Anchoring of Osmium Clusters to Silica†

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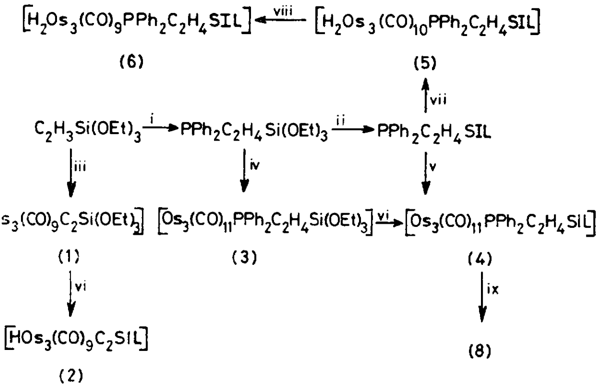
Summary Clusters of the types $[Os_3(CO)_{11}PPh_2R]$, $[H_2Os_3(CO)_{10}PPh_2R]$, and $[HOs_3(CO)_9CCR']$ have been anchored to silica and characterised by i.r. spectroscopy (R = C_2H_4SIL, R′ = SIL, SIL = silica gel.)

Interaction of metal carbonyl clusters with refractory supports has been studied recently as a potential way of preparing a highly uniform dispersion of metal particles.[1] Two problems arise from this approach. Firstly sintering can occur during the attempted thermal labilisation of the carbonyl ligands[2] and secondly these materials are difficult to characterise. We report specific syntheses of a variety of osmium carbonyl cluster complexes anchored to silica by appended ligands. This approach was adopted to counter the two problems of direct interaction between the cluster and the support; sintering should be less acute and characterisable analogues can be readily prepared.



Scheme. i, PPh_2H, u.v. ii, Silica gel, toluene, reflux. iii, $[Os_3(CO)_{12}]$, n-octane, reflux. iv, $[Os_3(CO)_{12}]$, toluene, reflux. v, $[Os_3(CO)_{11}MeCN]$, CH_2Cl_2, 20 °C. vi, Silica gel, benzene, reflux. vii, $[H_2Os_3(CO)_{10}]$, hexane, 20 °C. viii, Hexane, reflux. ix, n-Nonane, reflux.

The reactions carried out are presented in the Scheme. $C_2H_3Si(OEt)_3$, $PPh_2C_2H_4Si(OEt)_3$, and $PPh_2C_2H_4SIL$ (SIL = silica gel) were used as complexing agents.[3] Under conditions similar to those in which ethylene reacts with $[Os_3(CO)_{12}]$ to give $[H_2Os(CO)_9CCH_2]$,[4] vinyltriethoxysilane yields $[HOs_3(CO)_9CCSi(OEt)_3]$ (**1**) in high yield. This reaction is unusual in that the vinyl group is completely dehydrogenated; complexes of this type are normally prepared from terminal acetylenes.[5] Refluxing a benzene solution of (**1**) with silica gel leads to (**2**), the anchored version of (**1**), as identified by its carbonyl vibrations.

$[Os_3(CO)_{12}]$ and $PPh_2C_2H_4Si(OEt)_3$ in refluxing toluene give rise to $[Os_3(CO)_{11}PPh_2C_2H_4Si(OEt)_3]$ (**3**) and the di- and tri-substituted clusters. The anchored complex (**4**) was prepared by interaction of (**3**) with silica gel and also by the reaction of $[Os_3(CO)_{11}MeCN]$[6] with $PPh_2C_2H_4SIL$ at room temperature. The phosphinated silica complexes were characterised by comparison of their carbonyl stretching vibrations with those of the PPh_2Et analogue‡ (see Table). The i.r. spectra of (**4**) and $[Os_3(CO)_{11}PPh_2Et]$ are displayed in the Figure. The close agreement between them indicates that (**4**) was prepared specifically by these two routes. In contrast, direct interaction of $[Os_3(CO)_{12}]$ and $PPh_2C_2H_4SIL$ in refluxing toluene gives a material which exhibits a very broad spectrum and may contain a mixture of mono- and di-substituted products with the former predominating.

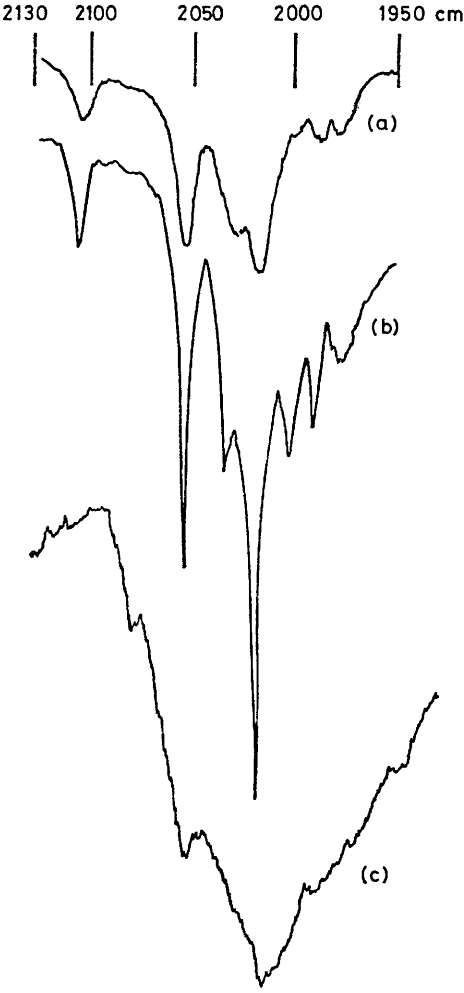


Figure. I.r. spectra of (a) (**4**) in Nujol mull, (b) $[Os_3(CO)_{11}PPh_2Et]$ in cyclohexane, and (c) the product of refluxing $[Os_3(CO)_{12}]$ with $PPh_2C_2H_4SIL$ in toluene in a Nujol mull.

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† No reprints available.

‡ A simple procedure was recently adopted to characterise a polymer bound $Ir_4(CO)_{11}PPh_2R$ complex (J. J. Rafalko, J. Lieto, B. C. Gates, and G. L. Schrader, Jr., *J.C.S. Chem Comm.*, 1978, 540).

TABLE. Carbonyl stretching frequencies of anchored and free clusters[a]

Compound	ν_{CO}/cm^{-1}
(**1**)	2102·5 w, 2077 vs, 2054 vs, 2020 vs, 2016·5 sh, 1983 sh, 1981 m
(**2**)	2078 s, 2054 s, 2022 s, 2014 s, 1983 m
[$Os_3(CO)_{11}PPh_2Et$]	2107 m, 2054s, 2035 s, 2019 vs, 2002 m, 1990 m, 1976 m, 1950 w
(**4**)	2107 m, 2054 s, 2035 s, 2019 vs, 2003 m, 1990 m, 1980 m
[$H_2Os_3(CO)_{10}PPh_2Et$]	2105·5 m, 2066 s, 2051 s, 2024·5 vs, 2016 sh, 2007 ms, 1999 m, 1982·5 m, 1972 m
(**5**)	2103 m, 2065 s, 2049 s, 2023 vs, br, 1984 m
[$H_2Os_3(CO)_9PPh_2Et$]	2097·5 m, 2054 s, 2019 s, 2010 vs, 1994 w, 1987·5 w, 1977·5 m, 1970 m, 1949 m
(**6**)	2095 m, 2063 sh, 2053 s, 2034 sh, 2015 vs, 1979 sh
(**7**)	2086·5 m, 2065 vs, 2044 s, 2010 sh, 2007 s, 1991 s, 1983 w, 1972 w
(**8**)	2094 w, 2075 m, 2061 sh, 2043 s, 2010 vs, br, 1960 sh

[a] Spectra of discrete complexes were recorded in cyclohexane solution and those of anchored materials in Nujol mulls.

Anchoring of [$H_2Os_3(CO)_{10}$] can also be effected at room temperature since it forms an adduct (**5**) with appended as well as free phosphine.[7]

Preliminary work on comparative reactivity studies of these free and anchored clusters indicates that identical reactivity between the two states cannot be assumed. Like its PPh_2Et counterpart,[7a] (**5**) readily loses one carbonyl group to form [$H_2Os_3(CO)_9PPh_2C_2H_4SIL$] (**6**) as the major product. However there is a divergence in behaviour between the anchored complex (**4**) and [$Os_3(CO)_{11}PPh_2Et$]. Refluxing the latter complex in n-nonane for 5 h causes conversion (*ca.* 80%) into [$Os_3(CO)_9PEtC_6H_4$] (**7**). Compound (**4**), however, yields an off-white material (**8**) with a substantially different i.r. spectrum (see Table).

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