

Preliminary communication

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

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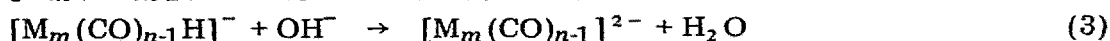
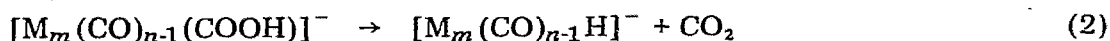
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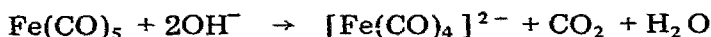
Summary

The compound $\text{Os}_5(\text{CO})_{16}$ reacts with base (OH^-) to produce $[\text{Os}_5(\text{CO})_{15}]^{2-}$. The compounds $\text{Os}_6(\text{CO})_{18}$, $\text{Os}_7(\text{CO})_{21}$ and $\text{Os}_8(\text{CO})_{23}$ react with the same base to undergo cluster fragmentation to yield the dianions $[\text{Os}_5(\text{CO})_{15}]^{2-}$, $[\text{Os}_6(\text{CO})_{18}]^{2-}$ and $[\text{Os}_7(\text{CO})_{20}]^{2-}$, 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:



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.:



We now report studies of the reaction of OH^- (KOH/MeOH) with the binary osmium clusters $\text{Os}_5(\text{CO})_{16}$, $\text{Os}_6(\text{CO})_{18}$, $\text{Os}_7(\text{CO})_{21}$ and $\text{Os}_8(\text{CO})_{23}$. Reaction of base (OH^-) with $\text{Os}_5(\text{CO})_{16}$ follows the usual course to produce $[\text{Os}_5(\text{CO})_{15}]^{2-}$:



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





In each case the dianion was isolated as its $[(\text{Ph}_3\text{P})_2\text{N}]^+$ salt and was fully characterised on the basis of analytical and spectroscopic data. Reaction of these dianions with acid (H^+) produces the dihydrido clusters $\text{H}_2\text{Os}_5(\text{CO})_{15}$, $\text{H}_2\text{Os}_6(\text{CO})_{18}$ and $\text{H}_2\text{Os}_7(\text{CO})_{20}$. The species $[\text{Os}_5(\text{CO})_{15}]^{2-}$, $[\text{Os}_6(\text{CO})_{18}]^{2-}$, $\text{H}_2\text{Os}_5(\text{CO})_{15}$ and $\text{H}_2\text{Os}_6(\text{CO})_{18}$ have been reported previously [1]. The anion $[\text{Os}_7(\text{CO})_{20}]^{2-}$ and corresponding dihydride $\text{H}_2\text{Os}_7(\text{CO})_{20}$ are new. Interestingly, the novel hydrido-carbido species $\text{H}_2\text{Os}_7(\text{CO})_{19}\text{C}$ has been obtained in very small yield from the reaction of $\text{Os}_3(\text{CO})_{12}$ with water [2] at elevated temperatures.

The compound $\text{Os}_5(\text{CO})_{16}$ 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 $\text{Os}_6(\text{CO})_{18}$ ($S = 6$), $\text{Os}_7(\text{CO})_{21}$ ($S = 7$), and $\text{Os}_8(\text{CO})_{23}$ ($S = 7$) 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 $\text{Os}_5(\text{CO})_{16}$ ($S = 6$) undergoes reaction to produce $[\text{Os}_5(\text{CO})_{15}]^{2-}$ ($S = 6$) which is also electron-precise. In contrast, the electron-deficient compounds $\text{Os}_6(\text{CO})_{18}$, $\text{Os}_7(\text{CO})_{21}$ and $\text{Os}_8(\text{CO})_{23}$ undergo reaction to remove a capping group $\text{Os}(\text{CO})_3$ and generate an electron-precise species, $[\text{Os}_5(\text{CO})_{15}]^{2-}$ ($S = 6$) or $[\text{Os}_6(\text{CO})_{18}]^{2-}$ ($S = 7$), or a "less electron-deficient" species $[\text{Os}_7(\text{CO})_{20}]^{2-}$ ($S = 7$).

The generality of this approach has yet to be justified. At present osmium is unique in giving a series of binary carbonyls $\text{Os}_m(\text{CO})_n$ ranging from $m = 1$ to $m = 8$, and spanning electron-rich systems e.g. $\text{Os}_3(\text{CO})_{12}$ ($S = 6$), to electron-deficient systems, e.g. $\text{Os}_8(\text{CO})_{23}$ ($S = 7$).

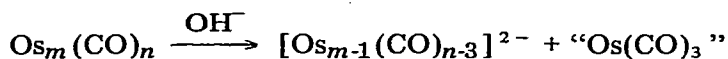
TABLE 1

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
$\text{Os}_5(\text{CO})_{16}$	6	Trigonal bipyramid	Trigonal bipyramid
$\text{Os}_6(\text{CO})_{18}$	7	Capped trigonal bipyramid	Capped trigonal bipyramid
$\text{Os}_7(\text{CO})_{21}$	7	Capped octahedron	Capped octahedron
$\text{Os}_8(\text{CO})_{23}$	7	Bicapped octahedron	?
$[\text{Os}_5(\text{CO})_{15}]^{2-}$	6	Trigonal bipyramid	?
$[\text{Os}_6(\text{CO})_{18}]^{2-}$	7	Octahedron	Octahedron
$[\text{Os}_7(\text{CO})_{20}]^{2-}$	7	Capped octahedron	?

^aBy X-ray analysis.

Thus, these reactions may be summarised as:



$$m = 6 \quad n = 18$$

$$m = 7 \quad n = 21$$

$$m = 8 \quad n = 23$$

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. $\text{Rh}_6(\text{CO})_{16}$ and $\text{Ru}_6\text{C}(\text{CO})_{17}$ ($S = 7$), undergo reaction to produce the electron-precise dianions $[\text{Rh}_6(\text{CO})_{15}]^{2-}$ and $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$, in contrast to the behaviour shown by the electron-deficient $\text{Os}_6(\text{CO})_{18}$,

Acknowledgements

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References

- 1(a) C.R. Eady, B.F.G. Johnson and J. Lewis, *Chem. Commun.*, (1976) 302;
- (b) C.R. Eady, J.J. Guy, B.F.G. Johnson, J. Lewis, M.C. Malaterta and G.M. Sheldrick, *Chem. Commun.*, (1976) 807.
- 2 C.R. Eady, B.F.G. Johnson and J. Lewis, *J. Chem. Soc. Dalton*, (1977) 838.