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Preliminary communication

Products from the pyrolysis of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$

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Some time ago we reported the formation of $Ru_6C(CO)_{17}$ and $Ru_6C(CO)_{14}$(arene) from the reaction of $Ru_3(CO)_{12}$ with the appropriate arene under reflux[1]. Similar observations were made by others[2]. The presence of the isolated carbon atom was later confirmed by single crystal X-ray analysis of both $Ru_6C(CO)_{17}$[3] and $Ru_6C(CO)_{14}[(CH_3)_3C_6H_3]$[4] but the origin of this carbon remained uncertain. We now report that the carbide is also produced by the thermal decomposition of $Ru_3(CO)_{12}$ in a sealed tube and in the complete absence of solvent thereby confirming our initial assumption[1] that the carbon is produced by the reduction of a coordinated carbonyl group. In addition we report the formation of several new polynuclear osmium carbonyls by the pyrolysis of $Os_3(CO)_{12}$ using the same method.

Dodecacarbonyltriruthenium was heated at ~150° in a sealed tube for 12 h. The product $Ru_6C(CO)_{17}$ was separated from some residual $Ru_3(CO)_{12}$ by thin layer chromatography and identified on the basis of its mass spectrum and infrared data. Yields of the product are moderately low (5%) and this method offers no particular advantage over that employing n-butyl ether as solvent[5] although yields are improved by higher temperatures. We have also reexamined the reaction of $Ru_3(CO)_{12}$ with benzene under reflux and although we were not able to improve significantly on the yields of the carbide produced we did note that, contrary to our previous report[1], small amounts of $Ru_6C(CO)_{14}$ (benzene) are produced.

The formation of $Ru_6C(CO)_{17}$ by this direct method led us to examine the corresponding reaction of $Os_3(CO)_{12}$ since one of the problems encountered with this carbonyl has been the lack of a suitable solvent system. On heating $Os_3(CO)_{12}$ in a sealed tube at 195–200° for 12 h a dark brown reaction product was obtained. After extraction into ethyl acetate followed by separation by thin layer chromatography seven components were obtained. One was identified as $Os_3(CO)_{12}$, the others were found to be polynuclear materials based on four, five, six, seven and eight osmium atom units. All were identified by mass spectroscopic analysis and if the criteria previously established for polynuclear carbonyl systems are obeyed[6] they may be formulated as $Os_4(CO)_{13}$ (yellow), $Os_5(CO)_{16}$

(pink), $Os_6(CO)_{18}$ (brown), $Os_7(CO)_{21}$ (orange), $Os_8(CO)_{23}$ (yellow-orange) and $Os_5(CO)_{15}C_4$ (dark purple). Further characterisation of these products is difficult. All exhibit fairly simple infrared spectra in the terminal M–CO region and no bands assignable to bridging CO groups have been observed (Table 1). With the exception of $Os_4(CO)_{13}$ it is possible to assign a plausible structure to each of these carbonyls on the basis of the Effective Atomic Number rule without invoking multiple bonding between the metal atoms concerned. Apart from $Os_6(CO)_{18}$ to which we assign an octahedral structure with three terminal CO's per osmium, such an exercise is not particularly useful and we must await the results of single crystal X-ray analysis.

TABLE 1

INFRARED SPECTRA OF THE POLYNUCLEAR OSMIUM CARBONYL SPECIES (1700–2200 cm^{-1})

Compound	ν(CO) (cm^{-1})	Solvent
$Os_4(CO)_{13}$	2077s, 2064s, 2052s, 2018m(sh), 2014m, 1998w	n-heptane
$Os_5(CO)_{16}$	2063vs, 2056m(sh), 2047s, 2039s, 2010wb, 1992mb, 1964w	cyclohexane
$Os_6(CO)_{18}$ [a]	2101w, 2072s, 2059s, 2035s, 2028m, 2024m(sh), 2017w(sh), 1999w	cyclohexane
$Os_7(CO)_{21}$ [b]	2105, 2078, 2070, 2065, 2054, 2033, 2026, 1994	cyclohexane
$Os_8(CO)_{23}$ [b]		
$Os_5(CO)_{15}C_4$	2086m, 2073m(sh), 2067s, 2042vw, 2034vw, 2022w(b), 2016w(b), 2003w	cyclohexane

[a] There are also present several very weak bands in the region 1924–1993 cm^{-1} which possibly arise from ^{13}CO (natural abundance).

[b] These compounds have not been obtained spectroscopically pure; the spectrum is of a mixture of the two species.

In view of the ease with which $Ru_6C(CO)_{17}$ is produced it is perhaps surprising that no evidence for the formation of $Os_6C(CO)_{17}$ has been found. It is possible that the thermal decomposition of $Ru_3(CO)_{12}$ to the carbide goes via $Ru_6(CO)_{18}$. We are therefore examining the thermal decomposition of $Os_6(CO)_{18}$ in detail.

We feel that we should emphasise that an essential part of this work is the use of thin layer chromatography. As is often the case in this area only small amounts of material are available and separation cannot be satisfactorily achieved using column chromatography

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