Electronic Supplementary Information:

Characterisation of $Os_3(CO)_{12}$ deposited MCM-41 and related structures:

Supports	Surface area (m^2g^{-1})
MCM-41	1344
Al-MCM41	1233
$Os_3(CO)_{12}$/MCM-41	1203

Table S1: BET specific surface areas of support materials used for the preparation of the catalysts.

MCM-41:

Before calcination, the XRD pattern (Fig.S1) of the MCM-41 is similar to the patterns published in the literature: it exhibits the four peaks at low angles (2°) corresponding to the d_{100}, d_{110}, d_{200}, d_{210} reflections of a regular hexagonal array of pores. These indicate a lattice parameter $a_0 = 47.3$ Å. It also gives a broader peak at higher angles that corresponds to the non-crystalline amorphous silica.
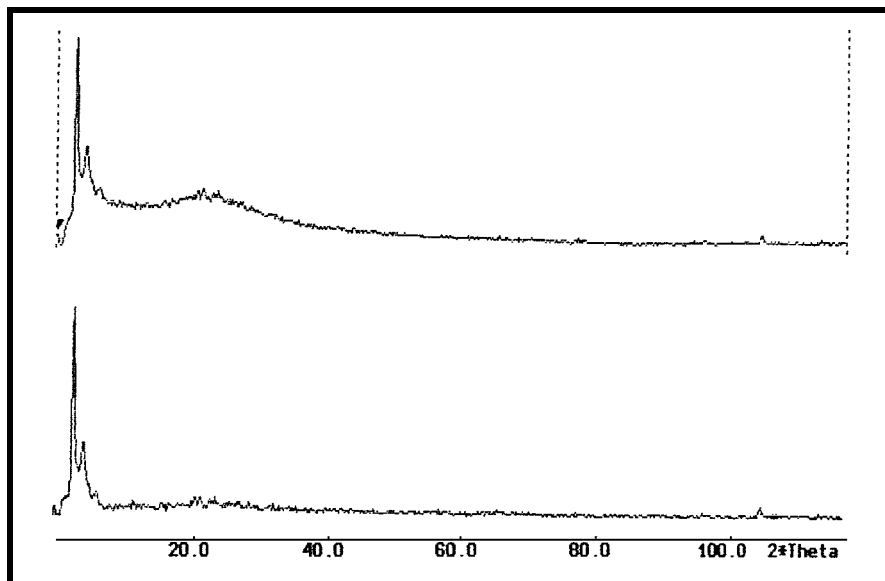

Fig. S1: XRD patterns of MCM-41 (original method) before calcination.

After calcination (Fig.S2), it exhibits one sharp peak at $2\theta = 2°$ corresponding to the d_{100} reflection, which gives a lattice parameter of a = 43.3 Å; it also exhibits a broad peak at higher angles. Thus, the calcination process has apparently induced a reduction in the pore diameter (which equals the lattice parameter minus the thickness of the walls).
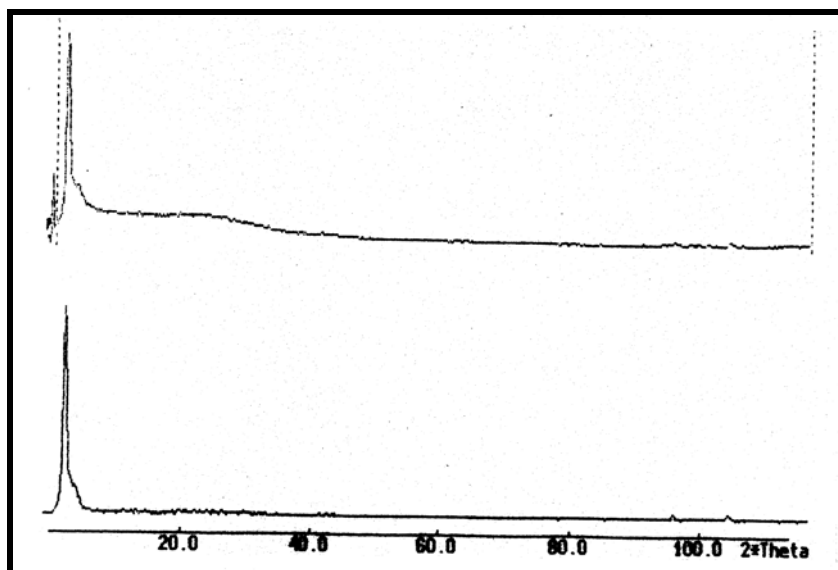
Fig. S2 XRD patterns of MCM-41 after calcination.

Al-MCM4

Incorporation of aluminium inside the MCM-41 framework does not seem to alter its well-ordered mesoporous structure as can be clearly observed from transmission electron micrographs.

$Os_3(CO)_{12}$ deposited MCM-41 and related structures

TEM studies of these catalysts clearly show a very well ordered mesoporous structure which consists in regular hexagonal arrays of channels. This structure is similar to the unmodified MCM-41, which indicates that the CVD of osmium precursors $Os_3(CO)_{12}$ does not affect the well-ordered structure of the support. It is also noted that the effects of calcination, initial Os loading, nature of Os precursor do not significantly alter the overall structure of this support. A TEM micrograph is shown in Fig.S3.
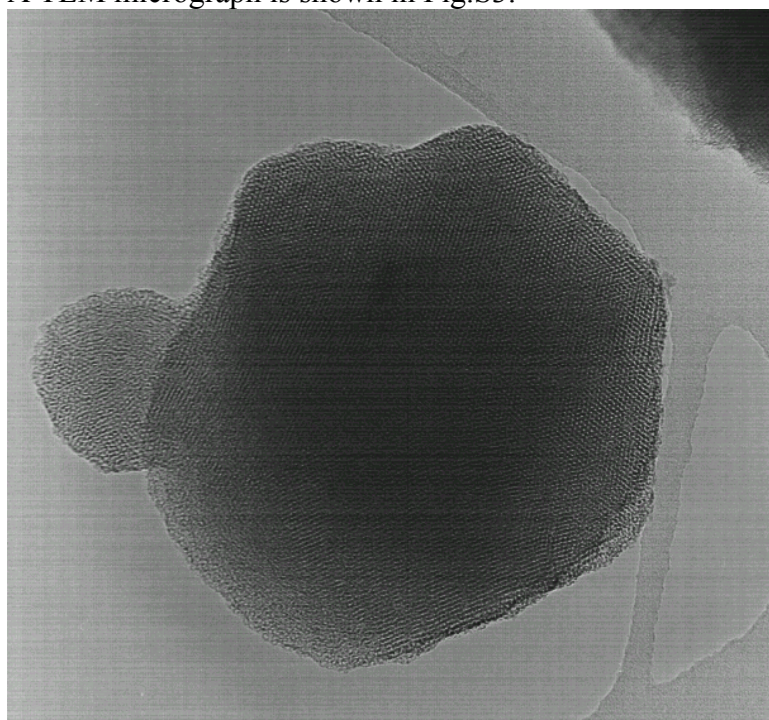

Fig. S3 TEM micrograph of $32mgOs_3(CO)_{12}/Al$-MCM41[220C].

Nature and Stability of surface Os species

Temperature programmed decomposition in helium is known to be one of the most powerful techniques in characterising the surface species of osmium/silica catalysts prepared *via* CVD method. The surface Os carbonyl species will undergo a number of surface reactions (thermal decomposition, oxidation, etc) at different temperatures. Hence, by following their decomposition products (CH_4, H_2, H_2O, CO, CO_2) the nature of the particular surface species and their stability can be revealed. CO_2 evolution has been reported to be the most revealing profile. As a result, it is extensively studied here. We found that CO_2 evolution pattern basically consists in a small peak at around 200°C, a larger broad peak (the major feature) between 300°C and 400°C and a shoulder in the major peak at around 400°C. These features are consistent with the previous TPDe features reported in heating $Os_3(CO)_{12}/SiO_2$ under an inert gas flow in a programmable manner [C. Dossi, A. Fusi, E. Grilli, R. Psaro, R. Ugo and R. Zanoni, *J. Catal.*, 1990, **123**, 181]

It is however noted that the highest temperature used for all the previous TPDe studies was about 400°C. Here, we observe a new sharp but small peak in the temperature range of 480-600°C by further ramping the TPDe to 600°C. According to the literature, formation of CO_2 from the surface Os carbonyl species mainly arises from the reactions of a particular carbonyl group with its neighbour groups. Typically, two carbonyl groups in a close proximity react and evolve carbon dioxide out. The high temperature sharp CO_2 peak is attributed to the reaction of the remaining isolated carbonyl species with surface oxygen species.

Effect of initial Os loading

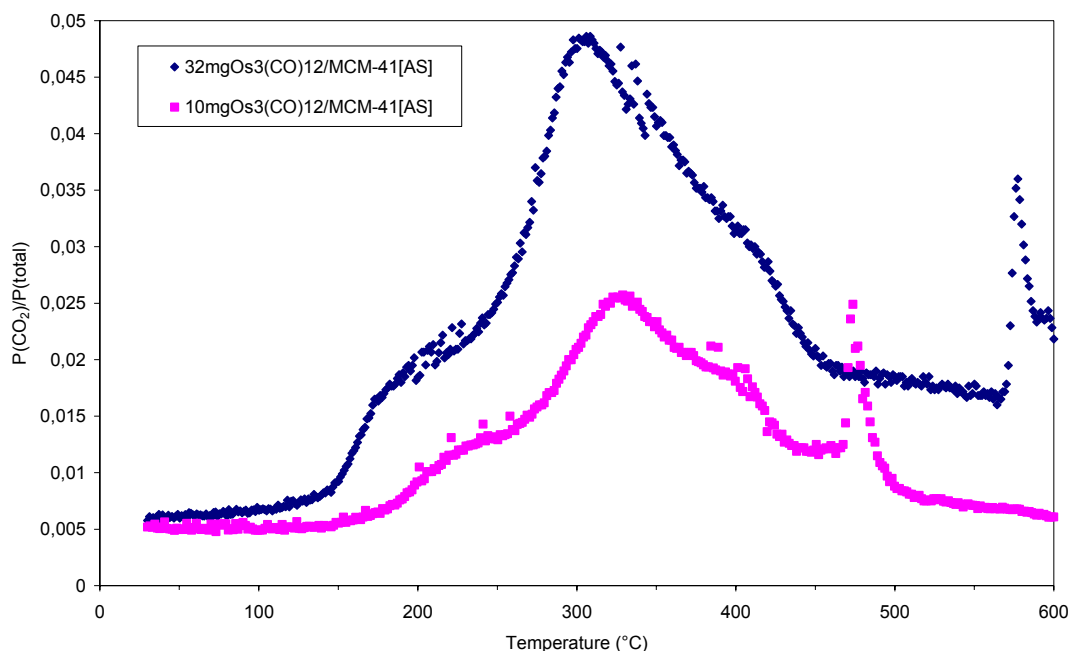*Fig. S4 TPDe spectra of 32mgOs$_3$(CO)$_{12}$/MCM-41[AS] and 10mgOs$_3$(CO)$_{12}$/MCM-41[AS].*

As mentioned in the text the CVD technique will only produce chemically anchored species (< one monolayer coverage) since under our preparation conditions, all the physisorbed species would have been desorbed. It is therefore interesting to compare high and low loading CVD samples, which may reflect different nature of the anchored species. It can be seen from Figure S4 that reducing the initial amount of $Os_3(CO)_{12}$ from 32 to 10 mg results in a shift of the major broad peak towards higher temperatures but also in a shift of the high

temperature sharp CO_2 peak to lower temperatures. Reproducibility of this observation is confirmed. The major decomposition peak is shifted from 308°C to 330°C, indicating the presence of more stable forms of carbonyl species against carbon dioxide formation (a high degree of the shoulder peak at 400°C) in $10mgOs_3(CO)_{12}/MCM-41[AS]$. The intensities of the peaks are also attenuated by a factor of two to three, indicating that less reactive species are present in the low loading catalyst.

Oxidative state of the surface species (XPS)

X-ray photoelectron spectroscopy was used to determine the concentration of the surface species and their oxidation state. All the binding energies are referenced to the binding energy of the carbon C 1s peak at 284.6 eV.

As can be seen from Table S2, XPS confirms the presence of Os on the catalysts surfaces. It also shows that the concentration of these Os surface species is low (atomic concentrations between 0.4 and 0.9%, Si/Os atomic ratios between 19 and 32). The binding energies of Os 4f7/2 are found to be between 52.3 and 52.7 eV, which implies an oxidation state similar to Os(IV) in OsO_2 (reported to be between 52.0 and 52.7 eV). This shows that some Os carbonyl species have been transformed into anchored Os-oxygen species after exposure to air.

Catalyst	Surface concentration (atom%)		Atomic ratios			Binding energies (eV)	
	Os	Al	Si/Al	Si/Os	Al/Os	Si2p3/2	Os4f7/2
Al(1)-MCM41	0	3.63	5.37	-	-	103.6	-
$32mgOs_3(CO)_{12}/MCM-41[AS]$	0.90	0	-	19.3	0	103.6	52.3
$32mgOs_3(CO)_{12}/Al-MCM41[AS]$	0.44	5.55	2.54	32.5	12.8	103.2	52.4
$32mgOs_3(CO)_{12}/MCM41[220C]$	0.58	4.17	3.83	27.4	7.15	103.2	52.5
$32mgOs_3(CO)_{12}/Al-MCM41[220C]$	0.70	8.44	2.19	26.3	12.0	103.1	52.7

Table S2: XPS data for some Os catalysts.

Methodologies for reaction in the dihydroxylation of *trans*-stilbene:

Testing conditions:

trans-stilbene (96% purity) and 4-methylmorpholine N-oxide (97%, NMO) were purchased from Aldrich and used without further purification. *trans*-stilbene (188 mg / 1 mmol) was introduced in a 50.0 mL Pyrex round-bottom flask together with 18 mg of catalyst, NMO (125 mg / 1 mmol) as the oxidant. Twenty milliliters of a 9:1 (v/v) mixture of acetone and water was added as the solvent. The reaction mixture was vigorously stirred using a magnetic stirrer and heated to 40°C using an oil bath and a hotplate. It was kept at atmospheric pressure under a flow of dry nitrogen for 96 h.

Product analysis:

The liquid reaction mixtures were analysed in two steps. First, using HPLC, a Perkin-Elmer Series 200 lc pump equipped with a reverse phase C-18 column (Brownlee, ValueLine Spheri-5 C18, 220mm × 4.6 mm, lot 15G6-002, part no. 402259) and a Diode Array Detector 235C with the detection wavelengths set at 245 and 255 nm. A mixture of acetonitrile and water was used as the mobile phase with a total flow rate of 1.5 cm^3 min^{-1}. This has made it possible to separate, within 15 minutes, the 1,2-diphenylethane-1,2-diol (hydrobenzoin) from the other reaction by-products, namely benzaldehyde, benzil, benzoin, *trans*-stilbeneoxide (epoxide) and deoxybenzoin (Scheme 1). The yield to the diol product was obtained after carefully calibrating the equipment with standard compounds (all purchased from Aldrich and used without further purification) of known concentrations using the provided Turbochrom Chromatography Workstation software (Version 4.1(2F12)), linked to the HPLC *via* a PE NELSON 600 Series LINK.

The reaction mixtures were then injected in a Perkin-Elmer HPLC, equipped with a Series 200 lc pump, a chiral column purchased from Hichrom (Regis Technologies, Pirkle covalent, (SS) Whelk-01 10/100, 250 mm x 4.6 mm) and a Diode Array Detector 235C, with the detection wavelengths set at 220 and 255 nm. A mixture of hexane and isopropanol (99:1) was used as the mobile phase with a total flow rate of 2 cm^3 min^{-1}. Products were separated within 60 min. Quantitative analysis was made possible by carefully calibrating the equipment with a solution in acetonitrile of standard compounds of known concentrations (RS-hydrobenzoin, RR-hydrobenzoin, SS-hydrobenzoin, 99% purity, purchased from Aldrich) using the Turbochrom Chromatography Workstation software (Version 4.1(2F12)), linked to the HPLC via a PE NELSON 600 Series LINK. All results were repeatedly analysed more than two times to confirm reproducibility of the measurements.
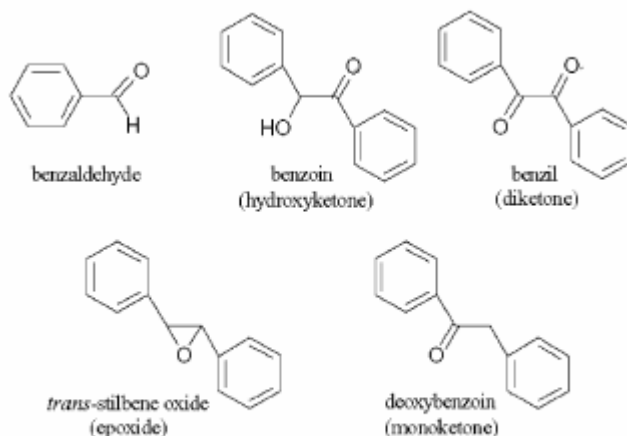

Fig. 4. *trans*-stilbene dihydroxylation by-products detected under our reaction conditions.

Scheme S1 (more details on testing methodologies could refer to: V. Caps, I. Paraskevas, S. C. Tsang, *Appl. Catal. A*, 2003, **252**, 37)