An Improved Synthesis of Os$_6$ Raft-like Clusters

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The new, activated, raft clusters [Os$_6$(CO)$_{20}$(MeCN)] and [Os$_6$(CO)$_{19}$(MeCN)$_2$] have been prepared by the coupling of two Os$_3$ units in a reaction involving PdCl$_2$ as catalyst; they react readily with ligands L (L = PR$_3$, CO) to generate a range of planar Os$_6$ clusters, and with Me$_3$NO–MeCN to form [Os$_6$(CO)$_{18}$(MeCN)$_3$].

One of the significant problems in cluster chemistry is the need for improved specificity in synthetic routes. In this communication we report a method by which two triosmium units are combined to produce planar hexaosmium clusters in high-yield; a feature of such complexes being the presence of labile organic substituents.
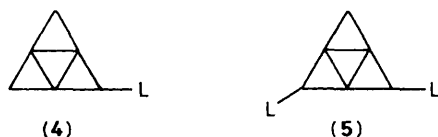
In general, binary carbonyl clusters of osmium require moderate to vigorous conditions to induce chemical reaction usually resulting in the formation of a number of products in low yield. However, if a suitable activated group is present then reactions can be carried out under mild conditions often with a high degree of specificity. In Os$_3$ cluster chemistry, for example, the compounds [Os$_3$(CO)$_{11}$(MeCN)] and [Os$_3$(CO)$_{10}$(MeCN)$_2$] (1) hold an important position; the ease with which the MeCN ligand is displaced by other substrates, such as alkenes and alkynes, has led to the isolation of many,
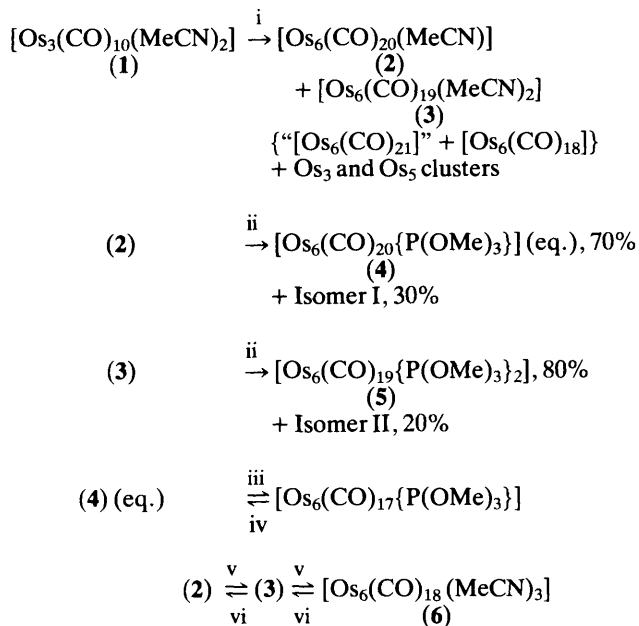
Table 1.

	$E_{1/2}(V)^a$		ΔE_p (mV)	
	1st wave	2nd wave	1st wave	2nd wave
$[Os_6(CO)_{20}\{P(OMe)_3\}]$ (ax.)	−0.96	−1.12	65	90
$[Os_6(CO)_{20}\{P(OPh)_3\}]$ (ax.)	−1.01	−1.27	62	57
$[Os_6(CO)_{20}\{P(Ph)_3\}]$ (eq.)	−1.02	−1.30	67	62
$[Os_6(CO)_{20}\{P(OMe)_3\}]$ (eq.)	−1.09	−1.28	67	85
$[Os_6(CO)_{20}\{P(OPh)_3\}]$ (eq.)	−1.15	−1.38	64	72
$[Os_6(CO)_{19}\{P(OMe)_3\}_2]$ (5)	−1.24	−1.46	80	85
$[Os_6(CO)_{19}\{P(OMe)_3\}_2]$	−1.24	−1.43	60	75
$[Os_6(CO)_{18}\{P(OMe)_3\}_3]$	−1.42	−1.62	68	125
$[Os_6(CO)_{18}\{P(OMe)_3\}_3]$	−1.28	−1.49	75	140
$[Os_6(CO)_{17}\{P(OMe)_3\}_4]$	−1.43	−1.60	—	—
$[Os_6(CO)_{16}\{P(OMe)_3\}_5]$	−1.58	−1.78	64	85
$[Os_6(CO)_{15}\{P(OMe)_3\}_6]$	−1.84	−2.04	62	75
$[Os_6(CO)_{20}\{MeCN\}]$	−0.98	−1.22	68	114
$[Os_6(CO)_{19}\{MeCN\}_2]$	−1.20	—	—	—

[a] All potentials quoted vs. Ag/Ag$^+$.

Schematic representation of (4) and (5).

$$[Os_3(CO)_{10}(MeCN)_2] \xrightarrow{i} [Os_6(CO)_{20}(MeCN)]$$
(1) → (2)
$$+ [Os_6(CO)_{19}(MeCN)_2]$$
(3)
$$\{\text{``}[Os_6(CO)_{21}]\text{''} + [Os_6(CO)_{18}]\}$$
$$+ Os_3 \text{ and } Os_5 \text{ clusters}$$

(2) $\xrightarrow{ii}$ $[Os_6(CO)_{20}\{P(OMe)_3\}]$ (eq.), 70%
(4)
$+$ Isomer I, 30%

(3) $\xrightarrow{ii}$ $[Os_6(CO)_{19}\{P(OMe)_3\}_2]$, 80%
(5)
$+$ Isomer II, 20%

(4) (eq.) $\underset{iv}{\overset{iii}{\rightleftharpoons}}$ $[Os_6(CO)_{17}\{P(OMe)_3\}]$

$$(2) \underset{vi}{\overset{v}{\rightleftharpoons}} (3) \underset{vi}{\overset{v}{\rightleftharpoons}} [Os_6(CO)_{18}(MeCN)_3]$$
(6)

Scheme 1. *Reagents and conditions:* i, PdCl$_2$, room temp., CH$_2$Cl$_2$, 3 h; ii, excess of P(OMe)$_3$, room temp., CH$_2$Cl$_2$, 5 min.; iii, toluene, 110 °C, 16 h; iv, toluene, 100 °C, 10 h, 50 atm CO; v, Me$_3$NO–MeCN; vi, CO–CH$_2$Cl$_2$.

previously inaccessible compounds and reaction intermediates.[1,2]

The new functionalised reagents $[Os_6(CO)_{20}(MeCN)]$ (2) and $[Os_6(CO)_{19}(MeCN)_2]$ (3) have been prepared in good yield from (1) in a simple coupling reaction (see Scheme 1). In a typical reaction, compound (1) in CH$_2$Cl$_2$ solution was treated with a small, catalytic, amount of PdCl$_2$. After stirring for *ca.* 3 h the solution changed from pale yellow to an intense blue colour. After filtration and separation by column

chromatography (eluant: CCl$_4$ 75%, CHCl$_3$ 20%, MeCN 5%) eight compounds were obtained in varying yields. The compounds $[Os_6(CO)_{20}(MeCN)]$ (2) and $[Os_6(CO)_{19}$-$(MeCN)_2]$ (3) were by far the major products, being obtained in yields of 46% and 30% respectively. The other Os$_6$ products, *viz.* $[Os_6(CO)_{21}]$† and $[Os_6(CO)_{18}]$, accounted for a further 12% and the remaining 12% was made up of various Os$_3$ and Os$_5$ derivatives. This method clearly offers a considerably improved route to the planar hexanuclear osmium clusters than that previously reported which involved the carbonylation of Os$_6$(CO)$_{18}$.[3]

The new compounds were identified primarily on the basis of their mass spectroscopic data‡ and on their reactions with P(OMe)$_3$ to produce the compounds $[Os_6(CO)_{21-n}$-$\{P(OMe)_3\}_n]$ (n = 1 or 2). Their i.r. spectra, which exhibit bands in the region 1900—2100 cm^{-1} assignable to ν_{CO} and ν_{CNR} stretching modes, and their ^1H n.m.r. spectra, which show a singlet resonance due to MeCN, are consistent with this structural assignment.

The usefulness of these compounds as precursors to a range of planar or raft-like cluster compounds has been investigated. In particular they allow a controlled replacement of groups

† Previously considered to be Os$_6$(CO)$_{20}$.

‡ *Selected spectroscopic data:* (2), ν_{max}. (CO) 2124w, 2089s, 2073s, 2037s, 2022s, 2004m, 1995m, and 1961m cm^{-1} (CH$_2$Cl$_2$); n.m.r. (CD$_2$Cl$_2$): ^1H, δ 2.87 (s, 3H, MeCN); $^{13}C\{^1H\}$ (−20 °C), 28.9 (s, Me), 116.4 (s, CN); mass *m/z* 1756 (1753).

(3), ν_{max}. (CO) 2109w, 2069s, 2061s, 2022sh,s, 2014s, 1998m, 1985m,sh, and 1954w cm^{-1} (CH$_2$Cl$_2$); n.m.r. (CD$_2$Cl$_2$): ^1H, δ 2.85 (s, 6H, 2 × MeCN); mass *m/z* 1766 (1766).

(4), ν_{max}. (CO) 2127vw, 2091s, 2107sm, 2041vs, 2022s, 2000w, and 1959w cm^{-1} (CH$_2$Cl$_2$); n.m.r. (CD$_2$Cl$_2$): ^1H, δ 3.85 (d, *J* 11.1 Hz, 9H, 3 × OMe); mass *m/z* 1836 (1836).

(5), ν_{max}. (CO) 2115w, 2075s, 2062m, 2031vs, 2014m, 1992m, and 1950vw cm^{-1} (CH$_2$Cl$_2$); n.m.r. (CD$_2$Cl$_2$): ^1H, δ 3.68 (d, *J* 12.2 Hz, 18 H, 6 × OMe); $^{31}P\{^1H\}$, −58.37 [d, *J*(PP) 7 Hz, P(OMe)$_3$], −61.35 p.p.m., [d, *J*(PP) 7 Hz, P(OMe)$_3$].

(6), ν_{max}. (CO) 2091w, 2051w, 1996s, 1970w, and 1945w cm^{-1} (CH$_2$Cl$_2$).

Isomer I, ν_{max}. (CO) 2119w, 2084r, 2054m, 2035vs, 2015m, 1990sh, 1983m, 1950w (CH$_2$Cl$_2$); n.m.r. (CD$_2$Cl$_2$): ^1H, δ + 3.64, (d, 11.2 Hz, 9H, 3 × OMe); mass *m/z* 1836 (1836).

Isomer II, ν_{max}.(CO) 2017m, 2066r, 2042m, 2024vs, 2007s, 1985m, 1975m, 1946vw cm^{-1} (CH$_2$Cl$_2$); n.m.r. (CD$_2$Cl$_2$): ^1H, δ 3.85 (d, *J* 11.83 Hz, 18H, 6 × OMe); mass *m/z* 1930 (1932).
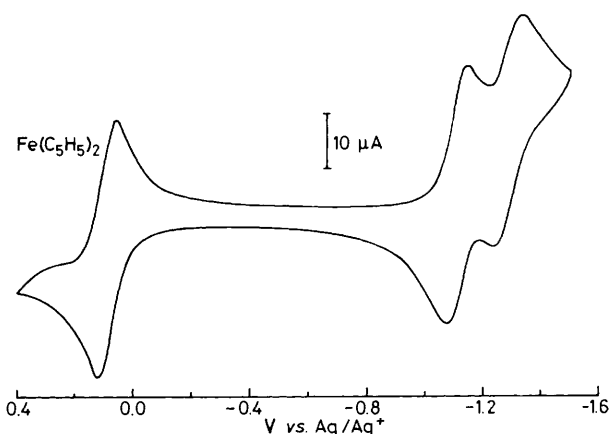
Figure 1. The cyclic voltammogram of $[Os_6(CO)_{20}\{P(OMe)_3\}]$ (eq.).

within the Os_6 raft structures. Thus, treatment of (2) or (3) with an excess of $P(OMe)_3$ in CH_2Cl_2 at room temperature produces the compounds $[Os_6(CO)_{20}\{P(OMe)_3\}]$ (4) (eq. = equatorial, ax. = axial) and $[Os_6(CO)_{19}\{P(OMe)_3\}_2]$ (5) respectively in quantitative yield. In each case two isomeric forms are observed (Scheme 1). Previous X-ray studies of the complexes (4), (5) (prepared from $[Os_6(CO)_{21}]$), and the compound $[Os_6(CO)_{17}\{P(OMe)_3\}_4]$ showed that all the $P(OMe)_3$ ligands occupied equatorial sites. The geometries of alternative isomers prepared from the corresponding aceto-nitrile derivatives have not been established with certainty but are believed to be equatorial isomers. Other related derivatives [L = PPh_3 or $P(OPh)_3$] have also been prepared by the same route.[4] In addition, we have found that compound (2) reacts with an equimolar amount of Me_3NO in MeCN to generate (3) in quantitative yields and that (3) reacts similarly to produce $[Os_6(CO)_{18}(MeCN)_3]$ (6).

Passage of CO through a solution of (2), (3), or (6) in CH_2Cl_2 leads to the formation of the binary carbonyl $[Os_6(CO)_{21}]$.[5] The characterisation of this compound rests almost entirely on its mass spectrum which exhibits a molecular ion at $m/z = 1738$. Thermolysis of the phosphite derivatives forms the closed-up substituted clusters, $[Os_6(CO)_{18-n}\{P(OMe)_3\}_n]$. Thus quantitative yields of $[Os_6(CO)_{17}\{P(OMe)_3\}]$[6] are obtained on heating the appropriate precursor material in toluene (at 110 °C for 16 h) (Scheme 1).

These reactions are reversible and illustrate the intercon-version of $[Os_6(CO)_{18}]$ and $[Os_6(CO)_{21}]$ derived species. Thus, treatment of, for example, $[Os_6(CO)_{17}\{P(OMe)_3\}]$ in toluene with CO (50 atm, 100 °C, 10 h) gives good yields of $[Os_6(CO)_{20}\{P(OMe)_3\}]$ (eq.).[7]

The hexanuclear osmium rafts have a rich redox chemistry. Using polarographic and voltammetric methods we have examined fourteen compounds in the $[Os_6(CO)_{21-x}L_x]$ series. In general the compounds undergo two reversible one electron transfer steps as exemplified by $[Os_6(CO)_{20}\{P(OMe)_3\}]$ (eq.) (Figure 1). Reduction potential values are given in Table 1. As the number of ligands L increases then the reduction potentials are shifted to more negative values. This is taken to indicate an increase in energy of the LUMO caused by the inductive effects of the donor ligands.

Our observation that these compounds can be reduced to the corresponding dianions provides experimental confirma-tion of Mingos' theoretical calculations which predicted the existance of such a low-lying unfilled molecular orbital in the hexanuclear raft systems.[8]

The nature of the initial coupling reaction is unclear. It is known that carbonyl substitution reactions of cluster com-pounds may be catalysed by a variety of species including $PdCl_2$. It is tempting to suggest that in this case $PdCl_2$ induces ligand dissociation to generate an active, ligand deficient Os_3 cluster unit, which interacts with the original Os_3 material to produce one Os_6 derivative. However, the correct interpreta-tion of this reaction must await further studies.

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