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Chemisorption and Catalysis by Metal Clusters

I. Characterisation of Materials Obtained by Impregnation of $Os_3(CO)_{12}$ and $Os_6(CO)_{18}$ onto Silica, Alumina, and Titania

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$Os_3(CO)_{12}$ and $Os_6(CO)_{18}$ were impregnated onto silica, alumina, and titania and characterised in the freshly impregnated state and in states achieved by subjecting the freshly impregnated material to (i) washing, (ii) heating to 523K (temperature-programmed decomposition), and (iii) storage at room temperature. The original clusters interact with the support surfaces and are converted to a family of species A of empirical formula $Os_n(CO)_{xn}C_{yn}$, where the most likely value of n is 12, $2.0 \leq x \leq 3.0$, and $0.0 \leq y \leq 0.4$. Retention of osmium–osmium bonding in species A is demonstrated by ultraviolet/visible reflectance spectroscopy and the upper limit of n is suggested by electron microscopy. Infrared spectra of species A contain three bands and indicate the presence of carbonyl ligands bonded to osmium atoms in formal zero, partial negative, and partial positive oxidation states. Species A chemisorbs carbon monoxide and oxygen at 293K, the extent of oxygen chemisorption being the same as that of strong CO chemisorption. A bridged structure for adsorbed-CO is proposed. $[^{18}O]CO$ adsorbed onto species A does not equilibrate, even at high temperatures, with linearly bonded $[^{16}O]CO$-ligands, confirming that adsorbed-CO and ligand-CO are different states of bound CO. CO_2 is formed, probably by a Boudouard reaction, during temperature-programmed decomposition of all freshly impregnated materials, and hence species A prepared in this way may contain ligand-C. Speculations as to likely cluster structures for species A are presented. Chemisorption and catalytic properties will be described in later papers.

INTRODUCTION

The preparation of metal catalysts from metal cluster compounds may provide a means of combining the high reactivity associated with heterogeneous metal catalysts and the high selectivity characteristic of some catalytically active metal complexes in homogeneous solution. Special selectivities may also be obtained if novel site structures can be achieved. Interest in this field is widespread (*1–5*).

Much effort has been expended in developing processes whereby metal clusters may be anchored to functionalised supports (e.g., phosphinated polymers (*6*) or phosphinated silicas (*7*)). These materials fulfill the role of model systems and studies of their properties are valuable. However, the instability of polymer supports at elevated temperatures and the modifying effects of phosphorus on reactivity at metal centres has led us to the view that such materials are unlikely to be robust catalysts. On the other hand, catalysts consisting of metal clusters held at the surfaces of conventional supports by strong cluster–support interac-

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tions appear more promising, provided processes that favour sintering can be inhibited.

In this series of papers we describe the physical, chemisorption, and catalytic properties of materials obtained via the impregnation of a wide range of Group 8 metal cluster compounds onto oxidic supports, including silica, alumina, and titania. The impregnated materials normally require thermal activation before they exhibit catalytic activity. Reactions studied include hydrogenations of unsaturated hydrocarbons, of carbon monoxide and of carbon dioxide, and alkane hydrogenolysis. The kinetics of these reactions and the selectivities achieved differ considerably, in some cases, from those exhibited by conventional supported catalysts prepared from metal salts. This being the case, it will be necessary, because of the volume of work to be described, to report separately our studies of physical characterisation, chemisorption properties, and catalytic properties. This paper is concerned with the characterisation of materials obtained by the impregnation of silica, alumina, and titania with solutions of $Os_3(CO)_{12}$ and $Os_6(CO)_{18}$, and of the effects of washing or heating these materials. Chemisorption properties, presented briefly here, will be described in detail in Section II, and catalytic properties in Section III. (All materials described in this paper as "heated to 523K" were catalysts for the reactions described above.)

Characterisation requires the use of as many techniques as are informative, and the application of each technique at each stage of catalyst preparation. Accordingly, we used (i) electron probe microanalysis to judge how evenly or otherwise osmium-containing entities are distributed over the support, (ii) temperature-programmed decomposition to evaluate the Os : CO balance in the metal-containing entities, (iii) ultraviolet/visible reflectance spectroscopy to determine whether osmium–osmium bonding has been retained, (iv) infrared spectroscopy to monitor the characteristics of the carbonyl ligands of the osmium-containing entities, and (v) transmission electron microscopy to determine whether crystalline osmium is formed. In addition, the degree of chemical unsaturation of the osmium-containing entities was examined by measurements of carbon monoxide adsorption.

The chief concern of this work was to determine whether these osmium cluster compounds are necessarily degraded to mononuclear osmium entities, as is claimed by other workers (*8*), or whether cluster nuclearity can be retained or increased.

EXPERIMENTAL

Instrumentation. Electron probe microanalysis was carried out using a Link Systems Model 290-2KX energy-dispersive spectrometer attached to a Cambridge Instruments Geoscan.

Temperature-programmed decomposition was recorded by the following procedure. A sample weighing 0.300 g was placed on a sintered glass disc in a vertical tube through which helium flowed at 23 ml (STP) min^{-1}. A furnace around the tube enabled the sample temperature to be raised at a steady rate of 10° min^{-1} from 293 to 523K. Temperatures were measured by means of a thermocouple located in the catalyst bed. The gas stream leaving the decomposition chamber contained He, CO, CO_2, C_2H_4, and C_2H_6; the hydrocarbons and CO_2 were condensed in a trap at 77K, and the CO passed on to a chromatograph where its instantaneous concentration was detected. Later, the trap was warmed and the yields of CO_2, C_2H_4, and C_2H_6 were estimated. Small quantities of hydrogen, if evolved, would not have been detected.

Infrared spectra were obtained by use of a Perkin–Elmer 580B spectrophotometer. Precise wavenumber measurements of the absorption maxima were made with reference to the standard wavenumber values of the rotational lines in the vibration–rotation spectrum of CO. The recording of the CO spectrum was followed immediately by the exchange of the carbon monoxide cell for the metal carbonyl sample without stopping the scan. Under these conditions the spectral bandpass was 1.4 cm^{-1}, and the scan rates were 18.8 cm^{-1} min^{-1} for the range above 2000 cm^{-1} and 9.4 cm^{-1} min^{-1} for the range below 2000 cm^{-1}; a 10-fold expansion was used on the abscissa. An accuracy of better than ± 1 cm^{-1} for ν_{max} values of sharply defined carbonyl stretching bands was thus readily achieved, and reproducibility was excellent. For somewhat broader bands the overall accuracy of ν_{max} measurements was never worse than ± 2 cm^{-1}. Ultraviolet/visible spectra were obtained by use of a Pye-Unicam SP 700 spectrophotometer fitted with an SP 735 diffuse reflectance attachment; the cell was constructed according to the pattern published by Zecchina *et al.* (*9*). Electron microscopy was carried out using a JEOL JEM 100C instrument capable of a resolution of 0.5 nm; when used to examine conventional metal/silica catalysts this instrument renders visible metal particles down to 0.8 nm in diameter. CO-chemisorption was measured volumetrically; the catalyst sample was placed in a glass vessel of known volume and connected to a stainless-steel high-vacuum system capable of a base pressure of 10^{-8} Torr (1 Torr = 133.3 N m^{-2}). Pressures in the sample vessel and in attached calibrated volumes were measured by a pressure transducer, or a calibrated thermal conductivity gauge (LKB). CO (>99.95%) and [^{18}O]CO (99 atom %) were used as received.

Catalyst preparation. $Os_3(CO)_{12}$ and $Os_6(CO)_{18}$ were prepared by literature methods (*10, 11*). Each was recrystallized and its purity was examined by HPLC. $Os_3(CO)_{12}$ contained no detectable impurities; $Os_6(CO)_{18}$ was >99% pure, the <1% impurity being $Os_3(CO)_{12}$. Supports used were alumina (Aluminium Oxid C (Degussa)), silica (Cab-O-Sil), and titania (Tioxide). The titania, which was prepared specially for this investigation from an organic titanate, was anatase; it had a purity of >99.9% and a silica content of <100 ppm. Each support was dried by heating to 773K for 16 h in a stream of dry nitrogen. The surface areas of the dried materials, measured by the BET method of N_2 physisorption, were: silica, 110 ± 5 m^2 g^{-1}; alumina, 97 ± 5 m^2 g^{-1}; titania, 43 ± 5 m^2 g^{-1}. Supports were impregnated with solutions of $Os_3(CO)_{12}$ in dichloromethane and of $Os_6(CO)_{18}$ in 1,2-dichloroethane, the solutions being added to suspensions of support. Evaporation to dryness was carried out in a stream of dry nitrogen at 313K, and all of the cluster compound appeared to be impregnated onto the support. Weights of cluster carbonyl and of support were such as to give 2.0% by weight of osmium in all catalysts.

The supported materials, however they have been treated, are referred to as $Os_3(CO)_{12}$/silica, $Os_6(CO)_{18}$/titania, etc. This nomenclature is intended to convey that they were prepared by impregnation of the stated cluster carbonyl onto the support; it is *not* intended to denote the stoichiometry of the supported osmium-containing entities.

RESULTS

I. Characterisation of Impregnated Materials

Examination of the six impregnated materials in the fresh state by low-power optical microscopy (magnification 2000×) revealed the presence of small coloured crystals on the white supports. Electron probe microanalysis confirmed for all samples that there were small areas of high osmium density and larger areas of low osmium density (Fig. 1a). Our impregnation procedure clearly gives an uneven initial distribution of osmium-containing species on the support.

Figure 2 presents the solid-state infrared spectrum of $Os_3(CO)_{12}$ as a nujol-mull, and the spectra of $Os_3(CO)_{12}$ impregnated onto the three supports. Spectrum (a) contains 16 bands; the same 16 bands are pre-

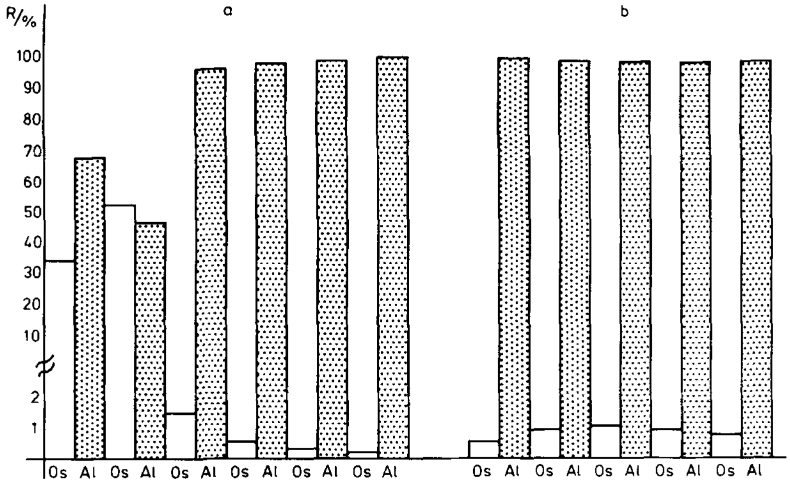

FIG. 1. Relative abundance, R, of osmium and of aluminium in $Os_3(CO)_{12}$/alumina determined by electron probe microanalysis (a) immediately after impregnation and (b) after heating the freshly impregnated sample to 523K *in vacuo*.

sent in the spectra of $Os_3(CO)_{12}$/silica and $Os_3(CO)_{12}$/titania. $Os_3(CO)_{12}$/alumina showed all bands except that at 1956 cm^{-1}. The same solid-state spectrum was obtained for $Os_3(CO)_{12}$ when the sample was prepared in a KBr disc. Figure 3 shows analogous spectra for $Os_6(CO)_{18}$ as a nujol-mull and for $Os_6(CO)_{18}$ impregnated onto the three supports. Spectra reported in the literature for such supported clusters prepared by a different method contain many fewer absorption bands (*12*).

Ultraviolet/visible diffuse reflectance spectra were studied because, for $Os_3(CO)_{12}$, bands at 385 and 330 nm have been assigned, respectively, to $\sigma^{*\prime} \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ transitions involving orbitals associated with osmium–osmium bonds (*13*). Thus these spectra provide evidence for or against the retention of a clustered state at each stage of catalyst preparation. Silica- and alumina-supported materials were examined; spectra of similarly treated blank supports contained no absorption bands. The technique was not applicable where titania was used as the support because this material is opaque to radiation in the range 220–400 nm. Repeat preparations gave reproducible spectra.

Table 1 provides evidence for the retention of molecular integrity in $Os_3(CO)_{12}$ and $Os_6(CO)_{18}$ on impregnation, in agreement with the results from infrared spectroscopy. However, the spectra of both silica- and alumina-supported $Os_3(CO)_{12}$ contain bands above 400 nm which are not present in the starting material, but which are close to bands at 442 and 595 nm observed in the spectrum of $Os_6(CO)_{18}$.

II. Characterisation of the Impregnated Materials after Heating to 523K

Chemical changes occurred on heating the impregnated materials to 523K. The stoichiometry of the change and the products formed were examined by temperature-programmed decomposition, and information concerning the transformed species was obtained spectroscopically. Changes in the capacities of the materials to adsorb carbon monoxide were examined as a function of heat treatment, and further information on the final states of the materials was obtained by electron microscopy.

Temperature-programmed decomposition. Each of the six cluster-compound/support combinations was heated in a flow of helium from 293 to 523K, and the evolved

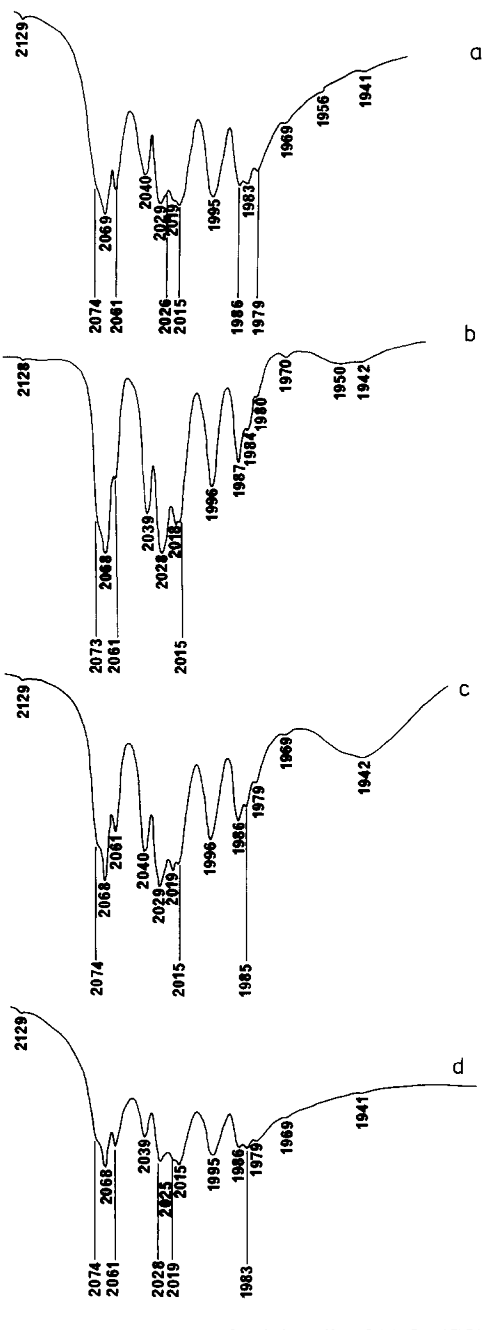

FIG. 2. Infrared spectra of nujol-mulls of (a) $Os_3(CO)_{12}$; (b) $Os_3(CO)_{12}$/titania; (c) $Os_3(CO)_{12}$/alumina; (d) $Os_3(CO)_{12}$/silica.

gases were analyzed. The manner of the progressive loss of carbon monoxide is shown in Fig. 4; none was desorbed from $Os_6(CO)_{18}$/silica or from $Os_6(CO)_{18}$/alumina. The gases evolved are listed in Table 2. Carbon monoxide loss was least for silica-supported materials and greatest for titania-supported materials; however, more than 50% of the ligand-CO was always retained. Evolution of ethene and ethane indicates reaction between the cluster compound and hydroxyl groups of the support.

Diffuse reflectance spectroscopy. Ultraviolet/visible diffuse reflectance spectra were obtained for materials heated in vacuum to 323, 373, 423, 473, and 523K. The typical effects of the progressive heat treatments are shown for $Os_3(CO)_{12}$/alumina in Fig. 5. Changes in the spectra were gradual and spectral features were retained even by materials heated to 473 and 523K. Although the spectra of the four original impregnated materials differed from each other, the process of heating to 473K transformed them to materials having similar spectra (Table 1).

A sample of $Os_3(CO)_{12}$/alumina was heated to 523K as described, cooled to 293K, and exposed to 100 Torr CO; this procedure caused an increase in intensity of the band at 613 nm (Fig. 6), but no other band was affected.

Infrared spectroscopy. As samples were heated, so their spectra changed from the 16-band system (Figs. 2, 3) to a simple 3-band system (Figs. 7, 8), the bands being at 1950 ± 15 cm^{-1} (s), 2030 ± 10 cm^{-1} (s), and 2122 ± 3 cm^{-1} (w). The relative intensities of these three bands, for the six samples, are given in Table 2. No bands attributable to carbonate or carboxylate were observed. Again, osmium-containing species showed identical spectra after heating to 523K, irrespective of the cluster or support used.

Isotherms for the adsorption of carbon monoxide and oxygen. Isotherms for CO adsorption at 293K were obtained using the freshly impregnated materials; adsorption by similarly treated blank support, where it occurred, has been subtracted. Isotherms showed a steeply rising extent of adsorption with pressure at low equilibrium pressures (<0.2 Torr, primary adsorption re-

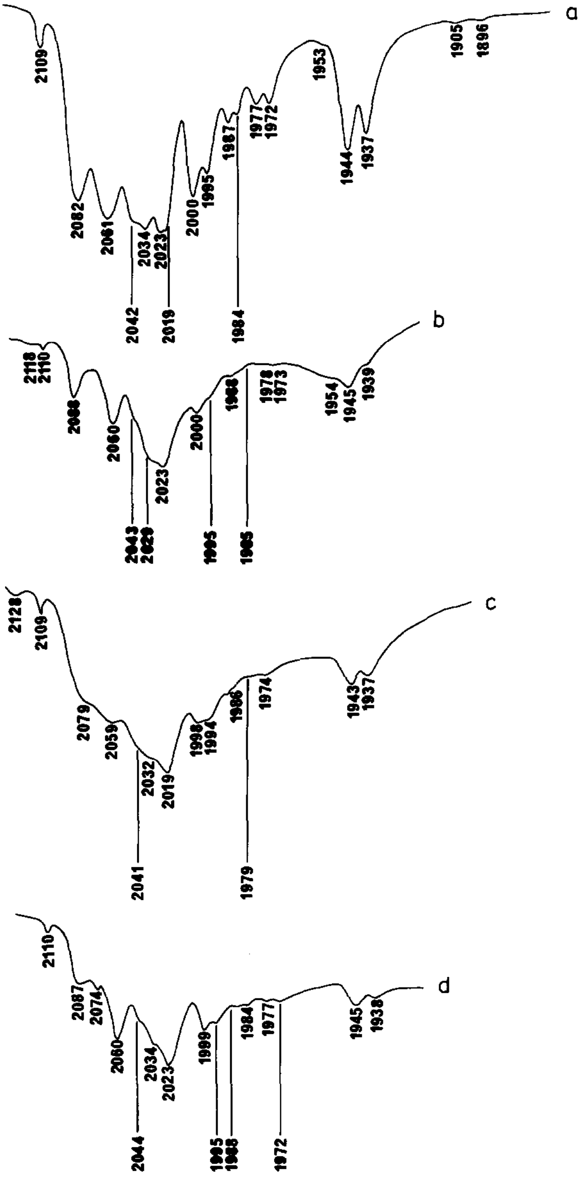

FIG. 3. Infrared spectra of nujol-mulls of (a) $Os_6(CO)_{18}$; (b) $Os_6(CO)_{18}$/titania; (c) $Os_6(CO)_{18}$/alumina; (d) $Os_6(CO)_{18}$/silica.

gion) followed by a secondary region (0.2–1.0 Torr) where additional carbon monoxide was adsorbed. Samples which had been heated and pumped to 523K, and cooled to 293K, adsorbed larger quantities of carbon monoxide than the freshly impregnated materials (Table 3).

This adsorbed material was completely removed as CO by pumping and heating to 523K. The possibility of interconversion between adsorbed-CO and ligand-CO was examined using [^{18}O]carbon monoxide as the adsorbate and various samples, each heated to 523K and cooled to 293K, as adsorbent. No interconversion between adsorbed [^{18}O]carbon monoxide and carbonyl

TABLE 1

Peak Maxima, λ_{max}, in Ultraviolet/Visible Absorbance and Reflectance Spectra

	Sample[a]	λ_{max} (nm)																				
Reference compounds	$Os_3(CO)_{12}$[b]			244			289		329			394										
	$Os_6(CO)_{18}$[b]	209		242			296			355		394		442	463		530		595			
	$Os_{10}C(CO)_{24}^{2-}$[c]	226	228					312	341			387				485				667	781	
Freshly impregnated samples	3/A		229	250			292	314					411	431					602			893
	3/S	226					287		328					431						649		
	6/A		228		266					342				427		495			595			
	6/S	222					292		328		370		413		452				606			
Heated samples	3/A[d]	223	230		263	273	286	320				394					540		613			870
	3/S	224	230			278	291	315			370		417			476		581	602		714	
	6/A[d]	226	231		269		283	317				394					540		613			
	6/S	225	230				294		331		376	400		424	450				595	658		
Washed samples	3/A	222	230				290	303	333						450				617			881
	3/S	226				274			335			394				488			613			862
	6/A		236				298					394			467				613		769	
	Assignments	Metal–ligand charge-transfer			Unassigned			$\sigma \rightarrow \sigma^*$			$\sigma^{*\prime} \rightarrow \sigma^*$			Unassigned								

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[a] Code: 3 = $Os_3(CO)_{12}$; 6 = $Os_6(CO)_{18}$; A = alumina; S = silica.

[b] In solution in cyclohexane.

[c] In solution in ethanol.

[d] Heated to 523K.

TABLE 2

Temperature-Programmed Decomposition of Supported $Os_3(CO)_{12}$ and $Os_6(CO)_{18}$ over the Range 293–523K, and the Relative Intensities of the Three Bands in the Infrared Spectra of Each Species A So Produced

	Loss[a] (%)	Products of TPD (%)				Number of CO-ligands retained per Os atom present (±0.1)	Relative band intensities (%)		
		CO	CO_2	C_2H_4	C_2H_6		~2122 cm^{-1}	~2030 cm^{-1}	~1950 cm^{-1}
$Os_3(CO)_{12}$/alumina	40	88	9	3	tr[b]	2.2	6	45	49
$Os_3(CO)_{12}$/silica	27	92	8	tr	0	2.8	10	46	44
$Os_3(CO)_{12}$/titania	47	90	9	1	tr	2.0	6	51	44
$Os_6(CO)_{18}$/alumina	15	0	91	7	2	2.2	4	44	52
$Os_6(CO)_{18}$/silica	5	0	100	0	0	2.8	8	46	46
$Os_6(CO)_{18}$/titania	27	82	16	2	0	2.0	13	50	37
$Os_6(CO)_{18}$/alumina[c]						3.0[d]	6	49	45

[a] Total carbon loss expressed as the percentage of CO-ligands converted to products.
[b] tr = Trace = <0.5%.
[c] Sample in which spreading of osmium entities over the support surface, and the simultaneous conversion of a 16-band spectrum to a 3-band spectrum, occurred at room temperature.
[d] Deduced from subsequent temperature-programmed decomposition.

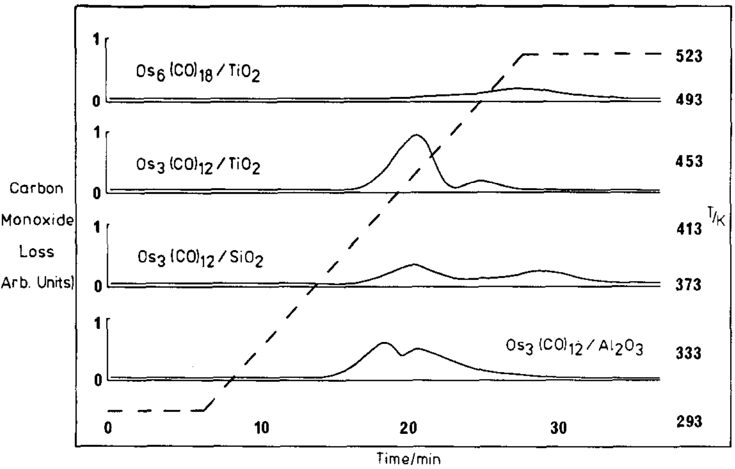


FIG. 4. Carbon monoxide evolutions in temperature-programmed decompositions.

ligands was observed either during the measurement of the isotherm or during subsequent heating to 523K to remove the adsorbed gas.

The chemisorption of oxygen at 293K onto $Os_3(CO)_{12}$/titania previously heated to 523K was also studied. The isotherms showed a considerable adsorption at low equilibrium pressures (<0.2 Torr) followed by a plateau. The amount of oxygen adsorbed at an equilibrium pressure of 0.2 Torr was close to the amount of carbon monoxide adsorbed at the same equilibrium pressure.

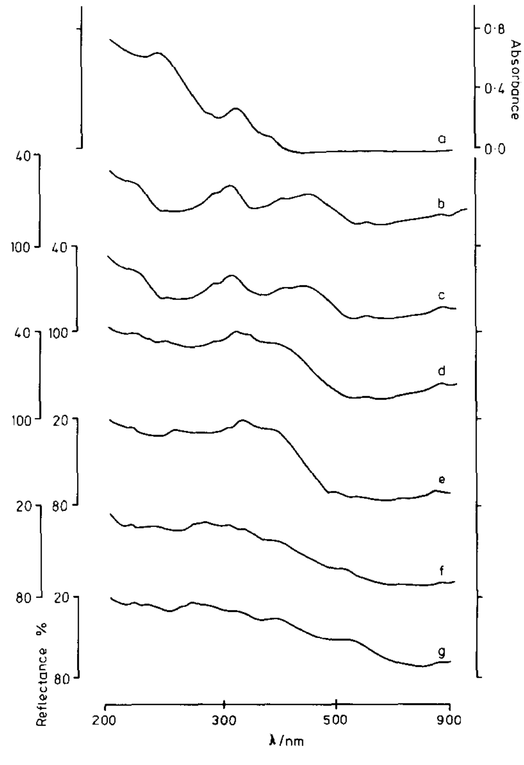


FIG. 5. Ultraviolet/visible spectra. Absorbance spectrum of $Os_3(CO)_{12}$ in cyclohexane versus a cyclohexane reference (a); diffuse reflectance spectra versus an alumina reference of freshly impregnated $Os_3(CO)_{12}$/alumina (b), and of (b) after heating *in vacuo* to 323K (c), 373K (d), 423K (e), 473K (f), and 523K (g).

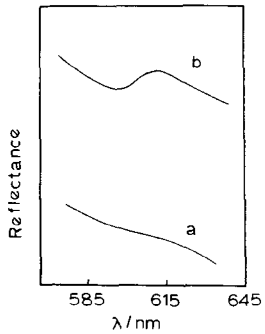


FIG. 6. Effect of adsorbed-CO on the ultraviolet/visible reflectance spectrum. Freshly impregnated $Os_3(CO)_{12}$/alumina heated to 523K *in vacuo* and cooled to 293K gave spectrum (a). This material, subsequently exposed to 100 Torr CO at 293K and evacuated, gave spectrum (b). The sample, after further heating to 523K *in vacuo* and cooling to 293K, gave a spectrum indistinguishable from (a). The full spectrum is given in Fig. 5g.

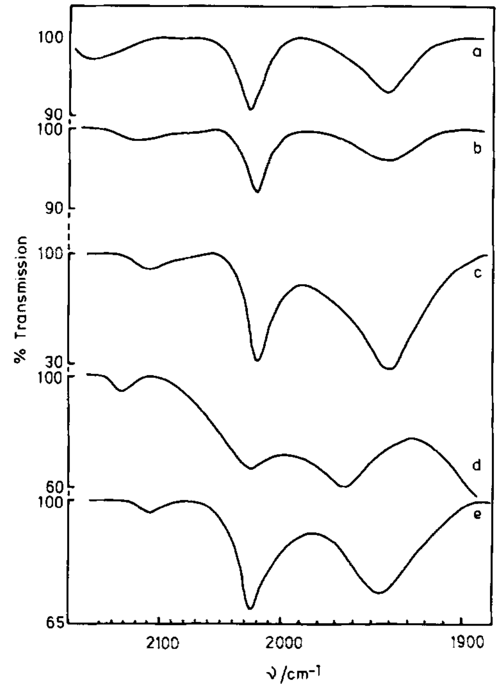


FIG. 7. Infrared spectra of various $Os_3(CO)_{12}$/support combinations: (a) washed $Os_3(CO)_{12}$/alumina; (b) washed $Os_3(CO)_{12}$/titania; (c) impregnated $Os_3(CO)_{12}$/alumina after heating to 523K; (d) $Os_3(CO)_{12}$/silica after heating to 523K; (e) $Os_3(CO)_{12}$/titania after heating to 523K.

Electron microscopy. Only silica-supported materials were suitable for high-resolution transmission electron microscopy. $Os_3(CO)_{12}$/silica and $Os_6(CO)_{18}$/silica, after heating to 523K, each gave micrographs which contained features which suggested the presence of very small osmium-containing species. The size of these features was close to the limit of resolution (~0.8 nm). Measurement of the micrographs indicated that for both $Os_3(CO)_{12}$/silica and $Os_6(CO)_{18}$/silica 99% of the features were less than 1.0 nm in diameter.

III. Characterisation of Washed Impregnated Materials

TABLE 3

Carbon Monoxide Adsorption at 293K

	CO adsorbed[a] µmol (g catalyst)⁻¹	
	Freshly impregnated sample	Sample after heating to 523K
$Os_3(CO)_{12}$/alumina	0.0	6.0
$Os_3(CO)_{12}$/silica	1.5	17.5
$Os_3(CO)_{12}$/titania	0.9	41.3
$Os_6(CO)_{18}$/alumina	0.0	28.5
$Os_6(CO)_{18}$/silica	2.0	5.5
$Os_6(CO)_{18}$/titania	0.9	8.5

[a] Equilibrium pressure = 0.2 Torr.

Freshly impregnated samples were washed to remove $Os_3(CO)_{12}$ or $Os_6(CO)_{18}$ which had not interacted with the support surface. Washed samples were examined spectroscopically to determine whether osmium carbonyl entities were retained on the supports. The degree of unsaturation of these entities was examined by carbon monoxide chemisorption.

Silica- and alumina-supported samples were examined by ultraviolet/visible diffuse

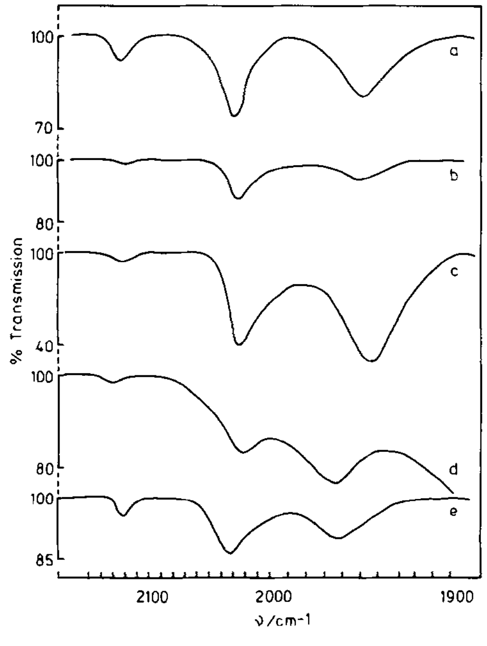


FIG. 8. Infrared spectra of various $Os_6(CO)_{18}$/support combinations: (a) washed $Os_6(CO)_{18}$/alumina; (b) washed $Os_6(CO)_{18}$/titania; (c) $Os_6(CO)_{18}$/alumina after heating to 523K; (d) $Os_6(CO)_{18}$/silica after heating to 523K; (e) $Os_6(CO)_{18}$/titania after heating to 523K.

reflectance spectroscopy (Table 1). Spectra obtained are similar, except in respect to reduced intensity, to those observed for the heated samples.

Infrared spectra of washed samples are shown in Figs. 7 and 8. The positions of the bands and the relative band intensities in the spectra of the washed alumina- and titania-supported materials are very similar to those obtained for the same materials heated to 523K. No carbonyl bands were observed in the spectra of the washed silica-supported materials.

The isotherm for carbon monoxide adsorption onto washed $Os_6(CO)_{18}$/titania resembled closely that measured for carbon monoxide adsorption onto freshly impregnated $Os_6(CO)_{18}$/titania.

DISCUSSION

The majority of the cluster/support combinations described in this paper exhibit catalytic activity which, in some cases, differs considerably from that of conventional supported osmium. As a first step towards the development of the understanding of this catalysis we discuss the physical character of these materials in their freshly impregnated, washed, and thermally activated states.

The Freshly Impregnated State

Our impregnation procedure gives a heterogeneous distribution of osmium-containing entities over the surface of each support (optical microscopy and electron probe microanalysis (Fig. 1a)) and where local osmium concentration is high the species present is crystalline starting material (i.e., $Os_3(CO)_{12}$ or $Os_6(CO)_{18}$, infrared spectroscopy (Figs. 2, 3)). Ultraviolet/visible spectra (Table 1) are consistent with the presence of the original cluster compound, but bands at wavelengths greater than 400 nm indicate additionally the formation of species of a second kind. The small capacity of the freshly impregnated materials to chemisorb CO (Table 2) is likewise attributed to the presence of a second type of osmium-containing species, since $Os_3(CO)_{12}$ and $Os_6(CO)_{18}$ do not chemisorb CO.

The Washed State

The properties of the species of the second kind became more apparent when the $Os_3(CO)_{12}$ or $Os_6(CO)_{18}$ crystals were removed from the supports by washing. A low concentration of evenly distributed osmium-containing species was retained on the support which gave a weak three-band infrared spectrum (Figs. 7, 8) fundamentally different from the spectra of the starting materials for which no evidence remained. Ultraviolet/visible spectra of washed materials (Table 1) confirmed that the evenly distributed material was responsible for the bands above 400 nm. Such spectra also contained bands below 400 nm that were not previously resolved when the original cluster compounds were present. The extent of CO adsorption by washed samples was similar to that by freshly impregnated samples; this confirmed that CO adsorption occurred only on the evenly distributed species.

Nomenclature: Species A

Three-band infrared spectra were obtained not only for the washed samples discussed above but also for self-spread and thermally activated materials. We know from the TPD results that species giving these spectra can differ with respect to their Os : CO ratio and they may also differ with respect to osmium nuclearity. It appears that these samples considered together contain a family of related osmium-containing species; in this discussion we refer to all members of the family as "species A."

Heated Samples

The intensities of the infrared and ultraviolet/visible spectra were such as to show that species A was a minority species in the freshly impregnated materials and in samples heated to about 423K. Above 423K changes occurred so that by 523K no spectral features attributable to $Os_3(CO)_{12}$ or

$Os_6(CO)_{18}$ remained, but features attributable to species A had greatly strengthened. No crystals of the initial cluster compound were visible by optical microscopy in materials heated to 523K and electron probe microanalysis showed an even spread of osmium-containing material over the support (Fig. 1b). Thus the heating procedure facilitated both the diffusion of osmium-containing entities over the support and the conversion of the original cluster compounds to species A. Ultraviolet/visible spectra showed that osmium-osmium bonding was retained in these species A. These entities could not be removed from any of the supports by washing, which suggests the presence of a metal–support interaction.

The amount of carbon monoxide lost from each cluster/support combination during temperature-programmed decomposition measurements depended upon both the complex and the support (Table 2). Remarkably, although the Os : CO ratio varied from 1 : 2.8 to 1 : 2.0, the infrared spectra showed the same three bands with *similar relative intensities* irrespective of the ratio (Table 2); we return to this matter later.

The Self-spread State

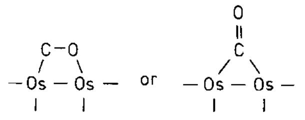
When freshly impregnated samples of supported $Os_6(CO)_{18}$ were left to stand at room temperature in the dark for some weeks migration of osmium-containing entities occurred until all osmium was evenly distributed over the surface of the support as species A. Migration was particularly slow over silica, but faster over alumina and titania. Temperature-programmed decomposition of these self-spread samples gave results similar to those reported in Table 2 for freshly impregnated $Os_6(CO)_{18}$/support combinations. *Therefore* $Os_6(CO)_{18}$ *can be converted into one member of the species A family without loss of carbon monoxide.*

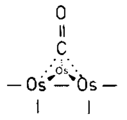
In contrast, $Os_3(CO)_{12}$/support combinations showed no tendency to achieve a self-spread state at room temperature.

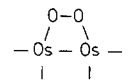
Retention of Osmium–Osmium Bonding in Species A

Tyler *et al.* (*13*) have shown that ultraviolet/visible spectra provide evidence concerning metal–metal and metal–ligand bonding in (unsupported) $Os_3(CO)_{12}$ and other cluster compounds. By analogy, for washed, self-spread, and heated samples containing only species A, we assign bands below 250 nm to metal–ligand charge-transfer transitions and bands in the range 300–400 nm to transitions involving orbitals associated with osmium–osmium bonds (Table 1). Hence we conclude that each species A contains an osmium cluster framework. This conclusion is supported by the spectrum of $[Ph_3P_2N^+]_2[Os_{10}C(CO)_{24}{}^{2-}]$, which is also given in Table 1; *this spectrum is remarkably similar to that of species A.*

Bands above 400 nm are given both by species A and by $Os_6(CO)_{18}$ and $Os_{10}C(CO)_{24}{}^{2-}$ in solution, but not by $Os_3(CO)_{12}$. Although some bands may be due to *d–d* transitions, it appears that the bands above 400 nm are mostly characteristic of a clustered state of considerable nuclearity. When carbon monoxide was adsorbed at room temperature onto a sample of $Os_3(CO)_{12}$/alumina previously heated to 523K the band at 613 nm was considerably enhanced (Fig. 6), whereas the metal–ligand charge-transfer band at 223 nm was not. This demonstrates that the band at 613 nm is associated with adsorbed-CO and that this form of bound carbon monoxide is distinguishable from the remaining CO-ligands which we assume retain the linear structure that they possess in the original cluster compounds. We suggest that this adsorbed-CO has a bridged structure (A) or possibly a capped structure (B) in keeping with Tyler *et al.* (*13*), who propose that metal–ligand charge-transfer transitions involving bridged carbonyl should occur in the visible region. Such structures are consistent with the retention of osmium–osmium bonding.


(A)


(B)


(C)

No spectral evidence for adsorbed-CO was obtained in the infrared region. Adsorbed-CO entities were fewer in number than the ligand-CO entities, usually by more than an order of magnitude (see below), and we would not wish to suppose that all adsorbed-CO entities have exactly the same structure. There may be a range of closely related bridged and capped structures. Thus, even if the extinction coefficients for adsorbed-CO and ligand-CO were similar, the band for the former might reasonably be weak and broad, and go undetected.

The amounts of CO and O_2 strongly adsorbed were the same. This is consistent with the state of strongly adsorbed O_2 being structure (C), which is proposed in Section II on the basis of chemisorption measurements.

Electron microscopy of $Os_3(CO)_{12}$/silica and of $Os_6(CO)_{18}$/silica heated to 523K showed the presence of osmium-containing entities having diameters near the limit of resolution (~0.8 nm). We suggest that a process of cluster growth occurs during heating terminating at a nuclearity in the region, say, 12–18.

The Infrared Spectra of Species A

The three-band infrared spectra given by all species A resemble spectra reported by other investigators (*8*) who have concluded that $Os_3(CO)_{12}$ and $Os_6(CO)_{18}$ break down at support surfaces to mononuclear $Os(CO)_2$ and $Os(CO)_3$. Each dissociated species should, from group theory considerations, give rise to a pair of absorption bands, and a spectrum of a mixture should thus give four bands. The centre band of the observed three-band spectra has been proposed to arise by overlap of one band from each of the two pairs. The above investigators (*8*) did not record ultraviolet/visible spectra nor were the chemisorption properties of the materials investigated.

Any attempt to interpret our infrared spectra of species A in terms of cluster dissociation to mononuclear entities collapses on several grounds. The self-spread species derived from $Os_6(CO)_{18}$/alumina or the heated $Os_6(CO)_{18}$/silica have stoichiometries close to Os : CO = 1 : 3 yet they gave all three bands. Species which TPD show to be Os : CO = 1 : 2 gave the same three bands with much the same ratio of intensities (Table 2). Moreover, although the highest- and lowest-frequency bands move somewhat from spectrum to spectrum (Figs. 7, 8), in no case is there any evidence that the centre band contains two components. Thus we reject the notion that cluster dissociation to $Os(CO)_2$ and/or $Os(CO)_3$ is responsible for the three-band infrared spectra given by our materials.

As an alternative, and bearing in mind the evidence for the clustered state of osmium presented above, we propose the spectra to be due to carbon monoxide bonded to a metal-like aggregate of osmium atoms. CO adsorbed on polycrystalline osmium gives rise to a band at 2030 cm^{-1} (*14*); for comparison with the clustered state we consider this to be equivalent to CO bonded to an osmium atom in the zero oxidation state. By analogy with the interpretation of frequency shifts for cationic, neutral, and anionic carbonyl species formed in argon matrices at low temperature (*15*), we attribute the band at about 1950 cm^{-1} to CO bonded to an osmium atom in a fractionally negative formal oxidation state and the band at about 2120 cm^{-1} to CO bonded to osmium in a fractionally positive formal oxidation state. Frequency shifts of ±100

cm^{-1} or thereabouts for a change in formal oxidation state of ±1 are comparable with those reported for many analogous carbonyls of V, Cr, Mn, Fe, Co, and Ni in matrix isolation work (*15*).

The presence of the three bands in all spectra indicates that these three oxidation states of osmium are present in all members of the family of species A. The relative populations of the three oxidation states are less easy to assess because, in general, as the vibrational frequency of a CO stretching band in these systems decreases, its extinction coefficient increases (*15*). Thus the fractionally positive and negative formal oxidation states of osmium may well be present in roughly comparable quantity, with the zero oxidation state predominating over both.

Three oxidation states have been identified in an X-ray study of $Os_6(CO)_{18}$ by Mason *et al.* (*16*); the ratios are $+1:0:-1 = 1:1:1$. The three states may be retained in the dimerisation or trimerisation of Os_6 units (see below).

Such CO-vibration frequencies are known to depend on environment (e.g., on solvent for species in solution) (*17*). For our materials, the frequency shifts were characteristic of support environment.

The Metal–Support Interaction

Failure to remove any of species A from the supports by washing hints at the presence of chemical bonding between the clustered entity and the support. Shifts in the bands of the infrared spectra of species A provide further evidence for metal–support interactions. The support surfaces are mildly basic (*18*). Strong base, such as methanolic KOH, reacts with $Os_6(CO)_{18}$ causing it to fragment to $Os_5(CO)_{15}^{2-}$ (*19*), whereas weak base, such as iodide ion, simply reduces $Os_6(CO)_{18}$ to $Os_6(CO)_{18}^{2-}$ (*20*). The action of the support surface is expected to be closer to that of iodide ion, and hence we envisage that partial electron donation will occur from the support to osmium; in turn, this will result in increased electron donation from osmium to antibonding π-orbitals of carbon, thus weakening the carbon–oxygen bond. The overall effect should provide for a lowering of the frequency of the band attributed to CO bonded to such an osmium atom. Alumina and titania surfaces are more basic than those of silica, and hence bands should appear at lower frequency for species A/alumina and species A/titania than for species A/silica. The recorded values for CO bonded to osmium in the fractionally negative formal oxidation state are 1944, 1946, and 1963 cm^{-1} in agreement with this expectation (Figs. 7, 8).

Carbon Dioxide Formation

Carbon dioxide was produced during temperature-programmed decomposition (Table 2), as were small yields of C_2 hydrocarbons. Equations (1) and (2) are two processes whereby carbon dioxide may be formed; the first is a Boudouard reaction, and the second is a variant of the water gas shift reaction.

$$2CO(ligand) \rightarrow C(ligand) + CO_2(g) \quad (1)$$

$$2OH(support) + CO(ligand) \rightarrow O(support) + H_2(g) + CO_2(g) \quad (2)$$

We ascribe the majority of CO_2 formation to Eq. (1) because various studies (*21*) have shown that as the carbon–oxygen bond in $MC{\equiv}O$ is weakened so the formation of CO_2 is favoured, and *vice versa.* Experiments with our catalysts show that, generally, ligand-CO breakdown to CO_2 increases with increasing electron donation from the supports. Other information confirms this view: (i) we infer in Section II (*22*) the presence of ligand-carbon in species A from adsorption measurements, (ii) we show in Section III (*22*) that CO_2 is normally a primary product of CO hydrogenation over species A in a static reactor, and (iii) the extent of CO_2 formation described here sometimes exceeds the likely capacity of the supports to supply incipient water by dehydration.

Hydrogen present in C_2 hydrocarbons must originate in the support. The catalytic activity of species A in a flow system was insufficient for C_2 production to be attributed to CO_2 hydrogenation following the water gas shift, or to the hydrogenation of ligand-CO (*22*). We attribute hydrocarbon formation to an interaction of OH(support), or of water formed by dehydration of the support, with C(ligand) formed in Eq. (1). Any methane formed in such a reaction would have been eluted, with the carbon monoxide, and in such small yield would not have been detected.

Empirical Formulae of Species A

Species A obtained by heating to 523K thus has the general formula $Os_n(CO)_{xn}C_{yn}Z_{zn}$, where Z represents adsorption sites and, in addition, some osmium atoms are involved in cluster–support interactions. From information in Tables 2 and 3 (assuming that all CO_2 formation occurs by Eq. (1) and that the number of adsorption sites is twice the number of CO molecules adsorbed) the empirical formulae for species A are as follows:

$Os_3(CO)_{12}$/silica	$Os_n(CO)_{2.8n}C_{0.1n}Z_{0.3n}$
$Os_3(CO)_{12}$/alumina	$Os_n(CO)_{2.2n}C_{0.1n}Z_{0.15n}$
$Os_3(CO)_{12}$/titania	$Os_n(CO)_{2.0n}C_{0.2n}Z_{0.8n}$
$Os_6(CO)_{18}$/silica	$Os_n(CO)_{2.8n}C_{0.1n}Z_{0.15n}$
$Os_6(CO)_{18}$/alumina	$Os_n(CO)_{2.2n}C_{0.4n}Z_{0.5n}$
$Os_6(CO)_{18}$/titania	$Os_n(CO)_{2.0n}C_{0.1n}Z_{0.2n}$

Clearly, for the number of carbon atoms to be integral and for $Z \geq 2$ (as is required by structure A), *n* must take a minimum value in the region of 12, in agreement with the conclusions from electron microscopy.

Possible Structure Types for Species A

Dimerisation or trimerisation of Os_6 units provides a simple interpretation of the likely nuclearity of those species A formed by heating to 523K. Where experiments have involved heating $Os_3(CO)_{12}$/support combinations, it must be further supposed that Os_3 units first dimerise to give Os_6 clusters; this is reasonable because $Os_6(CO)_{18}$ and higher-nuclearity clusters are prepared by the pyrolysis of $Os_3(CO)_{12}$ (*11, 23*). In addition, evidence from the solution chemistry of polynuclear metal carbonyls provides a precedent for such aggregation. For example, reduction of $Rh_4(CO)_{12}$ in the presence of base under mild conditions gives a Rh_{12} cluster (Eq. (3)) (*24*).

$$2Rh_4(CO)_{12} + 2OH^- \rightarrow [Rh_{12}(CO)_{30}]^{2-} + CO_2 + 5CO + H_2O \quad (3)$$

An analogous situation could clearly obtain at the surface of our supports.

We offer the following speculation as to the structure of the dimer. Little atomic relaxation is required to convert the bicapped tetrahedral structure of $Os_6(CO)_{18}$ to a trigonal prismatic configuration which is then ideally suited for dimerisation to structure (I) (Fig. 9, path *a*). This dimer retains the 1 : 1 : 1 ratio of −1, 0, and +1 oxidation states of osmium, although the trimer produced by an extension of this process would be relatively enriched in the +1 oxidation state.

Our interpretation of the infrared spectra of species A above suggested that zero was the most prevalent oxidation state for osmium. In this connection we note that direct condensation of two bicapped tetrahedra (Fig. 9, path b) can give structure (II) in which all osmium atoms are in the zero oxidation state. Except for the absence of an osmium atom at the centre, structure (II) is a fragment of hexagonal close packing, and it is in this structure that osmium crystallises.

Twelve osmium atoms grouped as in these structures and protected against sintering by ligand-CO might be expected to show three-band infrared spectra on the grounds proposed above, but with additional intragroup band splittings. That no such splitting is evident may indicate that the Os : CO ratios listed in Table 2 are mean values for each preparation, and that this ratio varies somewhat from one species A

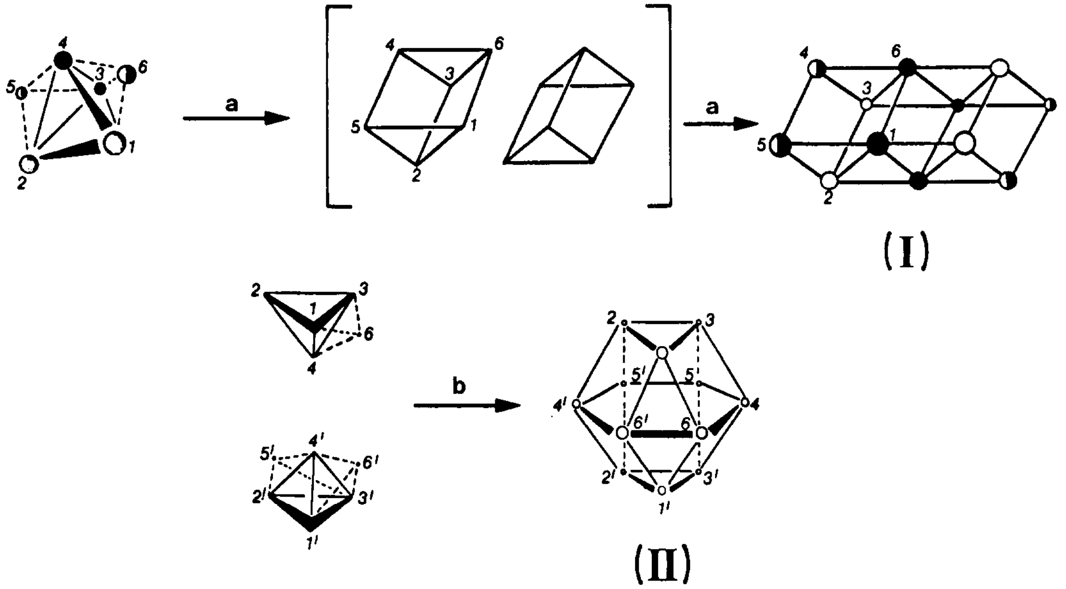


FIG. 9. Two dimerisations of bicapped tetrahedral Os_6 units. In (a), open circles, half-filled circles, and filled circles represent osmium atoms in formal 0, −1, and +1 oxidation states, respectively. In (II), all osmium atoms are formally in the zero oxidation state. In each Os_6 unit the osmium atom numbered 5 caps the face formed by those numbered 2, 3, and 4, and that numbered 6 caps the face formed by those numbered 1, 3, and 4. No attempt has been made to reproduce metal–metal bond lengths to scale.

cluster to the next in each preparation. This is not unexpected; the precise constitution of each species A will be determined by the environment of the support surface at the point where dimerisation occurred and will have been governed in part by the detailed nature of the cluster–support interaction that was achieved. Since each support presents a chemically and energetically heterogeneous surface on the atomic scale, it is to be expected that there may be some variation with respect to the numbers of CO-ligands (and C-ligands) attached to the Os_{12} entities.

The maximum dimension of the cluster framework in the dimers is about 0.8 nm, and in a timer produced by path *a* about 1.1 nm. Our experience of transmission electron microscopy with a wide range of osmium clusters, and of conventional catalysts containing Re, Os, or Ir, is such as to make us confident that such Os_{18} units and possibly Os_{12} units would be visible as features having an apparent size close to our limit of detection.

The variability of the Os : CO ratio in species A and the likelihood that it contains carbon and enters into chemical interactions with the support suggest that structures (I) and (II) may undergo further structural modifications. Indeed, the interesting catalytic properties of these materials may be related to their capacity to undergo configurational changes under reaction conditions.

Relationship with Previously Published Work

Having thus established to our satisfaction that the clustered state may be retained in catalytically active material, we consider again the work of Knözinger, Basset, Ugo, and their co-workers, who propose cluster degradation to mononuclear osmium species during catalyst preparation (*8*). Our supports were extensively dehydroxylated before impregnation with cluster compound, whereas the above workers appear to have employed more heavily hydroxylated supports. Surface hydroxyl concentration, hydroxyl reactivity, and osmium loading (our loadings are higher than those used by Knözinger *et al.* (*8*, *25*)) will each play a part in determining the course of reaction of the cluster compounds with the support; the effects of these parameters have yet to be examined in a systematic manner. Our observations of enhancement of nuclearity on heating the freshly impregnated materials are consistent with our having the less reactive support surfaces.

That our materials and those of Knözinger and Zhao (*8*) are different can be shown by a further example. These workers demonstrated reversible de- and re-carbonylation (over a period of 20 h at 645K) of their material that gave the three-band infrared spectrum. We repeated this experiment with species A derived from $Os_3(CO)_{12}$/titania. Admission of 20 Torr $[^{18}O]CO$ at 645K gave 13% $[^{16}O]CO$, 11% $[^{18}O]CO$, 53% $[^{16}O]CO_2$, 10% $[^{16}O, {}^{18}O]CO_2$, and 13% $[^{18}O]CO_2$ after only 0.3 h. Clearly, reaction and randomisation of oxygen isotopes occurred, showing that our species A has a chemistry different from that of the osmium-containing species prepared by Knözinger and Zhao.

The results of this investigation emphasize (i) the delicate balance of the chemistry in a system in which the Os–Os bonds and the Os–CO bonds are of comparable strength, (ii) the importance of the use of well-characterised supports, and (iii) the importance of the use of as many techniques as possible in the characterisation of cluster-derived catalysts.

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