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FEATURE ARTICLE

Linked arene clusters

Brian F. G. Johnson,* Caroline M. Martin and Paul Schooler

University Chemical Laboratory, Lensfield Road, Cambridge, UK CB2 1EW

The synthesis, isolation and characterisation of a number of $[2_n]$cyclophane transition metal clusters with nuclearities ranging from four to twelve atoms is described. The primary objective of this work has been to prepare molecules composed of alternating cyclophane and cluster subunits which may be considered as precursors to novel organometallic polymer chains and networks. This aim has been achieved to a certain degree using the [2.2.2]paracyclophane ligand, which has been shown to interact with metal clusters (*e.g.* tetracobalt nonacarbonyl) *via* all three of its aromatic rings. Also, the dimerisation of a hexaruthenium-[2.2.2]paracyclophane complex has yielded a remarkable dodecanuclear bis-arene cluster which may form the basis for a novel linear polymeric chain containing only metal atoms in the backbone. We have also been able to demonstrate that the coordinated [2.2.2]paracyclophane unit is able to embrace metal ions such as Ga^I and Ag^I giving rise to a concomitant change in the observed IR spectrum of the attached cluster. This perspective highlights these areas of research and also examines the factors controlling coordination mode preferences of the $[2_n]$cyclophane ligand and the central cluster nuclearity and geometry.

The interaction between both transition and main group metal ions with a variety of $[2_n]$cyclophane ligands has been of considerable interest to chemists for several decades.[1] These complexes were initially prepared in order to explore the unusual properties exhibited by the $[2_n]$cyclophane ligands which stem from the overlap of their π molecular orbitals and give rise to highly unique electronic and structural effects.[2] More recently, however, interest has been further stimulated by the potential for the $[2_n]$cyclophane ligands to serve as bridging units between redox-active metal centres in organometallic polymers and networks. Materials of this type are expected to exhibit a wide range of potentially interesting electrical and non-linear optical properties.[3]

The graphitic interaction

Over the past few years we have been actively involved in the study of organometallic cluster complexes, in particular, those containing coordinated arene ring systems.[4] The work described in this article was initially stimulated by the trends that emerged from a detailed examination of the solid-state structures of a number of bis-arene clusters of the type $[Ru_6C(CO)_{11}(arene)_2]$.[5] These investigations revealed an overwhelming tendency for the organic rings to become interlocked thus forming layers of organic substrate interspersed by layers of cluster units. Such layering was invariably found to be a result of the face-to-face (although typically off-centred) arrangement of aromatic ligands in adjacent molecules at distances comparable to that obeserved in graphite. It was also discovered that these packing interactions are propagated throughout the entire solid and result in the formation of supramolecular chains and stacks.[5]

This study revealed that it was primarily the difference in bonding mode adopted by the arene ligands (η^6 or μ_3) combined with their arrangement around the metallic core (*cis* or *trans*) that determined the packing motif within the crystal structure. For example, the two isomeric clusters *trans*-$[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)_2]$ **1** and $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **2** adopt different packing regimes in the solid-state (Fig. 1). In **1**, the molecules are arranged in long columnar structures with an interarene separation of 3.52 Å [Fig. 1(*a*)].[6]

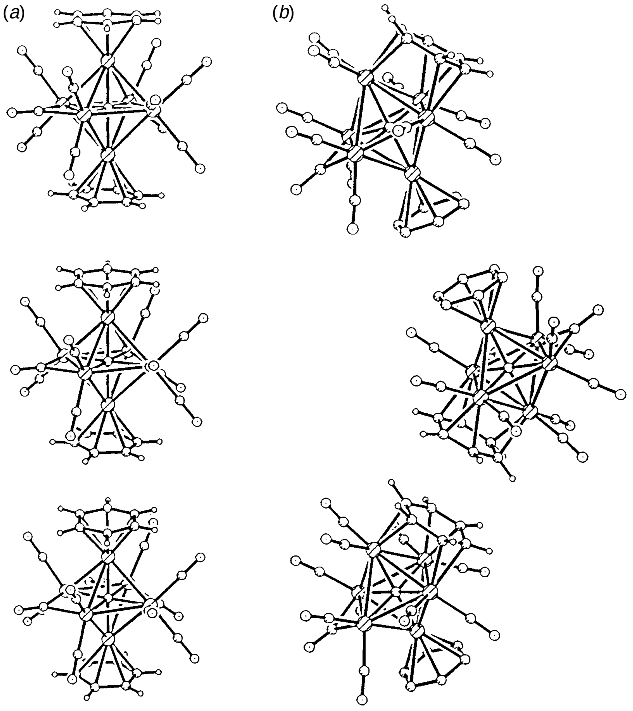


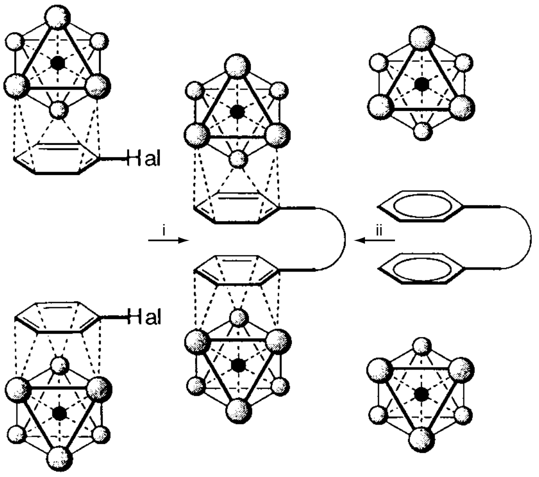
Fig. 1 Solid state packing of (*a*) $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)_2]$ **1** as rods; and of (*b*) $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **2** as snakes

Such a macromolecular structure arises from the arrangement of the arene rings which lie in parallel planes on the central cluster unit and permit the formation of a linear supramolecular rod. In **2**, however, the arene ligands are carried in planes which meet at a dihedral angle of 45°. As would be expected, this results in the introduction of kinks in the columnar structures producing supramolecular snakes instead [Fig. 1(*b*)].[7] In compound **2**, it should also be noted that the only close interactions observed between adjacent molecules in the crystal structure occur between η^6–η^6 bound rings and μ_3–μ_3 bound rings at distances of 3.29 and 3.56 Å, respectively. Although η^6–μ_3 interactions are known for other arene clusters, such as in the crystal structure of $[Os_3(CO)_6(C_6H_6)_2]$,[8] none are observed in that of compound **2**.

The study of these arene–arene interactions is of fundamental importance. This is because it is through such interactions that a mechanism in which charge transfer may occur throughout the crystalline lattice may be envisaged. Furthermore, one could speculate that it may be possible to create strong chemical bridges between adjacent arene clusters thus generating novel two-dimensional polymeric cluster chains and three-dimensional networks. It was with these ideas in mind that the class of ligands known as the cyclophanes, with their unique combination of strong chemical bridges linking aromatic rings and ability to transfer charge through space from one arene ring to the next within the same molecule, were considered as highly appropriate cluster linking groups.[9]

Linking arene clusters: the cyclophanes

There are two fundamentally different approaches which may be taken in order to produce linked arene clusters. The first involves the generation and subsequent coupling of activated arene clusters, while the second involves the addition of clusters to a pre-linked arene ligand (Scheme 1). The first approach has proved to be extremely difficult. In this case, the linkage of two arenes involves the initial preparation of halogenated arene cluster derivatives which are then coupled by the use of a reagent such as sodium metal. Such halogenated arene ligands are known to undergo C–halogen bond cleavage upon heating with transition metal carbonyls,[10] while attempting to halogenate the arene whilst coordinated to the cluster is difficult because transition metal carbonyl clusters are usually insufficiently robust to survive the harsh reaction conditions required. It should be noted, however, that the coupling of chromium tricarbonyl arene complexes has been successfully achieved and therefore the possiblity of linking arene clusters in an analogous manner cannot be entirely excluded. In these chromium compounds, the metal may be considered to remove π electron density from the bonded arene and thereby permit the face-to-face coupling of the fragments with enhanced yield.[11] In principle, these effects should be even greater if arene clusters can be coupled in the same way.



Scheme 1 The two principal routes to arene cluster linkage: i, cluster addition before coupling; ii, coupling before cluster addition

The more attractive approach is to use pre-linked arene ligands. Following a review of the literature, it was decided that the [2$_n$]cyclophanes would be an ideal class of ligand for our purpose.[12] These are a family of molecules whose structures generally consist of stacked aromatic rings held in close proximity by ethano bridges. They are rigid, well defined, and moderately accessible by relatively simple synthetic procedures. Typically, they possess strained molecular structures due to the strength of the electronic repulsions between the arene rings, and they have unusual electronic properties which stem from an ‘end-on’ overlap of π electron density giving essentially a single π-electron system. As mentioned earlier, this overlap should provide the additional possibility of electronic communication between bridged cluster units. Cyclophane linkages that may act as one, two or three-dimensional connectors such as [2.2]paracyclophane,[13] [2.2.2]paracyclophane,[14] and tetramesitylene[15] respectively, are currently available (Fig. 2). An example of how one can envisage such ligands being used in the construction of supramolecular networks is illustrated in Fig. 3 for the [2.2.2]paracyclophane ligand. In this case the triangular ligand can be seen to participate in the formation of hexagonal arrays in analogy to graphite with transition metal clusters forming the edges and cyclophane ligands the nodes.

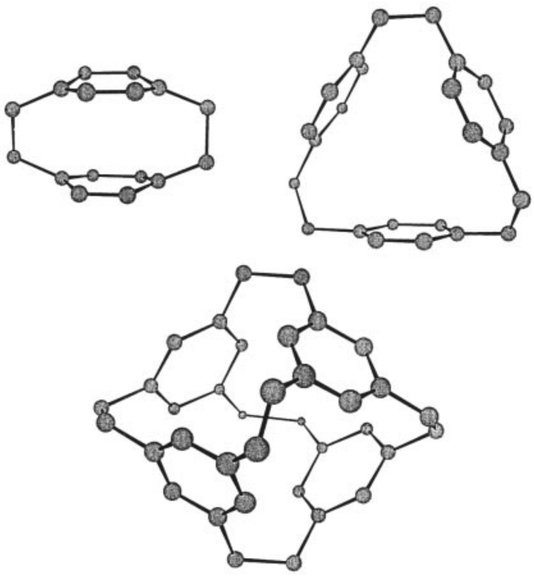


Fig. 2 The molecular structures of [2.2]paracyclophane (top left), [2.2.2]paracyclophane (top right) and tetramesitylene (bottom), respectively

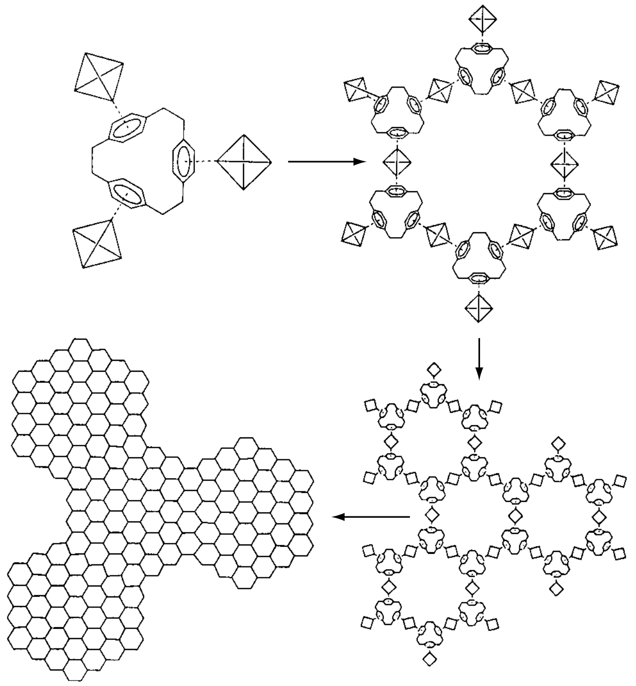


Fig. 3 The construction of a supramolecular hexagonal two-dimensional network using metal centres linked by the [2.2.2]paracyclophane ligand

[2.2]Paracyclophane clusters

Research in this area was initiated using the simplest of the [2$_n$]cyclophane ligands, [2.2]paracyclophane. The cluster chemistry of [2.2]paracyclophane has recently been reviewed,[16] and therefore only a short account will appear here. [2.2]Paracyclophane carbonyl clusters of ruthenium with nuclearities between two[17] and eight[18] have been structurally characterised and shown to display arene bonding modes ranging from η^6, to μ_2-η^3 : η^3 and μ_3-η^2 : η^2 : η^2.[17–19] There is, however, a marked tendency for the [2.2]paracyclophane to adopt the facial μ_3 coordination mode, and this is particularly apparent in the hexaruthenium carbido cluster $[Ru_6C(CO)_{14}(arene)]$ where the simpler arenes (benzene, toluene, xylene and mesitylene) tend to adopt the apical η^6 mode.[20] This effect is also apparent from work on the redox coupling reaction of $[Ru_5C(CO)_{14}]^{2-}$ and $[(C_{16}H_{16})Ru(NCMe)_3]^{2+}$ in which the cyclophane ligand, initially bound in an η^6 manner to a single metal atom, migrates during the course of the reaction to produce $[Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ in which the ligand is bound to a triangular metal face.[21]

It is evident, however, that none of the [2.2]paracyclophane compounds observed to date contain separate cluster moieties linked through a cyclophane unit. The reason for this is believed to originate from the through-space resonance effect within the ligand, whereby the electron-withdrawing nature of the cluster attached to one ring deactivates the second uncoordinated ring toward further cluster association. This effect appears to be so large that even single metal fragments such as chromium tricarbonyl will not coordinate to the second ring, and instead, complete displacement of the cluster occurs with the formation of $[Cr(CO)_3(C_{16}H_{16})]$. Therefore, the aims of more recent work have been to achieve cluster linkage using substituted or alternative types of [2*n*]cyclophane ligand.

Isomerisation and substitution effects

An important aspect of this work is to consider how the nature of the ligand influences the bonding mode adopted upon coordination to a metal cluster. Hence, an investigation into how different bridge substituted [2.2]cyclophanes effect cluster coordination patterns was undertaken. The molecular structures of two isomeric cluster species, $[Ru_6C(CO)_{14}(p\text{-}C_{16}H_{16})]$ **3** and $[Ru_6C(CO)_{14}(m\text{-}C_{16}H_{16})]$ **4**, have been determined by X-ray diffraction and a third, $[Ru_6C(CO)_{14}(o\text{-}C_{16}H_{16})]$ **5**, inferred by spectroscopy (Fig. 4).[20,22] The *para*-substituted ligand is found to adopt a facial μ_3 coordination mode upon the hexaruthenium carbido core, while the *meta*- and *ortho*-isomers prefer to adopt the η^6 bonding mode, interacting with a single metal atom only. There are two possible explanations for this behaviour. Firstly, it may be due to the superior donor capability of [2.2]paracyclophane over [2.2]meta- and [2.2]orthocyclophane, whereby the extensive overlap of π molecular orbitals in the *para*-isomer allows for sufficient supply of electron density for the three metal atoms.[23] There is little, if any, overlap of π molecular orbitals in the *meta*- and *ortho*-isomers and hence, they can be envisaged as only being able to support a single metal atom. This effect has been demonstrated electrochemically for $[Ru_6C(CO)_{14}(C_{16}H_{16})]$, whereby the *para*-isomer is far more difficult to reduce than either the *meta*- or *ortho*-isomers (−0.937, −0.893 and −0.890 V, respectively). Alternatively, the difference in coordination mode may be explained by the inherent distortion of the aromatic rings within the cyclophanes themselves (Fig. 5).[24] In [2.2]paracyclophane, the aromatic rings are convex, bulging outwards from the centre of the molecule due to inter-arene repulsion. Thus, in [2.2]paracyclophane the π orbitals are oriented outwards in such a way that they would be expected to interact more effectively with a trimetallic face than a single metal atom. However, in the *meta*-isomer the aromatic rings are concave, with the π orbitals oriented towards a focal point and thus the ligand is predisposed to interact with only a single metal atom. Furthermore, the distortion of the rings in both [2.2]para- and [2.2]metacyclophanes cause the aromatic C–H bonds to bend out of the plane. In [2.2]paracyclophane this occurs such that the C–H bonds point toward the centre of the molecule and in [2.2]metacyclophane such that they point away. Since the C–H bonds bend away from the underlying metal triangle in, for example $[Os_3(CO)_9(\mu_3\text{-}C_6H_6)]$,[25] it is therefore unsurprising that [2.2]paracyclophane adopts the facial bonding mode on the hexaruthenium cluster. Similarly, since the C–H bonds point toward the metal atom in mononuclear arene complexes it is not surprising either that the [2.2]metacyclophane ligand adopts an apical bonding mode.[26] In [2.2]orthophane the aromatic rings are planar and therefore presumably the preference of this ligand for the apical η^6 mode is not as strong as that of the *meta*-isomer.[27]

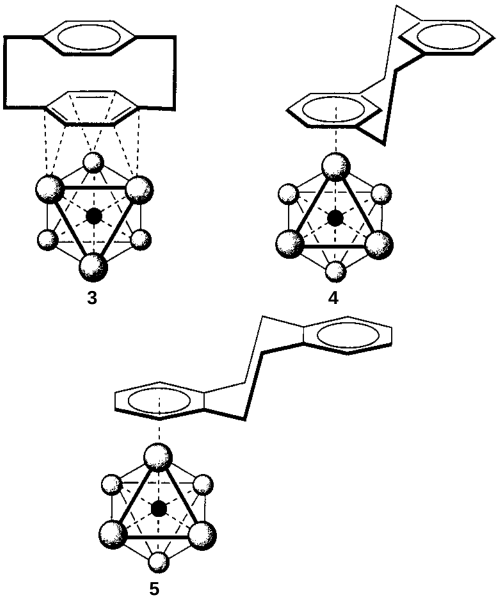

3
4
5

Fig. 4 The structures of three isomeric hexaruthenium [2.2]cyclophane clusters

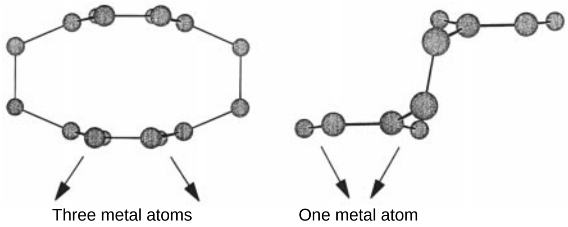
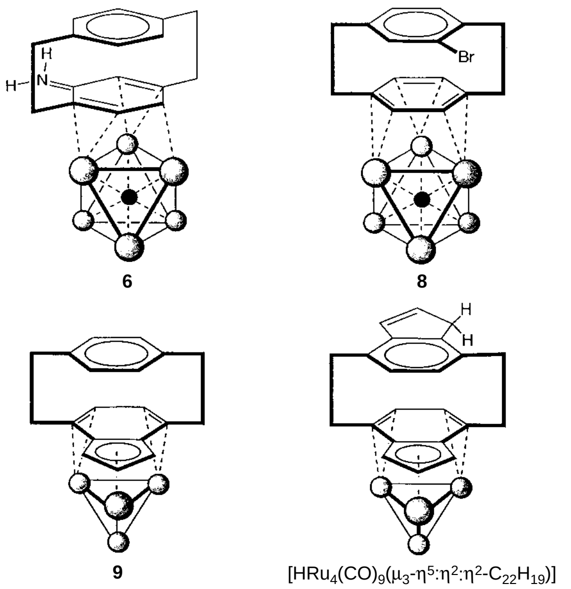


Fig. 5 The molecular structure of (left) [2.2]paracyclophane compared with (right) [2.2]metacyclophane.

Asymmetry

Since [2.2]paracyclophane interacts with metal clusters differently to its monoarene analogue, *para*-xylene,[20] it also seemed important to question whether [2.2]paracyclophane ligands bearing substituents upon their aromatic rings would interact differently from their monomeric analogues; and in cases where this substitution was not symmetrical, it would also be of interest to establish which ring the cluster unit would prefer to coordinate. In this regard, an investigation into the interaction of several ring-substituted [2.2]paracyclophane ligands with ruthenium carbonyl clusters has been carried out; the result of which is illustrated in Fig. 6.[28] It has been shown that the cluster unit always coordinates to the amine substituted ring of the 4-amino[2.2]paracyclophane ligand,[29] whereas it coordinates to the unsubstituted ring of 4-bromo[2.2]paracyclophane.[30] This behaviour may be explained in terms of the relative activating or deactivating effect of the substituents. The amino substituent is thought to push electron density onto the ring, thus making it more activated toward cluster association (as demonstrated by the planar geometry of the nitrogen). In fact, a closer analysis of the metal–ligand interface in $[Ru_6C(CO)_{14}(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}C_{16}H_{15}NH_2)]$ **6** suggests that the metal triangle interacts with only five aromatic carbon atoms (Fig. 7); the sixth (that attached to the nitrogen atom) remaining uncoordinated, possibly because it possesses insufficient electron density. The octahedral cluster retains the required electron count of 86 if the



6 **8**

9 $[HRu_4(CO)_9(\mu_3\text{-}\eta^5:\eta^2:\eta^2\text{-}C_{22}H_{19})]$

Fig. 6 The structures of some ring-substituted [2.2]paracyclophane ruthenium clusters: the 4-amino[2.2]paracyclophane cluster $[Ru_6C(CO)_{14}(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}C_{16}H_{15}NH_2)]$ **6**; the 4-bromo[2.2]paracyclophane cluster $[Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{15}Br)]$ **8**; the [2.2]parabenzoindenophane cluster $[HRu_4(CO)_9(\mu_3\text{-}\eta^5:\eta^2:\eta^2\text{-}C_{19}H_{17})]$ **9**; and the *anti*-[2,2]paraindenophane cluster $[HRu_4(CO)_9(\mu_3\text{-}\eta^5:\eta^2:\eta^2\text{-}C_{22}H_{19})]$

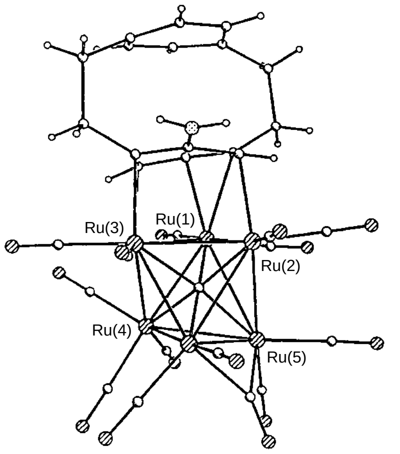
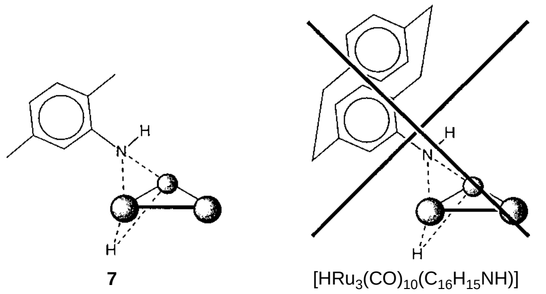


Fig. 7 The molecular structure of $[Ru_6C(CO)_{14}(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}C_{16}H_{15}NH_2)]$ **6**

substituted cyclophane is considered as a six electron donating dienyl ligand. It should be noted that this complex, to our knowledge, is the only example of an aniline ring coordinated to a cluster *via* its aromatic ring; other aromatic amine containing compounds such as 2,5-dimethylaniline yield N–H bond activated species only, *e.g.* as with the compound $[HRu_3(CO)_{10}(C_6H_3Me_2NH)]$ **7** (Fig. 8).[31] Presumably 4-amino-[2.2]paracyclophane cannot form such a compound because of the steric constraints imposed by the second aromatic ring.

In contrast, the bromo substituent in $[Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{15}Br)]$ **8**, is thought to deactivate the ring toward cluster coordination by pulling electron density away from it, and hence the cluster coordinates to the unsubstituted ring by default. Again this compound is unusual because contrary to the comments made above, the C–Br bond does not undergo oxidative-cleavage. In this example the resistance to C–Br cleavage is probably because the cyclophane unit blocks the path to an aryne or 'cyclophyne' type cluster.[32]

These results suggest that the cluster exerts a significant directing influence upon the substitution chemistry of a coordinated cyclophane ligand. From this, it may be further concluded that the coordinated ring, in for example $[Ru_6C(CO)_{14}(p\text{-}C_{16}H_{16})]$ **3**, should be activated towards nucleophilic attack in aromatic substitution reactions, whereas the uncoordinated ring should be more susceptible to electrophilic attack by default. Hence, in aromatic substitution reactions which employ mild conditions (that is conditions mild enough for the metal clusters to survive such as in the reaction of $[Ru_6C(CO)_{14}(C_6H_6)]$ with phenyllithium[33]), such clusters could be used to prepare unusually substituted [2.2]paracyclophane compounds not easily accessible *via* alternative routes.



7 $[HRu_3(CO)_{10}(C_{16}H_{15}NH)]$

Fig. 8 The structure of the N–H activated cluster $[HRu_3(CO)_{10}(C_6H_3Me_2NH)]$ **7** formed from 2,5-dimethylaniline. 4-Amino-[2.2]paracyclophane does not form an analogous compound, probably due to steric reasons.

Finally, the interaction of the [2.2]parabenzoindenophane[34] and *anti*-[2.2]paraindenophane[35] ligands with transition metal clusters has been investigated in collaboration with Prof. Henning Hopf of Braunschweig, Germany (Fig. 6). Although the former ligand possesses both a benzene and an indene face, it has been found that cluster coordination occurs only *via* the condensed indene face as in, for example, the tetranuclear cluster $[HRu_4(CO)_9(C_{19}H_{17})]$ **9** (Fig. 9). Here the ligand undergoes C–H bond activation which converts the cyclopentadiene ring to a cyclopentadienyl system; as such the cluster coordinates to the ring that is richest in π electron density *via* an η^9-(cyclopentadienyl–diene) interaction. Despite this predisposition of the indene face in [2.2]parabenzoindenophane, *anti*-[2.2]paraindenophane has also been shown to bond to only one cluster unit even though it possesses two indene rings suitable for cluster coordination (Fig. 6). This again is probably due to through space deactivation effects. All attempts to add monometallic fragments such as $[Mo(CO)_4]^+$ and $[FeCp]^+$ to the second cyclopentadiene ring, or to link these *anti*-[2.2]indenophane ruthenium carbonyl clusters by reaction with $FeCl_2 \cdot 2thf$ have so far been unsuccessful.[36]

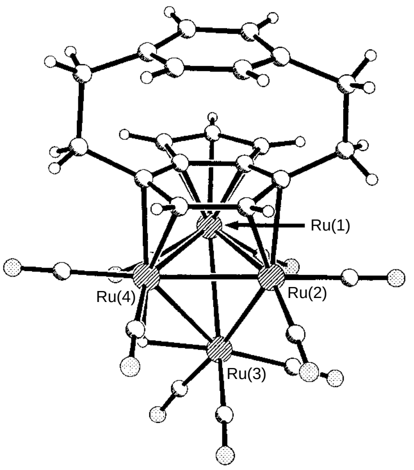
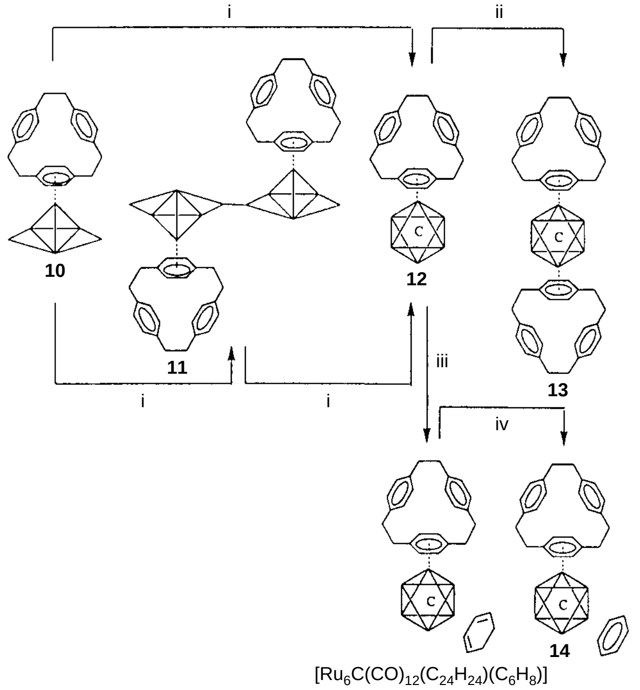


Fig. 9 The molecular structure of $[HRu_4(CO)_9(\mu_3\text{-}\eta^5:\eta^2:\eta^2\text{-}C_{19}H_{17})]$ **9**

The interaction of [2.2.2]paracyclophane with ruthenium carbonyl clusters

[2.2.2]Paracyclophane does not yield the diverse range of products observed for [2.2]paracyclophane when reacted with

$[Ru_3(CO)_{12}]$ under similar reaction conditions.[16] Instead, the thermolysis of [2.2.2]paracyclophane with 3 molar equiv. of $[Ru_3(CO)_{12}]$ in octane under reflux over a 6 h period affords just three new complexes: $[Ru_6(CO)_{15}(\eta^6\text{-}C_{24}H_{24})]$ **10** (5%), $[Ru_{12}(CO)_{28}(\eta^6\text{-}C_{24}H_{24})_2]$ **11** ($\approx 0.1\%$) and $[Ru_6C(CO)_{14}(\eta^6\text{-}C_{24}H_{24})]$ **12** (30%) (Scheme 2).[37] These may be readily separated by thin layer chromatography on silica using dichloromethane–hexane (1 : 2, v/v) as eluent. In each of these compounds the central cluster unit is based on a hexanuclear metal framework but of differing geometries. In compound **10**, the metal atoms are arranged as a doubly edge-bridged tetrahedron (an 88 valence electron cluster). By analogy to the mesitylene complex, $[Ru_6(CO)_{15}(\eta^6\text{-}C_6H_3Me_3)]$,[38] the arene ligand in compound **10** is coordinated in an η^6 manner to the apex of the central tetrahedron that is not involved in edge-bridging, and a dihapto (η^2-μ_4) carbonyl ligand is located in each of the butterfly sites. This compound may be converted by heating in octane to the octahedral hexaruthenium carbido cluster, $[Ru_6C(CO)_{14}(\eta^6\text{-}C_{24}H_{24})]$ **12**, in which the arene again coordinates to a single metal atom. An intermediate compound, $[Ru_{12}(CO)_{28}(\eta^6\text{-}C_{24}H_{24})_2]$ **11**, is also isolated in trace amounts during this conversion, and the molecular structure of this compound **11** is shown in Fig. 10. It is formally a dodecaruthenium bis-arene cluster, which makes it the largest arene cluster prepared by our group to date. This molecule contains a fused bis-(doubly edge-bridged tetrahedron) metallic framework in which ten of the metal atoms are essentially coplanar—all those except the two that carry the cyclophane ligands. It is easy to envisage the process by which compound **11** may be derived from **10** by the simple removal of a single carbonyl ligand from one of the edge-bridging metal atoms and the dimerisation of the resultant unsaturated species to produce the 174 valence electron cluster. The two hexaruthenium units of this cluster are related by an inversion centre and the linking metal–metal bond is located between two edge-bridging metal atoms. Two of the carbonyl ligands which were terminal at the edge-bridging metal atom in compound **10** migrate to a bridging position, possibly in order to stabilise the new linkage in compound **11**. Despite the change of the local arrangement of carbonyl ligands at the linkage, the η^2-μ_4-CO ligands are retained in the four butterfly sites of compound **11**.



Scheme 2 Routes to some [2.2.2]paracyclophane ruthenium clusters. *Reagents and conditions*: i, $[Ru_3(CO)_{12}]$, heat in octane; ii, $C_{24}H_{24}$, heat in nonane; iii, cyclohexa-1,3-diene with 2.2 equiv. Me_3NO in CH_2Cl_2; and iv, heat in hexane or 1.1 equiv. Me_3NO in CH_2Cl_2.

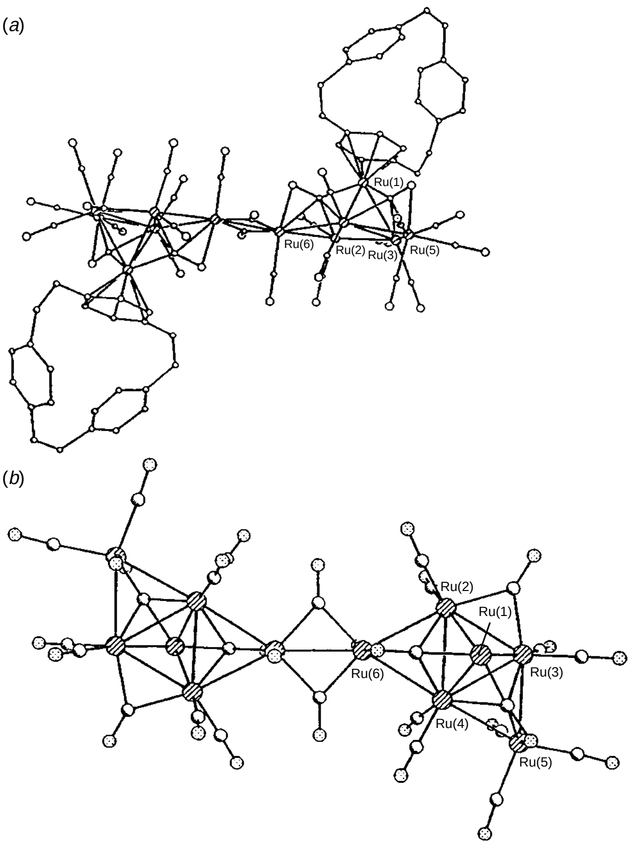
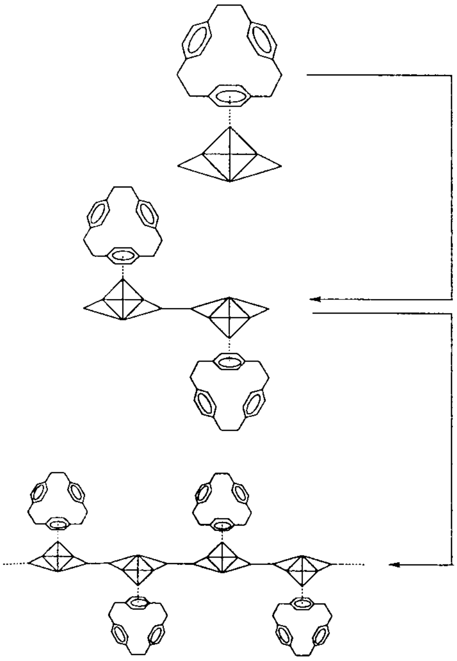


Fig. 10 The molecular structure of $[Ru_{12}(CO)_{28}(\eta^6\text{-}C_{24}H_{24})_2]$ **11**, with (*a*) and without (*b*) the [2.2.2]paracyclophane ligands, respectively

Since compounds **10** and **11** both possess two edge bridging metal atoms, and compound **10** can dimerise to form compound **11** upon the loss of a carbonyl ligand, it should be possible, at least in principle, for further oligomerisation to occur such that a polymeric material based solely on a metal backbone could be prepared (Scheme 3). However, as yet all attempts to induce further oligomerisation by thermal, chemical or photolytic means have resulted in the now well established closure of the metallic core[39] to form the octahedral hexaruthenium carbido cyclophane cluster $[Ru_6C(CO)_{14}(\eta^6\text{-}C_{24}H_{24})]$ **12**. It should also be noted that the loss of a carbonyl ligand from the cluster, followed by dimerisation of the resulting unsaturated fragments, as observed in the conversion of **10** to **11**, also provides a mechanism to explain the unexpected and generally observed irreversibility of arene cluster reductions during cyclic voltammetry.

An additional arene ligand may also be introduced onto the monocyclophane hexaruthenium carbido cluster **12**. The reaction of compound **12** with an excess of [2.2.2]paracyclophane in refluxing nonane yields the *trans*-bis-arene derivative $[Ru_6C(CO)_{11}(\eta^6\text{-}C_{24}H_{24})_2]$ **13**, while a related mixed arene cluster, $[Ru_6C(CO)_{11}(\eta^6\text{-}C_{24}H_{24})(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **14**, in which the cyclophane ligand adopts an apical mode and the benzene ligand a facial bonding mode (Fig. 11 and Scheme 2), is obtained from the reaction of **12** with cyclohexadiene and trimethylamine *N*-oxide.[40] Compounds **13** and **14** are of particular relevance to our objective of preparing organometallic network precursors since the cluster acts as a bridge between two arene ligands here.

The [2.2.2]paracyclophane ligand has also been shown to undergo reaction with $[Ru_5C(CO)_{15}]$, and the cluster $[Ru_5C(CO)_{12}(\eta^6\text{-}C_{24}H_{24})]$ **15** is the sole product formed during thermolysis in heptane.[37] In this compound, the cyclophane replaces all three carbonyl ligands on one basal metal atom of



Scheme 3 The dimerisation of $[Ru_6(CO)_{15}(\eta^6\text{-}C_{24}H_{24})]$ **10** to $[Ru_{12}(CO)_{28}(\eta^6\text{-}C_{24}H_{24})_2]$ **11** and the hypothetical metal based polymer $[Ru_6(CO)_{14}(\eta^6\text{-}C_{24}H_{24})]_n$

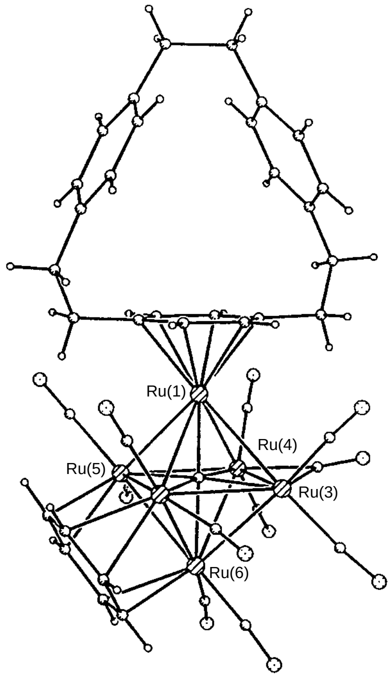
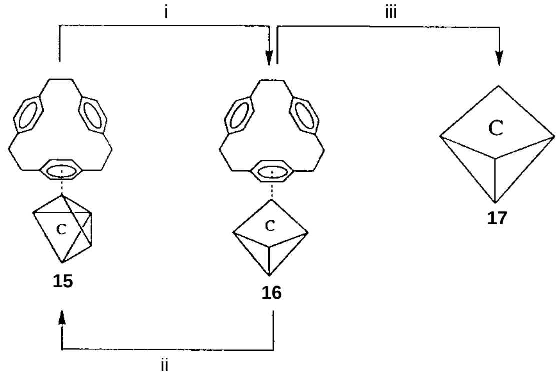


Fig. 11 The molecular structure of $[Ru_6C(CO)_{11}(\eta^6\text{-}C_{24}H_{24})(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **14**

the parent square pyramidal cluster. Under an atmosphere of carbon monoxide, compound **15** undergoes the reversible addition of a carbonyl ligand to form the bridged butterfly complex, $[Ru_5C(CO)_{13}(\eta^6\text{-}C_{24}H_{24})]$ **16** (Scheme 4). This is thought to occur by a mechanism similar to that observed for the analogous benzene cluster, *i.e.* by the coordination of a carbonyl ligand at the metal carrying the arene (formally that richest in electron density) with the concomitant breakage of a base–apex metal–metal bond.[41] However, the unrivalled degree of isomerism displayed by the benzene analogue is not displayed by the [2.2.2]paracyclophane complex (benzene can not only adopt the basal-η^6 bonding mode upon the square pyramidal cluster $[Ru_5C(CO)_{12}]$, but also the apical-η^6 and facial μ_3 modes).[42] Instead, continuous exposure to a carbon monoxide atmosphere causes compound **16** to release the cyclophane ligand and form the binary cluster, $[Ru_5C(CO)_{16}]$ **17**. Compound **17** possesses the same bridged butterfly metal geometry as the analogous osmium cluster.[43]



Scheme 4 The reactivity of $[Ru_5C(CO)_{12}(\eta^6\text{-}C_{24}H_{24})]$ **15**. *Reagents and conditions*: i, CO bubble in CH_2Cl_2 over 5 min; ii, N_2 bubble in CH_2Cl_2; iii, 1 atm CO over CH_2Cl_2 for 1 day.

A correlation between the chemical shifts of coordinated and uncoordinated aromatic ring protons in ruthenium–[2.2]paracyclophane clusters of differing nuclearities and bonding modes has been discussed in detail elsewhere.[16] This family of ruthenium–[2.2.2]paracyclophane clusters also show marked trends in their ^1H NMR spectra as illustrated in Table 1. It appears that the magnitude of the chemical shift of both the coordinated and free cyclophane rings is somewhat dependent on both the metal to carbonyl ratio of the cluster and, if present, the coordination mode of the second arene ligand. For example, the mean chemical shift of the aromatic protons on the bound ring of the cyclophane moves to higher field as the metal to carbonyl ratio falls and the electron-withdrawing power of the cluster increases. The difference in the chemical shift of the aromatic protons between $[Ru_6C(CO)_{11}(\eta^6\text{-}C_{24}H_{24})_2]$ **13** and $[Ru_6C(CO)_{11}(\eta^6\text{-}C_{24}H_{24})(\eta_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **14** may be related to the magnitude of interaction between the cyclophane and the cluster. This is weaker for compound **14** because of the influence of the second arene which being in the facial coordination mode is the more tightly bound of the two arene ligands.

Table 1 ^1H NMR characteristics of several ruthenium [2.2.2)paracyclophane clusters

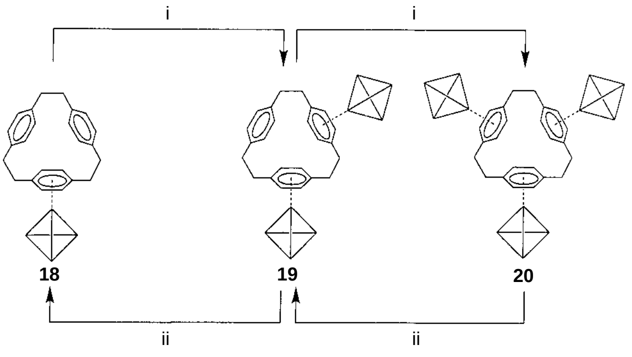
	Compound	M : CO ratio	Mean δ of bound aromatic protons	Mean δ of free aromatic protons
10	$[Ru_6(CO)_{15}(C_{24}H_{24})]$	2.50	5.82	6.82
15	$[Ru_5C(CO)_{12}(C_{24}H_{24})]$	2.40	5.54	6.83
12	$[Ru_6C(CO)_{14}(C_{24}H_{24})]$	2.33	5.25	6.74
14	$[Ru_6C(CO)_{11}(C_{24}H_{24})(C_6H_6)]$	1.83	5.26	6.76
13	$[Ru_6C(CO)_{11}(C_{24}H_{24})_2]$	1.83	5.01	6.69

The [2.2.2]paracyclophane ligand has been observed only in the apical η^6 bonding mode in ruthenium carbonyl clusters. This is in contrast to [2.2]paracyclophane which tends to adopt the facial μ_3-mode, and again this may possibly be attributed to the observation that the aromatic rings in [2.2.2]paracyclophane adopt a more planar configuration than those in [2.2]paracyclophane.

The interaction of [2.2.2]paracyclophane and cobalt carbonyl clusters

The reaction of [2.2.2]paracyclophane with an excess of $[Co_4(CO)_{12}]$ in hexane, affords three new cluster complexes:

$[Co_4(CO)_9(\eta\text{-}C_{24}H_{24})]$ **18** (20%), $[\{Co_4(CO)_9\}_2(\eta\text{-}C_{24}H_{24})]$ **19** (2%) and $[\{Co_4(CO)_9\}_3(\eta\text{-}C_{24}H_{24})]$ **20** ($\approx$ 0.1%). These may be readily separated by thin layer chromatography on silica using dichloromethane–hexane (1 : 3, v/v) as eluent (Scheme 5).[44]



Scheme 5 The interconversion of compounds $[\{Co_4(CO)_9\}_n(\eta\text{-}C_{24}H_{24})]$ (n = 1, 2 and 3). *Conditions*: i, $[Co_4(CO)_{12}]$, heat in hexane; ii, heat in toluene {clusters removed from cyclophane as $[Co_4(CO)_9(\text{toluene})]$}.

Complex **18** may be conveniently converted to **19** and in turn **19** to **20** by the progressive addition of $[Co_4(CO)_{12}]$ in hexane. Conversely, compound **20** ejects a cluster unit to form **19** and then another to form **18** when heated in toluene. This process occurs *via* arene exchange whereby the metal clusters are transferred from the cyclophane ligand to the toluene forming $[Co_4(CO)_9(\eta^6\text{-}C_6H_5Me)]$. The molecular structures of compounds **18** and **19** have been established by single crystal X-ray diffraction and are shown in Fig. 12(*a*) and (*b*), respectively. In both molecules the coordinated rings of the cyclophane ligands are bound to a single metal atom in an η^6-manner and lie parallel to, and staggered with respect to, the more distant underlying metal triangle. Compounds **19** and **20** are the first examples of metal clusters linked by a cyclophane ligand, and are of particular interest as potential precursor sub-units for the construction of one and two-dimensional organometallic networks and polymers discussed above. Furthermore, preliminary electrochemical analyses, although complex, suggest the existence of electronic communication between the metal clusters in compounds **19** and **20**.[44]

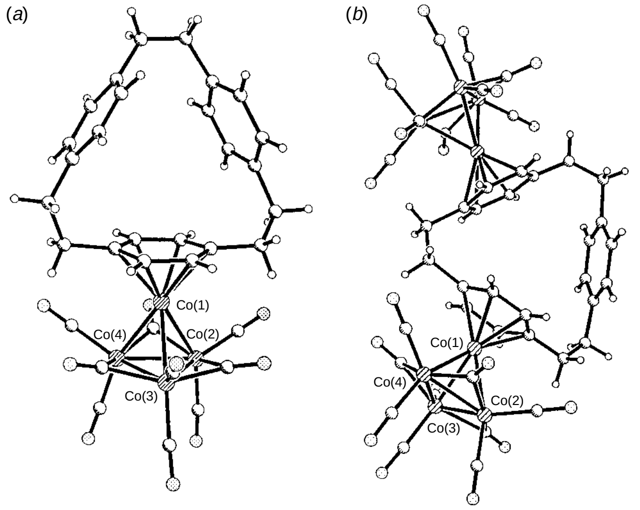


Fig. 12 The crystal structures of (*a*) $[Co_4(CO)_9(\eta\text{-}C_{24}H_{24})]$ **18**; and (*b*) $[\{Co_4(CO)_9\}_2(\eta\text{-}C_{24}H_{24})]$ **19**

The binding of soft metal cations

It has been known for some time that metal atoms and ions may bond to [2.2.2]paracyclophane by *endo*-coordination as well as *exo*-coordination.[45] In *endo*-coordination the metal atom resides in or near the ligand cavity such as in the π cryptates formed with Ga^I and Ag^I salts.[46,47] It has also been possible to demonstrate this effect using the ruthenium [2.2.2]paracyclophane clusters described herein.[37] For example, the addition of either Ga^I or Ag^I salts brings about a considerable change in the IR (carbonyl) spectrum of the parent cluster. This effect may be considered to occur as a consequence of the reduction in the electron density available for carbonyl π back donation which in turn causes a shift of the spectrum to higher wavenumbers. Table 2 illustrates this point for the complexes $[Ru_6C(CO)_{14}(\eta^6\text{-}C_{24}H_{24}Ag)][BF_4]$ **21** and $[Ru_6C(CO)_{14}(\eta^6\text{-}C_{24}H_{24}Ga)][GaCl_4]$ **22**. A comparison of the IR values of these two compounds with those of the parent cluster $[Ru_6C(CO)_{14}(\eta^6\text{-}C_{24}H_{24})]$ **12** indicates a clear shift. The magnitude of this shift may be rationalised in terms of the strength of the cation–cyclophane interaction. This is greater for the gallium(I) ion which is thought to be located at the centre of the cyclophane cavity than for silver which only remains at the edge (Fig. 13).[14,46] This behaviour does not extend to the [2.2.2]paracyclophane complexes of cobalt (and even of chromium tricarbonyl) which undergo extensive decomposition on treatment with either Ga^I or Ag^I salts presumably by some redox reaction.

Table 2 IR characteristics (carbonyl region) of $[Ru_6C(CO)_{14}(C_{24}H_{24})]$ **12** in the presence and absence of soft metal cations

Compound	Formula	ν_{CO}/cm^{-1} CH_2Cl_2
12	$[Ru_6C(CO)_{14}(C_{24}H_{24})]$	2074, 2023 and 1813
21	$[Ru_6C(CO)_{14}(C_{24}H_{24})Ag][BF_4]$	2084, 2045 and 1878
22	$[Ru_6C(CO)_{14}(C_{24}H_{24})Ga][GaCl_4]$	2089, 2051 and 1894

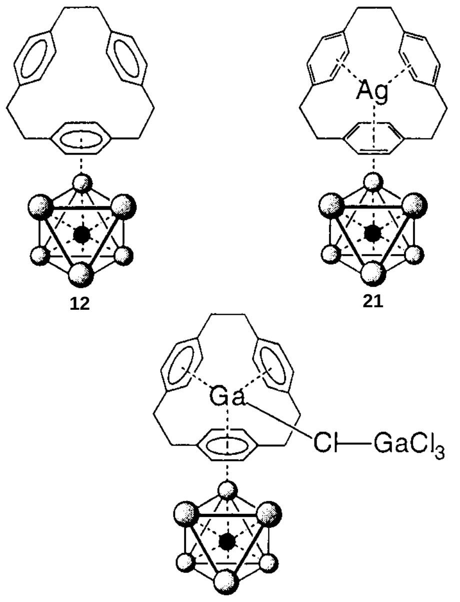


Fig. 13 The binding of Ga^I and Ag^I cations to $[Ru_6C(CO)_{14}(\eta^6\text{-}C_{24}H_{24})]$ **12**

Conclusions

Several novel compounds have been described which will, hopefully, in due course serve as potential building blocks for one- and two-dimensional cluster polymers and networks. These include $[Ru_{12}(CO)_{28}(\eta^6\text{-}C_{24}H_{24})_2]$ **11**, in which there is a metal containing back-bone; $[Ru_6C(CO)_{11}(\eta^6\text{-}C_{24}H_{24})_2]$ **13** and $[Ru_6C(CO)_{11}(\eta^6\text{-}C_{24}H_{24})(\mu_3\text{-}\eta^2 : \eta^2 : \eta^2\text{-}C_6H_6)]$ **14**, in which hexaruthenium clusters link two arene ligands together; and

$[\{Co_4(CO)_9\}_2(\eta\text{-}C_{24}H_{24})]$ **19** and $[\{Co_4(CO)_9\}_3(\eta\text{-}C_{24}H_{24})]$ **20**, in which a [2.2.2]paracyclophane bridges two and three tetracobalt clusters, respectively. It should be noted, however, that as yet we have been unable to sustain chain growth in any of these examples. In the case of compound] **11**, the induction of further oligomerisation instead results in conversion to monomeric closed octahedral hexaruthenium carbido clusters. Although it has been possible to prepare ruthenium carbonyl clusters containing two arene ligands it has, so far, proved difficult to introduce a second ruthenium cluster onto the cyclophane ligand. This is thought to be due to the interaction between the cyclophane molecule and the ruthenium cluster being too strong to permit the addition of further metallic units, and the cyclophane being unable to supply sufficient electron density to satisfy two cluster cores. For cobalt, however, each aromatic ring of the [2.2.2]paracyclophane ligand may be utilised in cluster coordination. So far, the introduction of a second cyclophane ligand onto the tetrahedral Co_4 core has been unsuccessful, which is possibly due to the weakness of the metal–arene interaction (as demonstrated by arene exchange reactions with toluene) which permits multiple complexation of clusters by a single ligand, but is too weak to allow the substitution of further carbonyl ligands by a poorer π-accepting cyclophane ligand.

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Prof. Brian F. G. Johnson is Professor of Inorganic Chemistry in the Department of Chemistry, the University of Cambridge, Cambridge CB2 1EW. He obtained his PhD from the University of Nottingham (1963). He then spent postdoctoral positions at M.I.T. and the University of Manchester where he became a lecturer (1965). Lectureships were also held at University College London (1967–1970) and the University of Cambridge (1970–1990). He held the Crum Brown Chair of Inorganic Chemistry at the University of Edinburgh (1990–1995) before returning to Cambridge (1995). He was elected as a Fellow of the Royal Society (1991) and Fellow of the Royal Society of Edinburgh (1992).

Dr Caroline M. Martin is an associate lecturer in the Department of Chemistry, the University of Cambridge, Cambridge CB2 1EW. She obtained her PhD from the University of Edinburgh (1994) and she held a postdoctoral fellowship at University College London for one year before moving to her current post (1995).

Paul Schooler is a final year PhD student under the supervision of Prof. Brian F. G. Johnson in the Department of Chemistry, the University of Cambridge, Cambridge, UK CB2 1EW. He will soon take up a postdoctoral position at Texas A.&M. University (October 1998) under the supervision of Prof. F. Albert Cotton.

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