Alkyne and Alkyne-Arene Complexes of Ruthenium.

Ruth Louise Mallors

Doctor of Philosophy.

The University of Edinburgh.

1995.

Declaration

The research presented in this thesis was carried out by the author, Ruth Louise Mallors at the Chemistry Laboratories of The University of Edinburgh between October 1991 and July 1994. It is the authors own original work unless otherwise acknowledged . None of the research described within this thesis has been submitted for any other qualification at any other establishment.

Acknowledgements.

The completion of this thesis would not have been possible without the encouragement and support that I have received over the last three and a half years from a long, long list of colleagues, friends and family.

First and foremost my most sincere thanks go to Professor Brian Johnson who during my time at Edinburgh surpassed 'Supervisor' status as he willingly cajoled and urged me to this point in time. Brian's never ending stream of enthusiasm for his subject was infectious and I thank him for sharing this with me whilst at Edinburgh. My extended thanks also go to Janet Hayes who unwittingly made my short stay at Edinburgh so pleasurable.

This thesis would not have been possible without the continued assistance of the 'workers' within the department, all the technical staff in the nmr and mass spectroscopy labs and personnel in the stores, thank you. Special thanks go to the excellence and patience provided to me by the crystallographers Sandy Blake, Simon Parsons, Jeremy Rawson, Scott Ingram and Dario Braga for the deciphering of incomprehensible numbers into crystal structures. Gratitude is also extended to David Reed in the nmr group for preparing, decoding and plotting of the enclosed COSY nmr spectra.

During my time at Edinburgh I had the good fortune to share lab space with numerous people who managed to either keep me going or calm me down which ever was the necessary evil and I thank them all.

My gratitude is extended to the University of Edinburgh for financial support.

Last but by no means least I wish to thank my family and friends for their patience and encouragement throughout my writing up, it would never have been completed but for them.

Contents.

Chapter Three.

Chapter Four.

Numbering of Compounds.

1. $[Ru_6C(CO)_{17}]$
2. $[Ru_6C(CO)_{15}(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)]$
3. $[Ru_6C(CO)_{14}(\mu:\eta^2:\eta^2\text{-}Me_2C_2)(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)]$
4. $[Ru_6C(CO)_{13}(Me_2C_2)_2]$
5. $[Ru_6C(CO)_{12}(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)_3]$
6. $[Ru_6C(CO)_{10}(Me_2C_2)_4]$
7. $[Ru_6C(CO)_{14}(\mu:\eta^2:\eta^2\text{-}Ph_2C_2)(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)]$
8. $[Ru_6C(CO)_{15}(MeC_2Et)]$
9. $[Ru_6C(CO)_{14}(MeC_2Et)(Me_2C_2)]$
10. $[Ru_6C(CO)(MeC_2Et)(Me_2C_2)_2]$
11. $[Ru_6C(CO)(MeC_2Et)(Me_2C_2)(Ph_2C_2)]$
12. $[Ru_6C(CO)_{12}(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)(\eta^6\text{-}C_6H_6)]$
13. $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)]$
14. $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)]$
15. $[Ru_6C(CO)_{14}(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)(\eta^6\text{-}C_6H_5Me)]$
16. $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4Me_2)]$
17. $[Ru_6C(CO)_{14}(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)(\eta^6\text{-}C_6H_4Me_2)]$
18. $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)]$
19. $[Ru_6C(CO)_{14}(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)(\eta^6\text{-}C_6H_3Me_3)]$
20. $[Ru_6C(CO)_{14}(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$
21. $[Ru_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$
22. $[Ru_6C(CO)_{14}(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$
23. $[Ru_6C(CO)_{14}(Me_2C_2)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$

List of Figures and Schemes Within the Text.

Chapter One.

Chapter Two.

Chapter Three.

Chapter One

Introduction Cluster Alkyne Complexes.

This Chapter will begin with some of the reasons for the study of cluster alkyne complexes. The reaction procedures employed to prepare these complexes will then be discussed followed by a brief electron counting analysis and the interaction of alkynes with metal centres. The Chapter will close with a synopsis of the cluster μ_6-carbido heptadecacarbonyl *hexa*ruthenium which this thesis is based upon.

1.1 The study of Transition Metal Clusters and Alkynes.

Over the past twenty years and more the field of organometallic chemistry has expanded to such an extent that it is now feasible to sub-divide it into integral topics. The content of this thesis is mostly dedicated to the area of alkyne-cluster chemistry and more specifically to the cluster μ_6-carbido heptadecacarbonyl *hexa*ruthenium and it's reactions with some alkynes. The depth of alkyne-cluster chemistry in it's entirety is beyond the scope of this text and only the study of homometallic clusters, in particular the iron triad, will be investigated.

There are two fundamental reasons behind the study of alkyne-cluster complexes. These complexes are believed to be useful models for the chemisorption of small molecules on metal surfaces[1,2] and also for the ability of the cluster to 'activate' the carbon-carbon triple bond upon coordination,[3,4] *i.e.* make the alkyne more susceptible to certain types of reaction. Analogies have been made between the coordination modes of alkynes and carbon monoxide to numerous metal centres on the same cluster and by altering the substituents of the alkyne ligand the number of coordination modes between an alkyne and a cluster increases.[5] In other words the diversity of the alkyne as a ligand is immense and hence the interest in its reactions with cluster fragments. It is believed that the interaction of a small molecule like an alkyne and a molecular metal cluster will mimic interactions of alkynes chemisorbed onto a metal surface, this is commonly referred to as the cluster-surface analogy and has been the subject of many review articles.[1,2,6-10] The advantage of studying discrete molecular clusters as opposed to metal surfaces is that cluster complexes can be analysed by high resolution techniques, for example infrared spectroscopy and nuclear magnetic resonance spectroscopy. These techniques cannot be employed in the study of metal surfaces due to bulk metal characteristics.

It is also believed that an in depth knowledge of alkyne cluster complexes would lead to an improved understanding of homogeneous and heterogenous catalysis exercised in a variety of important industrial processes. However, due to the lack of reliable thermochemical data and only a few examples of clusters behaving as catalysts[11-13] the cluster-surface analogy is something of a debatable point. Nevertheless, the study of alkyne-cluster complexes has emphasised the diversity of the bonding modes available to the hydrocarbon ligand and it is likely that the continued study in this area will provide a greater understanding of processes such as hydrogenation, dehydrogenation, isomerisation, polymerisation, *etc.*.

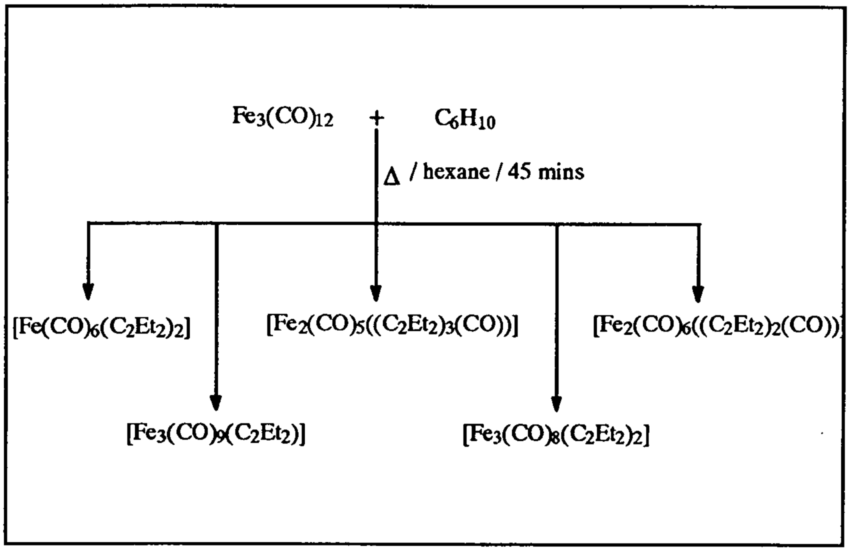
The second reason for the sustained interest in these complexes is the increasing importance of acetylene in industrial processes. Acetylene is returning to the forefront of chemical production as the shortage of oil reserves becomes increasingly obvious. The preparation of acetylene from conventional methods and carbon monoxide/ hydrogen mixtures form coal gas are dated processes and in need of modifications, hence the continued study of this area.[5,14-16]

1.2 Preparative Routes into Cluster-alkyne Complexes.

The study of cluster-alkyne complexes has received considerable attention and reviews have been presented in the literature that cover the majority of aspects in this area.[5,17] The routes employed to access cluster-alkyne derivatives can be split into two categories, thermolytic and chemically activated processes.

1.2.1. Thermolytic Preparation of Cluster-Alkyne Complexes.

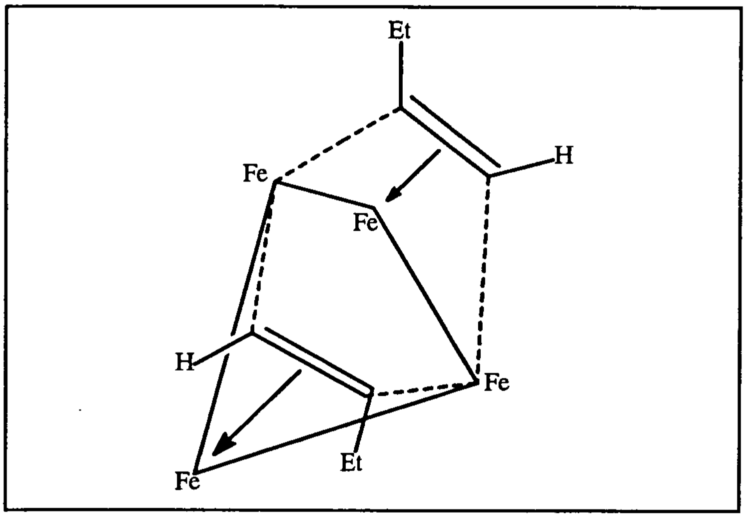
The use of thermolysis in the iron triad, $M_3(CO)_{12}$, (M=Fe, Ru, Os) has been studied to such an extent that conclusions about reaction products can be drawn.[17] The general reaction takes the *tri*-metallic carbonyl unit, $M_3(CO)_{12}$ with the necessary alkyne in an appropriate hydrocarbon under reflux conditions for prolonged periods of time. *Tri*-nuclear products have the general formula $M_3(CO)_{10}L$ or $M_3H(CO)_{10}(L\text{-}H)$ and $M_3(CO)_9L$ or $M_3H(CO)_9(L\text{-}H)$ where L denotes the coordinating alkyne and donates from four to six electrons to the cluster. This type of reaction rarely proceeds without the additional formation of *mono*-, *di*-, and *tetra*-nuclear species. An early example of this type of process is the reaction between *tri*-iron dodecacarbonyl and hex-3-yne in refluxing heptane[18]. It is also apparent that the alkyne is able to react with carbon monoxide obtained from the cluster. Seven products are obtained from this reaction as shown in Scheme 1.2.1(i).



Scheme 1.2.1(i). Reaction products from $Fe_3(CO)_{12}$ plus hex-3-yne.

A *tetra*-iron complex $Fe_4(CO)_{11}(HC_2Et)$[19] has been prepared by the reaction of $Fe_3(CO)_{12}$ in refluxing heptane in the presence of but-1-yne, HC_2Et. The usual tetrahedral arrangement of the metal atoms is not observed in the reaction product.

The four iron atoms are at the vertices of a tetrahedrally distorted square. Each metal atom bears two terminally bound carbonyl ligands, one CO group symmetrically bridges an Fe-Fe edge whilst the remaining two CO's asymmetrically bridge Fe-Fe bonds. The but-1-yne ligands are σ and π-bonded to all four of the metal atoms of the cluster. Two σ-bonds are formed from the acetylenic carbon atoms of each alkyne to two Fe atoms on opposite vertices and two π-bonds are formed to other Fe atoms. The structure is shown in Scheme 1.2.1(ii).



Scheme 1.2.1(ii). Schematic Structure of $Fe_4(CO)_{11}(HC_2Et)$.

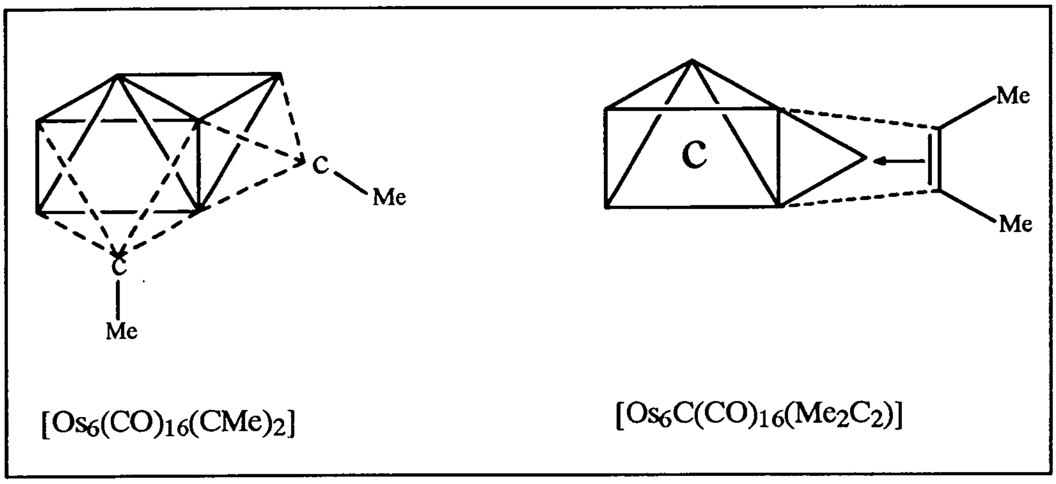
In the case of *tri*-ruthenium clusters, the thermal reaction of $Ru_3(CO)_{12}$ and alkynes does not go beyond the formation of *tetra*nuclear species. It has been shown that routes into *hexa*ruthenium arene complexes employ this technique,[20] *i.e.* heating $Ru_3(CO)_{12}$ in refluxing hydrocarbon in the presence of the desired arene results in the cluster build-up to the *hexa*ruthenium derivative. This observation for arene complexes and not alkyne complexes is probably a result of the high boiling points of the arene and the hydrocarbon employed. (This reaction works well for arenes toluene, xylene and mesitylene but not benzene which has a much lower boiling point). In the thermolytic processes used for alkyne-cluster complexes lower boiling point hydrocarbon solvents have been utilised to date, *e.g.* hexane, there seems to be no apparent reasoning for this limitation other than the probable decomposition of the alkyne at higher temperatures.

When the *tri*-metallic cluster *tri*-osmium dodecacarbonyl, $[Os_3(CO)_{12}]$ is employed in thermolytic reactions with alkynes, the high yield products are *tri*-nuclear species. This selectivity of reaction product has been attributed to the stronger metal-metal bonds of osmium compared to ruthenium and iron analogues.[5]

The other main conclusion to be made from the reactions of *tri*-nuclear complexes and alkynes is that due to the high temperatures and prolonged reaction times the likelihood of carbon-carbon triple bond fragmentation to produce oligomerisation[21] or polymerisation is far greater.[24]

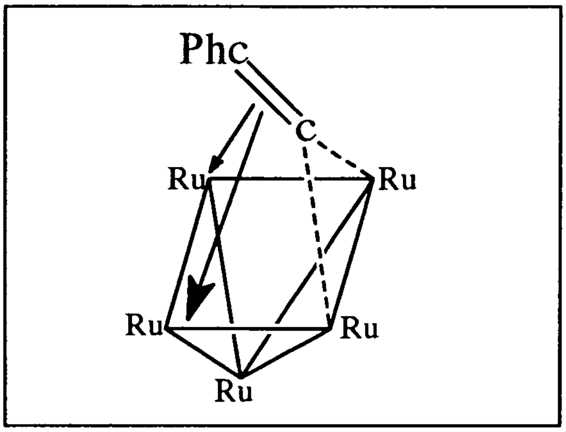
Thermal reactions involving clusters of nuclearity greater than three have been less well studied. In the case of *tetra*nuclear species the majority of work concerning metallic clusters and small organic molecules has dealt with the reactions of alkenes. It can be difficult to assess when looking at reaction products whether the bound organic fragment has been derived from the alkyne or alkene as the alkene/alkyne reagent can result in the same product being formed.[17]

Higher nuclearity systems of osmium systems have received some attention and in the case of the hexaosmium cluster three effects have been observed.[17] Firstly, there is metal framework modification, secondly the C-C multiple bond may rupture and finally dimerisation of the alkyne/alkene may occur. This is illustrated by the reaction[22] of $Os_6(CO)_{18}$ with ethylene in *n*-decane. Two products were isolated from the reaction, $Os_6(CO)_{18}(CMe)_2$ and $Os_6C(CO)_{16}(C_2Me_2)$. The former complex is defined by a *mono*capped square based pyramid of osmium atoms. The two organic units derived as a result of the fragmentation of the olefin molecule are said to be donating three electrons each to the overall electron count even though they are in different bonding modes. One ligand caps the square base of the metal cage interacting with all four metals; the second ligand bridges the triangulated face created by the sixth osmium atom which forms the 'cap' and two basal atoms. The second reaction product has a different geometry of metal atoms; the square based pyramid is still intact with the sixth osmium bridging a basal edge but not bonding to the apex of the pyramidal arrangement. A single carbide atom lies *ca* 0.20Å below the square plane coordinating symmetrically to the four basal osmium atoms and interacting with the apical osmium. The ethylene molecule has dimerised to produce a C_4H_6 unit which was formulated as but-2-yne. The alkyne coordinates to the metal frame via a π-interaction to the osmium atom bridging the basal edge and two σ-interactions to the basal atoms of the triangular face. These two complexes are given schematically in Scheme 1.2.1(iii).



Scheme 1.2.1(iii). Complexes $Os_6(CO)_{18}(CMe)_2$ and $Os_6C(CO)_{16}(C_2Me_2)$.

There is a rare example in the literature of a high nuclearity carbonyl cluster of ruthenium that reacts with an alkyne under thermal conditions[23]. A *penta*nuclear species is generated under thermal conditions by the reaction of the *mono*-substituted complex $Ru_3(CO)_{11}(PPh_2C{=}CPh)$[23] in heptane. The major product of the reaction as a result of cluster breakdown is the complex $Ru_2(CO)_6(PhC{=}C)(PPh_2)$; a *hexa*nuclear product was also reported but not fully characterised. The *penta*nuclear species, $Ru_5(CO)_{13}(C{=}CPh)(PPh_2)$ was fully characterised by spectroscopic methods and a crystallographic study. The square based pyramidal array of ruthenium atoms was the first structurally characterised example of such a geometry for ruthenium. The phosphido group bridges a basal edge of the pyramid and all the carbonyl groups are terminally bound. The acetylene group has adhered to the base of the pyramid. The alkyne interacts through two π-interaction to the two metal atoms that it symmetrically bridges and σ-bonds to the opposite basal atoms. The structure is shown diagrammatically in Scheme 1.2.1(iv).

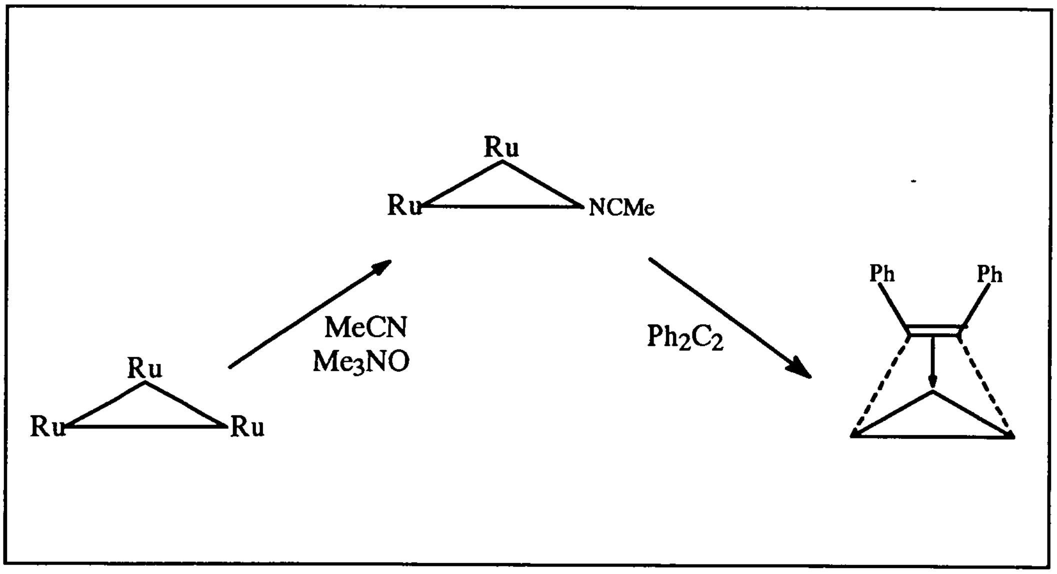


Scheme1.2.1(iv). Schematic representation of $Ru_5(CO)_{13}(C{=}CPh)(PPh_2)$.

Preparation of alkyne cluster complexes using thermal reaction techniques leads to a variety of products with no method for assessing what nuclearity the product will take, *i.e.* these reactions are highly unselective. The use of high temperatures and long reaction times also leads to fragmentation [22],polymerisation [24] and interaction of the alkyne with carbonyl groups on the cluster [18]. These factors have presented a need to develop reaction procedures into cluster alkyne complexes which will provide a degree of selectivity over reaction materials.

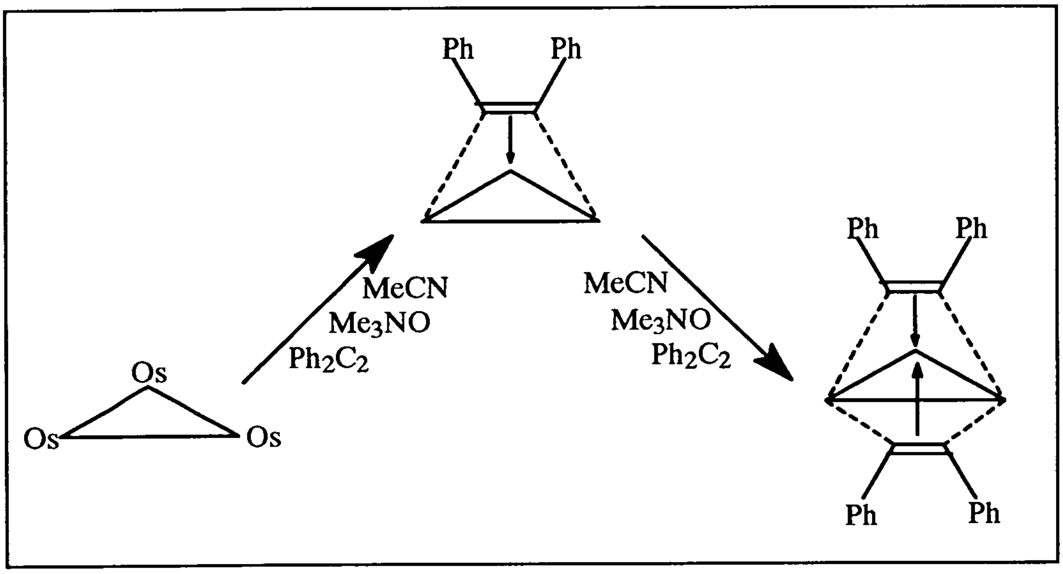
1.2.2. Chemical Activation as Means to Prepare Cluster-alkyne Complexes.

The use of trimethylamine N-oxide was first reported in 1974 by Shvo and Hazum [25] to remove organic fragments from iron complexes. The use of the reagent Me_3NO is now extensive in the field of organometallic chemistry and this is no more obvious than in the select area of cluster arene [26] complexes. The Me_3NO is able to selectively remove carbonyl ligands from a transition metal carbonyl compound as carbon dioxide leaving the fragment NMe_3 as a weakly bound ligand on the metal cage. In such a reaction the ligand MeCN is frequently added to the solution to afford 'stabilised' intermediates. For example, $Ru_3(CO)_{10}(NCMe)_2$[27] is prepared from $[Ru_3(CO)_{12}]$ in the presence of MeCN and stoichiometric amounts of Me_3NO. This type of cluster is said to be 'activated' as the *bis*-acetonitrile species is unstable for long periods of time but reacts well with the required alkyne ligand, in this case diphenylacetylene, Ph_2C_2, at room temperature to produce the complex $[Ru_3(CO)_{10}(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}Ph_2C_2)]$. The complex comprises of a triangle of ruthenium atoms each bearing three terminally bound carbonyl ligands and one CO group bridges across a Ru-Ru edge. The diphenylacetylene bridges the face of the metallic face coordinating *via* a π-interaction to one metal centre and two σ-interactions to the other two metal centres. Alternatively, the reaction can be carried out with the designated organic ligand present in solution to yield the required product in one step. The reactions are depicted in Scheme 1.2.2(i).



Scheme 1.2.2(i). Preparation of $[Ru_3(CO)_{10}(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}Ph_2C_2)]$.

The preparation of *mono*- and *bis*-substituted alkyne complexes using mild reaction routes has been reported for *tri*osmium dodecacarbonyl. The complex $[Os_3(CO)_{12}]$ is treated with Me_3NO in the presence of MeCN to yield the intermediate $[Os_3(CO)_{11}(MeCN)]$[28]. At room temperature this activated species then reacts with ethylene to produce $[Os_3(CO)_{10}(C_2H_4)]$, where the alkene is interacting with only one metal centre. The complex $[Os_3(CO)_{10}(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Ph_2)]$ in which the alkyne bridges the *tri*-osmium face is prepared in a similar fashion., *ie* substitution of two carbonyl groups by the action of Me_3NO in the presence of MeCN to yield the *di*-substituted complex $[Os_3(CO)_{10}(MeCN)_2]$ which readily undergoes further substitution to afford $[Os_3(CO)_{10}(C_2Ph_2)]$. This compound will then undergo the reaction again to produce to a bis-alkyne derivative $[Os_3(CO)_8(C_2Ph_2)]^{29}$ in which the two alkynes 'sandwich' the metal core. The reaction is given in Scheme 1.2.2(ii).

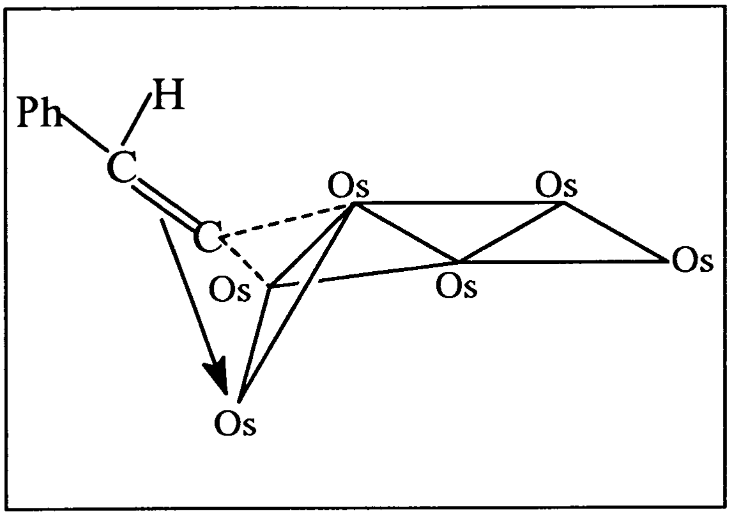


Scheme 1.2.2(ii). Synthesis of *mono*- and *bis*-substituted complexes of osmium.

It is worth noting that in these reactions no other nuclearity of cluster is prepared and the alkyne does not undergo further reaction which only serves to emphasise the selectivity of the reaction procedure.

This route of substituting carbonyls for MeCN using Me_3NO has also been employed in the preparation of *hexa*nuclear complexes of osmium. The parent complex $[Os_6(CO)_{21}]^{30}$ which has a raft geometry reacts with stoichiometric amounts of Me_3NO in the presence of MeCN to produce $[Os_6(CO)_{20}(MeCN)]$ which readily reacts in dichloromethane with the terminal alkyne HC_2Ph at room temperature to yield the compound $[Os_6(CO)_{20}(C{=}C(H)Ph)]$; the molecular structure of the compound has been determined by a crystallographic study and is given in Scheme

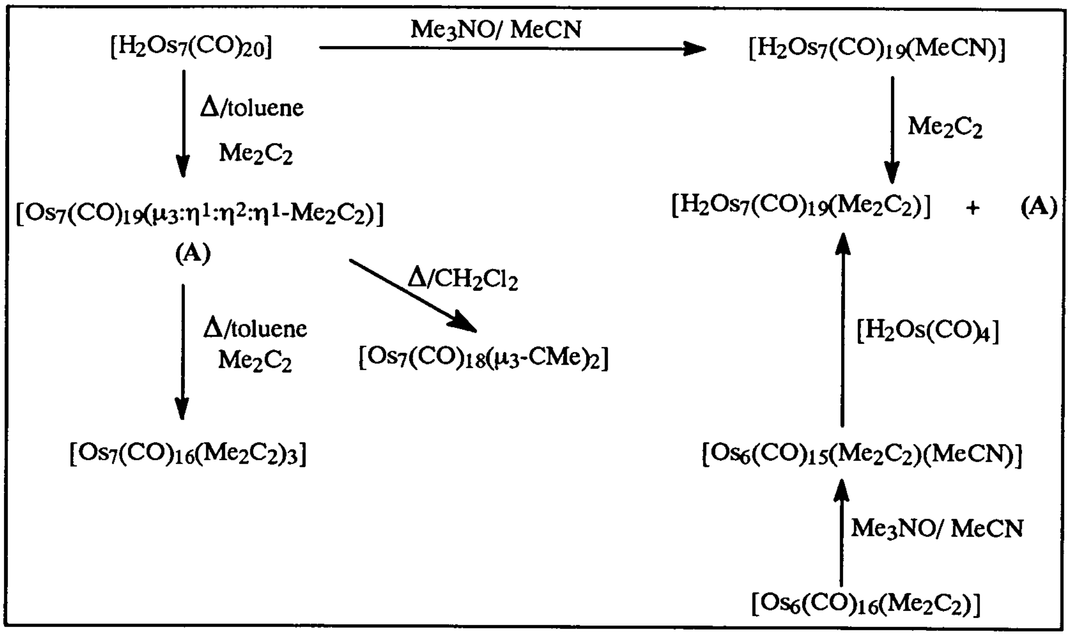
1.2.2(iii).



Scheme 1.2.2(iii) Schematic of $[Os_6(CO)_{20}(C{=}C(H)Ph)]$.

The metal geometry now consists of a chain of four triangles sharing three common edges, three of the triangles are essentially co-planar with the fourth making an angle of 34° with the plane of the three. It is this fourth, bent triangle that is capped by the organic moiety derived from the alkyne HC_2Ph. There are two σ-interactions and one π-interaction from the ligand to the metal core. The terminally bound hydrogen was not located crystallographically due to the absorption effects of the four osmium atoms but bond angles of the bound organic and also data from the ^1H nmr spectrum infer that the atom is located at the acetylenic carbon bearing the phenyl ring.

The use of Me_3NO as reagent to remove stoichiometric numbers of carbonyl ligands to prepare desirable reaction products would appear to be an attractive synthetic route; it offers selectivity and control in the reaction procedure. A series of reactions have been carried out using the heptaosmium cluster $[H_2Os_7(CO)_{20}]^{31}$ in which it has been reacted with but-2-yne under different reaction conditions, namely thermolytic and chemical activation. The parent complex, $[H_2Os_7(CO)_{20}]$ was reacted with an excess of but-2-yne in toluene under reflux conditions to yield the derivative $[Os_7(CO)_{19}(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}Me_2C_2)]$. Further thermolysis of this species in refluxing toluene in the presence of excess quantities of Me_2C_2 will yield a *tris*-but-2-yne complex $[Os_7(CO)_{16}(Me_2C_2)_3]$. The alkyne unit of the complex $[Os_7(CO)_{19}(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}Me_2C_2)]$ will fragment when the complex is subjected to further pyrolysis in dichloromethane to produce $[Os_7(CO)_{18}(\mu_3\text{-}CMe)_2]$. In comparison, activation of $[H_2Os_7(CO)_{20}]$ to $[H_2Os_7(CO)_{19}(MeCN)]$ using Me_3NO and acetonitrile followed by the addition of Me_2C_2 at room temperature yields the compound $[H_2Os_7(CO)_{19}(Me_2C_2)]$. This complex can also be obtained from the cluster $[Os_6(CO)_{16}(Me_2C_2)]$ and it's reaction with acetonitrile and Me_3NO to form $[Os_6(CO)_{15}(Me_2C_2)(MeCN)]$ which then reacts further with the monomeric dihydro species $[H_2Os(CO)_4]$. These reactions are given in Scheme 1.2.2(iv).



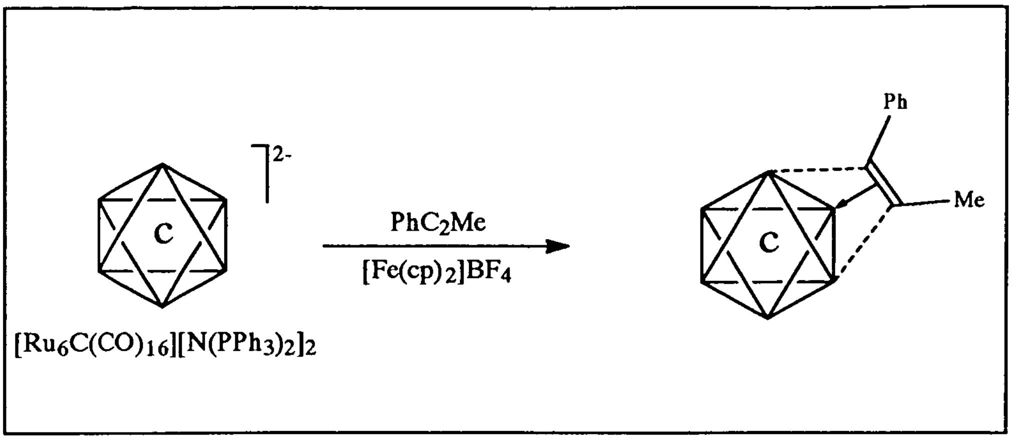
Scheme 1.2.2(iv). Thermolytic and Chemical Activation of $[H_2Os_7(CO)_{20}]$.

These reactions highlight the differences in reaction products using thermal and chemical activation. In the thermolytic reactions the hydride ligands are lost and the alkyne fragments upon prolonged heating. In contrast, chemical activation of the parent cluster $[H_2Os_7(CO)_{20}]$ yields derivatives in which the hydrides may or may not be lost but more importantly the alkyne has retained it's integrity.

The use of photolysis in the preparation of cluster alkyne compounds is not widespread. The complex $[H_2Os_6(CO)_{18}]$[32] was photolysed for 35 hours in the presence of phenylacetylene to yield as the major product $[H_2Os_5(CO)_{15}(C{=}CPh)]$. The metal cage consists of a butterfly arrangement with a fifth osmium Os atom bridging the 'wing-tip' atoms. The organic group coordinates via three σ-interactions and π-bonds with a fourth metal atom. The selectivity of this type of reaction is not as pronounced as that of the Me_3NO/MeCN route.

The most recent publication reporting the use of photolysis uses a mixed metal cluster $[Ru_5PtC(CO)_{16}]$[33] which after 12 hours irradiation produces three compounds, $[Ru_6C(CO)_{15}(\mu_3\text{-}C_2Ph_2)]$, $[Ru_6C(CO)_{13}(\mu_3\text{-}C_2Ph_2)_2]$ and $Ru_5PtC(CO)_{13}(\mu_2\text{-}C_2Ph_2)(\mu_3\text{-}C_2Ph_2)]$[34]. The two homometallic compounds both comprise of a regular octahedron of Ru atoms with alkynes bonded in the $\mu_3{:}\eta^1{:}\eta^2{:}\eta^1$ fashion to *tri*-ruthenium faces. In the case of the heterometallic derivative the metal core has under gone rearrangement from the octahedral array to a *mono*-capped square based pyramid with the interstitial carbon atom sitting in the base of the pyramid as it does in $[Ru_5C(CO)_{15}]$[35]. The two alkynes are bound in different bonding modes, one bridges the triangular face created by two basal Ru atoms and the Pt atom in the $\mu_3{:}\eta^1{:}\eta^2{:}\eta^1$- mode. The second ligand is bonded, more unusually, perpendicularly across the edge formed by the apex of the pyramid and the Pt atom in $\mu_2{:}\eta^2{:}\eta^2$-fashion through two π-interactions.

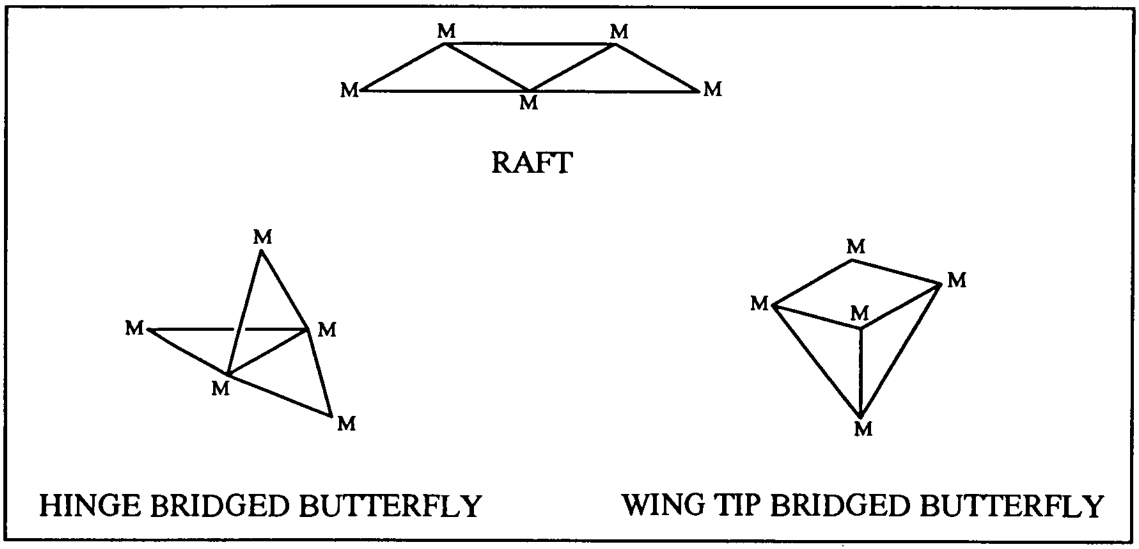
Electrochemical activation has also been reported in the preparation of a series of *hexa*ruthenium carbido alkyne clusters[36]. The dianion $[Ru_6C(CO)_{16}]^{2-}$ reacts with alkynes in solution in the presence of 2 equivalents of either of the oxidants $[Fe(cp)_2]BF_4$ or $FeCl_3$ resulting in the formation of a series of products with the general formula $[Ru_6C(CO)_{15}(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-alkyne})]$. The complex $[Ru_6C(CO)_{15}(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}MeC_2Ph)]$ was the subject of a crystallographic study; the regular octahedron had remained intact with the alkyne bound across a *tri*-ruthenium face in the $\mu_3{:}\eta^1{:}\eta^2{:}\eta^1$-bonding mode. This reaction seemed very appealing, *i.e.* a degree of control over reaction products was feasible, but further substitution of the cluster by a second alkyne was not deemed possible by this route. The reaction is given in Scheme 1.2.2(v).



Scheme 1.2.2(v). Electrochemical Preparation of $[Ru_6C(CO)_{15}(\mu_3:\eta^1:\eta^2:\eta^1\text{-}MeC_2Ph)]$

1.3 Electron Counting and Bonding Considerations.

Electron counting in alkyne substituted complexes is treated in a similar fashion to other cluster systems where the ligands are considered as species which donate electrons to the overall count, *i.e.* they do not possess donor/acceptor properties of their own. Initially electron counting for alkyne-cluster complexes was based on the 'Effective Atomic Number' rule (EAN) where the skeletal framework is held together by a network of two-centre two-electron bonds[37]. This rule works well for low nuclearity clusters but quickly breaks down for high nuclearity derivatives. This observation led to the development of the 'Polyhedral Skeletal Electron Pair Theory', (PSEPT) allowing a possible structure to be formulated from the total number of skeletal bonding pairs[38]. Molecular orbital calculations show that a closed polyhedron with n vertex atoms is held together by (n+1) skeletal bonding pairs. A *nido* polyhedron with one vertex vacant is held together by (n+2) skeletal pairs and an *arachno* polyhedron, with two vacant vertices is held together by (n+3) pairs. Further more, more open structures are obtainable by adding additional pairs of electrons. This structural analysis is usually applied solely to metal atoms but by considering an alkyne as an external ligand providing two skeletal CR units it is possible to assert PSEPT to cluster alkyne complexes. However, there are still some short comings of this bonding approach. Geometric possibilities of higher nuclearity complexes are much greater in number for a certain electron count than those of low nuclearity species. For example, *penta*nuclear species with an electron count of 76 may well be one of three structural geometries; a raft type structure and two butterfly arrangements, one where the fifth atom bridges the butterfly wing tips and the other with the fifth atom bridging the hinge of the butterfly. These geometries are shown in Scheme 1.3(i).



Scheme 1.3(i). Possible Geometries with same Electron Count.

In other words PSEPT may be able deduce a number of geometric possibilities for an electron count but it is unable to assign a geometry specifically. This theory was originally developed for borane clusters which result in larger *closo* structures as nuclearity increases. In transition metal cluster compounds however as nuclearity increases the geometry may be a result of faces of a smaller cluster being 'capped' by a an additional metal atom, *i.e.* as you increase the nuclearity of the cluster a larger *closo* polyhedron is not necessarily achieved. This approach can be considered equivalent to adding a capping atom/group to a *closo* cluster polyhedron without formally adding an electron pair.

Calculations of possible geometries adopted by higher nuclearity clusters have been assessed[39-45] but have focused on the metal core and disregarded any associated ligands. The polyhedral skeletal electron pair theory was reassessed by Mingos[46] to include non-conical fragments and condensed polyhedra[47]. As a result of this study it is now possible to account for all platinum group metal condensed polyhedral cluster complexes.[14]

In conclusion, there is no ultimate electron counting method for alkyne-cluster complexes that will successively predict specific structural geometries. It is however possible to narrow possible geometries down by applying the EAN rule to the cluster and then pin-pointing either one or a few geometries.

1.4 Bonding of Alkynes to Clusters.

An alkyne ligand has the ability to bond with one to four metal atoms at any one time. In practice, the observation of an alkyne coordinating to only one metal is rarely observed due to the desire of the ligand to interact with neighbouring metal centres within the cluster.[5] The interaction of the alkyne with one metal centre of a cluster may occur when substituents either on the cluster or on the ligand itself force the alkyne into this situation, usually due to steric hindrance.

The interaction of an alkyne with two metal centres can theoretically take several forms. The alkyne could lie perpendicularly to a metal-metal bond interacting *via* σ–bonds, or alternatively it may interact again perpendicular to the metal-metal bond but interact through π-interactions. The ligand could also lie parallel to the metal-metal bond coordinating through σ-interactions. A final situation could arise from the ligand interacting through a σ and a π-interaction. In practice, such coordination modes for homometallic cluster compounds are rarely observed.[5]

The majority of alkyne-cluster complexes fall in the category of the ligand interacting with three metal centres. There are two possible coordination modes for this to occur; the first is a σ-, 2π-interaction where the ligand donates 5 electrons to the electron count of the cluster. The other possibility is the π-, 2σ-interaction where-by the alkyne donates 4 electrons to the electron count. These coordination modes are given in Scheme 1.4(i).

σ, 2π-interaction
5 electron donor

π, 2σ-interaction
4 electron donor

Scheme 1.4(i). An Alkyne Interacting with Three Metal Centres.

The second bonding mode is by far the most commonly observed in alkyne cluster chemistry regardless of the number of metal centres of the cluster (nuclearity>3). The alkyne coordinates through a π-interaction to one metal centre and two σ-interactions to the remaining two centres; the metal centres are arranged in a triangle. The alkyne lies above the metal face usually at an angle of 70° to the plane bending towards the π-interaction. Upon coordination the alkyne is said to become 'alkene-like' in character; the C-C multiple bond lengthens from 1.2Å in the free ligand to 1.3-1.45Å and the linear 180° C-C-C bond in the uncoordinated alkyne reduces to 120-150°.

The interaction with four metal centres has also been observed. Cluster complexes of nuclearity four are frequently tetrahedral in geometry, but the coordination of an alkyne to a *tetra*-nuclear cluster demands either a planar or butterfly arrangement of metal atoms. The compound *tetra*-cobalt dodecacarbonyl will react with stoichiometric amounts of alkyne under gentle reflux conditions to yield blue *tetra*-cobalt butterfly complexes where the alkyne sits in the butterfly parallel to the hinge.[48, 49]

The complex $[Ir_4(CO)_8(C_2(COOMe)_2)_4]$[50] is a rare example of a square planar geometry of Ir group metal atoms with a *tetra*-substituted olefin. The metal centres are each coordinated to two terminally bound carbonyl ligands. The two alkynes lie parallel to the metal plane above and below bond purely through σ-interactions to the metal centres.

In conclusion alkynes can interact with one to four metal centres but it would seem out of preference coordinate to three metal centres in the face bridging $\mu_3:\eta^1:\eta^2:\eta^1$-mode regardless of the nuclearity of the cluster.

1.5 μ_6-Carbido Heptadecacarbonyl Hexaruthenium.

The hexaruthenium carbonyl cluster can be prepared by several routes[20,51-53]. The first recorded preparation of the cluster was in 1967 by Johnson *et. al.* which was a result of the thermolytic reaction of $[Ru_3(CO)_{12}]$ in refluxing arene solvents. Initial characterisation of the complex was by spectroscopic methods, mass spectrometry confirming the presence of the interstitial carbido atom.[20,51] The structure was confirmed in 1969 crystallographically.[54] The structure showed that the six ruthenium atoms were arranged in a regular octahedron. Of the seventeen carbonyl ligands sixteen are terminally bound to Ru centres, the seventeenth bridges an equatorial Ru-Ru edge. The interstitial carbido atom was located at the centre of the cage and is known to be derived from a carbonyl ligand.[55] The preparative route mostly frequently employed utilises a high temperature autoclave reaction in which *tri*-ruthenium dodecacarbonyl is reacted under an ethylene atmosphere.[51] In the complex $[Ru_6C(CO)_{17}]$ the interstitial atom is believed to offer the complex a stability such that during reaction rearrangement of the cluster is minimal[36,55]. The result of this is that substitution reactions can be assessed without the added complication of cluster degradation and rearrangements, that is the cluster acts as a substrate for reactions to occur at.

1.6 References for Chapter One.

1. E.L.Muetterties., *Angew. Chem. Int. Ed. Engl.* 1978, **17**, 545.

2. E.L.Muetterties, T.N.Rhodin, E.Band, C.F.Bruker, W.R.Pretzer., *Chem. Rev.*, 1979, **79**, 91.

3. E.L.Muetterties. *Bull. Soc. Chim. Belg.*, 1976, **85**, 451.

4. E.L.Muetterties. *Bull. Soc. Chim. Belg.*, 1975, **84**, 453.

5. E.Sappa, A.Tirripicchio, P.Braunstein, *Chem. Rev.*, 1983, **83**, 203.

6. R.Ugo., Catal. Rev., 1975, 11, 225.

7. R.L.Burwell, Jr., *Chem. Eng. News.*, 1966, **44**, 56.

8. E.L.Muetterties, *Science.*, 1977, **196**, 839.

9. E.L.Muetterties, *Pure Appl. Chem.*, 1982, **54**, 83.

10. B.C.Gates, L.Guczi, K.Krozinger, Eds., *'Metal Clusters in Catalysis'*, Elsevier, Amsterdam, 1986.

11. Y.Blum, Y.Shvo., *J. Organomet. Chem.*, 1984, **263**, 93.

12. A.Basu, S.Bhaduri, K.Sharma., *J. Organomet. Chem.* 1987, **319**, 407.

13. M.Bianchi, M.Matteoli, G.Menchi, P.Frediani, S.Pratesi, F.Piancenti., *J. Organomet. Chem.*, 1980, **198**, 73.

14. R.Cypres., *Actual Chim.*, 1978, **6/7**, 20.

15. R.P.A.Sneeden., *Actual. Chim.*, 1979, **1**, 31.

16. R.P.A.Sneeden., *Actual. Chim.*, 1979, **2**, 31.

17. P.R.Raithby, R.J.Rosales., *Adv. Inorg. Chem. and Radiochem.*, 1985, **29**, 169.

18. S.Aime, L.Milone, E.Sappa, A.Tirripicchio, M.Tirripicchio Camellini., *J. Chem. Soc. Dalton.*, 1979, 1155 and Ref's *therein.*

19. E.Sappa, A.Tirripicchio, M.Tirripicchio Camellini., *J.Chem. Soc. Dalton.*, 1978, 419.

20. B.F.G.Johnson, J.Lewis, R.D.Johnstone., *J. Chem. Soc. Chem. Commun.*, 1967, 1057.

21. E.Sappa, A.Tirripicchio, A.M.M. Lanfredi., *J. Chem. Soc. Dalton.*, 1978, 552.

22. For example: C.R.Eady, J.M.Fernandez, B.F.G.Johnson, J.Lewis, P.R.Raithby, G.M.Sheldrick., *J. Chem. Soc. Chem. Commun.*, 1978, ~~461~~.
421

23. A.J.Carty, S.A.Mclaughlin, N.J.Taylor., *J. Amer. Chem. Soc.*, 1981, **103**, 2456 and Ref's *therein.*

Dalton

24. For Example: G.Ferraris, G.Gervasio., *J. Chem. Soc.*, 1974, 1813.

25. Y.Shvo, E.Hazum., *J. Chem. Soc. Chem. Commun.*, 1974, 336.

26. B.F.G.Johnson, P.J.Dyson, D.Braga, F.Grepioni., *Chem. Rev.*, 1994, **94**, 1585 and Ref's *therein.*

27. G.A.Foulds, B.F.G.Johnson, J.Lewis., *J. Organomet. Chem.* 1985, **296**, 147.

28. B.F.G.Johnson, J.Lewis, D.A.Pippard., *J. Chem. Soc. Dalton*, 1981, 407.

29. B.F.G.Johnson, R.Khattar, F.T.Lahoz, J.Lewis, P.R.Raithby., *J. Organomet. Chem.*, 1987, **319**, C51-C57.

30. J.G.Jeffery, B.F.G.Johnson, J.Lewis, P.R.Raithby, D.A.Welch., *J. Chem. Soc. Chem. Commun.*, 1986, 318.

31. D.Braga, F.Grepioni, B.F.G.Johnson, J.Lewis, J.A.Luniss., *J.Chem. Soc. Dalton*, 1992, 1101.

32. D.H.Farrar, G.R.John, B.F.G.Johnson, J.Lewis, P.R.Raithby, M.J.Rosales, *J. Chem. Soc. Chem. Commun.*, 1981, 86.

33. R.D.Adams, W.Wu., *J. Cluster Science*, 1991, **2**, 271.

34. R.D.Adams, W.Wu., *Organomets.* 1993, **12**, 1238.

35. B.F.G.Johnson, J.Lewis, J.N.Nicholls, J.Puga, P.R.Raithby, M.J.Rosales, M.McPartlin, W.Clegg., *J. Chem. Soc. Dalton,* 1983, 277.

36. S.R.Drake, B.F.G.Johnson, J.Lewis, G.Connole, M.McPartlin., *J. Chem. Soc. Dalton,* 1990, 995.

37. C.A.Tolman., *Chem. Rev.*, 1972, **11**, 768.

38. K.Wade., *Adv. Inorg. Chem. and Radiochem.* 1976, **18**, 1.

39. G.Ciani, A.Sirroni, *J. Organomet. Chem.*, 1980, **197**, 233.

40. J.W.Lauher., *J. Amer. Chem. Soc.* 1978, **100**, 5303.

41. J.W.Lauher., *J. Amer. Chem. Soc.* 1978, **101**, 2604.

42. B.K.Teo., *Inorg. Chem.*, 1984, 23.

43. B.K.Teo., G.Logoni, F.R.K.Chung, *Inorg. Chem.*, 1984, **23**, 1257.

44. G.Ciani, A.Sironi., *J. Organomet. Chem.*, 1981, **20**, 233.

45. A.J.Stone., *Inorg. Chem.* 1981, **20**, 563.

46. D.M.Evans, D.M.P.Mingos., *Organomets.*, 1983, **2**, 435.

47. D.M.P.Mingos, *J. Chem. Soc. Chem. Commun.*, 1983, 706.

48. U.Kruche, W,Hubel., *Chem. Ber.*, 1961, **94**, 2829.

49. L.F.Dahl, D.L.Smith., *J. Chem. Soc. Dalton.*, 1962, **84**, 2451.

50.P.F.Helveldt, B.F.G.Johnson, J.Lewis, P.R.Raithby, G.M.Sheldrick., *J. Chem. Soc. Chem. Commun.*, 1978, 340.

51. B.F.G.Johnson, R.D.Johnston, J.Lewis, *J. Chem. Soc. Dalton,* 1968, 2865.

52. B.F.G.Johnson, J.Lewis, S.W.Sankey, K.Wong, M.Mcpartlin, W.J.H.Nelson., *J. Organomet. Chem.*, 1980, **191**, C3.

53. C.M.T.Hankey, J.R.Shapley., *Inorg. Chem.*, 1982, **21**, 3816.

54. A.Sirigu, M.Bianchi, E.Benedetti., *J. Chem. Soc. Chem. Commun.* 1969,596.

55. J.S.Bradley, G.B.Ansell, E.W.Hill., *J. Amer. Chem. Soc.*, 1979, **101**, 7417.

Chapter Two.

Step-wise Addition of Alkynes onto a Hexaruthenium Cluster.

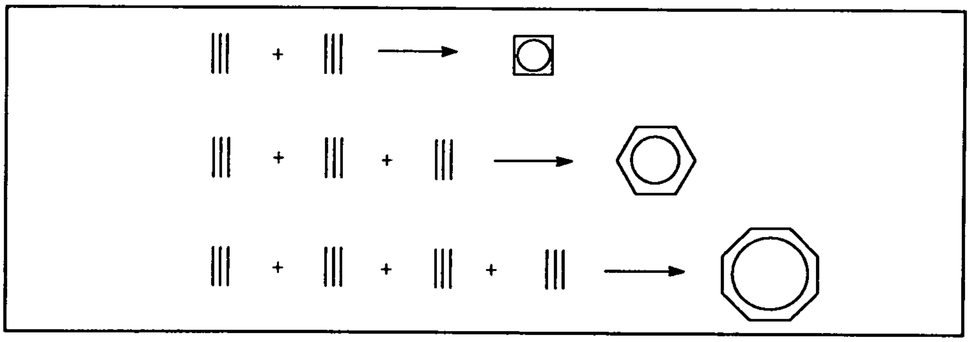
This chapter will begin by discussing the original hypothesis behind the work and the goals that were to be attained. It will then go on to look at the step-wise addition of successive but-2-yne ligands onto the metal frame work of the hexaruthenium carbonyl cluster $[Ru_6C(CO)_{17}]$; the one step reactions that also lead to these substituted compounds will be assessed. The final section of the chapter will deal with the addition of a variety of alkyne functionalities onto the $[Ru_6C(CO)_{17}]$ cluster.

2.1 Introduction.

The chemistry of low nuclearity carbonyl clusters containing substituted alkyne ligands is a rich and extensively studied area of organometallic chemistry[1,2]. The work investigating that of high nuclearity clusters bearing alkyne groups has, in comparison received little attention. The alkyne ligand is of particular interest to the organometallic chemist due to its unique diverse properties not observed by other organic ligands, *eg* its ability to bond in over fifteen different coordination modes donating from two[3] to five[4] electrons to a system. This was discussed in Chapter One. Also of major significance in this area of chemistry is the reported relationship between small organic fragments bound to a metallic surface and those bound to a transition metal cluster, *ie* the cluster surface analogy[5-10]. For these selected reasons only the study of high nuclearity carbonyl clusters and their reactivity towards alkyne groups is of immense importance and interest.

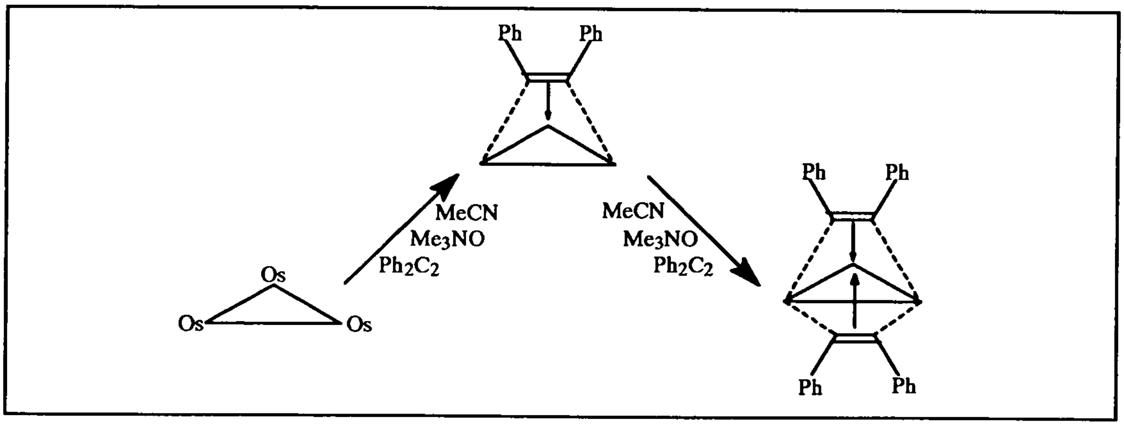
Our own reasons for initiating work into the study of the hexaruthenium carbonyl system with alkynes was two fold. Primarily we wished to synthesise a series of complexes that contained alkyne ligands substituted onto the metal core and to establish how many organic groups the cluster could bear and whether the ligand would undergo polymerisation to yield aromatic functionalities; this is highlighted in Scheme

2.1.1.



Scheme 2.1.1. Possible Polymerisations to Produce Arene Groups.

To date relatively few cluster complexes containing only two alkyne derivatives have been reported[11] and polymerisation[12] has been observed but is not a common occurrence. An example of two alkyne units on a cluster is that of $[Os_3(CO)_8(Ph_2C_2)_2]$[13], prepared from $[Os_3(CO)_{10}(Ph_2C_2)]$ in a dichloromethane/acetonitrile solution in the presence of excess Ph_2C_2 and stoichiometric amounts of Me_3NO. The ligands lie above and below the triangular plane in the facially bound mode, $\mu_3{:}\eta^1{:}\eta^2{:}\eta^1$. This is a rare example of a *bis*-alkyne derivative where the ligands have remained independent of each other.The reaction sequence is given in Scheme 2.1.2.

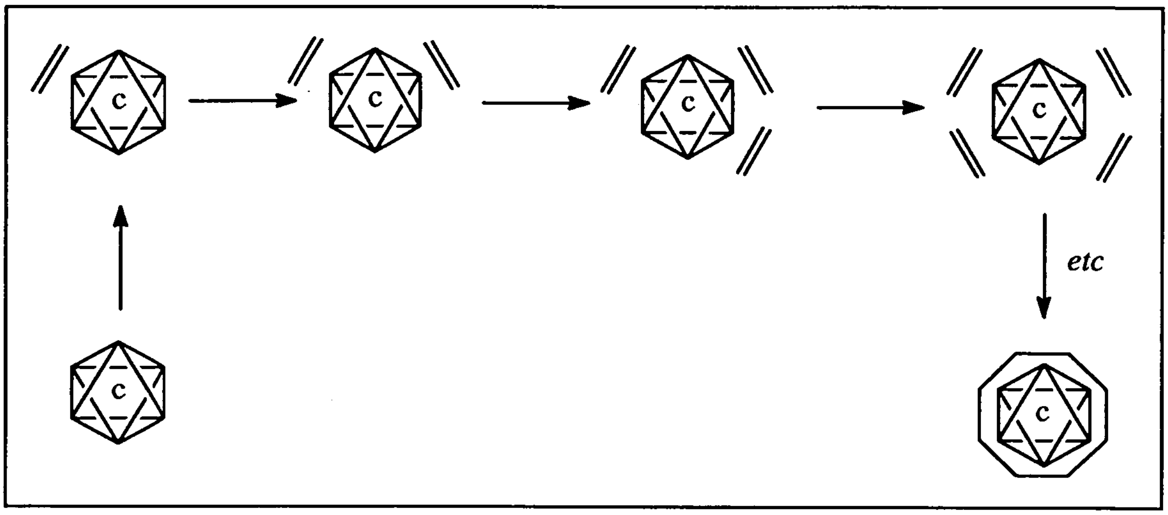


Scheme 2.1.2. Preparation of $Os_3(CO)_8(Ph_2C_2)_2]$.

An unusual heptaosmium complex bearing three but-2-yne ligands has been prepared, $[Os_7(CO)_{16}(Me_2C_2)_3]$[14], by the extended pyrolysis of $[H_2Os_7(CO)_{20}]$ in toluene in the presence of the alkyne. The complex to date has only been characterised spectroscopically so binding modes of the alkyne cannot be assessed fully, *i.e.* whether the alkyne has remained as but-2-yne or whether it has fragmented.

Alkynes sometimes polymerise to yield metallocycles as in the case of $[Ru_3(CO)_8(C_{12}H_{18})]$[15]. Prepared from a refluxing solution of $[Ru_3(CO)_{12}]$ in heptane in the presence of 4-methylpent-2-yne, the two alkynes have oligomerised to form a diene component and one of the metal-metal bonds has ruptured leaving the three ruthenium atoms in a bent arrangement. The organic is bound *via* two sigma and two π-interactions. Examples of high nuclearity ruthenium derivatives are rarer still thus necessitating their study.

Further down the line of study it was hoped that the synthesis of a complex where the hexaruthenium cluster was enveloped in an organic cage would be possible, much as the carbido atom of $[Ru_6C(CO)_{17}]$ is encapsulated in the centre of the metallic cage. It is envisaged that through a series of successive substitutions followed by alkyne polymerisations such a complex could be prepared, this is depicted in Scheme 2.1.3.



Scheme 2.1.3. Possible encapsulation of $[Ru_6C(CO)_{17}]$

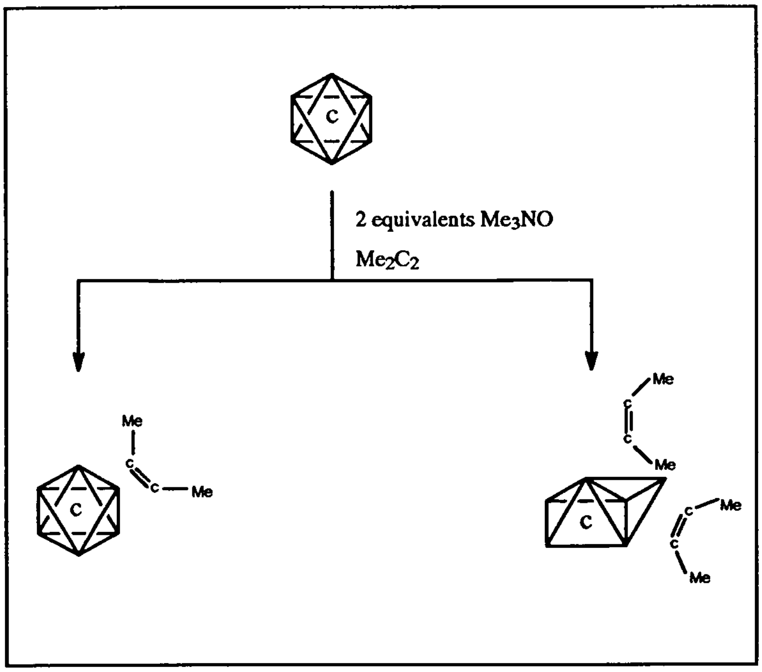
The complex $[Ru_6C(CO)_{15}(MeCH{=}CH\text{-}CH{=}CHMe)]$[12] shows the coordination of a *di*-alkyne ligand formed by the polymerisation of ethylene onto the metal cluster, the two alkene double bonds interact *via* π-interactions to adjacent metal atoms. More recently Adams[11] has reported the synthesis of a hexaruthenium carbonyl cluster in which the ligand 1,3,5-hexatriene is bound to two metal atoms *via* an allyl η^4-interaction and an η^2-mode. The hexatriene ligand would seem to be 'wrapping' itself around the cluster.

Synthetic procedures employed to attain alkyne derived cluster complexes involve thermolysis, chemical activation and photolytic activation[1,2]. In the case of the synthesis of hexaruthenium compounds thermolysis has been ruled out because of low selectivity and a high degree of decomposition involved. Hexaruthenium arenes can be prepared by heating $[Ru_3(CO)_{12}]$ in refluxing octane in the presence of the desired aromatic[22], it is known however that by carrying out similar reactions in the presence of alkynes the cluster build up of $[Ru_3(CO)_{12}]$ is limited to tetranuclear species[2]. Reports have been made of photolysing solutions of a mixed metal cluster, $[Ru_5PtC(CO)_{16}]$[17] in the presence of diphenylacetylene yielding *mono*- and *di*-substituted complexes[18] and although the reaction yields were reported as moderate (38% for the monosubstituted component) reaction times are long, *ca.*16 hours.

The use of trimethylamine N-oxide was first reported in the early 1970's[19] and was found to stoichiometrically remove carbonyl ligands from the carbonyl cluster compounds. The oxidative decarbonylation reagent Me_3NO can be used in the presence of the weakly coordinating acetonitrile to yield highly reactive, or 'activated' intermediates. These acetonitrile derivatives are rarely isolated from the reaction mixture but reacted further *in situ* in the presence of the organic ligand to form the desired product. The established synthetic route into the preparation of penta-[20] and hexaruthenium[21] arene complexes uses Me_3NO in stoichiometric amounts in the presence of 1,3-cyclohexadiene avoiding the necessity of the acetonitrile intermediates. It was also decided at this early stage of investigation that alkynes bereft of any α-hydrogen atoms would be used so that complexes could be studied without problems of *in situ* polymerisation occurring.

2.2 Synthesis of $[Ru_6C(CO)_{15}(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)]$, 2 and $[Ru_6C(CO)_{14}(\mu:\eta^2:\eta^2\text{-}Me_2C_2)(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)]$, 3.

To a cooled solution of the complex $[Ru_6C(CO)_{17}]$ and the ligand but-2-yne, Me_2C_2 in dichloromethane 2 molar equivalents of trimethylamine-N-oxide, Me_3NO were added to afford the new complexes μ_3: η^1 η^2: η^1-but-2-yne μ_6-carbido pentadecacarbonyl hexaruthenium, $[Ru_6C(CO)_{15}(\mu_3: \eta^1 \eta^2: \eta^1\text{-}Me_2C_2)]$, **2** and $\mu:\eta^2:\eta^2$-but-2-yne $\mu_3:\eta^1:\eta^2:\eta^1$-but-2-yne μ_5-carbido tetradecacarbonyl hexaruthenium, $[Ru_6C(CO)_{14}(\mu:\eta^2:\eta^2\text{-}Me_2C_2)(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)]$, **3** in moderate yields, as shown in Scheme 2.2.1



Scheme 2.2.1. Synthesis of $[Ru_6C(CO)_{15}(Me_2C_2)]$ and $[Ru_6C(CO)_{14}(Me_2C_2)_2]$.

Complex **3** will be discussed in greater detail at a later stage. The red/brown complex, **2** was purified using tlc with a solution of dichloromethane:hexane, (1:4 v/v) as eluent. The initial molecular formula was determined by mass spectroscopy. In the mass spectrum a strong parent peak was observed at m/z 1090 (calc.1092) followed by the sequential loss of fifteen carbonyl ligands. A singlet at δ 3.00ppm was observed in the ^{1}H nmr spectrum and may be assigned to the methyl groups of the bound alkyne. Crystals of high enough quality for a crystallographic study were grown by slow evaporation at -25°C of a dichloromethane/hexane solution. The molecular structure is shown in Figure 2.2a along with significant bond lengths and angles.

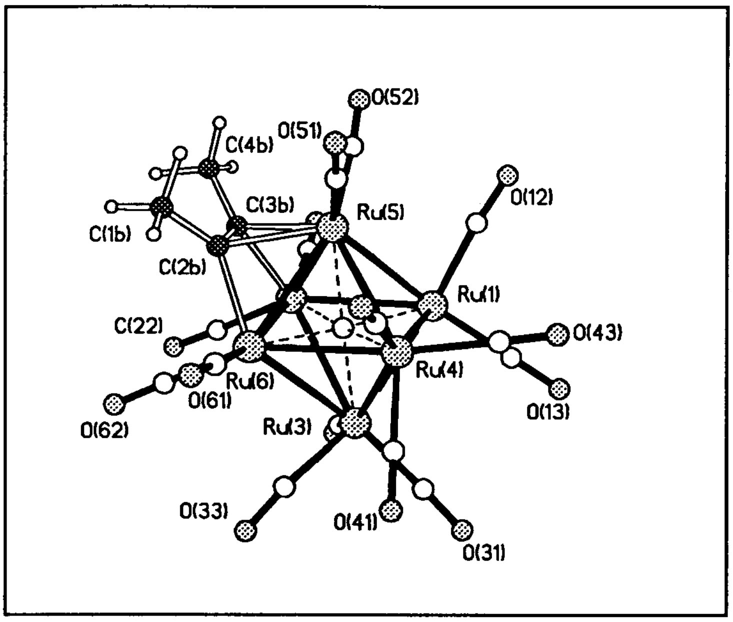


Figure 2.2a: the molecular structure of $[Ru_6C(CO)_{15}(\mu_3: \eta^1:\eta^2: \eta^1 - Me_2C_2)]$ showing the atom labelling scheme. Bond lengths (Å) and significant angles (°): Ru(1)-Ru(2) 2.935(7), Ru(1)-Ru(3) 2.844(7), Ru(1)-Ru(4) 2.901(7), Ru(1)-Ru(5)2.953(7), Ru(2)-R(3) 2.985(7), Ru(2)-Ru(5) 2.766(7). Ru(2)-Ru(6) 2.810(7), Ru(3)-Ru(4) 2.920(7), Ru(3)-Ru(6) 2.985(7), Ru(4)-Ru(5)2.911(7), Ru(4)-Ru(6) 2.865(7), Ru(5)-Ru(6) 2.806(7); Ru(1)-C 2.061(5), Ru(2)-C 2.015(5), Ru(3)-C 2.039(5), Ru(4)-C 2.056(5), Ru(5)-C 2.084(5), Ru(6)-C 2.013(5); mean Ru-C(CO) 1.899; mean C-O 1.065; Ru(2)-C(3B) 2.083(5), Ru(5)-C(2B) 2.183(5), Ru(5)-C(3B) 2.196(5), Ru(6)-C(2B) 2.055(5); C(1B)-C(2B) 1.525(8), C(2B)-C(3B) 1.385(8), C(3B)-C(4B) 1.510(8); mean Ru-C-O 176.0(5).

As can be seen the octahedral array of ruthenium atoms has remained intact but with a slight distortion arising due to the presence of the organic fragment. This is clearly illustrated from a comparison of Ru-Ru bond distances. Thus, the triangular face Ru(5)-Ru(2)-Ru(6) where the ligand is bound has a mean distance of 2.799 Å whilst the mean Ru-Ru distance in the remainder of the cluster is 2.922Å, 0.128Å longer. This can be attributed to the organic fragment pulling electron density away from the cluster core and resulting in a contraction of ruthenium bond lengths where there is direct contact between the alkyne and the triangular face. All the carbonyl groups are bound terminally with a mean Ru-C-O bond angle of 176.0(5)° (range 170.5(5)-179.6(5)°); the bridging carbonyl group of the parent cluster $[Ru_6C(CO)_{17}]$[22] is no longer present. It is clear that the carbido atom has shifted out of its central location towards the face on which the alkyne is coordinated. This can be highlighted by looking at bond distances, Ru(2)-C, 2.015Å compared to Ru(4)-C, 2.056Å (difference of 0.041Å) and Ru(6)-C, 2.013Å *cf.* Ru(1)-C, 2.061Å (difference of 0.048Å) across the edge involved in sigma inteactions with the alkyne and in the case of the pi-interaction at Ru(5)-C 2.084Å *cf.* Ru(3)-C 2.039Å (difference of 0.045Å). Reasons for this anomaly are not clear; given the uncertainty of deducing chemical shifts (movements) of active nuclei it would appear inappropriate to discuss this matter further at this time. Upon coordination to the metal core in the commonly observed μ_3:$\eta^1\eta^2$:η^1 bridging mode[1,2] across three metal atoms the alkyne ligand has become more 'alkene-like' in character. The C-C-C bond angles are now 124.4(5) and 124.7(5)° compared to 180° in the free ligand. Further evidence for this increased alkene character comes from the C=C multiple bond length; in this complex the C=C multiple bond is 1.385(8)Å compared to 1.2Å in the unbound moiety; these changes of bond lengths and angles are typical of an alkyne coordinated in the face bridging mode[23]. The two single bond lengths are fairly typical examples at 1.525(8) and 1.510(8)Å. The alkyne sitting across the face forms an angle of 70° to the plane of the three metal atoms bending towards Ru(5).

2.3 Attempted displacement of the ligand with carbon monoxide.

A solution of the complex $[Ru_6C(CO)_{15}(\mu_3$: η^1:η^2: η^1 - $Me_2C_2)]$ in dichloromethane was prepared. Over a period of four hours carbon monoxide gas was bubbled through the brown solution at room temperature. Every twenty minutes an infrared spectrum was recorded. Over this length of time there was no apparent reaction. It had been hoped that the organic ligand would be sufficiently labile to be displaced from the hexaruthenium unit by the carbon monoxide, this was not the case. The stability of these complexes has been reported in the past [24] and is said to be related to the presence of the interstitial carbido atom.[25]

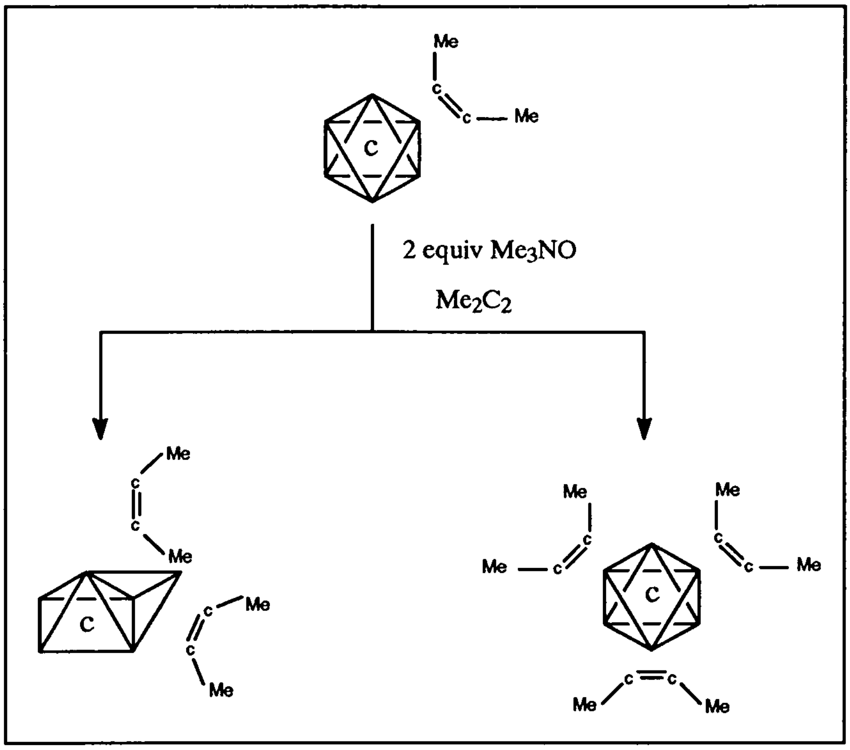
2.4 Reaction of $[Ru_6C(CO)_{15}(\mu_3: \eta^1:\eta^2: \eta^1 - Me_2C_2)]$ in an autoclave under a carbon monoxide atmosphere.

The known cluster $[Ru_5C(CO)_{15}]$[26] is prepared by reacting $[Ru_6C(CO)_{17}]$ in heptane at 85°C under a carbon monoxide atmosphere, pressure 70 atmospheres for 3.5 hours. Thus, it was thought that $[Ru_6C(CO)_{15}(\mu_3: \eta^1:\eta^2: \eta^1 - Me_2C_2)]$ may undergo a similar carbonylation reaction. The synthesis was carried out under the same conditions as outlined above. From the reaction red needle-like crystals were afforded; an infrared spectrum showed that the material was the cluster $[Ru_6C(CO)_{17}]$ and that the alkyne had been displaced but no carbonylation to a pentaruthenium derivative had occurred. It had been anticipated that this reaction could proceed one of two ways; firstly that the hexaruthenium cluster would undergo a carbonylation reaction to yield a pentaruthenium derivative with the alkyne remaining intact or that the pentaruthenium cluster would be formed but with the alkyne displaced. The synthesis of pure hexaruthenium carbonyl was not accounted for. Analysis of the heptane solution was not carried out at the time and was assumed to contain decomposition materials. Work is being carried on this reaction with a view to locating the alkyne and assessing what form it has taken, *eg* whether it has polymerised or not.

2.5. Reaction of $[Ru_6C(CO)_{15}(Me_2C_2)]$ with 2 molar equivalents of Me_3NO and Me_2C_2.

The complex $[Ru_6C(CO)_{15}(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)]$ was dissolved in dichloromethane and then cooled to -78°C. At low temperature an excess of ligand was added. Two molar equivalents of Me_3NO in dichloromethane was introduced to the solution. The solution reached room temperature after a further 30 minutes of stirring; the solution changed from a dark red-brown colour to cloudy brown. Solvent was removed under reduced pressure and the residues purified by tlc with a solution of dichloromethane-hexane (3:7 v/v) as an eluent. Products were eluted in the order $[Ru_6C(CO)_{14}(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)(\mu:\eta^2:\eta^2\text{-}Me_2C_2)]$, **3** first and *tris*-$\mu_3:\eta^1:\eta^2:\eta^1$-but-2-yne

μ_6-carbido dodecacarbonyl hexaruthenium $[Ru_6C(CO)_{12}(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)_3]$, **5** second. The overall reaction is highlighted in Scheme 2.5.1.



Scheme 2.5.1. Synthesis of $[Ru_6C(CO)_{14}(Me_2C_2)_2]$ and $[Ru_6C(CO)_{12}(Me_2C_2)_3]$.

The presence of compound **3** was confirmed by infrared spectroscopy, which likewise showed that compound **5** was new material; this material will be discussed later in the text. The mass spectrum of **3** exhibited a parent peak at m/z 1118, giving rise to the molecular formula $[Ru_6C(CO)_{14}(Me_2C_2)_2]$. In the ^1H nmr spectrum the two expected singlets of equal intensity at δ 2.88 and 3.29ppm were observed and may be assigned to the face capping and edge bridging modes respectively. Crystals suitable for a crystallographic study were afforded by the slow evaporation of a dichloromethane-hexane layer at -25°C. The molecular structure of $[Ru_6C(CO)_{14}(Me_2C_2)_2]$ is shown in Figure 2.5a.

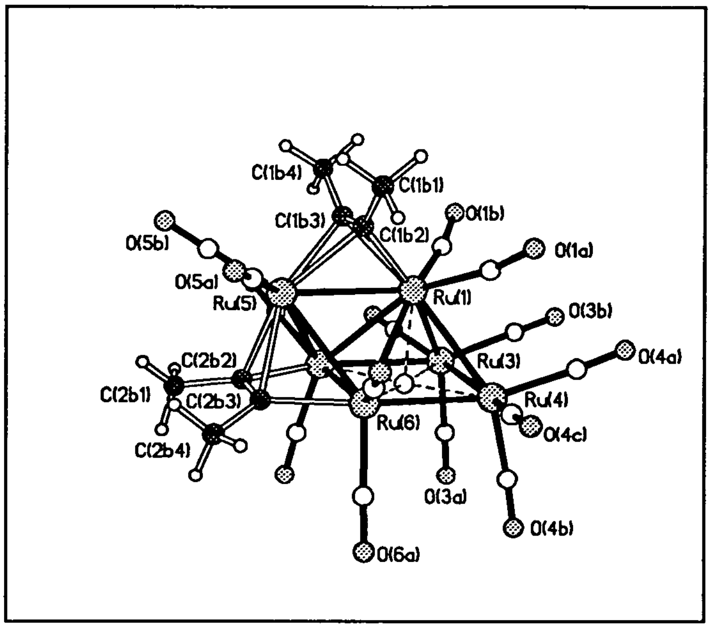


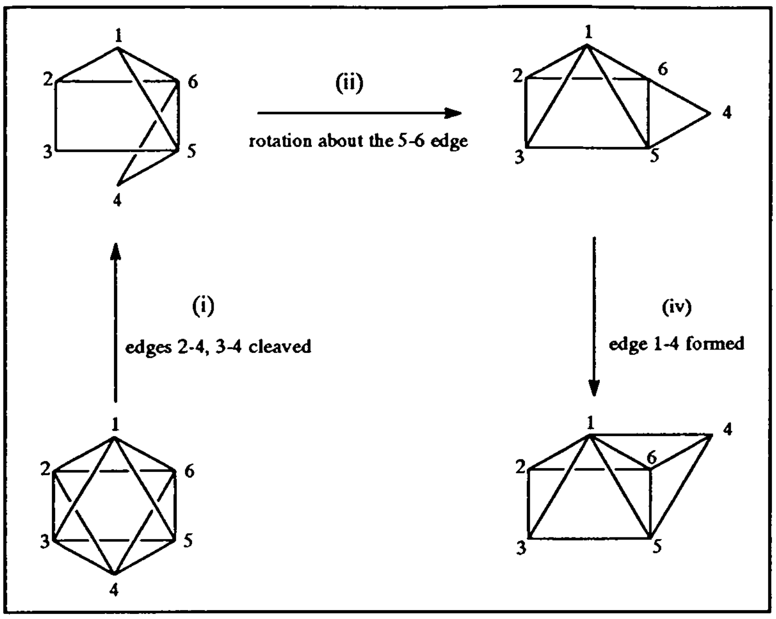
Figure 2.5a: the molecular structure of $[Ru_6C(CO)_{14}(\mu:\eta^2:\eta^2 - Me_2C_2)(\mu_3:\eta^1:\eta^2:\eta^1 -Me_2C_2)]$ showing the atom labelling scheme. Bond lengths(Å) and relevant angles(°): Ru(1)-Ru(2) 2.8603(10), Ru(1)-Ru(3) 2.8405(10), Ru(1)-Ru(4) 2.8364(10), Ru(1)-Ru(5) 2.8775(10), Ru(1)-Ru(6) 2.8740(10), Ru(2)-Ru(3) 2.8816(10), Ru(2)-Ru(5) 2.8171(10), Ru(2)-Ru(6) 2.8295(10), Ru(3)-Ru(4) 2.8174(10), Ru(4)-Ru(6) 2.8815(10), Ru(5)-Ru(6) 2.8288(10); Ru(1)-C 2.086(9), Ru(2)-C 2.004(8), Ru(3)-C 2.019(8), Ru(4)-C 2.019(8), Ru(6)-C 2.030(8); mean Ru-C(CO) 1.909; mean C-O 1.133; mean Ru-C-O 175.5; Ru(1)-C(1B2) 2.165(9), R(1)-C(1B3) 2.179(9), Ru(5)-C(1B2) 2.184(9), Ru(5)-C(1B3) 2.231(9), Ru(2)-C(2B2) 2.072(9), Ru(5)-C(2B2) 2.072(9), Ru(5)-C(2B3) 2.251(10), Ru(6)-C(2B3) 2.092(10); C(1B1)-C(1B2) 1.479(13), C(1B2)-C(1B3) 1.336(14), C(1B3)-C(1B4) 1.466(13); C(2B1)-C(2B2) 1.525(13), C(2B2)-C(2B3) 1.377(13), C(2B3)-C(2B4) 1.520(13); C(1B1)-C(1B2)-C(1B3) 139.4(9), C(1B2)-C(1B3)-C(1B4) 143.6(8), C(2B1)-C(2B2)-C(2B3) 123.1(8), C(2B2)-C(2B3)-C(2B4) 126.2(9).

The molecular structure comprises of a square based pyramid of ruthenium atoms with the sixth ruthenium atom capping the face of the Ru(1), Ru(3) and Ru(6) triangle. Ru-Ru distances range from 2.817(9) to 2.882(10)Å, (average 2.850Å). The longest metal-metal distances, Ru(2)-Ru(3), 2.882Å and Ru(4)-Ru(6), 2.882Å involve the sigma interactions from one of the coordinated alkynes at the basal Ru(2) and Ru(6)atoms, this effect was also observed in $[Ru_6C(CO)_{15}(Me_2C_2)]$. The interstitial carbido atom has remained intact now located in the base of pyramid as in other Ru_5C complexes;[25-28] it is displaced out of a central location towards Ru(2). All fourteen carbonyl ligands are bound terminally with an average Ru-C-O bond angle of 175.5°

(range 167.7(8)-178.5(8)°). The two carbonyl groups situated on Ru(1) with Ru-C-O bond angles of 167.7(8) and 169.1(9)° are bent out of a linear arrangement, this is probably because of the accumulative effects of limited space due to the alkyne bound across the Ru(1)-Ru(5) metal edge and the six carbonyl groups on the basal ruthenium atoms Ru(3) and Ru(4). The two alkynes are bound differently to the metal core. The first alkyne is bonded in the familiar face bridging mode, μ_3:η^1:η^2:η^1 [1,2] across the Ru(2)-Ru(5)-Ru(6) triangle. There are two separate sigma interactions to Ru(2) and Ru(6) and a π-interaction to Ru(5). The alkyne has increased in alkene characteristics upon coordination with C-C-C bond angles of 123.1(8) and 125.2(6)° and a C=C multiple bond distance of 1.377(13)Å, (*cf.* 180° and 1.2Å in free acetylene). The second ligand is bound, more unusually, perpendicularly across two metal atoms Ru(1) and Ru(5) and involves two π-interactions from the C=C multiple bond, one to each metal atom; a bonding mode commonly observed in dinuclear complexes[29]. The second ligand has attained some alkene characteristics on coordinating to the metal core the effects are not as marked as those for the facially bound ligand[23]. This is exemplified by assessing the bond angles and lengths of the ligand. The C-C-C bond angles are 139.4(9) and 143.6(8)° and the C=C multiple bond length is 1.336Å; *i.e.* the angles have been reduced and the bond lengthened but not as extensively as in the facially bound group. Few examples of *bis*-alkyne complexes have appeared in the literature and complexes where the two ligands are bound in different bonding modes are rarer still.

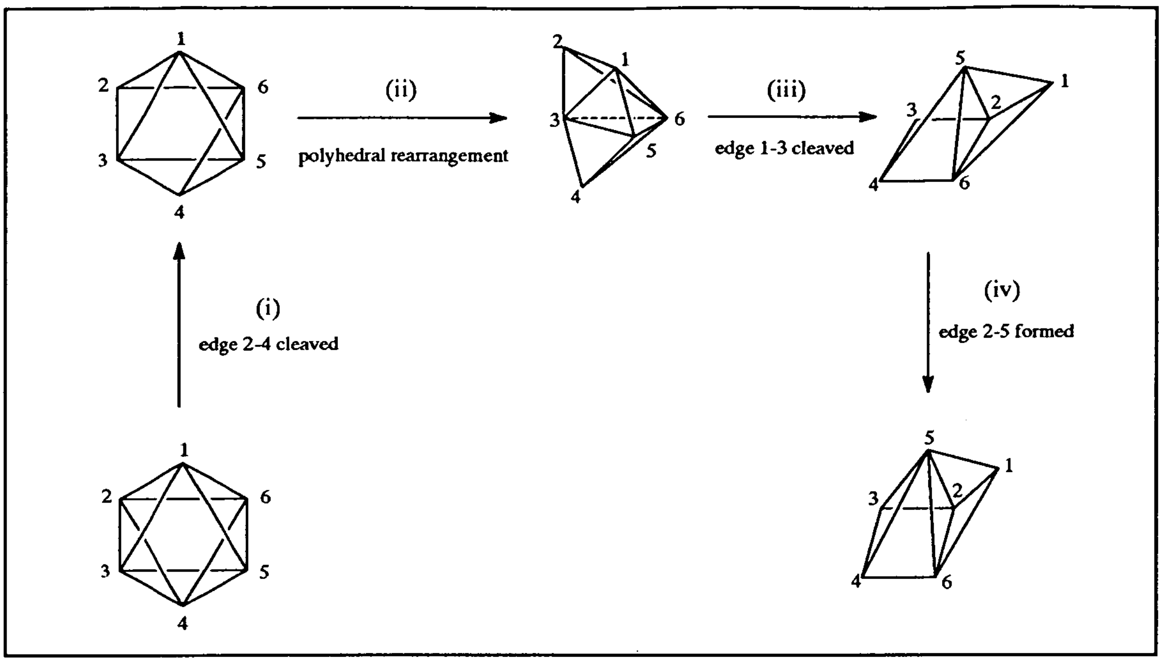
The rearrangement that the hexaruthenium carbido unit has undergone is unusual in itself in that the carbido atom has been noted[24,25] to offer stability to the ruthenium cage limiting rearrangement, whereas in complexes with no interstitial atom rearrangements are more frequently observed[30,31]. Highlighting an example of this behaviour is the reaction of the activated osmium derivative, $[Os_6(CO)_{17}(NCMe)]$[21] with alkynes which results in a variety of products. One such product is $[Os_6(CO)_{17}(\mu\text{-}H)(\mu_4\text{-}\eta\text{-}CCEt)]$ where the metal frame work has under gone rearrangement from the *bi*capped tetrahedron to a tetrahedron, one edge of which is bridged by a fifth osmium atom and the triangle thus formed is bridged by the sixth osmium atom. The α-hydrogen of the alkyne has migrated onto the metal frame and the dehydrogenated alkyne bridges three metal atoms in the familiar $\mu_3:\eta^1:\eta^2:\eta^1$-mode. It should, however be recognised that this reaction was carried out under severe conditions, namely long reflux times at elevated temperatures and the alkyne employed here was more susceptible to rearrangement due to the presence of the α-hydrogen. Reaction conditions for the synthesis of $[Ru_6C(CO)_{14}(Me_2C_2)]$, **2** were considerably milder and but-2-yne is not as likely to rearrange due to the absence of any α-hydrogens.

The mechanism of this rearrangement process is not clear, and as yet there is no experimental evidence available to aid clarification. It is possible however to speculate about a possible pathway. Polyhedral rearrangements have received extensive attention by Johnson and *co-workers*[32-35] who have devised the polyhedral-ligand model. The model, on a purely theoretical basis, accounts for many polyhedral rearrangements. It states that for any polyhedral rearrangement in the cluster unit M_m, one might reasonably expect a pathway in which the change in cohesive energy is kept to a minimum; *ie* rearrangement is expected to occur by the cleavage of one M-M contact or one polyhedral edge at a time. It is important to consider M-M contacts as 'fluid' and not fixed, non-flexible bonds. In the rearrangement of complex **2** to **3**, it is possible to envisage two possible mechanistic pathways. In the first case for a possible mechanism two edges could be broken, namely 2-4 and 3-4 which would leave a square based pyramid defined by vertices 1, 2, 3, 5 and 6 with 1 as the apical atom. If the triangle given by vertices 4, 5, and 6 then pivots about the 6-5 edge followed by a new edge being formed between vertices 1 and 4, the new polyhedron has been reached. A complex with the intermediate structure of the square based pyramid with on basal edge being bridged has been cited in the literature, $[Os_6(CO)_{17}(\mu_4\text{-HCCEt})]$[21] and has according to skeletal electron pair theory the required electron count of 88. This possible pathway is highlighted in Scheme 2.5.2.



Scheme 2.5.2. Possible mechanism for rearrangement of [$Ru_6C(CO)_{14}Me_2C_2)_2$], I.

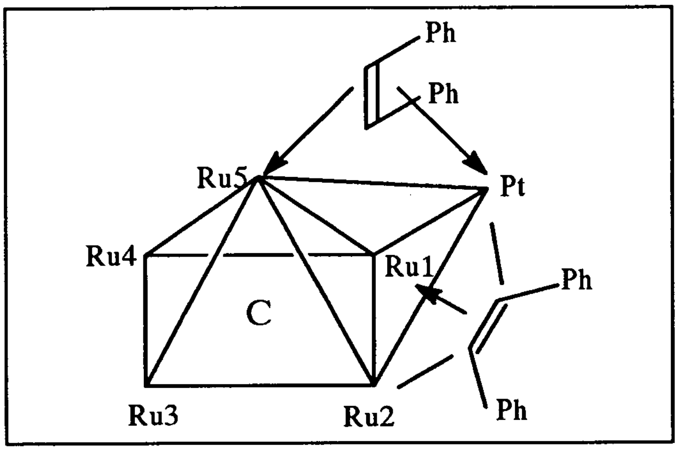
In a second possible pathway two edges are also broken. The first edge cleaved is 2-4. This is followed by the polyhedral rearrangement to a bicapped tetrahedron defined by vertices 1, 3, 5, and 6, edge 3-6 is absent and faces 1, 3, 6 and 3, 5, 6 are capped by vertices 2 and 4 respectively. A second edge, 1-3 is then cleaved to leave the capped square based pyramid, formation of the edge 2-5 completes the mechanism. This is highlighted in Scheme 2.5.3.



Scheme 2.5.3. Possible mechanism for the rearrangement of $[Ru_6C(CO)_{14}(Me_2C_2)_2]$, II.

In both cases two edges of the polyhedron have been broken and it would be difficult to decide on the basis of likely cohesive energies involved which would be the preferred route. However, the second mechanism appears to be a much more 'fluid' approach. These possible pathways, although simplistic do seem to offer logical, if highly speculative, mechanisms for the conversion of an octahedron to a capped square based pyramid but as already stated there is no experimental evidence as yet.

According to polyhedral skeletal electron pair theory[2,35] the predicted electron count for a capped square based pyramid structure is 86; the electron count of $[Ru_6C(CO)_{14}(Me_2C_2)_2]$ is 88. The substitution of a second alkyne group on to the complex $[Ru_6C(CO)_{15}(Me_2C_2)]$, **2** (electron count 86) was expected to proceed with the substitution of two carbonyl ligands which donate a total of four electrons to the overall count, the incoming alkyne making up the deficit by 're-donating' four electrons. However, only one carbonyl group is displaced and the cluster undergoes rearrangement. It is assumed that the alkyne bound across the edge is donating four electrons to count as it is perpendicular to the M-M contact;[23] alkynes only donating two electrons to a complex tend to be located parallel to the M-M bond. An example is the compound $[Ir_4(CO)_8(C_2(COOMe)_2)_4]$[36] where the four iridium atoms are arranged in a square, two of the alkynes bridge the face lying above and below the square plane. The remaining two ligands bridge opposing Ir-Ir edges and lie parallel to the bonds. The cluster is a 64 electron complex which is consistent with the count for a planar arrangement of four metal atoms in which the edge bridging functionalities donate two electrons each to the overall count. So, returning to the problem of the count of complex **3** it is assumed that both alkyne functionalities, although in different bonding modes donate four electrons each to the count. A related compound $[Ru_5PtC(CO)_{13}(\mu:\eta^2:\eta^2\text{-}Ph_2C_2)(\mu_3:\eta^2:\eta^1:\eta^1\text{-}Ph_2C_2)]$[18] has recently been reported in the literature and is shown schematically in Scheme 2.5.4

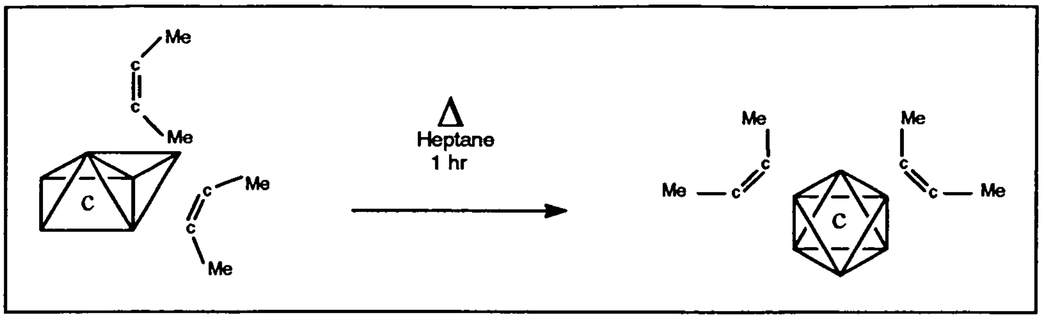


Scheme 2.5.4. Schematic representation of $[Ru_5PtC(CO)_{13}(\mu:\eta^2:\eta^2\text{-}Ph_2C_2)(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Ph_2C_2)]$

The cluster was prepared by photolysing $[PtRu_5C(CO)_{16}]$[17] in the presence of the ligand diphenylacetylene, Ph_2C_2.[18] This complex also undergoes the octahedron to capped square based pyramid rearrangement with the Pt atom in the capping position, the alkyne ligands are bound perpendicularly across the Pt-Ru(5) edge and facially across the Pt-Ru(1)-Ru(2) triangle and the electron count is 88, *i.e.* rich by 2 electrons. However, the excess electrons have been accounted for here; an examination of the Ru(1)-Ru(5) and Ru(2)-Ru(5) interactions shows that they are considerably longer at 3.023(2) and 3.107(2)Å respectively compared to an average M-M distance of 2.843(2)Å in the remainder of the cluster. This lengthening has been attributed to a weakening of the metal-metal bonds due to the presence of excess electrons. The analogous contacts in **3**, namely Ru(1)-Ru(6) (2.8744(10)Å) and Ru(1)-Ru(2) (2.8820(10)Å) both lie within the range of all Ru distances of the complex, 2.817(10)-2.882(10)Å, *i.e.* show no lengthening. The parent clusters, $[Ru_6C(CO)_{17}]^{22}$ and $[Ru_5C(CO)_{15}]^{24}$ have Ru distances in the ranges 2.872(7)-3.034(5)Å and 2.800(2)-2.882(2)Å respectively; compared to $[Ru_6C(CO)_{17}]$ the Ru distances in **3** are on the whole shorter and are comparable to those in $[Ru_5C(CO)_{15}]$. Concluding then it would appear that there is no immediate explanation for the anomalies of the complex, $[Ru_6C(CO)_{14}(Me_2C_2)_2]$.

2.6. Conversion of $[Ru_6C(CO)_{14}(Me_2C_2)]$ to $[Ru_6C(CO)_{13}(Me_2C_2)_2]$, (I).

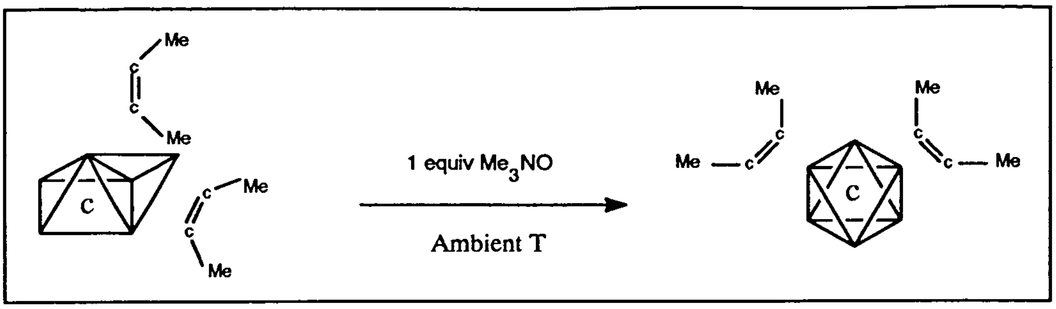
The failure to obtain the complex $[Ru_6C(CO)_{13}(Me_2C_2)_2]$ in which the two alkynes coordinate to an octahedral array of ruthenium atoms directly from $[Ru_6C(CO)_{17}]$ led us to examine the conversion of complex **3** to the required product by removal of a carbonyl ligand. The compound was heated in heptane for 1 hour under reflux conditions; the reaction was monitored periodically by infrared spectroscopy and spot tlc. Once it was clear that no further reaction was occurring solvent was removed *in vacuo*. Using a mixture of dichloromethane-hexane (3:7 v/v) as eluent and tlc products were eluted in the following order, $[Ru_6C(CO)_{14}(Me_2C_2)_2]$, **3** and $[Ru_6C(CO)_{13}(Me_2C_2)_2]$, **4**. The first indications of obtaining the *bis* but-2-yne derivative with the alkynes coordinating to a regular octahedron came from the infrared spectrum which showed a similar profile of bands to that of the known compound $[Ru_6C(CO)_{13}(Ph_2C_2)_2]^{18}$. In the mass spectrum a parent peak at m/z 1090amu was followed by the sequential loss of 13 carbonyl ligands confirming that $[Ru_6C(CO)_{13}(Me_2C_2)_2]$ had been prepared. Further evidence came from the ^1H nmr spectrum which exhibited an intense singlet at δ2.98 ppm. The reaction is highlighted in scheme 2.6.1.



Scheme 2.6.1. Thermal conversion of $[Ru_6C(CO)_{14}(Me_2C_2)_2]$ to $[Ru_6C(CO)_{13}(Me_2C_2)_2]$.

2.7 Conversion of $[Ru_6C(CO)_{14}(Me_2C_2)]$ to $[Ru_6C(CO)_{13}(Me_2C_2)_2]$, (II).

As has previously been discussed Me_3NO can be used selectively to remove a certain number of carbonyl groups. Complex **3** was known to be electron rich due to the presence of an additional carbonyl ligand; it was thus thought that Me_3NO could be used to remove the extra carbonyl to reach the $[Ru_6C(CO)_{13}(Me_2C_2)_2]$ derivative. In the preparation of $[Ru_6C(CO)_{14}(C_6H_6)]$[21] from $[Ru_6C(CO)_{17}]$ and 1,3-cyclohexadiene, three molar equivalents of Me_3NO are employed to selectively remove three carbonyl units from the parent cluster. A by-product of the reaction is the diene derivative $[Ru_6C(CO)_{15}(1,3\text{-}C_6H_8)]$ which can be successfully converted to the benzene derivative by using one molar equivalent Me_3NO at room temperature. With this reaction sequence in mind one molar equivalent of Me_3NO was added to a stirred solution of $[Ru_6C(CO)_{14}(Me_2C_2)_2]$ in dichloromethane at ambient temperature. After stirring the solution for a further 20 minutes solvent was reduced to a minimum volume; products were then isolated by tlc using a dichloromethane-hexane solution (3:7 v/v) as eluent. Starting material, $[Ru_6C(CO)_{14}(Me_2C_2)_2]$, **3** was retrieved from the reaction along with the new complex $[Ru_6C(CO)_{13}(Me_2C_2)_2]$, **4**. The reaction is depicted in Scheme 2.7.1.



Scheme 2.7.1. Chemical conversion of $[Ru_6C(CO)_{14}(Me_2C_2)_2]$ to $[Ru_6C(CO)_{13}(Me_2C_2)_2]$

All attempts to crystallise this material failed, on the occasions that crystals of suitable quality for a crystallographic study were obtained it was found that the unit cell was that of $[Ru_6C(CO)_{14}(Me_2C_2)_2]$; *i.e.* compound 4 had reverted to the starting material.

2.8. Reaction of $Ru_6C(CO)_{14}(Me_2C_2)_2$ with carbon monoxide.

The stimulus behind this reaction was to hopefully observe stepwise loss of the alkyne ligands in the presence of carbon monoxide. The complex $[Ru_6C(CO)_{14}(Me_2C_2)_2]$ as a red solution in dichloromethane was stirred for four hours under an atmosphere of carbon monoxide and was monitored periodically by infrared spectroscopy and spot tlc. After this period of time no apparent reaction had occurred. The reactant $[Ru_6C(CO)_{14}(Me_2C_2)_2]$ is therefore assumed to be relatively stable not reverting to starting material nor undergoing carbon monoxide insertion into the C=C multiple bond.

2.9 Synthesis of a Novel *Tris*-alkyne Hexaruthenium Complex.

The complex $[Ru_6C(CO)_{14}(Me_2C_2)_2]$ was dissolved in dichloromethane and cooled to -78°C. The ligand Me_2C_2 was added to the red solution in excess quantities. Two molar equivalents of Me_3NO in dichloromethane were added dropwise to the solution over a period of 5 minutes. The solution was stirred for a further 30 minutes during which time it reached room temperature and darkened in colour. The solution was concentrated to a minimum volume under reduced pressure; residues were purified by tlc using a solution of dichloromethane-hexane (3:7 v/v) as eluent. Products were isolated in the following order, $[Ru_6C(CO)_{14}(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)(\mu:\eta^2:\eta^2\text{-}Me_2C_2)]$, **3** (5%) and $[Ru_6C(CO)_{12}(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)_3]$, **5** (39%). Compound **5** exhibited a parent peak at m/z 1116 in the mass spectrum leading to the molecular formula $[Ru_6C(CO)_{12}(Me_2C_2)_3]$. In the ^1H nmr a singlet was observed at δ 2.86ppm. Crystals of complex **5** were produced by the slow evaporation of a dichloromethane-hexane layer at -25°C. The molecular structure of $[Ru_6C(CO)_{12}(Me_2C_2)_3]$ is shown in Figure 2.9a.

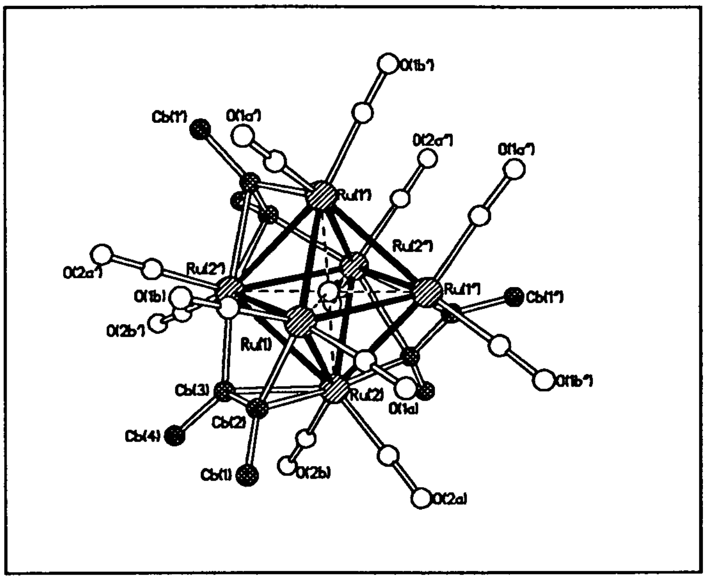
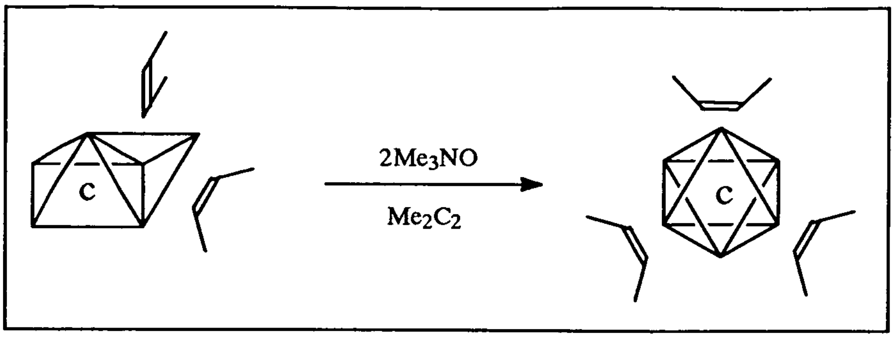


Figure 2.9a: The molecular structure of[$Ru_6C(CO)_{12}(\mu_3:\ \eta^1:\ \eta^2:\ \eta^1\ \text{-}\ Me_2C_2)_3$] showing the atom labelling scheme. Important bond lengths(Å) and angles(°) for one of the crystallographic units: Ru(1)-Ru(2) 2.9257(4), Ru(1)-Ru(1') 2.8730(5), Ru(1)-Ru(1") 2.8730(5), Ru(1)-Ru(2') 2.9476(4), Ru(2)-Ru(1") 2.9476(4), Ru(2)-Ru(2') 2.9359(5), Ru(2)-Ru(2") 2.9359(5); Ru(1)-C 2.020(3), Ru(2)-C 2.110(3), Ru(1')-C 2.020(3), Ru(1")-C 2.020(3), Ru(2')-C 2.110(3), Ru(2")-C 2.110(3); Ru(1)-C(1A) 1.868(4), Ru(1)-C(1B) 1.889(4), Ru(2)-C(2A) 1.873(4), Ru(2)-C(2B) 1.898(4); C(1A)-O(1A) 1.146(5), C(1B)-(1B) 1.138(4), C(2B)-O(2B) 1.137(4), C(2B)-O(2B) 1.137(4); mean Ru-C-O 178.1(4); Ru(1)C(b2) 2.035(3), Ru(2)-C(b2) 2.342(3), Ru(2)-C(b3) 2.284(3), Ru(2')-C(b3) 2.147(3); C(b1)-C(b2) 1.495(5), C(b2)-C(b3) 1.369(5), C(b3)-C(b4) 1.518(5); C(b1)-C(b2)-C(b3) 125.6(3), C(b2)-C(b3)-C(b4) 121.5(3).

The molecular structure of $[Ru_6C(CO)_{12}(Me_2C_2)_3]$ was solved using the DIRDIFS program and exhibits three fold crystallographic symmetry. The metallic cage comprises of a regular octahedron of ruthenium atoms encapsulating a central carbido atom. Ru-Ru bond distances are in the range 2.8730(5)-2.9476(5)Å (mean 2.9198(5)Å). The carbido atom has remained intact though once again it has been displaced out of the centre of the framework. The shorter Ru-C(carbido) bond distance of 2.020(3)Å is observed at Ru atoms bearing two carbonyl groups and one Ru-C(alkyne) sigma interaction, *i.e.* Ru(1), Ru(1') and Ru(1"); the longer Ru-C(carbido) distance of 2.110(3)Å occurs at Ru(2), Ru(2') and Ru(2") which are involved in the bonding of two carbonyls, a sigma Ru-C(alkyne) bond and a Ru-C(alkyne) pi-interaction. The overall effect is that the carbide lies closest to the Ru(1)-Ru(1')-Ru(1") face where each of the metals are involved with a sigma Ru-C(alkyne) interaction only. All the carbonyl ligands are terminally bound with slight deviations from linearity, mean Ru-C-O bond angle 178.1(4)° (range 177.4(3)-179.2(4)°) Each of the but-2-yne ligands bridges a triangular Ru_3 face in the $\mu_3:\eta^2:\eta^1:\eta^1$ mode. The alkyne character of the ligand has diminished with a C=C multiple bond length of 1.369(5)Å and C-C-C bond angles of 121.5(3) and 125.6(3)°. Although the ligand is essentially at angle of 70° to the plane of the Ru_3 face, it is not parallel to the metal face as in $[Ru_6C(CO)_{15}(Me_2C_2)]$, **2**. This is highlighted by examining the Ru-C(alkyne) distances of the sigma interactions; Ru(1)-C(b2) is 2.035(3)Å whilst Ru(2')-C(b3) is 2.147(4)Å, a difference of 0.112Å. This could be attributed to the fact that Ru(2') is also involved with a pi-interaction from C(b1') causing lengthening of the Ru-C bond, whilst Ru(1) bears no such interaction thus the bond is shorter.

In this reaction it had been our intention to substitute a further two carbonyls with a third but-2-yne ligand onto the metallic core. The mass spectrum confirmed that this had occurred with the observed parent peak at m/z 1116amu. This led to the formulation of $[Ru_6C(CO)_{12}(Me_2C_2)_3]$ and an electron count of 88. After the study of $[Ru_6C(CO)_{14}(Me_2C_2)_2]$ which showed that there had been a rearrangement from an octahedron to a monocapped square based pyramid, it was thought that complex **5** would have shown a similar rearrangement with having an unusual electron count. The ^1H nmr spectrum was expected to show two, possibly three separate resonances if there had been some reorientation of the cluster; however only a singlet was observed at δ 2.86ppm, *i.e.* all protons are in the same environment. This was confirmed by the molecular structure and the reaction is highlighted in Scheme 2.9.1.



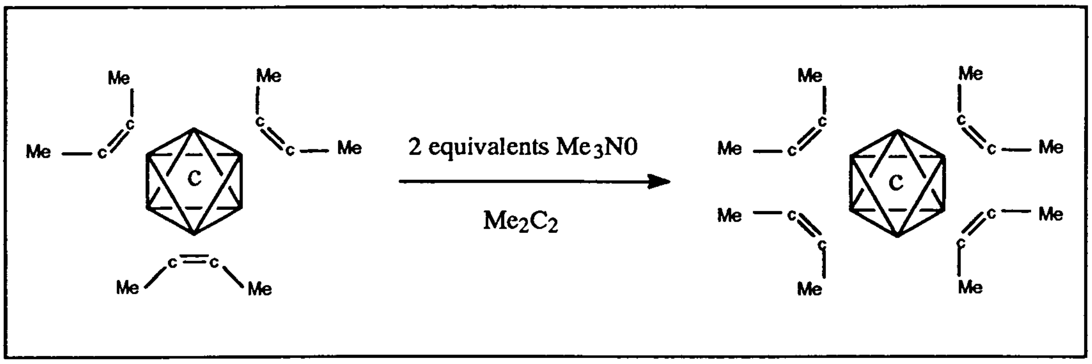
Scheme 2.9.1. Synthesis of $[Ru_6C(CO)_{12}(Me_2C_2)_3]$ from $[Ru_6C(CO)_{14}(Me_2C_2)_2]$.

2.10. Attempted Cyclization of *tris*-butyne hexaruthenium $[Ru_6C(CO)_{12}(Me_2C_2)_3]$.

The compound $[Ru_6C(CO)_{12}(Me_2C_2)_3]$ was heated in hexane under reflux conditions for five hours. The reaction was monitored by infrared spectroscopy periodically during this time. The reaction did not proceed as hoped and starting material was retrieved in 80% yield. This reaction emphasises the stability of these complexes. This has been shown previously[24,25,28] when *mono*-substituted alkyne complexes of hexaruthenium have been heated for several days in toluene under reflux conditions and retrieved in near quantitative yields. Such complexes with alkynes containing an α-H in similar conditions undergo rearrangements which involves H-migration from the alkyne onto the metal core and thus, the formation of an alkyilidene derivative. This stability of the *mono*- and *tri*-substituted alkyne derivatives has been attributed to the presence of the interstitial carbido atom[24,25,28]. In *hexa*- and *hepta*-osmium alkyne based clusters such stability is not observed and the metal cores under go major skeletal rearrangements on prolonged heating[30,31].

2.11. Reaction of $[Ru_6C(CO)_{12}(Me_2C_2)_3]$with 2 equivalents of Me_3NO and Me_2C_2.

To a solution of $[Ru_6C(CO)_{12}(Me_2C_2)_3]$ in dichloromethane at -78°C, but-2-yne was added. Two molar equivalents of Me_3NO in dichloromethane was introduced slowly to the solution. After 30 minutes stirring to reach room temperature the dark brown solution was concentrated to a minimum volume *in vacuo*. Residues were purified using tlc and a solution of dichloromethane-hexane (3:7, v/v). Products isolated were unreacted starting material [$Ru_6C(CO)_{12}(Me_2C_2)_3$], **5** and [$Ru_6C(CO)_{10}(Me_2C_2)_4$], **6**. The reaction is depicted in Scheme 2.11.1.



Scheme 2.11.1. Synthesis of [$Ru_6C(CO)_{10}(Me_2C_2)_4$], 6 from [$Ru_6C(CO)_{12}(Me_2C_2)_3$].

To date the only data available on complex **6** is infrared and mass spectra. The infrared spectrum is very simple, as was that of [$Ru_6C(CO)_{12}(Me_2C_2)_3$], suggesting a high degree of symmetry in the complex. In the mass spectrum a parent peak at m/z 1114amu followed by the loss of several carbonyl ligands gives rise to the molecular formula $Ru_6C(CO)_{10}(Me_2C_2)_4$. With such a limited amount of data available it is only possible to speculate about the possible structure of this material. One such suggestion could be that the octahedral array of ruthenium atoms has remained intact with ten carbonyls displaced around this core. The four alkynes could be arranged such that they occupy faces of the cluster in a tetrahedral fashion. If this was the case then the complex could be said to resemble the structure of $Rh_6(CO)_{16}$[37] where four carbonyls bridge four tetrahedrally displaced faces.

2.12. One Step Reactions to Hexaruthenium Alkyne Derivatives.

Up until now the stepwise reactions outlined to reach *tri-* and *tetra*-substituted alkyne derivatives have involved taking stoichiometric amounts of trimethylamine N-oxide to remove two carbonyls at a time. It has also been shown that the addition of four, six and eight molar equivalents to a reaction will, in a one step process yield complexes **3**, **5** and **6**. The addition of either three or four molar equivalents of Me_3NO to $Ru_6C(CO)_{17}$ will always yield the complex $[Ru_6C(CO)_{14}(Me_2C_2)_2]$ and not $[Ru_6C(CO)_{13}(Me_2C_2)_2]$. Problems that arise from this pathway are firstly, the presence of large quantities of Me_3NO leads to increased decomposition of $Ru_6C(CO)_{17}$. Secondly the yields of such 'one-pot' reactions versus a stepwise approach are much smaller, this is shown in Table 2.12a This data confirms that the stepwise mechanism is the much preferred route into these alkyne substituted complexes with a high selectivity of reaction products.

Moles Me_3NO	**% 2**	**% 3**	**% 4**	**% 5**
2	37	12	-	-
4	29	25	-	-
6	12	15	28	-
8	12	11	10	9

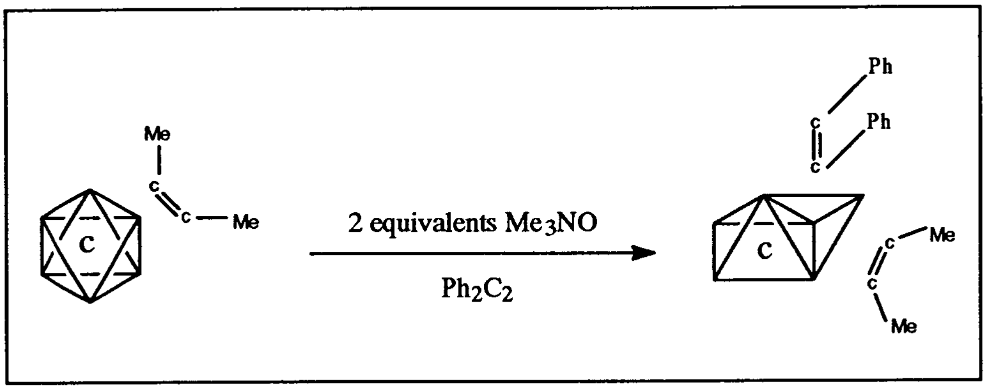
Table 2.12a. % yields of reactions of $Ru_6C(CO)_{17}$ and Me_3NO.

2.13. Reactions Involving Alkynes Other Than But-2-yne.

So far it has been shown that but-2-yne can be added to $Ru_6C(CO)_{17}$ in a series of steps yielding *mono-*, *di-*, *tris-*, and *tetrakis-*substituted compounds. As previously stated the stimulus behind this work was two-fold; firstly to produce cluster cores encapsulated in organic fragments and secondly to observe polymerisation of the organic units. With this second aim foremost, it was decided to look at the substitution of carbonyl groups by a variety of alkynes so that if polymerisation were to occur then organic chains would contain a high variety of R-groups.

2.14 Reaction of $Ru_6C(CO)_{15}(Me_2C_2)$ with 2 molar equivalents of Me_3NO and Ph_2C_2.

The complex $Ru_6C(CO)_{15}(Me_2C_2)$ was taken up in dichloromethane and cooled to -78°C; diphenylacetylene, Ph_2C_2 was added to the red solution. Two molar equivalents of Me_3NO in dichloromethane was introduced to the solution over a period of 5 minutes. After stirring the solution for a further 30 minutes to attain room temperature the solution had darkened in colour. Solvent was removed *in vacuo* and residues were purified by tlc using a solution of dichloromethane-hexane (3:7, v/v) as eluent. Two products were identified, unreacted starting material, $[Ru_6C(CO)_{15}(Me_2C_2)]$, **3** and μ_3:η^1:η^2:η^1-but-2-yne μ_6-carbido tetradecacarbonyl μ:η^2:η^2-diphenylacetylene hexaruthenium, $[Ru_6C(CO)_{14}(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)(\mu:\eta^2:\eta^2\text{-}Ph_2C_2)]$, **7**. This overall reaction is shown is shown in Scheme 2.14.1.



Scheme 2.14.1. Synthesis of $[Ru_6C(CO)_{14}(Me_2C_2)(Ph_2C_2)]$ from $[Ru_6C(CO)_{15}(Me_2C_2)]$.

The infrared spectrum of **7** exhibited a similar band pattern as $[Ru_6C(CO)_{14}(Me_2C_2)_2]$, **3** leading to an initial assessment of **7** to be $[Ru_6C(CO)_{14}(Me_2C_2)(Ph_2C_2)]$. In the mass spectrum a parent peak at m/z 1242 was observed followed by the loss of several carbonyl functionalities again pointing towards the formulation $[Ru_6C(CO)_{14}(Me_2C_2)(Ph_2C_2)]$. The ^1H nmr spectrum showed a singlet at δ2.89ppm and a multiplet at δ7.32ppm, confirming the presence of the two alkynes. Crystals of this compound were afforded from a solution of dichloromethane at -10°C.

The molecular structure of $[Ru_6C(CO)_{14}(Me_2C_2)(Ph_2C_2)]$ is shown in Figure 2.14a.

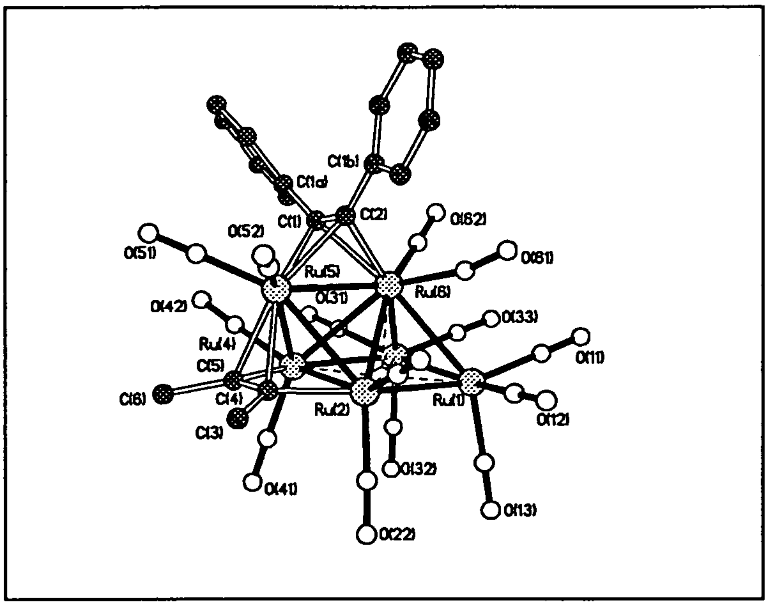
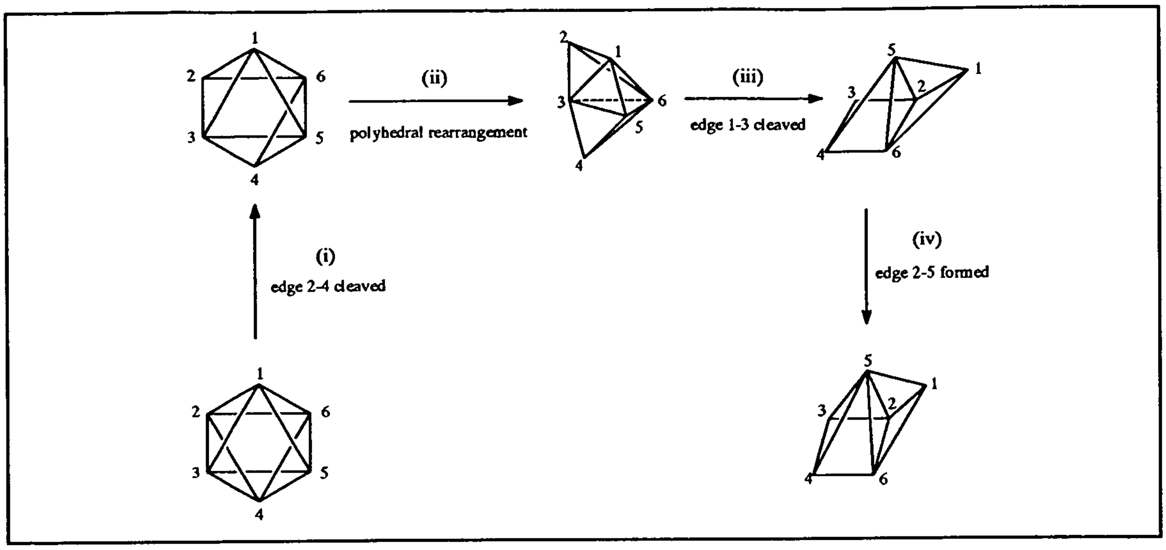


Figure 2.14a. The molecular structure of $[Ru_6C(CO)_{14}(Me_2C_2)(Ph_2C_2)]$ showing the atom labelling scheme. Significant bond lengths (Å) and angles (o): Ru(1)-Ru(2) 2.9023(5), Ru(1)-Ru(3) 2.8268(7), Ru(1)-Ru(6) 2.8465(5), Ru(2)-Ru(4) 2.8086(6), Ru(2)-Ru(5) 2.8787(5), Ru(2)-Ru(6)2.8788(5), Ru(3)-Ru(4) 2.8797(5), Ru(3)-Ru(6) 2.8539(5), Ru(4)-Ru(5) 2.8078(5), Ru(4)-Ru(6) 2.8870(4), Ru(5)-Ru(6) 2.8630(4); Ru(3)-Ru(1)-Ru(2) 90.259(10), Ru(1)-Ru(2)-Ru(4) 89.268(10), Ru(2)-Ru(4)-Ru(3) 91.089(10), Ru(4)-Ru(3)-Ru(1) 89.367(10); Ru(1)-C 2.009(3), Ru(2)-C 2.030(3), Ru(3)-C 2.034(3), Ru(4)-C 2.005(3), Ru(6)-C 2.101(3); mean Ru-C(CO) 1.902(4); mean C-O 1.136(4); Ru(5)-C1 2.232(3), Ru(5)-C2 2.168(3), Ru(6)-C1 2.147(3), Ru(6)-C2 2.180(3); Ru(2)-C4 2.083(3), Ru(4)-C5 2.092(3), Ru(5)-C4 2.238(3), Ru(5)-C5 2.241(3); C1-C2 1.319(4), C1-C1A 1.471(4), C2-C1B 1.476(3); C1A-C1-C2 140.4(3), C1-C2-C1A 1380(3); C3-C4 1.515(4), C4-C5 1.371(4), C5-C6 1.524(4); C3-C4-C5 124.2(3), C4-C5-C6 124.6(3).

The metal core comprises of a square based pyramid with a sixth ruthenium atom, Ru(5) capping the Ru(2)-Ru(4)-Ru(6) triangular face. M-M distances lie in the range 2.8086(6) - 2.9023(5)Å (mean 2.8576(7)Å). The base of the pyramid is not uniformly square and this is exemplified by examining the Ru-Ru-Ru bond angles; the largest bond angle of 91.089(10)° lies at Ru(2)-Ru(4)-Ru(3), smaller bond angles at Ru(1)-Ru(2)-Ru(4), 89.268(10)° and Ru(1)-Ru(3)-Ru(4), 89.367(10)° and at Ru(2)-Ru(1)-Ru(3) the bond angle 90.259(10)° . These distortions have been attributed to the accumulative effects of a capping metal atom and the two bound organic fragments. The interstitial carbido atom lies at the centre of the distorted square base. All fourteen carbonyls are terminally bound, mean bond angle Ru-C-O 175.9(4)°. The two carbonyls at Ru(6) show increased deviation from linearity than other CO moieties of the complex. This was also observed in $[Ru_6C(CO)_{14}(Me_2C_2)_2]$, **3** and was attributed to the limited space around the metal centre caused by the presence of the perpendicular alkyne and the basal carbonyl ligands. The two alkyne groups are bound like those in **3**. The but-2-yne ligand bridges the face Ru(2)-Ru(4)-Ru(6) in a μ_3:η^1:η^2:η^1 mode. The C(4)-C(9) bond lies parallel to the metal face as shown by the similar σ-bond distances, Ru(2)-C4, 2.083(3)Å and Ru(4)-C5, 2.092(3)Å. Atoms C(4) and C(5) are involved in a π-interaction to Ru(5). The C(4)-C(5) bond length has increased from 1.2Å in the free state to 1.371(4)Å upon coordination. The bond angles C(3)-C(4)-C(5), 124.2(3)° and C(4)-C(5)-C(6), 124.6(3)° have also increased from 180° in the free ligand[15]. The second ligand, bound perpendicular to the Ru(5)-Ru(6) edge shows alkene characteristics with a C=C multiple bond length of 1.319(4)Å and bond angles C(1A)-C(1)-C(2), 140.4(3)° and C(1)-C(2)-C(1B), 138.0(3)°. The two phenyl rings point away from each other, minimising any form of interaction between the two groups.

Comparing the two structures of **7** and **3** many similarities are observed; the alkynes are bound in identical bonding modes, carbonyls occupy the same locations and they both have electron counts of 88 rather than the predicted count of 86. There is no explanation for this abnormality.

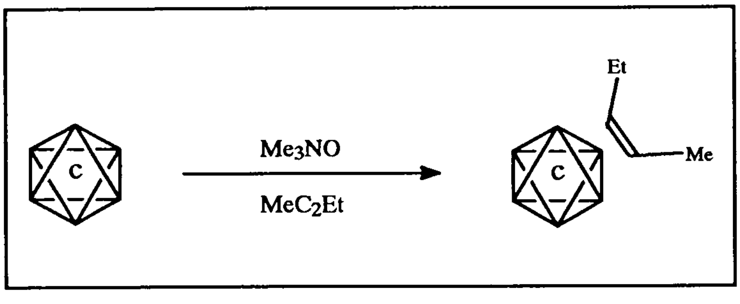
The preparation and characterisation of this mixed alkyne derivative may provide some insight into the mechanism of the rearrangement. As mentioned previously it is thought that the breaking of two edges may lead from the octahedron to the *mono*-capped square based pyramid. The Me_2C_2 ligand bound facially does not appear to move in the rearrangement. If the Me_2C_2 ligand bridges the face of apexes 1-2-6; there is a π-interaction with apex 1 and two σ-interactions at apexes 2 and 6, when the cluster undergoes the proposed rearrangement, all three of these interactions would remain intact in the final product. In $[Ru_6C(CO)_{14}(Me_2C_2)(Ph_2C_2)]$ the Me_2C_2 ligand is still face capping as in the starting material $[Ru_6C(CO)_{15}(Me_2C_2)]$ and the second alkyne is now bridging the edge apex 1-5. Of course this does not explain 'why' the rearrangement occurs but does suggest a means by which it may transpire. Scheme 2.5.3 is shown again to highlight a possible mechanism.



Scheme 2.5.3. Possible mechanism for rearrangement of [$Ru_6C(CO)_{14}(Me_2C_2)$], II.

2.15. Reaction of $Ru_6C(CO)_{17}$ with 2 molar equivalents of Me_3NO and MeC_2Et.

To a cooled solution of the material [$Ru_6C(CO)_{17}$] and pent-~~1~~2-yne, MeC_2Et in dichloromethane, 2 molar equivalents of Me_3NO in dichloromethane was introduced dropwise. The solution, initially red, attained room temperature over a 30 minute period accompanied by a darkening of the solution. The complex [$Ru_6C(CO)_{15}(MeC_2Et)$], **8** was isolated as a red/brown product by concentrating the solution *in vacuo*, followed by purification using tlc and a solution of dichloromethane-hexane (3:7, v/v) as eluent. The reaction sequence is given in Scheme 2.15.1.



Scheme 2.15.1. Synthesis of [$Ru_6C(CO)_{15}(MeC_2Et)$] from [$Ru_6C(CO)_{17}$].

Attempts at crystallisation of this complex have proved unsuccessful and the characterisation has been provided by infrared, mass and ^1H nmr spectroscopy. the infrared spectrum exhibited similar symmetry to that of $[Ru_6C(CO)_{15}(Me_2C_2)]$, **2**. Table 2.15a shows this data.

Complex	**Infrared Data.**				
Me_2C_2	2088, (w)	2036, (sh)	2044, (vs)	2021, (m)	2013, (m)
MeC_2Et	2087, (w)	2036, (sh)	2042, (vs)	2021, (m)	2011, (m)

Table 2.15a. Infrared data for $[Ru_6C(CO)_{15}(Me_2C_2]$and $[Ru_6C(CO)_{15}(MeC_2Et)]$

In the mass spectrum a parent peak at m/z 1106amu followed by the loss of several carbonyl ligands gave rise to the formulation $[Ru_6C(CO)_{15}(MeC_2Et)]$. Evidence from the ^1H nmr spectrum was not as definitive as hoped but indicate the presence of the desired product. The ^1H nmr spectrum along with a COSY analysis are given in Figure 2.15b.

At a first inspection of this complex it may be expected that the ligand may give rise to a singlet, a quartet and a triplet in the nmr spectrum. This initial approach could lead to the analysis of the spectrum of the complex was used in the following discussion of the observed resonanances in the spectrum. For the complex $[Ru_6C(CO)_{15}(Me_2C_2)]$, **2** a singlet was observed in the ^1H nmr spectrum at δ3.00ppm and was assigned to the six methyl protons of the but-2-yne moiety. Assuming that methyl protons of $[Ru_6C(CO)_{15}(MeC_2Et)]$, **8** would appear in a similar region, a singlet at δ3.00ppm was tentatively assigned to the three methyl protons of pent-2-yne. It was also anticipated that the predicted quartet would fall in the same frequency region. An apparent quartet was observed, centred at δ3.1ppm and was provisionally assigned to the CH_2 protons of the ethyl group. The triplet anticipated for the CH_3 protons of the ethyl group was expected to appear at lower frequencies as it was remote from metallic

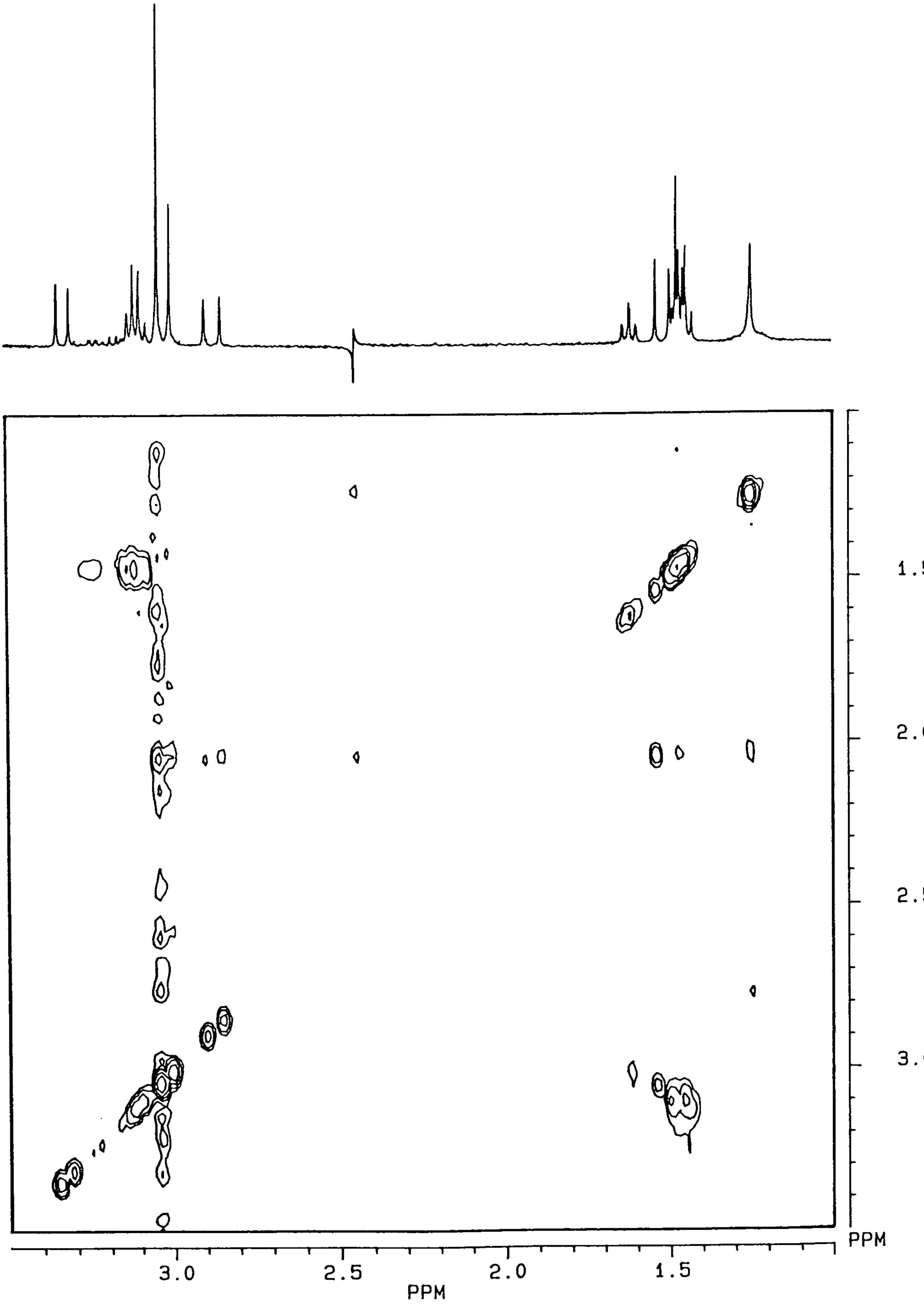
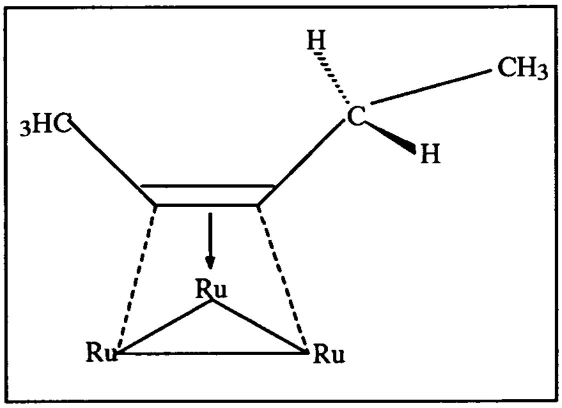


Figure 2.15b. ^1H nmr and COSY Spectra for [$Ru_6C(CO)_{15}(MeC_2Et)$].

core. In the spectrum resonances are observed at δ1.61, (triplet), δ1.53, (singlet) and δ1.47ppm (multiplet). The COSY spectrum analysis showed that the 'quartet' at δ3.1ppm correlated with the multiplet at δ1.47ppm. The relative integral for these signals were *ca.* 2:3 respectively. This means that the complex multiplet at δ1.47 is entirely due to the three protons of the CH_3 section of the ethyl group.

In the spectrum rather more signals were observed than can be accounted for in this basic analysis of the spectrum. This could be due to two factors, either impurities in the sample or the presence of diastereoisomers. This second effect can be explained by looking at the protons of the ethyl group of the coordinatied alkyne. In the diagram below the ligand and the tri-ruthenium face of the complex $[Ru_6C(CO)_{15}(Me_2C_2)]$ to which it is coordinated is shown.

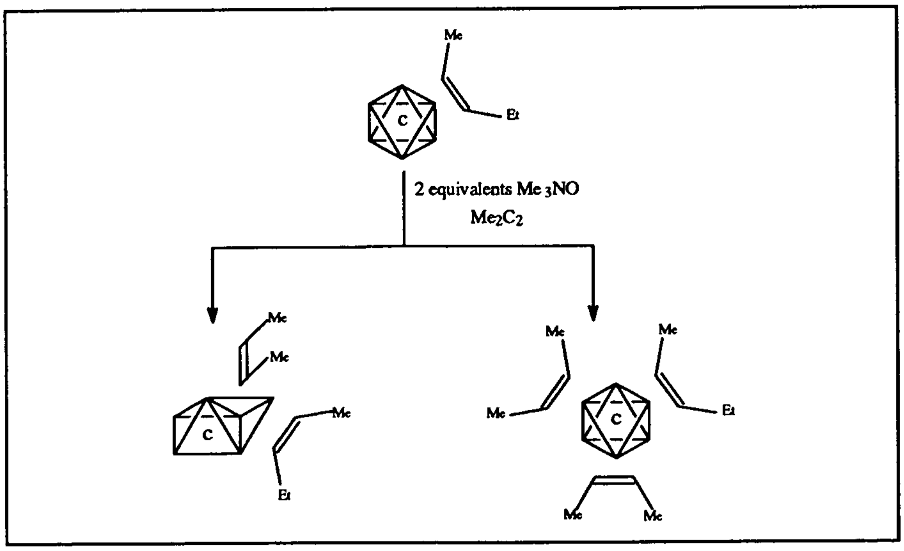


2.15.2Coordination of Pent-2-yne to a *Tri*-ruthenium Face of $[Ru_6C(CO)_{15}(MeC_2Et)]$

From this aspect it can be seen that the two protons of the methylene carbon can face 'in' and 'out' of the page. Rotation of the C-C single bond between the methylene carbon and the acetylenic carbon atom of the C=C multiple bond through 180° will leave the two methylene protons effectively unchanged with respect to their starting postions, however the methyl group would be in a different position with respect to it's own strating position. Therefore the methylene protons are not the same as one another, and hence the likelihood of diastereoisomers. The resultant effect of the presence of diastereoisomers would lead to a complicated ^1H nmr spectrum as the ethyl group would give rise to an ABX_3 type spectrum where by the protons as the methylene group would not only couple with the methyl protons but also with each other and the methyl group woul now couple independently to each of the two methylene protons. Further assignment of resonances in the spectrum was not deemed possible at this time as the spectrum exhibited a lot of background noise resulting in an unclear spectrum.

2.16. Reaction of $[Ru_6C(CO)_{15}(MeC_2Et)]$ with Me_3NO and Me_2C_2.

The starting material $[Ru_6C(CO)_{15}(MeC_2Et)]$ was dissolved in dichloromethane. As a ligand but-2-yne was introduced to the red solution at -78°C. Two molar equivalents of Me_3NO in dichloromethane were added dropwise over 5 minutes. The reaction mixture warmed to room temperature over 30 minutes, resulting in a darkening of the solution. Solvent was reduced to a minimum volume *in vacuo*. Residues were separated by tlc using a solution of dichloromethane-hexane (3:7, v/v) as eluent. Products were eluted as follows, $[Ru_6C(CO)_{15}(MeC_2Et)]$, **8** $[Ru_6C(CO)_{14}(MeC_2Et)(Me_2C_2)]$, **9** and $[Ru_6C(CO)_{12}(MeC_2Et)(Me_2C_2)_2]$, **10**. The reaction is depicted in Scheme 2.16.1.



Scheme 2.16.1. Reaction of $[Ru_6C(CO)_{15}(MeC_2Et)]$ with Me_3NO and Me_2C_2.

Complex **9** was initially identified by a comparison of the infrared spectra of itself with that of $[Ru_6(CO)_{14}(Me_2C_2)_2]$. In Table 2.16a infrared data is provided.

Complex.	**Infrared Data**					
3	2083(w)	2044(sh)	2039(s)	2025(s)	2012(m)	2001(w)
9	2082(m)	2046(sh)	2039(s)	2022(s)	2009(m)	1993(w)

Table 2.16a. Infrared data of compounds 3 and 9(cm^{-1}).

As can be seen the spectra show similarities leading to conclude that the carbonyl ligands of the two complexes are probably in similar geometries. In the mass spectrum a parent peak at m/z 1132amu gave rise to a formulation of $[Ru_6C(CO)_{14}(MeC_2Et)(Me_2C_2)]$. The ^1H nmr spectrum for the complex was intricate and the assignment of resonances was based on the assumption that proton signals for $[Ru_6C(CO)_{14}(Me_2C_2)(MeC_2Et)]$, **9** would appear at similar frequencies to those on $[Ru_6C(CO)_{15}(Me_2C_2)]$, **2** and $[Ru_6C(CO)_{14}(Me_2C_2)_2]$, **3** whose frequencies (ppm) are given in Table 2.16b as a point of reference.

Complex.	**^1H nmr Data.**	
$Ru_6C(CO)_{15}(Me_2C_2)$	3.00, 6H	-
$Ru_6C(CO)_{14}(Me_2C_2)_2$	2.88, 3H, μ_3	3.29, 6H, μ_2

Table 2.16b. ^1H nmr frequencies(ppm) of complexes 2 and 3.

From the infrared spectrum it was assumed that the complex, $[Ru_6C(CO)_{14}(Me_2C_2)(MeC_2Et)]$ had a similar geometry as that of complex **3**, *i.e.* one alkyne was face capping and the other edge bridging. In complex **7**, $[Ru_6C(CO)_{14}(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)(\mu_2:\eta^2:\eta^2\text{-}Ph_2C_2)]$ prepared by the reaction of $[Ru_6C(CO)_{15}(Me_2C_2)]$ with diphenylacetylene, Ph_2C_2 it was observed that the original but-2-yne group remained face capping whilst the second organic fragment coordinated in the edge bridging mode. Assuming that the same procedure of substitution occurred for complex **9**, *i.e.* the pent-2-yne remained facially bound and the but-2-yne bonded in the $\mu:\eta^2:\eta^2$-mode, resonances in the spectrum can start to be assigned, though only tentatively. The ^1H nmr and COSY spectra are given in Figure 2.16c.

As in the case of the the complex $[Ru_6C(CO)_{15}(MeC_2Et)]$ the initial assesment of the ^1H nmr spectrum was probably over simplistic based on assumptions that diastereoisomers were not present. This was discussed in some detail in Section 2.16. The following discussion of the ^1H nmr spectrum is based on there being no such diastereoisomers present. The methyl groups of the but-2-yne ligand could reasonably be expected to split into two independent singlets because of the asymmetry of the compound, induced by the pent-2-yne ligand. As stated previously the edge bridging but-2-yne of complex **3** showed a resonance at δ3.29ppm. In the ^1H nmr spectrum of complex **9** two singlets of equal intensity were observed at δ3.31 and 3.28ppm and have been tentatively assigned to the six protons of the but-2-yne ligand on a comparison basis to the resonances observed in **3**. The resonance pattern expected for the pent-2-yne ligand as outlined previously was that of a singlet, a quartet and a triplet. The methyl protons of but-2-yne in a face bridging coordination in **3** were observed at δ2.88ppm; assuming then that the three methyl protons of pent-2-yne in complex **9** would appear as a singlet in a similar frequency range the singlet labelled as (c) in the spectrum has been speculatively assigned to these protons. Assessing signal intensities, the ratio of intensity of signals a:b:c is 3:3:3 as it should be which points further to these assignments

Examining the spectrum for the predicted quartet and triplet of the ethyl fragment assignment of signals becomes increasingly difficult. Two apparent quartets are observed, centred at δ3.12ppm and 3.21ppm, a multiplet at δ1.45ppm is also observed. These frequencies are in the same areas as those observed in $[Ru_6C(CO)_{15}(MeC_2Et)]$, . The COSY spectrum shows that the two 'quartets' are related to the multiplet at δ1.45ppm confirming the presence of the ethyl fragment. It is not possible to assign any of these resonances to any specific proton group at this stage.

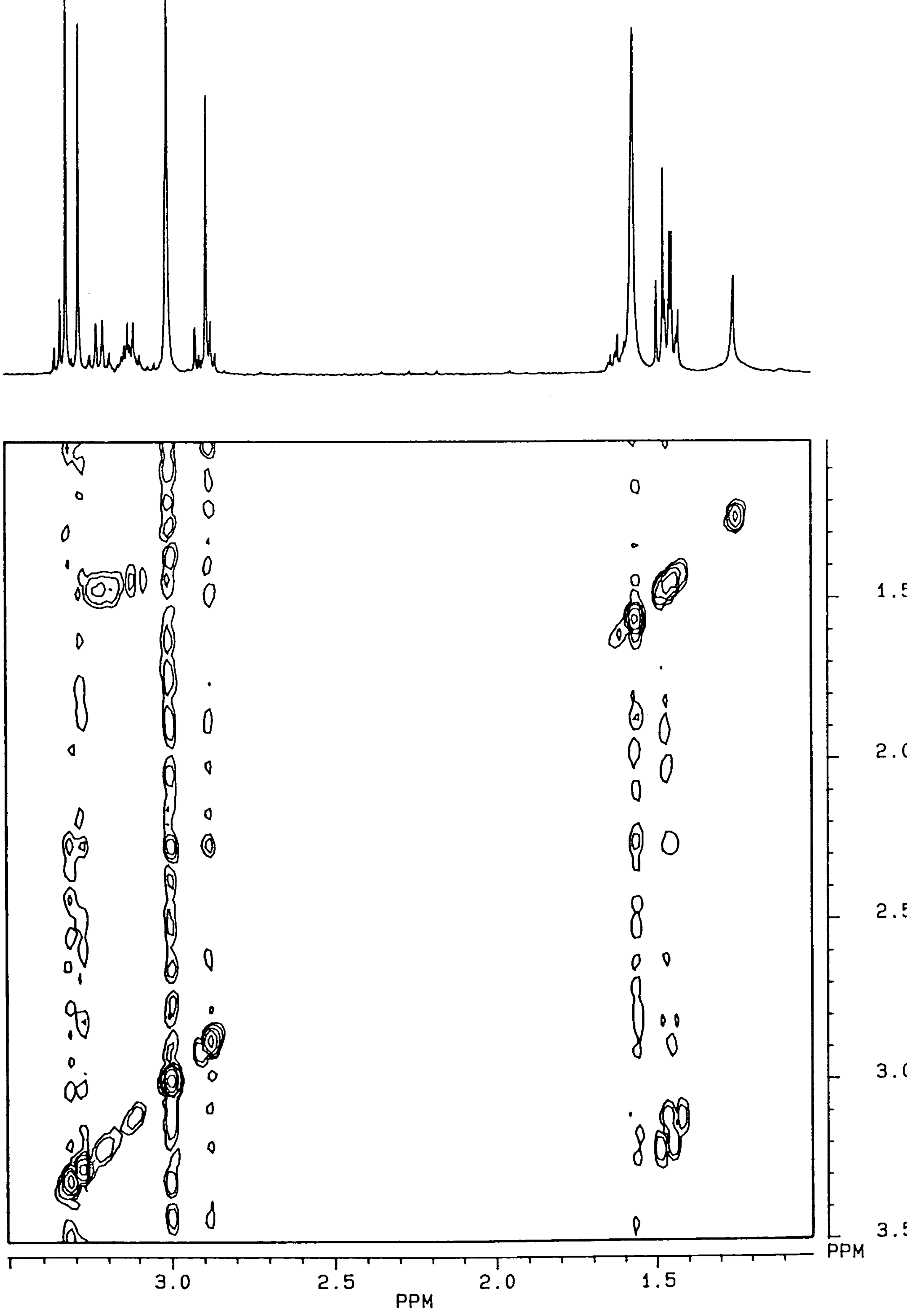


Figure 2.16c. ^{1}H nmr and COSY Spectra for $[Ru_6C(CO)_{14}(MeC_2Et)(Me_2C_2)]$

The spectrum of the complex is very complicated and as already stated could be the result of diastereoisomers due to the presence of the pent-2-yne ligand, how this arises is discussed in Section 2.16. There is also the possibilty of geometrical isomers as a result of the *mono*-capped square based pyramid rearranging in solution to the octahedral array of metal atoms. The previous discussion focused on the possibility of the *mono*-capped square based pyramid. A second isomer is purely speculative and would probably involve the dissociation of a carbonyl group to yield $[Ru_6C(CO)_{13}(Me_2C_2)(MeC_2Et)]$, some evidence for its existence may be present in the ^1H nmr spectrum. Complex **4**, $[Ru_6C(CO)_{13}(\mu_3\text{-}Me_2C_2)_2]$ has been characterised by infrared, mass spectroscopy and ^1H nmr spectroscopy. In the ^1H nmr spectrum of this derivative a singlet at δ2.99ppm was observed and attributed to the twelve protons of the two but-2-yne ligands. In isomer 2 it could reasonably be expected that the CH_3 groups on the but-2-yne and pent-2-yne ligands would appear as singlets in a similar region. In the actual spectrum a broad singlet at δ3.00ppm was observed and could tentatively be assigned to these proton groups. Looking at some of the relative intensities, intensities of the two 'quartets' are similar and the approximate ratio of either of the two 'quartets' with the singlet at δ3.00ppm is roughly 1:4. If isomer 2 were present the ratio of CH_2:CH_3 protons would be 2:9 or 1:4.5; thus the singlet, labelled as (g) in the spectrum is speculatively assigned to the nine CH_3 protons of isomer two.

To reiterate the assignment of signals in this spectrum is speculative and based solely on the comparison of frequencies between $[Ru_6C(CO)_{14}(Me_2C_2)(MeC_2Et)]$ and complexes **2** and **3**. The spectrum is complicated by the likely presence of diastereoisomers and geometrical ismoers in the solution. Work is currently being investigated in an attempt to clarify the situation.

Complex **10**, $[Ru_6C(CO)_{12}(MeC_2Et)(Me_2C_2)_2]$ has been characterized by infrared and mass spectroscopy only. The molecular ion, M^+ was observed at m/z 1130amu followed by the loss of several carbonyl ligands. The band shape in the infrared spectrum of the complex was compared to that of $[Ru_6C(CO)_{12}(Me_2C_2)_3]$, **5** and this is given in Table 2.16d.

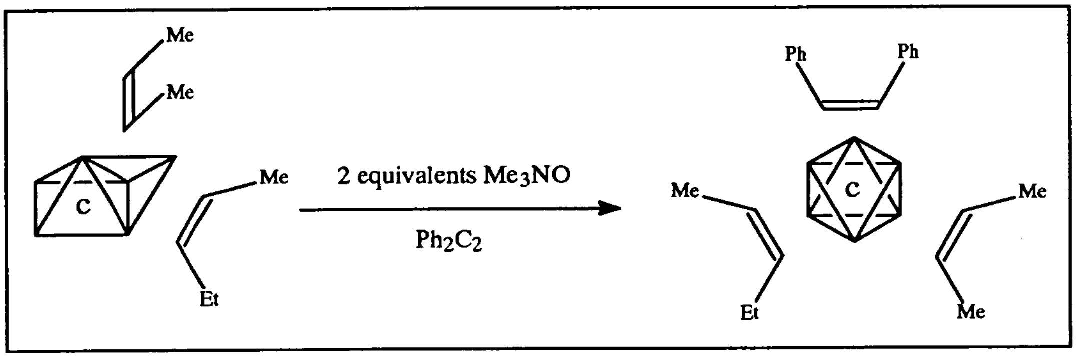
Complex.	**Infrared Data.**		
5	2074(vw)	2026(vs)	2002(m)
10	2074(vw)	2023(vs)	1997(m)

Table 2.16d. Infrared data for complexes 5 and 10.

The complex was tentatively assigned to be $[Ru_6C(CO)_{12}(MeC_2Et)(Me_2C_2)_2]$ from the mass spectrum and the infrared spectrum suggested that the molecular geometry of the product would be comparable to that of $[Ru_6C(CO)_{12}(Me_2C_2)_3]$.

2.17. Reaction of $[Ru_6C(CO)_{14}(MeC_2Et)(Me_2C_2)]$, 2 equivalents Me_3NO and Ph_2C_2.

A solution of $[Ru_6C(CO)_{14}(MeC_2Et)(Me_2C_2)]$ in dichloromethane was cooled to -78°C, and diphenylacetylene, Ph_2C_2 added. Two molar equivalents Me_3NO in dichloromethane was added slowly to the red solution. After warming to room temperature the solution was concentrated to a minimum volume under reduced pressure. The residues were separated by tlc using a solution of dichloromethane-hexane (3:7.v/v) as eluent. Products were isolated as follows, $[Ru_6C(CO)_{14}(MeC_2Et)(Me_2C_2)]$, **9** and $[Ru_6C(CO)_{12}(MeC_2Et)(Me_2C_2)(Ph_2C_2)]$, **11**. The reaction is given in Scheme 2.17.1.



Scheme 2.17.1. Preparation of $[Ru_6C(CO)_{12}(MeC_2Et)(Me_2C_2)(Ph_2C_2)]$

This derivative has been characterized by infrared, mass and ^{1}H nmr spectroscopy. In the mass spectrum a parent peak was observed at m/z 1254amu which gave the initial formula $[Ru_6C(CO)_{12}(MeC_2Et)(Me_2C_2)(Ph_2C_2)]$. The infrared spectrum was compared to the spectrum of $[Ru_6C(CO)_{12}(Me_2C_2)_3]$ and showed a similar band profile, leading to conclude that the molecular geometries of the carbonyl ligands at least was very similar. The infrared data is shown in Table 2.17a.

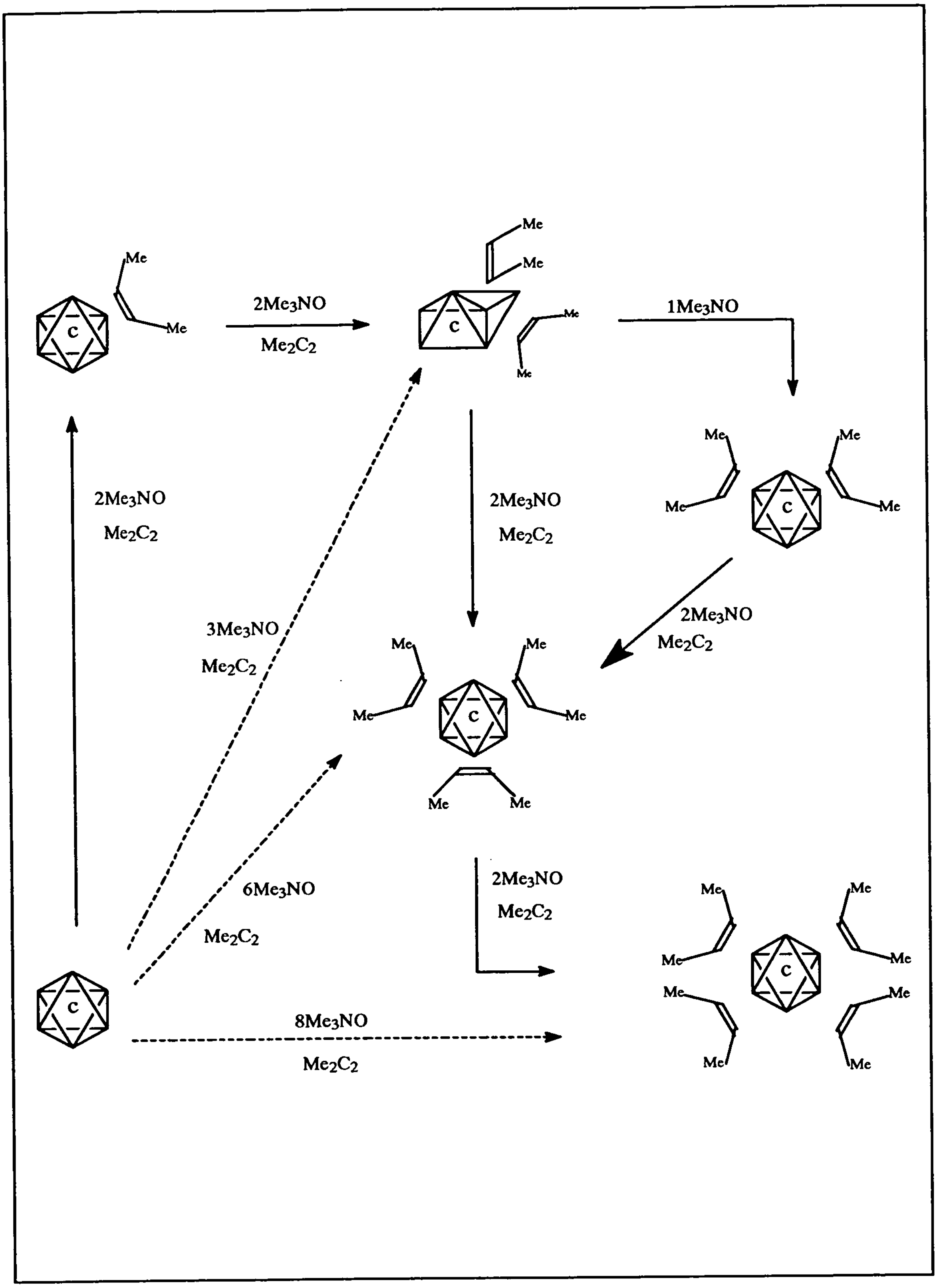
Complex	**Infrared Data.**				
5	2074(vw)	2037(sh)	2026(vs)	2002(m)	1966(vw)
11	2064(vw)	2038(sh)	2025(vs)	2001(m)	1963(vw)

Table 2.17a. Infrared frequencies of complexes 5 and 11(cm^{-1}).

The ^{1}H nmr spectrum confirmed the presence of the organic functionalities but signals did not resolve well resulting in broad resonances. A broad set of resonances was observed at δ2.5-3.0ppm. This is the area characteristic of methyl type protons bound to C=C multiple bond coordinated to a metal cluster. A resonance was also observed at δ1.4ppm where it has been shown for the CH_3 protons of the ethyl portion of pent-2-yne to be located. Two multiplets centred at δ7.1 and 7.2ppm were tentatively assigned to the aromatic protons of the diphenylacetylene ligand. Apart from the provisional assignment of these aromatic protons no further resonances were attributed to specific protons. The spectrum suggested the presence of the required organic fragments but conclusions are tentative.

2.18 Concluding Remarks.

In the first section of this Chapter the reactions of the hexaruthenium carbonyl cluster, $[Ru_6C(CO)_{17}]$ with the alkyne but-2-yne were investigated. Prior to the initiation of the investigation it had been decided that mild reaction routes would be employed so as to enforce an element of control over the ensuing reactions. It has been shown that through the use of stoichiometric amounts of the oxidative decarbonylation reagent trimethylamine-N-oxide, Me_3NO carbonyl ligands can be systematically subsitituted for the alkyne ligand in a step-wise fashion. From this series of reactions *mono*, *bis*, *tris* and *tetrakis*-substituted complexes of the parent compound, $[Ru_6C(CO)_{17}]$ have been prepared. It was also shown that the same complexes could be prepared in one-pot preparations. These reactions are shown in Scheme 18.1. Of particular interest, is the observed rearrangement of the regular octahedral array of ruthenium atoms in the complex $[Ru_6C(CO)_{15}(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}Me_2C_2)]$ which upon further reaction with Me_3NO and alkyne rearranges to the mon-capped square based pyramid found in the compound $[Ru_6C(CO)_{14}(\mu{:}\eta^2{:}\eta^2\text{-}Me_2C_2)(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}Me_2C_2)]$. The reaarangement is unusual for the metal core of Ru_6C, which is known for it's increased stabilty under mild reaction conditions. Possible mechanistic pathways have been offered in the text but no experimental data is available at present to substantiate these mechanisms. The preparation and structural characterisation of the *tris*-butyne derivative, $[Ru_6C(CO)_{12}(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}Me_2C_2)_3]$ is believed to be the first known example of its kind to be reported. Work was also initiated into the preparation of some mixed alkyne derivatives with moderate success. Further work in this area would include the reactions involving alkynes containing α-hydrogens to ascertain whether these material would polymerise



Scheme 18.1. Stepwise Synthesis of Alkyne Ruthenium Complexes.

2.19 References for Chapter Two.

1. E.Sappa, A.Tirripicchio, P.Braunstein., *Chem. Rev.*, 1983, **83**, 203.

2. P.R.Raithby, M.J.Rosales.,*Adv.Inorg.Chem.and Radiochem.*, 1985, **29**, 169.

3. B.F.G.Johnson, J.Lewis, D.Pippard, P.R.Raithby, *J.Chem.Soc., Chem.Commun.*,1978, 551.

4. M.Evans, M.Hursthouse, E.W.Randall, E.Rosenberg, L.Milone, M.Valle, *J.Chem.Soc., Chem.Commun.*, 1972, 545.

5. R.Ugo. *Catal.Rev.* 1975, **11**, 225.

6. R.L.Burwell., *Chem.Eng.News.*, 1966, **44**, 56.

7. E.L.Muetterties., *Bul.Soc.Chim.Belg.*, 1975, **84**, 959.

8. E.L.Muetterties., *Science.*, 1977, **196**, 839.

9. E.L.Muetterties., *Angew.Chem.Int.Ed.Engl.*, 1978, **17**, 545.

10. E.L.Muetterties, T.N.Rhodin, E.Band, C.F.Bucker, W.R.Pretzer., *Chem.Rev.*, 1979, **71**, 91.

11. R.D.Adams, W.Wu., *Organometallics*, 1993, 1072

12. P.F.Jackson, B.F.G.Johnson, J.Lewis, P.R.Raithby, G.J.Will, M.M^{c}Partlin, W.J.H.Wilson., *J.Chem.Soc., Chem.Commun.*, 1980, 1190.

13. B.F.G.Johnson, R.Khattar, F.J.Lahoz, J.Lewis, P.R.Raithby., *J.Organomet.Chem.*, 1987, **319**, C51.

14. D.Braga, F.Grepiono, B.F.G.Johnson, J.Lewis, J.A.Luniss., *J. Chem. Soc. Dalton,* 1992, 1101.

15. E.Rosenberg, S.Aime, L.Milone, E.Sappa, A.Tirripicchio, A.M.M.Lanfredi., *J.Chem.Soc.DaltonTrans.*, 1981, 2023.

16. B.F.G.Johnson, R.D.Johnston, J.Lewis., *J.Chem.Soc., Chem.Commun.*, 1967, 1057.

17. R.D.Adams, W.Wu., *J.Cluster Sci.*, 1991, **2**, 271.

18. Adams,R.D., Wu, W.,*Organometallics*, 1993, **12**, 1238.

19. Y.Shvo, E.Hazum., *J. Chem. Soc. Chem. Commun.*, 1974, 336.

20. P.J.Bailey, D.Braga, P.J.Dyson, F.Grepioni, B.F.G.Johnson, J.Lewis, P.Sabatino., J.Chem.Soc., Chem.Commun., 1992, 177.

21. P.J.Dyson, B.F.G.Johnson, J.Lewis, M.Martinelli, D.Braga, F.Grepioni., *J. Amer. Chem. Soc.,* 1993, **115**, 9062.

22. Sirigu, Bianchi, Benedetti, *J. Chem. Soc. Chem Commun.*, 1969, 596.

23. D.M.Hoffmann, R.Hoffmann, C.R.Fisel, *J. Am. Chem. Soc.*,1982, **104**, 3858.

24. G.Conole, S.R.Drake,B.F.G. Johnson, J.Lewis, M.M^{c}Partlin, *J. Chem. Soc. Dalton Trans.*, 1990, 995.

25. J.S.Bradley, G.B.Ansell, E.W.Hill., *J. Amer. Chem. Soc.*, 1979, **101**, 7417.

26. B.F.G.Johnson, J.Lewis, J.N.Nicholls, J.Puga, P.R.Raithby, M.J.Rosales, M. M^{c}Partlin, W.Clegg, *J. Chem. Soc. Dalton Trans.*, 1983, 277.

27. M.Tachikawa, E.L.Muetterties, *Prog. Inorg. Chem.*, 1981, **28**, 203.

28. J.R.Bradley, *Adv. Organomet. Chem.*, 1983, **22**, 1.

29. for example F.A.Cotton, J.D.Jamerson, B.R.Stults, *J. Am. Chem. Soc.*, 1976, **98**, 1774.

30 .M.P.Gomez-Sal, B.F.G.Johnson ,J.Lewis ,R.A.Kamuradin P.R.Raithby; *J. Chem. Soc., Chem. Commun.*, 1985,1662.

31. C.R.Eady, J.M.Fernandez, B.F.G.Johnson, J.Lewis, P.R.Raithby, G.M.Sheldrick, *J.Chem.Soc. Chem. Commun.*, 1978, 421.

32. B.F.G.Johnson, Transition Metal Clusters, Wiley.

33. B.F.G.Johnson, *J.Chem.Soc., Chem.Commun.*, 1986, 27.

34. A.Rodger, B.F.G.Johnson, *Polyhedron*, 1988, **12**, 1107.

35. P.F.Helveldt, B.F.G.Johnson, J.Lewis, P.R.Raithby, G.M.Shel;drick, *J.Chem.Soc. Chem. Commun.*, 1978, 340.

36. E.R.Corey, L.F.Dahl, W.Beck., *J. Amer. Chem. Soc.*, 1963, **85**, 1202.

Chapter Three.

Arene-alkyne complexes of *Hexa*ruthenium Carbonyl.

This Chapter opens with a synopsis of some of the reactions that have been reported in which arene groups bonded to a central cluster unit have undergone some kind of transformation either chemically or in the manner in which they are bound to the cluster unit. The synthesis and characterisation of a series of complexes bearing both arene and alkyne ligands on the *hexa*ruthenium cluster $[Ru_6C(CO)_{17}]$, are then discussed in detail and the strong similarities in the compounds are emphasised.

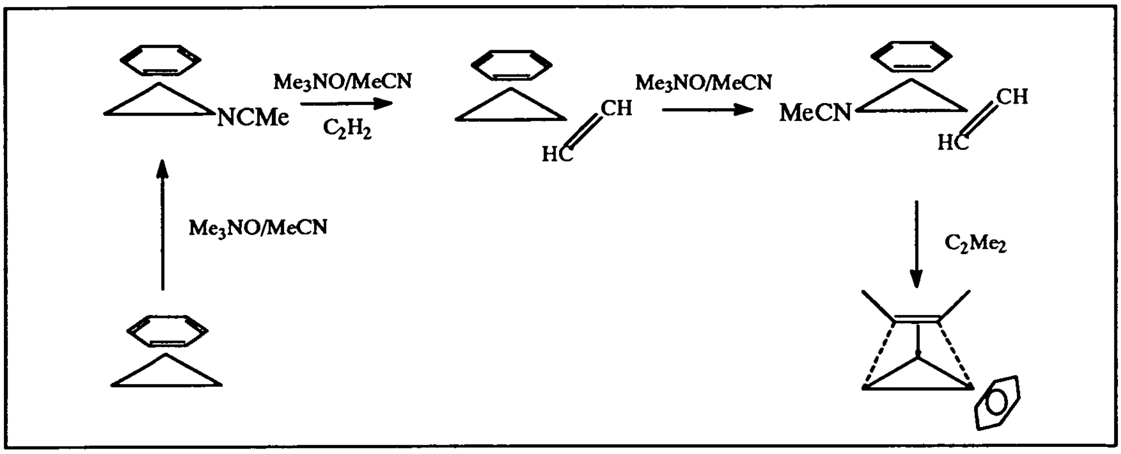
3.1 Introduction.

The study of arene complexes has received considerable attention in recent years[1] with particular studies being undertaken of the types of bonding modes employed by the arenes onto the cluster surface. There are several bonding modes[2-10] but two are more frequently observed than others. Firstly, there is the more conventional η^6-terminal bonding mode in which the arene ligates to one metal centre *via* π-interactions and donates six electrons to the electron count of the complex. The second mode is that of the face capping bond, $\mu_3:\eta^2:\eta^2:\eta^2$. Here, the arene interacts with three metal centres in a triangular array and again donates six electrons to the overall electron count. The face capping mode is of particular importance since it may be considered to model the alternate long-short C-C interactions observed for the benzene ligand adsorbed on the Rh(111)[11] and Os(001)[12] single crystal metal surfaces.

We were interested in the 'flexibility' of the arene functionality which is apparently able to modify its coordination mode according to outside influences, *e.g.* other ligands. The arene ligand has been shown to undergo C-H cleavage[13], migration[14] from one location on the cluster to another, and complete displacement[15] from the cluster.

It has been shown in earlier work that the benzene ligand in the complex $[Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]^{16}$ will undergo C-H cleavage to yield a benzyne group, $[\mu_2\text{-}H_2Os_3(CO)_9(C_6H_4)]$ on irradiation for 13 hours in toluene.[13] The C_6H_4 ligand, previously donating six electrons to the complex as the aromatic group C_6H_6, is now acting as a four electron donor and is said to resemble a coordinated alkyne. The benzyne group coordinates to the metal face *via* a single π-interaction and two σ-interactions and lies at an angle of 70° to the triangular metallic face. The two displaced hydrogen atoms have migrated to the cluster core to form independent μ_2-hydrogen bridges.

Benzene migration has been observed in *tri*nuclear complexes in which the arene ligand moves from the μ_3-face capping mode to a η^6-terminal site. The compound $[Os_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$,[16] for example has been shown to undergo such a process. When treated with $Me_3NO/MeCN$ the activated cluster $[Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(MeCN)]$ is formed and the labile acetonitrile ligand is then readily displaced by ethylene to yield the new complex $[Os_3(CO)_8(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(C_2H_4)]$. Further activation with $Me_3NO/MeCN$, followed by the addition of but-2-yne yields the complex $[Os_3(CO)_7(\eta^6\text{-}C_6H_6)(Me_2C_2)]$. The overall reaction is depicted in Scheme 3.1.1.

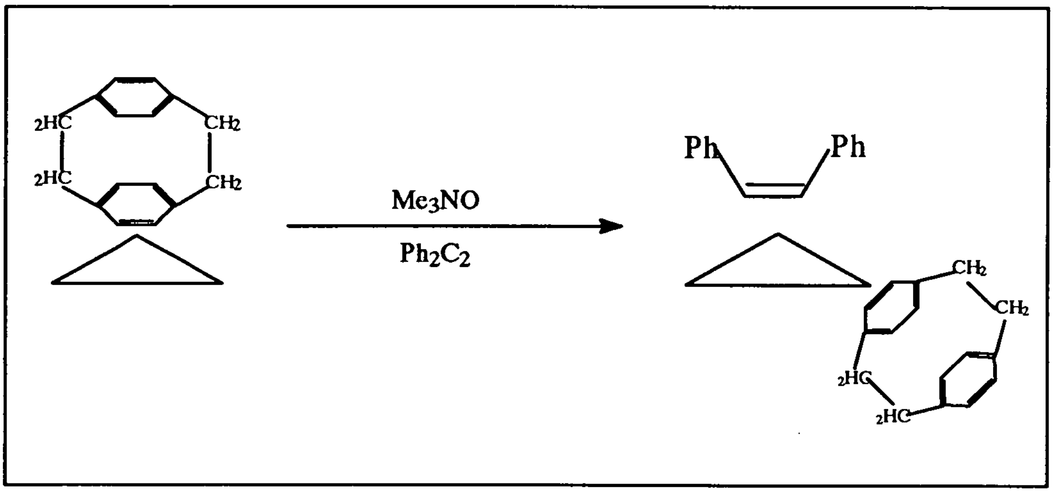


Scheme 3.1.1. Benzene Migration on a *Tri*osmium Cluster.

The ethylene and MeCN ligands have been displaced upon reaction with but-2-yne and the benzene moiety has migrated from the μ_3-face capping mode to a η^6-terminal position. The alkyne ligand bridges the *tri*osmium face and interacts *via* a π-interaction and two σ-interactions.

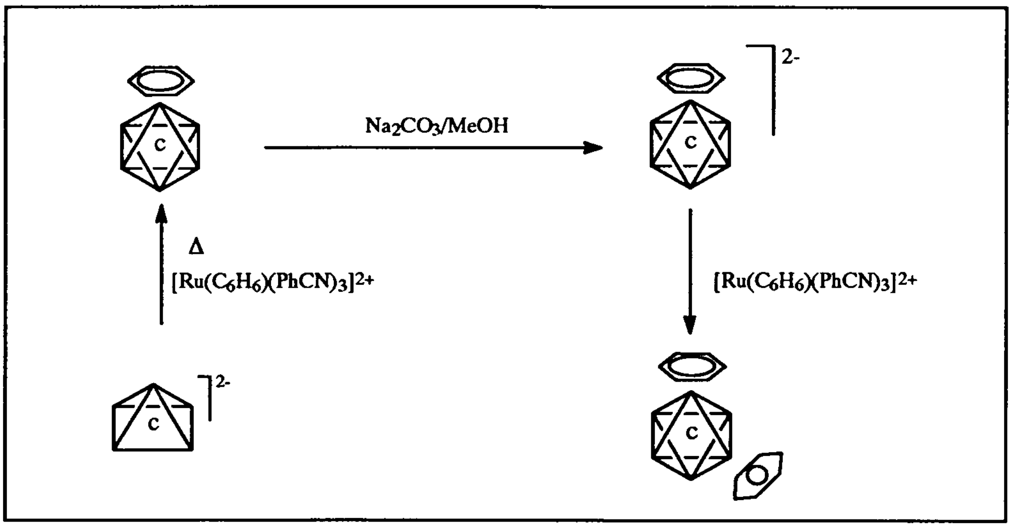
In the case of the ruthenium analogue $[Ru_3(CO)_9(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$,[17] benzene migration is also observed but under different conditions.[18] Here, the cluster is subjected to prolonged pyrolysis in dichloromethane in the presence of diphenylacetylene, Ph_2C_2. Once again the benzene functionality shifts from the facially bound site on the cluster to a terminal position. The alkyne, as in the *tri*osmium case, bonds to the *tri*-ruthenium cluster in the 2σ-, π-face bridging manner. Carbonyl insertion has also taken place, presumably by insertion into one of the Ru-C σ-bonds.

Migration of an aromatic ligand has transpired with no CO insertion in the case of $[Ru_3(CO)_9(C_{16}H_{16})]$,[19] ($C_{16}H_{16}$ = 2.2-[paracyclophan]) which when reacted with Me_3NO in the presence of diphenylacetylene at low temperatures, the face capping ligand migrates to the terminal position and the Ph_2C_2 ligand bridges the *tri*ruthenium face.[20] This is depicted pictorially in Scheme 3.1.2.



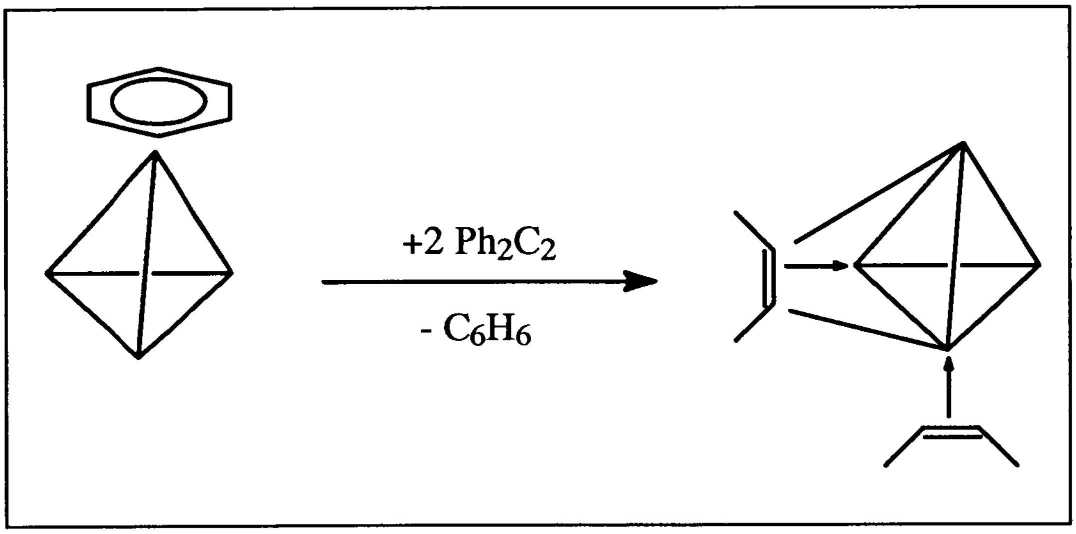
Scheme 3.1.2 Migration of 2.2-paracyclophan on a *Tri*-ruthenium Cluster.

Migration of a terminally bound arene to a face capping mode has been reported[21]. The reagent $[Ru(C_6H_6)(PhCN)_3]^{2+}$ can be employed as a 'capping' reagent in which the $[Ru(C_6H_6)]$ fragment caps a metal face . The preparation of the *bis*-benzene *hexa*ruthenium complex from the compound $[N(PPh_3)_2]_2[Ru_5C(CO)_{14}]$[22] employs this tactic. The *penta*nuclear parent cluster is heated under reflux conditions in dichloromethane in the presence of the 'capping' complex, $[Ru(C_6H_6)(PhCN)_3]^{2+}$; this produces the *mono*-substituted arene cluster, $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)]$. Further reduction of this complex through the utilisation of Na_2CO_3/MeOH to the dianionic species, $[Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_6)]^{2-}$ followed by the addition of an aliquot of $[Ru(C_6H_6)(PhCN)_3]^{2+}$ yields the *bis*-arene complex, $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)]$. The arene ligand has shifted from the terminal bonding site in the capping compound to a face-capping mode on the cluster core. It is not clear if the arene disengages from the Ru centre of $[Ru(C_6H_6)(PhCN)_3]^{2+}$ or whether there is ruthenium displacement from the *hexa*ruthenium core. This reaction is outlined pictorially in Scheme 3.1.3.



Scheme 3.1.3. Arene migration , terminal to face-capping.

The displacement of an arene from a cluster has been cited in the literature and involves the presence of an incoming alkyne ligand.[15] The *tetra*-osmium compound, $[H_2Os_4(CO)_{10}(\eta^6\text{-}C_6H_6)]$[23] is reacted with $Me_3NO/MeCN$ to form the activated intermediate $[H_2Os_4(CO)_9(\eta^6\text{-}C_6H_6)(MeCN)]$. This then readily reacts with the ligand diphenylacetylene resulting in the production of $[H_2Os_4(CO)_9(Ph_2C_2)_2]$.[15] The arene ligand has been displaced from the cluster by the two alkyne ligands; it is interesting to note that the two Ph_2C_2 groups are bound to the metal core in different bonding modes. One ligand bridges a *tri*osmium face in a $\mu_3:\eta^1:\eta^2:\eta^1$-bonding mode, whilst the other ligand interacts with only one metal centre. The reaction is given diagrammatically in Scheme 3.1.4.



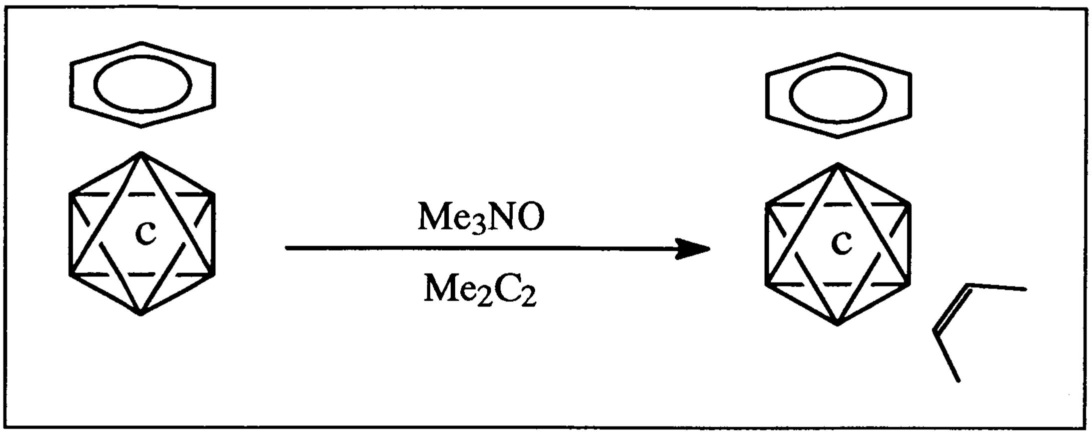
Scheme 3.1.4. Displacement of benzene from a cluster.

So far, the discussion has been concerned with the ability of the arene ligand to migrate over the cluster from one bonding site to another and on how it may be displaced from the cluster all together. It would seem that these effects can be brought about by the presence of an alkyne ligand which seems to preferentially bridge a triangulated face of a cluster compound. To date, systems studied have included *tri*- and *tetra*nuclear systems. The remainder of this chapter is dedicated to the synthesis and characterisation of a series of *hexa*ruthenium complexes that contain both arene and alkyne ligands. Our interest in this field was to ascertain whether the alkyne ligand would have any influence on the bonding nature of the coordinated arene ligand.

The preparation of *hexa*ruthenium arene complexes was reported in the late 1960's by Johnson and *co-workers*[24] and involves pyrolysis of $[Ru_3(CO)_{12}]$[25] and the required arene in octane for long periods of time. This process works fairly well for toluene, xylene and mesitylene but not so well for benzene which has a much lower boiling point. A much improved route for the preparation of the benzene *hexa*ruthenium[26] derivative involves the direct reaction of 1,3-cyclohexadiene with $[Ru_6C(CO)_{17}]$[27] using the degradative decarbonylation reagent, Me_3NO to remove the necessary number of carbonyl ligands. The benzene moiety is formed *in situ* by C-H activation of the diene ligand. The preparation of *hexa*ruthenium arene derivatives used in the ensuing work employs both of these routes and typical reactions are given in Chapter Four.

3.2 Reaction of $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)]$, 14 with 2 molar equivalents Me_3NO and Me_2C_2.

The compound $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)]$, **13** was dissolved in dichloromethane and the resulting red solution was cooled to -78°C. An excess of the ligand but-2-yne was added to the solution followed by the dropwise introduction of two molar equivalents of Me_3NO in dichloromethane. The solution attained room temperature after a further 30 minutes stirring. At this stage the infrared spectrum showed that there was unreacted starting material present but the intermittent taking of spot tlc samples during the reaction showed that the reaction was not going to proceed any further at this stage. Solvent was removed under reduced pressure. Dark brown residues were purified by tlc using a solution of dichloromethane-hexane (3:7, v/v) as eluent. Products were eluted as follows, $[Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_6)(\mu_3\text{:}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-}Me_2C_2)]$, **12**, 39% and $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)]$, **13**, 12%. The reaction is given diagrammatically in Scheme 3.2.1 .



Scheme 3.2.1. Synthesis of [$Ru_6C(CO)_{12}(\eta^6$-$C_6H_6)(\mu_3$:η^1:η^2:η^1-$Me_2C_2)$], 12.

The product, **12**, was initially characterised as [$Ru_6C(CO)_{12}(\eta^6$-$C_6H_6)(\mu_3$:η^1:η^2:η^1-$Me_2C_2)$] by infrared, mass and ^1H nmr spectroscopy. The mass spectrum exhibited a parent peak at m/z 1086amu (calc. 1086) followed by the sequential loss of several carbonyls. The ^1H nmr spectrum confirmed the presence of both organic moieties with resonances a δ5.79ppm (s, 6H) and 2.89ppm (s, 6H). Crystals of the complex were grown by the slow diffusion of a dichloromethane-hexane layer at -25°C and the molecular and crystallographic studies established by single crystal X-ray diffraction analysis. The molecular structure of [$Ru_6C(CO)_{12}(C_6H_6)(Me_2C_2)$], **12** is shown in Figure 3.2a.

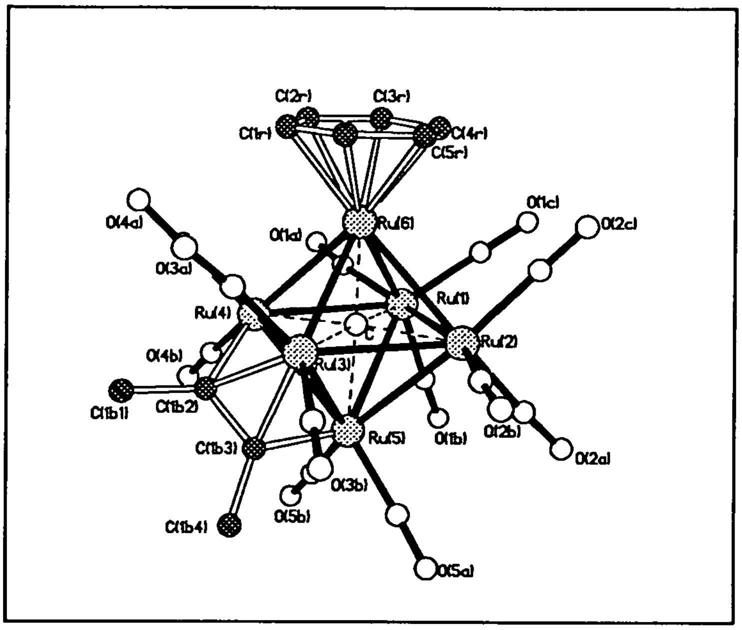


Figure3.2a. The molecular structure of $[Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_6)(\mu_3\text{:}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-}Me_2C_2)]$. Significant bond lengths (Å) and angles (°) for $[Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_6)(\mu_3\text{:}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-}Me_2C_2)]$are given: Ru(1)-Ru(2) 2.8534(8), Ru(1)-Ru(4) 2.9739(8), Ru(1)-Ru(5) 2.9379(7), Ru(1)-Ru(6) 2.8668(8), Ru(2)-Ru(3) 3.0135(8), Ru(2)-Ru(5) 2.8769(8), Ru(2)-Ru(6) 2.8735(8), Ru(3)-Ru(4) 2.7674(8), Ru(3)-Ru(5) 2.7883(8), Ru(3)-Ru(6) 2.8780(7),Ru(4)-Ru(5) 2.8107(7), Ru(4)-Ru(6) 2.8738(8); Ru(1)-C 2.034(6), Ru(2)-C 2.059(6), Ru(3)-C 2.086(6), Ru(4)-C 2.036(6), Ru(5)-C 2.038(6), Ru(6)-C 1.957(5); mean Ru-C(CO) 1.897(8), range 1.880(7)-1.927(7); mean C-O 1.143(8), range 1.130(7)-1.152(7);Ru(3)-C(1B2) 2.178(5), Ru(3)-C(1B3) 2.184(6), Ru(4)-C(1B2) 2.075(6), Ru(5)-C(1B3) 2.066(6); C(1B2)-C(1B3) 1.403(8); C(1B1)-C(1B2)-C(1B3) 123.9(5), C(1B2)-C(1B3)-C(1B4) 123.9(5).

The regular octahedron previously observed in $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)]$, **13** has been retained in the new complex $[Ru_6C(CO)_{12}(\mu_3\text{:}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-}Me_2C_2)(\eta^6\text{-}C_6H_6)]$, **12**. Ruthenium bond distances lie in the range 2.7674(8) - 3.0135(8)Å, mean 2.8762(8)Å. The lengthening of the Ru(2)-Ru(3) bond has been attributed to the presence of the π-interaction at Ru(3) from atoms C(1B2) and C(1B3); as the π-interaction pulls electron density away from the metal atom this causes a 'weakening' effect, thus the bond lengthens. The carbido atom is displaced out of the essentially central location towards the arene bearing atom, Ru(6). This can be highlighted by an assessment of Ru-C bond lengths; Ru(6)-C 1.957(6)Å compared to Ru(5)-C 2.083(6)Å which lies opposite is 0.126Å longer. All the carbonyl ligands are bound terminally with Ru-C-

O angles in the range 172.1(6)-179.2(6)°, mean 175.9(6)°. The alkyne ligand has coordinated to the cluster in the μ_3:η^1:η^2:η^1-face capping across the Ru(3)-Ru(4)-Ru(5) triangular face. Atoms C(1B2) and C(1B3) are involved in a π-interaction with Ru(3) and separate σ-interactions to Ru(4) and Ru(5) respectively. Bond distances and angles of the alkyne ligand show that the ligand still exhibits 'alkene-like' characteristics as observed in the parent compound [$Ru_6C(CO)_{15}(Me_2C_2)$], **2**. The C=C multiple bond measures 1.403(6)Å and the two C-C-C angles are both 123.9(5)°. The benzene ligand has remained in the η^6-terminal bonding mode donating a total of six electrons to the overall count of the complex.

3.3 Preparation of [$Ru_6C(CO)_{12}(\eta^6$-$C_6H_5Me)(Me_2C_2)$],15 from [$Ru_6C(CO)_{14}(\eta^6$-$C_6H_5Me)$],14.

The complex [$Ru_6C(CO)_{14}(\eta^6$-$C_6H_5Me)$], **14** was taken up in dichloromethane resulting in a red solution. But-2-yne was introduced to the solution at -25°C followed by the dropwise addition of two molar equivalents Me_3NO in dichloromethane. After a further 30 minutes of vigorous stirring the solution had reached room temperature and darkened in colour. All volatiles were removed under reduced pressure. The dark brown residues were purified by tlc using a solution of dichloromethane-hexane (3:7, v/v) as eluent. Products were isolated as follows, [$Ru_6C(CO)_{12}(\eta^6$-$C_6H_5Me)(\mu_3$:η^1:η^2:η^1-$Me_2C_2)$], **15** in moderate yield, 42% and unreacted starting material [$Ru_6C(CO)_{14}(\eta^6$-$C_6H_5Me)$], **14** 18%. The new compound, **15** was initially characterised by mass and ^1H nmr spectroscopy. In the mass spectrum a parent peak at m/z 1100amu (calc. 1100) was followed by the sequential loss of several carbonyl ligands; this led to the formulation [$Ru_6C(CO)_{12}(\eta^6$-$C_6H_5Me)(\mu_3$:η^1:η^2:η^1-$Me_2C_2)$]. In the ^1H nmr spectrum, resonances at δ 5.82 (d,2H), 5.70 (m, 3H), 2.88 (s, 6H) and 2.35 (s, 3H) ppm were observed confirming the presence of he two organic ligands. The preparation of crystals from a dichloromethane/hexane solution led to a crystallographic study of the complex. The molecular structure of $[Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_5Me)(\mu_3\text{:}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-}Me_2C_2)]$ is shown in Figure 3.3a.

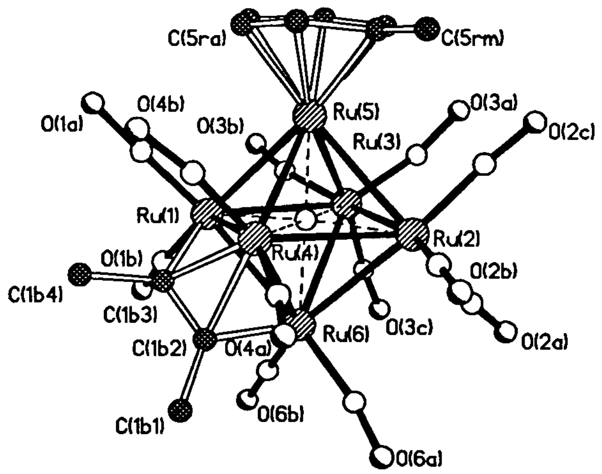


Figure 3.3a. The molecular structure of $[Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_5Me)(\mu_3\text{–}Me_2C_2)]$. Significant bond lengths (Å) and angles (°) are given for $[Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_5Me)(\mu_3\text{–}Me_2C_2)]$. are given. Ru(1)-Ru(3) 2.924(4), Ru(1)-Ru(4) 2.770(4), Ru(1)-Ru(5) 2.885(4), Ru(1)-Ru(6) 2.792(4), Ru(2)-Ru(3) 2.842(4), Ru(2)-Ru(4) 3.059(4), Ru(2)-Ru(5) 2.908(4), Ru(2)-Ru(6) 2.859(4), Ru(3)-Ru(5) 2.853(4), Ru(3)-Ru(6) 2.977(4), Ru(4)-Ru(5) 2.861(4), Ru(4)-Ru(6) 2.779(4); Ru(1)-C 2.07(4), Ru(2)-C 2.02(4), Ru(3)-C 2.03(4), Ru(4)-C 2.08(4), Ru(5)-C 1.99(4), Ru(6)-C 2.01(4); Ru-C(CO), range 1.80(3)-1.93(4), mean 1.878(4); C-O, range 1.08(4)-1.26(4), mean 1.17(5); Ru-C-O, range 164.2(33)-178.6(30), mean 1171.4(33); Ru(1)-C(1B3) 2.06(3), Ru(6)-C(1B2) 2.09(3), Ru(4)-C(1B2) 2.25(3), Ru(4)-C(1B3) 2.17(3); Ru(5)-C(5RA) 2.19(3), Ru(5)-C(5RB) 2.33(4), Ru(5)-C(5RC) 2.16(5), Ru(5)-C(5RD) 2.27(4), Ru(5)-C(5RE) 2.23(5), Ru(5)-C(5RF) 2.28(4); C(1B1)-C(1B2) 1.48(5), C(1B2)-C(1B3) 1.40(4), C(1B3)-C(1B4) 1.52(3); C(5RA)-C(5RB) 1.44(6), C(5RA)-C(5RF) 1.41(5), C(5RB)-C(5RE) 1.39(7), C(5RC)-C(5RD) 1.40(6), C(5RC)-C(5RE) 1.38(7), C(5RD)-C(5RF1) 1.47(5), C(5RE)-C(5RM) 1.60(9).

The octahedral array of the six ruthenium atoms has remained intact though slightly distorted. Ru-Ru bond distances lie in the range 2.770(4)-3.059(4)Å, mean 2.876(4)Å. The shortest M-M contact is that of Ru(1)-Ru(4), 2.770(4)Å and the longest Ru(2)-Ru(4), 3.059(4)Å. The short Ru-Ru bond is comparable to the Ru(6)-Ru(6) bond, 2.779(4)Å; both of these bonds contain Ru atoms that bear either a π-interaction (Ru(4)) or a σ-interaction (atoms Ru(1) and Ru(6)). This bond 'strengthening' is attributed to the effects of the σ-interactions increasing electron density around the metal centres. The Ru(2)-Ru(4) bond, 3.059(4)Å the longest M-M contact in the complex is a result of the π-interaction at Ru(4) withdrawing electron density away from the metal centre, leading to a 'weakening' effect of the bond. The interstitial carbon atom, essentially central is displaced out of the square plane of Ru(1)-Ru(3)-Ru(2)-Ru(4) towards Ru(5) which is bonded to the arene ligand. This is highlighted by an assessment of the relevant bond lengths, Ru(5)-C 1.99(4)Å compared to Ru(6)-C 2.01(4)Å. The toluene ligand has remained in the η^6-terminal bonding mode at the apical site Ru(5) and donates six electrons to the overall count of the complex. The incoming but-2-yne ligand bridges the triangular face Ru(1)-Ru(4)-Ru(6). Atoms C(1B2) and C(1B3) are involved in a π-interaction to Ru(4) and two separate σ-interactions to Ru(6) and Ru(1) respectively. The alkyne ligand upon coordination shows increased 'alkene-like' characteristics, *ie* the C=C multiple bond has lengthened to 1.40(4)Å and the C-C-C angles have reduced to 124.3(28) and 123.0(27)°.

3.4 Preparation of $[Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_4Me_2)(Me_2C_2)]$ from $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4Me_2)]$.

The compound $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4Me_2)]$ was dissolved in dichloromethane to produce a red solution. An excess of ligand, but-2-yne was added to the solution at -78°C. Two molar equivalents of Me_3NO in dichloromethane were introduced to the solution over a 5 minute period. On warming to room temperature the solution became cloudy and darker in colour. Solvent was reduced to a minimum volume under reduced pressure. Products were isolated by tlc using a dichloromethane-hexane (3:7, v/v) solution as eluent. Components of the reaction were eluted as follows, $[Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_4Me_2)(\mu_3\text{:}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-}Me_2C_2)]$ as a brown band in moderate yield, 40% and unreacted starting material $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4Me_2)]$, 15%. Initial characterisation of the new material was provided by mass and ^1H nmr spectroscopy. In the mass spectrum a parent peak at m/z 1114amu (calc. 1114) was observed followed by the loss of several carbonyl ligands in succession; this led to the initial formulation of the complex to be [$Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_4Me_2)(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}Me_2C_2)$]. In the ^1H nmr spectrum the presence of organic ligands was confirmed by the observation of signals at δ5.45 (m) and δ5.79(m)ppm; these were attributed to the aromatic protons of the xylene ligand. Two singlets at δ2.89ppm and δ2.40ppm were attributed to the methyl protons of the alkyne and the xylene ligand respectively. Suitable crystals for a crystallographic study were nucleated from a dichloromethane-hexane solution at -25°C. The molecular structure of [$Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_4Me_2)(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}Me_2C_2)$] is shown in Figure 3.4a.

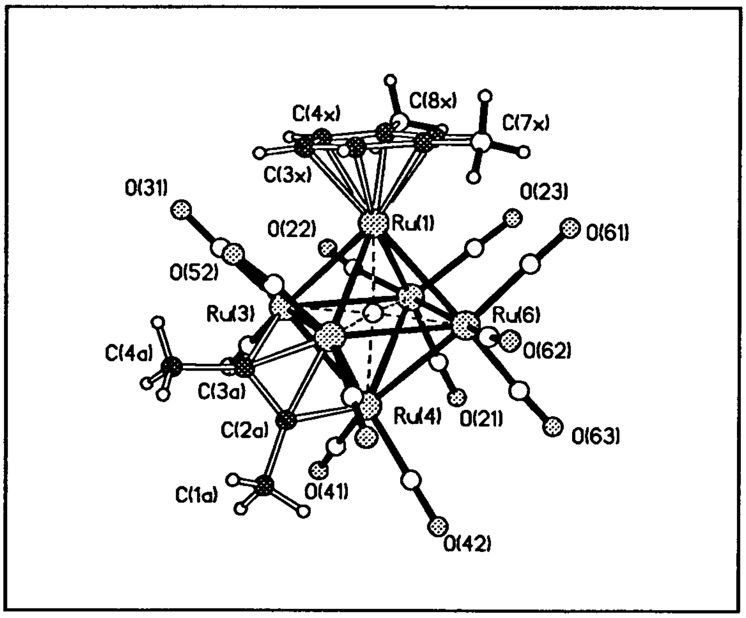


Figure 3.4a. The molecular structure of [$Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_4Me_2)(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}Me_2C_2)$]. Significant bond lengths(Å) and angles(°) are given. Ru(1)-Ru(2) 2.8636(8), Ru(1)-Ru(3) 2.8470(8), Ru(1)-Ru(5) 2.8881(10), Ru(1)-Ru(6) 2.8852(9), Ru(2)-Ru(3) 2.9526(9), Ru(2)-Ru(4) 2.9391(10), Ru(2)-Ru(6) 2.8301(8), Ru(3)-Ru(4) 2.7948(9), Ru(3)-Ru(5) 2.7949(8), Ru(4)-Ru(5) 2.7765(9), Ru(4)-Ru(6) 2.9121(9), Ru(5)-Ru(6) 2.9733(8); Ru(1)-C 1.959(6), Ru(2)-C 2.026(6), Ru(3)-C 2.018(6), Ru(4)-C 2.056(6), Ru(5)-C 2.071(6), Ru(6)-C 2.059(6); Ru-C(CO), range 1.879(6)-1.917(6), mean 1.895(6); C-O, range 1.133(8)-1.155(8), mean 1.141(8); Ru-C-O, range 171.0(6)-179.0(6), mean 176.3(6); Ru(1)-C(1X) 2.264, Ru(1)-C(2X) 2.241(6), Ru(1)-C(3X) 2.193(6), Ru(1)-C(4X) 2.232(6), Ru(1)-C(5X) 2.275(6), Ru(1)-C(6X) 2.212(6); Ru(3)-C(3A) 2.059(6), Ru(4)-C(2A) 2.067(6), Ru(5)-C(2A) 2.177(6), Ru(5)-C(3A) 2.193(6); C(1X)-C(2X) 1.417(8), C(2X)-C(3X) 1.397(9), C(3X)-C(4X) 1.423(9), C(4X)-C(5X) 1.408(8), C(5X)-C(6X) 1.418(9), C(6X)-C(1X) 1.412(9), C(1X)-C(7X) 1.497(9), C(5X)-C(8X) 1.506(9); C(1A)-C(2A) 1.506(8), C(2A)-C(3A) 1.393(8), C(3A)-C(4A) 1.515(8); C(1A)-C(2A)-C(3A) 123.0(5), C(2A)-C(3A)-C(4A) 124.5(6).

The ruthenium framework observed in $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4Me_2)]$, **16** is still present in the new complex $[Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_4Me_2)(\mu_3\text{:}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-}Me_2C_2)]$, **17**. Ruthenium bond lengths range from 2.7768(9)Å to 2.9733(8)Å, (mean 2.8715(10)Å); the shortest M-M contact is Ru(4)-Ru(5), 2.7765(9)Å and compares well to the contacts Ru(3)-Ru(4), 2.7949(8)Å and Ru(3)-Ru(5) 2.7948(9)Å. These three bonds form the triangular face Ru(3)-Ru(4)-Ru(5) which bears the alkyne ligand. This 'contracting' of bond lengths was also observed in the complex $[Ru_6C(CO)_{15}(Me_2C_2)]$, **2** and was attributed to the effects of the bound alkyne. The carbido atom is displaced towards Ru(1) which is bonded to the arene ligand; the distance Ru(1)-C is 1.959(6)Å compared to a mean distance of 2.046(6)Å for the remaining Ru-C distances. The twelve carbonyl ligands are distributed around the cluster such that Ru(2) and Ru(6) are bonded to three carbonyl ligands whilst Ru(3), Ru(4) and Ru(5) are bonded to two ligands each. All twelve carbonyl groups are terminally bound as shown by the Ru-C-O angles ranging from 171.0(6) to 179.0(6)°, mean 176.3(6)°. The terminally bound aromatic ligand in the parent complex, $[Ru_6C(CO)_{14}(C_6H_4Me_2)]$ is found in the same mode here and donates a total of six electrons to the overall count. The but-2-yne ligand as previously stated bridges the Ru(3)-Ru(4)-Ru(5) face with a π-interaction to Ru(5) and two σ-interactions to Ru(3) and Ru(4). The alkyne shows increased 'alkene' properties with the C=C multiple bond measuring 1.393(8)Å and the C-C-C angles of 123.0(5) and 124.5(6)°.

3.5 Synthesis of $[Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_3Me_3)(Me_2C_2)]$ from $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)]$.

A solution of the complex $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)]$, **18** in dichloromethane was prepared. An excess of ligand, but-2-yne was added to the solution at -78°C. Two molar equivalents of Me_3NO in dichloromethane was slowly introduced to the solution in a dropwise fashion. The solution attained room temperature after a further 30 minutes stirring. Solvent was removed *in vacuo* and residues separated by tlc using a solution of dichloromethane-hexane (3:7, v/v) as eluent. Products were eluted in the following order, $[Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_3Me_3)(\mu_3\text{:}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-}Me_2C_2)]$, **19**, 39% and

$[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)]$, **18**, 14%. Mass and ^1H nmr spectroscopy were used to determine the formulation of the complex and to confirm the presence of ligands. In the mass spectrum a parent peak at m/z 1288amu (calc. 1288) led to the formula $[Ru_6C(CO)_{12}(C_6H_3Me_3)(Me_2C_2)]$. The observation of resonances in the ^1H nmr spectrum at δ 5.71ppm (s, 3H), δ 2.39ppm (s, 9H) and δ 2.86ppm (s, 6H) confirmed the presence of the two organic functionalities. Crystals suitable for a diffraction study were prepared by the slow diffusion of a dichloromethane-hexane layer at -25°C. The molecular structure of $[Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_3Me_3)(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}Me_2C_2)]$ is shown in Figure 3.5a.

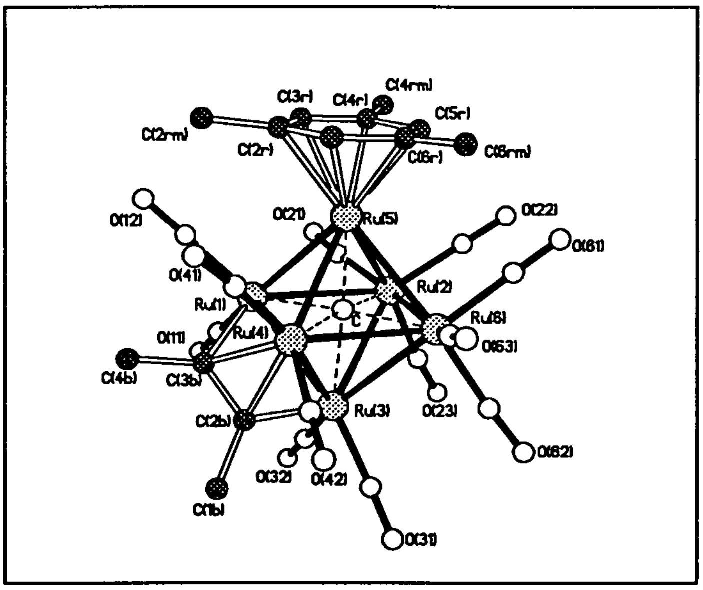


Figure 3.5a. The molecular structure of $[Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_3Me_3)(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}Me_2C_2)]$. Bond lengths(Å) and angles (°) are given. Ru(1)-Ru(2) 2.9771(8), Ru(1)-Ru(3) 2.7969(8), Ru(1)-Ru(4) 2.8132(8), Ru(1)-Ru(5) 2.8615(8), Ru(2)-Ru(3) 2.9277(8), Ru(2)-Ru(5) 2.8794(8), Ru(2)-Ru(6) 2.8551(8), Ru(3)-Ru(4) 2.7617(8), Ru(3)-Ru(6) 2.9299(8), Ru(4)-Ru(5) 2.8991(8), Ru(4)-Ru(6) 2.9244(8), Ru(5)-Ru(6) 2.8638(8); Ru(1)-C 2.023(6), Ru(2)-C 2.014(6), Ru(3)-C 2.057(6), Ru(4)-C 2085(6), Ru(5)-C 1.959(6), Ru(6)-C 2.066(6); Ru-C(CO), range 1.870(8)-1.912(7), mean 1.891(8); C-O, range 1.132(9)-1.151(9), mean 1.141(9); Ru-C-O, range 172.6(6)-179.2(6), mean 176.2(6); Ru(1)-C(3B) 2.061(6), Ru(3)-C(2B) 2.070(6), Ru(4)-C(2B) 2.184 (6), Ru(4)-C(3B) 2.182(6); Ru(5)-C(1R) 2.253, Ru(5)-C(2R) 2.269(8), Ru(5)-C(3R) 2.243(8), Ru(5)-C(4R) 2.250(8), Ru(5)-C(5R) 2.207(7), Ru(5)-C(6R) 2.258(6); C(1B)-C(2B) 1.512(9), C(2B)-C(3B) 1.398(9), C(3B)-C(4B) 1.496(9); C(1R)-C(2R) 1.398(11), C(2R)-C(3R) 1.431(11), C(3R)-C(4R) 1.375(11), C(4R)-C(5R) 1.420(11), C(5R)-C(6R) 1.403(10), C(6R)-C(1R) 1.1.423(10); C(1B)-C(2B)-C(3B) 123.9(6), C(2B)-C(3B)-C(4B) 125.2(6).

The integrity of the cluster frame has remained undisturbed throughout the reaction with Ru-Ru bond distances in the range 2.7617(8)-2.9771(8)Å, mean 2.8740(8)Å. There are three noticeably shorter Ru-Ru bonds, namely Ru(1)-Ru(3) 2.7969(8)Å, Ru(1)-Ru(4) 2.8132(8)Å and Ru(3)-Ru(4) 2.7617(8)Å; these three bonds form the ruthenium triangle onto which the alkyne ligand is bound. The encapsulated carbido atom is displaced towards the arene bearing metal centre Ru(5); Ru(5)-C 1.959(6)Å compared to an average Ru-C distance of 2.049(6)Å in the remainder of the cluster. The twelve carbonyl ligands are linearly bound with Ru-C-O angles lying in the range 172.6(6) - 179.2(6)°, mean 176.1(6)°. Atoms Ru(2) and Ru(6) are bonded to three CO groups whilst Ru(1), (3) and (4) are connected to two carbonyl ligands. The bonding of the mesitylene group has undergone no change from the terminal position found in the starting material. The but-2-yne ligand is bonded across the Ru(1)-Ru(3)-Ru(4) face with σ-interactions to Ru(1) and Ru(3) and a π-interaction to Ru(4). The coordinated alkyne now exhibits the characteristic alkene-like parameters, *ie* C=C multiple bond length has lengthened from 1.2Å to 1.398(9)Å and bond angles have increased from 180° to 123.9(6)and 125.2(6)°.

3.6 Comparison of Preceding Arene-alkyne Complexes.

The complexes $[Ru_6C(CO)_{14}(arene)(Me_2C_2)]$, arene = C_6H_6, C_6H_5Me, $C_6H_4Me_2$, $C_6H_3Me_3$ all bear striking similarities to one another. In all cases the aromatic ligand has not been obviously influenced by the presence of the Me_2C_2 ligand, *ie* it has not migrated to an alternative site on the cluster nor has it been displaced. The similarities and differences between the structures will now be assessed.

Firstly in all cases the reaction of the $[Ru_6C(CO)_{14}(arene)]$ and but-2-yne has resulted in the displacement of two carbonyl ligands one of which is the bridging CO group. In analogy with the ligand distribution of the parent carbonyl cluster $[Ru_6C(CO)_{17}]$ and in all the *mono-* and *bis*-substituted arene derivatives, where one of the carbonyl ligands bridges a metal-metal bond in the equatorial plane of the cluster, one of the two alkyne carbons interacting with the triangular face spans an equatorial cluster edge. In other words the μ-ligand takes the place of the bridging CO usually present in other [$Ru_6C(CO)_{17}$] derivatives. The geometrical constraint due to the coordination of the second C atom of the unsaturated fragment to the metal core, though, causes the observed deviation from the planarity of the five membered system thus formed. In each of the compounds the three shortest metal-metal bonds are the three which form the *tri*-ruthenium face which the alkyne bridges. The alkyne bonds in the same way to the cluster core in each case. The alkyne coordinates to the lower half of the cage if the upper half is designated as that which is involved with the bonding to the aromatic ligand. The familiar μ_3:η^1:η^2:η^1 mode is observed, with the π-interaction at an equatorial Ru atom and the two σ-interactions to an equatorial and an apical atom.

The carbido atom in the series [$Ru_6C(CO)_{14}$(arene)] is displaced out of the central location towards the arene bearing atom. This effect, frequently observed in hexaruthenium arene derivatives bearing a terminally bound aromatic ligand is poorly understood. It has been explained in terms of the bonding properties of the arene causing the metal atom to be electron defecient and hence the carbido atom shifting towards the arene bound Ru atom. It has also been explained in terms of a contraction of orbitals around the metal centre as the pi-interactions of the bound arene againg pull electron density away from the metal centre and thus 'sucks' the carbido atom towards itself. What is clear is that due to a lack of substantial data no definitive reasoning can be provided at this time. The table below shows the ruthenium-carbido distances of the series of complexes $Ru_6C(CO)_{14}$(arene) and $Ru_6C(CO)_{12}$(arene)(alkyne).

ARENE	Ru_6C(arene)	Ru_6C(arene)(Me_2C_2)
Benzene	1.935	1.957
Toluene	1.937	1.990
Xylene	1.913	1.959
Mesitylene	1.900	1.959

Table 3.6.1. Ruthenium Carbido bond lengths (Å)

As can be seen, without exception the Ru-C distance in the [Ru_6C(arene)(alkyne)] complexes has increased, *ie* moved away from the arene bearing Ru atom, upon coordination of the alkyne. This obviuosly is a result of the coordination of the alkyne to the cluster and could possibly be related to the different π-acceptor abilities of the carbonyl and alkyne ligands. Carbon monoxide is a strong pi-acceptor ligand whilst the alkyne is less so, *i.e.* it is a weaker pi-acceptor though this clearly does not explain why the carbido atom shifts away from the cluster.

The final anomaly concerns the ^1H NMR spectra of these derivatives. In the table below the aromatic NMR signals for the compounds [$Ru_6C(CO)_{14}$(arene)] and [$Ru_6C(CO)_{12}$(arene)(Me_2C_2)] are shown , where arene equals benzene, toluene, xylene and mesitylene.

Arene	**Ru_6C(arene)**	**Ru_6C(arene)(alkyne)**
Benzene	5.56(s, 6H)	5.79(s,5H)
Toluene	5.3(s,5H), 2.15(s,3H)	5.82(d,2H), 5.7(m,3H), 2.35(s,3H)
Xylene	5.54(m,2H), 5.32(dd,2H),2.26(s,6H)	5.77(m,2H), 5.46(m,2H), 2.40(s, 6H)
Mesitylene	5.3(s,3H), 2.23(s, 9H)	5.71(s,3H), 2.39(s,9H)

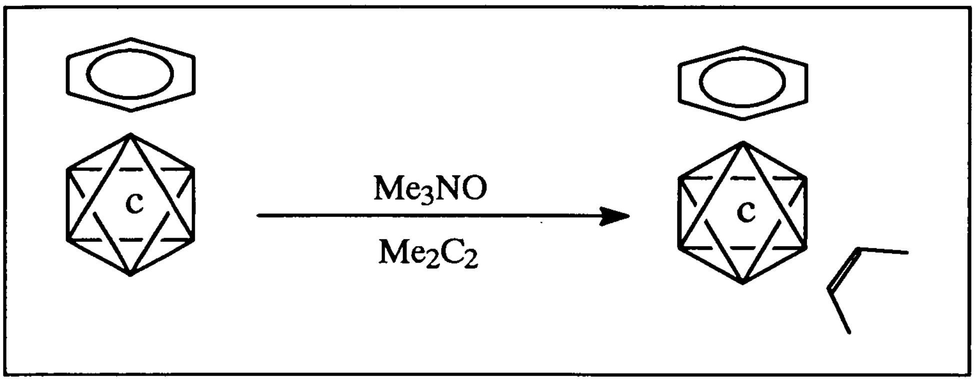
Table 3.6.2. ^1H NMR shifts(ppm) of Ru_6C(arene) and Ru_6C(arene)(alkyne) in $CDCl_3$.

Without exception the resonances assigned to aromatic protons and the protons of the methyl groups bound to the rings have shifted approximately 0.2 ppm to higher frequencies. The characteristic shift to lower frequencies of a bound arene is well established but poorly understood and in discussions to clarify the situation the metal-bond anisotropy, modifications of ring current and electron density changes have been assessed. Metal-arene π-back-bonding is most apparent, increasing the electron density at the ring. This effectively results in a change in the nature of the carbon atoms of the aromatic ligand, *viz* a shift in sp^2 to sp^3 character. More simply, as the ligand coordinates to the cluster it becomes *less* aromatic and *more* aliphatic, Hence the shift to lower frequencies in the NMR spectrum. We believe that as the alkyne coordinates to the $[Ru_6C(CO)_{14}(arene)]$ fragment the arene is becoming more aromatic in character because of the increased competition for electron density from the cluster.

As discussed previously, the primary objective of this study was to ascertain the effects of an incoming alkyne group on a series of hexaruthenium arene complexes. In smaller cluster complexes the alkyne has had a substantial effect on the complex; it has been observed that the arene has changed bonding modes or been displaced entirely from the metal. The effects here were not nearly so dramatic but it can be stated that the alkyne has had an influence on the aromatic group .

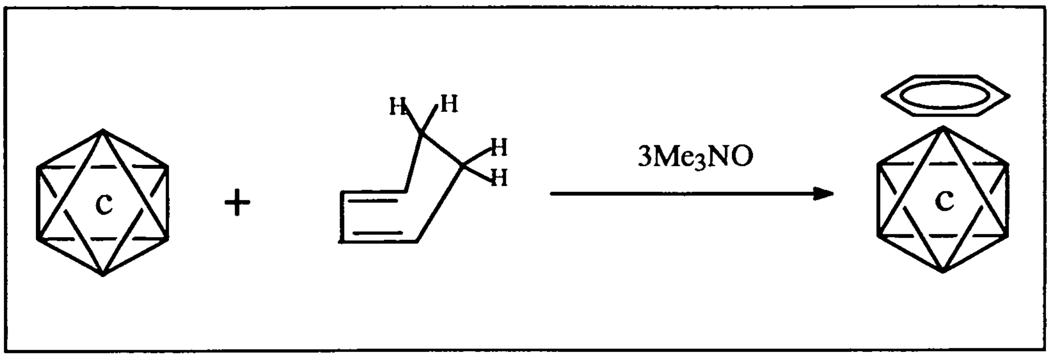
3.7 An Alternative Route to Arene-Alkyne Derivatives.

The reactions in the preceding discussion have taken the arene substituted complex and reacted it with trimethylamine-N-oxide in the presence of the alkyne but-2-yne to produce an arene-alkyne hexaruthenium complex. This is shown schematically in Scheme 3.7.1.



Scheme 3.7.1. Preparation of *Hexa*ruthenium Arene-alkyne Derivatives.

An alternative route into these complexes has been devised for the *hexa*ruthenium benzene-butyne system. The preparative route into *hexa*ruthenium benzene[26] is a well established reaction and involves reacting hexaruthenium carbonyl with three molar equivalents Me_3NO in the presence of 1,3-cyclohexadiene. The cyclohexadiene undergoes dehydrogenation *in situ* to produce a benzene ligand which coordinates to the cluster in the terminal η^6-bonding mode. This reaction is shown in Scheme 3.7.2.



Scheme 3.7.2. Preparation of [$Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$].

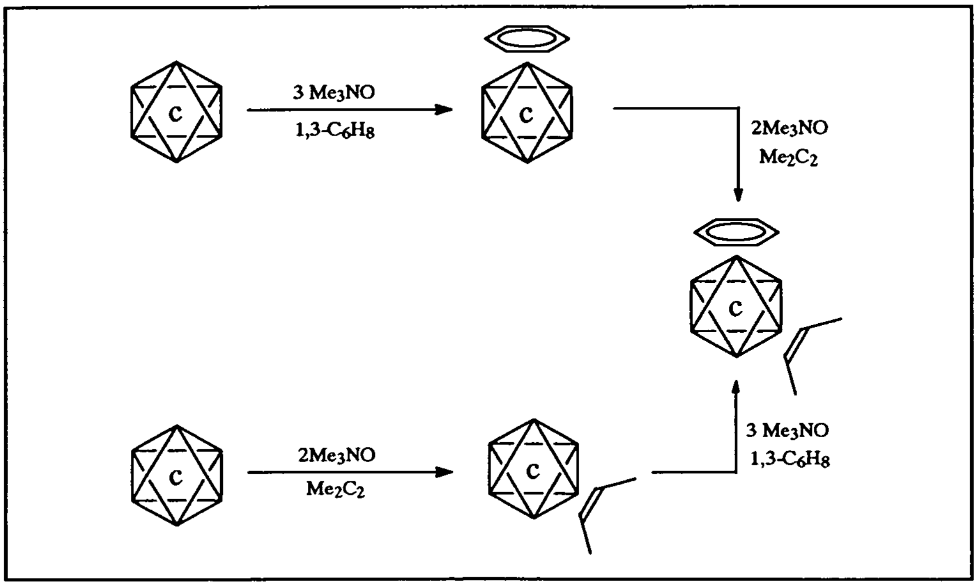
Thus it was thought that the reaction of [$Ru_6C(CO)_{15}(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}Me_2C_2)$] and Me_3NO in the presence of 1,3-cyclohexadiene would result in the formation of the benzene-but-2-yne *hexa*ruthenium complex.

3.8 Preparation of [$Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}Me_2C_2)$] *via* an Alternative Route.

The complex [$Ru_6C(CO)_{15}(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}Me_2C_2)$] was prepared as discussed in Section 2.2 of Chapter Two. The compound [$Ru_6C(CO)_{15}(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}Me_2C_2)$] was dissolved in dichloromethane and an excess of the ligand 1,3-cyclohexadiene was introduced to the solution, the resulting red solution was then cooled to -78°C. Three molar equivalents Me_3NO in dichloromethane were added to the cold solution in a dropwise manner over an eight minute period. The reaction vessel was removed from the acetone/dry ice bath and allowed to warm to room temperature over 30 minutes. All volatiles were removed under reduced pressure to leave red-brown residues in the flask. A minimum amount of dichloromethane was added to the solids. Reaction products were isolated by tlc using as eluent a solution of dichloromethane/ hexane (2:3 v/v). Two products were isolated; at the top of the tlc plate was unreacted starting material, [$Ru_6C(CO)_{15}(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}Me_2C_2)$]. This was followed by a second brown band of the material [$Ru_6C(CO)_{15}(\eta^6\text{-}C_6H_6)(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}Me_2C_2)$]. The characterisation of this second complex was confirmed by infrared, mass and ^1H nmr spectroscopies. No new compounds were isolated from this reaction.

3.9 Comparison of the Two Reaction Routes into Arene-Alkyne Derivatives.

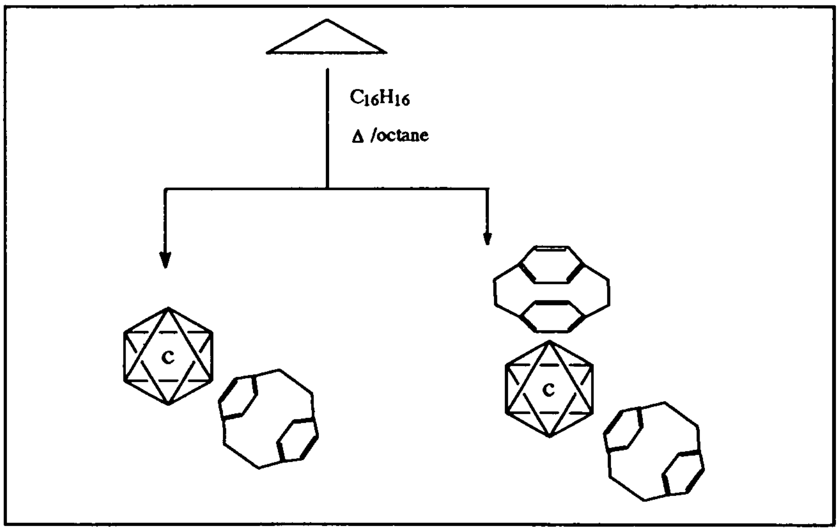
The two routes employed in the preparation of the complex hexaruthenium benzene-butyne are easy to compare in terms of productivity and cleanliness of reaction. In the first route the first step of preparation is that of the hexaruthenium benzene from hexaruthenium carbonyl and 1,3-cyclohexadiene using Me_3NO to remove the necessary number of carbonyls. This reaction produces $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)]$ in approximately 25% yield along with a series of other reaction products. the second step reacts the arene complex with but-2-yne to produce the desired benzene-but-2-yne derivative in ~40% yield. This reaction is very clean with only one distinct product and some unreacted staring material being prepared. In the alternative route the primary step is the synthesis of the compound $[Ru_6C(CO)_{15}(\mu_3\text{:}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-}Me_2C_2)]$, which is produced in good yields of ~37%. This material is then reacted with 1,3-cyclohexadiene to yield $[Ru_6C(CO)_{15}(\eta^6\text{-}C_6H_6)(\mu_3\text{:}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-}Me_2C_2)]$ in 28% yields. The two reactions are given schematically in Scheme 3.9.1.



Scheme 3.9.1. Routes into *Hexa*ruthenium Benzene-Butyne

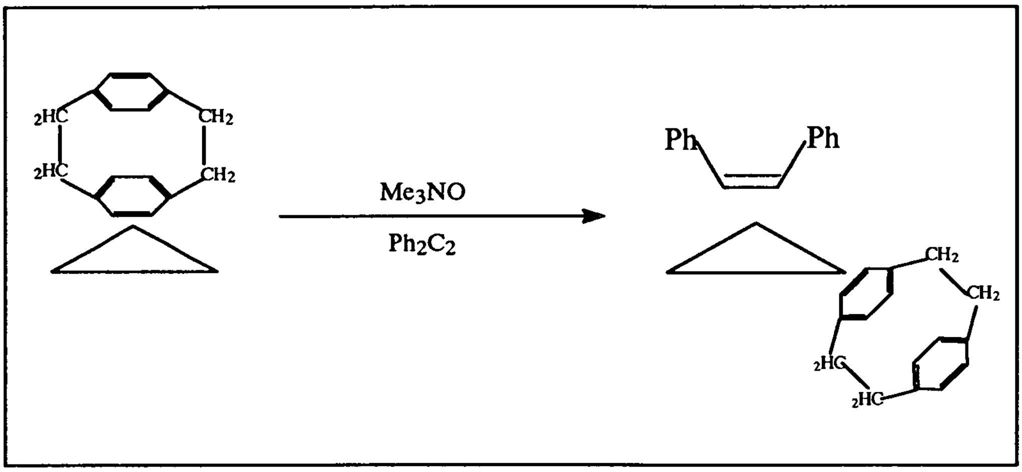
There is little to choose in the two reactions as both have one step that is low yielding whilst the other may be higher; in the first route the first step is lower yielding and not very clean whilst the second phase of the reaction is high yieldin g and very succinct in what it produces. The alternative reaction has a high yielding first step but a much lower one in the second step. In other words the steps in both reactions which involve the 1,3-cyclohexadiene are the ones which result in lower product quantities.

All the above reactions involve a complex containing a η^6-bound arene. The final reaction to be looked at in this chapter is that of $[Ru_6C(CO)_{14}(C_{16}H_{16})]$[23] and but-2-yne. The ligand 2.2-paracyclophan, $C_{16}H_{16}$ is an usual ligand, it contains two aromatic rings which are linked by two CH_2CH_2 arms so that the rings are parallel to one another. The complex is prepared by the thermolysis of $[Ru_3(CO)_{12}]$ and the ligand in octane for several hours. The reaction produces the products $[Ru_6C(CO)_{14}(C_{16}H_{16})]$ and $[Ru_6C(CO)_{11}(C_{16}H_{16})_2]$. The overall reaction is given in Scheme 3.9.2 below.



Scheme 3.9.2. Preparation of $[Ru_6C(CO)_{14}(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$from $[Ru_3(CO)_{12}]$.

The complex $[Ru_6C(CO)_{14}(\mu_3:\eta^2:\eta^2:\eta^2-C_{16}H_{16})]$ was the first example of a *mono*-substituted arene complex with the arene in the face capping mode and not terminally bound. Having looked at the reactions of complexes containing the η^6-bound arene with but-2-yne in some depth it seemed natural to look at the reaction of $[Ru_6C(CO)_{14}(\mu_3:\eta^2:\eta^2:\eta^2-C_{16}H_{16})]$ with but-2-yne to observe the possible influence of the alkyne on the face capping mode. As stated previously the face capping 2.2paracyclophan ligand of $[Ru_3(CO)_9(C_{16}H_{16})]$ shifts to a terminal position when reacted with diphenylacetylene and Me_3NO at -78°C. The reaction is given in Scheme 3.9.3



Scheme 3.9.3. Reaction of $[Ru_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2-C_{16}H_{16})]$ with Ph_2C_2 and Me_3NO.

It would seem that movement from the face bridging mode to the terminal site occurs with some ease, with this in mind it was decided that the complex $[Ru_6C(CO)_{14}(\mu_3:\eta^2:\eta^2:\eta^2-C_{16}H_{16})]$ would be reacted with but-2-yne to observe any changes in the coordination mode of the aromatic ligand.

3.10. Reaction of $[Ru_6C(CO)_{14}(C_{16}H_{16})]$ with Me_2C_2 and Me_3NO.

The complex $[Ru_6C(CO)_{14}(\mu_3:\eta^2:\eta^2:\eta^2-C_{16}H_{16})]$ was dissolved in dichloromethane and cooled to -78°C. An excess of the ligand Me_2C_2 was added to the solution. Two molar equivalents of Me_3NO in dichloromethane were introduced to the solution in a dropwise manner over a five minute period. The reaction was removed from the acetone/dry ice bath and stirred for a further 20 minutes at room temperature. The reaction products were isolated by reducing the reaction mixture to a minimum volume followed by tlc using as eluent a solution of CH_2Cl_2:hexane (3:7, v/v). Products were eluted as follows, a bright yellow band of $[Ru_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})][Ru_6C(CO)_{12}(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)]$ and $[Ru_6C(CO)_{14}(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})(Me_2C_2)]$ both as brown bands on the tlc plate. The compound $[Ru_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$[19] is a known complex and shall not be dealt with here. $[Ru_6C(CO)_{12}(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)]$ was initially characterised by infrared, mass spectroscopy and ^1H NMR spectroscopy. In the mass spectrum a parent peak was observed at M^+ 1220 amu, this led to the initial formulation of $[Ru_6C(CO)_{12}(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})(\mu_3:\eta^1:\eta^1:\eta^2\text{-}Me_2C_2)]$. In the ^1H NMR spectrum a singlet at δ 3.07 ppm led to the conclusion that the alkyne had reacted with the parent complex. Signals at δ 7.43, 3.41, 3.30 and 2.79 ppm also confirmed the presence of the 2.2-paracyclophan ligand. The infrared spectrum showed peaks at higher frequencies with a different symmetry pattern to the $[Ru_6C(CO)_{12}(\eta^6\text{-}arene)(Me_2C_2)]$ series. Crystals of suitable quality for a crystallographic study were afforded by the slow evaporation of dichloromethane and hexane at -30°C. The molecular structure of $[Ru_6C(CO)_{12}(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)]$ is given in Figure 3.10a.

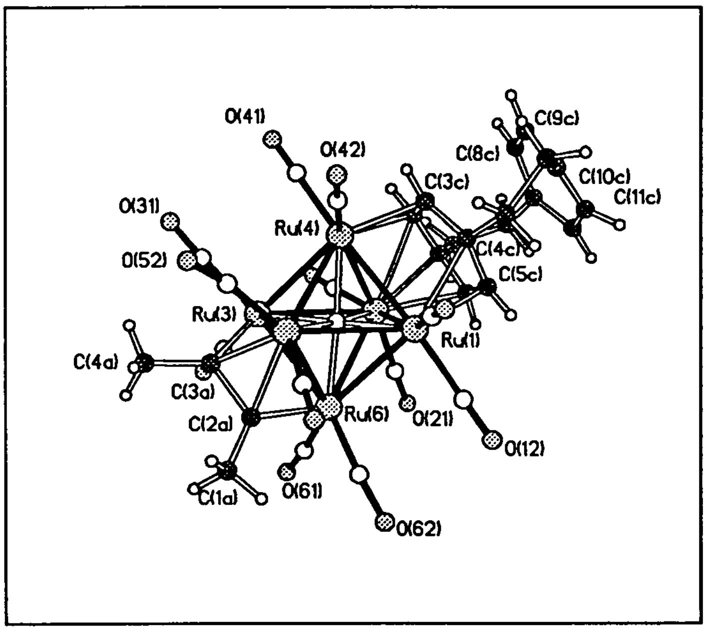


Figure 3.10a. The Molecular Structure of $[Ru_6C(CO)_{12}(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2]$. Significant bond lengths(Å) and angles(°) for $[Ru_6C(CO)_{12}(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2]$. are given. Ru(1)-Ru(2) 2.886(4), Ru(1)-Ru(4) 2.816(4), Ru(1)-Ru(5) 2.954(4), Ru(1)-Ru(6) 2.895(4), Ru(2)-Ru(4) 2.900(4), Ru(2)-Ru(6) 2.922(5), Ru(3)-Ru(5) 2.777(4), Ru(3)-Ru(5) 2.820(5), Ru(4)-Ru(5) 2.899(4), Ru(5)-Ru(6) 2.795(5); Range 2.77(5)-2.992(5), mean 2.884(5); Ru(1)-C 2.01(3), Ru(2)-C 2.01(3), Ru(3)-C 2.03(3), Ru(4)-C 2.07(3), Ru(5)-C 2.12(3), Ru(6)-C 2.00(3); Ru-C(CO) range 1.84(4)-1.93(4), mean 1.88(4); C-O range 1.07(5)-1.24(5), mean (1.15)(5); Ru-C-O range 170.0(4)-179.0(4), mean 174.4(4); C(1a)-C(2a) 1.43, C(2a)-C(3a)1.55, C(3a)-C(4a) 1.48; C(1c)-C(2c) 1.38(5), C(2c)-C(3c) 1.48(5), C(3c)-C(4c)1.40(5), C(4c)-C(5c) 1.41(5), C(5c)-C(6c) 1.50(5), C(6c)-C(1c) 1.37(5), C(1c)-C(13c) 1.58(5), C(4c)-C(15c) 1.53(5), C(7c)-C(14c) 1.41(5), C(7c)-C(8c) 1.44(5), C(7c)-C(12c) 1.48(5), C(8c)-C(9c), C(9c)-C(10c) 1.46(5), C(10c)-C(11c) 1.33(5), C(10c)-C(16c) 1.43(5), C(11c)-C(12c) 1.41(6), C(13c)-C(14c)-1.49(6), C(15c)-C(16c) 1.63(5); C(1a)-C(2a)-C(3a) 122.0(4), C(2a)-C(3a)-C(4a) 123.0(3).

The crystallographic data obtained for this study was of poor quality, as reflected in the final R-factor of 12%. Thus, although a discussion of the complex is viable no set conclusions can be made about bond lengths and angle parameters.

The complex is based on the familiar octahedral array of six ruthenium atoms encapsulating a central carbido atom. Metal-metal distances lie in the range 2.777(4) -2.992(4)Å, mean 2.884(5)Å compared to a range of 2.794(1)-2.990(1)Å and average of 2.902(1)Å in the parent compound. Bearing in mind the larger errors involved for the arene-alkyne complex there is little difference in the metal-metal distances when looking at the ranges, however the average Ru-Ru bond length for $[Ru_6C(CO)_{12}(\mu_3:\eta^2:\eta^2:\eta^2-C_{16}H_{16})(\mu_3:\eta^1:\eta^2:\eta^1-Me_2C_2)]$ is 0.018Å shorter than in $[Ru_6C(CO)_{14}(\mu_3:\eta^2:\eta^2:\eta^2-C_{16}H_{16})]$. This is not surprising as the Ru-Ru bonds involved in coordinating to the alkyne are three of the shortest at Ru(3)-Ru(5) 2.77(5), Ru(3)-Ru(6) 2.820(5), Ru(5)-Ru(6) 2.795(5)Å in the complex, thus reducing the average bond length. The ruthenium-carbido distances lie in the range 2.00(3)-2.12(3)Å. This extra long Ru-C bond of 2.12(3)Å occurs at Ru(5) which is involved in a π-interaction from carbon atoms C(2a) and C(3a) of the but-2-yne ligand; this effect was also observed in the compound $[Ru_6C(CO)_{15}(Me_2C_2)]$. The effect of the alkyne is a distinct possibility but definitive conclusions are not possible due to the large errors involved from the crystallographic data. There are twelve linearly bound carbonyl ligands which are distributed evenly over the cluster. One of the rings of the paracyclophane ligand is still coordinted to a triangular face of the metal core *via* three π-interactions. In analogy with other facially coordinated six membered rings, the mid-points of alternating C-C bonds in the C_6 interacting system are, in a first approximation, eclpised over the three metal atoms. It can be observed, though, that the coordinated ring shows a certain degree of torsion with respect to the underlying Ru_3 fragment. In fact, the Ru-C bond length distribution is spread over a wide range of distances, the alterneting average values for the shortest and the longest distances being 2.164Å and 2.404Å respectively, (Δ = 0.24Å). The torsion of the ligand toward a near ecplipsing of the C atoms over the metals has also been observed in all the previously reported Ru clusters carrying the face capping [2.2]-paracyclphane ligand[19] although the extent of deformation varies from compound to compound. This conformational flexibility is likely to be the effect of intermolecular forces acting on the protruding 2.2-paracyclophane ligand.

The bonding of the alkyne is found to be coordinating in the face bridging mode across the *tri*-ruthenium face Ru(3)-Ru(5)-Ru(6). There is a π-interaction to Ru(5) and two σ-interactions to Ru(3) and Ru(6). As was seen in the $[Ru_6C(CO)_{12}(\eta^6-arene)(Me_2C_2)]$ compounds discussed previously the π-interaction is to an equatorial ruthenium atom.

The table below highlights the ^1H NMR frequencies observed for $[Ru_6C(CO)_{12}(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}Me_2C_2)]$ and $[Ru_6C(CO)_{12}(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})]$.

$[Ru_6C(CO)_{12}(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})]$	$[Ru_6C(CO)_{12}(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1Me_2C_2)]$
7.44(s,4H)	7.43(s,4H)
3.43(s,4H)	3.41(s, 4H)
3.40(m, 4H)	3.30(m,4H)
2.98(m,4H)	2.79(m,4H)
-	3.07(s, 6H)

Table 3.10.2. ^1H NMR frequencies (ppm) for 2.2-paracyclophan derivatives.

The signals at δ7.43 and 7.44ppm relate to the four protons on the aromatic ring not coordinated to the cluster; signals at δ3.41 and 3.43ppm have been assigned to the four protons of the coordinated ring. The data shows that unlike the $[Ru_6C(CO)_{12}(\eta^6\text{-arene})(Me_2C_2)]$ series the aromatic protons signals have remained unchanged in their positions. The signals related to the aliphatic protons closest to the uncoordinated ring, δ 2.79 and 2.98ppm have shifted by 0.19 ppm, there is no obvious explanation for this anomaly.

3.11 Concluding Remarks.

To reiterate, the background to this work was an examination of the reactions of a series of *hexa*ruthenium arene complexes with alkynes to assess the influence of the alkyne on the coordination type of the arene ligand. In previous studies coordinated arenes have been shown to migrate over the cluster to a different bonding site or have been displaced from the metal core completely by the incoming alkyne. In our work neither of these effects have been observed. This is possibly because of the size of the cluster since other work in this area has focused on *tri-* and *tetra*-nuclear species[5-7]. In the case of the face capping benzene on the *tri*-osmium cluster $[Os_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2-C_6H_6)]$, the migration of the arene to a terminal site has been attributed to the preferential $\mu_3:\eta^1:\eta^2:\eta^1$ bonding mode of the alkyne moiety and its over-riding tendency to bond to the facial site. It would seem that the *tri*-osmium cluster is unable to bond two ligands facially simultaneously, *i.e.* one on either side of the cluster to form a 'sandwich' complex; hence the migration of the arene. The addition of the second alkyne results in the displacement of the arene completely which leads one to conclude that the cluster preferentially selects the alkyne over the arene. In our study, the cluster is larger than the *tri*-osmium unit, with six metal atoms creating eight triangular faces, the cluster is able to accommodate both ligands without imposing any restraints on either of the two ligands. This is particularly so in the $[Ru_6C(CO)_{12}(\mu_3:\eta^2:\eta^2:\eta^2-C_{16}H_{16})(Me_2C_2)]$ system where the cluster core can accommodate the face bridging modes of both the arene and the alkyne. No obvious structural changes have occurred in these reactions but it would seem that the ligands are 'communicating' with each other. This is particularly evident in the η^6-arene series when assessing the ^1H NMR resonances. The shift in signals appears to be a direct consequence of the incoming alkyne. To sum up, the reaction of *hexa*ruthenium arene complexes with alkynes results in a series of compounds in which the arene has not migrated to an alternative site nor has it been displaced from the cluster as the cluster is of sufficient size to accommodate both the ligands.

Further work in this area would include the reacting the arene-alkyne complexes with trimethylamine-N-oxide and but-2-yne to assess whether the cluster would be able to bear two alkyne units as well as the arene or whether the arene would be displaced.

3.12 References for Chapter Three.

1. P.J.Dyson, B.F.G.Johnson, D.Braga, F.Grepioni., *Chem. Rev.,* 1994, **94**, 1620

2. η^1: K.Shelly, D.C.Finster, Y.L.Lee, W.R.Scheidt, C.A.Reed., *J.Amer.Chem.Soc.*, 1985, **107**, 5955.

3. η^2: H.van der Heijden, A.G.Orpen, P.Pasman., *J.Chem.Soc., Chem. Commun.*, 1985, 1576.

4. η^3: A.Keasey, P.M.Bailey, P.M.Maitlis., *J.Chem.Soc., Chem.Commun.*, 1978, 142.

5. η^4: J.A.Bandy, M.L.H.Green, D.O'Hare, K.Prout. *J.Chem.Soc.Chem.Commun.*, 1984, 1402

6. η^6: H.Le Bosec, D.Touchard, P.H.Dixneuf., *Adv.Organomet.Chem.*, 1991, **29**, 163 and references therein.

7. μ_2-η^2:η^2: W.D.Harman, H.Taube., *J.Amer.Chem.Soc.*,1987, **109**, 1883.
and H.Omori, H.Suzuki, Y.Take, Y.Moro-oka, *Organometallics*, 1989, **8**, 2270.

8. μ_2-η^3:η^3: K.Jonas, G.Koepe, L.Schieferstein, R.Mynott, C.Kruger, Y.H.Tsai, *Angew. Chem.Int.Ed.Engl.*, 1983, **22**, 620.

9. μ_2-η^4:η^4: K.Jonas, V.Wiskamp, Y.H.Tsai, C.Kruger., *J.Amer.Chem.Soc.*, 1983, **105**, 5480.

10. μ_2-η^6:η^6: W.H.Lamanna, W,B,Gleason, D.Britton., *Organometallics*, 1987, **6**, 1583.

11. M.A.Van Hove, R.F.Lin, G.A.Somarjai, *J.Amer.Chem.Soc.*, 1986, **108**, 2532.

12. F.P.Netzer, H.H.Green, H.Kuhlenbeck, M.Neuman., *Chem.Phys.Lett.*, 1987, **133**, 49.

13. M.A.Gallup, B.F.G.Johnson, J.Lewis, A.M^{c}Camely, R.N.Perutz, *J. Chem. Soc. Chem. Commun.*, 1988, 1071.

14. for example, D.Braga, F.Grepion, B.F.G.Johnson, J.Lewis, M.Martinelli, M.A.Gallup., *J. Chem. Soc. Chem. Commun.*, 1990, 53.

15. H.Chen, B.F.G.Johnson, J.Lewis., *J. Organomet. Chem.*, 1991, **405**, C22.

16. M.P.Gomez-Sal, B.F.G.Johnson, J.Lewis, P.R.Raithby, A.H.Wright., *J. Chem.*

Soc. Chem. Commun., 1985, 1682.

17.B.F.G.Johnson, J.Lewis, M/Martinelli, A.H.Wright, D.Braga, F.Grepioni., *J. Chem. Soc., Chem. Commun.*, 1990, 364.

180. D.Braga, M.A.Gallup, F.Grepioni, B.F.G.Johnson, J.Lewis, M.Martinelli, E.Parisini., *J. Chem. Soc., Dalton.*, 1992, 804.

19. A.J.Blake, D.Braga, P.J.Dyson, F.Grepioni, B.F.G.Johnson, C.M.Martin, E.Parisini., *Organometallics.*, 1994, **13**, 2113.

20. A.J.Blake, P.J.Dyson, S.Ingham, B.F.G.Johnson, C.M.Martin., *Organometallics.*, 1995, **14**, 862.

21. M.A.Bennet, A.K.Smith., *J. Chem. Soc., Dalton.*, 1974, 233.

22.B.F.G.Johnson, J.Lewis, W.J.H.Nelson, J.N.Nicholls, J.Puga, P.R.Raithby, M.J.Rosales, M.Schroder, M.D.Vargas., *J. Chem. Soc., Dalton.*, 1983, 2447.

23. D.Braga, H.Chen, F.Grepioni, B.F.G.Johnson, J.Lewis, E.Parisini., *J. Chem. Soc., Dalton* 1991, 215.

24. B.F.G. Johnson, R.D.Johnston, J. Lewis., *J. Chem. Soc. (A)*, 1968, 2865.

25.C.R.Eady, P.F.Jackson, B.F.G.Johnson, J.Lewis, M.C.Malatesta, M.McPartlin, W.J.H.Nelson., *J. Chem. Soc.Dalton*, 1980, 383.

26. P.J.Dyson, B.F.G.Johnson, J.Lewis, M.Martineli, D.Braga, F.Grepioni., *J. Amer. Chem. Soc.*, 1993, **115**, 9062.

27. B.F.G.Johnson, J.Lewis, M.Martinelli, S.W.Sankey, K.Wong, M.McPartlin, W.J.H.Nelson., *J. Organomet. Chem.*, 1980, **191**, C3.

Chapter Four.

Experimental for Chapters Two and Three.

4.1 General Specifications.

All experiments were carried out with the exclusion of air under an inert atmosphere of nitrogen using freshly distilled solvents unless otherwise stated. Ruthenium Chloride Dihydrate was purchased from Hereaus Silica and Metals Limited. Triruthenium dodecacarbonyl[1], $Ru_3(CO)_{12}$ and Hexaruthenium carbido heptadecacarbonyl[2], $Ru_6C(CO)_{17}$ were prepared by literature methods with no further modifications typical reactions are provided in the text. The 250ml autoclave used was supplied by Berghoff Limited and fitted with a PTFE liner and magnetic stirrer.

Ligands unless otherwise stated were purchased from Aldrich Chemicals and used without further purification prior to use. Trimethylamine-N-oxide dihydrate, also supplied by Aldrich Chemicals, was initially dried by a Dean and Stark distillation in benzene and then sublimed before use. Low temperatures of -78°C were achieved using an acetone/dry ice bath.

4.2. Analytical Techniques.

4.2.1 Infrared Spectroscopy.

Infrared spectra were recorded on a Perkin Elmer 1710 Series Fourier transformer instrument, calibrated against CO_2 . Solution cells fitted with NaCl windows (0.5mm path length) supplied by Specac Limited were employed. Unless otherwise stated samples were recorded in dichloromethane or hexane.

4.2.2 ^1H nmr Spectroscopy.

All ^1H nmr spectra were recorded on either Bruker WH 200 or 360 fourier transform instruments. Unless otherwise stated samples were run in deuterated trichloromethane, $CDCl_3$. An internal lock was used for all accumulations at all temperatures.

4.2.3 Mass Spectra.

Positive fast atom bombardment mass spectra were measured on a Kratos MS5OTC device. The instrument was run in positive mode using CsI as standard. Samples were dissolved in a minimum volume of acetone prior to being added to the liquid matrix.

4.2.4 Crystallographic Studies.

X-ray crystal diffraction data was collected on a Stoe Stadi-4-circle-diffractometer. For data collected at low temperatures, an Oxford cryosystems device was employed. Where necessary the appropriate data is provided in the text.

Techniques used for growing crystals suitable for crystallographic studies were either slow diffusion using mostly dichloromethane and hexane layers or slow evaporation with a mixture of various solvents, *eg*. dichloromethane and toluene. Where it is appropriate specific details of technique are provided in the text.

4.2.5. Purifications.

Separations of reaction mixtures were carried out chromatographically on silica gel. Small scale separations were performed using thin layer chromatography (tlc) on glass plates supplied by Merck. The plates, 20x20cm, were coated with silica gel 60 F_{254}, thickness 0.25cm. Eluent details (standard laboratory grade solvents) are specified in the text. For larger scale preparations a 50cm glass column (diameter 2cm) fitted with a sintered glass frit and Young's tap was used. A 250ml solvent reservoir was adapted to take nitrogen pressurisation. Silica gel, 60 mesh was used as packing material supplied by Fluka Chemicals.

4.3. Preparations of Starting Materials for Chapters Two and Three.

4.3.1. Preparation of $[Ru_3(CO)_{12}]$.

Ruthenium trichloride hydrate (4.5g) was placed in a 250ml PTFE liner with 150ml methanol and a large magnetic stirring bar. The reaction vessel was then placed into the autoclave and sealed. The solution was heated for 10 hours at 125°C, under a carbon monoxide pressure of 65-70 atmospheres. The reaction was left to cool slowly under pressure over a period of at least 10 hours. Orange crystals of $[Ru_3(CO)_{12}]$ were washed with 2 x 20ml hexane and then dried under a flow of dinitrogen gas. The reaction typically produced 3-3.5g of $[Ru_3(CO)_{12}]$.

4.3.2. Preparation of $[Ru_6C(CO)_{17}]$ from $[Ru_3(CO)_{12}]$.

The complex $[Ru_3(CO)_{12}]$ (1.1g, 1.721mmol) and 100ml HPLC grade heptane were reacted in the 250ml PTFE liner in the autoclave for 3 1/2 hours at 85°C under an ethylene pressure of 30 atmospheres. The reaction was left to cool for 7 hours; the dark red crystals of $[Ru_6C(CO)_{17}]$ were washed with 2 x 15ml of hexane before being dried under a dinitrogen atmosphere. The reaction typically yielded 0.4-0.5g of the hexaruthenium carbonyl.

4.3.3 Typical Reaction to Prepare $[Ru_6C(CO)_{14}(arene)]$, arene = toluene, xylene, mesitylene, [2.2]-paracyclophan.

$[Ru_3(CO)_{12}]$ (0.50g, 0.789mmol) in octane (25ml) containing an excess of the required arene was heated to a vigorous reflux for 3 hours. The solvent was removed *in vacuo* and products isolated by column chromatography using a solution of dichloromethane-hexane (1:4, v/v) as eluent. Product yields range from 8 - 15% in this type of reaction.

4.3.5 Typical Synthesis of $[Ru_6C(CO)_{14}(C_6H_6)]$.

$[Ru_6C(CO)_{17}]$ (100mg, 0.091mmol) in dichloromethane (30ml) containing excess 1,3-cyclohexadiene (1.5ml) was cooled to -78°C. The solution was treated with Me_3NO (15mg, 0.20mmol) added dropwise in 5ml dichloromethane over 5 minutes. The reaction mixture was stirred for a further 25 minutes and brought to room temperature, after which time the solution had darkened in colour from red to brown. Volatiles were removed *in vacuo* and products isolated by tlc using a dichloromethane-hexane solution (3:7, v/v) as eluent. $[Ru_6C(CO)_{14}(C_6H_6)]$ was isolated in moderate yields of 24% along with $[Ru_6C(CO)_{15}(C_6H_8)]$ which could be converted to the benzene derivative upon reaction with an aliquot of Me_3NO at room temperature.

4.4. Experimental Details for Chapter Two.

2.2 Reaction of $Ru_6C(CO)_{17}$ with 2 molar equivalents Me_3NO and Me_2C_2.

$Ru_6C(CO)_{17}$ (120mg, 0.109mmol) was dissolved in 60ml dichloromethane. The red solution was cooled to -78°C. Me_2C_2 was added in excess, followed by the dropwise addition of Me_3NO (17mg, 0.219mmol) in 5ml dichloromethane over 5 minutes. The solution was the allowed to warm to room temperature over 30 minutes changing in colour to dark brown, . Infrared spectroscopy at this point confirmed consumption of starting material. The solvent was removed *in vacuo* and products $[Ru_6C(CO)_{15}(Me_2C_2)]$, **2** (37%) and $[Ru_6C(CO)_{14}(Me_2C_2)_2]$, **3** (12%), both brown in colour, were isolated by tlc using a dichloromethane-hexane solution (1:4, v/v) as eluent. Crystals of **2** suitable for crystallographic studies were provided by slow diffusion at -25°C from a dichloromethane-hexane layer.

Spectroscopic data $Ru_6C(CO)_{15}(Me_2C_2)$: IR (hexane) ν (CO)/cm^{-1}: 2088(w), 2044(vs), 2036(s,sh), 2021(m), 2013(m), 1944(vw). ^1H nmr ($CDCl_3$) δ/ppm 3.00(s, 6H). Positive fast atom bombardment mass spectrum /amu , M^+ obs. 1090, (calc. 1092).

Crystallographic data: formula: $Ru_6C_{20}H_6O_{15}$, M_r:1092.67, crystal size/mm:0.25x0.20x0.15, system:monoclinic, space group:P_{21}/n, a/Å:14.338(3), b/Å:11.686(7), c/Å:16.018(3), α/°:90, β/°:95.416(17), γ/°:90, U/$Å^3$:2972, Z:4, F(000):2040, D_c/gcm^{-3}:2.716, μ(Mo - Kα)/cm^{-1}:33.18, 2σ range/°:30 - 32, ω scan width/°:0.96 + 0.347tanθ, measured reflections:3820(3343 unique), unique observed reflections:F>4σ(F) 2908, No. of refined parameters:370, R:2.18, R_w:2.86, S:1.034, T/K:150.

2.3 Reaction of $[Ru_6C(CO)_{15}(Me_2C_2)]$ with carbon monoxide at ambient temperature.

$[Ru_6C(CO)_{15}(Me_2C_2)]$ (0.65mg, 0.060mmol) was taken up into 50ml dichloromethane in a 3-necked round bottomed flask fitted with a stopper, carbon monoxide inlet and bubbler. Carbon monxide gas was bubbled through the red-brown solution for four hours. The reaction was monitored periodically by infrared spectroscopy and spot tlc. No reaction was seen to occur. Starting material was retrieved from the reaction mixture by tlc in 95% yield.

2.4 Reaction of $[Ru_6C(CO)_{15}(Me_2C_2)]$ in heptane under a carbon monoxide atmosphere.

$[Ru_6C(CO)_{15}(Me_2C_2)]$ (85mg, 0.078mmol) was stirred in an autoclave in 50ml heptane under a carbon monoxide pressure of 70 atmospheres for 3 1/2hrs; the reaction mixture was left to cool for 12 hours. A dark brown solution was decanted off from red crystals. Infrared spectroscopy confirmed that the dark red crystals obtained were $[Ru_6C(CO)_{17}]$.

2.5 Reaction of $[Ru_6C(CO)_{15}(Me_2C_2)]$ with 2 molar equivalents Me_3NO and Me_2C_2.

$[Ru_6C(CO)_{15}(Me_2C_2)]$ (90mg, 0.081mmol) and an excess of Me_2C_2 was taken up in 30ml dichloromethane and then cooled to -78°C. Me_3NO (13mg, 0.161mmol) in 5ml dichloromethane was added slowly to the solution over a period of 5 minutes. For 30 minutes the solution was stirred, darkening in colour and reaching room temperature. Solvent was reduced to a minimum volume *in vacuo*. Using dichloromethane-hexane (3:7 v/v) as eluent products $[Ru_6C(CO)_{14}(Me_2C_2)_2]$, **3** (35%) and $[Ru_6C(CO)_{12}(Me_2C_2)_3]$, **5** (7%) were isolated by tlc. Crystals of **3** of suitable quality for a crystallographic study were prepared by the slow evaporation of a solution of dichloromethane and hexane at -25°C.

Spectroscopic data $[Ru_6C(CO)_{14}(Me_2C_2)_2]$: IR(hexane)$\nu$(CO)/cm-1: 2083(w), 2070(vw), 2044(sh), 2039(vs), 2025(s), 2012(m), 2001(vw), 2997(vw), 1981(vw), 1969(vw). ^{1}H nmr ($CDCl_3$) δ/ppm 2.88(s, 6H), 3.29(s,6H). Positive fast atom bombardment mass spectrum /amu, M$^+$ obs.,1116, (calc. 1118).

Crystallographic data $[Ru_6C(CO)_{14}(Me_2C_2)_2]$: formula: $Ru_6C_{23}H_{12}O_{14}$, M_r: 1118.76, Crystal size/mm: 0.50x0.30x0.25, System: triclinic, Space Group: P-1, a/Å: 9.966(5), b/Å: 10.618(5), c/Å: 15.776(8), $\alpha/^\circ$: 73.59(3), $\beta/^\circ$: 84.23(3), $\gamma/^\circ$: 70.117(23), U/Å^3 : 1506, Z: 2, F(000): 1052, D_c /gcm^{-3} : 2.467, μ(Mo-Kα)/cm^{-1} : 29.44, 2σ Range/$^\circ$: 28 - 32, ω Scanwidth/$^\circ$: 1.20 + 0.347tanθ, Measured Reflections: 4374(3829unique), Unique Observed reflections: F>4σ(F) 3464, No. of refined parameters: 285, R: 5.72, R_w: 8.43, S: 1.229, T/K :150.

Crystallographic data $[Ru_6C(CO)_{14}(Me_2C_2)_2]$: formula: $Ru_6C_{23}H_{12}O_{14}$, M_r: 1118.76, Crystal size/mm: 0.50x0.50x0.40, System: monoclinic, Space Group: $P2_1/n$, a/Å: 9.6593(8), b/Å: 10.2056(20), c/Å 16.1402(15), $\beta/^\circ$: 93.393(9), U/Å^3 : 3000, Z: 4, F(000): , D_c /gcm^{-3} : 2.477, μ/mm^{-1} : 3.009 ψ-scan absorption correction: T_{min}=0.104, T_{max}=0.129R[F>4σ(F)] 4.10, $R_w[F^2]$: 19.4% for 3891 data and 388 parameters. The final difference synthesis max. and min. were 1.31 and -1.84e A^{-3}, respectively.

2.6 Conversion of $[Ru_6C(CO)_{14}(Me_2C_2)_2]$ to $[Ru_6C(CO)_{13}(Me_2C_2)_2]$, (I).

$[Ru_6C(CO)_{14}(Me_2C_2)_2]$ (50mg, 0.045mmol) was heated in 50ml heptane under reflux conditions for 1 hour. The reaction was monitored by infrared spectroscopy and spot tlc, eluent dichloromethane-hexane (3:7 v/v). Solvent was removed *in vacuo* and products $[Ru_6C(CO)_{14}(Me_2C_2)_2]$, 3(45%) and $[Ru_6C(CO)_{13}(Me_2C_2)_2]$, 4(38%) were isolated by tlc using a mixture of dichloromethane-hexane (3:7 v/v) as eluent.

Spectroscopic data $[Ru_6C(CO)_{13}(Me_2C_2)_2]$. IR($CH_2Cl_2$)$\nu$(CO)/cm^{-1}: 2077(m), 2042(s), 2021(vs), 1996(w), 1978(w). ^{1}H nmr ($CDCl_3$): δ/ppm 2.98(s, 12H). Positive fast atom bombardment mass spectrum/amu, M$^+$ obs., 1090 (calc.1090).

2.7 Conversion of $[Ru_6C(CO)_{14}(Me_2C_2)_2]$ to $[Ru_6C(CO)_{13}(Me_2C_2)_2]$, (II).

$[Ru_6C(CO)_{14}(Me_2C_2)_2]$ (70mg, 0.063mmol) in 40ml dichloromethane was treated with Me_3NO (5mg,0.063mmol) in 5ml dichloromethane at room temperature.

The reaction mixture was stirred for 20 mins and monitored by spot tlc. Solvent was removed under reduced pressure. Using a solution of dichloromethane-hexane (3:7 v/v) as eluent products $[Ru_6C(CO)_{14}(Me_2C_2)_2]$, **3**(40%) and $[Ru_6C(CO)_{13}(Me_2C_2)_2]$, **4**(33%) were isolated by tlc.

2.8 Reaction of $[Ru_6C(CO)_{14}(Me_2C_2)_2]$ with carbon monoxide at ambient temperature.

$[Ru_6C(CO)_{14}(Me_2C_2)_2]$ (60mg, 0.537mmol) was dissloved in 50ml dichloromethane. Carbon monoxide was bubbled through the solution at room temperature for 1 hour. The reaction was monitored by infrared spectroscopy. Solvent was removed under reduced pressure and starting material was isolated in 95% yield using tlc and a solution of dichloromethane-hexane, (2:3 v/v) as eluent.

2.9 Reaction of $[Ru_6C(CO)_{14}(Me_2C_2)_2]$ with 2 molar equivalents of Me_3NO and Me_2C_2.

$[Ru_6C(CO)_{14}(Me_2C_2)_2]$ (70mg, 0.063mmol) was dissloved in 40ml dichloromethane and then cooled to -78°C. An excess of Me_2C_2, was added to the red-brown solution, followed by the dropwise addition of Me_3NO (10mg, 0.125mmol) in 5ml dichloromethane. The solution was stirred for a further 30 minutes to reach room temperature resulting in an overall darkening of the solution. Products $[Ru_6C(CO)_{14}(Me_2C_2)_2]$, **3** (5%), $[Ru_6C(CO)_{12}(Me_2C_2)_3]$, **5** (39%) and $[Ru_6C(CO)_{10}(Me_2C_2)_4]$, **6** (7%) were isolated by reducing the solution to a minimum volume *in vacuo* and then separating the reaction mixture by tlc using a solution of dichloromethane-hexane (3:7 v/v) as eluent. Crystals of a suitable quality for a crystallographic study were prepared by the slow evaporation of a dichloromethane-hexane layer at -25°C.

Spectroscopic data $[Ru_6C(CO)_{12}(Me_2C_2)_3]$. IR(hexane) $\nu(CO)/cm^{-1}$: 2083(w), 2074(w), 2048(vw), 2037(sh), 2026(vs), 2013(sh), 2002(sh), 1966(w). ^1H nmr ($CDCl_3$): δ/ppm 2.86(s, 15H). Positve fast atom bombardment mass spectrum /amu M^+ obs., 1116 (calc. 1116).

Crystallographic data $[Ru_6C(CO)_{12}(Me_2C_2)_3]$. Formula: $Ru_6C_{25}H_{18}O_{12}$, M_r: 1116.81, system: trigonal, space group: R-3, a/Å: 16.73837(11), c/Å: 37.505(3), U/Å^3 : 9099.7, Z: 12, crystal size/mm^{-3} : 0.35x0.15x0.15, D_c/gcm^{-3}: 2.466, μ/mm^{-1}: 2.971, ψ-scan absorption correction: T_{min} 0.588, T_{max} 0.663, $R[F > 4\sigma(F^2)]$: 2.08 and $R_w[F^2]$ 5.03% for 4432 data and 264 parameters. The final difference synthesis max. and min. were 0.48 and -0.44e Å^{-3} respectively.

2.10 Reaction of $[Ru_6C(CO)_{12}(Me_2C_2)_3]$ in hexane.

$[Ru_6C(CO)_{12}(Me_2C_2)_3]$ (45mg, 0.040mmol) was taken up in 50 ml hexane and heated for 5 hours under reflux conditions. The reaction was monitored every 20 minutes by spot tlc and infrared spectroscopy. No apparent reaction occurred. All solvent was removed *in vacuo* and starting material was retrieved in 80% yield by tlc using a dichloromethane-hexane solution (2:3 v/v) as eluent.

2.11 Reaction of $[Ru_6C(CO)_{12}(Me_2C_2)_3]$ with 2 molar equivalents Me_3NO and Me_2C_2.

$[Ru_6C(CO)_{12}(Me_2C_2)_3]$ (75mg, 0.067mmol) was dissolved in 40ml dichloromethane and then cooled to -78°C. An excess of Me_2C_2 was added to the brown solution. Two molar equivalents of Me_3NO (10mg, 0.134mmol) in 5ml dichloromethane was introduced to the solution over 5 minutes. After a further 30 minutes of stirring to let the reaction reach room temperature solvent was removed *in vacuo*. Products were separated by tlc using a solution of dichloromethane-hexane (3:7 v/v) in the following order, $[Ru_6C(CO)_{12}(Me_2C_2)_3]$, **5** (22%) and $[Ru_6C(CO)_{10}(Me_2C_2)_4]$, **6** (15%).

Spectroscopic data for $[Ru_6C(CO)_{10}(Me_2C_2)_4]$: IR (CH_2Cl_2) ν(CO)/cm^{-1} 2077(m), 2034(vs), 2021(sh), 2013(sh), 1980(vw). Positive fast atom bombardment mass spectrum, M^+ obs. 1114 (calc. 1114).

2.12 Reaction of $[Ru_6C(CO)_{17}]$ with Me_2C_2 and 4 molar equivalents of Me_3NO.

$[Ru_6C(CO)_{17}]$ (130mg, 0.119mmol) was dissolved in 60 ml dichloromethane. The solution was cooled to -78°C and excess quantities of Me_2C_2 added. Over a period of 5 minutes Me_3NO (36mg, 0.475mmol) in 5ml dichloromethane was added dropwise to the solution. The reaction mixture was stirred for a further 30mins to reach room temperature, resulting in a colour change of red to dark brown. Products $[Ru_6C(CO)_{15}(Me_2C_2)]$, **2** (29%) and $[Ru_6C(CO)_{14}(Me_2C_2)]$, **3** (25%) were isolated by tlc using a solution of dichloromethane-hexane (1:4 v/v) as eluent.

2.12 Reaction of $[Ru_6C(CO)_{17}]$ with Me_2C_2 and 6 molar equivalents Me_3NO.

$[Ru_6C(CO)_{17}]$ (120mg, 110mmol) was dissolved in 60ml dichloromethane, then cooled to -78°C. Me_2C_2 was introduced to the solution followed by the dropwise addition of Me_3NO (50mg, 0.658mmol) in 10ml dichloromethane. Over a 30 minute period the solution darkened in colour and attained room temperature. An infrared spectrum confirmed complete consumption of starting material. Solvent was reduced in volume under reduced pressure. Products $[Ru_6C(CO)_{15}(Me_2C_2)]$, **2** (12%), $[Ru_6C(CO)_{14}(Me_2C_2)_2]$, **3** (15%) and $[Ru_6C(CO)_{12}(Me_2C_2)_3]$, **5** (28%) were isolated by tlc and a solution of dichloromethane-hexane (3:7, v/v) as eluent.

2.12 Reaction of $[Ru_6C(CO)_{17}]$ with 8 molar equivalents Me_3NO and Me_2C_2.

$[Ru_6C(CO)_{17}]$ (100mg, 0.091mmol) was dissolved in 60ml dichloromethane before being cooled to -78°C. An excess of but-2-yne was added to the solution followed by the dropwise addition of 8 molar equivalents Me_3NO (55mg, 0.731mmol) in 10ml dichloromethane. After 30 minutes stirring to reach room temperature the solution had darkened in colour. Solvent was reduced to a minimum volume under reduced pressure before separating products by tlc with a solution of dichloromethane-hexane (3:7, v/v). Components of the reaction were eluted in the order $[Ru_6C(CO)_{15}(Me_2C_2)]$, **2** (12%), $[Ru_6C(CO)_{14}(Me_2C_2)_2]$, **3** (11%), $[Ru_6C(CO)_{12}(Me_2C_2)_3]$, **5** (10%), $[Ru_6C(CO)_{10}(Me_2C_2)_4]$, **6** (9%).

2.14 Reaction of $[Ru_6C(CO)_{15}(Me_2C_2)]$ with 2 equivalents Me_3NO and Ph_2C_2.

$[Ru_6C(CO)_{15}(Me_2C_2)]$ (100mg, 0.092mol) was dissolved in 50ml dichloromethane and cooled to -78°C. Ph_2C_2 in excess was added to the solution followed by the dropwise addition of Me_3NO (0.014mg, 0.184mmol) in 5ml dichloromethane. The reaction mixture was stirred for a further 30 minutes to reach room temperature. Products $[Ru_6C(CO)_{15}(Me_2C_2)]$, **2** (15%), and $[Ru_6C(CO)_{14}(Me_2C_2)(Ph_2C_2)]$, **7** (33%), were isolated by tlc using a solution of dichloromethane-hexane (3:7, v/v) as eluent.

Spectroscopic data $[Ru_6C(CO)_{14}(Me_2C_2)(Ph_2C_2)]$. IR($CH_2Cl_2$) ν(CO)/cm^{-1}: 2082(s), 2042(vs), 2025(s), 2009(m), 1996(w). ^{1}H nmr ($CDCl_3$) δ/ppm 2.89 (s, 6H), 7.32 (m, 10H). Positive fast atom bombardment mass spectrum/amu, M$^+$ obs. 1242 (calc. 1242).

Crystallographic data $[Ru_6C(CO)_{14}(Me_2C_2)(Ph_2C_2)]$. Formula: $Ru_6C_{33}H_{16}O_{14}$, M_r: 1242.88, Crystal size/mm: 0.47x0.31x0.23, System: monoclinic, Space group: $P2_1/n$, a/Å: 17.494(2), b/Å: 12.336(2), c/Å: 17.479(2), α/° : 90, β/°: 98.73, γ/°: 90, U/Å^3: 3728.4(8), Z: 4, F(000): 2360, D_c/gmm^{-1}: 2.214, μ(Mo-Kα)/mm^{-1}: 2.434, σ range/°: 2.79-24.99, Measured reflections: 13267, Unique observed reflections: F>2σ(F) 13267, No. of refined parameters: 13209, R[F>2σ(F)]: 2.68%, $R_w[F^2]$:4.92%, S: 1.085, T/K: 253, Final difference synthesis max. and min./eÅ^{-3} 0.377 and -0.438.

2.15 Reaction of $[Ru_6C(CO)_{17}]$ with 2 equivalents of Me_3NO and MeC_2Et.

$[Ru_6C(CO)_{17}]$ (100mg, 0.091mmol) was dissolved in 60ml dichloromethane and then cooled to -78°C. MeC_2Et was introduced to the solution in excess amounts followed by the dropwise addition of Me_3NO (14mg, 0.183mmol) in 5ml dichloromethane. The reaction was stirred for a further 30 minutes to reach room temperature which was accompanied by the darkening of the solution in colour. $[Ru_6C(CO)_{15}(MeC_2Et)]$, **8** (41%) was isolated by tlc using a solution of dichloromethane-hexane (3:7 v/v) as eluent.

Spectroscopic data $[Ru_6C(CO)_{15}(MeC_2Et)]$. IR($CH_2Cl_2$) ν(CO)/cm^{-1}:2088(s), 2034(s,br), 2021(s,br), 1979(vw), 1961(vw). ^{1}H nmr ($CDCl_3$) δ/ppm 3.00(s, 3H), 3.1(q, 2H), 1.47(m, 3H). Positive fast atom bombardment mass spectrum/amu, M$^+$ 1106 (calc. 1106).

2.16 Reaction of $[Ru_6C(CO)_{15}(MeC_2Et)]$ with 2 equivalents Me_3NO and Me_2C_2.

$[Ru_6C(CO)_{15}(MeC_2Et)]$ (85mg, 0.077mmol) was taken up in 50ml dichloromethane and then cooled to -78°C. Me_2C_2, in excess, was added to the solution followed by the dropwise addition of Me_3NO (12mg, 0.154mmol) in 5ml dichloromethane. The solution was warmed to room temperature over a period of 30 minutes. $[Ru_6C(CO)_{15}(Me_2C_2Et)]$, **8** (22%) and $[Ru_6C(CO)_{14}(MeC_2Et)(Me_2C_2)]$, **9** (35%) and $[Ru_6C(CO)_{12}(MeC_2Et)(Me_2C_2)_2]$, **10**, (12%) were isolated by tlc using a dichloromethane-hexane (3:7 v/v) solution as eluent.

Spectroscopic data for $[Ru_6C(CO)_{14}(MeC_2Et)(Me_2C_2)]$: IR($CH_2Cl_2$) υ(CO)/$cm^{-1}$: 2082(s), 2046(s,sh), (2039(vs), 2022(vs), 2009(s, br), 1993(vw), 1977(vw). ^1H nmr ($CDCl_3$) δ/ppm 3.31(s, 3H), 3.28 (s,3H), 2.88 (s, 3H), 3.12(q, 2H), {3.21(q, 2H)}, 1.45(m, 3H). Positive fast atom bombardment mass spectrum/amu, M^+ 1132, (calc.1132).

Spectroscopic data for $[Ru_6C(CO)_{12}(MeC_2Et)(Me_2C_2)_2]$: IR($CH_2Cl_2$) ν(CO)/$cm^{-1}$: 2079(vw), 2062(vw), 2052(vw), 2023(vs), 1997(s), 1956(w, br). Positive fast atom bombardment mass spectrum/amu, M^+ obs. 1025 (calc. 1025).

2.17 Reaction of $[Ru_6C(CO)_{14}(MeC_2Et)(Me_2C_2)]$ with 2 equivalents of Me_3NO and Ph_2C_2.

$[Ru_6C(CO)_{14}(MeC_2Et)(Me_2C_2)]$ (75mg, 0.066mmol) was dissolved in 50ml dichloromethane and cooled to -78°C. Ph_2C_2 was introduced to the solution followed by the slow addition of Me_3NO (0.010mg, 0.133mmol) in 5ml dichloromethane. The solution was stirred for 30 minutes to allow the reaction to warm to room temperature, the solution darkened in colour. Products $[Ru_6C(CO)_{14}(MeC_2Et)(Me_2C_2)]$,**9**(20%) and $[Ru_6C(CO)_{12}(MeC_2Et)(Me_2C_2)(Ph_2C_2)]$, **10** (17%) was isolated by tlc with a mixture of dichloromethane-hexane (3:7v/v) as eluent.

Spectroscopic data $[Ru_6C(CO)_{12}(MeC_2Et)(Me_2C_2)(Ph_2C_2)]$. IR($CH_2Cl_2$) ν(CO)/$cm^{-1}$: 2064(w), 2038(sh), 2025(vs), 2001(m),1963(vw). ^1H nmr ($CDCl_3$) δ/ppm 7.1(m,5H), 7.2(m, 5H), 2.5-3.0 (m, 11H), 1.4(m, 3H). Positive fast atom bombardment mass spectrum/amu, M^+ 1254 (calc. 1254).

4.5. Experimental Details for Chapter Three.

3.2 Reaction of $[Ru_6C(CO)_{14}(C_6H_6)]$ with 2 equivalents of Me_3NO and Me_2C_2.

$[Ru_6C(CO)_{14}(C_6H_6)]$ (85mg,0.078mmol) was dissolved in 50ml dichloromethane and then cooled to -78°C. Me_2C_2 was added to the solution, followed by the dropwise addition of Me_3NO (12mg, 0.205mmol) in 5 ml dichloromethane. The solution was warmed to room temperature with continuous stirring over 30 minutes. Products $[Ru_6C(CO)_{12}(C_6H_6)(Me_2C_2)]$, **12**, (40%) and $[Ru_6C(CO)_{14}(C_6H_6)]$, **13** (15%) were isolated by tlc, eluent 70:30, hexane:dichloromethane.

Spectroscopic data $[Ru_6C(CO)_{12}(C_6H_6)(Me_2C_2)]$: IR($CH_2Cl_2$) ν(CO)/cm^{-1} 2057(m), 2019(s), 2011(s), 1996(s,br), 1958(w,br), 1938(vw). ^{1}H nmr δ/ppm (arene) 5.79(s,6H), (alkyne) 2.89(s,6H). Positive fast atom bombardment mass spectrum/amu, M$^+$ obs., 1086 (calc. 1086).

Crystallographic data $[Ru_6C(CO)_{12}(C_6H_6)(Me_2C_2)]$: formula: $Ru_6C_{23}H_{12}O_{12}$; M_r: 1086.75; T/K: 150.0(2); wavelength/Å:0.71073; crystal system: orthorhombic; space group: P212121; a/Å: 13.020(3); b/Å:13.647(2); c/Å:15.751(3); α/°:90; β/°: 90; γ/°: 90; U/Å^3: 2798.8(9); Z: 4; D_c/gcm^{-3}: 2.579; absorption coefficient: 2040; crystal size/mm: 0.30x0.25x0.20; θ range for data collection/°: 2.52 to 22.49; reflections collected: 3249; independent reflections: 2082[R(int) = 0.0177]; absorption correction: ψ scans; max. and min. transmission: 0.298 and 0.250; refinement method: full-matrix least-squares on F^2; data / restraints / parameters: 2074 / 0 / 372; goodness-of-fit on F^2; 1.096; final R indices [I > 2sigma(I)]: R1 = 0.0147, wR2 = 0.0330; R indices (all data); R1 = 0.0167, wR2 = 0.0364; absolute structure parameter: 0.18(5); larges diff. peak and hole/eÅ^{-3}: 0.267 and -0.299.

3.3 Reaction of $[Ru_6C(CO)_{14}(C_6H_5Me)]$ with 2 equivalents Me_3NO and Me_2C_2.

$[Ru_6C(CO)_{14}(C_6H_5Me)]$ (95mg,0.086mmol) was dissolved in 50ml dichloromethane. At -78°C Me_2C_2 in excess was added , followed by the dropwise addition of Me_3NO (13mg, 0.173mmol) in 5ml dichloromethane. The solution was stirred for a further 30 minutes and changed in colour from red to brown. Products

$[Ru_6C(CO)_{12}(C_6H_5Me)(Me_2C_2)]$, **15**, (43%) and $[Ru_6C(CO)_{14}(C_6H_5Me)]$, **14**, (22%) were isolated by tlc, using, as eluent, a dichloromethane-hexane solution (3:7, v/v). **Spectroscopic data $[Ru_6C(CO)_{12}(C_6H_5Me)(Me_2C_2)]$:** IR($CH_2Cl_2$) ν(CO)/$cm^{-1}$ 2056(m), 2018(s), 2010(s), 1996(s,br), 1956(m,br). ^1H nmr ($CDCl_3$) δ/ppm (arene) 5.82(d,2H), 5.70(m,3H), 2.35(s,3H), (alkyne)2.88(s,6H). Positive fast atom bombardment mass spectrum/amu, M^+ obs.,1102 (calc. 1102).

Crystallographic data $[Ru_6C(CO)_{12}(C_6H_5Me)(Me_2C_2)]$: This is not given as the structure was not completed due to poor crystallographic data.

3.4 Reaction of $[Ru_6C(CO)_{14}(C_6H_4Me_2)]$ with 2 equivalents Me_3NO and Me_2C_2.

$[Ru_6C(CO)_{14}(C_6H_4Me_2)]$ (85mg,0.076mmol) was dissolved in 50ml dichloromethane and cooled to -78°C. Me_2C_2 was introduced to the solution followed by the dropwise addition of Me_3NO (12mg, 0.152mmol) in 5ml dichloromethane over 5 minutes. The reaction mixture was stirred for a further 30 minutes to allow the reaction to warm to room temperature. Products $[Ru_6C(CO)_{12}(C_6H_4Me_2)(Me_2C_2)]$, **17** (32%) and $[Ru_6C(CO)_{14}(C_6H_4Me_2)]$, **16** (12%) were separated facilitating tlc type procedures with a solution of dichloromethane-hexane (3:7, v/v) acting as eluent. **Spectroscopic data $[Ru_6C(CO)_{12}(C_6H_4Me_2)(Me_2C_2)]$** IR($CH_2Cl_2$) ν(CO)$cm^{-1}$: 2056(s), 2017(vs), 2009(vs), 1996(s,br), 1988(sh), 1954(w), 1934(vw). ^1H nmr ($CDCl_3$) δ/ppm m, 2H), 5.72(d, 1H), 5.46(s,1H), 2.88(s, 6H), 2.40(s, 6H). Positive fast atom bombardment mass spectrum/amu$^+$ M^+obs. 1114 (calc. 1114).

Crystallographic data $[Ru_6C(CO)_{12}(C_6H_4Me_2)(Me_2C_2)]$: Formula: $Ru_6C_{25}H_{16}O_{12}$; M_r 1114.8; T/K: 150.0(2); wavelength/Å: 0.71073; crystal system:orthorhombic; space group: $Pna2_1$; a/Å:14.312(4); b/Å:14.368(4); c/Å:14.259(4); α/°:90; β/°:90; γ/°:90; U/$Å^3$:2932.1(14); Z:4; D_c/gcm^{-3}:2.522; absorption coefficient/ mm^{-1}: 3.073; F(000):2104; crystal size/mm 0.31x0.19x0.19; θ range for data collection/°:2.84-30.06; index ranges: -1<=h<=20, -1<=k<=20, -1<=l<=20; reflections collected:6187; independent reflections:4669 [R(int) = 0.0195]; absorption correction: semi-empirical ψ scans; max. and min. transmission: 0.290 and 0.251; refinement method: full-matrix least squares on F^2; data/restraints/parameters: 4668 / 1 / 392; goodness-of-fit on F^2: 1.090; final R indices[I > 2sigma(I)]: R1 = 0.0264, wR2 = 0.0480; R indices (all data): R1 = 0.0318, wR2 = 0.0511; absolute structure parameter: -0.06(4); largest diff. peak and hole/Åe-3: -0.735 and -0.707.

3.5 Reaction of $[Ru_6C(CO)_{14}(C_6H_3Me_3)]$ with two equivalents Me_3NO and Me_2C_2.

$[Ru_6C(CO)_{14}(C_6H_3Me_3)]$ (85mg, 0.075mmol) was dissolved in dichloromethane (50ml), the resulting red solution was cooled to -78°C. But-2-yne was added to the cold solution in excess quantities followed by the dropwise introduction of Me_3NO (11mg, 150mmol) in dichloromethane (5ml). After a further 30 minutes stirring the solution had attained room temperature and had darkened in colour. Solvent was removed under reduced pressure. The brown residues were separated by tlc using a solution of dichloromethane-hexane (3:7, v/v) as eluent. Products were eluted in the following order, $[Ru_6C(CO)_{12}(C_6H_3Me_3)(Me_2C_2)]$, **19**, 39% and $[Ru_6C(CO)_{14}(C_6H_3Me_3)]$, **18**, 14%.

Spectroscopic data $[Ru_6C(CO)_{12}(C_6H_3Me_3)(Me_2C_2)]$: IR($CH_2Cl_2$): ν(CO)/$cm^{-1}$ 2057(m), 2019(vs), 2011(vs), 1996(s), 1957(w), 1938(vw). ^1H nmr ($CDCl_3$): δ/ppm (arene) 5.71(s, 3H), 2.39(s, 9H), δ(alkyne) 2.86(s, 6H). Positive fast atom bombardment mass spectrum/amu, M^+ obs. 1128 (calc. 1128).

Crystallographicdata $[Ru_6C(CO)_{12}(C_6H_3Me_3)(Me_2C_2)]$: Formula: $Ru_6C_{26}H_{18}O_{12}$; M_r: 1128.8; crystal size/mm: 0.50x0.50x0.40; crystal system: monoclinic; space group;$P2_1/n$; a/Å: 9.981(3); b/Å: 18.419(5); c/Å:18.363(7); α/°: 90; β/°: 96.82(3); γ/°: 90; U/$Å^3$: 3352; Z: 4; F(000): 2136; D_c/gcm^{-1}: 2.236; μ(Mo-Kα)/cm^{-1}: 26.42; 2σ range/°: 24-26; measured reflections: [F>4σ(F)] 33712; No. of refined parameters 422; R: 2.83; Rw: 3.68; s: 0.849; T/K: 150.0(1).

3.8 Alternative Preparative Route for $[Ru_6C(CO)_{12}(C_6H_6)(Me_2C_2)]$.

$[Ru_6C(CO)_{15}(Me_2C_2)]$, **2** (75mg, 0.077 mmol) was taken up in 50ml dichloromethane and then cooled to -78°C. At this lowered temperature an excess of the ligand 1,3-cyclohexadiene (1ml) was introduced to the brown solution. Three molar equivalents of Me_3NO (15.5mg, 0.206mmol) in 5ml dichloromethane were subsequently added to the solution in a dropwise manner over a five minute duration.

Removal of the reaction vessel from the acetone/dry ice bath and a further 30 minutes of stirring allowed the solution to warm to room temperature and darken in colour. All volatiles were removed *in vacuo* to yield brown residues. Products were isolated by tlc using a solution of dichloromethane-hexane (3:7, v/v) as eluent. $[Ru_6C(CO)_{12}(Me_2C_2)(C_6H_6)]$, **13** was isolated in 28% yield and confirmed by its infrared spectrum.

3.10 Preparation of $[Ru_6C(CO)_{12}(C_{16}H_{16})(Me_2C_2)]$ from $[Ru_6C(CO)_{14}(C_{16}H_{16})]$.

A solution of $[Ru_6C(CO)_{14}(C_{16}H_{16})]$ (85mg, 0.70mmol) in 50ml dichloromethane was prepared and then cooled to -78°C. But-2-yne was added to the solution in excess amounts followed by the dropwise introduction of Me_3NO (10.5mg, 0.140mmol) in 5ml dichloromethane over a 5 minute period. Removal of the reaction from the ice bath and an additional 30 minutes stirring rendered the reaction complete. All volatiles were removed under reduced pressure to leave dark brown residues in the reaction vessel. Reaction products were isolated by tlc, facilitating a dichlorormethane-hexane (3:7, v/v) solution as eluent. Products were eluted in the following order, $[Ru_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$, **21**, 38%, $[Ru_6C(CO)_{12}(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)]$, **22**, 19% and $[Ru_6C(CO)_{12}(C_{16}H_{16})(Me_2C_2)]$ **23**, 13%. $[Ru_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ was a known compound and was identified from published data.

Spectroscopic data $[Ru_6C(CO)_{12}(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)]$, 22: IRν(CO)/cm^{-1}: 2068(m), 2056(w), 2029(sh), 2017(vs), 2003(sh), 1984(w, br), 1940(vbr). ^{1}H nmr ($CDCl_3$) δ7.43(s, 4H), 3.41(s, 4H), 3.30(m, 4H), 3.07(s, 6H), 2.79(m, 4H). Positive fast atom bombardment mass spectrum, M$^+$ obs.: 1220 (calc. 1216).

Crystallographic data $[Ru_6C(CO)_{12}(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)]$ (plus toluene as solvent of crystallization): Formula: $Ru_6C_{40}H_{30}O_{12}$; M_r: 1309.06; T/K: 150.0(2); wavelength/Å: 0.71073; crystal system: monoclinic; space group: $P2_1/n$; a/Å: 9.784(6); b/Å: 26.157(12); c/Å: 16.0165(5); α/°: 90; β/°: 97.66(4); γ/°: 90; U/Å^3: 4062(3); Z: 4; D_c/gcm^{-3}: 2.140; absorption coefficient/mm^{-1}: 2.236; F(000): 2520; crystal size/mm: 0.58x0.23x0.12; θ range for data collection/°: 2.57 to 22.52; index ranges: -10<=h<=10, 0<=k<=28, 0<=l<=17; reflections collected: 5316; independent reflections: 5304 [R(int) = 0.0665]; absorption correction: DIFABS; max. and min. transmission: 1.249 and 0.705; refinement method: full-matrix least-squares on F^2; data/ restaints/ parameters: 5197 / 0/ / 263; goodness-of-fit on F^2: 1.128; final R indices [I> 2 sigma(I)]: R1 = 0.1154, wR2 = 0.2441; R indices (all data): R1 = 0.2089, wR2 = 0.4073; largest diff. peak and hole/ eÅ^{-3}: 1.537 and -1.522.

Spectroscopic data $[Ru_6C(CO)_{12}(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})(\mu_3:\eta^1:\eta^2:\eta^1\text{-}Me_2C_2)]$, 23: IR ($CH_2Cl_2$) ν(CO)/cm-1:2050(m), 2013(ssh), 2008(vs), 1997(sh), 1982(w,br), 1952(vw). ^1H nmr ($CDCl_3$) δ/ppm 7.43 (s, 4H), 3.42 (s, 4H), 3.33(m, 4H), 3.08(s, 6H), 2.75(m, 4H). Positive fast atom bombardment mass spectrum/amu, M^+ obs. 1216 (calc. 1216).

4.6 References for Chapter Four.

1. C.R.Eady, P.F.Jackson, B.F.G.Johnson, J.Lewis, M.C.Malatesta, M.McPartlin, W.J.H.Nelson., *J. Chem. Soc.Dalton*, 1980, 383.

2. B.F.G.Johnson, J.Lewis, M.Martinelli, S.W.Sankey, K.Wong, M.McPartlin, W.J.H.Nelson., *J. Organomet. Chem.*, 1980, **191**, C3.