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The synthesis of ruthenium and osmium carbonyl clusters with unsaturated organic rings [1]

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Contents

Abstract

The reactivity of some ruthenium and osmium carbonyl clusters towards unsaturated organic ligands is described.

Keywords: Cluster; Arene; Carbonyl; Ruthenium; Osmium

1. Introduction

The interaction of small organic molecules with transition metal clusters has received a great deal of attention over the last few decades. The reasons for this are manifold, but are largely derived from the observation that the structure and reactiv-

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[1] Dedicated to Professor Dr. Kees Vrieze on the occasion of his 25th anniversary as professor of inorganic chemistry.

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ity of organic fragments coordinated to clusters differ from those coordinated to mononuclear complexes and approach the properties observed for those chemisorbed on a metal surface. Clearly, if an organic moiety can adopt a multicentre bonding site on a metal surface it cannot be accurately modelled by a single metal atom, whereas even the smallest cluster may act as a reasonable structural model. When accurate surface structures are obtained and compared with crystallographically determined cluster complexes it has been found that the ligand-cluster, adsorbate-surface interactions are remarkably similar.

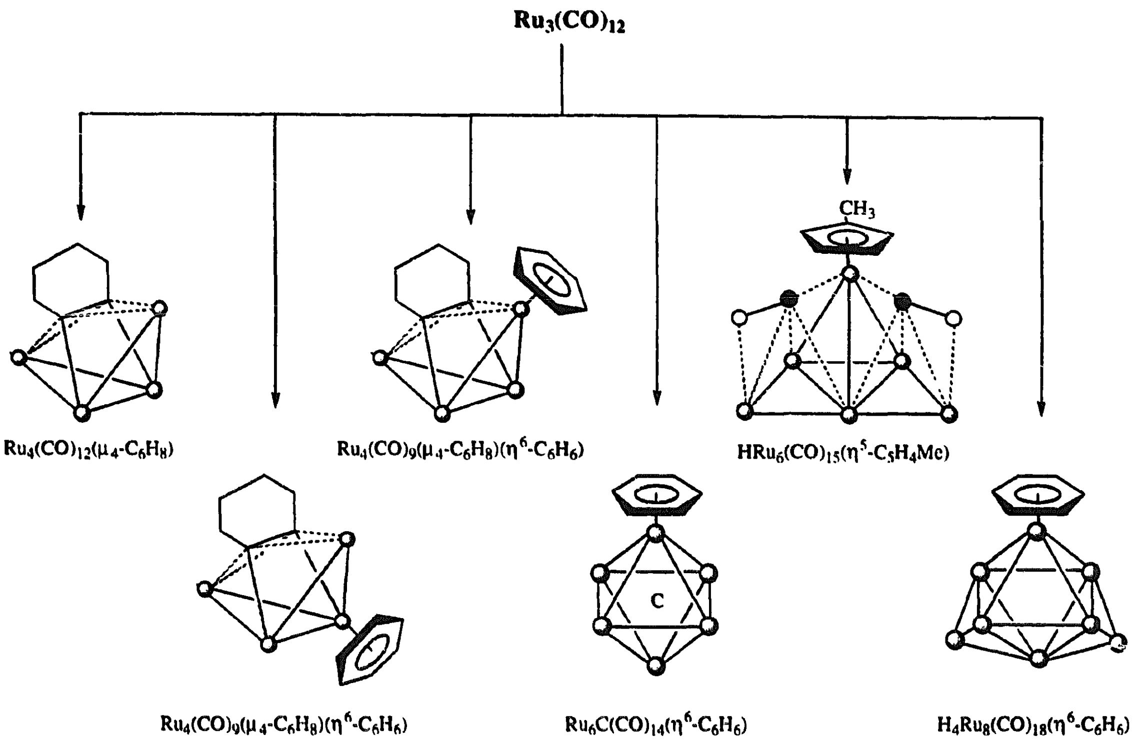
The incorporation of unsaturated organic molecules into transition metal clusters has been well met by the synthetic chemist. The organic molecules employed in these studies are often the same as those used in the organometallic chemistry of mononuclear complexes, *e.g.* alkenes, alkynes, allyls, cyclopentadienyls, arenes and a host of other compounds with one or more unsaturated bonds. These types of compound have been reviewed on numerous occasions and are even beginning to appear in text books [1]. Our research group have directed their efforts towards the synthesis and characterisation of clusters with unsaturated carbocyclic molecules containing between four and eight carbon atoms. We have also prepared metallacycles, while other workers have focused their attention to heterocyclic rings. This article is not intended to be comprehensive; instead, we describe some recent results obtained from our laboratory and also highlight some of the more unusual aspects of this work.

2. Thermal reactions

Thermolysis has been widely employed in the preparation of organometallic cluster-ring complexes. The general method involves direct reaction between a transition metal carbonyl cluster and the appropriate ligand. Simple substitution reactions rarely take place, and a mixture of reaction products with varying nuclearities is usually formed. This comes as no surprise since thermolysis has been used as a means of generating high nuclearity carbonyl clusters of ruthenium and osmium for many years [2].

A recent thermolysis reaction which yielded some intriguing new compounds involves the reaction between [2.2]paracyclophane and $Ru_3(CO)_{12}$ in heptane or octane. Seven cyclophane-clusters with nuclearities ranging from three to eight have been isolated and their relationships explored; this has been reviewed elsewhere [3]. Similarly, thermolysis of $Ru_3(CO)_{12}$ in octane containing cyclohexene yields six products; these comprise: three butterfly clusters, $Ru_4(CO)_{12}(\mu_4\text{-}C_6H_8)$; two isomers of formula $Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\eta^6\text{-}C_6H_6)$, which differ only in the location of the benzene ligand; the hexaruthenium-carbido cluster $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$; the hexanuclear cluster, $HRu_6(CO)_{15}(\eta^5\text{-}C_5H_4Me)$; the *cis*-bicapped octahedral cluster, $H_4Ru_8(CO)_{18}(\eta^6\text{-}C_6H_6)$ (Scheme 1) [4-6].

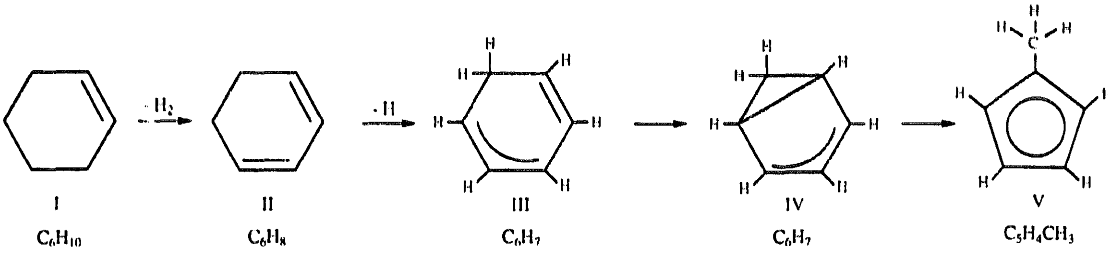
The tetraruthenium butterfly and the hexaruthenium-carbido clusters have both been reported previously, the former as a product from the reaction of $Ru_3(CO)_{12}$ with cyclohexa-1,3-diene in refluxing octane [7], and the latter complex has been prepared by a number of different routes including an extended thermolysis in benzene [8]. Perhaps the most unusual compound obtained from this reaction is



Scheme 1. The products obtained from the thermolysis of $Ru_3(CO)_{12}$ with cyclohexa-1,3-diene in octane.

the one in which the C_6-ring has undergone contraction to form a methylcyclopentadienyl ring, *viz.* $HRu_6(CO)_{15}(\eta^5\text{-}C_5H_4Me)$. The cluster core consists of a tetrahedral Ru_4 arrangement with two edge bridging Ru-atoms thereby forming two *pseudo*-butterflies which are bridged by η^2 carbonyl ligands. This metal geometry is quite unusual, although it has been observed before [9,10]. The methylcyclopentadienyl ligand adopts an η^5 bonding mode. As yet, we have been unable to establish the precise mechanism by which the ring undergoes contraction. However, it is considered that the contraction process must occur after dehydrogenation and a possible mechanism can be postulated (Scheme 2).

The mechanism involves the initial dehydrogenation of the cyclohexene to a cluster-stabilised cyclohexadienyl (C_6H_7) fragment. At this stage transannular addition followed by hydrogen transfer provide a plausible possibility.



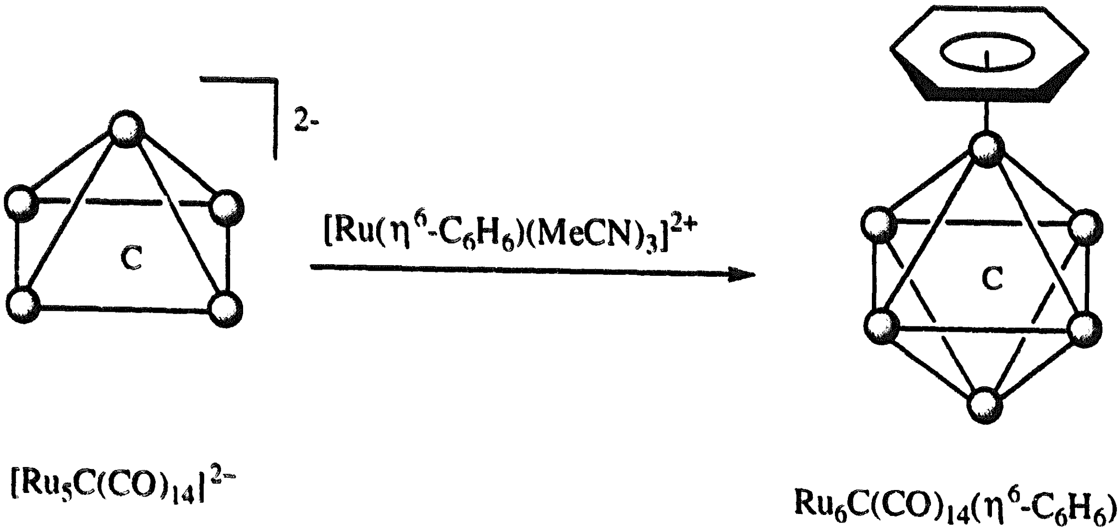
Scheme 2. A possible mechanism for the ring contraction observed in the formation of $HRu_6(CO)_{15}(\eta^5\text{-}C_5H_4Me)$.

3. Ionic coupling reactions

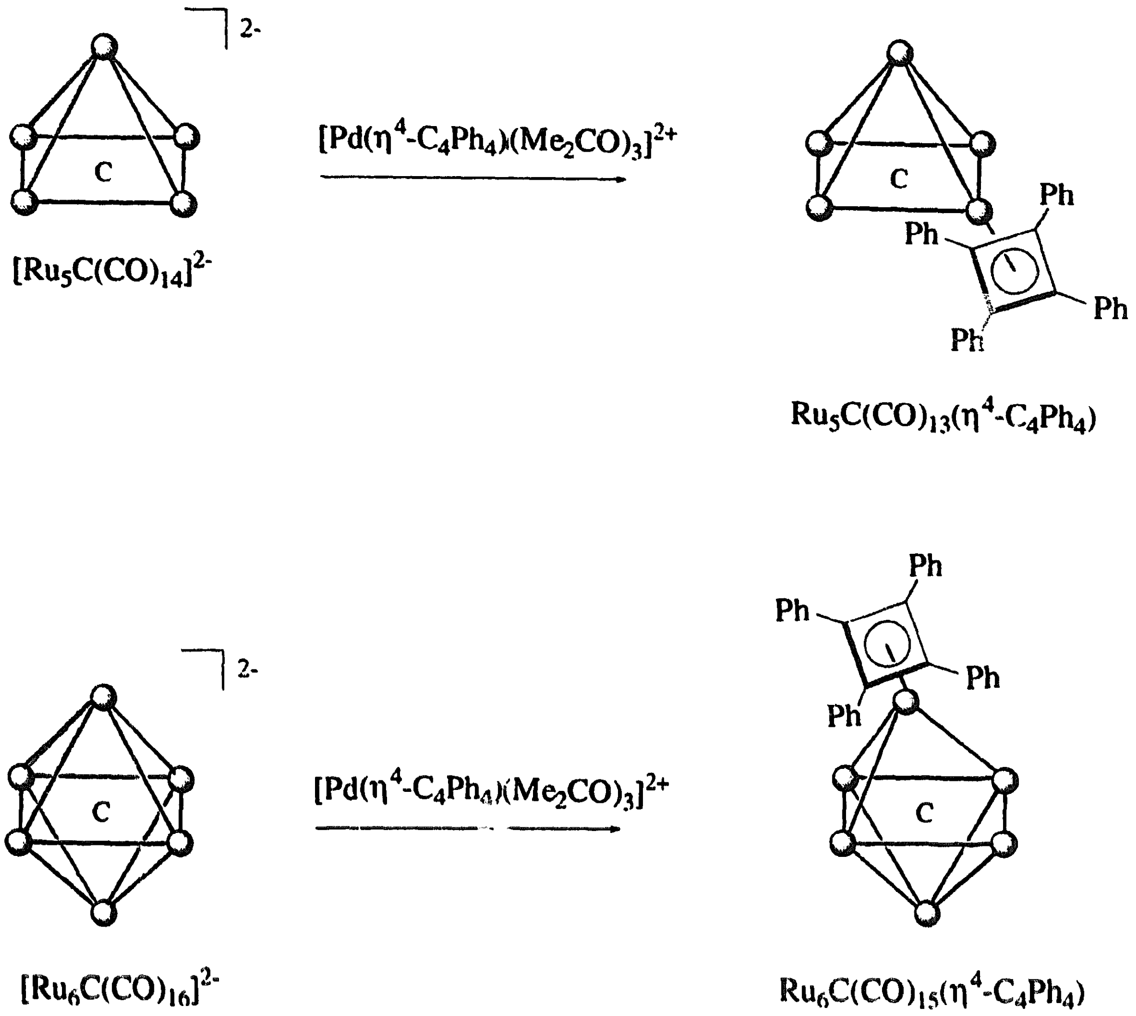
Ionic coupling reactions have been used to synthesise a wide number of clusters, not just those with organic ligands. The introduction of arenes, principally benzene, has been greatly facilitated by the use of the dicationic metal fragment, $[M(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ (M = Ru and Os), which reacts with a variety of dianionic cluster compounds to yield neutral clusters containing the benzene moiety plus one additional metal atom [11–13]. Other arenes, *i.e.* toluene, xylene and mesitylene, have also been introduced into clusters in this way. The first application of this technique was reported for the reaction with the pentanuclear dianion, $[Ru_5C(CO)_{14}]^{2-}$, affording the hexanuclear-carbido cluster, $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$, in almost quantitative yield (Scheme 3) [14].

More recently we used the solvated palladium fragment, $[Pd(\eta^4\text{-}C_4Ph_4)(Me_2CO)_2]^{2+}$, in conjunction with the cluster dianions, $[Ru_5C(CO)_{14}]^{2-}$ and $[Ru_6C(CO)_{16}]^{2-}$ [15]. Instead of obtaining the expected mixed-metal redox condensation products from these reactions, the homonuclear clusters $Ru_5C(CO)_{13}(\eta^4\text{-}C_4Ph_4)$ and $Ru_6C(CO)_{15}(\eta^4\text{-}C_4Ph_4)$ were produced (Scheme 4).

In these redox mediated ligand exchange reactions the palladium fragment is believed to cap a ruthenium face prior to the ligand exchange process. Owing to the steric bulk of the tetraphenylcyclobutadiene ligand it bonds to a basal ruthenium atom in the square-based pyramidal pentaruthenium cluster $Ru_5C(CO)_{13}(\eta^4\text{-}C_4Ph_4)$ which has an Ru–Ru connectivity of three (compared with the apical Ru-atom which has a connectivity of four); in the octahedral cluster the ruthenium atom to which the C_4Ph_4 ligand is coordinated has one considerably elongated Ru–Ru contact, effectively reducing its Ru–Ru connectivity from four to three. The Ru–Ru edges involving the Ru-atom to which the cyclobutadiene ligand is bonded are longer than the distance which is generally considered to constitute a bond (3.213 Å), otherwise the mean Ru–Ru bond length in the cluster is 2.882 Å (with lengths ranging from



Scheme 3. Ionic coupling with an increase in cluster nuclearity.



Scheme 4. Ionic coupling ligand transfer reactions with retention of the cluster nuclearities.

2.823 to 2.968 Å). Extended Hückel calculations were used to compare the structures of this distorted molecule with that of the related binary carbonyl-cluster, $Ru_6C(CO)_{17}$. It was found that the observed structural changes (*i.e.* substitution of two terminal CO ligands by C_4Ph_4) result in a significant reduction in the Ru–Ru reduced overlap population, and consequently a weakened bond.

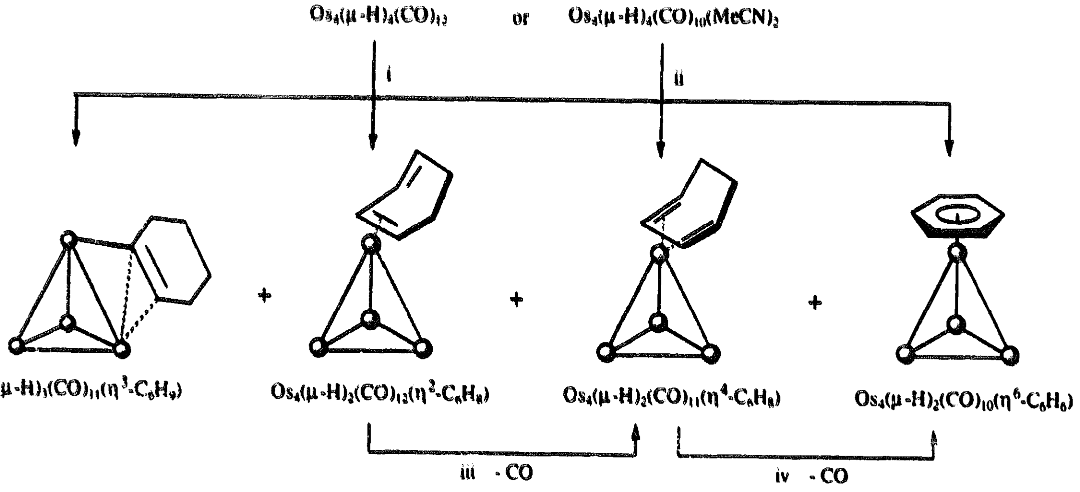
We have also applied this synthetic technique to other clusters. For example, reaction of $[Pd(\eta\text{-}C_4Ph_4)(Me_2CO)_2]^{2+}$ with the octahedral cluster $[Os_6(CO)_{18}]^{2-}$ results in the formation of the bicapped-tetrahedral cluster, $Os_6(CO)_{16}(\eta^4\text{-}C_4Ph_4)$ [16]. The characterisation of this product is based entirely on spectroscopic data, and remains tentative.

4. Chemical activation

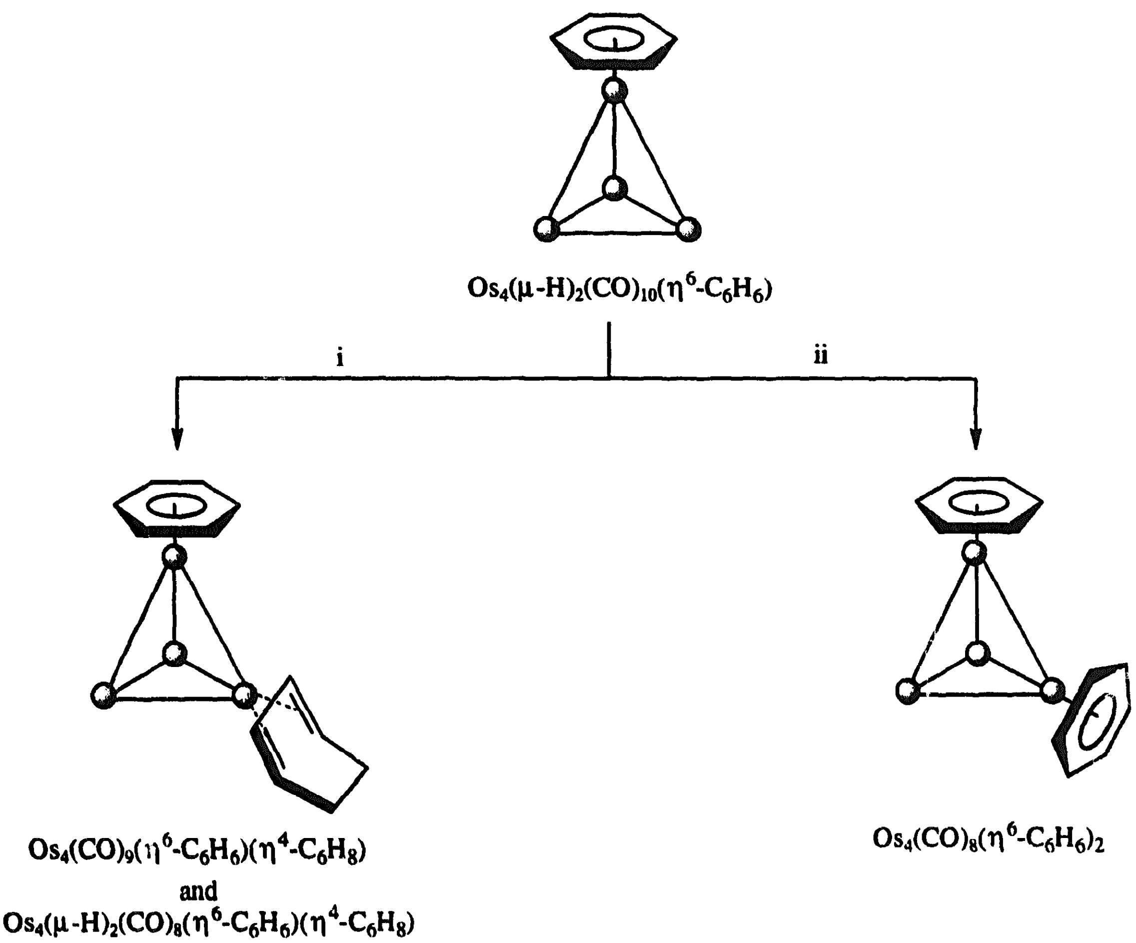
The use of Me_3NO as an oxidative decarbonylation reagent (removing coordinated CO as CO_2) in stoichiometric amounts has been well documented. It is generally used in combination with a coordinating solvent (typically acetonitrile) which is later displaced by a suitable ligand in a subsequent step. Alternatively, Me_3NO can be used in a non-coordinating solvent containing the appropriate ligand so that direct substitution takes place.

For example, the reaction of $Os_4(\mu_2\text{-}H)_4(CO)_{10}(MeCN)_2$ with cyclohexa-1,3-diene in CH_2Cl_2 at room temperature for 6 h, or the direct reaction of $H_4Os_4(CO)_{12}$ with Me_3NO in CH_2Cl_2 in the presence of cyclohexa-1,3-diene gives several products (Scheme 5) [17,18]. The four major compounds obtained include $Os_4(\mu\text{-}H)_3(CO)_{11}(\eta^3\text{-}C_6H_9)$ (previously reported [19]), $Os_4(\mu\text{-}H)_2(CO)_{12}(\eta^2\text{-}C_6H_8)$, $Os_4(\mu\text{-}H)_2(CO)_{11}(\eta^4\text{-}C_6H_8)$ and $Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)$. In a series of separate experiments we have further established that on heating $Os_4(\mu\text{-}H)_2(CO)_{12}(\eta^2\text{-}C_6H_8)$ in hexane it undergoes conversion to compound $Os_4(\mu\text{-}H)_2(CO)_{11}(\eta^4\text{-}C_6H_8)$, which in turn undergoes conversion to compound $Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)$. Clearly, the clusters, $Os_4(\mu\text{-}H)_2(CO)_{12}(\eta^2\text{-}C_6H_8)$, $Os_4(\mu\text{-}H)_2(CO)_{11}(\eta^4\text{-}C_6H_8)$ and $Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)$, emerge as a closely related series. As a CO ligand is lost, additional electron-pair donation from the C_6-ring is observed, paralleling the change from an η^2 to an η^4 and then to an η^6 bonding configuration. The conversion of the diene ligand to benzene necessitates not only the loss of a CO ligand, but also the concomitant cleavage of two C–H bonds and loss of H_2.

The photochemistry of these derivatives has also been investigated. On irradiation in toluene and in the presence of cyclohexa-1,3-diene, the same range of derivatives are produced as those obtained from the thermal route. Another activated cluster, $Os_4(\mu\text{-}H)_4(CO)_{11}(NMe_3)$ reacts similarly. Again, in a separate experiment, we have established that on irradiation $Os_4(\mu\text{-}H)_2(CO)_{11}(\eta^4\text{-}C_6H_8)$ is smoothly converted into $Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)$. These observations lead us to believe that the same process, *i.e.* CO-ejection, is the primary step for both the thermal and photolytic reactions; by this means 58-electron coordinatively unsaturated intermediate compounds are formed, and these then undergo reaction with the appropriate substrate.



Scheme 5. Products obtained from the reaction of $Os_4(\mu_2\text{-}H)_4(CO)_{10}(MeCN)_2$ with cyclohexa-1,3-diene. *Reagents*: (i) C_6H_8/3 eq. Me_3NO; (ii) C_6H_8; (iii) and (iv) Δ/hexane.



Scheme 6. Reaction of $Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)$ with cyclohexa-1,3-diene and benzene. Reagents: (i) C_6H_8, 3 eq. Me_3NO; (ii) C_6H_6, 3 eq. Me_3NO.

The product $Os_4(\mu\text{-}H)_3(CO)_{11}(\eta^3\text{-}C_6H_9)$ is commonly observed under all reaction conditions studied. For this product to be formed, the cyclohexa-1,3-diene is required to undergo partial hydrogenation and C–H bond formation, and also C–H cleavage and C–C σ-bond formation. This cluster does not appear to be an active intermediate in the formation of clusters $Os_4(\mu\text{-}H)_2(CO)_{12}(\eta^2\text{-}C_6H_8)$, $Os_4(\mu\text{-}H)_2(CO)_{11}(\eta^4\text{-}C_6H_8)$ and $Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)$; instead, it appears to undergo conversion into a benzyne derivative [20].

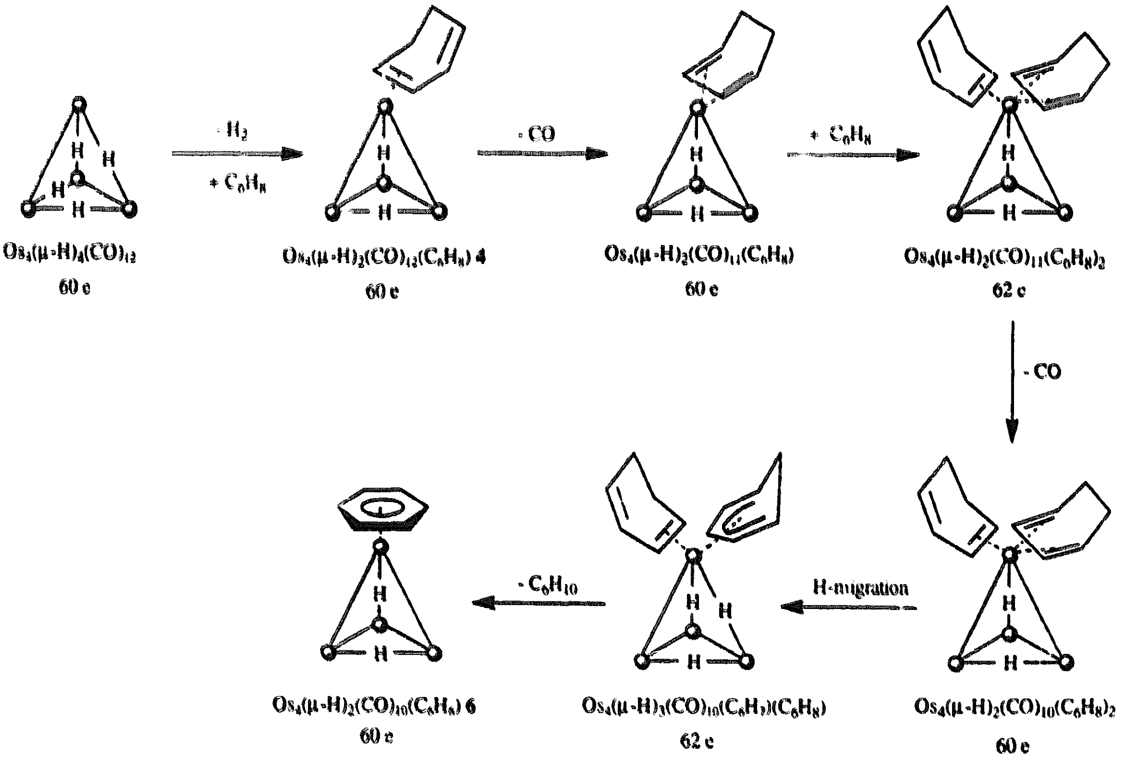
$Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)$ undergoes further reaction with Me_3NO in the presence of cyclohexa-1,3-diene to produce $Os_4(CO)_9(\eta^4\text{-}C_6H_8)(\eta^6\text{-}C_6H_6)$ and $Os_4(\mu\text{-}H)_2(CO)_8(\eta^4\text{-}C_6H_8)(\eta^6\text{-}C_6H_6)$. If benzene is used in the place of cyclohexa-1,3-diene a new product, tentatively characterised as $Os_4(CO)_8(\eta^6\text{-}C_6H_6)_2$, results in low yield (Scheme 6).

It is known that the tetranuclear cobalt cluster $Co_4(CO)_9(\eta^6\text{-}C_6H_6)$ readily undergoes arene exchange with C_6H_5Me, $C_6H_4Me_2$ and $C_6H_3Me_3$ [21]. In contrast, the face-capping benzene moieties found in clusters based on Ru_3, Os_3 and Ru_6C units are far more resistant to exchange. We have attempted to carry out arene exchange reactions with a wide range of clusters but with only very limited success [22]. However, we have found that the tetraosmium cluster, $Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)$, undergoes arene exchange [23]; by heating in toluene $Os_4(\mu\text{-}H)_2(CO)_{10}(C_6H_5Me)$ is produced and on heating in octane in the presence of xylene $Os_4(\mu\text{-}H)_2(CO)_{10}(C_6H_4Me_2)$ is formed. There is no evidence to suggest that these substitutions are reversible.

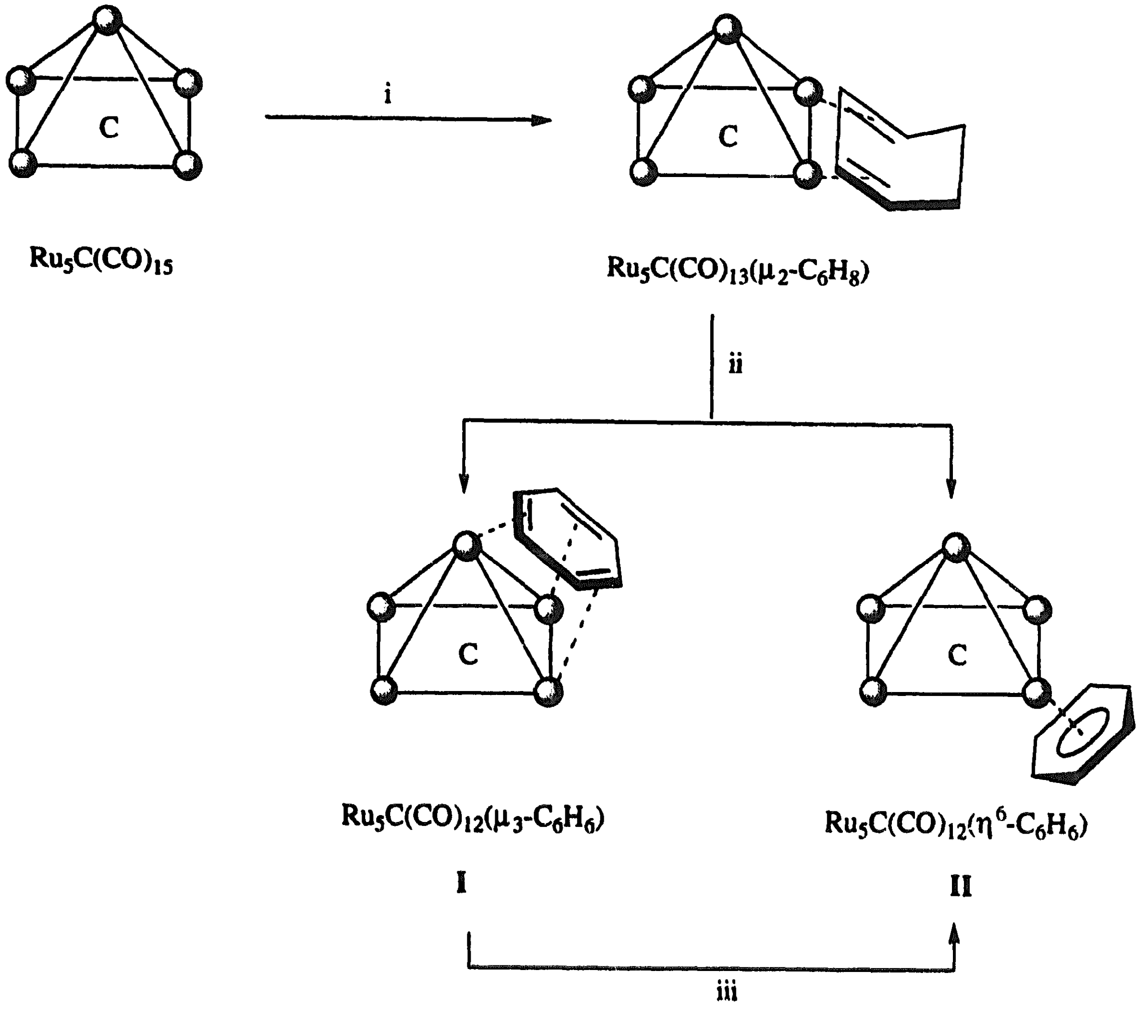
The mechanism by which some of these conversions take place is of some interest. We tend to believe that, given the formation of $Os_4(\mu\text{-}H)_3(CO)_{11}(\eta^3\text{-}C_6H_9)$ involves both the hydrogenation and isomerisation of coordinated cyclohexa-1,3-diene and that the formation of $Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)$ involves the dehydrogenation of the same diene, the reaction sequence requires both the presence of a "sacrificial" and a "benefactor" molecule of cyclohexa-1,3-diene and suggests the mechanism shown in Scheme 7.

A series of benzene clusters based on the square-pyramidal cluster, $Ru_5C(CO)_{15}$, have also been synthesised using a systematic approach involving the direct reaction of the cluster with cyclohexadiene and Me_3NO (Scheme 8) [24]. Using two equivalents of Me_3NO the diene cluster, $Ru_5C(CO)_{13}(\mu_2\text{-}C_6H_8)$, is produced. This cluster, which contains an edge bridging diene moiety, undergoes reaction with a further molecular equivalent of Me_3NO in dichloromethane to give two isomeric benzene products, $Ru_5C(CO)_{12}(\mu_3\text{-}C_6H_6)$ **I** and $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$ **II**; in this latter complex the benzene is bonded to a ruthenium atom on the base of the square pyramid.

The proposed mechanism for the conversion of the diene to the benzene in this



Scheme 7. A possible mechanism for the formation of $Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)$.



Scheme 8. The synthesis of benzene derivatives of $Ru_5C(CO)_{15}$. *Reagents*: (i) C_6H_8/2 eq. Me_3NO; (ii) 1 eq. Me_3NO; (iii) Δ/hexane.

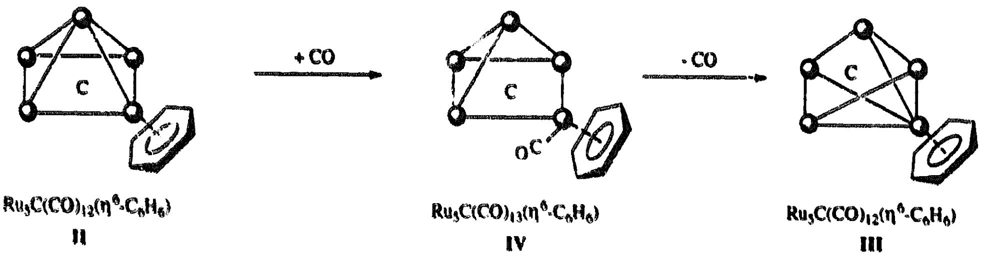
reaction is believed to involve a cyclohexadienyl intermediate. The first step in the dehydrogenation process may be envisaged as the creation of a vacant coordination site on the cluster surface by the oxidative removal of CO to CO_2 by Me_3NO. This is followed by the oxidative addition of a C–H bond of the diene to generate the hydrido-hexadienyl cluster $HRu_5C(CO)_{12}(C_6H_7)$, in which the C_6H_7 moiety is expected to lie over a trimetal face. The required second C–H bond cleavage must occur by an alternative route since only one equivalent of Me_3NO is required. One can speculate that this second C–H cleavage is brought about by an initial cluster rearrangement, probably *via* a square-pyramidal to bridged-butterfly interconversion. This type of interconversion is well documented for $Ru_5C(CO)_{15}$ upon reaction with small nucleophiles [25], and will be elaborated shortly. Such an interconversion would generate an activated coordination site, providing the driving force for the second required C–H bond cleavage, and hence the formation of the bridged-butterfly species $H_2Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$. Evolution of dihydrogen would result in regeneration of the square-pyramidal Ru_5C unit, and hence, $Ru_5C(CO)_{12}(\mu_3\text{-}C_6H_6)$.

Upon mild thermolysis in hexane, $Ru_5C(CO)_{12}(\mu_3\text{-}C_6H_6)$ **I** can be quantitatively and irreversibly converted into $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$ **II**. A third isomer, in which the benzene bonds solely to the apical metal of the pyramid (**III**), can be produced *via* the intermediacy of a bridged butterfly complex (**IV**) upon nucleophilic addition of $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$ **II** with CO in dichloromethane under ambient conditions (see Scheme 9). In this reaction, cleavage of an Ru–Ru bond along the apical-basal edge involving the ruthenium atom to which the benzene ring is attached has taken place. The new bridged butterfly cluster, $Ru_5C(CO)_{13}(\eta^6\text{-}C_6H_6)$ **IV**, affords the apical-isomer on expulsion of the "additional" carbonyl moiety, on standing under N_2. On heating the apical-isomer **III** in hexane for a prolonged period conversion to the basal-isomer **II** occurs.

The benzene-clusters $Ru_5C(CO)_{12}(\mu_3\text{-}C_6H_6)$ **I** and $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$ **II** react further with Me_3NO and cyclohexa-1,3-diene to yield the benzene–diene species $Ru_5C(CO)_{10}(\mu_3\text{-}C_6H_6)(\mu_2\text{-}C_6H_8)$ and $Ru_5C(CO)_{10}(\eta^6\text{-}C_6H_6)(\mu_2\text{-}C_6H_8)$ [26]. Thus far it has not been possible to convert these benzene–diene complexes into *bis*(benzene) derivatives.

Reaction of $Ru_5C(CO)_{15}$ with cyclohexa-1,4-diene, in an analogous method to that described above, results in the isolation of the $Ru_5C(CO)_{13}(\mu_2\text{-}C_6H_8\text{-}1,4)$ [27]. In this compound the 1,4-diene has retained its unconjugated form. In all other cases employing cyclohexa-1,4-diene, isomerisation to the 1,3-diene takes place on coordination. The subsequent chemistry of $Ru_5C(CO)_{13}(\mu_2\text{-}C_6H_8\text{-}1,4)$ is analogous to that described for the other isomer. A second cyclohexa-1,4-diene may also be introduced into the cluster and the diene ligands in the resulting product, $Ru_5C(CO)_{11}(\mu_2\text{-}C_6H_8\text{-}1,4)_2$, occupy different sites which may undergo exchange detectable on the NMR time scale (see below).

An isomer of this compound, $Ru_5C(CO)_{11}(\eta^4\text{-}C_6H_8)_2$, in which 1,3-dienes bond in η^4 fashion to alternate Ru-atoms on the square-base has also been prepared [26]. This compound reacts with CO under ambient conditions to give $Ru_5C(CO)_{12}(\mu_3\text{-}C_6H_6)$ **I** and $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$ **II**. Whilst this reaction does not seem straightforward to rationalise, we believe the mechanism involves the square based pyramid↔trigonal bipyramid interconversion common to this system. Initial uptake of CO would result in cleavage of a Ru–Ru bond, and on reformation of the square-based pyramidal core, expulsion of one diene ring must take place rather than loss of CO. The same mechanism in operation for the conversion of the diene to benzene (see above) can now be applied.



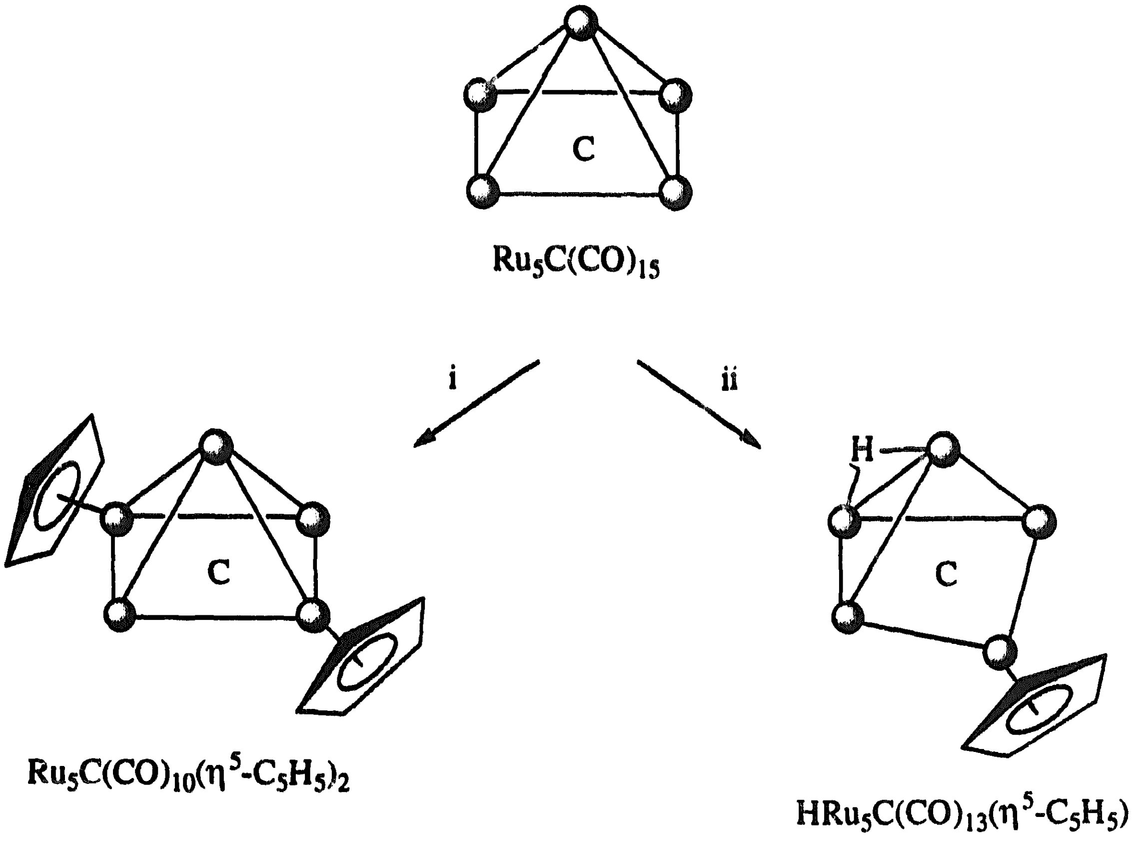
Scheme 9. The reversible reaction of $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$ with CO.

Cyclopentadienyl rings may also be introduced into the cluster using Me_3NO in the presence of C_5H_6 yielding the *bis*(C_5H_5) complex, $Ru_5C(CO)_{10}(\eta^5\text{-}C_5H_5)_2$ [28]. A *mono*(C_5H_5) cluster, $HRu_5C(CO)_{13}(\eta^5\text{-}C_5H_5)$, may be prepared but from an entirely different route [29]. This involves the reaction of $Ru_5C(CO)_{15}$ with NaC_5H_5 followed by the addition of HBF_4. The structure of the metal atom skeleton in $Ru_5C(CO)_{10}(\eta^5\text{-}C_5H_5)_2$ remains unchanged from that of the starting material, whereas that of $HRu_5C(CO)_{13}(\eta^5\text{-}C_5H_5)$ constitutes a bridged-butterfly arrangement (Scheme 10).

Apart from the work carried out on the Os_4 and Ru_5C clusters, similar chemistry has also been developed for other cluster systems, in particular, based on Ru_3 [30] and Ru_6C [31] cluster cores.

5. Photolysis

Photolysis has been used to prepare a range of tricobalt clusters in which photochemically reactive fragments are generated [32]. However, photolysis has only been used with limited success in the preparation of ruthenium clusters [33] although it has proved very useful in bringing about certain isomerisations and rearrangements.

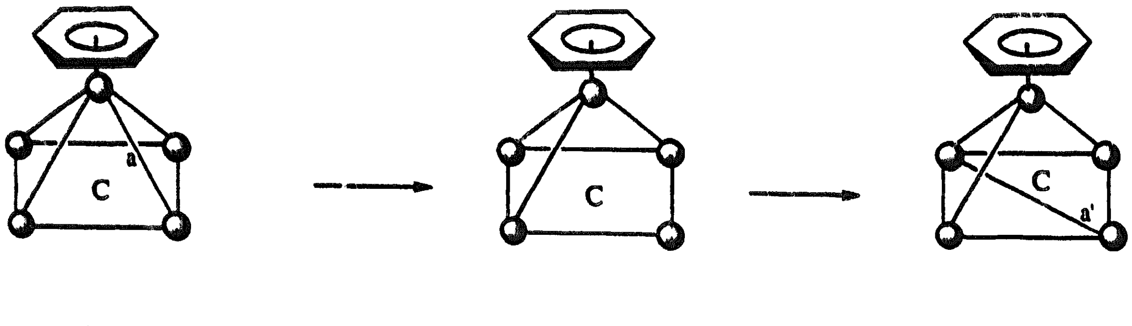


Scheme 10. The synthesis of cyclopentadienyl derivatives of $Ru_5C(CO)_{15}$. *Reagents*: (i) C_5H_6/5 eq. Me_3NO; (ii) NaC_5H_5 followed by HBF_4.

Two systems which have been studied by thermolysis in some depth include the pentaruthenium system (see above), and the triosmium system, $Os_3(CO)_9(\mu_3\text{-}C_6H_6)$. In $Ru_5C(CO)_{12}(C_6H_6)$, three structural forms based on the location of the benzene ligand about the central Ru_5C core have been identified, *i.e.* $Ru_5C(CO)_{12}(\mu_3\text{-}C_6H_6)$ **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 [34]. Heating **I** in hexane for 4 h results in quantitative conversion to **II** (Scheme 8). The preparation of isomer **III** is less straightforward; it involves first the formation of the bridged-butterfly adduct, $Ru_5C(CO)_{13}(\eta^6\text{-}C_6H_6)$, 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. Heating **III** for 40 h in hexane results in its irreversible conversion to **II**. This thermolysis was monitored by infrared spectroscopy: at no stage during the process was the presence of **I** observed, thereby ruling out the possibility of the facial isomer being an intermediate, and hence the need to consider a second alternative. 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 firstly Ru–Ru edge cleavage and then recombination (Scheme 11). The process involves cleavage of edge (a) (Ru_{apex}–Ru_{basal}) to generate the intermediate with a bridged-butterfly structure and then the formation of the new edge (a′) to regenerate the (new) square pyramidal structure. This *pseudo*rotation has the effect of *apparently* transferring 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 this work we believe that good evidence has been obtained for a mechanism related to this second type, although of course we are unable to differentiate between initiation involving a heterolytic or a homolytic bond fission. The compound, $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$ **II**, embedded within a polymethylmethacrylate (PMMA) film was photolysed for about 2 h, during which time its infrared spectrum was recorded every 10 min. Careful examination of the infrared spectra showed that as time progressed, an initial transformation from **II** to **III** takes place, and that cluster **I** is then generated from it.

The conversion of **II** to **III** found in the PMMA film is the reverse of that observed



Scheme 11. Proposed mechanism for the thermal isomerisation of **III** to **II**.

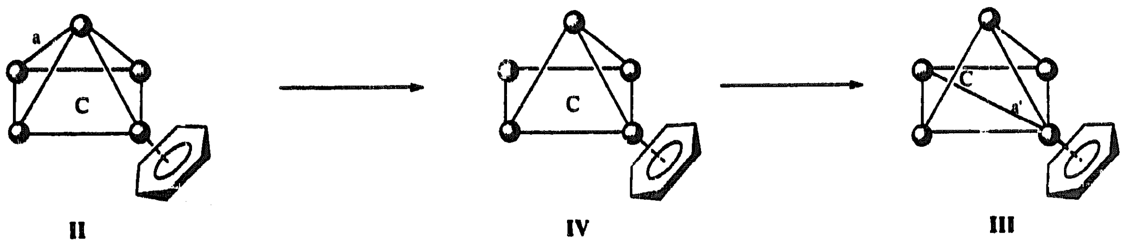
in solution, but clearly, since **I** is produced after the formation of **III** it cannot serve as the appropriate intermediate. However, the second mechanistic approach is probably responsible, *i.e.* *pseudo*rotation by Ru–Ru edge cleavage to bring about the correct rearrangement (Scheme 12). The thermal process is believed to proceed *via* the *heterolytic* bond fission pathway outlined above, whereas the photolytic process more probably proceeds *via* *homolytic* fission and the formation of a *diradical* intermediate. Nevertheless, from the geometric standpoint the nature of the proposed intermediates **IV** and **V** must be similar.

Photolysis of the triosmium–benzene cluster, $Os_3(CO)_9(\mu_3\text{-}C_6H_6)$ results in photoisomerisation to the dihydrido–benzyne cluster, $H_2Os_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_6H_4)$ [35]. The reverse process, however, has not been observed. Photolysis of the ruthenium analogue, $Ru_3(CO)_9(\mu_3\text{-}C_6H_6)$, results in its slow decomposition.

6. Chemical-induced migrations

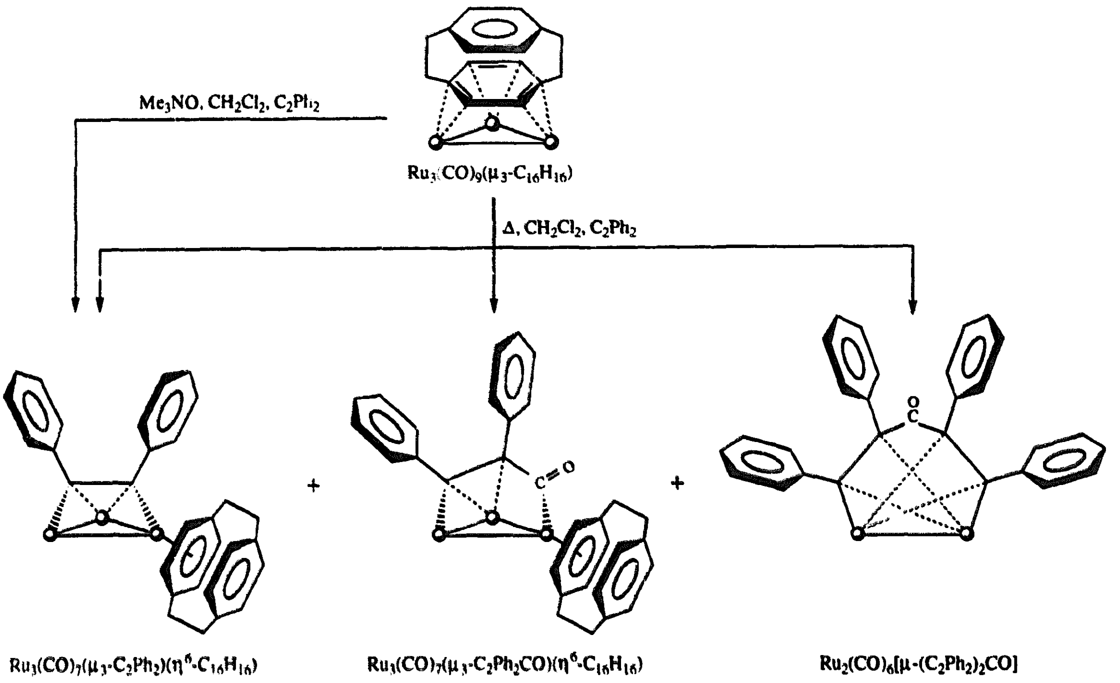
On reaction with alkynes, the benzene clusters, $M_3(CO)_9(\mu_3\text{-}C_6H_6)$ (M = Ru, Os), afford compounds in which the benzene has undergone migration from a face-capping to a terminal site with the alkyne adopting a face-capping position. The only difference between the corresponding reactions of the ruthenium [36] and osmium [37] derivatives is that, in the case of the ruthenium complex, a carbonyl group inserts between the alkyne ligand and the metal atom carrying the benzene moiety.

We have found that the reaction of the [2.2]paracyclophane cluster, $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})$, towards alkynes is somewhat more complicated [38]. It reacts with diphenylacetylene under two sets of conditions (thermal and chemical activation) to give the same major product, $Ru_3(CO)_7(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Ph_2)(\eta^6\text{-}C_{16}H_{16})$. In the thermal reaction, two additional products, $Ru_3(CO)_7(\mu_3\text{-}\eta^2\text{-}PhC_2PhCO)(\eta^6\text{-}C_{16}H_{16})$ and $Ru_2(CO)_6(\{\mu_2\text{-}\eta^1{:}\eta^2\text{-}C_2Ph_2\}_2\text{–}CO)$, are also obtained (Scheme 13). It has been found that the relative yields of compounds produced during this reaction depend critically on the thermolysis time, with the diruthenium complex formed in highest yields when the longest reaction period is employed. Clearly, the two trinuclear clusters are analogous to the ones obtained from the ruthenium- and osmium-benzene reactions. The dinuclear complex, $Ru_2(CO)_6(\{\mu_2\text{-}\eta^1{:}\eta^2\text{-}C_2Ph_2\}_2\text{–}CO)$, is highly unusual in that a ketone has been produced *via* a double CO-insertion reaction. While we do not fully understand the mechanism by which this process



II IV III

Scheme 12. Proposed mechanism for the photochemical isomerisation of II to III.



Scheme 13. Products from the reactions of $Ru_3(CO)_9(\mu_3\text{-}C_{16}H_{16})$ with diphenylacetylene.

takes place, it appears, from our observations, that $Ru_2(CO)_6(\{\mu_2\text{-}\eta^1\text{:}\eta^2\text{-}C_2Ph_2\}_2\text{-}CO)$ is derived from $Ru_3(CO)_7(\mu_3\text{-}\eta^2\text{-}PhC_2PhCO)(\eta^6\text{-}C_6H_6)$.

7. Dynamics

We have found that a large number of the organic ligands in these clusters undergo some type of dynamic process. For example, NMR spectroscopy indicates that the rings, whether bonded in terminal or face-capping mode, undergo rapid rotation although the barriers to rotation are slightly higher in the latter [39]. In a *bis*(toluene) cluster, $Ru_6C(CO)_{11}(C_6H_5Me)_2$, we have conducted labelling experiments which demonstrate that the rings migrate over the octahedral metal surface *via* a mechanism involving η^6 and μ_3 bonding interchange [40]. Although there is only limited spectroscopic data, it has been shown that dynamical processes may take place in the solid-state [41]. Calculations would suggest that these process are in fact very common [42].

We shall describe a highly unusual example of site exchange in a pentaruthenium cluster [43]. The ^1H NMR spectrum of $Ru_5C(CO)_{11}(\mu_2\text{-}C_6H_8\text{-}1,4)_2$ at 223 K comprises twelve signals, labelled A–L in Fig. 1, eight of which are of relative intensity one, and four of relative intensity two, with coupling constants of *ca.* 18 Hz and 7 Hz respectively. These data are consistent with the area one signals being due to the geminal CH_2 protons, each of which would be expected to be inequivalent to its partner. A series of homonuclear decoupling/NOE experiments carried out at 223 K showed signals A, B, D, E, F and H belonged to one C_6H_8 moiety, while signals C,

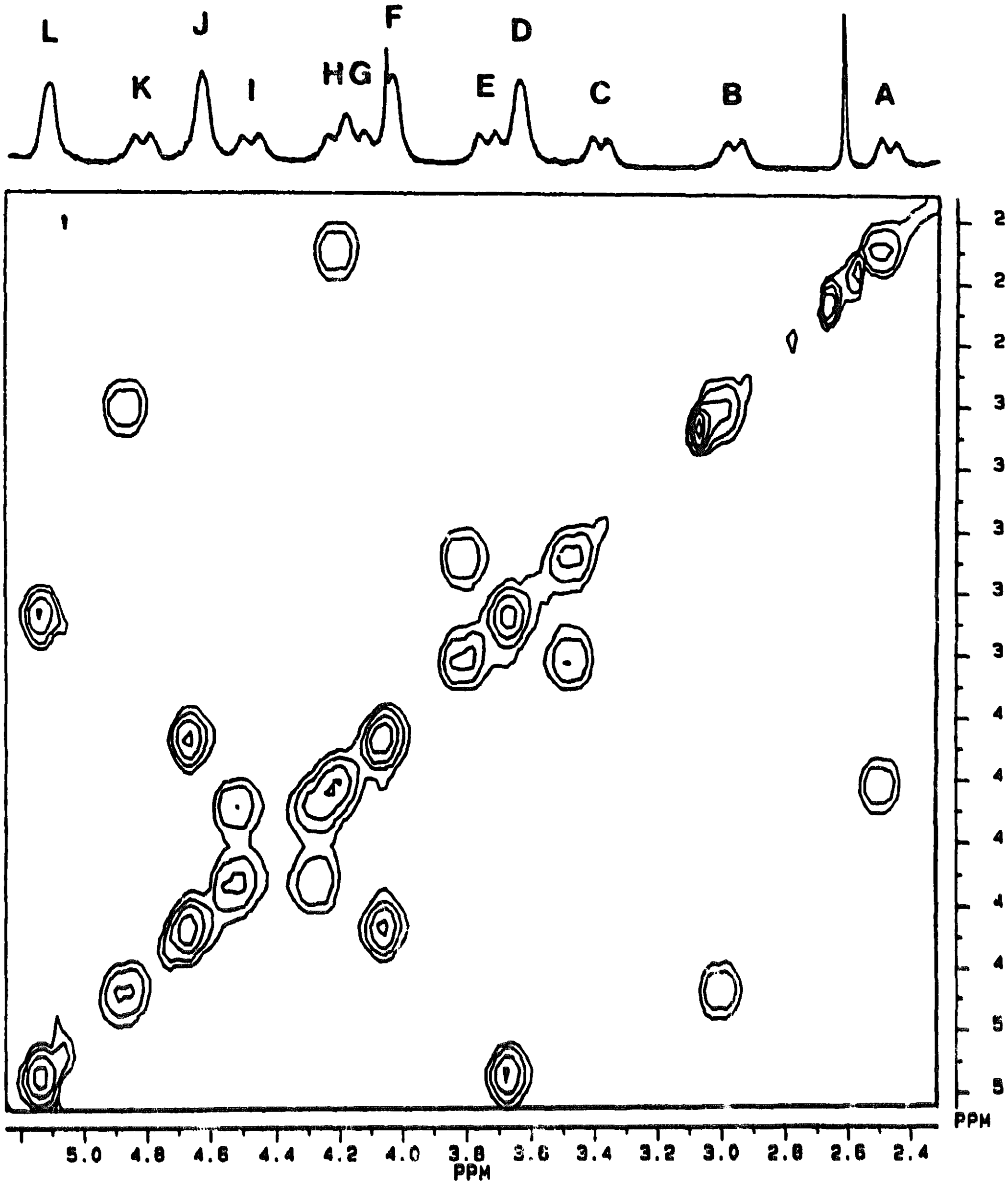


Fig. 1. The 360 MHz ^{1}H spectrum and ^{1}H 2-D EXSY spectrum of $Ru_5C(CO)_{11}(\mu_2\text{-}C_6H_8\text{-}1,4)_2$ obtained at 296 K.

G, I, J, K and L are associated with the other ring. The observation that the spectrum of $Ru_5C(CO)_{11}(\mu_2\text{-}C_6H_8\text{-}1,4)_2$ obtained at 296 K was broader than that obtained at 223 K suggests some exchange process. The EXSY spectrum (Fig. 1) carried out at 296 K, suggests that the two cyclohexadiene ligands begin to undergo site exchange. Cross-peaks are thus found between A and G, B and K, C and E, H and I, D and L, F and J.

It therefore appears that, at 296 K, the system exhibits two-site exchange. For a system exhibiting first-order exchange between two sites in the same molecule, it is possible to relate cross and diagonal peak intensities derived from EXSY spectra to

Scheme 14. The site exchange process in $Ru_5C(CO)_{11}(\mu_2\text{-}C_6H_8\text{-}1,4)_2$. The cyclohexa-1,4-diene ligands have been omitted with only their locations indicated on the scheme.

the exchange rate at the temperature at which the experiment was carried out. Assuming this to be the case, the rate of exchange was calculated as $31 \pm 5\ s^{-1}$ (Scheme 14). Further elevation of the temperature caused significant broadening, such that by 316 K all signals arising from diene ring protons were broadened. By 330 K there appeared to be just two broad signals forming; these gained an apparent doublet structure by 346 K. These signals are at δ values of 4.37 and 3.63 ppm, indicating that rapid rotation and flexing is also taking place. Residual underlying broadness made integration of these signals impossible, and further heating of the sample resulted in irreversible sample decomposition.

8. Summary

We have shown that the range of different synthetic methods commonly employed in the organometallic chemistry of mononuclear complexes may also be used to prepare organometallic cluster complexes. However, the reactions are often more complicated by virtue of the possibility of multicentre bonding and flexible cluster skeletons.

We are also looking at other, less traditional, activation techniques for preparing new compounds. These include the use of lasers [44] and microwaves [45].

Acknowledgements

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