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The reaction of $[Ru_{10}C(CO)_{24}][ppn]_2$ with carbon monoxide to yield $[Ru_3(CO)_{12}]$ and $[Ru_6C(CO)_{16}]^{2-}$

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Abstract

The dianion $[Ru_{10}C(CO)_{24}]^{2-}$ in CH_2Cl_2 reacts with CO under ambient conditions to produce quantitative amounts of the species $[Ru_3(CO)_{12}]$ and $[Ru_6C(CO)_{16}]^{2-}$; the hydrido-anion $[HRu_{10}C(CO)_{24}]^-$ reacts similarly to form $[Ru_3(CO)_{12}]$ and $[HRu_6C(CO)_{16}]^-$.

It has recently been reported [1] that triruthenium dodecacarbonyl, $[Ru_3(CO)_{12}]$ (**1**), reacts with the hexarutheniumhexadecacarbonylcarbido-dianion, $[Ru_6C(CO)_{16}]^{2-}$ (**2**), to produce the decaruthenium-carbido cluster dianion $[Ru_{10}C(CO)_{24}]^{2-}$ (**3**) [2] in high yields. The dianion **3** was shown by a single crystal X-ray analysis of its $[ppn]^+$ salt * to possess a tetracapped octahedral ruthenium core with a carbido-atom occupying the central octahedral interstitial site. It is thus isostructural with its well established Os_{10}-analogue, $[Os_{10}C(CO)_{24}]^{2-}$ (**4**). We now wish to report that, in marked contrast to **4**, dianion **3** (as its $[ppn]^+$ salt) reacts rapidly with carbon monoxide under very mild conditions (1 atm, 25°C) to regenerate the precursor materials **1** and **2** in quantitative amounts. This instability is remarkable and is in marked contrast to the corresponding osmium dianion which resists reaction with carbon monoxide and subsequent cluster fragmentation even under very vigorous conditions (1000 atm, 200°C).

On passing a stream of carbon monoxide through a solution of $[Ru_{10}C(CO)_{24}][ppn]_2$ in CH_2Cl_2 at room temperature the solution rapidly changed from the characteristic deep-green colour of **3** first to brown and then to orange. After removal of most of the CH_2Cl_2 *in vacuo* followed by TLC on silica and elution with CH_2Cl_2 : hexane (60 : 40%) the two compounds $[Ru_3(CO)_{12}]$ and $[Ru_6C(CO)_{16}][ppn]_2$ were isolated and identified on the basis of their spectroscopic data. Yields of these materials were virtually quantitative according to the equation given

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* $[ppn]^+$ = bis(triphenylphosphine)iminium.

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below. In a separate experiment the orange solution so obtained was heated under reflux when the green dianion $[Ru_{10}C(CO)_{24}]^{2-}$ was regenerated.

$$\begin{tikzcd}
{3[Ru_6C(CO)_{16}][ppn]_2} & {+\,4[Ru_3(CO)_{12}]} \arrow[r, shift left] & {3[Ru_{10}C(CO)_{24}][ppn]_2 + 24CO} \arrow[l, shift left] \\
(2) \arrow[d, shift left] & (1) & (3) \arrow[d, shift left, "HCl"] \\
{[HRu_6C(CO)_{16}][ppn]} \arrow[u, shift left] & {+\,[Ru_3(CO)_{12}]} \arrow[r, shift left] & {[HRu_{10}C(CO)_{24}][ppn]} \arrow[u, shift left] \arrow[l, shift left] \\
(6) & & (5)
\end{tikzcd}$$

We have previously shown [2] that the dianion **3** may be protonated with HCl, to generate the monohydrido-cluster anion $[HRu_{10}C(CO)_{24}]^-$ (**5**). We now find that this anion also reacts with carbon monoxide under similar mild conditions to produce **1** and $[HRu_6C(CO)_{16}]^-$ (**6**) and that this reaction is also reversible (see equation below). Cluster degradation of **3** may also be initiated by reaction with I_2. At low temperatures **3** reacts with I_2 to produce the red-brown monoanion $[Ru_{10}C(CO)_{24}I]^-$ (**7**), which, on the basis of its IR spectrum {ν(CO) (cm^{-1}) (CH_2Cl_2) 2087(w), 2053(vs) and 2011(s)} is considered to be isostructural with its osmium analogue [3]. At room temperature the reverse reaction occurs and **3** is regenerated.

$$\underset{(3)}{[Ru_{10}C(CO)_{24}]^{2-}} + 2I_2 \rightleftharpoons \underset{(7)}{[Ru_{10}C(CO)_{24}I]^-} + I_3^-$$

At higher temperatures further reaction occurs to produce a species which, on the basis of its mass spectrum ($m/e = 1264$) and other spectroscopic data, has been identified as the neutral diiodo-cluster $[Ru_6C(CO)_{14}I_2]$ (**8**). The same cluster **8** may also be produced via the direct reaction of the dianion **2** with I_2.

$$\underset{(2)}{[Ru_6C(CO)_{16}]^{2-}} + 4I_2 \rightleftharpoons \underset{(6)}{[Ru_6C(CO)_{16}I_2]} + 2I_3^-$$

Prolonged reaction of **3** with excess I_2 produces the polymeric compound $[Ru(CO)_2I_2]_n$ [4] which has also been characterised on the basis of its IR spectrum {ν(CO) (cm^{-1}) (Nujol) 2054(vs), 1994(s)}. This leads us to suggest that the overall reaction sequence corresponds to the equation:

$$[Ru_{10}C(CO)_{24}]^{2-} + 5I_2 \rightarrow [Ru_6C(CO)_{14}I_2] + 4[Ru(CO)_2I_2]$$

In conclusion, these observations clearly illustrate the danger of considering that cluster stability may be associated with interstitial site occupancy by main group atoms such as carbon. In this work the high stability of the octahedral dianion $[Ru_6C(CO)_{16}]^{2-}$ is apparent but the ease with which $[Ru_{10}C(CO)_{24}]^{2-}$ reacts with CO is surprising. We and others have observed that other interstitial species e.g. $[Ru_6N(CO)_{15}]^-$ and $[HRu_6N(CO)_{15}]$ also readily and spontaneously degrade to give $[Ru_5N(CO)_{14}]^-$ or $[HRu_5N(CO)_{14}]$ [5]. The observation that the hexanuclear ruthenium anions react readily with $[Ru_3(CO)_{12}]$ to produce Ru_{10} species indicates new and simple routes to high nuclearity clusters and these are being explored.

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