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**Preliminary communication**

# HYDROGENATION AND METALLATION OF ETHYLENE ON ANCHORED TRIOSMIUM CLUSTERS

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## Summary

An anchored ethylidyne complex, $H_3Os_3(CO)_8(CCH_3)PPh_2C_2H_4SIL$ (SIL = silica gel), is formed when $H_2Os_3(CO)_9PPh_2C_2H_4SIL$ and $Os_3(CO)_{11}PPh_2C_2H_4SIL$ are treated with ethylene and hydrogen.

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We report a comparative study of trinuclear osmium complexes in solution and anchored on silica gel as ethylene hydrogenation catalysts which has revealed the formation of a particular ethylidyne complex bound to the silica surface by an appended phosphine.

$$\begin{tikzcd}
\begin{array}{c}H_2Os_3(CO)_{10}PPh_2Et\\ \text{(I)}\end{array} \arrow[r, "\text{(i)}"] & \begin{array}{c}H_2Os_3(CO)_9PPh_2Et\\ \text{(II)}\end{array} \arrow[d, "\text{(iii)}"', "\text{(iv)}"] & \begin{array}{c}Os_3(CO)_{11}PPh_2Et\\ \text{(III)}\end{array} \arrow[l, "\text{(ii)}"'] \\
 & \begin{array}{c}HOs_3(CO)_9(CHCH_2)PPh_2Et\\ \text{(IV)}\end{array} \arrow[r, "\text{(v)}"] & H_2Os_3(CO)_8(CCH_2)PPh_2Et \arrow[d, "\text{(V)}"] \\
 & & \begin{array}{c}H_3Os_3(CO)_8(CCH_3)PPh_2Et\\ \text{(VI)}\end{array}
\end{tikzcd}$$

SCHEME 1. (i) refluxing hexane; (ii) $H_2$, refluxing n-octane; (iii) $C_2H_2$, 20°C; (iv) $C_2H_4$, 60 psig, 20°C; (v) refluxing heptane; (vi) $H_2$, refluxing n-octane.

We established the reactions depicted in Scheme 1, which indicate that phosphine substitution does not markedly alter the reactivity of $H_2Os_3(CO)_{10}$ [1,2], to determine likely temperatures for ethylene hydrogenation by the silica anchored derivatives $H_2Os_3(CO)_{10}PPh_2C_2H_4SIL$ (VII), $H_2Os_3(CO)_9PPh_2C_2H_4SIL$ (VIII) and $Os_3(CO)_{11}PPh_2C_2H_4SIL$ (IX) [3] (SIL = silica gel). Although $H_2Os_3(CO)_{10}$ catalyses alkene hydrogenations under 50 psig of $H_2$ at 50°C, [4],

$H_2Os_3(CO)_9PPh_2C_3H_6SIL$ has been found to be inactive towards propylene hydrogenation at 100°C [5].

Under a 4/1 mixture of ethylene (60 psig) and hydrogen (240 psig), we find that suspensions of VII and VIII in hydrocarbon solvents catalyse ethane formation at 75°C, as do those of IX at 110°C. Hydrocarbon solutions of I, II and III behave similarly to their anchored analogues and under these conditions formation of the two derivatives of $H_2Os_3(CO)_{10}$, VIII and II, is likely. After 20 h at 75°C, a solution of II afforded ~75 ethane molecules per cluster. Ethane yields from VIII at 75°C were estimated to be 2.5, 9 and 11.5 molecules per cluster after 4, 20 and 44 h reaction time, respectively, It appears that anchoring has reduced the reaction rate by a factor of ca. 8. Also catalytic activity deteriorates and this can be correlated with a change in the infrared spectra of the recovered silicas (Fig. 1). In addition to bands due to VIII, after 4 h there is a weak band at 2083 $cm^{-1}$, coincident with a strong $\nu(CO)$ absorption of $HOs_3(CO)_9(CHCH_2)PPh_2Et$ (IV), which is later lost. A third species increases in concentration up to 20 h reaction time and its IR spectrum was obtained by subtracting the 4 h spectrum from the 20 h one (Fig. 2a). There is little subsequent change so after 44 h this third species is still a major one. Comparison with the $\nu(CO)$ pattern of $H_3Os_3(CO)_8(CCH_3)PPh_2Et$ (VI) (Fig. 2c) indicates that the third species is probably $H_3Os_3(CO)_8(CCH_3)PPh_2C_2H_4SIL$ (X). Metallation of ethylene occurs as a deactivation process, as the $\mu_3$-C—$CH_3$ group blocks further catalytic hydrogenation.

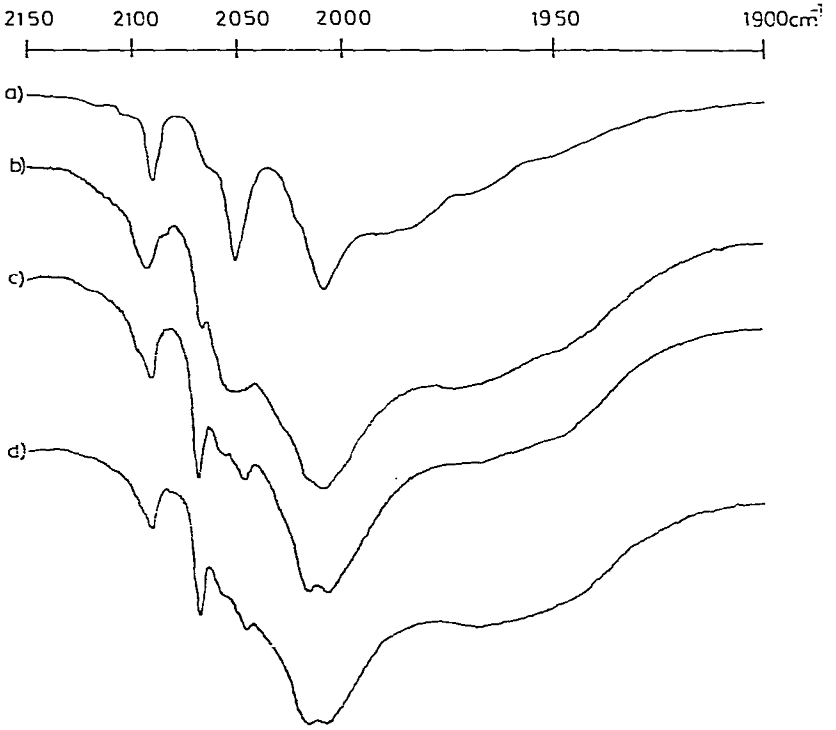

Fig. 1. IR spectra of Nujol mulls of silicas recovered from the reaction of $H_2$ (240 psig), $C_2H_4$ (60 psig) and $H_2Os_3(CO)_9PPh_2C_2H_4SIL$ (VIII) at 75°C after various reaction times. (a) VIII, (b) 4 h, (c) 20 h, (d) 44 h.

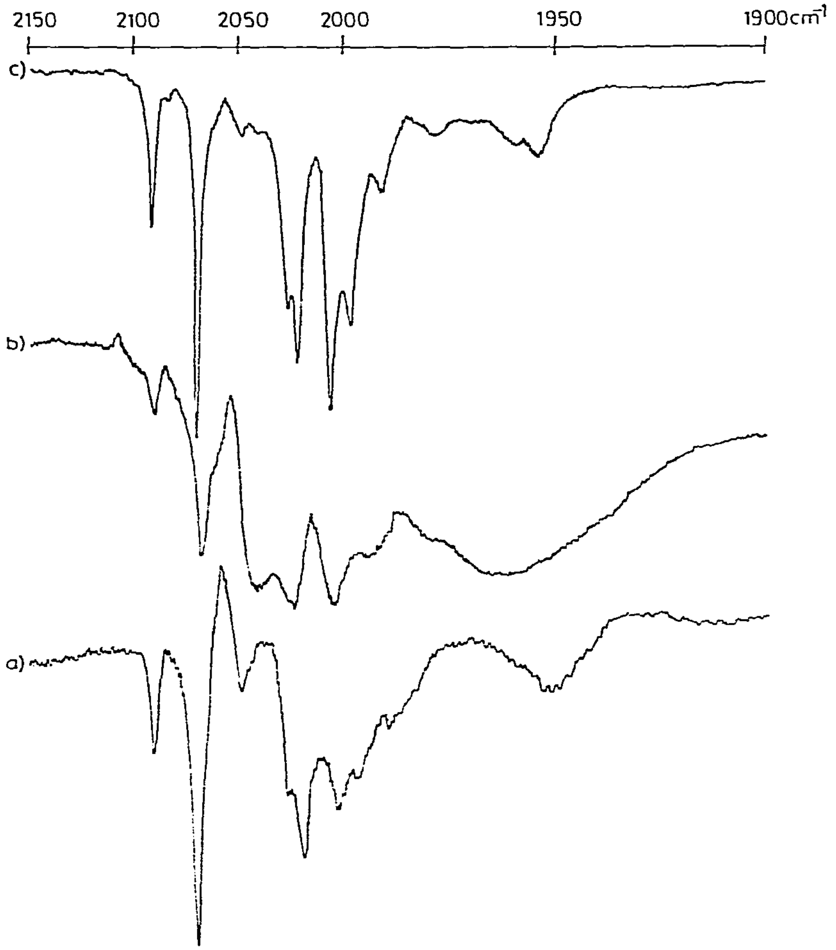

Fig. 2. (a) Difference spectrum between spectra 1c and 1b. (b) Difference IR spectrum between product from the reaction between $H_2$ (240 psig), $C_2H_4$ (60 psig) and $Os_3(CO)_{11}PPh_2C_2H_4SIL$ (IX) at 110°C and IX itself. (c) IR spectrum of $H_3Os_3(CO)_9(CCH_3)PPh_2Et$ (VI) in cyclohexane solution.

At 110°C under the same gas mixture (IX) gives a higher catalytic rate (60 turnovers/cluster after 20 h) and IR analysis of the recovered silica again indicates the presence of X (Fig. 2b). In addition, there are two broad $\nu$(CO) absorptions at 2030 and 1958 $cm^{-1}$ due to an unidentified osmium carbonyl species, which is also formed by heating IX to 120°C in vacuo.

In conclusion, these results demonstrate (a) that phosphine substitution does not inhibit the reactivity of $H_2Os_3(CO)_{10}$, (b) these anchored cluster materials undergo the associative reactions involved in ethylene hydrogenation more slowly than dissolved analogues and (c) a particular ethylidyne complex X, is formed at the silica surface.

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