

Preliminary communication

THE REDUCTION OF OSMIUM CARBONYL CLUSTERS BY NITRILES

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Summary

The clusters $\text{Os}_6(\text{CO})_{18}$, $\text{Os}_7(\text{CO})_{21}$ and $\text{Os}_8(\text{CO})_{23}$ are reduced to the anions $[\text{Os}_6(\text{CO})_{18}]^{2-}$, $[\text{Os}_7(\text{CO})_{20}]^{2-}$ and $[\text{Os}_8(\text{CO})_{22}]^{2-}$, respectively, by the action of nitriles RCN ($\text{R} = \text{Me, Et, CH}_2\text{C}(\text{Me})$); the kinetics of the reaction of $\text{Os}_6(\text{CO})_{18}$ with EtCN have been examined and reveal a third order dependence on nitrile concentration.

We have previously reported [1,2] that the cluster $\text{Os}_6(\text{CO})_{18}$ can be reduced to $[\text{Os}_6(\text{CO})_{18}]^{2-}$ under mild conditions by treatment with activated zinc or iodide ion, or electrochemically.

We now report that certain nitriles RCN ($\text{R} = \text{Me, Et, CH}_2\text{C}(\text{Me})$) effect the reduction of not only $\text{Os}_6(\text{CO})_{18}$ to $[\text{Os}_6(\text{CO})_{18}]^{2-}$, but also other high nuclearity osmium carbonyl clusters to their respective anions, as indicated in equations 1–3.

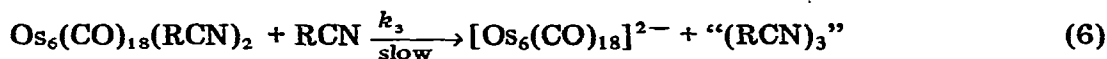
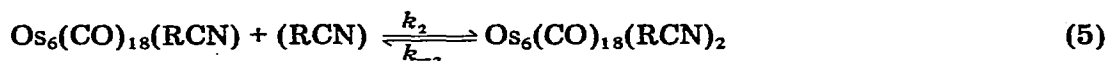


The rate depends on the nature of R ; reaction with EtCN usually being complete within a matter of minutes, but that with MeCN requiring several hours. Reduction can also be effected with $\text{CH}_2=\text{C}(\text{Me})\text{CN}$, but no reaction is observed with Cl_3CCN , no doubt reflecting the much weaker N -donor capacity of the latter substrate. From low temperature and mixed solvent experiments on both $\text{Os}_6(\text{CO})_{18}$ and $\text{Os}_7(\text{CO})_{21}$ with RCN ($\text{R} = \text{Me, Et}$), two intermediate species can be observed in the infrared carbonyl stretching region prior to the formation of $[\text{Os}_6(\text{CO})_{18}]^{2-}$ and $[\text{Os}_7(\text{CO})_{20}]^{2-}$, respectively. Attempts to isolate these intermediates lead only to the recovery of the original neutral clusters, suggesting the stepwise addition of nitrile to the cluster unit.

Kinetic analysis of the reduction of $\text{Os}_6(\text{CO})_{18}$ by EtCN gives an insight into

the course of reaction. Using an excess of EtCN, the reaction proceeds to completion in dichloromethane and may be conveniently followed by the slow (i.e. over a few hours) disappearance of the original neutral carbonyl bands at 2075vs, 2061vs, 2037s, 2029m(sh), 1999w and 1958w cm^{-1} , and growth of final product bands at 1992vs and 1915w cm^{-1} . Good linear pseudo-first order plots were obtained for 60–70% of reaction. Significantly, bands corresponding to the intermediate species were clearly discernible throughout the reaction, indicating a series of genuine equilibria.

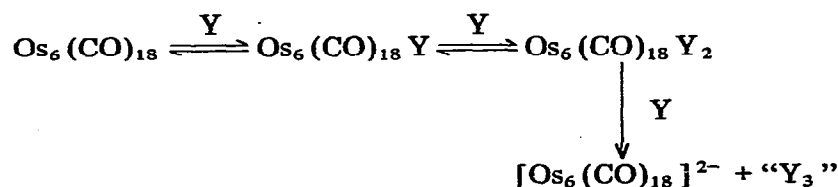
The rate of attack of EtCN on $\text{Os}_6(\text{CO})_{18}$ was found to vary with $[\text{EtCN}]$ [3] for nitrile concentrations up to 2.5 M. This may be rationalised in terms of a series of equilibria as shown in equations 4–6, for which both stationary state and pre-equilibria approaches lead to the rate expression (eq. 7); the experi-



$$\text{Rate} = K_1 K_2 k_3 [\text{Os}_6(\text{CO})_{18}] [\text{RCN}]^3 \quad (7)$$

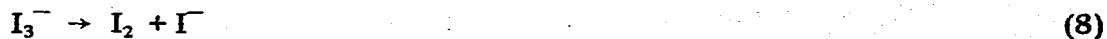
experimental dependence on $[\text{RCN}]^3$ satisfies such a mechanism. Such intermediate adduct formation is supported by the infrared spectroscopic data already mentioned.

The reduction of $\text{Os}_6(\text{CO})_{18}$ by I^- [2] is now considered to involve a similar mechanism, the observation of a second-order dependence on iodide concentration merely reflecting the difference in kinetic parameters between the two systems. Thus a general scheme for the reduction of $\text{Os}_6(\text{CO})_{18}$ is postulated as in Scheme 1.



SCHEME 1

The precise nature of “ Y_3 ” in the nitrile case is as yet uncertain, although ^1H NMR studies suggest a complex organic cationic species. The observation of iodine in the reaction of $\text{Os}_6(\text{CO})_{18}$ with iodide is thus explained as resulting from the formation of I_3^- and the subsequent dissociation process (eq. 8). The



reduction process involves the transformation of the capped trigonal bipyramidal geometry of $\text{Os}_6(\text{CO})_{18}$ into the regular octahedral arrangement of $[\text{Os}_6(\text{CO})_{18}]^{2-}$, which requires reorganisation of the metal framework. Similar arguments can be

applied to $\text{Os}_7(\text{CO})_{21}$ and $\text{Os}_8(\text{CO})_{23}$, both of which have "capping" $\text{M}(\text{CO})_3$ groups. Interestingly, the molecule $\text{Os}_5(\text{CO})_{15}$ does not undergo simple reduction with nitriles.

Finally, the anion $[\text{Os}_8(\text{CO})_{22}]^{2-}$ which has not been previously reported, can be acidified in situ to yield the new neutral hydrido species $\text{H}_2\text{Os}_8(\text{CO})_{22}$.

Acknowledgements

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References

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- 2 G.R. John, B.F.G. Johnson, J. Lewis and A.L. Mann, *J. Organometal. Chem.*, 171 (1979) C9.