Ruthenium Carbonyl Carbide Compounds

By B. F. G. JOHNSON, R. D. JOHNSTON, and J. LEWIS*
(*Department of Chemistry, The University, Manchester* 13)

HERE we report the preparation and characterisation of a new type of cluster compound, $Ru_6C(CO)_{17}$, and some of its derivatives, $Ru_6C(CO)_{14}$(arene), where arene = $CH_3{\cdot}C_6H_5$, $(CH_3)_2{\cdot}C_6H_4$, and $(CH_3)_3{\cdot}C_6H_3$. These compounds are unusual in that not only do they contain a cluster of six ruthenium atoms but also an *individual* carbon atom. With the exception of $Fe_5(CO)_{15}C$,[1] no other examples of this type of carbide compound are known. The nature of the carbon atom and its co-ordination number in these compounds are, as yet, unknown.[2]

The compounds were prepared by heating $Ru_3(CO)_{12}$ under reflux in the appropriate arene and the products, red $Ru_6C(CO)_{17}$ and purple $Ru_6C(CO)_{14}$(arene), separated by chromatography on a silica column. All are stable in air and soluble in non-polar solvents. In the infrared spectra in the CO stretching region a complex pattern of peaks is observed for $Ru_6C(CO)_{17}$, 2064s, 2049s, 2007w, 1993w, 1854w and it would appear that both terminal and bridging [or three-centre *cf.*, $Rh_6(CO)_{16}$[3]] CO groups may be present in these molecules. The presence of arene is confirmed by n.m.r. spectra which show signals due to ring protons and methyl protons only. Furthermore, the chemical shifts of these protons are upfield from those observed for free arene consistent with the view that the arene is acting as a six electron-donor in these systems [*e.g.*, for $Ru_6C(CO)_{14}$ (mesitylene) $\tau_H = 4{\cdot}70$; $\tau_{Me} = 7{\cdot}77$].

The most indicative evidence for the formulation of these compounds as Ru_6 carbides is provided by their mass spectra. With the parent carbonyl the molecular ion, $[Ru_6C(CO)_{17}]^+$ is observed together with ions corresponding to the stepwise loss of seventeen carbonyl groups, $[Ru_6C(CO)_{17-n}]^+$, (n = 1—17). The ion, $[Ru_6C]^+$, occurs in high abundance but no other singly-charged ions of lower m/e values are observed. (The mass of this ion has been confirmed by addition of calibrant during the running of the spectrum.) Doubly-charged ions, $[Ru_6C(CO)_{17-m}]^{2+}$ (m = 0—17), are also observed in very high abundances. The spectra of the arene derivatives are somewhat similar. In all cases parent molecular-ions are observed and the fragmentation scheme follows a loss of fourteen carbonyl groups to give $[Ru_6C(\text{arene})]^+$ which then breaks down to give ultimately $[Ru_6C]^+$. The corresponding doubly-charged ions are also present in high abundances. The calculated isotopic patterns of the parent molecular-ions agree closely with those observed in all cases.

In conclusion we must stress that the method of preparation and properties of $Ru_6C(CO)_{17}$ are very similar to those reported for $Ru_6(CO)_{18}$.[4] It is interesting to note that, whereas $Ru_6(CO)_{18}$ can readily be formulated on the basis of the effective atomic number rule for the ruthenium atoms, the carbide may be regarded as electronically equivalent to the $Rh_6(CO)_{16}$ cluster.[3,5]

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