DALTON
PERSPECTIVE

Arene cluster compounds

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The synthesis, isolation and characterisation of a wide and diverse range of arene clusters based on nuclearities of three to eight metal atoms are described. Their use as models for the chemisorption of benzene on the macromolecular surface are considered and matters relevant to the chemistry on the surface such as bonding type, mobility and reactivity discussed. Certain of these compounds readily undergo photoisomerisation to produce benzyne derivatives by cleavage of two C–H arene bonds. This process may be tuned by varying the nature of the other ligands present. In the solid many of the arene clusters exhibit strong arene–arene interactions which are 'graphitic-like' leading to the formation of chains, ribbons and snakes. Use of bridging bifunctional arenes such as [2.2]paracyclophane and PhCH=CHCH=CHCH=CHPh leads to useful monomeric precursors to arene cluster polymers.

Our interest in this area was originally stimulated[1] by the chance discovery of the arenehexaruthenium derivatives $[\mathrm{Ru_6C(CO)_{14}(C_6H_{6-n}Me_n)}]$ ($n = 0$–3) and the subsequent synthesis of the bis(benzene) derivative $[\mathrm{Ru_6C(CO)_{11}}(\eta^6\text{-}\mathrm{C_6H_6})(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}\mathrm{C_6H_6})]$.[2] The observation that in this latter interesting compound the benzene molecules adopted not only the familiar η^6 terminal bonding mode found in *e.g.* $[\mathrm{Cr}(\eta^6\text{-}\mathrm{C_6H_6})_2]$, but also the then highly unusual μ_3 face-capping mode, led us to investigate the chemistry of arene clusters in more detail.

Over the recent past we have developed a systematic and diverse chemistry of these materials, not only based on $\mathrm{Ru_6C}$ units, but also for a variety of clusters containing from three to eight metal atoms. For us, basically *four* patterns of interest have emerged, *viz.*, (*i*) the cluster–surface analogy, (*ii*) the photochemistry of arene clusters and C–H bond-cleavage reactions, (*iii*) graphitic-like interactions in the solid state leading to chains, snakes and ribbons and (*iv*) the generation of monomer and dimer precursors to conducting polymers. These themes are not independent; they rely heavily on one another. Nevertheless, each provides an excellent research area in its own right and undoubtedly other related areas of interest will emerge.

The Cluster–Surface Analogy

The idea behind these investigations emerged naturally from our studies of $[\mathrm{Ru_6C(CO)_{11}}(\eta^6\text{-}\mathrm{C_6H_6})(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}\mathrm{C_6H_6})]$. Our discovery of this compound corresponded with reports by Somerjai[3] and others of the interaction of benzene with the Rh(111) surface both in the presence of differing amounts of CO and in its absence. It seemed apparent to us that a clear relationship existed between our benzene–carbonyl cluster and the benzene–carbonyl–surface interaction (Fig. 1). The feeling that our systems, which were so easily studied by the usual vibrational (IR and Raman) spectroscopic techniques, NMR spectroscopy and diffraction methods (X-ray and neutron), might enable a clearer understanding of the surface chemistry led us to contemplate the synthesis of simple model compounds. In the limiting case, the single-crystal metallic surface may be regarded as being composed of approximately close-packed planar arrays of spheres extending infinitely in two dimensions. A consequence of this long-range periodicity is that the local atomic and electronic structure will be influenced by more distant atoms in both the surface and the bulk of the metal. Hence, adsorption of CO at one site will influence the characteristics of sites adjacent to (or even removed from) it. Recent advances in the dynamic theory of low-energy electron diffraction (LEED) by ordered absorbate overlayers has led to the structural characterisations of several metal surface–

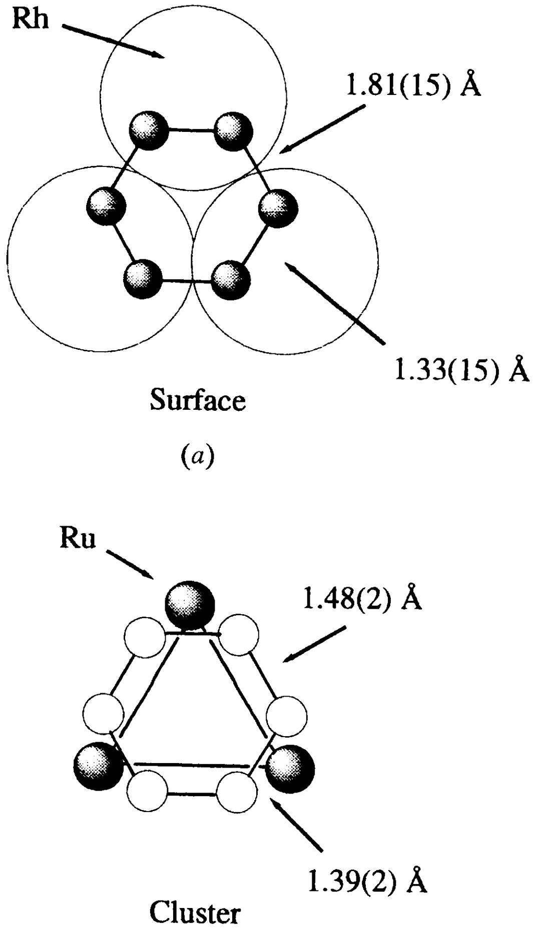


Fig. 1 Comparison of the bonding geometries for benzene on (*a*) the Rh(111) metal surface and (*b*) the hexaruthenium cluster, $[\mathrm{Ru_6C(CO)_{11}}(\eta^6\text{-}\mathrm{C_6H_6})(\mu_3\text{-}\mathrm{C_6H_6})]$

benzene complexes by Somerjai, van Hove and co-workers.[3] There are at least five possible sites that chemisorbed benzene may adopt on a close-packed atomically flat metal surface (Fig. 2). These are the 'on-top' site which has six-fold symmetry, the 'hollow' site with three-fold local symmetry and the 'bridge' site with two-fold symmetry. In each overlayer benzene is chemisorbed intact and lies parallel to the close-packed metal surface. Adsorption at a three-fold hexagonal close-packed (h.c.p.)-type site is clearly related to the μ_3 bonding mode adopted in $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$. In both cases the C_6 ring is expanded showing in-plane Kekulé distortions: C–C bond distances alternate between 1.31(15) and 1.83(15) Å, the short bonds lying above single atoms while the long C–C bonds form bridges linking pairs of metal atoms. Two-fold bridge-site occupancy has been substantiated on a Pt(111) structure with a distortion in molecular symmetry to C_{2v}. For us, the challenge to produce model cluster systems which correspond to these observations was raised.

The metal skeletons of high-nuclearity carbonyl cluster compounds are frequently structurally comparable to fragments of the bulk metallic lattice, *e.g.* $[Rh_{13}(CO)_{24}H_3]^{2-}$, $[Os_{10}C(CO)_{24}]^{2-}$ and $[Rh_{14}(CO)_{25}]^{4-}$ may be recognised as fragments of h.c.p., cubic close packed (c.c.p.) and body-centred cubic (b.c.c.) structures respectively.[4] The series of osmium clusters based on four, ten, twenty and thirty-five metal atoms, $[Os_4H_4(CO)_{12}]$, $[Os_{10}C(CO)_{24}]^{2-}$, $[Os_{20}(CO)_{40}]^{2-}$ and $[Os_{35}(CO)_{56}]^{2-}$, follow the c.c.p. growth sequence precisely. Significantly, in the dianion $[Os_{20}(CO)_{40}]^{2-}$, each face of the cluster corresponds directly to the metal(111) surface. Smaller carbonyl clusters are typically deltahedra and many of their metal-core configurations may be regarded as microscopic fragments of common close-packed lattices. However, the role of the ligand sphere in stabilising these bulk-like geometries should be appreciated, as should the case in which they undergo geometrical transformation as the overall electron count is modified, *e.g.* monocapped trigonal bipyramid in $[Os_6(CO)_{18}]$ (84e) to octahedral in $[Os_6(CO)_{18}]^{2-}$ (86e).

Structural comparisons between the chemisorbed state and metal clusters are best made when there is a correspondence in the metal, ligands, ligand coverage of the cluster or surface and in the crystallography. Detailed structural analysis of the gas–metal interface is currently only feasible for metal crystals having well defined flat surfaces. For chemisorption on these low-Miller-index surface planes the metal–ligand and –metal connectivity is respectively smaller and larger than for clusters, although on higher planes the metal co-ordination number decreases at irregular features such as step and kink sites.

Thus, our challenges as molecular chemists may be described as: (*a*) the production of systems containing arenes in bonding modes related to those supposed to exist on the surface; (*b*) the investigation of the change in electronic character and bonding mode of the arene as the number and type of metal atoms changes; (*c*) the monitoring of related changes in bonding as a function of ligand type and (*d*) the exploration of the migratory patterns that exist on the cluster surface and their relationship to motion in the bulk. In this paper some of our efforts made in response to these challenges are reported.

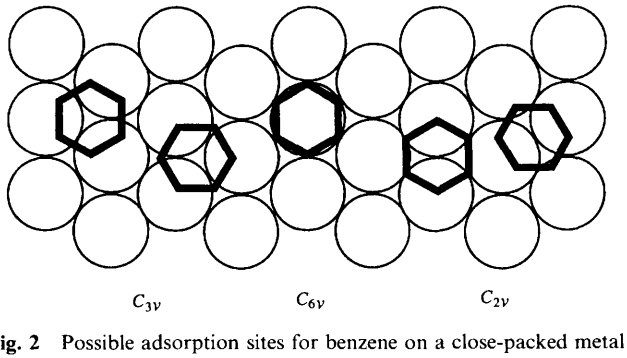


Fig. 2 Possible adsorption sites for benzene on a close-packed metal surface

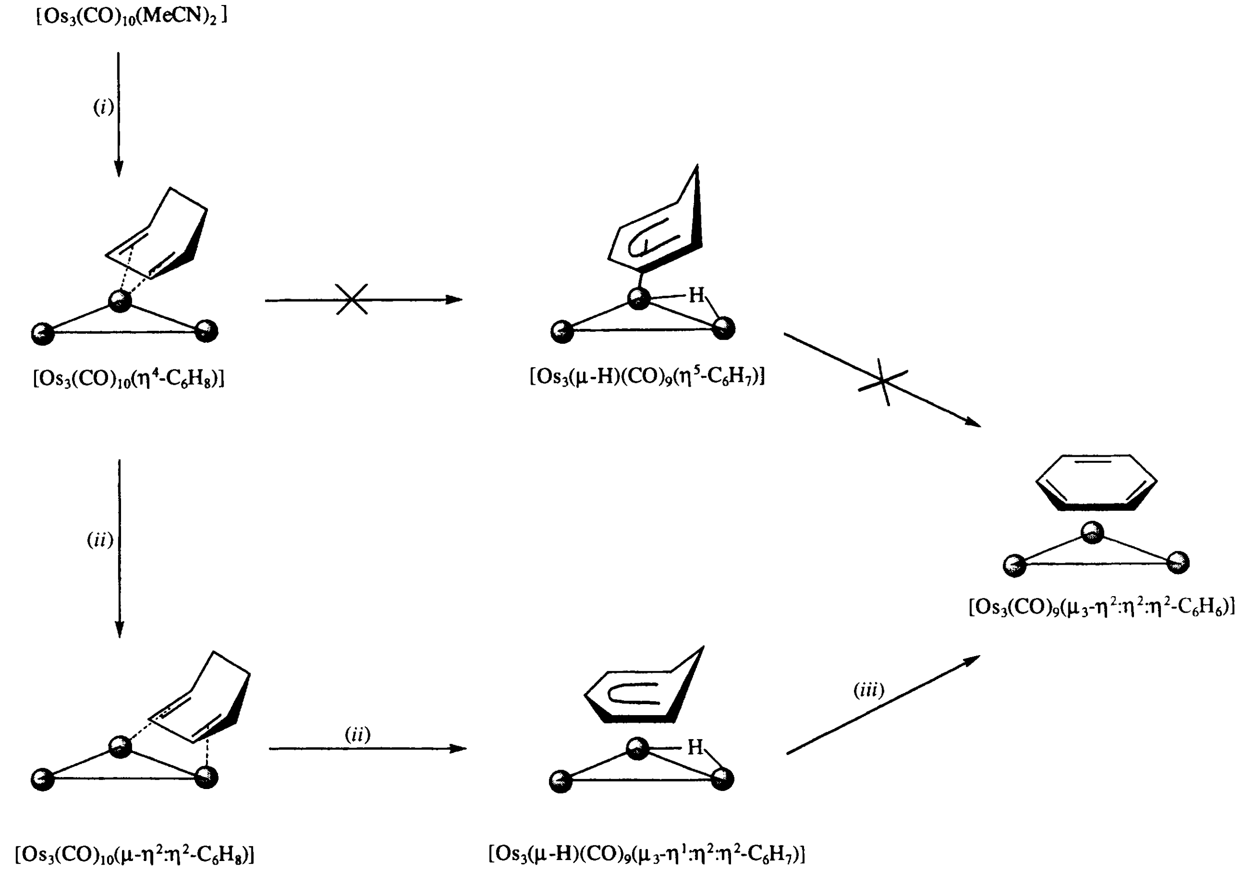
The model compounds $[M_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (M = Ru or Os)]

The simplest model of the [111] surface is the metal triangulo-arrangement found in the simplest clusters $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$. In this work we took advantage of this fact and explored routes to benzene–carbonyl models. We were lucky that our first attempted syntheses proceeded moderately easily and in favourable yields. The best routes to the ruthenium and osmium compounds $[M_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ are, however, different. For ruthenium, treatment of $[Ru_3(CO)_{12}]$ in dichloromethane with Me_3NO in the presence of an excess of cyclohexa-1,3-diene leads to the required product in a single-stage process.[5] The corresponding osmium derivative may be prepared in a related fashion (Scheme 1), but is best obtained from the very reactive unsaturated cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ (Scheme 2).[2] The molecular structures of the two compounds are, as expected, very similar.[2,6] In each case the central metal triangle supports the μ_3-bonded benzene and nine CO ligands. Owing to the greater precision of the ruthenium structure, the C–H vectors are seen to bend away from the C_6 plane and Ru_3 unit, in agreement with the Somerjai model. In addition, in both cases, the C_6 ring shows the expected Kekulé distortion. Clearly these compounds are good model systems. Detailed vibrational analysis of both these cluster and surface-adsorbed systems is currently under investigation.

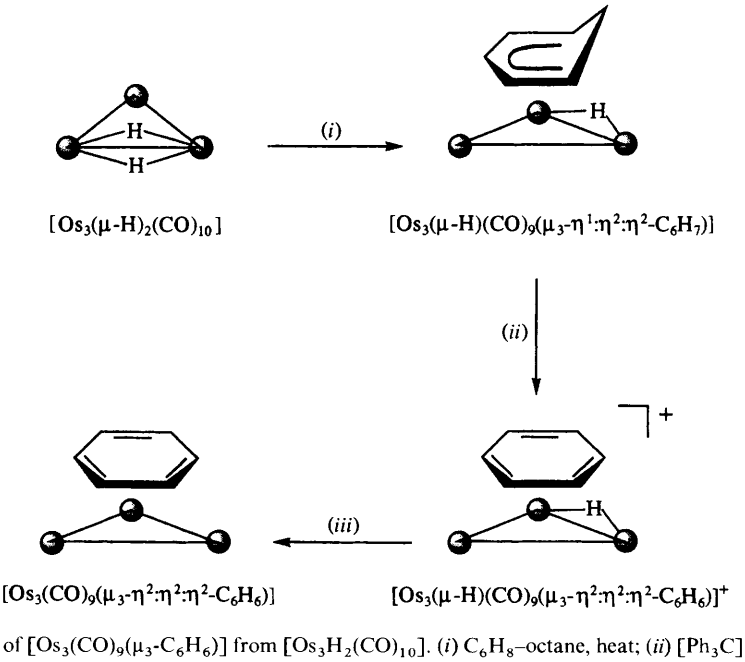
Many other 'model' systems have now been prepared and detailed synthetic routes to clusters based on M_4, M_5, M_6, M_7 and M_8 units have been devised. The Ru_6C system provides a good example of the synthetic routes employed and also the versatility of the benzene ligand, which may bond to produce a variety of geometric forms (Scheme 3).[7] One of our primary objectives in this aspect of the work has been to increase the number of benzene or related molecules supported by the cluster unit, leading ultimately to a system containing only benzene on the surface.

In our synthetic programme essentially the same approach has been employed for all systems under investigation. The initial cluster is activated by oxidative removal of CO as CO_2 by reaction with Me_3NO, followed by addition of cyclohexa-1,3-diene which usually bonds first through a single double bond and then through the 1,3-diene unit. By this means complexes containing six-membered rings bonded to central cluster units have been isolated and characterised.

The bonding mode adopted by the cyclohexadiene unit in these systems is *not* always the same.[5] For the Os_3 system we have good evidence to suggest that two forms of the compound $[Os_3(CO)_{10}(C_6H_8)]$ exist (Scheme 1). One, for which the molecular structure has been established by single-crystal X-ray analysis, with the diene bonded to *one* osmium atom. This compound is reluctant to undergo conversion either to the dienyl derivative by single C–H bond cleavage, or to the benzene derivative *via* the cleavage of two C–H bonds. In contrast, the second isomer, which we suppose contains the diene bridge bonding to *two* osmium atoms, readily undergoes conversion directly into $[Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$. This observation is significant, indicating that C–H bond cleavage, leading to a face-bridging arene, is assisted by multiple interactions with the cluster surface in this case. However, this cannot be the whole story, since in our studies of the Os_4 systems (Scheme 4) we have been able to isolate and characterise the complete range of intermediate compounds leading to the final benzene derivative.[8] It is important to note, however, that here the hexadiene molecule bonds to only *one* osmium atom and benzene apparently adopts only the η^6 terminal bonding mode. Similar behaviour is noted with the Co_4 systems where again only the η^6 mode for benzene is



Scheme 1 Synthesis of $[Os_3(CO)_9(\mu_3-C_6H_6)]$ from $[Os_3(CO)_{12}]$. (*i*) $C_6H_8-CH_2Cl_2$; (*ii*) octane, heat; (*iii*) $[Ph_3C][BF_4]$ followed by 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu)

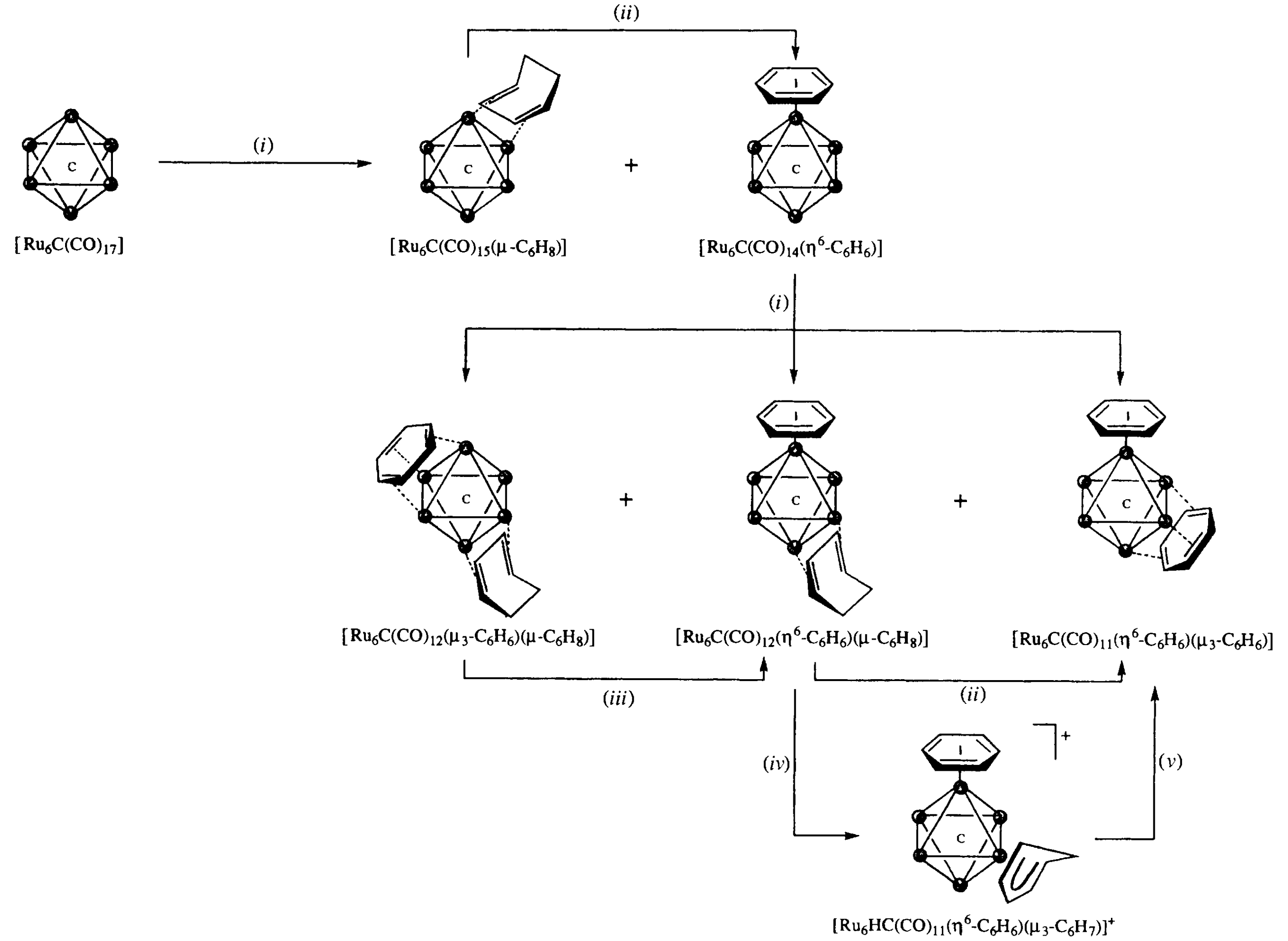


Scheme 2 Alternative synthesis of $[Os_3(CO)_9(\mu_3-C_6H_6)]$ from $[Os_3H_2(CO)_{10}]$. (*i*) C_6H_8–octane, heat; (*ii*) $[Ph_3C][BF_4]$; (*iii*) dbu

observed.[9] A feature of these Co_4 and Os_4 tetrahedral systems is the relative ease with which the terminally bonded arene undergoes exchange with an unco-ordinated arene. For both systems this exchange provides a highly convenient method of producing different arene cluster derivatives. However, this behaviour is not general and systems based on the Ru_6C unit are reluctant to undergo exchange.

In most other systems (*e.g.* Scheme 3) the diene is found to bridge one edge of the cluster polyhedron and on treatment of these complexes with Me_3NO, or on pyrolysis, smooth conversion into the appropriate benzene derivative is observed.[7]

For the Ru_6C series of compounds, benzene (and other arenes) adopt both μ_3 and μ bonding configurations.[2] With $[Ru_6C(CO)_{14}(arene)]$, apart from the derivative derived from [2.2]paracyclophane (see below), all arenes adopt the terminal



Scheme 3 Synthesis of benzene derivatives of $[Ru_6C(CO)_{17}]$. (*i*) $Me_3NO–C_6H_8$; (*ii*) Me_3NO; (*iii*) hexane, heat; (*iv*) $[Ph_3C][BF_4]$; (*v*) dbu

bonding mode and no evidence for face bridging has been found.[10] This is not the case for the bis(benzene) derivative, $[Ru_6C(CO)_{11}(C_6H_6)_2]$, which may be easily prepared from $[Ru_6C(CO)_{17}]$ using $Me_3NO–1,3\text{-}C_6H_8$ in a sequential manner. Here several different isomeric forms have been isolated. Significantly, these forms undergo exchange[11] but the barriers to isomer interconversion are relatively high. The mechanism by which isomerisation occurs has not been established, but we consider that the most likely route involves an intermediate in which the C_6 ring spans a polyhedral edge and is co-ordinated through two 'allyl' fragments within it. Although direct examples for this mode have not been found for the simple benzene derivatives, a compound containing benzene bound in this manner has been observed by others in $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}\eta^3:\eta^3\text{-}C_6H_6)]$[12] and we have fully characterised a related cyclophane derivative, $[Ru_2(CO)_6(\mu\text{-}\eta^3:\eta^3\text{-}C_{16}H_{16})]$ (Fig. 3).[13]

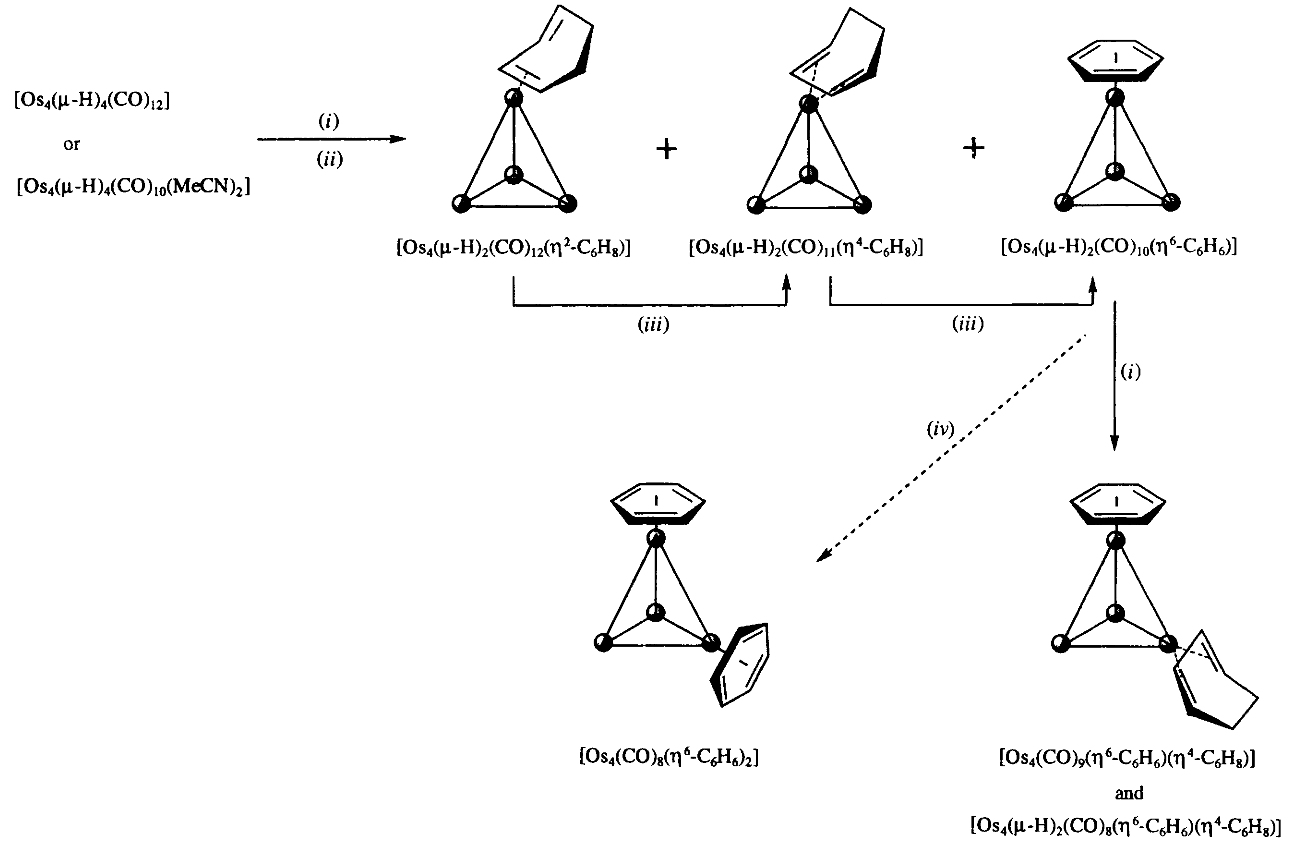
In general, the benzene compounds described so far cannot be prepared directly from the reaction of benzene with the appropriate cluster. The Co_4 system provides a rare example, where direct reaction does occur with either $[Co_2(CO)_8]$ or $[Co_4(CO)_{12}]$ to produce $[Co_4(CO)_9(C_6H_6)]$.[9] Interestingly, we have noted that in the reaction of $[Ru_3(CO)_{12}]$ with $Me_3NO–1,3\text{-}C_6H_8$ the presence of benzene greatly enhances the rate, although we have not established its role.[5] Benzyne, rather than benzene, derivatives of Os_3, *e.g.* $[Os_3(\mu\text{-}H)_2(CO)_9(C_6H_4)]$, are formed directly on reaction of the activated cluster $[Os_3(CO)_{10}(MeCN)_2]$ with C_6H_6; no evidence has been found that $[Os_3(CO)_9(C_6H_6)]$ is an intermediate in this reaction, but we have discovered that on irradiation or prolonged heating $[Os_3(CO)_9(C_6H_6)]$ is converted into the same benzyne derivative (see below).[14]

Electronic character and change in bonding mode of arene

A number of interesting features have emerged but we remain a long way from truly understanding the factors which govern the bonding mode adopted by arenes on the cluster surface. Apart from $[Ru_2(CO)_6(\mu\text{-}\eta^3:\eta^3\text{-}C_{16}H_{16})]$ we have no direct evidence for the bis(allyl) bonding mode (Fig. 3) although there is limited evidence to suggest the formation of unstable edge-bridged intermediates in the μ_3 to η^6 conversion process.[15]

The η^6 terminal bonding mode is commonly observed for all cluster nuclearities and seems to be independent of the metal–metal connectivities within the clusters, involving a connectivity (M–M) of two in $[M_3(CO)_7(R_2C_2)(C_6H_6)]$,[16] three in $[Os_4H_2(CO)_{10}(C_6H_6)]$,[8] $[Co_4(CO)_9(C_6H_6)]$[9] and $[Ru_5C(CO)_{12}(C_6H_6)]$[16] (basal isomer **1**) and four in $[Ru_5C(CO)_{12}(C_6H_6)]$[17] (apical isomer **2**) and $[Ru_6C(CO)_{14}(C_6H_6)]$.[7] Migration of the arene over the cluster surface to produce different isomeric forms may be induced chemically[16] or thermally.[17,18] At present there appears to be no correlation between the number of carbonyl groups also present and the arene bonding type. For systems containing more than one arene moiety, as in $[Ru_6C(CO)_{12}(C_6H_6)_2]$, we detect a slight tendency for face bonding to be preferred, but this may be more apparent than real!

One exciting observation which has arisen from our work is that the CH chemical shift in the ^1H NMR spectra of the range of η^6-bonded benzene derivatives $[Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)]$ (δ 5.93), $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)]$ (δ 5.56) and $[Ru_8H_4(CO)_{18}(\eta^6\text{-}C_6H_6)]$ (δ 5.40) undergoes a systematic variation as a function of the number of metals in the cluster unit.[19] Although great care should always be exercised in any correlation of this type, it is reasonable to assume that the shift



Scheme 4 Synthesis of some benzene derivatives of $[Os_4H_4(CO)_{12}]$. (*i*) 3.2 equivalents Me_3NO–CH_2Cl_2–1,3-C_6H_8; (*ii*) CH_2Cl_2–1,3-C_6H_8; (*iii*) heat, hexane; (*iv*) 3.2 equivalents Me_3NO–CH_2Cl_2–C_6H_6

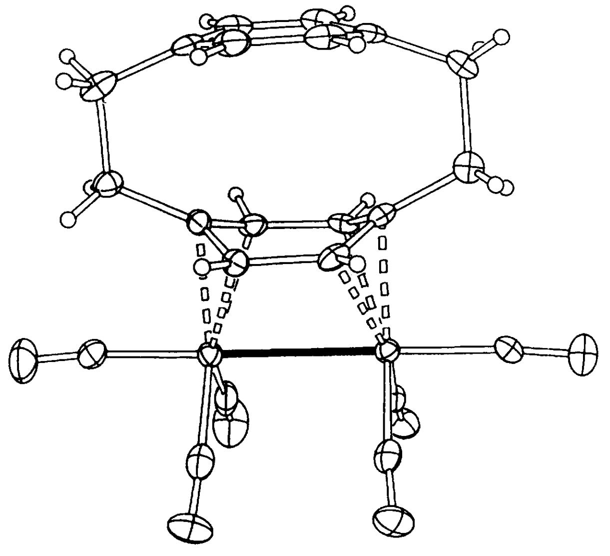


Fig. 3 Molecular structure of $[Ru_2(CO)_6(\mu\text{-}\eta^3:\eta^3\text{-}C_{16}H_{16})]$

reflects the change in electron density available for bonding on the cluster surface and, in any event, appears to be a more sensitive probe than *e.g.* the CO stretching vibration in carbonyl clusters.

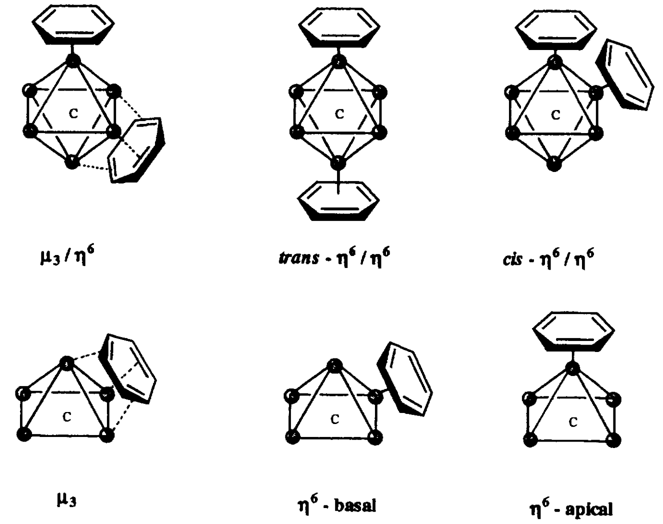
A similar variation is noted for the ^1H resonances of the two rings in face-capping [2.2]paracyclophane derivatives (see below).[20] In this case the degeneracy of the two rings is removed on co-ordination and the chemical shift observed at δ 6.51 for the parent ligand is seen to separate. As the number of metals increases from three to six the separation also increases; for $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ the values are δ 3.76 and 7.22 (Δ = 3.46) and for $[Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ the values are δ 3.43 and 7.44 (Δ = 4.01). In this case the bonding between the co-ordinated ring and the cluster affects its p_π interactions with the other ring. This is a particularly sensitive probe of the cluster surface and it would be interesting to examine the interactions of cyclophane with the bulk surface.

Bonding as a function of ligand type

Our investigations in this area have been limited to date. Undoubtedly the presence of CO on the cluster surface affects the nature and type of bonding mode adopted by the arene. In one key experiment we have observed that reaction of the triangulo-clusters $[M_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (M = Ru or Os) with alkynes R_2C_2 leads to the displacement of the benzene to a terminally bonded mode and the concomitant bond formation of the alkyne in the familiar 2σ, π mode across the triangular face to form the complex $[M_3(CO)_7(R_2C_2)(\eta^6\text{-}C_6H_6)]$.[16] For the series of compounds $[Os_3(CO)_8L(\eta^6\text{-}C_6H_6)]$ (L = C_2H_4, PR_3, *etc.*) the barrier to rotation of the C_6H_6 moiety is found to vary but not by very much.[21] At present we are studying the variation in the ^1H chemical shift for a series of compounds in which a CO ligand is replaced by a series of phosphine ligands with differing basicities.

Migratory patterns of the arene ligand over the cluster surface

As we have commented previously, a range of different isomeric forms have been observed for the series of bis-substituted compounds $[Ru_6C(CO)_{11}(C_6H_6)_2]$[7] (Scheme 5) and the monosubstituted system $[Ru_5C(CO)_{12}(C_6H_6)]$.[17] In each case almost every possible isomeric form is observed (except the bis-μ_3 form!) for $[Ru_6C(CO)_{11}(C_6H_6)_2]$. Interconversion is readily monitored spectroscopically but at no stage have stable forms been observed in which the arene straddles the edge. Nevertheless, we believe this to be the most likely intermediate (see above).



Scheme 5

Photochemistry of Arene Clusters and C–H Cleavage Reactions

We have observed that on irradiation of solutions of $[Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ in toluene the benzyne derivative $[Os_3H_2(CO)_9(\mu_3\text{-}\eta^2:\eta^1:\eta^1\text{-}C_6H_4)]$ is produced. Interest in this reaction centres around the activation of the two adjacent ring C–H bonds. Although the mechanism by which the photochemical reaction occurs has not been fully established, the accepted view is that Os–Os bond cleavage ($\sigma \longrightarrow \sigma^*$) occurs as the initial step. Although related work has not been carried out for other triosmium arene compounds containing C_6H_5Me, $C_6H_4Me_2$-1,3, $C_6H_3Me_3$-1,3,5, *etc.*, we have established that the direct reaction of a wide range of arenes with $[Os_3(CO)_{10}(MeCN)_2]$ generates the appropriate benzyne derivatives.[22] No evidence for the intermediate formation of μ_3-arene intermediate compounds has been found and it is probable that the reaction takes place in these instances *via* a μ-bonded intermediate. Evidence for a reaction of this kind has been found in our related studies of the reaction of cyclohexene with $[Os_4H_4(CO)_{12}]$ or $[Os_4H_4(CO)_{10}(MeCN)_2]$. Here, totally unexpectedly, cleavage of one of the 'olefin' C–H bonds to generate the cyclohexenyl derivative $[Os_4H_3(CO)_9(C_6H_9)]$, which undergoes a second C–H bond cleavage on heating to form the 'yne' derivative $[Os_4H_2(CO)_9(C_6H_8)]$, in which the C_6H_8 moiety spans the tetrahedral Os_4 face. Related studies of the corresponding ruthenium systems have led to the isolation of a series of yne-like complexes based on the $[Ru_4(CO)_{12}(C_6H_8)]$ unit but, in this case, presumably because of the weaker Ru–Ru bonds, the yne unit straddles a butterfly Ru_4 arrangement.[23] Again, olefinic C–H bond cleavage has occurred in preference to methylene CH_2 bond cleavage.

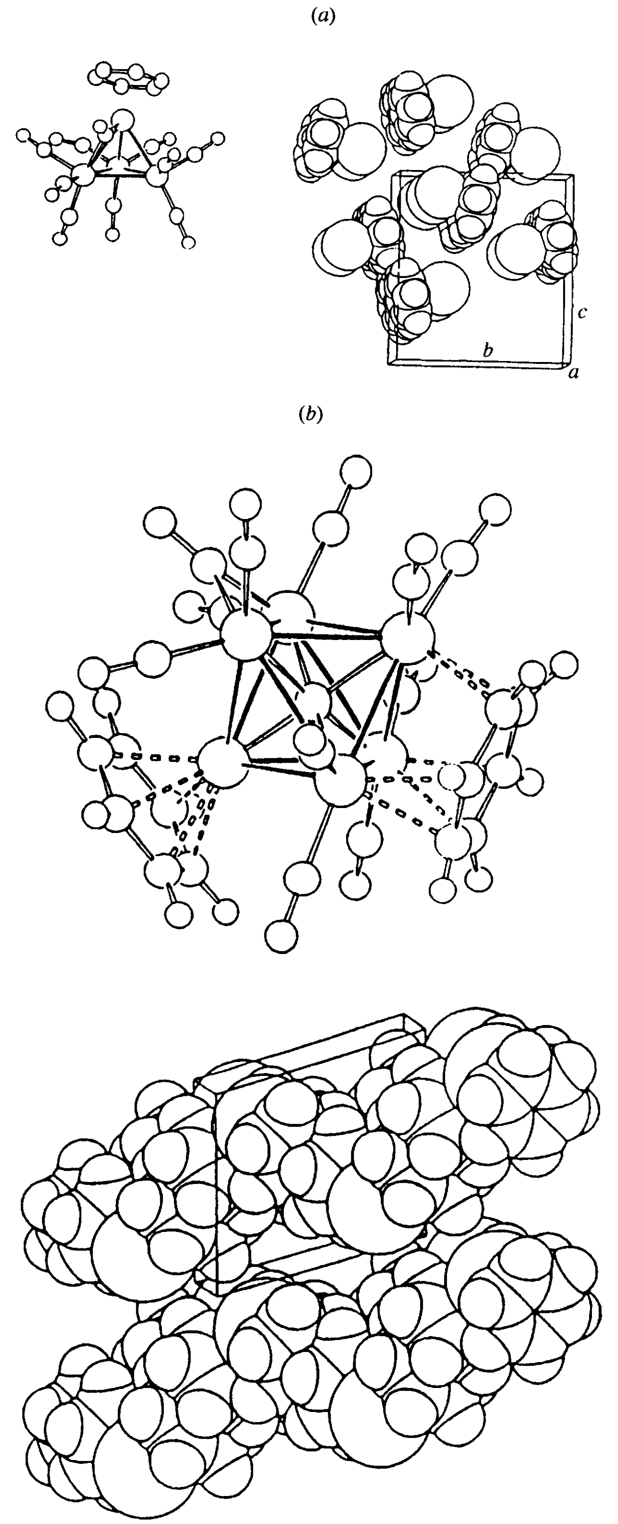


Fig. 4 Schematic representations of the molecular organisation in crystalline (*a*) $[Os_4H_2(CO)_{10}(\eta^6\text{-}C_6H_6)]$ and (*b*) $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}C_6H_6)]$

Graphitic-like Interactions in the Solid State

Many of the compounds reported in this article have been the subject of detailed analysis by X-ray diffraction studies on single crystals. Several points of interest emerge. For several of the monosubstituted derivatives, based on Os_4 and Ru_6C units with simple arenes, the organic rings are observed to interlock to produce layers of organic substrate and layers of the cluster units [Fig. 4(*a*) and (*b*)].[24] In the bis-substituted derivatives of Ru_6C the various different isomeric forms give rise to different crystallographic packing arrangements. Thus, in *trans*-$[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)_2]$ and *trans*-$[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)_2]$ the rings from adjacent molecules in the crystal are superimposed *albeit* with some displacement and the inter-ring distances are compatible with those observed in graphite. In these examples, interaction between the rings occurs throughout the solid, leading to molecular 'chains'. In the related system *cis*-$[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)_2]$ the interactions are similar but because of the distribution of the arenes about the Ru_6C cluster unit the 'graphitic-like' interactions lead to molecular 'snakes' throughout the solid. For the system $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}C_6H_6)]$ the η^6 rings on adjacent molecules in the solid interact in a graphitic-like manner as do the adjacent μ_3-ring systems. This also leads to molecular 'snakes' [Fig. 4(*b*)]. These interactions are of fundamental importance, particularly since they provide a mechanism or route by which charge

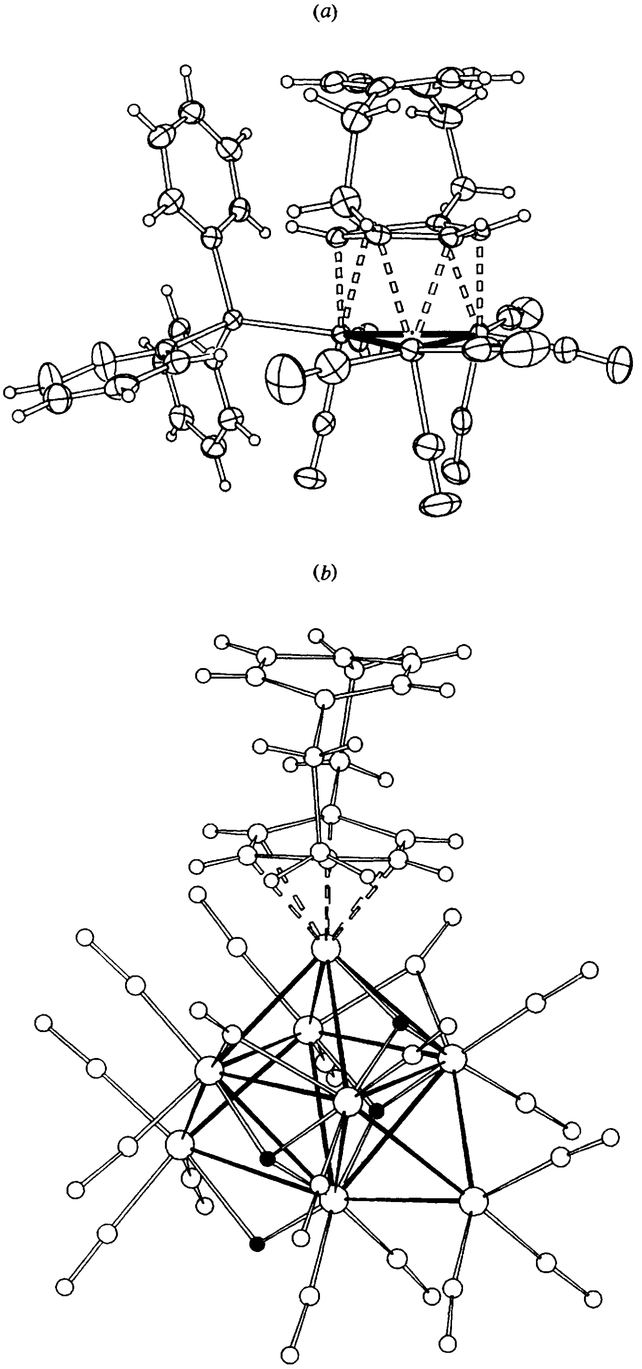


Fig. 5 Molecular structures of (*a*) $[Ru_3(CO)_8(PPh_3)(\mu_3\text{-}C_{16}H_{16})]$ and (*b*) $[Ru_8H_4(CO)_{18}(\eta^6\text{-}C_{16}H_{16})]$

transfer may occur throughout the lattice in well designated pathways. Very recently, using ultraviolet laser desorption mass spectrometry, we have recorded direct evidence for such aggregated species in the gas phase directly from neutral benzene molecular clusters. In an effort to extend the studies of this phenomenon we are currently investigating the formation of arene clusters containing much larger polycyclic systems. It is our intention to produce organometallic cluster materials in which ring–ring interactions are maximised. To date we have prepared $[Ru_3(CO)_9(C_{12}H_{10})]$ which shows the desired effect.[25]

Monomer and Dimer Precursors to Conducting Polymers

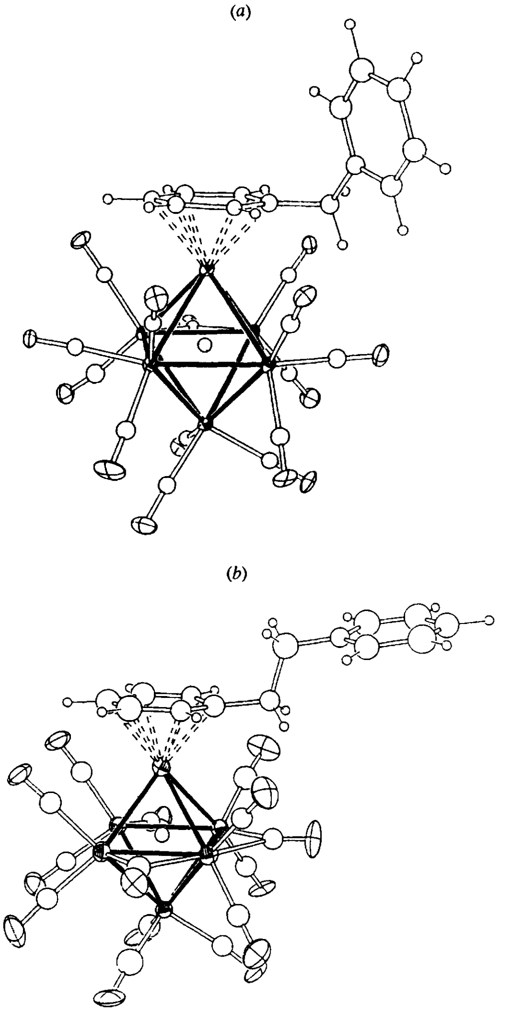


Fig. 6 Molecular structures of $[Ru_6C(CO)_{14}\{\eta^6\text{-}Ph(CH_2)_nPh\}]$ $[n = 1\ (a)\ \text{or}\ 2\ (b)]$

Following on from these studies (see above) we have synthesised a whole range of [2.2]paracyclophane cluster derivatives.[20] At the onset of these studies it was our intention to produce monomers with one cyclophane bonded to the central unit and then dimers in which the cyclophane moiety is bonded simultaneously to two separate cluster units and thereby serving as a bridge allowing each separate cluster unit to exchange electron density. Ultimately, our goal is to generate polymeric chains of such materials which hopefully will serve as conductors or semiconductors. We are also interested in producing clusters containing two cyclophane units which pack in chains, snakes or ribbons as with the simpler arenes, but through which charge transfer may be mediated. Examples of two [2.2]paracyclophane clusters which have been prepared and characterised are shown in Fig. 5. Several general features appear. First, the cyclophane ligand shows a marked tendency to function as a face cap rather than as an η^6 terminal group. However, this is not always the case and our attempts to prepare $[Ru_6C(CO)_{11}(C_{16}H_{16})_2]$, the first cluster with two face-capping rings, have resulted in the η^6, μ_3 complex. Secondly, as commented above, the ^1H NMR spectrum of the co-ordinated $C_{16}H_{16}$ ligand shows highly significant ^1H chemical shift values which appear to be sensitive to the number of metal atoms within the cluster. Finally, we have observed that in the compound $[Ru_6C(CO)_{12}(\mu_3\text{-}C_{16}H_{16})(\mu\text{-}C_6H_8)]$ it is the C atoms of the co-ordinated ring that sit directly above the metal atoms of the triangular face and not, as in all other cases, the C=C bond. Significantly, major changes in the configuration of the cyclophane rings are also observed.

In related studies we have prepared derivatives of linked arene systems such as $Ph(CH_2)_nPh$ (n = 0–2)[26] and PhCH=CH-

CH=CHCH=CHCH=CHPh.[27] Again, our objective is simply to produce cluster systems linked by an organo bridge and ultimately to produce organometallic cluster materials. The molecular structures of the series of compounds [$Ru_6C(CO)_{14}\{Ph(CH_2)_nPh\}$] have been established and a couple are shown in Fig. 6.

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