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# The formation of carbides in hexaruthenium carbonyl clusters ☆

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## Abstract

The introduction of carbido atoms into hexaruthenium clusters is discussed in terms of the cleavage of susceptible carbonyl ligands coordinated to non-carbido precursors. The isolation of an intermediate containing dihapto-carbonyl ligands in the well established synthesis of $[Ru_6C(CO)_{14}(\eta^6\text{-arene})]$ species by thermolysis of $[Ru_3(CO)_{12}]$ in the presence of the arene, and its demonstrated conversion to the carbide, a second hexaruthenium product and carbon dioxide, is interpreted in terms of a bimolecular mechanism involving cleavage of a dihapto-carbonyl ligand. With reference to this mechanism, the virtually quantitative conversion of $[Ru_6(CO)_{18}]^{2-}$ (**5**) into $[Ru_6C(CO)_{16}]^{2-}$ (**6**) and carbon dioxide which occurs at high temperature in solution is discussed, and an autocatalytic mechanism involving a bimolecular CO cleavage step is suggested. Finally, the conversion of $[Ru_6(CO)_{18}]^{2-}$ (**5**) into the neutral carbide $[Ru_6C(CO)_{17}]$ (**1**) by carbonyl ligand C–O cleavage induced by reaction with trifluoromethanesulfonic or trifluoroethanoic anhydrides is discussed.

*Keywords:* Carbido atoms; Hexaruthenium clusters; Carbonyl clusters

## 1. Introduction

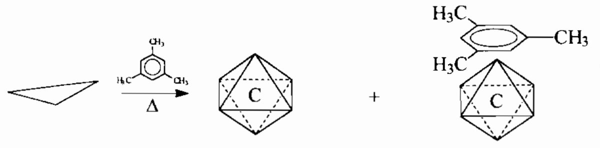
There has been a rapid growth in the number of high nuclearity ruthenium carbonyl clusters reported recently. Nuclearities now range to eleven and their syntheses mostly involve the solution thermolysis of lower nuclearity precursors in either protic (alcohol) solvents, leading to hydrido clusters [1], or aprotic (hydrocarbon or ether) solvents which generate species containing interstitial carbido ligands [2]. Whilst the majority of the carbido clusters of the cobalt subgroup metals have been synthesised by the use of halomethanes as an external source of carbon [3], those of the iron subgroup have invariably been derived from the thermally induced cleavage of coordinated carbon monoxide, as evidenced by a number of $^{13}C$ labelling experiments. Carbon dioxide has been detected as a by-product in a number of such reactions thus indicating the occurrence of a disproportionation of two CO ligands (Eq. (1)). It is significant that in ruthenium cluster build up

$$2CO \longrightarrow C + CO_2 \qquad (1)$$

reactions in aprotic media almost all species of a nuclearity of six or greater incorporate a carbido ligand and this nuclearity may therefore be identified as critical in the C–O cleavage process. This paper presents a discussion of the mechanisms involved in inducing this cleavage of CO brought about by the transformations of a hexaruthenium core.

## 2. Discussion

Although the first transition metal carbido cluster to be reported was $[Fe_5C(CO)_{15}]$, ruthenium provided the first examples of such clusters containing fully encapsulated carbido ligands; the octahedral $[Ru_6C(CO)_{17}]$ (**1**) and $[Ru_6C(CO)_{14}(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)]$ (**2**). These clusters were isolated from the solution resulting from the high temperature thermolysis of $[Ru_3(CO)_{12}]$ in 1,3,5-trimethylbenzene (mesitylene) (Eq. (2)) [4]. A more recent investigation of this reaction at a lower temperature of 97 °C lead to the isolation of two further hexaruthenium clusters containing not carbido ligands but $\mu_4\text{-}\eta^2$-coordinated carbonyl ligands; $[Ru_6(CO)_{13}(\mu_4\text{-}\eta^2\text{-}CO)_2(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)]$ (**3**) and



(2)

$[Ru_3(CO)_{12}]$ $[Ru_6C(CO)_{17}]$ (1) $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)]$ (2)

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☆ This paper is dedicated to Professor György Bor on the occasion of his 70th birthday.

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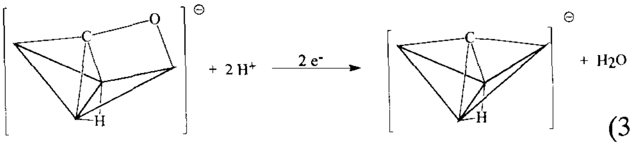
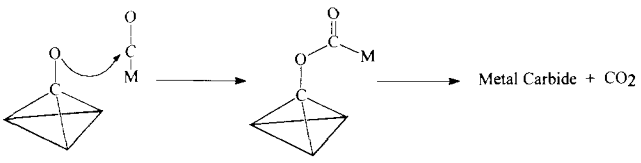
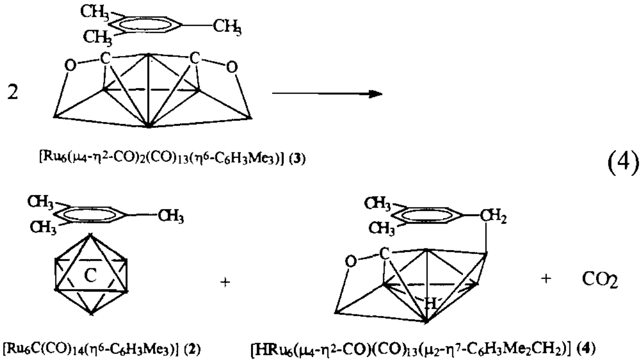
$[HRu_6(CO)_{13}(\mu_4\text{-}\eta^2\text{-}CO)(\mu_2\text{-}\eta^7\text{-}C_6H_3Me_2CH_2)]$ (**4**) [5]. Such dihapto-coordination of the carbonyl ligands leads to considerable weakening of the C–O bond as is evidenced by the C–O stretching frequencies of 1392 (symmetric) and 1423 (antisymmetric) $cm^{-1}$ assigned to the two ligands in **3**. Additionally, this coordination mode increases the nucleophilicity of the carbonyl oxygen which enables the dihapto-carbonyl in $[HFe_4(CO)_{13}]^-$ to be cleaved by protonation for example (Eq. (3)) [6]. Similarly, this effect forms the basis for the mechanism of CO cleavage proposed by Deeming [7] which involves combination of the oxygen nucleophilicity of a highly bridging carbonyl ligand with the carbon electrophilicity of a terminal carbonyl (Scheme 1).The isolation of clusters containing dihapto-carbonyl ligands in a synthesis of hexaruthenium carbido clusters is therefore significant and indicates their involvement in the formation of the carbide. This hypothesis is further supported by the observation that thermolysis of **3** in solution or solid state yields the carbide **2** in addition to the cluster **4**, $CO_2$ also being identified as a by-product (Eq. (4)). Since $CO_2$ is known to be produced in this reaction, an intramolecular disproportionation of two coordinated carbonyl ligands may be ruled out on the grounds of carbon stoichiometry since the carbide product **2** and its precursor **3** contain the same number of carbon atoms. Equally, the formation of two hexaruthenium clusters suggests a bimolecular mechanism as indicated in Eq. (4).



(3)



Scheme 1.



(4)

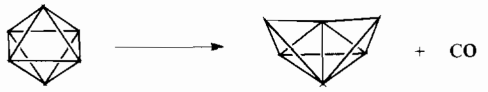
The mechanism of carbide formation therefore appears to involve the cleavage of an $\eta^2$-CO ligand of **3** via the nucleophilic attack of its oxygen on a terminal CO carbon on a second cluster molecule. Elimination of $CO_2$ from this intermediate generates the carbide coordinated to the first cluster and leaves the second deficient of one carbonyl ligand. Rearrangement of the carbide species to encapsulate the newly formed carbon leads to **2**, however the fate of its reaction partner is complicated by the fact that it is now unsaturated with the formula $[Ru_6(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)]$, an 84-electron system, the dihapto-carbonyl being a four-electron donor. However, the edge-bridged trigonal bipyramidal structure of the eventual form of this species requires an electron count of 86 as dictated by polyhedral skeletal electron pair theory. This unsaturation explains the activation of a mesitylene methyl group C–H bond leading to the transfer of a hydrido ligand to the metal core and the coordination of the resulting benzylic methylene to the cluster, a process which provides the required further two electrons for cluster bonding. The alternative of closing of the cluster core to a capped trigonal bipyramid (an 84-electron system as required) is not viable since the $\eta^2$ to $\eta^1$ conversion of the unique carbonyl necessarily involved in such a process would lead to the loss of a further two electrons from the system leaving 82, an electron count for which there are no viable hexanuclear cluster geometries. This carbide formation process is therefore analogous to that proposed in Scheme 1 except that the two precursors are not incorporated into a single carbide product but rather the carbonyl donor of the pair is isolated as a second product.

A second well characterised reaction which leads to the generation of a carbide in a hexaruthenium system involves the high temperature thermolysis of the octahedral dianion $[Ru_6(CO)_{18}]^{2-}$ (**5**) in diglyme at reflux (165 °C) which generates the carbide $[Ru_6C(CO)_{16}]^{2-}$ (**6**) (Eq. (5)) [8]. The reaction has also been found to proceed slowly at the lower temperature of 120 °C in the same solvent [9]. The formation of the carbide $[Ru_6C(CO)_{16}]^{2-}$ (**6**) occurs almost quantitatively (96% isolated yield) and $CO_2$ has been positively identified as a by-product by trapping as $BaCO_3$. This is therefore clearly another example of CO disproportionation carbide forming reaction. Eq. (5) suggests a unimolecular process and therefore an intramolecular reaction between coordinated carbonyl ligands in the carbide forming reaction. The precursor **6** contains two $\mu_3$-carbonyl ligands bridging diagonally opposite faces of the octahedral core [10], however, the adoption of the reaction geometry necessary for a $\mu_3$-CO oxygen to attack a terminal CO carbon coordinated to the same cluster core is difficult to envisage. Furthermore, any disso-

$$[Ru_6(CO)_{18}]^{2-} \xrightarrow{\Delta} [Ru_6C(CO)_{16}]^{2-} + CO_2 \qquad (5)$$

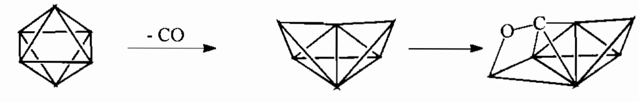
ciation of CO to such an end is precluded by the quantitative nature of the reaction. It is therefore suggested that the formation of the carbide in this system is bimolecular in nature.

Diprotonation of **5** yields the octahedral neutral dihydride $[H_2Ru_6(CO)_{18}]$ (**7**) which has been shown to spontaneously rearrange to the 84-electron capped trigonal bipyramidal $[H_2Ru_6(CO)_{17}]$ (**8**) with ejection of a carbonyl ligand both in solution and in the solid state (Eq. (6)) [11]. The capped trigonal bipyramid is of course the geometry from which the carbide precursor in the mesitylene containing system **3** is derived. At the elevated temperatures involved in the conversion of **5** to the carbide **6**, CO ejection to generate the dianion $[Ru_6(CO)_{17}]^{2-}$, the deprotonated analogue of **8**, is the most likely initial process. This species must also be based upon the capped trigonal bipyramidal geometry. The formation of such a structure in this system leads to a possible mechanism for the carbide formation since the potential for the formation of a C–O bond weakened $\mu_4$-$\eta^2$-carbonyl via the opening of one of the caps and insertion of an $\eta^2$-carbonyl now exists (Scheme 2). A bimolecular reaction between this $[Ru_6(CO)_{17}]^{2-}$ species and $[Ru_6(CO)_{18}]^{2-}$ (**5**) can now take place in which nucleophilic attack of the activated $\eta^2$-carbonyl oxygen on a terminal carbonyl on a molecule of **5** generates the carbide and $CO_2$. The cluster products of this reaction are $[Ru_6C(CO)_{16}]^{2-}$ (**6**) and a further molecule of $[Ru_6(CO)_{17}]^{2-}$ which may now be seen as the chain carrier in an autocatalytic reaction initiated by the loss of one molecule of CO from **5** (Scheme 3).



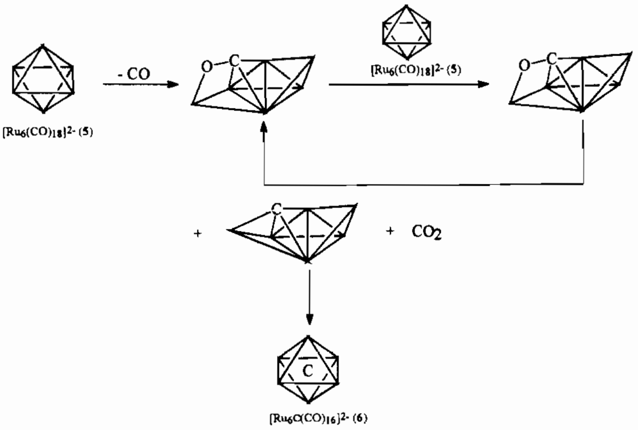
$[H_2Ru_6(CO)_{18}]$ (7) $[H_2Ru_6(CO)_{17}]$ (8) (6)

Although this mechanism is similar to that described for the conversion of **3** to the carbide $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)]$ (**2**), the carbide precursor **3** is equivalent to a neutral $[Ru_6(CO)_{18}]$ cluster and therefore has two fewer electrons than the dianionic system $[Ru_6(CO)_{18}]^{2-}$ (**5**). As a consequence, the non-carbido reaction product from the thermolysis of **3** is an unsaturated $[Ru_6(CO)_{17}]$ equivalent which derives the further two electrons which it requires for the formation of a stable structure by the oxidative addition of a methyl C–H bond and therefore appears as a second cluster product of the reaction. In contrast, the carbonyl donor in the anionic system is $[Ru_6(CO)_{18}]^{2-}$ (**5**) which is converted into the chain carrier $[Ru_6(CO)_{17}]^{2-}$ by the carbide formation process and can therefore reenter the reaction cycle, thus resulting in the formation of a single cluster product from this reaction.



$[Ru_6(CO)_{18}]^{2-}$ (5) $[Ru_6(CO)_{17}]^{2-}$ $[Ru_6(CO)_{17}]^{2-}$

Scheme 2.

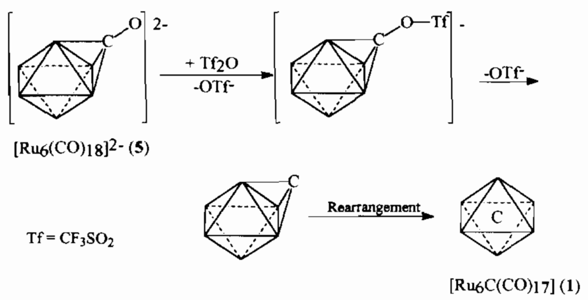


Scheme 3.

The generation of cluster carbides by chemical rather than thermal activation of a coordinated carbonyl ligand is less common, however a number of examples are known and all exploit the nucleophilicity of a bridging ($\mu_2$-, $\mu_3$-) carbonyl oxygen. One such example has already been introduced in the conversion of $[HFe_4(CO)_{13}]^-$ to $[HFe_4C(CO)_{12}]^-$ by strong acid (Eq. (3)). A more general approach is the reaction of an anionic cluster containing a susceptible carbonyl with acyl chloride to generate an intermediate metalloester which may be regarded as an incipient carbide coordinated to acetate. The reductive cleavage of such species derived from $[M_3(CO)_{11}]^{2-}$ (M = Fe, Ru, Os) has yielded the ketenylidene clusters $[M_3(CO)_9(CCO)]^{2-}$ [12], whilst $[Fe_4(CO)_{12}\{COC(O)CH_3\}]^-$ yields $[Fe_4C(CO)_{12}]^{2-}$ on similar treatment or $[HFe_4(CO)_{12}(CH)]$ with acid [13]. Similarly, the reaction of the octahedral cobalt cluster $[Co_6(CO)_{15}]^{2-}$ with $CH_3COCl$ has been found to lead directly to the carbido anion $[Co_6C(CO)_{14}]^-$ (Eq. (7)) [13].

$$3[Co_6(CO)_{15}]^{2-} + 2CH_3COCl \xrightarrow{+CO} 2[Co_6C(CO)_{14}]^- + 4[Co(CO)_4]^- + 2Cl^- + 2Co^{2+} + 2CH_3COO^- \qquad (7)$$

In a similar approach, it has been found that treatment of $[Ru_6(CO)_{18}]^{2-}$ (**5**) with strong acid anhydrides (trifluoroacetic or trifluoromethanesulfonic) leads directly to the neutral carbide $[Ru_6C(CO)_{17}]$ (**1**) in high yields (Scheme 4) [14]. The use of such anhydrides results in the intermediate formation of a system in which the incipient carbide is coordinated to the good anionic leaving groups trifluoroacetate or trifluoromethanesulfonate and the spontaneous cleavage of the C–O bond is therefore favoured. Such a process is most likely



Scheme 4.

also driven by the encapsulation of the resulting carbide within an octahedron of ruthenium atoms.

The two alternative routes to carbido clusters from $[Ru_6(CO)_{18}]^{2-}$ (**5**) are clearly related and both rely upon the nucleophilicity of bridging carbonyl oxygens. The interaction of this centre with a metal carbonyl as the electrophilic component leads to retention of the overall cluster charge with elimination of the neutral carbon dioxide thus yielding $[Ru_6C(CO)_{16}]^{2-}$ (**6**). However, with the formal involvement of a cationic electrophilic component ($CF_3CO^+$ for example), and the departure of the resulting leaving group as an anion, the dianionic charge of the cluster is removed in the formation of $[Ru_6C(CO)_{17}]$ (**1**).

## 3. Conclusions

The formation of carbido clusters is clearly highly complicated and a number of potential sources of an isolated carbon atom have been identified. For ruthenium, carbido formation is dominated by C–O cleavage and the production of $CO_2$. This may be achieved by a variety of processes but appears to be dependent upon the presence of a carbonyl oxygen with enhanced nucleophilicity which may attack an electrophilic carbonyl carbon, thus leading to an ester-type intermediate which may decompose to the carbide and $CO_2$. The stability of the octahedrally encapsulated carbide in the systems discussed here undoubtedly contributes to the driving force for the C–O cleavage processes described.

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