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Preliminary communication

PREPARATION AND PYROLYSIS OF SOME ISONITRILE DERIVATIVES OF TRIOSMIUM DODECACARBONYL

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Summary

The reaction of $Os_3(CO)_{12}$ with isonitriles in refluxing heptane solution gives the substituted complexes $Os_3(CO)_{12-n}(CNR)_n$ (R = Me, n = 1—2; R = p-$MeOC_6H_4$, n = 1—3; R = t-Bu or Ph, n = 1—4), pyrolysis of these derivatives in refluxing octane leads to the formation of higher nuclearity clusters, and the complexes $Os_6(CO)_{18-n}(CNR)_n$ (R = Me or t-Bu, n = 1—5) have been isolated.

The pyrolysis of $Os_3(CO)_{12}$ at elevated temperatures (210—260°C) leads to the formation of polynuclear osmium carbonyl species based on 5—8 osmium atoms [1]. Although organophosphine substituted derivatives can be pyrolysed at lower temperatures (ca 140°C in refluxing xylene), no osmium clusters containing more than 3 osmium atoms are formed. Instead a complicated mixture of trinuclear products is obtained in which fragmentation of the substituent ligand has occurred [2].

We now report that the isonitrile substituted derivatives $Os_3(CO)_{11}$ (CN-t-Bu) and $Os_3(CO)_{10}(CN\text{-t-Bu})_2$ may be pyrolysed at even lower temperatures (ca. 125°C in refluxing octane solution) to give the hexanuclear complexes $Os_6(CO)_{18-n}(CNBu\text{-t})_n$ (n = 2—4) in good yield. There is no evidence for ligand fragmentation in these reactions and, after a 24 h reaction period, the hexanuclear complexes together with some starting material are the only osmium-containing products which are present in solution. Hexanuclear complexes may also be prepared by the direct reaction of $Os_3(CO)_{12}$ with MeNC or t-BuNC in refluxing octane and by this means all the complexes in the series $Os_6(CO)_{18-n}(CNR)_n$ (n = 1—5) can be obtained. Molecular ions have been observed in the mass spectra of all the products and satisfactory analytical data have been obtained. Solution infrared studies show only terminally bonded carbonyl and isonitrile groups are present and suggest that a mixture of isomers is formed. ^1H NMR spectra (CD_2Cl_2 solution) show only a single resonance at room temperature in each case.

The trinuclear complexes themselves are prepared by refluxing $Os_3(CO)_{12}$ with the appropriate isonitrile in heptane solution. By this means the complexes $Os_3(CO)_{12-n}(CNR)_n$ have been prepared (R = Me, n = 1—2; R = p-$MeOC_6H_4$, n = 1—3; R = t-Bu, Ph, n = 1—4). A feature of interest of these complexes is their ^{13}C NMR spectra (CD_2Cl_2 solution) which reveal that at —60°C axially as well as equatorially substituted isomers are present. Indeed the mono- and di-substituted derivatives containing less sterically hindered isonitrile ligands, such as p-$MeOC_6H_4NC$, exist in solution exclusively as the axial isomers, indicating that this is the electronically preferred position of substitution. In contrast, the reaction of $Os_3(CO)_{12}$ with organophosphine ligands, which are presumably more bulky, has invariably been reported to give exclusively equatorial substitution [3,4]. For those isonitrile derivatives which exist in solution as a mixture of isomers, isomer interchange is observed to take place on the NMR timescale at around room temperature, suggesting that the observed isomer distribution is the result of thermodynamic rather than kinetic control.

The above results indicate that for $Os_3(CO)_{12}$ the partial substitution of carbonyl by isonitrile ligands greatly facilitates the pyrolysis reaction which leads to the generation of higher nuclearity clusters. The possibility of preparing higher nuclearity clusters of other transition metals by this means is being explored.

References

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