On the Chemisorption of [Ru₃(CO)₁₂] and [Os₃(CO)₁₂] on Silica and Alumina

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I.r. [δ(MH)], Raman [v(M–M)], and Ru K-edge E.X.A.F.S. data on the first chemisorption product of $M_3(CO)_{12}/SiO_2$ (M = Ru, Os) and $Os_3(CO)_{12}/Al_2O_3$, indicate a structure of type $(\mu\text{-H})M_3(CO)_{10}(\mu\text{-O}\text{—}O)$.
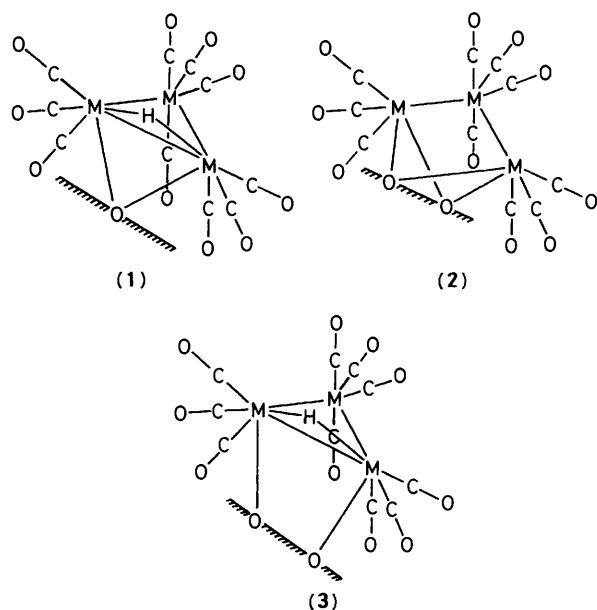
The chemisorption of $[Ru_3(CO)_{12}]$ on silica and $[Os_3(CO)_{12}]$ on silica and alumina is now generally agreed to afford similar types of species as the first observable product, based on an $(X)(Y)M_3(CO)_{10}$ unit.[1—6] It has, however, proved difficult to differentiate between the three alternative structures in Figure 1, partly owing to the problem of observing the bridging hydride site on the oxide surfaces. We report vibrational and

X-ray absorption spectroscopic evidence for the presence of such hydride sites.

Bent hydride bridges on heavy transition metal carbonyl cluster complexes typically exhibit weak 'in-plane' v(MH) i.r. absorptions in the $\sim$1100 to $\sim$1500 cm^{-1} range, coincident with strong bands from the inorganic support. More conveniently the out-of-plane bending mode of the v-HM$_2$ units

Table 1. Frequencies of hydride bending and metal–metal stretching vibrations of surface and model species.

Species	δ(M–H–M)/ cm^{-1}	v(M–M)/ cm^{-1}	Ref.
$Os_3(CO)_{12}$	—	161,120	13
$H_2Os_3(CO)_{10}$	730	187,142,97	8
$HOs_3(CO)_{10}(OMe)$	—	172,136,119	13
$HOs_3(CO)_{10}(OH)$	716	176,136,98	This work
$HOs_3(CO)_{10}(OSiPh_3)$	—	176,162w,135,104,97	This work
$Os_3(CO)_{10}(OEt)_2$	—	170,132,104	14
$HOs_3(CO)_{10}(O_2CH)$	740	161,150w,126,109,99	This work
$HOs_3(CO)_{10}(O_2CMe)$	744	160,130,99	This work
$HOs_3(CO)_{10}$- (MeCOCHCOMe)	733	159,120,102,86	This work
'HOs$_3$(CO)$_{10}$(O-SIL)'	708	—	This work
'HOs$_3$(CO)$_{10}$(O-AL)'	—	160,119,80	12
'HRu$_3$(CO)$_{10}$(O-SIL)'	682	201,162	This work; 6
$HRu_3(CO)_{10}(PPhH)$	670	186,157,149,125sh	This work

Table 2. Ru K-edge E.X.A.F.S. derived data on the initial chemisorption product of $Ru_3(CO)_{12}$ on silica.[a]

Back scattering shell	Ru–E/Å	Co-ordination number	Debye–Waller factor/Å²
Ru–C	1.90(0)	3.3	0.0046(4)
Ru–O	2.06(0)	3.8(4)	0.0023(3)
Ru–Ru	2.79(0)	2.0	0.0121(5)
Ru–C–O	3.06(0)	3.3	0.0035(8)

[a] Analysis used *ab initio* phase-shifts, 13 l values being used for all scattering paths excepting the reverse scattering term in the third order contribution to the Ru–C–O shell. Values without standard deviations were held fixed. The proportion of absorption affording E.X.A.F.S. used was 0.6 and inelastic effects modelled with an imaginary potential of -4 eV. R factor 16%, E_0 27.5(3) eV fitted on k^3 weighted Fourier filtered (0.97—3.62 Å) E.X.A.F.S. between 19 and 682 eV above the absorption edge. Ru–C–O bond angle estimated as 165(1)° (see text).

Figure 1. Three structure types for the first chemisorption product of $M_3(CO)_{12}/SiO_2$ (M = Ru, Os) and $Os_3(CO)_{12}/Al_2O_3$.

Figure 2. I.r. spectra of the first chemisorption product of $M_3(CO)_{12}/SiO_2$: (a) M = Os, (b) M = Ru in the region 530—720 cm^{-1}.
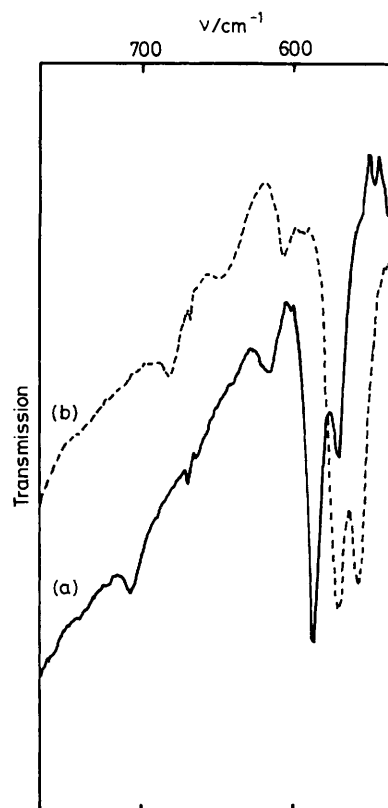
are more intense and occur in an i.r. window of silica at ~700 cm^{-1}.[7—9] In Figure 2 we present the i.r. spectra of the initial chemisorption product of the trinuclear carbonyls on silica in the region 770—530 cm^{-1}. In addition to the absorptions due to v(M–C) and δ(M–C–O) modes in the lower frequency section of this spectral range, there are additional bands (not exhibited by the support) assigned to δ(M–H–M) vibrations at 708 and 682 cm^{-1} for osmium and ruthenium respectively. These frequencies are similar to those observed in a series of model complexes (Table 1), several of which have been confirmed by ^{2}H substitution. So this direct spectroscopic evidence of the presence of the hydride ligand indicates that the species formed on silica at least is either of type (1) or (3) as depicted in Figure 1.

Structural information about the ruthenium species has been obtained by analysis of its ruthenium K-edge E.X.A.F.S. (recorded in fluorescence mode on Station 9.2 of the SRS at

the Daresbury Laboratory). Figure 3 presents the best fit obtained using the spherical wave-multiple scattering calculations[10] that have been previously used to assess M–C–O bond angles in cobalt carbonyl complexes.[11] Four shells at increasing radius can clearly be observed in the phase-corrected (on carbon) Fourier transform due to Ru–C, Ru–O, Ru–Ru, and Ru · · · O(carbonyl) interatomic distances. Only one Ru–Ru distance was refinable, consistent with the crystallographic data on osmium containing models of structure types (1) and (3), but inconsistent with type (2). The results of the data
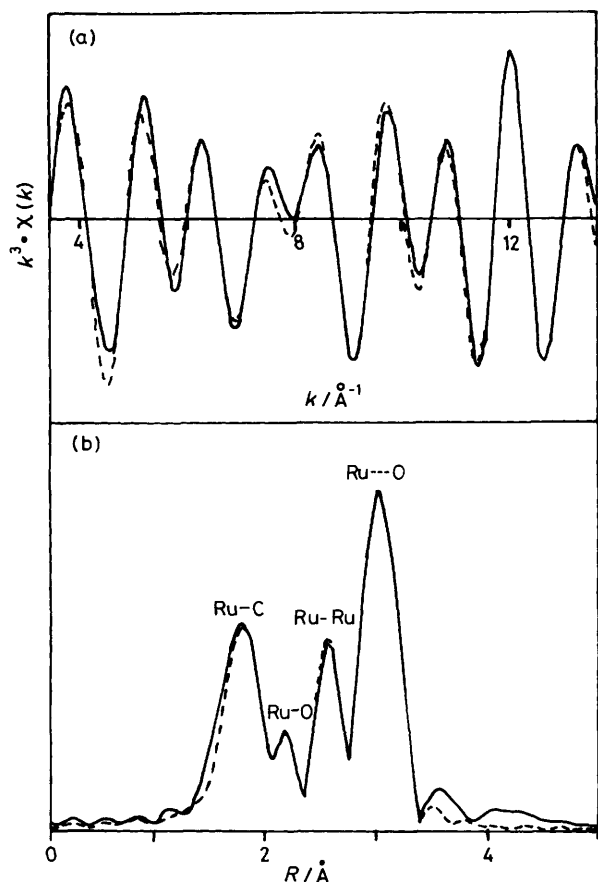
Figure 3. Fourier filtered experimental (—) and calculated (---) Ru K-edge E.X.A.F.S. results on the first chemisorption product of $Ru_3(CO)_{12}/SiO_2$: (a) $k^3\chi(k)$ vs. $k/\text{Å}^{-1}$, (ii) Fourier transform vs. $R/\text{Å}$.

analysis are presented in Table 2. All the bond distances so derived are within ~0.03 Å of those observed in model osmium species of the two hydrido-containing structure types; the similarity of the covalent radii of ruthenium and osmium would suggest that these are chemically reasonable values. Multiple scattering theory models the back scattering from the carbonyl oxygen atoms more closely than previous empirical approaches and the systematic reduction in this M · · · O distance observed in earlier analyses of osmium carbonyls is thus eliminated.[5] The best fit was obtained for a mean Ru–C–O angle of 165(1)°. However the value of this angle is highly correlated with the Debye–Waller factor for this shell (correlation matrix element of ~0.92) and a more reasonable standard deviation is 5°. The C–O distance derived from these data is 1.19 ± 0.03 Å. High correlation (0.93) between the co-ordination number of the minor Ru–O shell with the Debye–Waller factor rendered that value unreliable. Nevertheless, analysis of the Ru K-edge E.X.A.F.S. data supports models (1) or (3) for the surface species.

The most recent E.X.A.F.S. analysis of the Os $L(\text{iii})$ edge data on the $Os_3(CO)_{12}/Al_2O_3$ species is also consistent with either of these structure types.[15] Gates et al. have also reported the Raman spectrum of this species, which exhibits a clear band at 160 cm^{-1}, together with features at ~119 and 80 cm^{-1}.[12] We have collected Raman data in the v(M–M) region on a series of potential surface models and this indicates that

the structure types (1), (2), and (3) exhibit Raman bands attributable to the symmetric v(Os–Os) mode at ~175, ~170, and ~160 cm^{-1} respectively. The lower frequency bands are less clearly assignable, but it may be that the frequency of this mode may represent a fingerprint for the three structure types. Clearly the agreement with the $Os_3(CO)_{12}/Al_2O_3$ is closest for the models of type (3) in which two oxygen atoms rather than one are involved in chemisorption of the cluster. Whether these are geminal or vicinal groups is unknown.

This structure seems chemically plausible for two reasons in particular. First it is known that both *geminal* and *vicinal* silanediols exist on silica surfaces.[16] Secondly, the osmium clusters at least appear to be more stable with a bidentate oxygen bridge as in type (3). Evidence for this comes from a transformation of $HOs_3(CO)_{10}(OH)$ to $HOs_3(CO)_{10}(O_2CR)$ (R = H, Me, CF$_3$) even in dilute solution at 20 °C.[17] The initial interaction with the surface may be *via* one oxygen atom as in structure (1), but this suggests that the long-lived species considered here has probably reacted further.

In conclusion, the vibrational and E.X.A.F.S. data presented here strongly support the presence of hydride ligands in the three cluster/oxide systems discussed. The frequency of the symmetric v(Os–Os) vibration is most consistent, for $Os_3(CO)_{12}/Al_2O_3$ at least, with the involvement of *two* surface oxygens in cluster binding. It is of course possible that species (1) is present on the silica supported analogues.

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