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Benzene migration and isomer interconversion in $Ru_5C(CO)_{12}(C_6H_6)$: Comparison of solution and isolation matrix phenomena

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Abstract

The irradiation of $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$, in which the benzene is coordinated to a basal metal atom, embedded within a polymethylmethacrylate (PMMA) film leads to the formation of the η^6 apical isomer. On heating, the process is reversed and conversion of the η^6 apical into the η^6 basal isomer is observed. Possible mechanistic pathways for these processes are discussed.

Keywords: Ruthenium; Carbonyl; Benzene; Photolysis

1. Introduction

The square-pyramidal ruthenium cluster, $Ru_5C(CO)_{15}$, was first reported in 1983, as the product of the degradative carbonylation reaction of $Ru_6C(CO)_{17}$, which yields both the pentamer and ruthenium pentacarbonyl [1]. The iron [2] and osmium [3] analogues of this cluster are also known, the iron cluster being the first carbido-cluster to be definitively characterised. It has also been shown that the ruthenium cluster, $Ru_5C(CO)_{15}$, readily accepts two electrons from a suitable small nucleophile (Nu) under ambient conditions, to generate the stable adduct, $Ru_5C(CO)_{15}Nu$, in which the cleavage of one Ru–Ru bond has taken place, generating a bridged-butterfly metal atom topology (Scheme 1) [1]. It has been recognised that this property not only plays an important role in the cluster addition reaction but also in the mechanism by which reactions may occur on the cluster surface [4]. In our work we have used $Ru_5C(CO)_{15}$ as a template to model the chemistry displayed by chemisorbed cyclohexadiene and benzene at the metal surface, and have prepared a wide series of Ru_5C derivatives bearing cyclohexadiene and benzene ligands [5,6]. Migration of benzene from one bonding site to another has been observed in the series of compounds $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$, **I**, and the two isomers of $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$, **II** and **III** for the basal and apical isomers, respectively [5], and it is the isomerisation processes that these three isomers undergo which are dealt with in this paper. Here we report that we have observed a different isomerisation pattern on irradiation in polymer films (η^6 basal to η^6 apical) from that observed in solution under thermal conditions (η^6 apical to η^6 basal).

2. Results and discussion

In arene-cluster derivatives two bonding modes for benzene predominate; viz. the η^6 terminal and $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ face-bonding modes (Fig. 1) [7]. In $Ru_5C(CO)_{12}(C_6H_6)$ three structural forms, depending on the location of the benzene ligand about the central Ru_5C core, have been identified, viz. $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ **I**, and two isomers of $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$ in which the benzene bonds to either a basal (**II**) or the apical (**III**) ruthenium atom of the square-pyramid [5]. These isomers are illustrated in Fig. 2. It has been established that **I** is generated initially upon aromatisation of a bridging cyclohexadiene ligand in $Ru_5C(CO)_{13}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8)$ together with the expulsion of carbon monoxide and dihydrogen. Heating a solution of **I** in hexane (69°C) for 4 h results in quanti-

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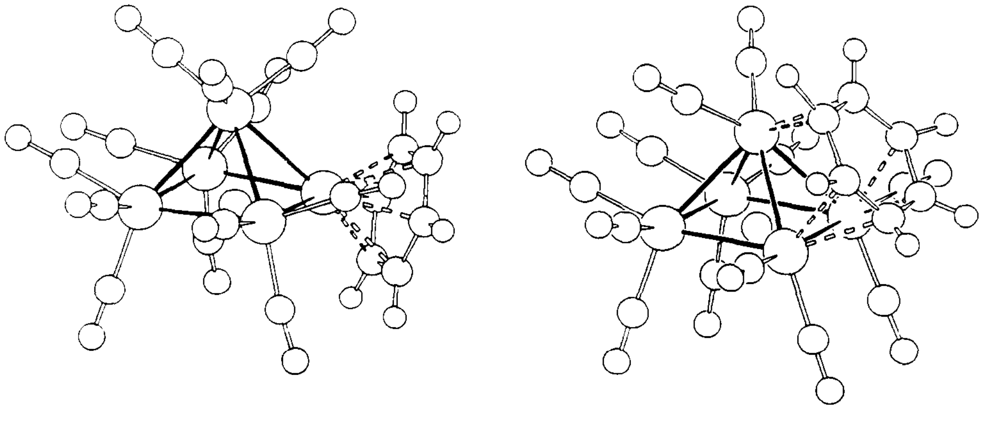
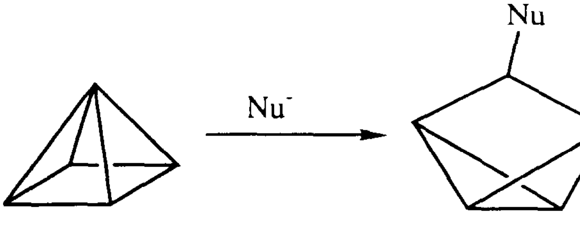


(a) (b)

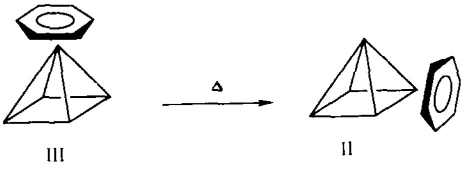
Fig. 1. The solid-state structure of: (a) $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$ II; (b) $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ I.

tative conversion into **II**. A kinetic study, with monitoring by ^1H NMR spectroscopy, yielded a very low value of ΔH^* (22 kJ mol^{-1}) together with a negative value for ΔS^* (−64 J mol^{-1}), indicating that the mechanism of this isomerisation involves a non-dissociative process [8]. The preparation of isomer **III** is less straightforward. It involves first the formation of the bridged-butterfly adduct, $Ru_5C(CO)_{13}(\eta^6\text{-}C_6H_6)$, **IV**, from **II** by the uptake of CO with the concomitant cleavage of the Ru–Ru bond connecting the ruthenium atom carrying the benzene ligand with the cluster apex, and then subsequent loss of CO to yield either **II** or **III** depending on the conditions employed [5]. Heating a solution of **III** for 40 h in hexane (69°C) results in its irreversible conversion into **II**, as depicted in Scheme 2.

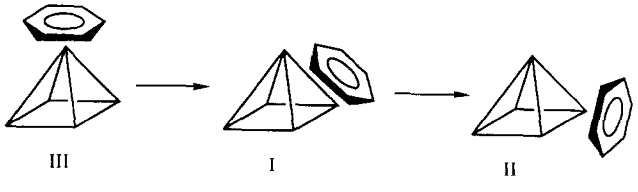
Initially, we proposed that the isomerisation of **III** to **II** proceeded via the intermediacy of **I**. This appeared to the logical sequence, with the benzene molecule slipping first from the η^6 terminal position to a position over the cluster face to form the $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ face-capping mode in **I** and then by further migration of the η^6 mode observed in isomer **II**, as shown in Scheme 3. This thermolysis was monitored by IR spectroscopy, and at no stage during the process was the presence of **I** observed, thereby ruling out the possibility of its being an intermediate, and so it was necessary to consider an alternative. In this, isomerisation may be considered to occur via a polyhedral rearrangement of the Ru_5 square-pyramidal cage via a bridged-butterfly structure, a process which involves first Ru–Ru edge cleavage and then recombination. This is illustrated in Scheme 4. The process involves cleavage of edge (a) (Ru_{apex}–Ru_{basal}) to generate the intermediate with a bridged-butterfly structure and then formation of the new edge (a′) to regenerate the (new) square pyramidal structure. This isomerisation has the effect of *apparently* transfering the benzene from the η^6 apical **III** to the η^6 basal position **II**. In reality the benzene remains attached to the same Ru-atom throughout the process and does not correspond to a migration in the "real" sense. In the light of earlier work we believe that the



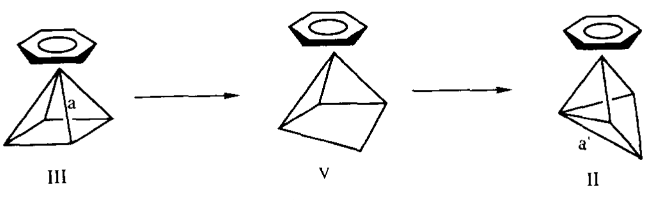
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

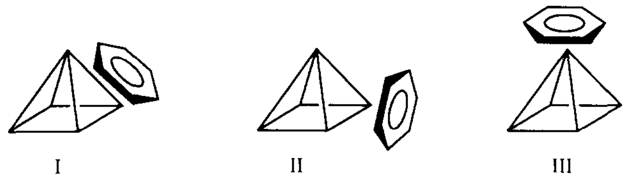
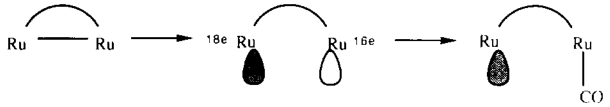


Fig. 2. Basal **II** and apical **III** isomers of $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$.



Scheme 5.

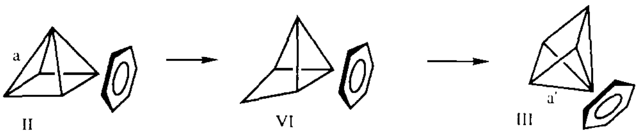
bridged-butterfly intermediate is brought about by the heterolytic fission of the Ru–Ru bond (which in a square-pyramidal structure such as this may be regarded as a conventional two-centre/two-electron bond) to generate one 16-electron metal centre and one 18-electron centre, see Scheme 5. As such it is a totally reasonable reaction intermediate for CO addition to **II** (at the coordinatively unsaturated Ru-atom) to produce **IV**.

We believe that the results provide good evidence for a mechanism related to this second type, although of course we are unable to differentiate between initiation involving a heterolytic and that involving a homolytic bond fission. The compound, $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$, **II**, embeded within a polymethylmethacrylate (PMMA) film was photolysed for about 2 h, during which its IR spectrum was recorded every 10 min. Careful examination of the IR spectra showed that an initial transformation from **II** to **III** takes place, and that cluster **I** is then generated from it. The IR carbonyl-stretching frequencies of the three isomers **I** to **III** recorded in pure form in PMMA are listed in Table 1, and by use of these values for the purpose of comparison the above inferences were made. Table 1 also contains spectral data for the corresponding species obtained in dichloromethane, illustrating that the structures of the molecules in solution and solid phases are the same.

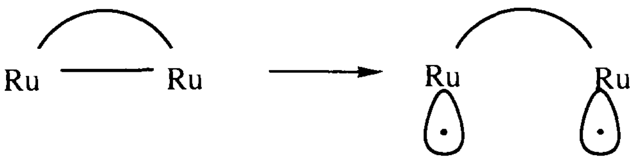
The conversion of **II** into **III** found in the PMMA film is the reverse of that observed in solution, but clearly because **I** is produced *after the formation* of **III** it cannot serve as the appropriate intermediate, as outlined in Scheme 3. However, the second mechanistic approach is probably responsible, i.e. isomerisation by Ru–Ru edge cleavage to bring about the correct rearrangement, as depicted in Scheme 6.

Table 1
IR carbonyl-stretching frequencies recorded in pure form in PMMA

Isomer	ν_{CO}(PMMA Film)	ν_{CO}(CH_2Cl_2)
I	2081 m, 2049 s, 2031 m, 2017 vs, 2000 w(sh).	2083 m, 2051 s, 2031 m(sh), 2019 s, 2000 w(sh).
II	2076 w, 2048 vs, 2031 m, 2008 s, 1991 w(sh).	2078 m, 2049 s, 2033 m, 2010 s, 1994 m(sh).
III	2075 w, 2069 w, 2048 m, 2030 m, 2009 vs.	2078 m, 2068 s, 2050 s, 2035 s, 2011 s.



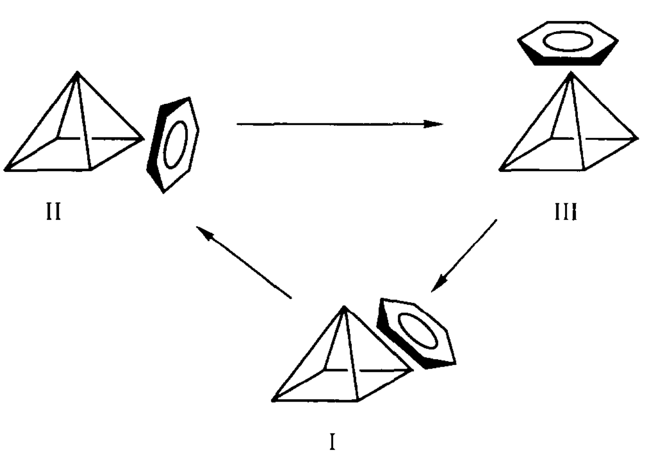
Scheme 6.



Scheme 7.

There is some limited evidence from the IR spectra for an intermediate **VI** initially observed on irradiation of the PMMA film, and a peak is also found at 2066 cm^{-1} which does not correspond to any of the known compounds. However, the nature of **VI** is difficult to establish. Although the process appears to be similar to that observed in solution, the thermal and photolytic processes are almost certainly different. We suggest that the thermal process proceeds via the *heterolytic* bond fission pathway outlined above, whereas the photolytic process probably proceeds via *homolytic* fission and the formation of a *diradical* intermediate, as depicted in Scheme 7. Nevertheless, from the geometric standpoint the proposed intermediates **V** and **VI** must be similar in nature. To date we have been unable to find evidence for the formation of the radical species, but further work is in hand.

In the PMMA film, an infinite cycle could, in principle, take place, following the sequence, **II** → **III** → **I** →



Scheme 8.

II etc. (Scheme 8). In reality, however, some decomposition occurs with time as photolysis proceeds.

It is also worth noting that the photolysis of these pentaruthenium–benzene clusters is different from that of the triosmium–benzene cluster, $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$. In this latter species photoisomerisation to the dihydrido-benzyne cluster, $H_2Os_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_6H_4)$, takes place. The reverse process, however, has not been observed [9]. Furthermore, migration of the benzene to the η^6 terminal mode is observed only on reaction with μ_3-bonding ligands, such as alkynes [10].

3. Experimental details

3.1. General

Photolysis was carried out at room temperature using a water-cooled 125 W medium-pressure mercury arc lamp, with the films placed 1 cm from the source. IR spectra were recorded on a Perkin-Elmer 1710 series FTIR spectrometer, calibrated with carbon dioxide. In the case of polymer films, a blank film was used for the background subtraction, while solution spectra were recorded in CH_2Cl_2 using NaCl cells (0.5 mm path length). The compounds $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$, **I** and $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$, **II** were prepared by published procedures [6]. Compound **III** was prepared from **II** by the published route [5].

The films in this study were prepared by the solvent-casting technique [11]. In a typical experiment (150 mg) of the polymer precursor [Diakon MG102 (polymethylmethacrylate) supplied by ICI Wilton] was dissolved in hot toluene (20 ml). When the solution had cooled a sample of the complex (typically 10 mg) was added, and the resulting solution was poured into a Petri dish (5 cm diameter). The solvent was allowed to evaporate during 24 h, and the resulting polymer film was extracted from the dish by adding distilled water, cutting around the edge, and allowing the film to float to the surface. The films were dried thoroughly prior to photolysis. All compounds were identified from their IR spectra, as described in Table 1.

3.2. Thermolysis in hexane

3.2.1. Thermolysis of $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ I in hexane.

A solution of $[Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$, **I**, (10 mg) in hexane (30 ml) was heated under reflux for 4 h, during which the colour the colour changed from red to black, and IR spectroscopy indicated complete conversion of the starting material to $[Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)]$ **II** (9 mg). This was confirmed by spot tlc, which revealed no other products, and that virtually no decomposition had taken place during the reaction.

3.2.2. Thermolysis of $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$, III, in hexane

A solution of $[Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)]$, **III**, (5 mg) in hexane (25 ml) was heated under reflux. After 40 h, IR spectroscopy indicated that the starting material had undergone complete conversion into $[Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)]$ **II** (5 mg). This was confirmed by spot tlc, which revealed no other products.

3.3. Photolysis in PMMA film

3.3.1. Photolysis of $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$ II in PMMA film

$Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$, **II**, was irradiated with unfiltered light for 1.75 h during which the film was monitored every 10 min by IR spectroscopy. The compound $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$, **III**, was detected after 20 min, and after 40 min the cluster $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ **I** was observed. The initially black film turned a reddish colour. Compounds **III** and **I** were monitored by the appearance of characteristic peaks in the IR spectrum.

3.3.2. Photolysis of $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ I in PMMA film

$Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ **I** was irradiated with unfiltered light for 2.5 h. Peaks corresponding to the isomers of $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$, **II** and **III**, were observed in the IR spectrum after 0.5 h and 2.5 h, respectively.

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References

[1] B.F.G. Johnson, J. Lewis, J.N. Nicholls, J. Puga, P.R. Raithby, M. McPartlin and W. Clegg, *J. Chem. Soc., Dalton Trans.*, (1983) 277.

[2] E.H. Braye, L.F. Dahl, W. Hubel and D.S. Wampler, *J. Am. Chem. Soc., 84* (1962) 4633.

[3] C.R. Eady, B.F.G. Johnson, J. Lewis, B.E. Reichert and G.M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, (1976) 271.

[4] D.H. Farrar, A.J. Poë and Y. Zheng, *J. Am. Chem. Soc., 116* (1994) 6252.

[5] D. Braga, F. Grepioni, P. Sabatino, P.J. Dyson, B.F.G. Johnson, J. Lewis, P.J. Bailey, P.R. Raithby and D. Stalke, *J. Chem. Soc., Dalton Trans.*, (1993) 985.

[6] D. Braga, P. Sabatino, P.J. Dyson, A.J. Blake and B.F.G. Johnson, *J. Chem. Soc., Dalton Trans.*, (1994) 393.
[7] D. Braga, P.J. Dyson, F. Grepioni and B.F.G. Johnson, *Chem. Rev.*, *94* (1994) 1585.
[8] P.J. Dyson, B.F.G. Johnson and D. Braga, *Inorg. Chim. Acta.*, *33* (1994) 3218.
[9] M.A. Gallop, B.F.G. Johnson, J. Lewis, A. McCamley and R.N. Perutz, *J. Chem. Soc., Chem. Commun.*, (1988) 1071.
[10] D. Braga, F. Grepioni, B.F.G. Johnson, J. Lewis, M. Martinelli and M.A. Gallop, *J. Chem. Soc., Chem. Commun.*, (1990) 53.
[11] T. Cassen, N. Geacintov and G. Oster, *J. Am. Opt. Soc.*, *58* (1968) 1217.