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Preliminary communication

The preparation of $Ru_5C(CO)_{15}$ and $Os_5C(CO)_{15}$

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SUMMARY

The carbido carbonyl complexes $Ru_5C(CO)_{15}$ and $Os_5C(CO)_{15}$ have been prepared and characterised.

Following the initial report by Braye and coworkers[1] of the synthesis and structural characterisation of the first transition metal carbonyl carbide $Fe_5C(CO)_{15}$ came reports of the preparation and X-ray analysis of the anion[2] $Fe_6C(CO)_{16}^{2-}$ and the neutral $Ru_6C(CO)_{17}$ [3,4] and $Ru_6C(CO)_{14}$(arene)[3,5]. More recently the rhodium anion[6] $Rh_6C(CO)_{15}^{2-}$ has been identified by full X-ray analysis and an improved synthetic route to $Fe_5C(CO)_{15}$ has been given[7]. In the case of the neutral $Ru_6C(CO)_{17}$ evidence[8] has been presented to suggest that the source of the carbon atom is a carbonyl group whereas the carbon in the Rh_6C system apparently arises from $CHCl_3$ [6]. We now report the preparation and characterisation of the ruthenium and osmium analogues of $Fe_5C(CO)_{15}$.

Reaction of α-$H_4Ru_4(CO)_{12}$ with ethylene (10–12 atm) at 130°C for ~1 h yields a dark brown-orange-solution. After filtration and removal of solvent in vacuo a dark brown residue is obtained. Separation by column chromatography on silica using hexane as eluent gives at least eight products amongst which are $Ru_6C(CO)_{17}$ and $Ru_5C(CO)_{15}$. Yields of these materials are moderate and very low (30% and ~1%) respectively. Although no evidence has yet been obtained for the formation of the pentanuclear carbide from the direct pyrolysis of α-$H_4Ru_4(CO)_{12}$ it is likely that the ethylene plays no part in the formation of this derivative.

Pyrolysis of $Os_6(CO)_{18}$ [8] in an evacuated Carius tube at 255° gives a dark brown material. Extraction into ethyl acetate, followed by filtration through kieselguhr gives a yellow solution which after removal of the solvent yields $Os_5C(CO)_{15}$ as yellow crystals (yield ~40%). Alternatively the carbide may be obtained from the direct pyrolysis of $Os_3(CO)_{12}$ but in this case yields are low (~10%) and the reaction obviously proceeds via the intermediate formation of $Os_6(CO)_{18}$.

TABLE 1

INFRARED SPECTRA OF $M_5C(CO)_{15}$ COMPOUNDS (CYCLOHEXANE) (2200–1600 cm^{-1})

Compound	*ν(CO) (cm⁻¹)*				
$Fe_5C(CO)_{15}$[a]	2098w	2050s	2031s	2012m	1991m
$Ru_5C(CO)_{15}$	–	2066vs	2034s	2016m	*b*
$Os_5C(CO)_{15}$	–	2078vs	2038s	2019m	*b*

[a] Ref. 7. [b] A very weak absorption is observed in this region.

The infrared spectra of $Ru_5C(CO)_{15}$ and $Os_5C(CO)_{15}$ in the carbonyl stretching region (see Table 1) are related to that of $Fe_5C(CO)_{15}$ recorded by Graham and coworkers[7]. Under electron impact the parent ion $M_5C(CO)_{15}^+$ together with ions $M_5C(CO)_{15-n}^+$ ($n = 1-15$) corresponding to the stepwise loss of fifteen CO groups are observed. As was observed in the mass spectrum of $Fe_5C(CO)_{15}$ the most intense ion corresponds to the simple carbide M_5C^+ but unlike the iron complex fragmentation of this unit does not occur except for the formation of small amounts of Ru_4C^+. In keeping with the enhanced stability observed with clusters of the 2nd and 3rd row transition metals the doubly-charged ions $M_5C(CO)_{15}^{2+}$ and $M_5C(CO)_{15-n}{}^{2+}$ are observed in relatively high abundance.

The synthetic routes employed in this work, particularly in the case of the osmium system, would again indicate that the source of the carbido-carbon is from the reduction of a coordinated carbonyl group. Pyrolysis of higher osmium carbonyl compounds based on Os_7 and Os_8 units also yields carbido complexes and these will be reported in due course. The chemistry of the "carbon atom" in these and other carbide systems is currently under investigation.

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