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Preliminary communication

The Reaction of $H_2Os_5(CO)_{15}$ with Nucleophilic Reagents

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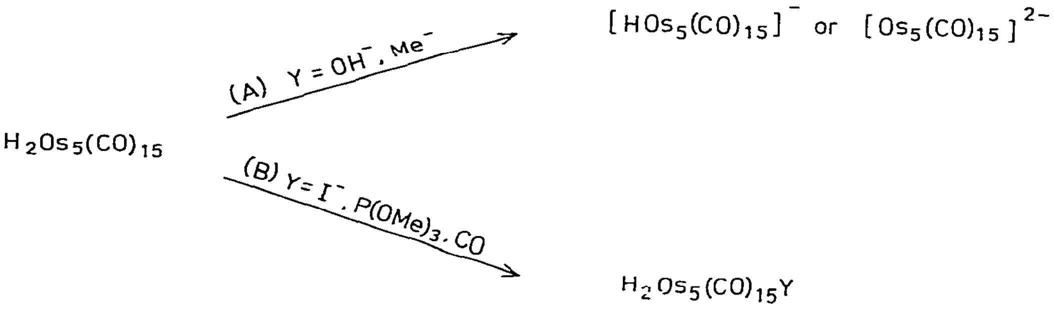
SUMMARY

The reaction of $H_2Os_5(CO)_{15}$ with nucleophiles Y leads either to deprotonation ($Y = OH^-$ or Me^-) or addition ($Y = I^-$, $P(OMe)_3$, or CO). The geometrical consequences of these reactions are discussed.

As part of our investigation into the chemistry of the higher osmium carbonyl clusters, we wish to report on the nature of nucleophilic attack on the dihydrocluster $H_2Os_5(CO)_{15}$. On reaction with nucleophiles such as OH^- and Me^-, deprotonation occurs to give either $[HOs_5(CO)_{15}]^-$ or $[Os_5(CO)_{15}]^{2-}$; the degree of deprotonation depending on the solvent employed. (Scheme 1,route A). In contrast, nucleophiles such as I^-,

$P(OMe)_3$ or CO react according to route B, Scheme 1, to give the adducts $[H_2Os_5(CO)_{15}I]^-$, $H_2Os_5(CO)_{15}[P(OMe)_3]$ or $H_2Os_5(CO)_{16}$. In these reactions a major structural transformation of the Os_5 unit occurs; changing from a trigonal bipyramidal geometry to an edge-bridged tetrahedral arrangement.



Scheme 1

$H_2Os_5(CO)_{15}$ is almost totally insoluble in methanol but on treatment with a 50-fold excess of methanolic KOH a deep red-brown solution is formed. On addition of excess $[PPN]^+Cl^-$ to this solution purple-brown crystals of $[PPN]_2{}^+[Os_5(CO)_{15}]^{2-}$ separate quantitatively. When KOH or MeLi in ether (4%) is added to a stirred solution of $H_2Os_5(CO)_{15}$ in warm dichloromethane, conversion to $[HOs_5(CO)_{15}]^-$ takes place, which again may be quantitatively precipitated as the $[PPN]^+$ salt.

When a 10-fold excess of $n\text{-}Bu_4NI$ is added to $H_2Os_5(CO)_{15}$ in refluxing dichloromethane a deep red solution is slowly formed. Thin layer chromatography (90% dichloromethane/10% hexane) of the reaction mixture after *ca*. 2 hours leads to a high yield (80%) of the pure red-brown product $[Bu_4N]^+[H_2Os_5(CO)_{15}I]^-$ (I) characterised by microanalysis, 'H n.m.r. [τ28.56(s) and 30.05(s), CD_2Cl_2, 35°C] and i.r. spectroscopy [ν_{CO} (CH_2Cl_2) 2089w, 2061vs, 2037s, 2026s, 2011w(sh) and 1985m(br) cm^{-1}]. Interestingly this anionic cluster reverts back to $H_2Os_5(CO)_{15}$ upon treatment with excess acid (H_2SO_4 in acetonitrile).

In a similar manner treatment of $H_2Os_5(CO)_{15}$ with a 50-fold excess of $P(OMe)_3$ in refluxing dichloromethane for approximately 20 hours and t.l.c. (as above) of the reaction mixture leads to the neutral orange-red cluster $H_2Os_5(CO)_{15}P(OMe)_3$ (II) also in good yield (67%). This was fully characterised by microanalysis, 'H n.m.r. [τ30.72(s) and 31.02(s), CD_2Cl_2, 35°C], i.r. spectroscopy [ν_{CO} (CH_2Cl_2) 2116w, 2070s, 2048vs, 2036s, 2014m(sh) and 1997w cm^{-1}] and mass spectrometry [$^m/_e$ 1497(M^+), (M^+-n CO), n = 1-15].

CO can also be added to $H_2Os_5(CO)_{15}$ but requires the more severe conditions of an autoclave. When $H_2Os_5(CO)_{15}$ in deoxygenated hexane is heated to 150°C for ca. 16 hours under a working pressure of 6 atmospheres of CO, a reasonable yield (40%) of the anticipated $H_2Os_5(CO)_{16}$ is obtained. An appreciable amount of decomposition also takes place, although the yield of product has yet to be optimised. Certainly this route to $H_2Os_5(CO)_{16}$ is an improvement on the pyrolysis of $Os_3(CO)_{12}$ in the presence of traces of water[1], where yields do not exceed 2%.

Infrared Spectra in the CO Stretching Region for

(a) $[H_2Os_5(CO)_{15}I]^-$, (b) $[H_2Os_5(CO)_{15}P(OMe)_3]$ and (c) $[H_2Os_5(CO)_{16}]$

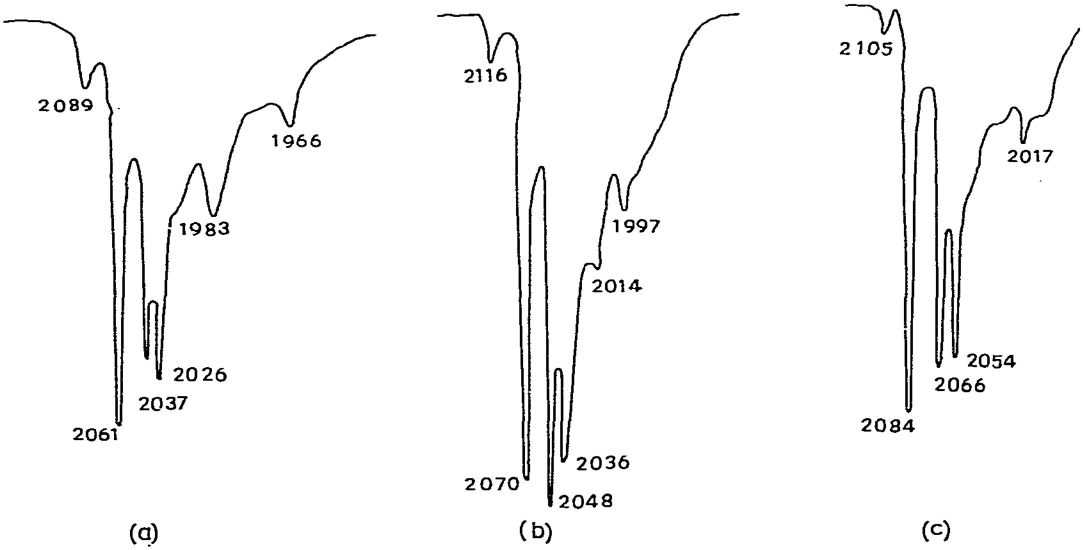
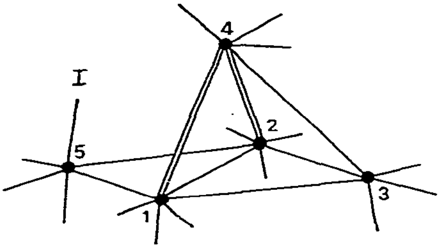


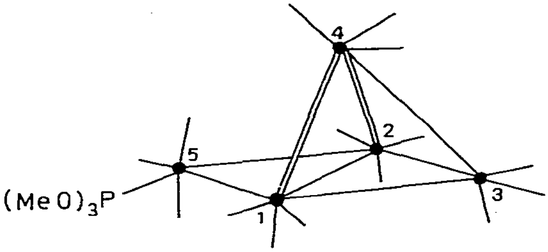
Figure 1

These dihydrides each have seven electron pairs available for cluster bonding and a square pyramidal metal geometry, similar to that found in $Fe_5(CO)_{15}C$ [2] and $Os_5(CO)_{15}P(OMe)$ [3], is predicted on the basis of the Wade Theory. In order to investigate the solid-state structures, crystals of $[Bu_4N]^+[H_2Os_5(CO)_{15}I]^-$ (I) and $H_2Os_5(CO)_{15}P(OMe)_3$ (II) suitable for X-ray analysis were grown by slow evaporation from dichloromethane. Their molecular structures are shown in Figures 2 and 3. A full report of these analyses will be given elsewhere.



(I)

Figure 2



(II)

Figure 3

The geometry of the metal atoms is not square pyramidal but is related to that found in $H_2Os_5(CO)_{16}$ [4] which consists of a tetrahedron of osmium atoms with one edge bridged by the fifth osmium atom. This alternative geometry may still be rationalised by skeletal electron counting procedures. It is fundamental to Wade's Theory that closo-, nido- and arachno-variants of the same polygon require the same number of skeletal electron pairs. It has been shown that a nido-capped octahedron is a suitable metal geometry for a six metal atom cluster having seven skeletal electron pairs. Thus, by analogy, the structure of the dihydrides (I) and (II) and $H_2Os_5(CO)_{16}$ may be looked upon as an arachno-capped octahedron which is a valid alternative geometry for five metal atoms and seven skeletal electron pairs (Figure 4). It is consistent with this description that the structure forms part of a close-packed array and the four osmium atoms Os(1), Os(2), Os(3) and Os(5) are roughly coplanar.

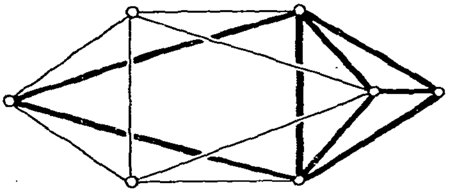


Figure 4

The only other cluster known[5] with a similar geometry is $Co_5(CO)_{11}[P(CH_3)_2]_3$ which has eight skeletal electron pairs. This structure cannot be explained by Wade's Theory, nor by the 18-electron rule; only a valence bond notation invoking canonical forms provides an acceptable picture of the bonding in this compound.

The difference in site preference for the I^- (axial on Os_5) and $P(OMe)_3$ (equatorial on Os_5) moietes is rationalised simply in terms of the much greater steric demands of the phosphite ligand. In both (I) and (II) the hydrogen atoms appear to bridge the long Os-Os bonds, Os(1)-Os(4) and Os(2)-Os(4). Significantly in $H_2Os_5(CO)_{16}$ these same edges appear to be bridged by the hydrogen atoms which suggests that the parent $H_2Os_5(CO)_{15}$ contains the two hydride ligands in the equatorial edge-bridging sites indicated (Figure 5).

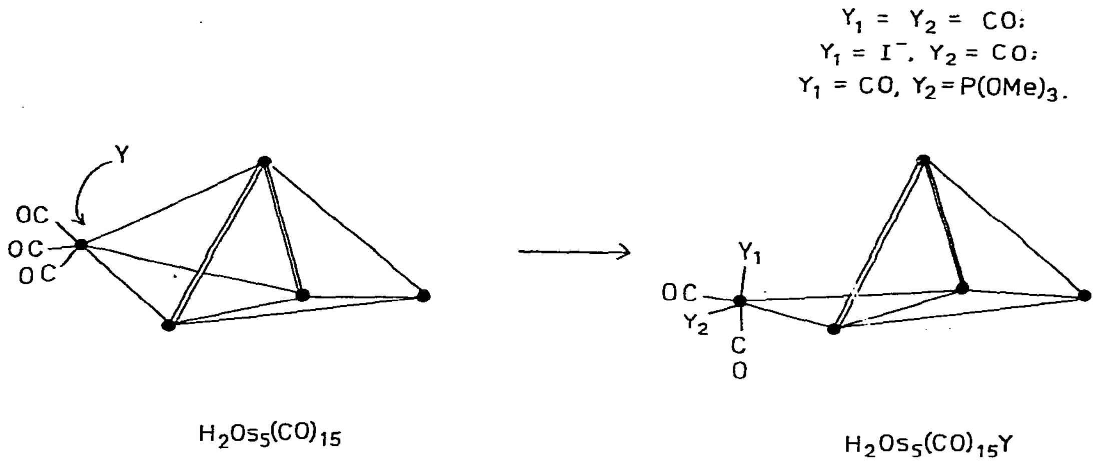


Figure 5

It is apparent from the above studies that while strongly basic nucleophiles tend to deprotonate $H_2Os_5(CO)_{15}$, those with much less basic character undergo addition to the cluster. $H_2Os_5(CO)_{15}$ is isoelectronic with $Os_5(CO)_{16}$ for which a trigonal bipyramidal structure has been determined[6] and a similar structure for $H_2Os_5(CO)_5$ is predicted both by the Wade Theory and the skeletal electron counting scheme. Thus, it is seen that the addition of nucleophiles such as I^-, $P(OMe)_3$ and even CO to $H_2Os_5(CO)_{15}$ results in cleavage of an Os-Os bond, followed by an opening out of the structure to yield the edge-bridged tetrahedral arrangement.

This provides a further example of the fascinating changes in structure that my be effected chemically in the reactions of the higher osmium carbonyl clusters, in sharp contrast to the widely varied chemistry of, for example, Os_3 derivatives where the basic Os_3 triangle usually remains intact. Indeed, the reversibility of (at least) $[H_2Os_5(CO)_{15}I]^-$ to $H_2Os_5(CO)_{15}$ upon treatment with acid demonstrates the exciting potential of facile structural transformations that may one day lead to catalysis by metal clusters.

ACKNOWLEDGMENTS

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