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Preliminary communication

THE SYNTHESIS OF CLUSTERS CONTAINING A μ_2-CO_2 LINKAGE

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Summary

The cluster anions $[HOs_3(CO)_{10}(\mu_2\text{-}CO_2)Os_5(CO)_{15}]^-$, $[HOs_3(CO)_{10}(\mu_2\text{-}CO_2)Os_7(CO)_{20}]^-$ and $[HOs_3(CO)_{10}(\mu_2\text{-}CO_2)Ru_6C(CO)_{16}]^-$ have been prepared from the reaction of the $[HOs_3(CO)_{11}]^-$ anion with the carbonyl clusters $Os_5(CO)_{16}$, $Os_7(CO)_{21}$ and $Ru_6C(CO)_{17}$, respectively.

In a previous communication [1] the preparation and full characterisation of the anionic nonaosmium carbonyl anion $[HOs_3(CO)_{10}(\mu_2\text{-}CO_2)Os_6(CO)_{17}]^-$ were reported. The presence of a μ_2-CO_2 linkage was confirmed by a full single crystal analysis of the $[Me_4N]^+$ salt. Here we report that the reaction of the $[HOs_3(CO)_{11}]^-$ anion with neutral carbonyls of the type $Os_5(CO)_{16}$, $Os_7(CO)_{21}$ and $Ru_6(CO)_{17}C$ provides a general route to μ_2-CO_2 species.

Treatment of $Os_5(CO)_{16}$ with $[HOs_3(CO)_{11}]^-$ in CH_2Cl_2 at room temperature leads to the formation of the octaosmium anion $[HOs_3(CO)_{10}(\mu_2\text{-}CO_2)Os_5(CO)_{15}]^-$ which may be separated and characterised as its $[(Ph_3P)_2N]^+$ or $[Me_4N]^+$ salt. The anionic species $[HOs_3(CO)_{10}(\mu_2\text{-}CO_2)Os_7(CO)_{20}]^-$ and $[HOs_3(CO)_{10}(\mu_2\text{-}CO_2)Ru_6C(CO)_{16}]^-$ have been prepared similarly from the corresponding reaction of $[HOs_3(CO)_{11}]^-$ with $Os_7(CO)_{21}$ and $Ru_6(CO)_{17}C$, respectively. The mechanism by which these reactions occur is not understood [1]. However, we have established that oxygen is necessary and the reactions may therefore be represented as:

$$Os_5(CO)_{16} + [HOs_3(CO)_{11}]^- \xrightarrow{\frac{1}{2}O_2} [HOs_3(CO)_{10}(\mu_2\text{-}CO_2)Os_5(CO)_{15}]^-$$

$$Os_7(CO)_{21} + [HOs_3(CO)_{11}]^- \xrightarrow{\frac{1}{2}O_2} [HOs_3(CO)_{10}(\mu_2\text{-}CO_2)Os_7(CO)_{20}]^-$$

$$Ru_6(CO)_{17}C + [HOs_3(CO)_{11}]^- \xrightarrow{\frac{1}{2}O_2} [HOs_3(CO)_{10}(\mu_2\text{-}CO_2)Ru_6(CO)_{16}C]^-$$

The highly coloured salts were characterised on the basis of their microanalytical data and on their infrared spectra which are recorded in Table 1. All exhibit a broad absorption at ca. 1260 cm^{-1} which is characteristic of the

μ_2-CO_2 ligand [1]. In their ^1H NMR spectra a highfield singlet in the region of τ 20—23 ppm was observed in all cases.

As with $Os_6(CO)_{18}$, both $Os_5(CO)_{16}$ and $Os_7(CO)_{21}$ contain three different types of Os atom. In $Os_5(CO)_{16}$ these correspond to $Os(CO)_3$ apical, $Os(CO)_3$ equatorial and $Os(CO)_4$ equatorial; and in $Os_7(CO)_{21}$ to the capping $Os(CO)_3$ unit and to the two different $Os(CO)_3$ moieties within the trigonal antiprism of the remaining six osmium atoms. It is not possible on the information at present available to decide upon the point of attack of the $[HOs_3(CO)_{11}]^-$ but in Fig. 1 and 2 we show one possibility.

In an attempt to extend this reaction further the reactions of $[HOs_3(CO)_{11}]^-$ with the neutral hydrido clusters $H_2Os_5(CO)_{15}$ and $H_2Os_6(CO)_{18}$ were investigated. The products were found to be the monoanionic species $[HOs_5(CO)_{15}]^-$ and $[HOs_6(CO)_{18}]^-$ and not the anticipated μ_2-CO_2 derivatives. The other product in each reaction was $HOs_3(CO)_{10}(OH)$. These reactions

TABLE 1

COLOUR, IR AND ^1H NMR SPECTRA, AND ANALYTICAL DATA FOR THE PRODUCTS CONTAINING CO_2 LINKED CLUSTER UNITS

$[HOs_3(CO)_{10}CO_2Os_6(CO)_{17}]^-$ brown-black	$\nu(CO)$ (CH_2Cl_2) 2111vw, 2082mw, 2074m, 2062mw, 2047m, 2028ms, 2013s, 1971vw, 1961vw cm^{-1}
	$\nu(C—O)$ (CH_2Cl_2) 1270 cm^{-1} (br)
	^1H $(CD_2Cl_2$, 40°C) τ 20.24 ppm
$[HOs_3(CO)_{10}CO_2Os_5(CO)_{15}]^-$ orange-brown	$\nu(CO)$ (CH_2Cl_2) 2107vw, 2069ms, 2058ms, 2036s, 2011vs (br), 1965w cm^{-1}
	$\nu(C—O)$ (CH_2Cl_2) 1260 cm^{-1} (br)
	^1H $(CD_2Cl_2$, 35°C) τ 22.52 ppm
	Found: C, 26.8; H, 1.7; N, 0.47%
	Calcd.: C, 26.5; H, 1.1; N, 0.49%
$[HOs_3(CO)_{10}CO_2Os_7(CO)_{20}]^-$ dark red-brown	$\nu(CO)$ (CH_2Cl_2) 2108vw, 2070ms, 2058ms, 2037vs, 2012.5(br), 1970w cm^{-1}
	^1H $(CD_2Cl_2$, 35°C) τ21.91 ppm
	Found: C, 24.2; H, 1.2; N, 0.33%
	Calcd.: C, 25.0; H, 0.9; N, 0.4%
$[HOs_3(CO)_{10}CO_2CRu_6(CO)_{16}]^-$ red	$\nu(CO)$ (CH_2Cl_2) 2107vw, 2077s, 2069m(sh), 2037m (sh), 2021s, 1973vw, 1970w(br) cm^{-1}.
	$\nu(C—O)$ (CH_2Cl_2) 1240 (br) cm^{-1}
	^1H $(CD_2Cl_2$, 40°C) τ 20.4 ppm
	Found: C, 31.0; H, 1.25; N, 0.8%
	Calcd.: C, 30.8; H, 1.45; N, 1.0%

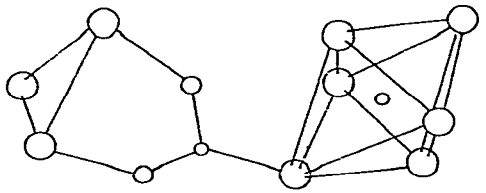

Fig.1. Possible structure of $[HOs_3(CO)_{10}(\mu_2$-$CO_2)Ru_6(CO)_{16}C]^-$.

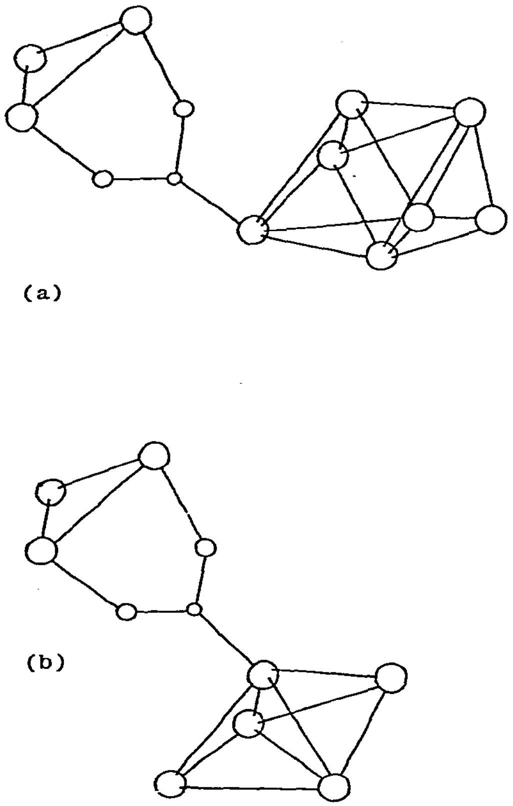

Fig.2. Possible structure of (a) $[HOs_3(CO)_{10}(\mu_2\text{-}CO_2)Os_7(CO)_{20}]^-$ and (b) $[HOs_3(CO)_{10}(\mu_2\text{-}CO_2)Os_5(CO)_{15}]^-$.

occur rapidly and go to completion in a matter of seconds under ambient conditions reflecting the strongly basic nature of the anion $[HOs_3(CO)_{11}]^-$ and the acidity of the dihydrido complexes. The formation of $HOs_3(CO)_{10}(OH)$ is difficult to understand. As reported previously [1] every attempt was made to exclude water from the reactions but the dihydride $H_2Os_3(CO)_{11}$ is known to react rapidly with H_2O to form $HOs_3(CO)_{10}(OH)$. In a related reaction $Os_5(CO)_{15}I_2$ was treated with $[HOs_3(CO)_{11}]^-$, in this case the reaction products were $HOs_3(CO)_{10}I$ and $[Os_5(CO)_{15}I]^-$:

$$H_2Os_5(CO)_{15} + [HOs_3(CO)_{11}]^- \rightarrow H_2Os_3(CO)_{11}(?) + [HOs_5(CO)_{15}]^-$$

$$H_2Os_6(CO)_{18} + [HOs_3(CO)_{11}]^- \rightarrow H_2Os_3(CO)_{11}(?) + [HOs_6(CO)_{18}]^-$$

$$H_2Os_3(CO)_{11} + H_2O \rightarrow HOs_3(CO)_{10}OH + H_2(?) + CO$$

$$Os_5(CO)_{15}I_2 + [HOs_3(CO)_{11}]^- \rightarrow HOs_3(CO)_{10}I + [Os_5(CO)_{15}I]^- + CO$$

It is of interest to compare these reactions with those more generally observed in the cluster carbonyl series. In general the reaction of anionic cluster carbonyls with neutral carbonyl clusters leads to cluster expansion. This has been clearly demonstrated by the work of Chini and his collaborators [2]. With the neutral binary carbonyls of osmium it would appear that the Os_m core ($m = 5$, 6 or 7) is effectively screened by the CO-sheath from attack by incoming substrate, in this case $[HOs_3(CO)_{11}]^-$. In this connection it is important to recall that attack by I^- on $Os_6(CO)_{18}$ leads not, as is commonly observed, to a iodometal derivative, but to $[Os_6(CO)_{18}]^{2-}$ [3]. Further work on this and other related reactions are currently in progress.

Acknowledgements

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