Pyrolysis Products of Ligand-supported Triosmium Clusters

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EXAFS analysis of the pyrolysis product of $[(\mu\text{-H})Os_3(CO)_{10}\{\mu\text{-S}[CH_2]_3Si(OMe)_{3-x}(O\text{-silica})_x\}]$ shows the average co-ordination sphere of osmium contains O, S, and Os at bonding distances in addition to carbonyl groups; in contrast, there is little evidence of retention of phosphorus co-ordination on pyrolysis of $[(\mu\text{-H})Os_3H(CO)_{10}\{PPh_2[CH_2]_2Si(OEt)_{3-x}(O\text{-silica})_x\}]$.

The interactions of $[(\mu\text{-H})_2Os_3(CO)_{10}]$ with phosphinated silica and $[Os_3(CO)_{12}]$ with thiolated silica have been shown to yield $[(\mu\text{-H})Os_3H(CO)_{10}\{PPh_2[CH_2]_2Si(OEt)_{3-x}(O\text{-silica})_x\}]$ (**1**)[1] and $[(\mu\text{-H})Os_3(CO)_{10}\{\mu\text{-S}[CH_2]_3Si(OMe)_{3-x}(O\text{-silica})_x\}]$ (**2**)[2] by i.r. spectroscopy. The carbonyl stretching vibrations are relatively sharp and good agreement with the spectra of close model complexes could be obtained. However, like the grafted cluster $[(\mu\text{-H})Os_3(CO)_{10}(O\text{-silica})]$ (**3**),[3,4] pyrolysis of (**1**) and (**2**) affords pale materials with broad ν(CO) absorptions in the i.r. region.[5,6] Three bands are observed for each pyrolysis product: from (**3**) 2122w, 2036s, and 1956m cm^{-1};[7] from (**1**) 2112vw, 2034s, and 1966s cm^{-1}; from (**2**) 2107w, 2027s, and 1967m cm^{-1}. This might be interpreted as indicating common surface species. There is no common agreement with the structure of these surface species on an unmodified silica surface. Some workers favour mononuclear sites,[8—10] while others favour di- or poly-meric units.[4,7,11,12] The effect of functional groups on these species is totally unknown. However, by applying the EXAFS technique, which has afforded structural information about surface species that is otherwise unobtainable,[13] we have obtained evidence for significant structural differences between the pyrolysis products on phosphinated and thiolated silica.

$$(\mu\text{-H})Os_3H(CO)_{10}\{PPh_2[CH_2]_2Si(OEt)_{3-x}(O\text{-silica})_x\}$$
(**1**)

$$(\mu\text{-H})Os_3(CO)_{10}\{\mu\text{-S}[CH_2]_3Si(OMe)_{3-x}(O\text{-silica})_x\}$$
(**2**)

$$(\mu\text{-H})Os_3(CO)_{10}(O\text{-silica})$$
(**3**)

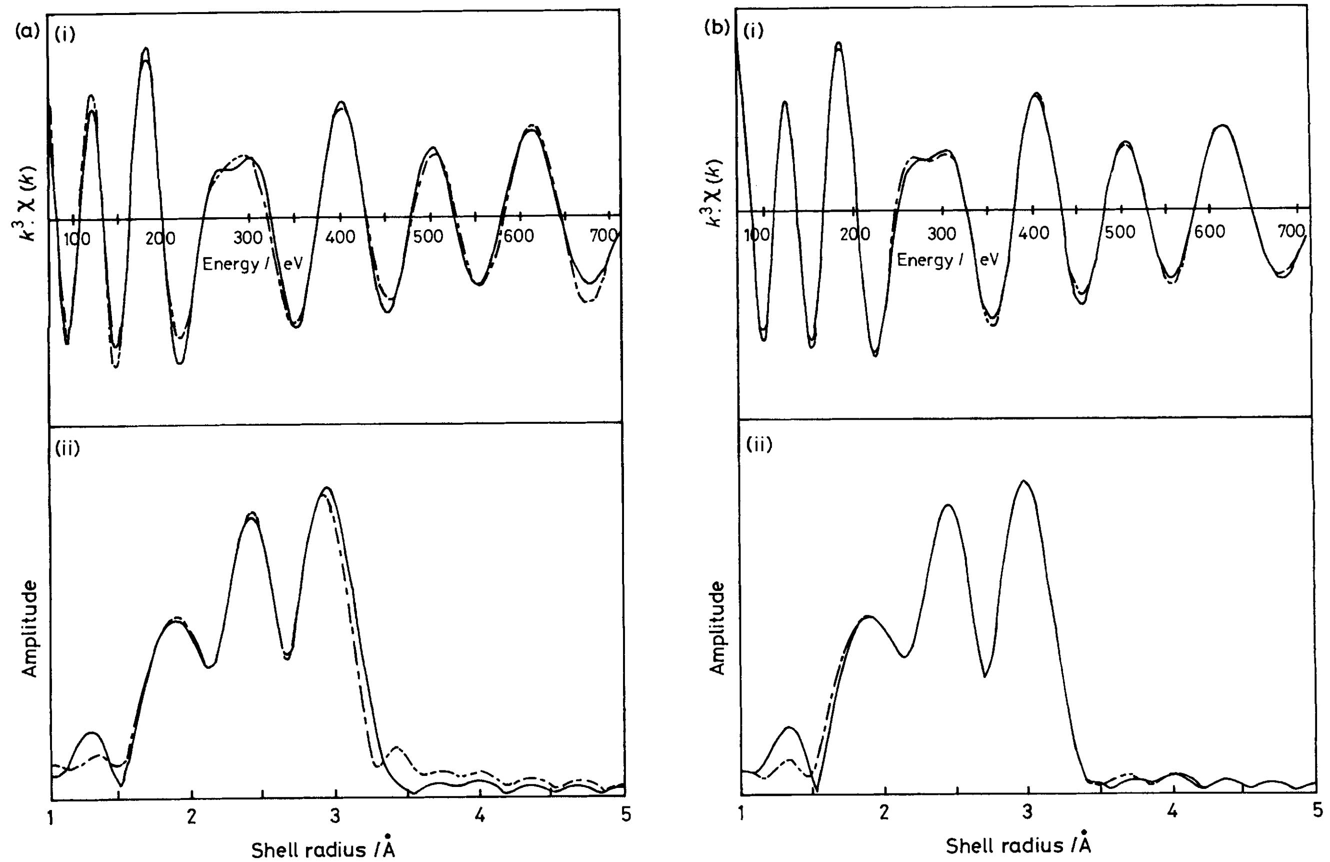

Figure 1. Calculated (- - -) and Fourier filtered experimental (——) plots of (i) $k^3.\ \chi(k)$ against photoelectron energy (eV) and (ii) the Fourier transform amplitude, corrected for carbon phase shifts, against distance (Å). Os L(III) edge spectra of the pyrolysed osmium cluster on thiolated silica (**5**): (a) four shell model (C, O, S, and O), giving a fit index of 0.44, (b) five shell model (C, O, S, Os, and O) giving a fit index of 0.16.

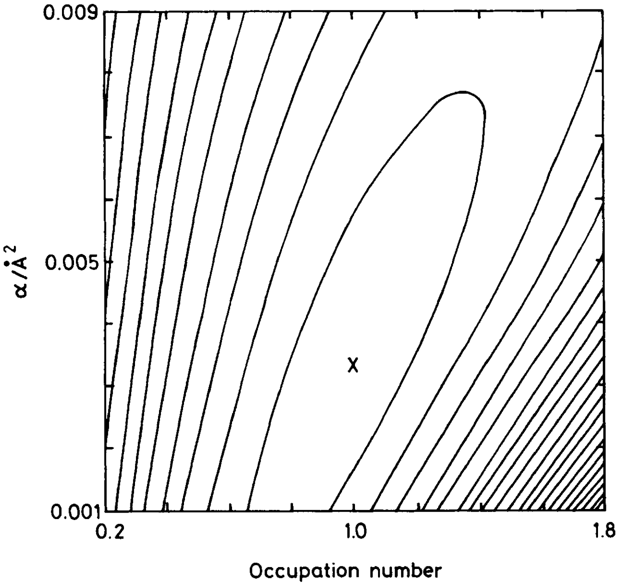

Figure 2. Contour map of the fit index values for the correlation between the sulphur occupation number and Debye–Waller factor for the pyrolysed osmium cluster on thiolated silica. Minimum fit index 0.17, lower contour 0.35, increment 0.38, upper contour 7.53.

Table 1. EXAFS derived occupation numbers (ON) and Debye–Waller factors ($\alpha = 2\sigma^2$) for model compounds.

Compound	Shell	ON_{Actual}	ON_{EXAFS}	$\alpha/Å^2$
$[Os_3(CO)_{12}]$	C	4	3.7(3)	0.007(1)
	Os	2	1.4(3)	0.006(1)
	O	4	3.2(4)	0.009(2)
$[Os_3H(CO)_{10}(OMe)]$	C	3.33	2.5(1)	0.005(1)
	O(br)	0.67	0.6(1)	0.019(3)
	Os	2.0	2.1(1)	0.012(1)
	O	3.33	2.6(1)	0.014(1)
$[Os_3H(CO)_{10}(SPr^n)]$	C	3.33	3.2(1)	0.005(1)
	S	0.67	0.52(5)	0.005(1)
	Os	2.0	2.6(1)	0.010(1)
	O	3.33	3.2(2)	0.012(1)
$[Os_3(CO)_{10}(OEt)_2]$	C	3.33	2.8(1)	0.007(1)
	O(br)	1.33	1.3(1)	0.002(3)
	Os	1.33	1.4(1)	0.010(1)
	O	3.33	3.2(1)	0.014(1)
	Os(br)	0.67	0.5(1)	0.008(1)

Table 2. Optimum fits obtained for the Os L(III) edge EXAFS data on (**4**) and (**5**).

	(**4**)			(**5**)		
Shell	ON	Radius/Å	α/Å	ON	Radius/Å	α/Å^2
C	1.6(1)	1.860(2)	0.0050(7)	2.2(3)	1.899(5)	0.007(2)
O	1.9(2)	2.233(2)	0.016(1)	1.8(4)	2.27(8)	0.020(5)
S	—	—	—	1.0(1)	2.41(1)	0.003(1)
Os	2.2(3)	2.816(4)	0.015(1)	1.8(7)	2.84(2)	0.013(4)
O	1.1(2)	2.867(5)	0.011(4)	1.0(4)	2.90(1)	0.005(5)

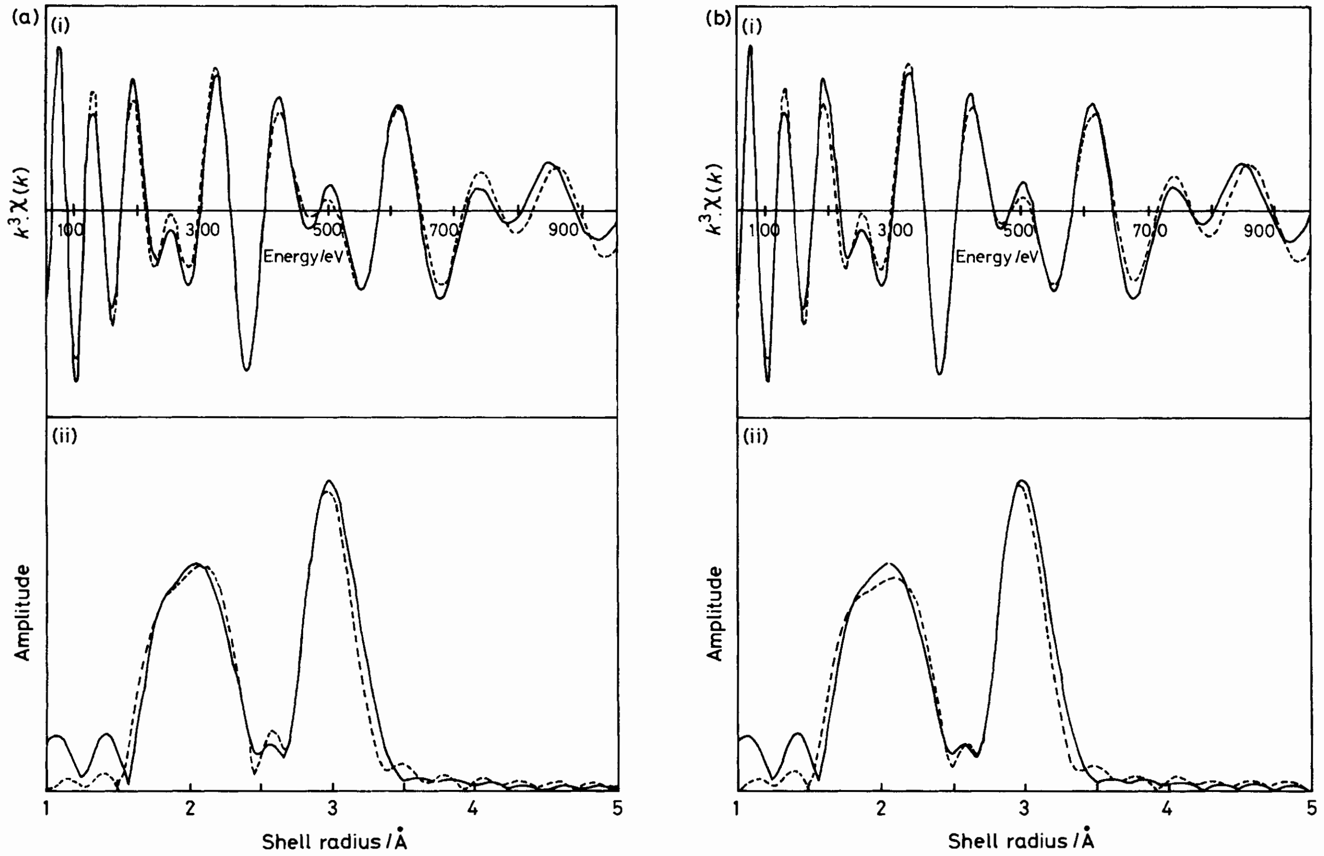

Figure 3. Calculated (- - -) and Fourier filtered experimental (——) plots of (i) k^3. $\chi(k)$ against photoelectron energy (eV) and (ii) the Fourier transform amplitude, corrected for carbon phase shifts, against distance (Å). Os L(III) edge spectra of the pyrolysed osmium cluster on phosphinated silica (**4**): (a) four shell model (C, O, Os, and O) giving a fit index of 0.52; (b) five shell model (C, O, P, Os, and O) giving a fit index of 0.48.

X-Ray absorption spectra of the Os L(III) edge of the pyrolysed samples of (**1**) and (**2**), labelled (**4**) and (**5**)† respectively, were recorded and the EXAFS extracted as described previously.[14,15] The EXAFS data for the two pyrolysis products, (**4**) and (**5**), were qualitatively different, indicating distinct co-ordination spheres. Analysis could not rely on fingerprinting by a close model compound, since none are known. So detailed curve fitting procedures were employed using a version of the program EXCURVE,[16] including routines for Fourier filtering and contour mapping of the fit index for two correlated variables (MAP). These contour maps are alternatives to the stacked plots previously used to assist analyses.[17] A particular concern was the estimation of shell occupation numbers, which are strongly correlated with the Debye–Waller factors. The results of floating the occupation number for four known compounds are presented in Table 1. In general, the MAP procedure seems a reliable guide and can be used to assist in model refinement. The errors estimated from the contour plots are comparable with those obtained by least squares methods. The occupation number is generally within 3σ of the true value, although the carbon co-ordination number is generally underestimated by 10—20%. Error analysis was by a method similar to that described by Cox[18] employing numerical estimates of the partial derivatives at the minimum.

The data for the thiolated silica pyrolysis product (**5**) were analysed initially in two Fourier filtered regions of *r* space. Fourier filtering removes noise and residual background and

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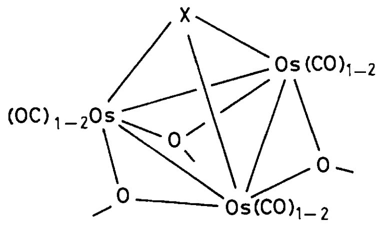
† The data will be deposited with the EXAFS data bank at the S.E.R.C. Daresbury Laboratory, Daresbury, Warrington WA4 4AD, U.K.



(A)

(**4**) X = CH$_x$ (if occupied)
(**5**) X = S (and CH$_x$)

thus aids refinement. The inner region (0.99—2.37 Å with no phase shift correction) required three shells, carbon, oxygen, and sulphur. Incrementing the complexity of the model from a single carbon shell by adding an oxygen as the second shell and sulphur as the third caused the fit index to drop from 2.90 through 1.27 to 0.16. Two shells (O and Os) were required to fit the outer region (2.37—3.11 Å) back transform. Introduction of a third shell which refined as osmium at 3.17 Å did not give a significant improvement to the fit at high photoelectron energies (>500 eV), where backscattering from heavy elements is dominant, and seems unwarranted. Hence two models were employed to fit the Fourier smoothed EXAFS data of (**5**). Each contained carbon, oxygen, sulphur, and oxygen shells, with the second model having an additional osmium. The fits of the EXAFS and Fourier transforms are presented in Figure 1. It appears that the inclusion of one osmium shell causes a significant improvement of the fit, at high energy in particular. The five shell model affords a close fit of both the EXAFS and Fourier transform, and, with the exception of the carbon oxygen (as noted previously),[14,15] gives plausible distances (Table 2). The Os–S shell is a relatively small component of the total backscattering. However a contour map of the occupation number against the Debye–Waller factor for that shell (Figure 2) indicates that the occupation number is defined within the range of ~0.9 to ~1.1.

A similar procedure was adopted for the data analysis on the phosphinated silica pyrolysis product (**4**). The outer radius region (2.16—3.06 Å) was entirely fitted by a two shell model *viz.* Os and O. Analysis of the inner region (0.61—2.16 Å) clearly revealed two shells due to carbon and oxygen. However, no significant improvement was obtained on the introduction of a phosphorus shell. Nevertheless, two models were again employed to fit data filtered over the whole *r*-space range. The four common shells were C, O, Os, and O, with phosphorus added in one model. The fits of the EXAFS and Fourier transform are presented in Figure 3. Inclusion of phosphorus affords little improvement in the fit, and all the parameters associated with that shell are ill-defined. In this case the four shell model is adequate to fit the data, and the results obtained are given in Table 2.

Translating these results into structural models is not straightforward since the data obtained are possibly the mean values of a number of species. However certain features are evident. Both materials exhibit co-ordination spheres of 1—2 CO groups, ~2 O atoms, and ~2 Os atoms. Additionally, (**5**) also contains a sulphur atom. The observation of a carbon shell with a higher occupation number than oxygen was not evident in any of the model systems in Table 1. This suggests that some other site, perhaps of form CH$_x$, may also occur in these materials. The osmium co-ordination number of 2 is consistent with triangles or chains. A plausible basic unit is shown as (A), which maintains the original cluster unit. In (**5**), the site X seems principally to be sulphur, perhaps abstracted from the surface thiolate, with the possibility of some other carbon donor also occurring. In contrast, any occupation of X in (**4**) is carbonaceous.

This study suggests that even in the pyrolysed form of ligand tethered clusters, there is some Os–Os bonding. Also, there is an evident divergence of behaviour between phosphinated and thiolated silica. The tendency for the metal to migrate from a phosphine to the support, on one hand, and to maintain sulphur co-ordination on the other may have considerable repercussions on the catalytic properties of these thermally activated materials.

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