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Preliminary communication

THE REACTION OF BASE (OH^-) WITH BINARY OSMIUM CARBONYLS: CLUSTER FRAGMENTATION

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Summary

The compound $Os_5(CO)_{16}$ reacts with base (OH^-) to produce $[Os_5(CO)_{15}]^{2-}$. The compounds $Os_6(CO)_{18}$, $Os_7(CO)_{21}$ and $Os_8(CO)_{23}$ react with the same base to undergo cluster fragmentation to yield the dianions $[Os_5(CO)_{15}]^{2-}$, $[Os_6(CO)_{18}]^{2-}$ and $[Os_7(CO)_{20}]^{2-}$, respectively.

It is well established that reaction of binary carbonyl compounds with base (OH^-) leads to the formation of anionic species according to the general scheme:

$$M_m(CO)_n + OH^- \rightarrow [M_m(CO)_{n-1}(COOH)]^- \quad (1)$$

$$[M_m(CO)_{n-1}(COOH)]^- \rightarrow [M_m(CO)_{n-1}H]^- + CO_2 \quad (2)$$

$$[M_m(CO)_{n-1}H]^- + OH^- \rightarrow [M_m(CO)_{n-1}]^{2-} + H_2O \quad (3)$$

The overall reaction, which corresponds to the formation of a dianionic species and the loss of a carbon monoxide ligand as CO_2, applies equally well to both mono-metal and cluster carbonyl compounds, e.g.:

$$Fe(CO)_5 + 2OH^- \rightarrow [Fe(CO)_4]^{2-} + CO_2 + H_2O$$

$$Rh_6(CO)_{16} + 2OH^- \rightarrow [Rh_6(CO)_{15}]^{2-} + CO_2 + H_2O$$

We now report studies of the reaction of OH^- (KOH/MeOH) with the binary osmium clusters $Os_5(CO)_{16}$, $Os_6(CO)_{18}$, $Os_7(CO)_{21}$ and $Os_8(CO)_{23}$. Reaction of base (OH^-) with $Os_5(CO)_{16}$ follows the usual course to produce $[Os_5(CO)_{15}]^{2-}$:

$$Os_5(CO)_{16} + 2OH^- \rightarrow [Os_5(CO)_{15}]^{2-} + H_2O + CO_2$$

In contrast, reaction with the Os_6, Os_7 and Os_8 clusters leads to cluster fragmentation action:

$$Os_6(CO)_{18} \xrightarrow{OH^-} [Os_5(CO)_{15}]^{2-} \quad (4)$$

$$Os_7(CO)_{21} \xrightarrow{OH^-} [Os_6(CO)_{18}]^{2-} \qquad (5)$$

$$Os_8(CO)_{23} \xrightarrow{OH^-} [Os_7(CO)_{20}]^{2-} \qquad (6)$$

In each case the dianion was isolated as its $[(Ph_3P)_2N]^+$ salt and was fully characterised on the basis of analytical and spectroscopic data. Reaction of these dianions with acid (H^+) produces the dihydrido clusters $H_2Os_5(CO)_{15}$, $H_2Os_6(CO)_{18}$ and $H_2Os_7(CO)_{20}$. The species $[Os_5(CO)_{15}]^{2-}$, $[Os_6(CO)_{18}]^{2-}$, $H_2Os_5(CO)_{15}$ and $H_2Os_6(CO)_{18}$ have been reported previously [1]. The anion $[Os_7(CO)_{20}]^{2-}$ and corresponding dihydride $H_2Os_7(CO)_{20}$ are new. Interestingly, the novel hydrido-carbido species $H_2Os_7(CO)_{19}C$ has been obtained in very small yield from the reaction of $Os_3(CO)_{12}$ with water [2] at elevated temperatures.

The compound $Os_5(CO)_{16}$ with six skeletal electron pairs is, according to the Wade Theory, electron-precise and, as a consequence has a regular trigonal bipyramidal geometry. The other members of the series $Os_6(CO)_{18}$ ($S = 6$), $Os_7(CO)_{21}$ ($S = 7$), and $Os_8(CO)_{23}$ ($S = 7$) are electron-deficient and, as a consequence, have capped-polyhedral geometries (Table 1). From the information at present available it would appear that the electron-precise $Os_5(CO)_{16}$ ($S = 6$) undergoes reaction to produce $[Os_5(CO)_{15}]^{2-}$ ($S = 6$) which is also electron-precise. In contrast, the electron-deficient compounds $Os_6(CO)_{18}$, $Os_7(CO)_{21}$ and $Os_8(CO)_{23}$ undergo reaction to remove a capping group $Os(CO)_3$ and generate an electron-precise species, $[Os_5(CO)_{15}]^{2-}$ ($S = 6$) or $[Os_6(CO)_{18}]^{2-}$ ($S = 7$), or a "less electron-deficient" species $[Os_7(CO)_{20}]^{2-}$ ($S = 7$).

The generality of this approach has yet to be justified. At present osmium is unique in giving a series of binary carbonyls $Os_m(CO)_n$ ranging from $m = 1$ to $m = 8$, and spanning electron-rich systems e.g. $Os_3(CO)_{12}$ ($S = 6$), to electron-deficient systems, e.g. $Os_8(CO)_{23}$ ($S = 7$).

TABLE 1

THE STRUCTURES OF THE BINARY CARBONYLS OF OSMIUM AS A FUNCTION OF SKELETAL ELECTRON PAIRS

Carbonyl	S (= Number of skeletal pairs)	Structure	
		Predicted	Found[a]
$Os_5(CO)_{16}$	6	Trigonal bipyramid	Trigonal bipyramid
$Os_6(CO)_{18}$	7	Capped trigonal bipyramid	Capped trigonal bipyramid
$Os_7(CO)_{21}$	7	Capped octahedron	Capped octahedron
$Os_8(CO)_{23}$	7	Bicapped octahedron	?
$[Os_5(CO)_{15}]^{2-}$	6	Trigonal bipyramid	?
$[Os_6(CO)_{18}]^{2-}$	7	Octahedron	Octahedron
$[Os_7(CO)_{20}]^{2-}$	7	Capped octahedron	?

[a] By X-ray analysis.

Thus, these reactions may be summarised as:

$$\mathrm{Os}_m(\mathrm{CO})_n \xrightarrow{\mathrm{OH}^-} [\mathrm{Os}_{m\text{-}1}(\mathrm{CO})_{n\text{-}3}]^{2-} + \text{“}\mathrm{Os(CO)_3}\text{”}$$

$m = 6 \quad n = 18$
$m = 7 \quad n = 21$
$m = 8 \quad n = 23$

No other osmium-containing product has been isolated from these reactions to date, and further work is in progress.

It is noteworthy that other electron-precise clusters, e.g. $Rh_6(CO)_{16}$ and $Ru_6C(CO)_{17}$ ($S = 7$), undergo reaction to produce the electron-precise dianions $[Rh_6(CO)_{15}]^{2-}$ and $[Ru_6C(CO)_{16}]^{2-}$, in contrast to the behaviour shown by the electron-deficient $Os_6(CO)_{18}$,

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