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Arene migration in ruthenium clusters: a kinetic study of the isomerisation of $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ to $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$

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Abstract

The migration of benzene in $Ru_5C(CO)_{12}(C_6H_6)$ from a $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ position to an η^6 site has been monitored by ^1H NMR spectroscopy at 313, 323, 333, 343 and 356 K. From this data a detailed kinetic analysis has been undertaken. Possible transition state species and thus a mechanism for this isomerisation process are postulated, and the results discussed in the broader context of benzene surface phenomena, which is re-evaluated where appropriate.

Key words: Kinetics and mechanism; Ruthenium complexes; Arene complexes; Carbonyl complexes

Introduction

The migration of benzene in monometallic complexes (usually $\eta^6 \leftrightarrows \eta^4 \leftrightarrows \eta^2$) has received significant attention over the years [1]. This is primarily due to interest in arene exchange phenomena, which has broad ranging implications from the synthesis of new arene–metal complexes, to enhancing the understanding of arene reactions catalysed by transition metals [1]. Until recently, with transition metal clusters, only the η^6 coordination mode had been observed for benzene. However, in 1985 a second and new bonding mode for benzene ($\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$) was discovered in which the ligand lies over a trimetal face [2]. Shortly after this discovery, it was observed that the face-bound benzene undergoes migration to give products in which the benzene is η^6-bound to a single metal atom [3–8]. The first example of benzene migration was reported for the trimetal clusters $M_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ (M = Ru, Os), and was achieved by chemical methods [3,4]. In the case of the osmium complex, a carbonyl can be replaced by acetonitrile from the reaction of equimolar quantities of $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ and Me_3NO in acetonitrile, yielding $Os_3(CO)_8(MeCN)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$. Substitution of acetonitrile by ethylene affords the π-bound alkene complex $Os_3(CO)_8(\eta^2\text{-}CH_2{\cdot}CH_2)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$, which may undergo further reaction with $Me_3NO/MeCN$ to produce the activated cluster $Os_3(CO)_7(C_2H_4)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(MeCN)$. This activated species readily reacts with alkynes (C_2RR') to form the complexes $Os_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2RR')$ (R = R' = H, Ph or Me; R = H, R' = Ph; R = Me, R' = Et) in which the benzene has migrated to a terminal position; the Os triangle being capped on one side by dimethylacetylene which bonds to the metal atoms via two σ-interactions and one π-interaction [4]. For the ruthenium analogue, direct reaction of $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ with alkynes in refluxing CH_2Cl_2 affords the cluster $Ru_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3{:}\eta^2\text{-}RC_2R'CO)$ (R = R' = Me, Ph or H; R = Ph, R' = H). The structure of the diphenylacetylene derivative $Ru_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3{:}\eta^2\text{-}PhC_2(PhCO)$ is similar to that described for Os, except that the C_2Me_2 ligand is replaced with the PhC=C(Ph)CO moiety, in which a carbonyl group has been inserted between one of the Ru–C σ-interactions [3].

More recently, benzene migration from $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ to η^6 has been induced thermally [5–8]. This process also requires the simultaneous migration of coordinated carbonyl ligands. For example, in the bis-benzene species

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$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ the μ_3-benzene has been found to migrate to a single ruthenium atom forming the *trans*-sandwich complex after thermolysis in nonane at 150 °C for several hours [5]. Alternatively, there is IR spectroscopic evidence to indicate that the $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ benzene migrates to a metal atom *cis* to that on which the other η^6 benzene bonds, on storage of the complex at −25 °C for a prolonged period [6]. This latter isomer may be converted back to its precursor $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ by heating in hexane. In fact, the migration process $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ to *cis*-$\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ and back is general for the arene–benzene species $Ru_6C(CO)_{11}(\eta^6\text{-arene})(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ (arene = C_6H_5Me, $C_6H_4Me_2$ and $C_6H_3Me_3$). The rate of the forward process increases with increasing methyl substitution of the arene ligand. As yet, an arene has not been observed to migrate over the entire cluster surface. It has been observed that when the two arene ligands are toluene, an equilibrium between $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5Me)$ and *trans*-$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)_2$ exists, and as temperature is raised, the concentration of the latter species increases [7]. This is in keeping with the previous observations. It has also been established that the migration of the toluene between sites takes place via a non-dissociative process.

The simplest system to study is the pentaruthenium cluster system [8] since the migration of the facial benzene to a single basal metal on the cluster occurs irreversibly at temperatures accessible to NMR spectroscopy over relatively short time periods. Also, the two benzene types may be readily distinguished by ^1H NMR spectroscopy, with singlets for the $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ and η^6 ligands at δ 4.12 and 5.93 ppm, respectively.

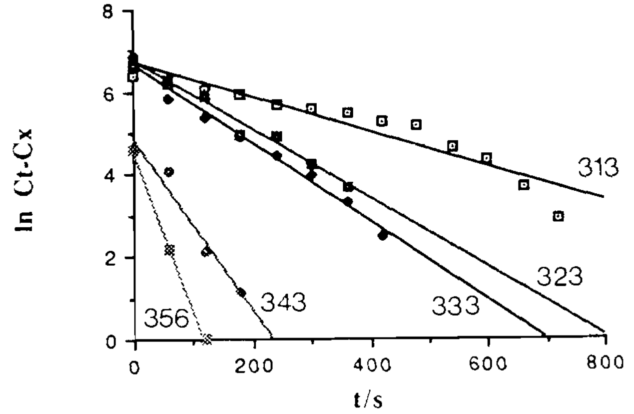

Fig. 1. Plots of ln $(C_t - C_x)$ vs. time at 313, 323, 333, 343 and 356 K. C_t is the concentration of $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ at time t; C_x is the final concentration of this cluster.

TABLE 1. The values of k estimated from the slopes in Fig. 1

T (K)	$k \times 10^4$ (s^{-1})
313	−42
323	−95
333	−335
343	−897
356	−2857

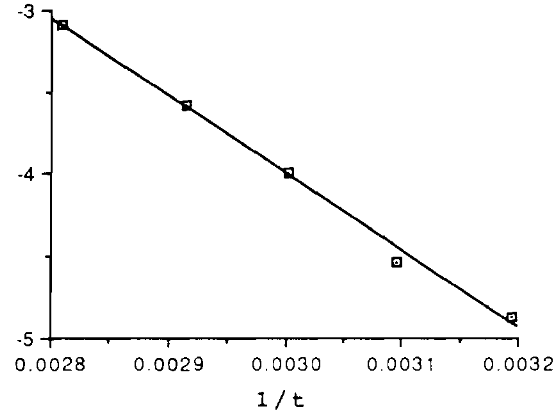

Fig. 2. Eyring plots of ln (k/t) vs. $1/t$ for the isomerisation of $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ to $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$.

Results and discussion

Kinetic analysis

We have monitored the isomerisation of $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ to $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$ at 313, 323, 333, 343 and 356 K in tetrachloroethane-d_2 by NMR spectroscopy. For each temperature at which measurements were made, the integral of the proton singlet resonance at δ 4.12 ppm, attributed to the face-capping benzene ring, was assessed to yield each of the plots shown in Fig. 1. The slopes of these graphs yield k, which are listed in Table 1, and in turn, these values were then employed in a linear form of the Eyring equation [9], and hence $\Delta H^\ddagger$, $\Delta S^\ddagger$ and $\Delta G^\ddagger_{298}$ were evaluated. The Eyring plot is illustrated in Fig. 2, and from this $\Delta H^\ddagger$ has been estimated as 21.6 kJ mol^{-1}, and $\Delta S^\ddagger$ as −64 J mol^{-1}, and hence, $\Delta G^\ddagger_{298}$ = 40.6 kJ mol^{-1}. The very low value of $\Delta H^\ddagger$ together with a negative value for $\Delta S^\ddagger$ indicates that the mechanism of this isomerisation involves an associative process. This is in agreement with other findings regarding the inability of the benzene to undergo exchange with other arenes (*vide infra*). Although caution should be exherted when comparing energy differences or energy barriers obtained by experiment with those obtained by theoretical calculations, it is interesting to mention in the context of this discussion that extended Hückel calculations have provided a value of *c*. 75 kJ mol^{-1} for the electronic barrier against movement of the benzene ring across the cluster [10]. This value was obtained from a simple model in which carbonyl motion was not included, and hence the concomitant motion of the carbonyls would appear to play an important role in the isomerisation process.

Any analysis raises the question as to the identity of the reaction transition state or intermediate (as yet unobserved by any spectroscopic technique in this case). To our mind there are two possible and reasonable transition states. The first involves a μ_2-η^3:η^3 type interaction of the benzene moiety with two basal ruthenium atoms of the cluster unit. There are bimetallic compounds which contain an arene bonding in a related manner and which provide good models for this suggestion [11]. In the second possible interaction with the same two ruthenium atoms the benzene adopts a μ_2-η^4:η^2 bonding mode (see Fig. 3). The former would require the additional formation of bridging CO ligands if the electron count on each ruthenium is to be sustained, while the latter allows for a stepwise comigration of the CO groups. Clearly, the former is the more symmetric and is therefore preferred. Qualitative results show that the toluene analogue, $Ru_5C(CO)_{12}(\mu_3$-η^2:η^2:η^2-$C_6H_5Me)$, undergoes migration at a rate faster than that of benzene. The only other arene analogue prepared contains the *p*-cymene aromatic ring system, and it was found to undergo isomerisation during separation on silica.

Arene exchange

Although the migration of the face-capping benzene in $Ru_5C(CO)_{12}(C_6H_6)$ to a terminal position is known to proceed via a non-dissociative mechanism, attempts were made to exchange the benzene for other arenes. It is known that in some systems in which the arene apparently adopts only the η^6 terminal bonding mode, e.g. $Co_4(CO)_9(\eta^6$-arene) and $H_2Os_4(CO)_{10}(\eta^6$-arene), arene exchange occurs quite readily [12]. It was thought that for the pentaruthenium complexes an arene could enter the cluster system as the benzene slipped to a terminal site, and ultimately displace the benzene ligand. However, thermolysis of $Ru_5C(CO)_{12}(\mu_3$-η^2:η^2:η^2-$C_6H_6)$ in toluene, xylene or mesitylenc gavc no indication of simple arene exchange. Other attempts to exchange the face-bound ring in the hexaruthenium system $Ru_6C(CO)_{14}(\mu_3$-η^2:η^2:η^2-$C_{16}H_{16})$ ($C_{16}H_{16}$ = [2.2]paracyclophane) in a similar manner proved to be equally unrewarding. Bis(arene) products of formula $Ru_6C(CO)_{11}(\mu_3$-η^2:η^2:η^2-$C_{16}H_{16})(\eta^6$-arene) were isolated from these reactions in low yield. Formulation of these bis(arene) products was made from IR spectroscopy and a knowledge of the prefered bonding of the respective arenes. We have already established that the tendency for arenes to adopt a facial position follows the order $C_{16}H_{16} > C_6H_6 > C_6H_5Me > C_6H_4Me_2$. Clearly, once an arene ring is bonded to either the penta- or hexaruthenium carbido clusters, regardless of the coordination mode, they are not readily displaced. Addition of donor solvents to facilitate such an exchange process or use of photolysis also seems of little consequence.

Relationship to surface chemistry

For metal surfaces, various adsorption sites have been recognised, some remain controversial, the most important are illustrated in Fig. 4; these being the so called 'Hollow' ($C3_{v\sigma d}$ or $C2_{v\sigma v}$), 'On top' (C_{6v}) and 'Bridge' (C_{2v}) symmetry sites [13]. In each case, the chemisorbed benzene remains intact, lying parallel to the metal surface. Benzene molecules have been observed in bridged sites on Pt(111) and Pd(111) crystal faces [14, 15], and in a hollow $C3_{v\sigma d}$ site on Rh(111) surfaces [16], both sites requiring the additional presence of CO. It would therefore appear that the co-chemisorption of C_6H_6 and CO generates new benzene arrangements (i.e. hollow and bridge sites) not present when benzene is adsorbed alone; this has been attributed to metal mediated charge transfer effects from benzene to CO [17]. In our studies we have observed by X-ray crystallography three of these four bonding types on metal clusters (or at least near to the ideal bonding). The 'On top' site is clearly analogous to the η^6 bonding

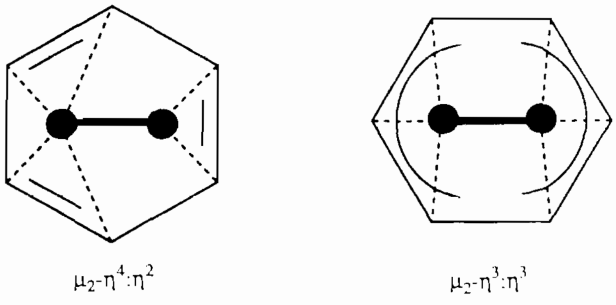

Fig. 3. Sketches illustrating the possible bonding of benzene in the transition state molecule in the isomerisation of $Ru_5C(CO)_{12}(\mu_3$-η^2:η^2:η^2-$C_6H_6)$ to $Ru_5C(CO)_{12}(\eta^6$-$C_6H_6)$.

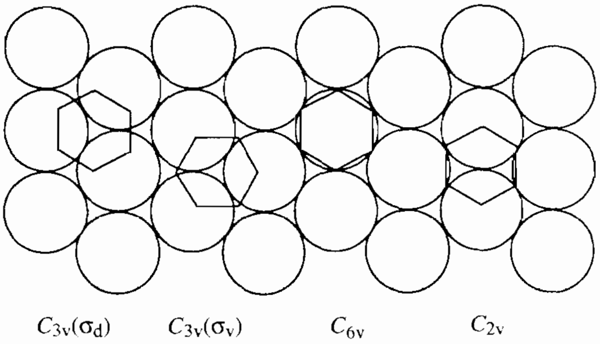

Fig. 4. The possible adsorption sites for benzene on a close-packed metal surface.

TABLE 2. IR spectra (ν(CO), cm^{-1}) recorded in dichloromethane

$Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$	2085 (m), 2063 (s), 2028 (s, sh), 2014 (s), 1890 (w, br).
$Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$	2077 (m), 2048 (s), 2033 (s, sh), 2010 (s).
$Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})$	2076 (w), 2039 (s), 2024 (vs), 1982 (w, br), 1940 (w, br), 1814 (w, br).
$Ru_6C(CO)_{11}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})$-($\eta^6$-arene)	2031 (s), 1996 (vs), 1944 (w), 1788 (w, br).

mode observed throughout transition metal arene chemistry. Both 'Hollow' symmetry sites have now been established in clusters in the solid state, although both deviate slightly from ideal symmetry. Face-capping benzene on clusters of differing metal and size (Ru3, Os3, Ru5, Ru6 and Os6) all show a bonding type analogous to the $C3_{v\sigma d}$ chemisorbed state. The mid-points of the C–C bonds lie over the metal atoms, although not precisely.

With [2.2]paracyclophane, a near eclipsing conformation of the C atoms of the ring with the ruthenium triangular face in $Ru_6C(CO)_{11}(\mu_3\text{-}C_{16}H_{16})(\mu_2\text{-}\eta^2:\eta^2\text{-}C_6H_8)$ is apparent, thus the coordination mode can be described as $\mu_3\text{-}\eta^1:\eta^1:\eta^1$ which is essentially that of the alternative 'Hollow' site, viz. $C3_{v\sigma v}$. The 'Bridge' (C_{2v}) symmetry site is yet to be established in M_3 or even bigger cluster systems. However, it is this which we postulate as the transition state in the isomerisation of benzene from a facial site to an η^6 terminal position, i.e. a bridging $\mu_2\text{-}\eta^3:\eta^3$ group, and is found in dinuclear species recently characterized [11]. Migration of benzene across a metal surface is important with respect to catalysis [18], although little is known about the mechanisms of such processes.

The C_6 ring of benzene in a hollow site is expanded, and exhibits in-plane Kekulé distortions: C–C bond distances alternate between 1.31(15) and 1.81(15) in Rh(111)/C_6H_6/CO [19], the short bonds lying above single metal atoms while the long C–C bonds straddle the metal–metal bonds. These features are remarkably similar to the analogous $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ benzene in metal clusters, although there are differences in the extent of localisation. The chemisorbed analogue of the $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ benzene, viz. benzene chemisorbed at a 'Hollow' site [20], exhibits the customary alternation of C–C bond lengths, the difference between long and short bonds being $\Delta = 0.50$ Å. The estimated standard deviations associated with this are large, and in the limiting case the difference is $\Delta = 0.20$ Å. In the triruthenium cluster, $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$, $\Delta = 0.04$ Å, which increases to $\Delta = 0.08$ Å in $[Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ [21], and for hexaruthenium clusters, the difference in bond length is typically $\Delta = 0.09$ Å. Although these observations are limited to only three cluster sizes, there is a clear trend showing that as nuclearity increases, the Kekulé distortions in the benzene ring increase accordingly. As long as this is taken into account, then reasonable analogies between the surface and cluster could be made between the regimes. Clearly, crystallographic studies of $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ benzene rings attached to larger clusters would be beneficial to confirm this pattern. It is possible, however, to estimate that a cluster of approximately thirty metal atoms would show distortions of the same order as a metal surface (assuming a linear relationship). This estimate is consistent with calculations which indicate that a cluster of metal atoms becomes metal-like at nuclearities ranging from 25 to 50 atoms [22].

Experimental

The cluster $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ was prepared according to the literature method [8b]. Toluene and *p*-cymene analogues were prepared in the same manner as that reported for benzene, merely exchanging cyclohexadiene for dihydrotoluene and dihydro-*p*-cymene, respectively, both of which were purchased from Aldrich Chemicals and used without further purification. The ^{1}H NMR measurements were made on a Bruker WM200 spectrometer, referenced to TMS. Line narrowing was applied prior to measurement of the peaks.

Thermolysis of $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ in octane–arene

In a typical reaction, the compound, $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ (10–15 mg) was heated to reflux in a solution of octane–arene (arene = toluene, xylene or mesitylene, 10% vol./vol.) for 6 h. The solvent was then removed *in vacuo* and the residue redissolved in a minimum amount of dichloromethane, and the product extracted by TLC eluting with dichloromethane–hexane (1:4). One black band was seen to elute, this was extracted and characterised on the basis of spectroscopic evidence as $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$ ($\sim$10%).

Thermolysis of $Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})$ *in octane–arene*

Typically, the compound, $Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})$ (20 mg) was heated to reflux in a solution of octane–arene (arene = toluene, xylene or mesitylene, 10% vol./vol.) for 6 h. The solvent was then removed *in vacuo* and the residue redissolved in a minimum amount of dichloromethane, and the products isolated by TLC using dichloromethane–hexane (1:4) as eluent. In order of elution, an orange and a brown band were extracted. The orange band was characterised as unreacted starting material ($\sim$10%), the brown band as a bis-arene product of formula $Ru_6C(CO)_{11}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})(\eta^6\text{-arene})$ ($\sim$10%).

IR (ν(CO)) stretching frequencies for these clusters are found in Table 2.

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