I.R. and E.X.A.F.S. Characterisation of a Supported Osmium Cluster Carbonyl

By BERNARD BESSON, B. MORAWECK, A. K. SMITH, and J. M. BASSET*
(*Institut de Recherches sur la Catalyse, 2, avenue Albert Einstein, 69626 Villeurbanne Cédex, France*)

and RINALDO PSARO, A. FUSI, and R. UGO*
(*Istituto di Chimica Generale e Inorganica d'ell Università, Centro C.N.R., 21 Via Venezia, 20133 Milano, Italy*)

Summary $Os_3(CO)_{12}$ and $Os_3(CO)_{10}(MeCN)_2$ react with silanol groups of silica at 150 and 25 °C, respectively, to give the grafted cluster $Os_3(CO)_{10}(H)(OSi\lesseqgtr)$ (**1**) which has been characterized by i.r. spectroscopy, gas phase analysis, and E.X.A.F.S.; the model compound $Os_3(CO)_{10}(H)(OSiPh_3)$, obtained by the reaction of $Os_3(CO)_{12}$ with Ph_3SiOH, confirms the structure of the surface compound (**1**).

THE use of transition metal cluster carbonyls to prepare highly dispersed metal catalysts on inorganic oxide supports is of considerable current interest;[1,2] studies of these systems can also give direct experimental evidence for the nature of the surface organometallic species and their chemistry.[3] Previous papers have considered the chemistry of $Rh_6(CO)_{16}$,[4,5] $Rh_4(CO)_{12}$,[6] and $Fe_3(CO)_{12}$[7] supported on different inorganic oxides. Also, formation of hydrocarbons upon heating various supported carbonyl clusters has been observed[8] and a recent report[9] discussed the anchoring of osmium carbonyl clusters to silica *via* phosphine or vinyl groups. We report here new ways of anchoring $Os_3(CO)_{12}$ to a silica surface by direct reaction of the molecular cluster with surface silanol groups.

On highly hydroxylated silica (Aerosil from Degussa, 200 m^2/g) degassed at 25 °C for 16 h under 10^{-5} Torr (denoted silica$_{25}$), the room temperature adsorption of $Os_3(CO)_{12}$ from CH_2Cl_2 solution leads to a simple physisorption of the original cluster. This is shown not only by spectroscopy (Figure 1) but also by chemical analysis of the gas phase above the impregnated silica surface which shows no significant amount of CO, CO_2, or H_2. (Separate experiments demonstrated that CO, CO_2, and H_2 cannot be adsorbed on silica at room temperature.)

$Os_3(CO)_{10}(H)(OSi\lesseqgtr)$ (**1**)	$Os_3(CO)_{10}(H)(OPh)$ (**2**)
$Os_3(CO)_{10}(OPh)_2$ (**3**)	$Os_3(CO)_{10}(H)(OSiPh_3)$ (**4**)

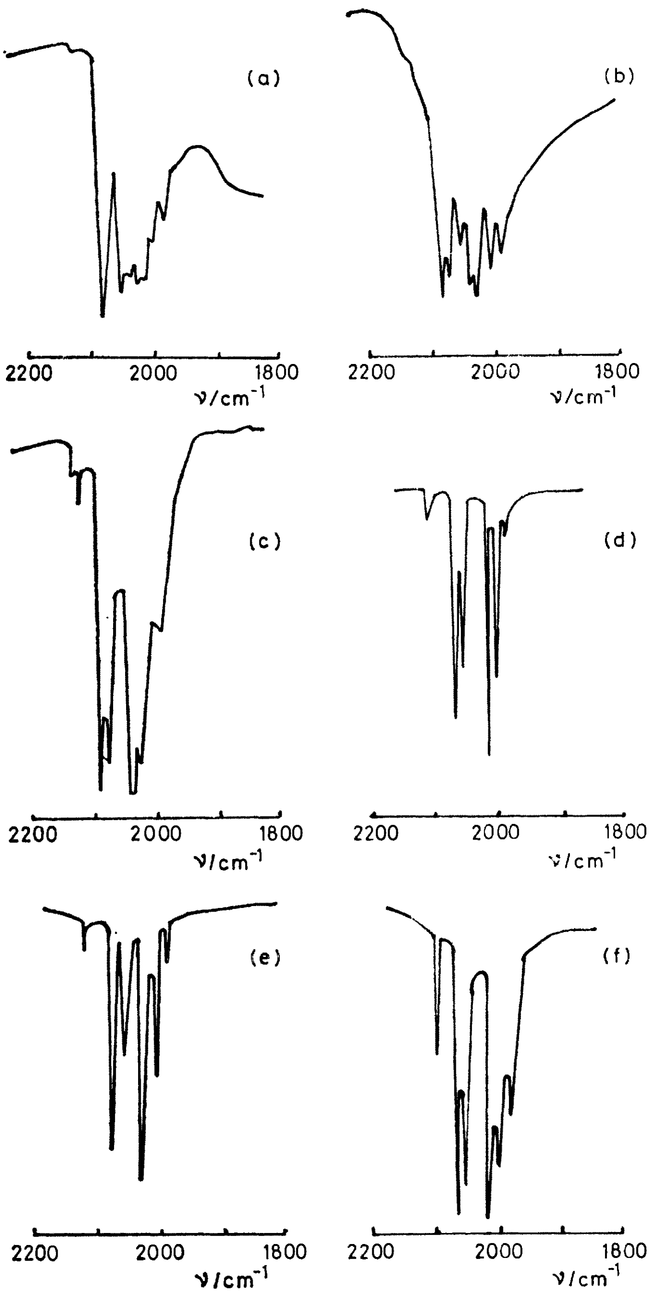


FIGURE 1. I.r. spectra of osmium cluster compounds in the ν(CO) region. (a) after impregnation of a silica$_{25}$ disc with $Os_3(CO)_{12}$ in CH_2Cl_2 solution and solvent removal; (b) $Os_3(CO)_{12}$ in Nujol mull; (c) (**1**); (d) (**2**) in cyclohexane solution (ref. 13); (e) (**3**) in cyclohexane solution (ref. 14); (f) (**4**).

When $Os_3(CO)_{12}$ physisorbed on silica$_{25}$ is heated at 150 °C for 4 h under argon, 2 mol of CO per mol of supported cluster are evolved without any significant H_2 or CO_2 evolution. The i.r. spectrum of the species obtained (**1**) is very different from that of the original cluster (Figure 1). The wavenumbers and the shape of the ν(CO) bands as well as the high ratio of CO to Os (10:3) suggest that a molecular cluster carbonyl is still present on the surface. In no case did the i.r. spectrum correspond to metallic osmium covered with CO which gives two broad bands at 2010 and 1860 cm^{-1}.[10] Since (**1**) is quite stable at room temperature, even in the open air, further characterisation using extended *X*-ray absorption fine structure (E.X.A.F.S.) was possible.

The K^3 Fourier transforms of the E.X.A.F.S. spectra of (**1**) and $Os_3(CO)_{12}$ were determined (Figure 2). The effect of the phase shift obtained from the known structure of $Os_3(CO)_{12}$[11] was 0·23 Å and, after correcting for the phase shift, the average Os–Os nearest neighbour distance for (**1**) was found to be 2·68 Å. This corresponds to a shortening of the average Os–Os distance with respect to that of the starting cluster $Os_3(CO)_{12}$ (average Os–Os distance of 2·88 Å[11]). The Fourier transform of the E.X.A.F.S. spectrum of (**1**) does not contain any peak which could be attributed to a second Os nearest neighbour, which confirms the lack of aggregation to metal particles.

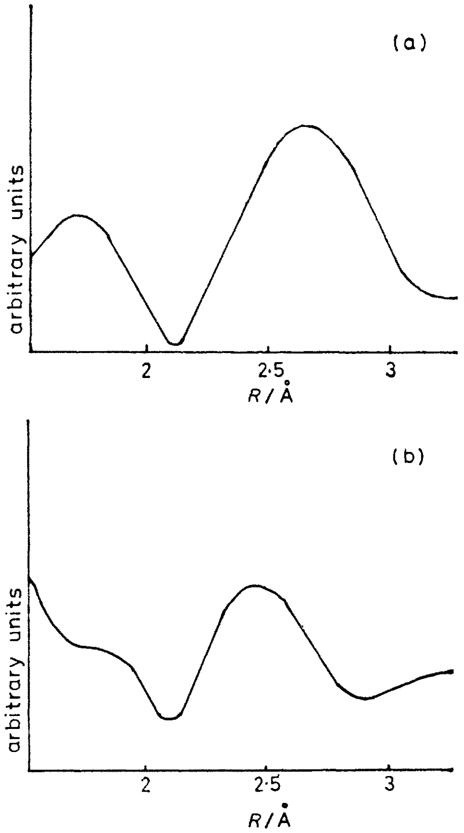


FIGURE 2. K_3 Fourier transform of the E.X.A.F.S. spectra of (a) $Os_3(CO)_{12}$ and (b) (**1**), without correction for the phase shift.

The species (**1**) can also be obtained by the reaction of $Os_3(CO)_{10}(MeCN)_2$[12] with silica$_{25}$ at room temperature with insignificant evolution of CO. Production of (**1**) from either $Os_3(CO)_{12}$ or $Os_3(CO)_{10}(MeCN)_2$ suggests that in this surface compound the Os_3 cluster framework is kept on the surface, without aggregation to a metal cluster carbonyl of higher nuclearity, or to a metal particle. In such cases the ratio CO/Os would decrease below 10:3 (3·33) [see for example $H_4Os_4(CO)_{12}$ (3·0), $Os_4(CO)_{13}$ (3·25), $Os_5(CO)_{16}$ (3·2), $Os_6(CO)_{18}$ (3·0), $Os_7(CO)_{21}$ (3·0), and $Os_8(CO)_{23}$ (2·87)].[13]

The combination of i.r. spectroscopy, E.X.A.F.S., and gas-phase analysis indicates that (**1**) has kept a metal–metal skeleton with CO carbonyl ligands corresponding to the possible surface reactions (1) and (2).

$$Os_3(CO)_{12} + SiOH \rightarrow Os_3(CO)_{10}(H)(O\text{–}Si\leqslant) + 2CO \quad (1)$$

$$Os_3(CO)_{12} + 2SiOH \rightarrow Os_3(CO)_{10}(O\text{–}Si\leqslant)_2 + H_2 + 2CO \quad (2)$$

In solution PhOH reacts with $Os_3(CO)_{12}$ to form either $Os_3(CO)_{10}(H)(OPh)$[14] (**2**) or $Os_3(CO)_{10}(OPh)_2$[15] (**3**). The surface reaction leading to (**1**) is probably a similar oxidative addition of a silanol group to an Os–Os bond of $Os_3(CO)_{12}$ leading to $Os_3(CO)_{10}(H)(OSi\leqslant)$ or $Os_3(CO)_{10}(OSi\leqslant)_2$. The model compound $Os_3(CO)_{10}(H)(OSiPh_3)$ (**4**) was prepared by the reaction of $Os_3(CO)_{12}$ with Ph_3SiOH (high field ^1H n.m.r. signal at δ 21·0 from Me_4Si) [equation (3)]. The i.r.

$$Os_3(CO)_{12} + Ph_3SiOH \longrightarrow (\mathbf{4}) + 2CO \quad (3)$$

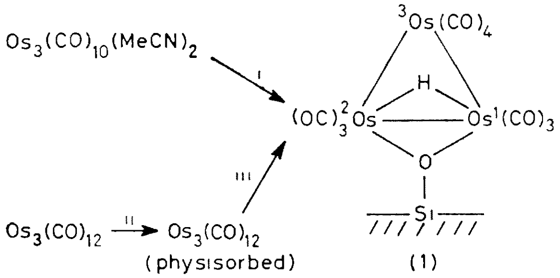
spectra of (**1**)—(**4**) are very similar (Figure 1 and Table).

TABLE. I.r. and ^1H n.m.r. data for osmium cluster compounds.

Compound	$\nu(CO)/cm^{-1}$	δ (H–Os)
$Os_3(CO)_{12}$[a]	2135vw, 2076vs, 2068s, 2048m, 2035sh, 2023s, 2003m, 1985m	
$Os_3(CO)_{12}/SiO_2$[b]	2135vw, 2070vs, 2048s, 2040s, 2025s, 2018sh, 1980m	
(**1**)[b] (25 °C)	2122w, 2088vs, 2075s, 2037vs b 1955w sh	—
(**4**)[c]	2107w, 2069s, 2055s, 2017s, 1997m, 1980m	21·0
(**2**)[c,d]	2112w, 2073vs, 2064m s, 2025vs, 2007m, 1991w sh, 1986mw	22·2
(**3**)[c,e]	2109w, 2076s, 2060ms, 2019vs, 2002ms, 1955mw	

[a] Nujol mull. [b] Silica disc. [c] Cyclohexane. [d] Ref. 13. [e] Ref. 14.

Since no H_2 is evolved in the reaction of $Os_3(CO)_{12}$ with surface silanol groups, the structure $Os_3(CO)_{10}(H)(OSi\leqslant)$, rather than $Os_3(CO)_{10}(OSi\leqslant)_2$, can be attributed to (**1**). The Scheme summarizes the results.



SCHEME. i, $\geqslant$SiOH, room temp., – MeCN; ii, silica$_{25}$, CH_2Cl_2, room temp.; iii, $\geqslant$SiOH, 150 °C, Ar, 4 h, – 2CO.

The species (**1**) is, to our knowledge, the first case of a grafted cluster in which the immobilisation results from an oxidative addition of a silanol group to a metal–metal bond. It is also the first supported cluster to be characterised using E.X.A.F.S. The shortening of the average Os–Os bond distance is probably more important for the Os(1)–Os(2) distance than for Os(3)–Os(1) and Os(3)–Os(2) distances, but the shape of the E.X.A.F.S. spectrum does not allow any distinction between the three Os distances. The species (**1**) is also a unique model of the well known metal–support interaction in heterogeneous catalysis, although, so far, the type of chemical interactions between zero-valent particles and support has not been elucidated. Here we present good evidence for a chemical bonding *via* siloxane bridges. Studies on alumina, in progress, tend to indicate related types of aloxane bridges with alumina-supported osmium clusters. Finally the high selectivity of this supported cluster towards methane in Fischer–Tropsch synthesis[8] might be related to the stabilisation of a triangular frame which could accommodate methylene fragments as shown by Calvert and Shapley.[16]

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