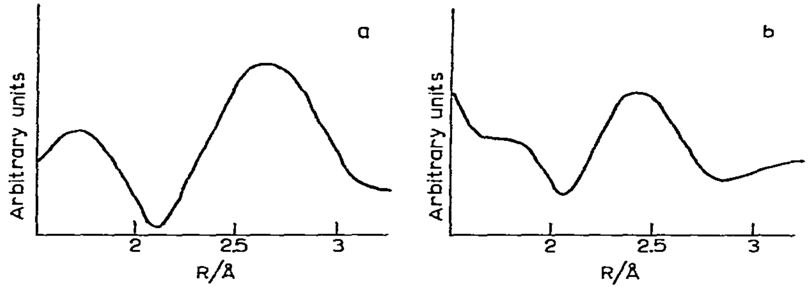


Fig. 6. K^3 Fourier transform of the EXAFS spectra. a) $Os_3(CO)_{12}$. b) $Os_3(CO)_{12}$ on silica$_{25}$ after heating at 150°C for 4 hours under argon (800 mmHg).

and of physisorbed $Os_3(CO)_{12}$ were determined (Fig. 6); the effect of the phase shift, calculated from the known structure of $Os_3(CO)_{12}$ [28], was 0.23 Å. After correction of the phase shift the average Os—Os nearest neighbour distance was 2.68 Å, corresponding to a shortening with respect to that of the starting cluster $Os_3(CO)_{12}$, which has an average Os—Os distance of 2.88 Å. Such a shortening, while small, would be expected if an oxidative addition takes place on one Os—Os bond of the Os_3 metal cage of $Os_3(CO)_{12}$. In fact, X-ray structures are reported for clusters of the type $Os_3(\mu\text{-}H)(\mu\text{-}X)(CO)_{10}$, (X = H, Cl, Br ...) [29]. A contraction of the bridged Os—Os distance occurs for small X, the smaller X the higher being the contraction.

The Fourier transform of the EXAFS of the intermediate surface species does not contain any peak which could be attributed to a second Os nearest neighbour, in agreement with the lack of aggregation to very small osmium particles and with the existence of a molecular species. Moreover, the resolution, the sharpness and the position of the carbonyl stretching absorption bands of species A do not suggest the formation of metallic particles of osmium, since such particles when covered with CO should give broad IR bands in the carbonyl stretching region [30].

The values of the stretching frequencies of the carbonyl absorption of this surface species, are closer to those of $Os_3(OPh)_2(CO)_{10}$ than to those of $Os_3H(OPh)(CO)_{10}$ (Table 1). We therefore examined the gas evolved during the thermal treatment of physisorbed $Os_3(CO)_{12}$ in order to ascertain if the surface oxidative addition proceeds via the reaction:

$$Os_3(CO)_{12} + HOSi\equiv \rightarrow Os_3(H)(OSi\equiv)(CO)_{10} + 2\ CO \qquad (1a)$$

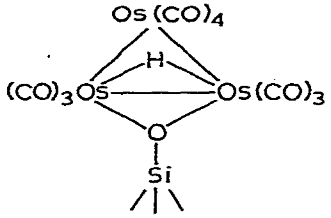
or

$$Os_3(CO)_{12} + 2\ HOSi\equiv \rightarrow Os(OSi\equiv)_2(CO)_{10} + H_2 + 2\ CO \qquad (2)$$

The gas evolution under static conditions (see Experimental section) is depicted in Fig. 7a. Up to about 150°C in vacuum there is evolution of about two moles of CO per mole of $Os_3(CO)_{12}$ but no significant amount of H_2, CH_4 or CO_2. This would suggest, therefore, a simple oxidative addition of one surface Si—OH group to physisorbed $Os_3(CO)_{12}$ according to eq. 1a. In agreement with this suggestion we found that the model compounds $Os_3(H)(OSiPh_3)(CO)_{10}$, prepared by reaction between $HOSiPh_3$ and $Os_3(CO)_{12}$ [31], and $Os_3H(OSiEt_3)(CO)_{10}$, prepared by reaction between $HOSiEt_3$ and $Os_3(H)(CH_3)(CO)_{10}$ [32], have IR spectra in the carbonyl stretching region very similar to that of species A (see Table 1 and Fig. 3f).

Finally, we found the almost immediate appearance of the characteristic IR spectrum of species A, accompanied by evolution of two moles of CH_3CN, in the impregnation of silica$_{25}$ and silica$_{500}$ with $Os_3(CH_3CN)_2(CO)_{10}$ [33] (Fig. 3g). This latter complex is known to form $Os_3(H)(X)(CO)_{10}$ species by reaction with HX under very mild conditions, with release of CH_3CN [33].

Taken overall, the results discussed above indicate that on silica, by treatment at about 100—150°C, the physisorbed clusters $Os_3(CO)_{12}$ is anchored to the surface by covalent bonding of the type:



This bonding is probably formed by:

$$Os_3(CO)_{12(\text{physisorbed})} + \geqslant SiOH \rightarrow 2\ CO + Os_3(H)(O{-}S\leqslant)(CO)_{10} \qquad (1a)$$

The reverse reaction was observed in the presence of carbon monoxide and

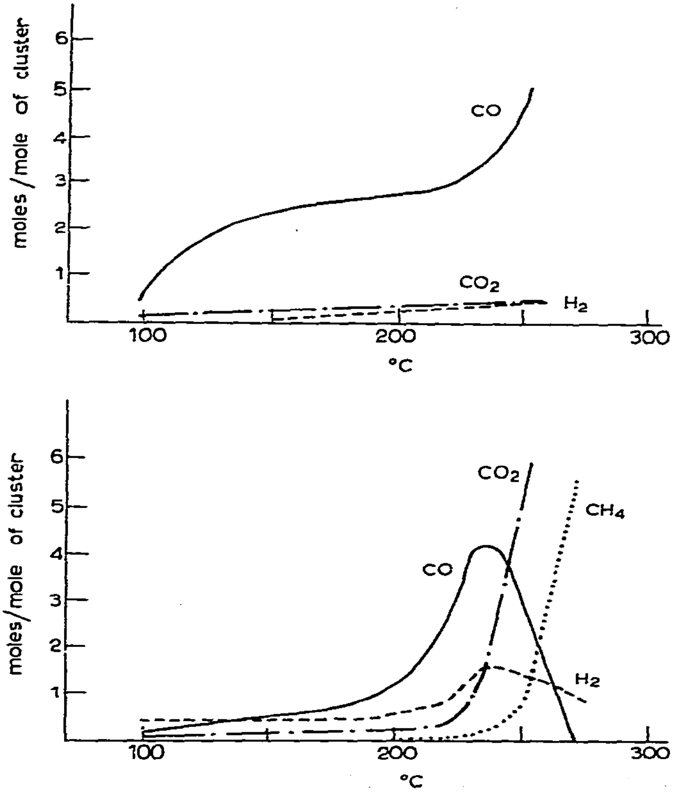


Fig. 7. Gas evolution under argon upon heat treatment. a) $Os_3(CO)_{12}$ on silica$_{25}$. b) $H_2Os_3(CO)_{10}$ on silica$_{25}$.

water:

$$Os_3(H)(O{-}Si\equiv)(CO)_{10} + 2\,CO \xrightarrow{H_2O} Os_3(CO)_{12} + H{-}O{-}Si\equiv \qquad (1b)$$

We therefore considered the possibility of a similar reaction in the homogeneous phase for model compounds. However neither $Os_3(H)(OPh)(CO)_{10}$ and $Os_3(OPh)_2(CO)_{10}$ reverts to $Os_3(CO)_{12}$ upon treatment at 50°C in hexane under a pressure of about 50 atm of CO, even when the solvent is wet. This result is not unexpected, since the reactivities of similar species in solution or on a surface can be very different, owing to the different nature of the inner and outer sphere interactions (e.g. solvation, hydrogen bonding, dielectric constant of the medium). For instance, we could not obtain $Os_3(H)(OSiPh_3)(CO)_{10}$ by reaction of $Os_3(CH_3CN)_2(CO)_{10}$ with $HOSiPh_3$ in acetonitrile, although this reaction takes place easily with Si—OH groups of the surface.

We also examined the behaviour of silica impregnated with $H_2Os_3(CO)_{10}$. In the absence of air the hydrido cluster $H_2Os_3(CO)_{10}$ is easily physisorbed as such on silica$_{25}$ (Fig. 4a and b1). Upon introduction of a partial pressure of CO (20 mmHg) at 25°C complete transformation into $H_2Os_3(CO)_{11}$ occurs in few hours (Fig. 8c). This behaviour is parallel to that reported in solution [34], and upon

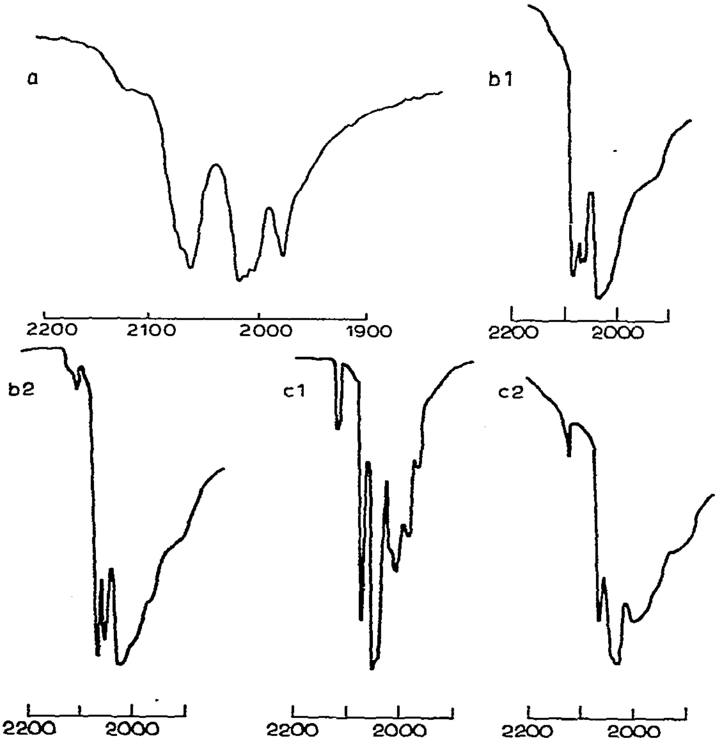


Fig. 8. IR spectra in the ν(CO) region (cm^{-1}). a) $H_2Os_3(CO)_{10}$ in Nujol mull. b1) $H_2Os_3(CO)_{10}$ impregnated on silica$_{25}$. b2) $H_2Os_3(CO)_{10}$ impregnated on silica$_{25}$ after treatment at 120°C for 16 hours under argon (800 mmHg). c1) $H_2Os_3(CO)_{11}$ in CH_2Cl_2 solution. c2) $H_2Os_3(CO)_{10}$ on silica$_{25}$ after exposure to CO (20 mmHg) at room temperature.

evacuation at room temperature the original cluster $H_2Os_3(CO)_{10}$ is re-formed. After heating under argon at about 100—150° C the spectrum of species A appeared (Fig. 8b2). The formation of species A was confirmed by the drastic color change from red-biolet at room temperature to yellow at ca. 150° C. Evolution of H_2 was also detected by chromatographic analysis (Fig. 7b) and was probably formed by the following reaction:

$$H_2Os_3(CO)_{10} + H{-}O{-}Si{\leqq} \rightarrow Os_3(H)(O{-}Si{\leqq})(CO)_{10} + H_2 \qquad (3)$$

We also investigated the nature of the surface species formed at higher temperatures. When $Os_3(CO)_{12}$ physisorbed on $silica_{25}$ or $silica_{500}$ was heated at 150° C for 4 hours under vacuum we could not identify the intermediate formation of triangular species covalently anchored to the surface. Under these condi-

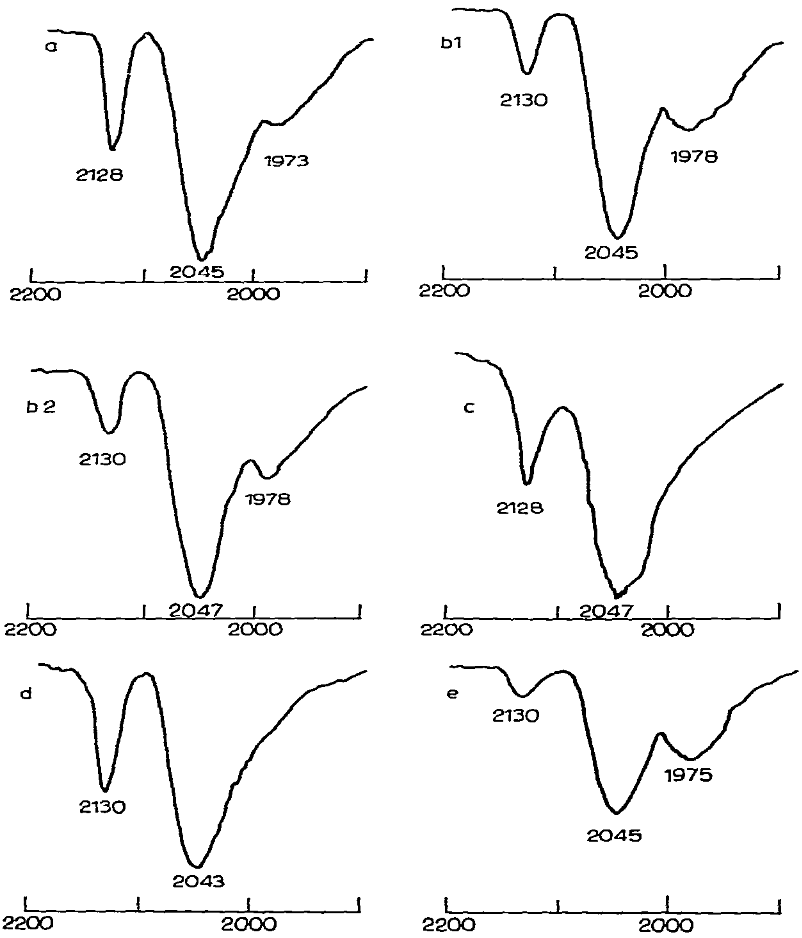


Fig. 9. IR spectra in the ν(CO) region (cm^{-1}). a) $Os_3(CO)_{12}$ on $silica_{25}$ after treatment under vacuum for 4 hours at 150° C. b1) $Os_3(CO)_{12}$ on $silica_{25}$ after treatment under vacuum for 4 hours at 200° C. b2) Same sample after treatment under vacuum for 17 hours at 250° C. c) Same sample after treatment under CO (500 mmHg) for 60 hours at 200° C. d) Sample after treatment under CO (200 mmHg) and H_2O (16 mmHg) for 60 hours at 200° C. e) Sample after treatment under vacuum for 5 hours at 300° C.

tions only a slow transformation occurred; affording after 4 or 5 hours a completely white sample characterised by three IR absorption bands, as shown in Fig. 9a (species B). This transformation is quicker at higher temperatures. Under argon, the three IR absorption bands are formed very slowly at temperatures above 200° C.

The same kind of spectrum is obtained by heating under vacuum not only the physisorbed cluster of comparable nuclearity, such as $H_2Os_3(CO)_{10}$, but also $Os_6(CO)_{18}$. The hexanuclear cluster is physisorbed unaltered in the presence or absence of air and remains stable up to 150° C (Fig. 10). At higher temperatures some transformations occur, but as for $Os_3(CO)_{12}$ we could not characterise any stable intermediate. In particular, owing to the complexity of the IR carbonyl absorptions of the original cluster there is a continuous overlap with the IR carbonyl bands of the new species which are thermally formed. The typical IR spectrum of species B, with the three absorption bands, appears only at temperature of about 200° C. The intensity ratios of the three bands are not always the same; in particular the intensity of the band at lower wavelength is dependent upon the temperature, and its intensity increases with both the temperature and the time of the thermal treatment. This band disappears after few hours upon addition of a partial pressure of CO (200—600 mmHg) at tempera-

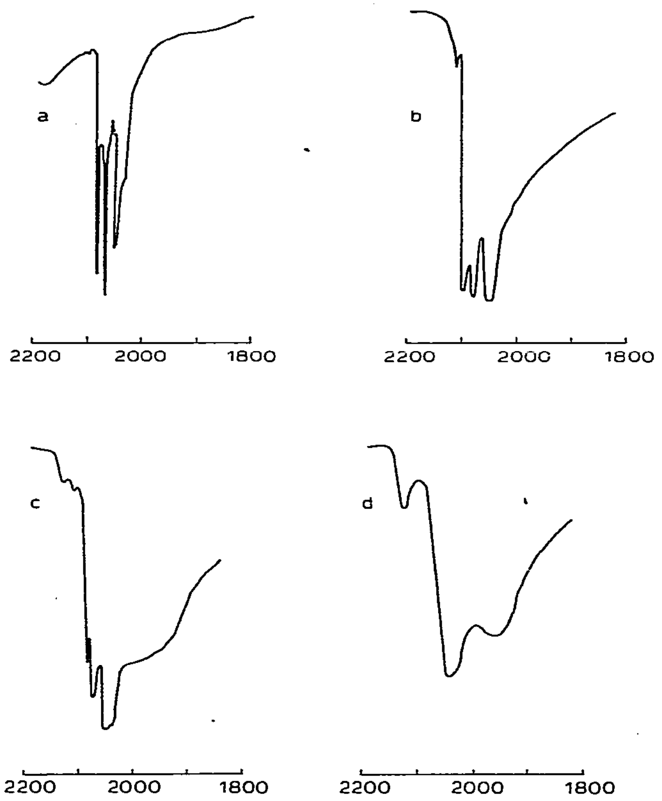


Fig. 10. IR spectra in the ν(CO) region (cm^{-1}). a) $Os_6(CO)_{18}$ in heptane solution. b) $Os_6(CO)_{18}$ after impregnation on silica$_{25}$. c) Same sample after treatment under argon for 3 hours at 150° C. d) Same sample after treatment under argon for 1 hour at 200° C.

tures between 100 and 200°C, while the band at about 2130 cm^{-1} simultaneously increases in intensity until a spectrum with only two strong and broad bands of constant intensity is obtained (Fig. 9c).

During the carbonylation process the broad, strong band centered at about 2045 cm^{-1} shifts to lower wavelengths by a few cm^{-1}. Upon heating under vacuum, the kind of spectrum of Fig. 9a is easily reobtained after few hours. The process of decarbonylation and recarbonylation can be repeated many times, suggesting the existence of a reversible carbonylation. If the carbonylation is carried out in the presence of a partial pressure of H_2O (normally 200 mmHg of CO and 18 mmHg of H_2O), the two final absorption bands centered at 2130 and 2043 cm^{-1} are much sharper; in particular the broad band at lower wavelengths decreases to about one quarter of the original band half width (Fig. 9d). It is quite difficult, even by prolonged treatment at about 300°C under vacuum, to obtain a final spectrum with only two IR absorption bands located at about 2045 and 1970 cm^{-1}, since the weak IR band at about 2130 cm^{-1} does not disappear completely (Fig. 9e).

The general patterns of the infrared spectra discussed above are comparable, both in position and relative intensity of the absorption bands, with those of known derivatives of Os^{II} such as $[Os(CO)_3X_2]_2$ (X = Cl, Br, I) and $[Os(CO)_2I_2]_n$ [21] (see Table 2). We repeated the synthesis of $[Os(CO)_3I_2]_2$ and $[Os(CO)_2I_2]_n$, and recorded their infrared spectra in Nujol mulls (Fig. 11A and B); they exhibit a pattern completely consistent in intensity and position of the bands with those reported in Fig. 9.

The appearance of the same species by thermal treatment of Os_3 or Os_6 clusters having different nuclearities would suggest complete rupture of the cluster metallic cage to form osmium species without metal—metal bonds. The EXAFS investigation on these samples confirmed this suggestion; the K^3 Fourier transform, which is shown in Fig. 12, shows the absence of any ordered Os—Os bond.

The formal oxidation of osmium from the zerovalent to the divalent state is in agreement with the observation of the positive effect of an oxygen atmos-

TABLE 2

Compounds	ν(CO) (cm^{-1})	Reference
$[Os(CO)_2(O{-}Si{\equiv})_2]_n$ [b]	2130m, 2045s(br), 1975m(br)	This work
$[Os(CO)_3(O{-}Si{\equiv})_2]_2$ [b]	2130m, 2045s(br)	This work
$[Os(CO)_2(O{-}Al{<})_2]_n$ [c]	2127m, 2034s(br), 1970m(br)	This work
$[Os(CO)_3(O{-}Al{\equiv})_2]_2$ [c]	2127m, 2034s(br)	This work
$[Os(CO)_3Cl_2]_2$ [d]	2134m, 2059s (α isomer) 2129m, 2048s, 2035s (β isomer)	21
$[Os(CO)_3Cl_2]_2/SiO_2$ [b] (25°C)	2140s, 2063vs(br)	This work
$[Os(CO)_3Br_2]_2$ [e]	2128s, 2042vs(br), 2000w(sh)	15
$[Os(CO)_3Br_2]_2/\eta\text{-}Al_2O_3$ [c] (400°C)	2124s, 2044s(br), 1992(sh)	15
$[Os(CO)_3I_2]_2$ [d]	2118s, 2050vs	This work
$[Os(CO)_2I_2]_n$ [a]	2112w, 2039s(br), 1980s(br)	This work
$[Ru(CO)_3I_2]_2$ [a]	2116m, 2059s, 2009m	36
$[Ru(CO)_2I_2]_n$ [a]	2050s, 1995s, 1975w(sh)	36
$[Os(CO)_3(O{-}SiPh_3)_2]_m$ [a]	2109m, 2023s	31
$[Os(CO)_3O]_4$ [e]	2093s, 2087m(sh), 2000(sh), 1988s(br), 1954w	37

[a] Nujol mull. [b] Silica disc. [c] Alumina disc. [d] CCl_4. [e] KBr disc.

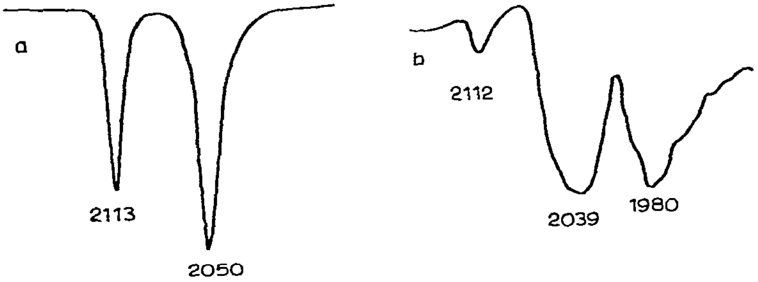


Fig. 11. IR spectra in the ν(CO) region (cm^{-1}). a) $[Os(CO)_3I_2]_2$ in CCl_4 solution. b) $[Os(CO)_2I_2]_n$ in Nujol mull.

phere on the breaking of the cluster frames. For instance under a partial pressure of 200 mmHg of O_2 the spectrum of Fig. 9a is obtained from different osmium clusters already at 100° C. The oxidation of the osmium atoms was also confirmed by a series of different experiments.

Upon treatment at 200° C under vacuum of $[Os(CO)_3Cl_2]_2$ physisorbed on silica$_{25}$, a slow incorporation of the $Os(CO)_3$ units into the silica surface takes place, since it is possible to isolate intermediate surface states in which both physisorbed $[Os(CO)_3Cl_2]_2$ and $Os(CO)_3$ units, probably bound to the silica surface via O—Si bonds, can be characterised by IR spectroscopy (Fig. 13). After 40 hours complete incorporation of the $Os(CO)_3$ units into the silica matrix is achieved, and the final IR spectrum is similar to that of Fig. 9a. Since we could not detect any other surface species by IR spectroscopy, we confidently suggest the following surface exchange reaction:

$$1/2[Os(CO)_3Cl_2]_2 + 2\ HOSi\lessgtr \rightarrow Os(CO)_3(OSi\lessgtr) + 2\ HCl \qquad (4)$$

We also obtained the same kind of surface species by CO reduction of commercial hydrated $OsCl_3$ adsorbed on silica$_{25}$. The treatment at 150° C under a partial pressure of CO causes a change of colour of the silica from green-brown to yellow and finally to white, and this is accompanied after a few hours by the appearance of an infrared spectrum of the type of Fig. 9a with three carbonyl absorption bands (Fig. 14a). Only after 40 hours did we obtain a spectrum with only two absorption bands, typical of the fully carbonylated samples (Fig. 14b). Interestingly we did not observe any other significant infrared carbonyl band during this treatment with CO; under these carbonylation conditions the

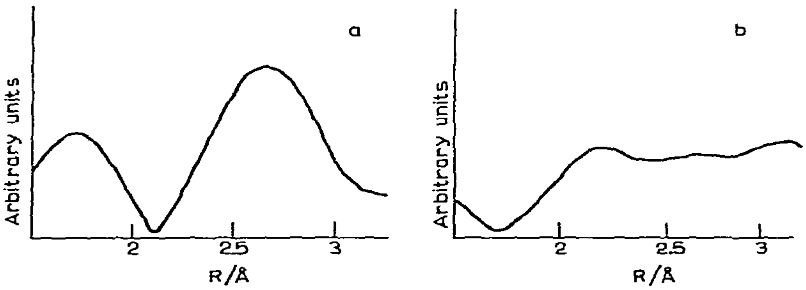


Fig. 12. K^3 Fourier transform of the EXAFS spectra. a) $Os_3(CO)_{12}$. b) $Os_3(CO)_{12}$ on silica$_{25}$ after heating at 150° C for 72 hours under argon (800 mmHg).

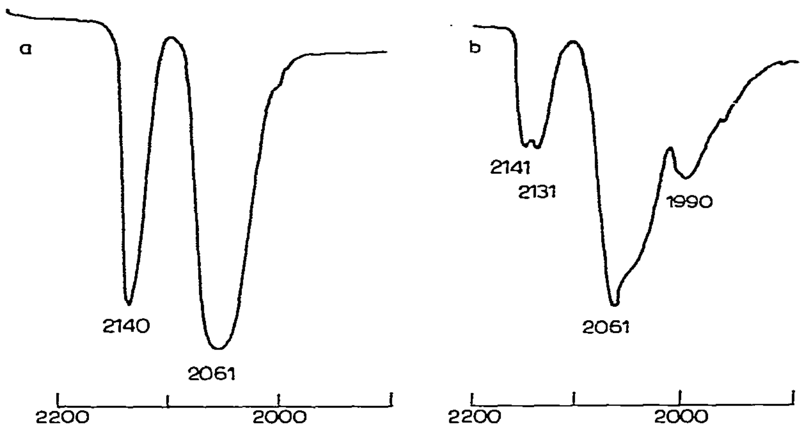


Fig. 13. IR spectra in the ν(CO) region (cm^{-1}). a) [Os(CO)$_3$Cl$_2$]$_2$ after impregnation on silica$_{25}$. b) Same sample after treatment under vacuum for 22 hours at 200°C.

band at about 1970 cm^{-1} is well defined, and cleaner than when obtained by thermal decarbonylation.

In this series of observations we think that we have provided good evidence that these surface species are oxidised divalent osmium units bound to the silica by —O—Si$\lessgtr$ bonds. In particular the species with IR bands at 2130 and 2045 cm^{-1} can be regarded as Os(CO)$_3$ units, since the features of the spectrum are typical of tricarbonyl species with local C_{3v} symmetry [25]. The species with absorption bands at 2130w, 2145s and 1975m cm^{-1}, characteristic of the decarbonylated state, can be assigned to Os(CO)$_2$ units. This assignment is based on the comparison of the observed infrared spectra with that of [Os(CO)$_2$I$_2$]$_n$ (see, for instance, Table 2 and Figs. 9 and 11). However, it must be pointed out that for simple Os(CO)$_2$ units, without particular polymeric arrangements, we should

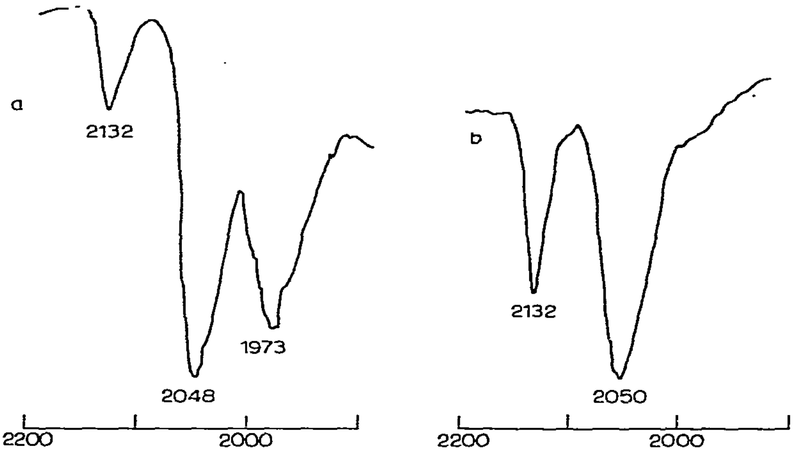


Fig. 14. IR spectra in the ν(CO) region (cm^{-1}). a) OsCl$_3$ physisorbed on silica$_{25}$ after treatment under CO (200 mmHg) for 16 hours at 150°C. b) Same sample after treatment under CO (500 mmHg) for 40 hours at 150°C.

expect a strong doublet in the IR spectrum, corresponding to the symmetric and asymmetric carbonyl stretching modes of the $Os(CO)_2$ units. Therefore, we suspect that the fully decarbonylated species is actually associated with a spectrum having only two strong absorption bands, centered at 2045 and 1975 cm^{-1}; the weak band at 2130 cm^{-1} could be due to residual $Os(CO)_3$ units which could not be decarbonylated even under drastic conditions. In fact, although the IR spectrum reported for $[Os(CO)_2I_2]_n$, which we have reproduced, has a weak band at 2112 cm^{-1}, the parent compound $[Ru(CO)_2I_2]_n$, which is better characterised, is reported to have only two strong absorption bands, at 2050 and 1995 cm^{-1} [36].

On the surface these carbonyl osmium units are probably linked together via oxygen bridges of the surface silanolate groups. In order to produce further evidence for this suggestion we synthesised the model compound $[Os(CO)_3(OSiPh_3)]_m$ [31], which shows an infrared spectrum very similar to that in Fig. 9b. It is noteworthy that a related polynuclear molecular species with oxygen bridges, e.g. $[Os(CO)_3O]_4$, has a spectrum which is similar in general pattern, but is complicated by the coupling of the different $Os(CO)_3$ units (Table 2) [37]. This observation suggests that the nuclearity of the bridged aggregates of Os^{II} is low; it is possible that the tricarbonyl species are dimeric, and that the thermal decarbonylation results in a higher aggregation as follows:

$$\frac{n}{2}\,[Os(CO)_3(OSi\text{—})_3]_2 \overset{\Delta}{\rightleftharpoons} [Os(CO)_2(OSi\equiv)_2]_n + nCO \qquad (5)$$

Thus the breadth of the band at 2050—2045 cm^{-1} may be due to the presence of a series of slightly different surface species with similar absorption bands in this region. We suggest the presence of different isomeric arrangements of the 3 CO units around the osmium atoms [19], of bridged aggregates higher than 2 $Os(CO)_3$ units, or of $Os(CO)_3$ units bridged by

instead of $OSi\equiv$ bridges [38].

It is relevant to note that the infrared spectra of $Os(CO)_3$ units obtained by surface reaction with silanols of physisorbed $[Os(CO)_3Cl_2]_2$ or by direct carbonylation of adsorbed commercial hydrated $OsCl_3$ are sharper than those ob-

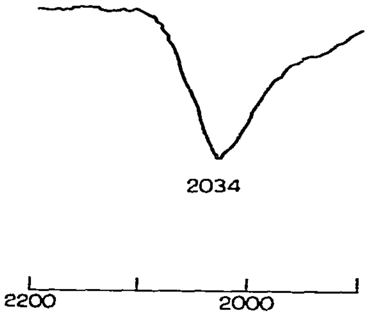


Fig. 15. IR spectra in the ν(CO) region (cm^{-1}) of $Os_3(CO)_{12}$ on $silica_{25}$ after treatment under H_2 (200 mmHg) for 20 hours at 400°C and subsequently exposed to CO (400 mmHg) at 25°C.

tained by thermal treatment of physisorbed clusters. This could be related to a lower aggregation of the carbonylated osmium units in the first case compared with those generated by thermal decomposition of osmium carbonyl clusters.

The divalent osmium carbonyl species are stable under vacuum up to ca. 300°C. Upon increasing the temperature up to 400°C, complete decarbonylation is observed, and the sample turns brown. However, recarbonylation under 400 mmHg of CO even at room temperature regenerates the two band spectrum of Fig. 9b, typical of the divalent $Os(CO)_3$ units, and the sample turns white again. Upon treatment with H_2 (200 mmHg) for 20 hours at 400°C a similar complete disappearance of the carbonyl bands occurs, but the sample turns gray. Introduction of 400 mmHg of CO at 25°C, gives a very broad absorption band, centered at about 2030 cm^{-1} (Fig. 15), while the sample remains gray.

Although the positions of the carbonyl absorption bands of carbon monoxide chemisorbed on metallic osmium are not well established, since conflicting data are reported [30], we confidently conclude, on the basis of the breadth of the absorption band, that we have produced metallic osmium on the silica surface. The osmium must be quite dispersed, since treatment at 250°C with a partial pressure of 560 mmHg of O_2, after 4 or 5 hours causes the colour of the sample to change from gray to brown. Introduction of carbon monoxide (400 mmHg at 25°C) leads to formation of divalent $Os(CO)_3$ species on the surface, suggesting a ready destruction and oxidation of the metallic osmium particles dispersed on the surface of silica.

2. Behaviour of $Os_3(CO)_{12}$ and $Os_6(CO)_{18}$ on η-alumina

As in the previous case, most of the work was devoted to $Os_3(CO)_{12}$. Two types of impregnations were used: one in the presence of air and the other in complete absence of air (argon and/or vacuum). In the latter case the alumina samples were pre-treated thermally under vacuum (10^{-5} mmHg) at 25°C (alumina$_{25}$) and 400°C (alumina$_{400}$) for 16 hours so as to provide a wide range of water or hydroxyl content of the support [24,39].

As in the case of silica, with any type of alumina or any type of pretreatment, a simple physisorption of $Os_3(CO)_{12}$ and $Os_6(CO)_{18}$ occurs, since the two clusters can be easily extracted from the support by treatment with a chlorinated solvent such as $CHCl_3$ or CH_2Cl_2. The IR spectra of $Os_3(CO)_{12}$ adsorbed on η-Al_2O_3 are poorly resolved compared with the corresponding spectra in Nujol mulls (Fig. 16). This poorer resolution could be attributed to a series of different and strong interactions of the carbonyl groups of the clusters with the OH or the Lewis acidic centers of the alumina surface. We suggest also that there are strong interactions since we did not (in contrast to the behaviour of the silica supported species) observe any sublimation of $Os_3(CO)_{12}$ upon treatment under high vacuum for more than 24 hours at temperatures up to 60—70°C.

In particular, the spectrum of $Os_3(CO)_{12}$ physisorbed on alumina$_{400}$ is slightly more resolved than that of $Os_3(CO)_{12}$ physisorbed on alumina$_{25}$, in agreement with a simpler surface composition [39]. A thermal treatment at 100°C under vacuum for about 3 hours of $Os_3(CO)_{12}$ physisorbed on alumina$_{25}$ produces some significant changes in the IR spectrum (Fig. 17a). In particular, a weak

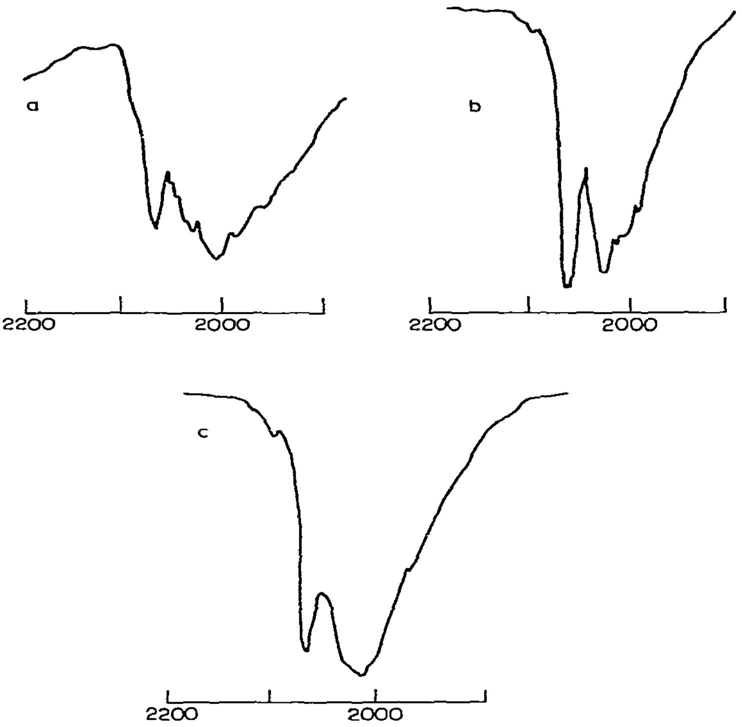


Fig. 16. IR spectra in the ν(CO) region (cm^{-1}). a) $Os_3(CO)_{12}$ after impregnation on alumina$_{25}$. b) $Os_3(CO)_{12}$ after impregnation on alumina$_{400}$. c) $Os_3(CO)_{12}$ after impregnation on alumina$_{25}$ in air.

but well-defined band appears at about 2109 cm^{-1}, together with a broad doublet centered at about 2070—2058 cm^{-1} while a broad band is centered at about 2010 cm^{-1}. This kind of spectrum (although characterised by a poor resolution) can be assigned to a surface species of the type $Os_3H(X)(CO)_{10}$ where X is a $-OAl{<}$ group of the surface. The position and shape of the IR absorptions of the spectrum shown in Fig. 17a are in agreement with those of the surface species, obtained by impregnation of alumina in the air with $Os_3(C_6H_8)(CO)_{10}$, which is thought, on the basis of chemical and IR evidence, to be $Os_3(H)(-OAl{<})(CO)_{10}$ [16].

However the intensity ratio of the doublet centered at 2070—2058 cm^{-1} and of the broad band centered at 2010 cm^{-1}, is different than that of the well characterised surface species $Os(H)(OSi{\leqslant})(CO)_{10}$, species A (Fig. 3a). This suggests that the transformation of the original cluster is not complete, since the high intensity of the broad absorption at about 2010 cm^{-1} is probably due to additional absorption of some unreacted $Os_3(CO)_{12}$.

A similar spectrum is obtained by treatment at 100°C for 3 or 4 hours under vacuum of $Os_3(CO)_{12}$ physisorbed on alumina$_{400}$, or by carrying out the same experiment under argon but on a sample in which $Os_3(CO)_{12}$ had been physisorbed in the presence of air (Fig. 17b and c). In these cases the ratio of the intensities of the bands centered at about 2070 and 2010 cm^{-1}, is not too far from that expected for a surface species of the type $Os_3(H)(OAl{<})(CO)_{10}$. Ob-

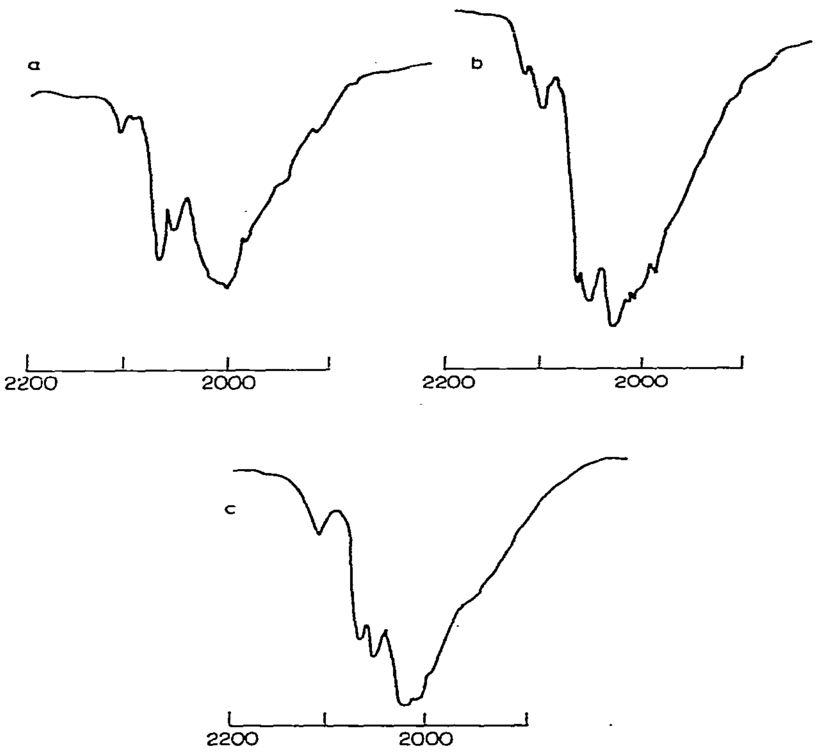


Fig. 17. IR spectra in the ν(CO) region (cm^{-1}). a) $Os_3(CO)_{12}$ on $alumina_{25}$ after treatment under vacuum for 3 hours at 100°C. b) $Os_3(CO)_{12}$ on $alumina_{400}$ after treatment under vacuum for 4 hours at 100°C. c) $Os_3(CO)_{12}$ on $alumina_{25}$ (impregnation in air) after treatment under argon for 1 hour at 100°C.

viously the breadth of the IR spectrum of Fig. 17, which contrasts with those from species A on silica, did not allow definite characterisation on the basis of this result alone. Therefore, we carried out additional experiments which gave further support for the formation of $Os_3(H)(OAl<)(CO)_{10}$ on the surface. Thus we obtained the same kind of IR spectrum as that shown in Fig. 17 by impregnation of $Os_3(CH_3CN)_2(CO)_{10}$ on η-$Al_2O_{3_{25}}$ and $Al_2O_{3_{400}}$. This experiment recalls that of Watson and Schrader using $Os_3(C_6H_8)(CO)_{10}$ [16]. In contrast with the results obtained on silica, on alumina CH_3CN is not evolved in the gas phase but is strongly bound to the alumina surface (as shown by infrared); this interaction probably occurs at the Lewis acid centers, which are acceptors for N-donor bases such as CH_3CN.

Additional evidence for the formation of $Os_3(H)(OAl<)(CO)_{10}$ on the surface was obtained from careful gas phase analysis above the $alumina_{25}$ sample after adsorption of $Os_3(CO)_{12}$ in CH_2Cl_2 under Ar (Fig. 18). Between 50 and 100°C about 2 moles of CO/mole of cluster are evolved without any significant evolution of H_2, CO_2 or CH_4. Similar results are obtained on $alumina_{400}$. Such evolution of gas is consistent with the following surface reaction:

$$Os_3(CO)_{12} + HOAl< \rightarrow Os_3(H)(OAl<)(CO)_{10} + 2\ CO \qquad (6)$$

In total, we have good evidence, confirming that of other authors [16], that,

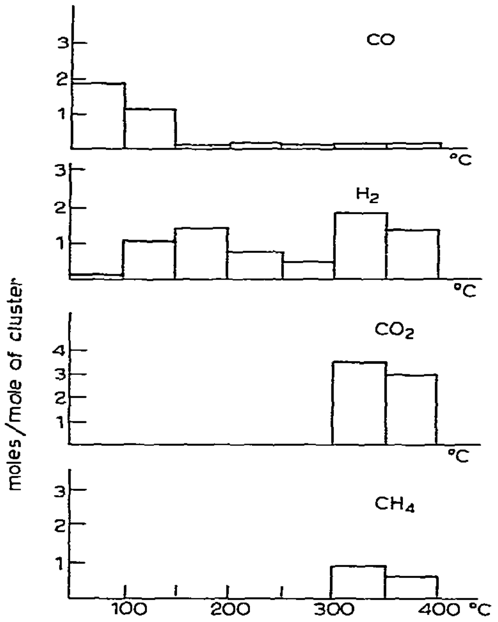


Fig. 18. Semi-dynamic experiment of gas evolution. $Os_3(CO)_{12}$ on alumina[25] under argon (800 mmHg).

as with silica, a triosmium carbonyl complex can be covalently attached to an alumina surface. However this triosmium carbonyl complex anchored to alumina is less thermally stable than that anchored to silica.

Prolonged treatment under vacuum at temperatures between 100 and 150°C produces a rapid and complete transformation of this surface species into a new one, characterised by a 3-bands spectrum (Fig. 19a), completely similar in form to that obtained on silica (Fig. 9a) under more drastic conditions. As on silica, the ratio of the intensities of the three bands depends on the temperature and duration of the thermal treatment: higher temperatures (200—250°C) and longer heating times increase the intensity of the band at 1970 cm^{-1}, with a corresponding decrease of that of the band at 2127 cm^{-1}. The introduction of a partial pressure of CO (400—500 mmHg) at about 200°C produces the complete disappearance of the band at 1970 cm^{-1}, with a parallel increase of the intensity of the band at about 2127 cm^{-1}; meanwhile, the broad and intense band, originally at 2035 cm^{-1}, shifts slightly to lower wavenumbers (Fig. 19c). If a partial pressure of 18 mmHg of H_2O is added to the 400—500 mmHg pressure of CO, the final spectrum has quite sharp bands (Fig. 19d). The intensity ratio of the two final bands is the same in all cases.

Upon heating under vacuum again, at 250°C, the band at 1970 cm^{-1} reappears, while the band at higher wavelengths decreases in intensity. However, even on prolonged heating at 300°C, this latter band never disappears completely, but the final IR spectrum is characterised by two strong and broad absorption bands at 2040 and 1970 cm^{-1}. The original surface species, with IR bands at 2127 and 2035 cm^{-1}, is restored by treatment with CO at 250°C.

In conclusion, there is evidence for the equilibrium existence of two surface species, as on silica, which are interconverted by a reversible carbonylation-

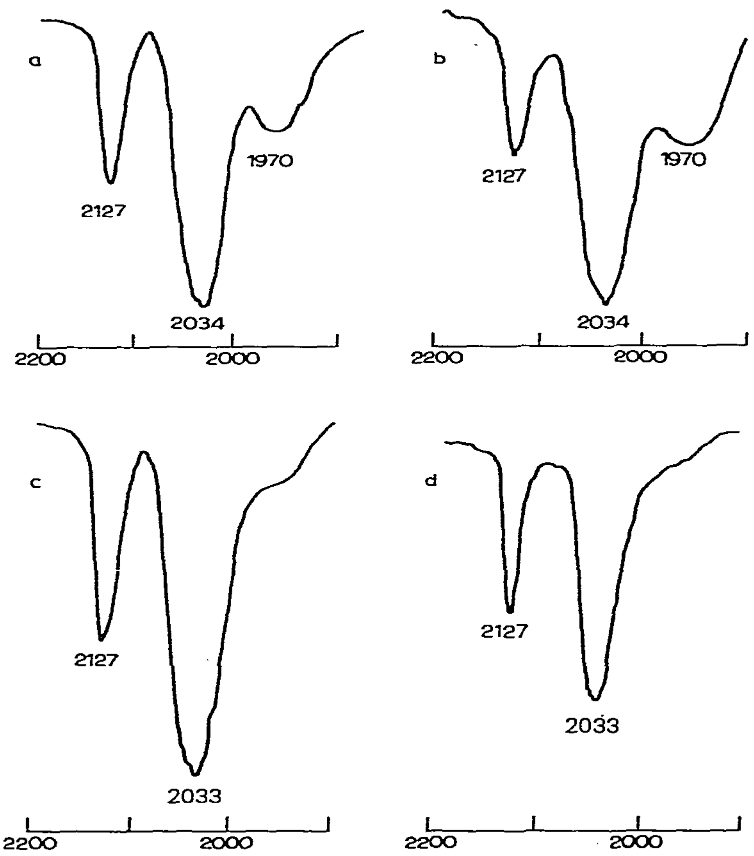


Fig. 19. IR spectra in the ν(CO) region (cm^{-1}). a) $Os_3(CO)_{12}$ on alumina$_{400}$ after treatment under vacuum for 15 hours at 150° C. b) Same sample after treatment under vacuum for 7 hours at 200° C. c) Same sample after treatment under CO (300 mmHg) for 40 hours at 200° C. d) Same sample after treatment under CO (200 mmHg) and H_2O (18 mmHg) for 42 hours at 250° C.

decarbonylation. The similarities of the IR spectra suggest a breakdown of the cluster frame to form mononuclear oxidised osmium species, bound covalently to the surface and arranged through OAl$<$ bridges in dimeric or polymeric aggregates.

We have shown that the spectra of Fig. 19 can be attributed to divalent osmium surface species of the type $Os(CO)_3$ and $Os(CO)_2$ as on silica surfaces. Thermal treatment at 200—250° C, under vacuum, of $Os_6(CO)_{18}$ and of $[Os(CO)_3Br_2]_2$, physisorbed on alumina$_{25}$ or alumina$_{400}$, generates the same species characterised by the same IR spectra and by similar thermal behaviour. Moreover the thermal (150° C) carbonylation of alumina impregnated with commercial hydrated $OsCl_3$ produce the same kind of species (Fig. 20). It is known that at such temperatures $OsCl_3$ is carbonylated to $[Os(CO)_3Cl_2]_2$ [21].

Additional evidence for the formation of a divalent osmium carbonyl species on the surface was obtained from the gas phase composition shown in Fig. 18. Between 100 and 250° C about 1.6 mole of CO per mole of cluster and about 3 moles of H_2 per mole of cluster are evolved. This gas evolution is consistent with

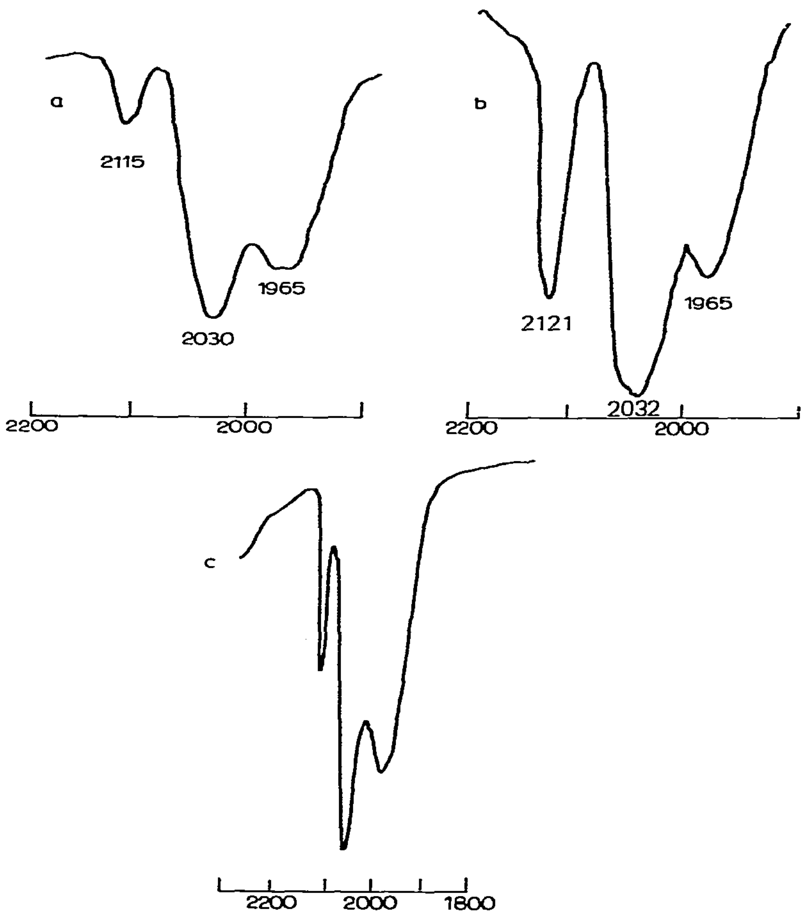


Fig. 20. IR spectra in the ν(CO) region (cm^{-1}). a) $Os_6(CO)_{18}$ on $alumina_{25}$ after treatment under vacuum for 2 hours at 200°C. b) $[Os(CO)_3Br_2]_2$ on $alumina_{400}$ after treatment under vacuum for 20 hours at 250°C. c) $OsCl_3$ on $alumina_{25}$ after treatment under CO (45 mmHg) for 16 hours at 150°C.

the mass balance corresponding to the following surface reactions:

$$\begin{array}{l} Os_3(H)(OAl\lessdot)(CO)_{10} \rightarrow CO + 3\,Os^{II}(CO)_3(OAl\lessdot)_2 + 3\,H_2 \\ \qquad\qquad\qquad\qquad +CO \upharpoonleft\downharpoonright -CO \\ \qquad\qquad\qquad 3\,CO + 3\,Os^{II}(CO)_2(OAl\lessdot)_2 + 3\,H_2 \end{array}$$

The important result is the evolution of 3 moles of H_2/mole of cluster which indicates the formation of an Os^{II} surface complex.

On η-alumina the Os^{II} surface carbonyl species are thermally stable under vacuum at up 300°C. At higher temperatures (e.g. 350°C) a slow decarbonylation occurs during about 30 hours, while the sample turns from white to pale-brown. This decarbonylation is reversible, since upon addition of carbon monoxide (400 mmHg) a white sample with two strong IR absorption bands at 2127 and 2035 cm^{-1} is slowly generated during 100 hours even at temperatures of 350°C.

The behaviour at higher temperatures depends quite strongly on the water

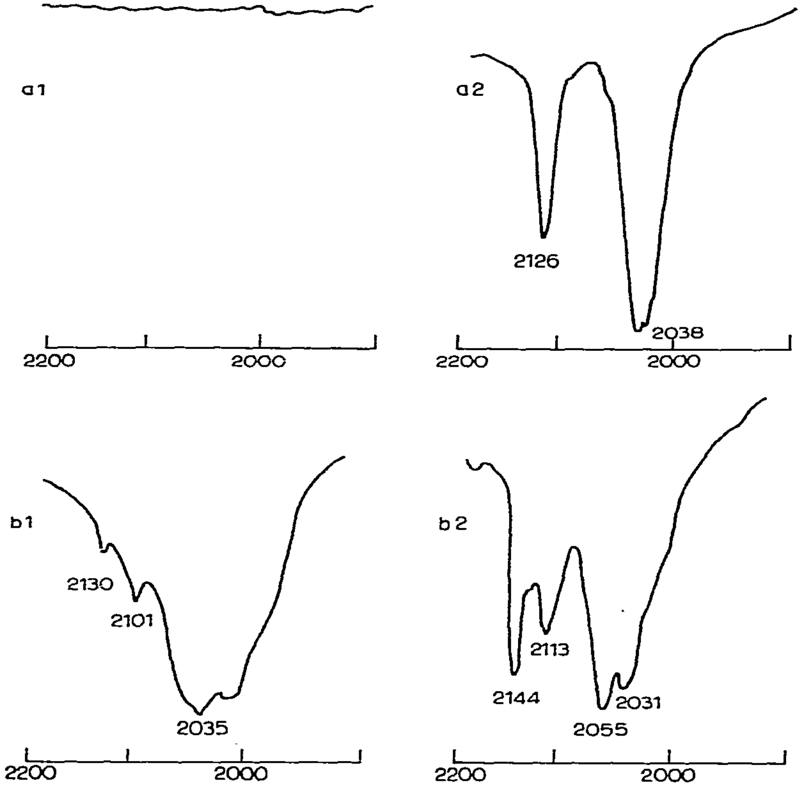


Fig. 21. IR spectra in the ν(CO) region (cm^{-1}). a1) $Os_3(CO)_{12}$ on alumina$_{25}$ after treatment for 30 hours at 350° C. a2) Same sample after treatment under CO (400 mmHg) for 100 hours at 350° C. b1) $Os_3(CO)_{12}$ on alumina$_{400}$ after treatment under vacuum for 14 hours at 400° C. b2) Same sample under CO (400 mmHg) for 46 hours at 400° C.

content of the surface, since a thermal treatment of 40—50 hours at temperatures between 350 and 400°C produces an irreversible decarbonylation if a partial pressure of water is not added. In this case a rather broad infrared spectrum in the carbonyl stretching frequencies area is obtained; however, by addition of 400 mmHg of carbon monoxide a complex, but quite sharp, series of IR absorp-

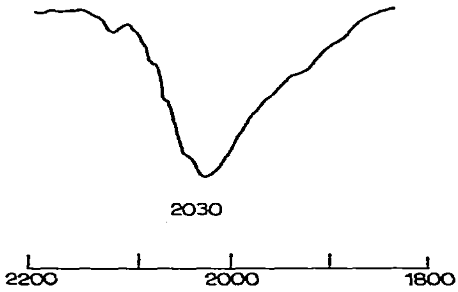


Fig. 22. IR spectra in the ν(CO) (cm^{-1}) region of $Os_3(CO)_{12}$ on alumina$_{400}$ under H_2 (500 mmHg) for 16 hours at 400° C and exposed subsequently to CO (500 mmHg) at 25° C.

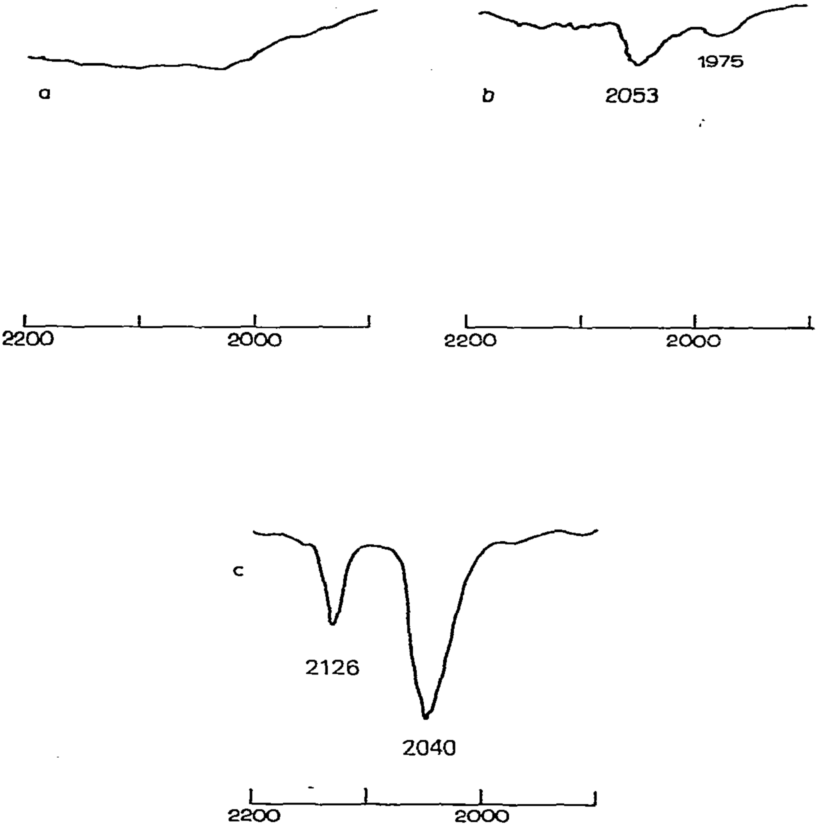


Fig. 23. IR spectra in the ν(CO) region (cm^{-1}). a) $OsCl_3$ on alumina[25] after treatment under H_2 (235 mmHg) for 23 hours at 500°C and subsequently exposed to CO (200 mmHg) at 25°C. b) Same sample after treatment under O_2 (300 mmHg) for 20 hours at 200°C and subsequently exposed to CO (500 mmHg) at 25°C. c) Same sample after treatment under CO (380 mmHg) for 18 hours at 200°C.

tion bands (Fig. 21) is obtained after 40—50 hours at 350—400°C. The sharpness and position of these bands would suggest the formation of a complex mixture of molecular osmium carbonyl species incapsulated in the alumina structure, but different from the Os^{II} species formed at temperatures below 350°C. We have not yet investigated in detail the nature of the carbonyl osmium species formed in this irreversible decarbonylation. It is of interest that even under these drastic conditions (heating under vacuum at 400°C for 40—50 hours) we did not observe the formation of detectable amounts of metallic particles of osmium generated by thermal decomposition. If this kind of thermal treatment is carried out after addition of water to the surface, only a reversible decarbonylation of the Os^{II} carbonyl surface species occurs, even at 400°C.

Metal particles are formed by similar prolonged thermal treatment (16 hours at 400°C) but only under 500 mmHg of H_2. The presence of metallic particles is indicated by the gray colour of the sample and by a broad IR absorption band centered at about 2030 cm^{-1} obtained after the reduction with hydrogen, by introduction of a partial pressure of carbon monoxide (Fig. 22). The metal particles must be quite large, since the carbon monoxide infrared absorption band is very broad. Interestingly, even the large metallic particles produced by hydrogen reduction are easily reoxidised after 20 hours of reaction with 300 mmHg of O_2 at 200° C. The sample turns from gray to pale brown and finally, by admission of carbon monoxide (300 mmHg at 200° C for 20 hours) to white. In parallel, the two-band IR spectrum (2126 and 2040 cm^{-1}) reappears, in agreement with an oxidation of metallic osmium to surface Os^{II} species (Fig. 23).

3. Stoichiometric and catalytic (under $CO + H_2$) hydrocarbon formation with the silica or alumina supported clusters or species derived therefrom

We have previously noted in a preliminary report [41] that thermal treatment of transition metal clusters physisorbed on silica or alumina, with different water contents, gives hydrocarbons at temperatures above 150—200° C in a closed vessel. Under $CO + H_2$ the reaction is catalytic. We consider separately below the stoichiometric formation of hydrocarbons arising from the surface reaction between carbonyl ligands and the water of the surfaces, and the catalytic reaction carried out in static or dynamic reactors.

3.1. Stoichiometric formation of hydrocarbons. When carried out in a closed vessel the thermal decomposition under Ar of $H_2Os_3(CO)_{10}$ adsorbed on $silica_{25}$ gives CH_4, CO_2 and H_2 above 220° C (Fig. 7b). A detailed examination of the evolved gases clearly indicates that a water gas shift reaction between gaseous CO and adsorbed water occurs above 220° C, while H_2 is simultaneously transformed into methane. Both reactions occur in a temperature range in which we have confirmed the formation of Os^{II} carbonyl species by IR spectroscopy. The same kind of experiment was carried out under H_2 with $Os_3(CO)_{12}$ adsorbed on $silica_{25}$ (Fig. 24). Above 250° C gaseous and adsorbed CO (vide supra) are converted mainly into methane, without any significant water gas shift reaction.

On alumina two types of experiments were conducted: thermal decomposition in a closed vessel and semi-dynamic thermal decomposition (Fig. 25a, b and Fig. 18). On $alumina_{25}$ in a static reactor, methane is formed at 150° C, which was rather unexpected. On $alumina_{400}$, formation of methane occurs at much higher temperature (above ca. 300° C). The semi-dynamic thermal decomposition also gives CH_4, H_2 and CO_2 at about the same temperature, 300° C (Fig. 18). Before this temperature we detected only the reversible decarbonylation of the Os^{II} carbonyl species discussed earlier.

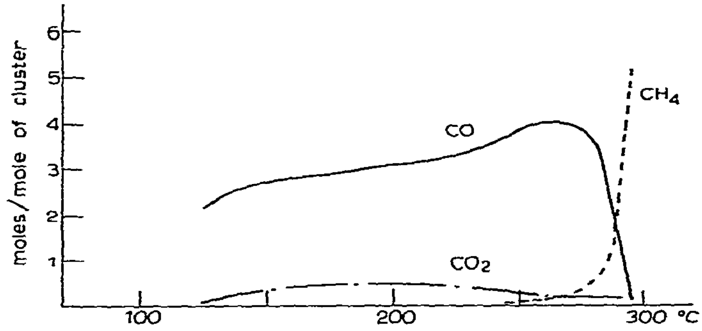


Fig. 24. Gas evolution during the thermal treatment of $Os_3(CO)_{12}$ impregnated on $silica_{25}$ under H_2 (400 mmHg).

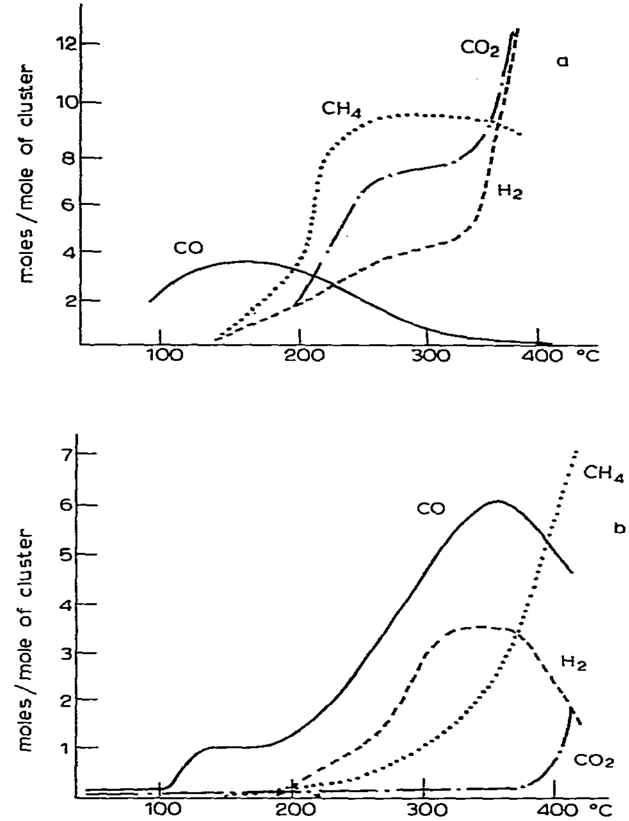


Fig. 25. Gas evolution during the thermal treatment under argon (800 mmHg) of: a) $Os_3(CO)_{12}$ on alumina$_{25}$. b) $Os_3(CO)_{12}$ on alumina$_{400}$.

We tentatively conclude that on silica, as on alumina, the formation of CH_4 generally parallels the water gas shift reaction at temperatures where the breakdown of the cluster into an Os^{II} carbonyl species has already occured. In the presence of hydrogen, the water gas shift reaction does not occur, but methane is formed at the same temperatures.

3.2. Catalytic formation of hydrocarbons under CO + H_2. We examined the hydrocarbon formation in a closed vessel under Fischer-Tropsch conditions (e.g. with a mixture 1 to 1 of CO and H_2) (P_{total} = 1 atm). The selective formation of methane is confirmed for a large range of temperatures on both silica and η-alumina (Fig. 26A, B, C). At lower temperatures, small but detectable amounts of C_2—C_3 hydrocarbons (both saturated and unsaturated) are produced, but above 300°C methane is virtually the only hydrocarbon formed. Comparable results are obtained by using as catalyst physisorbed $Os_3(CO)_{12}$ or the Os^{II} carbonyl species encapsulated in the oxide structure, formed by previous thermal treatment of the physisorbed clusters under vacuum. Experiments have been conducted in another laboratory [53] with the same catalysts under dynamic conditions. The selectivity for methane was very similar to that obtained in our static reactor, which indicates that methane formation does not arise from a secondary cracking of higher molecular weight hydrocarbons. Thus, although we have not carried out an extended investigation, it seems that stoichiometric and

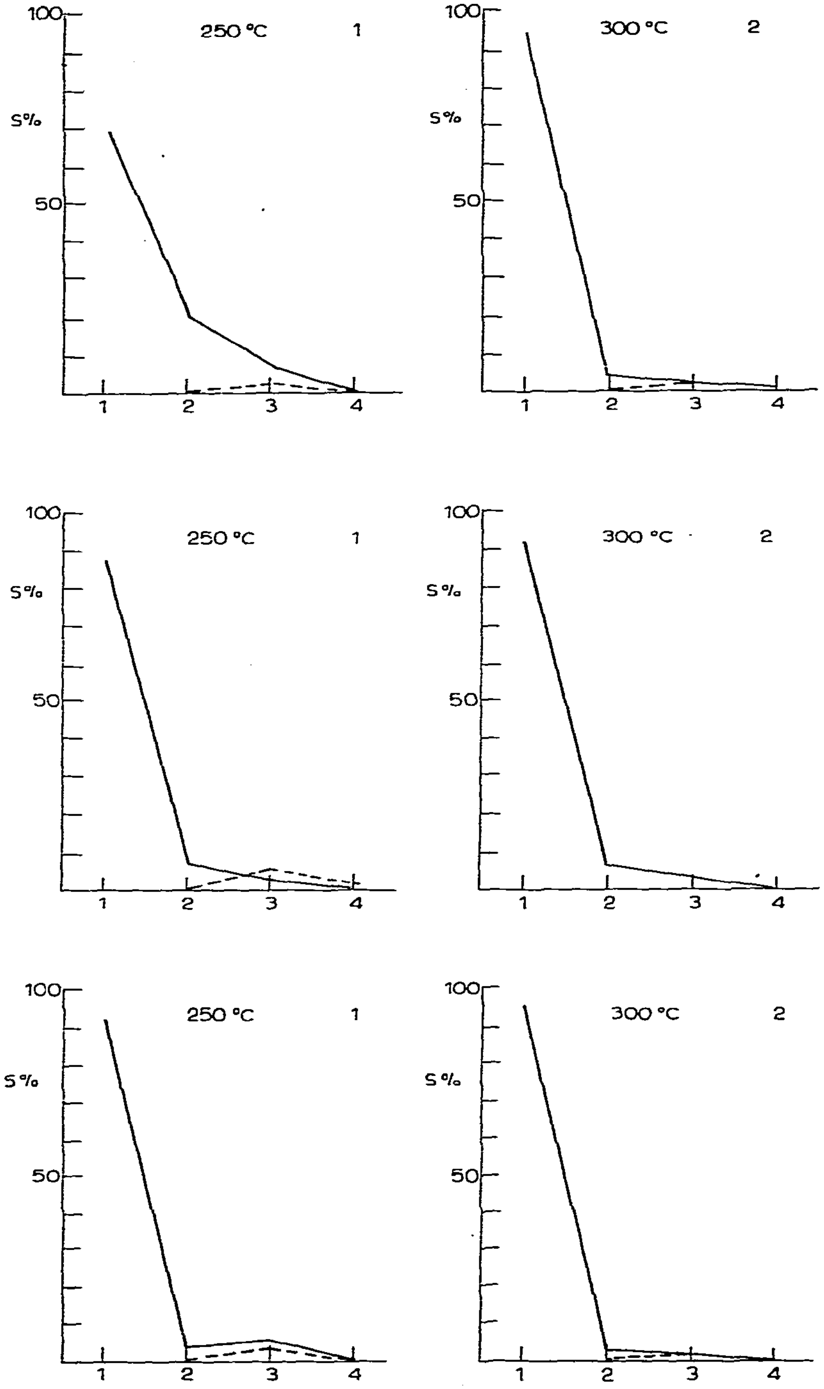


Fig. 26. Selectivities in the reaction CO + H_2. The selectivity *S* toward hydrocarbons is given in molar percentage. The number in abscissa represents the carbon chain length. The dashed line refers to olefins.
a) The catalyst precursor is $Os_3(CO)_{12}$ on silica$_{25}$. b) The catalyst precursor is $Os_3(CO)_{12}$ on alumina$_{25}$. c) The catalyst precursor is $Os_3(CO)_{12}$ on silica$_{25}$ after treatment at 200°C for 4 hours under argon (760 mmHg).

catalytic formation of methane do not occur on the cluster itself but on a degradation product of the cluster, which may be an osmium^{II} carbonyl species.

Unfortunately, no detailed studies have been published on the catalytic synthesis of hydrocarbons from H_2/CO mixtures over heterogeneous osmium catalysts of the Fischer-Tropsch type; in particular the work of Vannice on the Group VIII metals did not include osmium [43]. The only extended comparative investigation of the catalytic behaviour of the Group VIII metals is that by Fischer and coworkers [44]. A low activity of the osmium catalysts, to produce mainly gaseous hydrocarbons, has been reported [45]. If the selectivity of heterogeneous osmium catalysts can be estimated by extrapolation from the systems of low activity reported by Vannice (e.g. Pd, Pt, Ir), which selectivity produce only methane, the high selectivity for methane of our osmium catalytic systems would be as expected for a normal supported osmium metallic catalyst.

However, we cannot at present confidently identify our catalytic systems as a metallic supported catalysts, formed by decomposition and reduction of a physisorbed molecular carbonyl clusters of osmium. In fact, under the thermal conditions of our catalytic runs (250—300° C), we have previously observed mainly formation of molecular osmium carbonyl species encapsulated in the oxide structure. These species are quite stable even under hydrogen, since they are reduced very slowly to metallic osmium only above 300° C (with SiO_2) or 350—400° C (with Al_2O_3). These observations suggest that oxidised surface molecular species of osmium may be the only catalytic entities for the selective reduction of carbon monoxide to methane, although we cannot exclude the presence of tiny amounts of extremely divided metallic osmium particles, even within the range of stability of Os^{II} carbonyl species. With this limitation, our findings complement those of other authors who reported carbon monoxide reduction to low molecular weight hydrocarbons with metal clusters such as $Os_3(CO)_{12}$ in the homogeneous phase, including molten salts [46,47]. However, in our case the catalytic activity is not related to molecular metallic aggregates, such as metal carbonyl clusters, but to simple mononuclear oxidised osmium surface complexes.

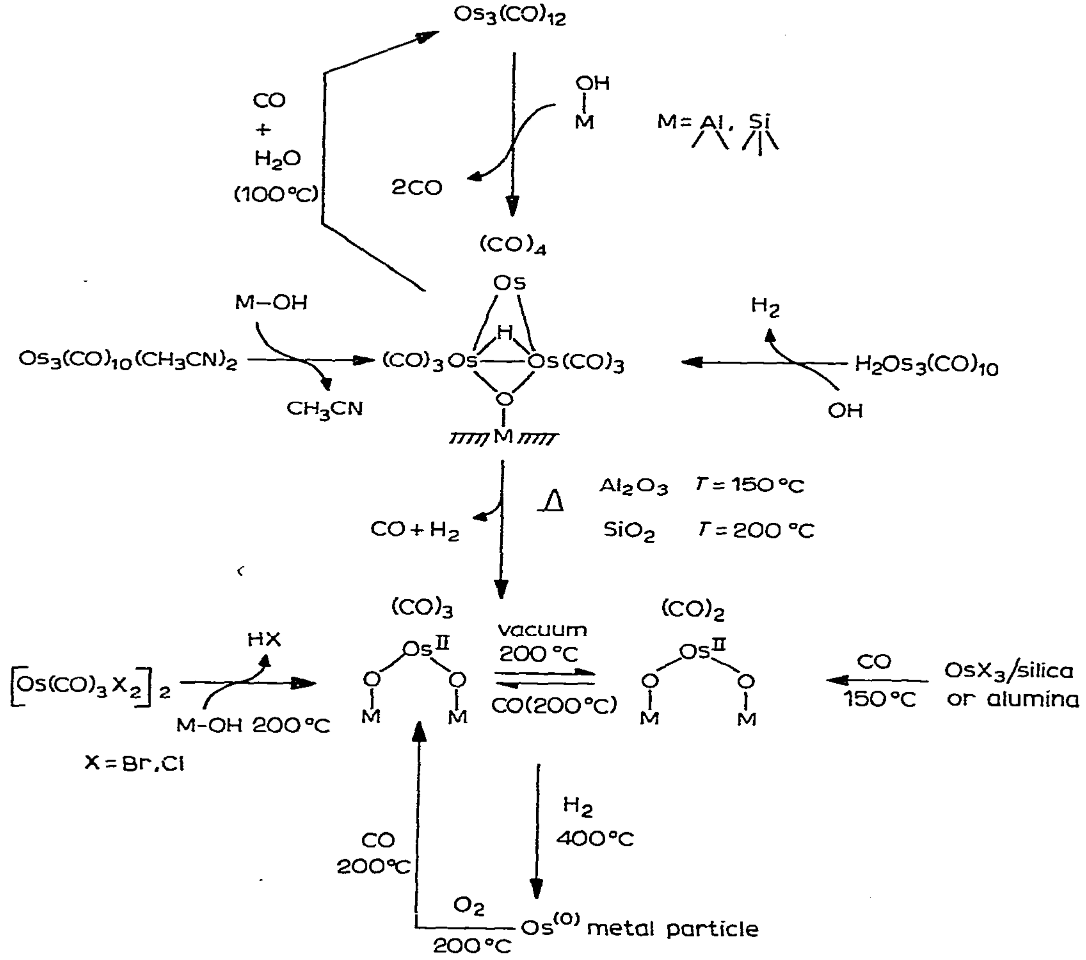
Conclusions

The behaviour of $Os_3(CO)_{12}$ and related osmium clusters on surfaces of alumina and silica seems to be very different from that of $Fe_3(CO)_{12}$ or $Rh_6(CO)_{16}$, which have been previously studied in our laboratories [1—5,9,42]. It more closely resembles that of $Ru_3(CO)_{12}$, recently studied by Bell, Yermakov et al. [48].

In contrast with $Fe_3(CO)_{12}$, which reacts readily with surface OH groups of alumina at room temperature to give anionic hydrides such as $[HFe_3(CO)_{11}]^-$, $Os_3(CO)_{12}$ or related osmium clusters can be stable as such on alumina or silica surfaces up to ca. 70° C (Scheme 1). Anionic hydrides of ruthenium were postulated by Kuznetsov et al. [48] for alumina supports, but were not definitely identified.

The thermal decomposition of the physisorbed cluster $Os_3(CO)_{12}$ does not seem to be initiated by a nucleophilic attack of surface water or surface OH groups followed by protonation of the carbonyl hydrido or carbonyl anionic

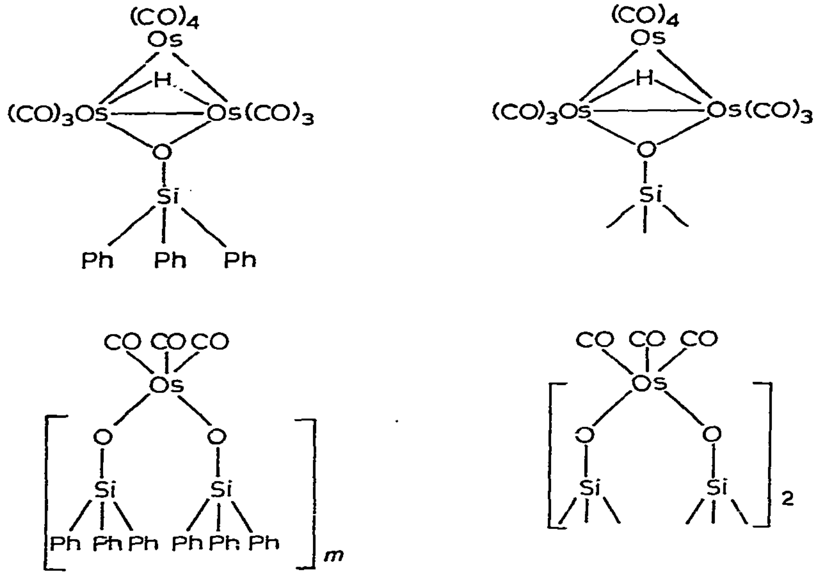
SCHEME 1



clusters as probably occurs with $Rh_6(CO)_{16}$ supported on alumina [3]. The absence of evolution of CO_2 in the early stage of the decomposition rules out such nucleophilic attack [49]. On the contrary, we have isolated a stable intermediate which is covalently bonded to the surface via an oxidative addition of M—OH surface groups (M = Si, Al) to the original cluster cage (Scheme 1). Thus the metal cage is attached to the surface by a covalent —M—O— cluster bond (M = Si, Al). The structure of such a surface species has also been confirmed by use of model compounds (Scheme 2). The attachment of a cluster to the surface of an oxide via Si—O—M bonds is, to our knowledge, the first example of grafting of a cluster via direct covalent bonding. There are known examples of grafting of a cluster to a surface via ligand exchange with a silica functionalised with anions or phosphine groups [17], via hydrogen bonding between the carbonyl ligands and the surface hydroxyl groups [3], via M—CO → Al- complexation [38,50], or via ionic interaction such as $[HFe_3(CO)_{11}]^-M^+$ (M = Al, Mg). Furthermore, such covalent attachment, for which the formal oxidation state of

SCHEME 2

MODEL COMPOUNDS OF SURFACE SPECIES



the osmium is different from zero, can be regarded as a model of the metal—support interaction which is frequently involved in heterogeneous catalysis.

With silica it seems to be possible to regenerate $Os_3(CO)_{12}$ from the covalently bonded cluster with CO + H_2O. It is possible that water hydrolyses the Si—O—Os_3 bond at the surface to produce $Os_3(H)(OH)(CO)_{10}$, which might be carbonylated to $Os_3(CO)_{12}$ with water evolution. This is an unusual observation, since in the homogeneous phase the related complex $Os_3(H)(OPh)(CO)_{10}$ is not reversibly carbonylated to $Os_3(CO)_{12}$ even in solvents containing water.

The breakdown of the grafted cluster occurs at ca. 200°C both on alumina and silica, with parallel oxidation of low valent osmium atoms to divalent osmium by surface OH groups and release of hydrogen. This oxidation process was first clearly demonstrated by Brenner and Burwell for $Mo(CO)_6$ supported on alumina [51]. The oxidised osmium(II) carbonyls surface species have been also obtained from $[Os(CO)_3X_2]_2$, X = Cl, Br, or by carbonylation of OsX_3 supported on silica or alumina. Their structures were confirmed by use of model compounds such as $[Os^{II}(CO)_3(O\text{—}Si(Ph)_3)_2]_m$.

For $Ru_3(CO)_{12}$ on alumina [48] or silica surfaces [52] formation of compounds of the type $[Ru(CO)_3X_2]_n$, $[Ru(CO)_4X_2]_n$ and $[Ru(CO)_2X_2]_n$, in which X represents an atom of the alumina or silica lattice have been observed. As in the case of ruthenium [48], the oxidised Os^{II} carbonyl surface species are thermally and chemically more stable than the corresponding Rh^{I} carbonyl surface species [3]. Thus they are not reduced by H_2O and CO to the original $Os_3(CO)_{12}$, in contrast to the behaviour of surface $Rh^{I}(CO)_2$. Moreover, while the $Rh^{I}(CO)_2$ species is readily reduced to metal by H_2O or H_2 below 100°C, the reduction of Os^{II} carbonyl species by H_2 occurs, very slowly, only above 300°C. Similar behaviour is found with Ru^{II} carbonyl species, but for iron the situation is quite different [42], since zerovalent particles of superparamagnetic iron can be obtained by thermal decomposition of $[HFe_3(CO)_{11}]^-$ or $Fe_3(CO)_{12}$ adsorbed on alumina and magnesia.

The chemical transformations which occur upon thermal treatment of the supported $Os_3(CO)_{12}$ cluster gives a series of well defined species. Interestingly, those transformations are followed by two simultaneous stoichiometric reactions, namely the water gas shift reaction and the formation of methane. From the range of temperatures at which these stoichiometric reactions occur, it seems reasonable to assume that they occur on the Os^{II} carbonyl species, which exhibit extraordinary high thermal and chemical stability. This would rule out the possibility that osmium metal particles are responsible for the stoichiometric reactions.

For the catalytic formation of methane under CO + H_2 with these supported Os species, the results again favour an Os^{II} carbonyl species rather than metallic particles as the catalyst. Although this is not fully confirmed, and deserves further study, the results of our investigation argue against the existence of metallic particles of osmium in Fischer-Tropsch reactions carried out below 300°C. We are currently investigating the possible formation and the nature of metallic particles under Fischer-Tropsch conditions.

In conclusion, as expected from their known kinetic stability towards CO substitution and reactivity towards various reagents, osmium metal clusters display a well defined surface organometallic chemistry associated with specific molecular surface species stable over a large range of temperatures and conditions.

We have presented the first unequivocal evidence for grafting of a metallic cage in which the immobilisation results from an oxidative addition of a surface OH group to a metal—metal bond. This is a unique model, corresponding to a molecular interaction, for the well known interactions between dispersed very small metal particles and supports reported for heterogeneous catalysis. We have also pointed out for the first time that this kind of interaction is dependent upon the water content of the surface and, of course, upon the nature of the support.

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