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Preliminary Communication

Reaction of $[(\mu\text{-H})Os_3(CO)_{11}]^-$ anion with dioxygen

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Abstract

The anion $[(\mu\text{-H})Os_3(CO)_{11}]^-$ reacts with dioxygen in solution to give a yellow species which further reacts with $Os_6(CO)_{18}$ to yield $[(\mu\text{-H})Os_3(CO)_{10}\cdot(\mu_2\text{-}O_2C)\cdot Os_6(CO)_{17}]^-$. The structure of the oxygen intermediate is proposed, and a mechanism of the reaction suggested.

The reaction of the anion $[(\mu\text{-H})Os_3(CO)_{11}]^-$ with $Os_6(CO)_{18}$ was carried out by workers in our group in an attempt to increase the cluster nuclearity systematically; the anion $[(\mu\text{-H})Os_3(CO)_{10}\cdot(\mu_2\text{-}O_2C)\cdot Os_6(CO)_{17}]^-$, containing discrete Os_6 and Os_3 units linked by a carboxylate bridge, was obtained [1–3] rather than the expected *closo*-Os_9 cluster. The reaction was repeated using, $Os_5(CO)_{16}$, $Os_7(CO)_{21}$ and $Ru_6C(CO)_{17}$ [4], and the similarly linked clusters, $[(\mu\text{-H})Os_3(CO)_{10}\cdot(\mu_2\text{-}O_2C)\cdot Os_5(CO)_{15}]^-$, $[(\mu\text{-H})Os_3(CO)_{10}\cdot(\mu_2\text{-}O_2C)\cdot Os_7(CO)_{20}]^-$ and $[(\mu\text{-H})Os_3(CO)_{10}\cdot(\mu_2\text{-}O_2C)\cdot Ru_6C(CO)_{16}]^-$, were obtained. More recently the related raft cluster, $[(\mu\text{-H})Os_3(CO)_{10}\cdot(\mu_2\text{-}O_2C)\cdot Os_6(CO)_{20}]^-$, was obtained from the reaction of $[(\mu\text{-H})Os_3(CO)_{11}]^-$ with two equivalents of $Os_3(CO)_{10}(NCMe)_2$ [5]. The bonding characteristic in all these complexes involves the formation of a "carboxylate bridge" between the two cluster units by addition of an $HOs_3(CO)_{10}$ fragment to carbonyl ligand of the higher nuclearity cluster, as illustrated in Fig. 1.

Herein we report the investigation of the mechanism of formation of these carboxylate-linked clusters. Study of the conditions of the reaction of $[(\mu\text{-H})Os_3(CO)_{11}]^-$ with $Os_6(CO)_{18}$ indicated that dioxygen was required for the formation of these carboxylate-linked species. In the absence of dioxygen, $[(\mu\text{-H})Os_3(CO)_{11}]^-$ acts as a one-electron reducing agent and reduces $Os_6(CO)_{18}$ to $[Os_6(CO)_{18}]^{2-}$. The CV of $[(Ph_3P)_2N][(\mu\text{-H})Os_3(CO)_{11}]$ in CH_2Cl_2 at 25°C showed two irreversible oxidations, at +0.23 V and +1.08 V *versus* Ag/AgCl; there were no observable reductions. The CV of $Os_6(CO)_{18}$ in CH_2Cl_2 at 25°C showed a quasi-reversible reduction at +0.14 V [6] *versus* Ag/AgCl. This suggests that the reduction of $Os_6(CO)_{18}$ by $[(\mu\text{-H})Os_3(CO)_{11}]^-$ is thermodynamically favourable. Analogous results were observed with $Os_5(CO)_{16}$, $Os_7(CO)_{21}$ and $Ru_6C(CO)_{17}$, the compounds being reduced to $[Os_5(CO)_{15}]^{2-}$, $[Os_7(CO)_{20}]^{2-}$ and $[Ru_6C(CO)_{16}]^{2-}$, respectively. The formation of $[(\mu\text{-H})Os_3(CO)_{10}\cdot(\mu_2\text{-}O_2C)\cdot Os_6(CO)_{17}]^-$ was found to arise from the product of the interaction of $[(\mu\text{-H})Os_3(CO)_{11}]^-$ with dioxygen in dichloromethane, acetone, chloroform or acetonitrile, at 25°C. This yielded a reactive species which could then interact with $Os_6(CO)_{18}$. Under the above conditions, the lifetime of this species in the presence of an excess of dioxygen was found to be < 5 min.

In order to elucidate the structure of the intermediate a series of spectroscopic studies of the reaction solution of oxygen and $[(\mu\text{-H})Os_3(CO)_{11}]^-$ was undertaken; the ESR spectrum showed no resonances were observable in the solution at 25 or −78°C, indicating the absence of any free radical species. The NMR spectrum of the solution showed the loss of a resonance at −13.64(s) (associated with the bridging hydride of $[(\mu\text{-}H)Os_3(CO)_{11}]^-$) and the simultaneous growth of a resonance at −17.30(s) associated with the bridging hydride of $[(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}CO_3)]^-$ which is absent in the carboxylate complexes). This signal then disappeared and new resonances at −10.96(s)

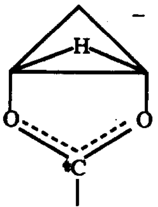

Fig. 1. The carboxylate-linked cluster $[(\mu\text{-H})Os_3(CO)_{10}\cdot(\mu_2\text{-}O_2C)\cdot Os_6(CO)_{17}]^-$.

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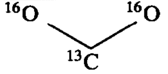
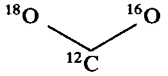
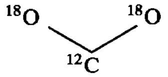
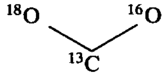
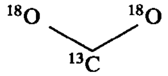
TABLE 1

	$Os_6(CO)_{18}$	$[(\mu\text{-H})Os_3(CO)_{11}]^-$	O_2	Carboxylate frequency (cm^{-1})
a	normal	normal	$^{16}O_2$	1268
b	^{13}C (*ca.* 50%)	normal	$^{16}O_2$	1268, 1244
c	normal	^{13}C (*ca.* 50%)	$^{16}O_2$	1268
d	normal	normal	$^{18}O_2$	1261, 1250
e	^{13}C (*ca.* 50%)	normal	$^{18}O_2$	1268, 1251, 1225

TABLE 2

Carboxylate bridge	Calculated frequency relative to 1268 cm^{-1}
	1240 cm^{-1}
	1252 cm^{-1}
	1238 cm^{-1}
	1224 cm^{-1}
	1210 cm^{-1}

and −14.52(s) ppm, of unequal intensity grew. The IR spectrum of $[(\mu\text{-H})Os_3(CO)_{11}]^-$ on exposure to oxygen showed a growth of an absorption at 891 cm^{-1} (not present in $[(\mu\text{-H})Os_3(CO)_{11}]^-$), which was indicative of an oxygen-oxygen single bond stretch; on standing, this absorption disappeared.

We previously used ^{13}C isotopic labelling to establish the nature of the carboxylate bridging group in the infrared spectra of the complexes. We have now extended this approach by use of ^{18}O labelled (*ca.* 99%) dioxygen gas. Table 1 summarises the results. The infra-red spectra of compounds (a), (b) and (c) establish that the carbon atom in the carboxylate bridge arises from the higher nuclearity cluster, whilst for (d) and (e) one oxygen atom in the bridge originates from dioxygen. The calculated values for the shifts in the frequencies of the various isotopic substitions are given in Table 2 [7]. Isotopic labelling was also used to allow monitoring of the isotopic composition of the gaseous products liberated in the reaction by infrared spectroscopy. Table 3 summarizes the results. Absorptions observed at 2360 and 2340 cm^{-1} correspond to $^{16}O{=}^{12}C{=}^{16}O$; those at 2330 and 2312 cm^{-1} correspond to $^{18}O{=}^{12}C{=}^{16}O$ (calculated at 2330 and 2311 cm^{-1});[7] $^{18}O{=}^{12}C{=}^{18}O$ was not observed (calculated at 2300 and 2283 cm^{-1}).[7] No $^{18}O{=}^{13}C{=}^{16}O$ (calculated as 2198 cm^{-1} and 2179 cm^{-1})[7] or $^{18}O{=}^{13}C{=}^{18}O$ bands (calculated as 2143 cm^{-1} and 2125 cm^{-1})[7] were observed. No carbon monoxide was observed. These results indicate that the carbon atom of the evolved carbon dioxide molecule originates from a carbonyl ligand of $[(\mu\text{-H})Os_3(CO)_{11}]^-$. The absorption attributed to the bridging carbonyl ligand in $[(\mu\text{-H})Os_3(CO)_{11}]^-$ disappeared on the reaction with dioxygen.

Dioxygen is also required to form the carboxylate bridge; one oxygen atom of the dioxygen molecule is incorporated into the bridge, and the other into the carbon dioxide evolved. Thus the carbon atom of the bridge originates from the $Os_6(CO)_{18}$ molecule whilst the carbon atom of the bridging carbonyl ligand in $[(\mu\text{-H})Os_3(CO)_{11}]^-$ is incorporated into the evolved carbon dioxide molecule.

The reactive species produced from the reaction of $[(\mu\text{-H})Os_3(CO)_{11}]^-$ with O_2 was treated with some other electrophiles, in an attempt to confirm its nature and its mode of reaction compared with that of $[(\mu\text{-H})Os_3(CO)_{11}]^-$. These reactions are summarized in Table 4, and reveal the change in the behaviour of $[(\mu\text{-H})Os_3(CO)_{11}]^-$ in the presence of oxygen.

TABLE 3

	$Os_6(CO)_{18}$	$[(\mu\text{-H})Os_3(CO)_{11}]^-$	O_2	Observed frequency of evolved CO_2 (cm^{-1})
a	normal	normal	$^{16}O_2$	2360, 2340
b	^{13}C (*ca.* 50%)	normal	$^{16}O_2$	2360, 2340
c	normal	normal	$^{18}O_2$	2360, 2340 and 2330, 2311
d	^{13}C (*ca.* 50%)	normal	$^{18}O_2$	2360, 2340 and 2330, 2311

TABLE 4

Reactant	Product from $[(\mu\text{-H})Os_3(CO)_{11}]^-$	Product from $[(\mu\text{-H})Os_3(CO)_{11}]^-/O_2$
HBF_4	$H_2Os_3(CO)_{11}$ [8]	$(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OH})$ [9]
CH_3CO^+	no apparent reaction	$(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}O_2CMe)$ [9]
Me_3O^+	$(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-COMe})$ [10]	$(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OMe})$ [9]

The above evidence for the production of the carboxylate-linked species may be interpreted mechanistically in terms as the interaction of $[(\mu\text{-H})Os_3(CO)_{11}]^-$ and O_2 to give a peroxyformyl anion, which reacts with the higher nuclearity carbonyl complex, the structure of which is shown in Fig. 2.

The peroxyformyl anion intermediate proposed accounts for the reactivity, isotopic distribution and the spectrocopic data observed; the hydride is observed at −17.30(s) ppm in the ^1H NMR spectrum, and the infrared absorption at 891 cm^{-1} is indicative of the stretching frequency of the oxygen–oxygen single bond [11].

In the absence of a suitable electrophile, the intermediate reacts further to produce species which do not react to give the carboxylate species with the clusters. The more abundant of these products (yield 35%) has been studied spectroscopically, and the structure is tentatively proposed in Fig. 3. The infrared spectrum in the carbonyl region shows the following absorptions; 2090 (w), 2050 (m), 2042 (m), 2001 (s) and 1976 (m). This carbonyl pattern is characteristic of the $Os_3(CO)_{10}$-type structure, *e.g.* $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-OH})$. The ^1H NMR spectrum shows a resonance at −10.966 ppm, assigned as a hydride bridging between two metal atoms. FAB mass spectoscopy shows a molecular ion peak at 1738.6 (M^+) (assimilated at 1735.2). The Raman spectrum shows a band at 1015 cm^{-1}, suggested to be from oxygen–oxygen single bond.

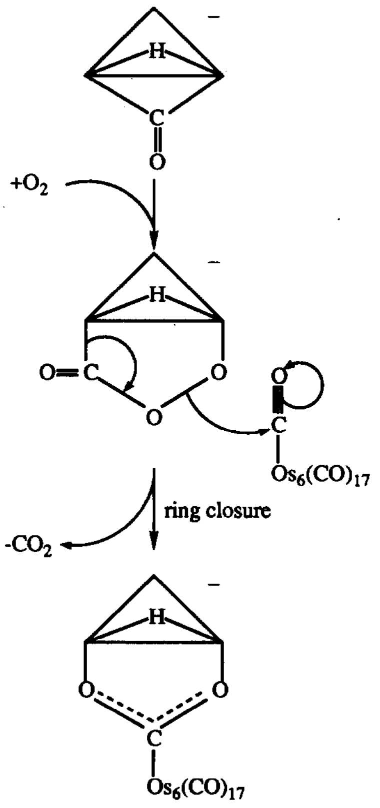


Fig. 2. Proposed mechanism for the formation of $[(\mu\text{-H})Os_3(CO)_{10}\cdot(\mu_2\text{-}O_2C)\cdot Os_6(CO)_{17}]^-$.

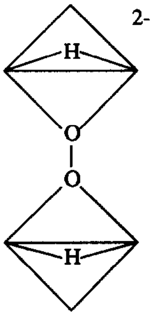


Fig. 3. Proposed final product of the reaction of the intermediate $[(\mu\text{-H})Os_3(CO)_{10}\cdot(\mu_2\text{-}O_3C)]^-$ in the absence of a suitable electrophile

We are attempting to obtain suitable crystals for an X-ray diffraction study.

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