

The Build-Up of Bimetallic Transition Metal Clusters

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The synthesis and reaction chemistry of high nuclearity transition metal carbonyl clusters is briefly reviewed, and new synthetic strategies leading to the “rational” synthesis of bimetallic clusters containing metal cores of over 1 nm in dimension are described. The solid state structures of a number of osmium/mercury, osmium/gold and ruthenium/copper bimetallic clusters are discussed with regard to the nature of their formation, and of their bonding and redox properties. Suggestions are made as to how the synthetic strategies can be adapted to prepare bimetallic clusters of industrially useful combinations of metals. Recent work showing that bimetallic nanoparticles prepared from clusters are catalytically active when anchored inside mesoporous silica is also discussed.

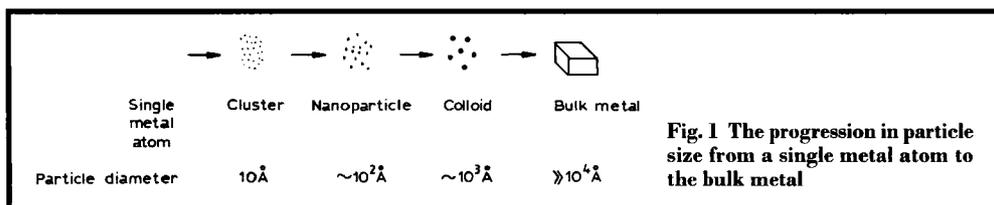
Transition metal carbonyl cluster chemistry has been an important and developing topic of research in organometallic chemistry for the last three decades (1). One of the main appeals of clusters is that they lie at the interface between “conventional” organometallic chemistry and the chemistry of colloids and of the bulk metal. Figure 1 illustrates the progression in particle size from a single atom through clusters, with metal core sizes of around 1 nm; nanoparticles, with sizes up to 100 nm; leading into the colloid regime; and then on to the bulk metal.

Indeed, at what size (number of metal atoms) does a metal cluster stop behaving like an organometallic complex, with bonding properties that can be described in terms of discrete molecular orbitals, and take on metallic properties, where the bonding can be described in terms of band structure? There is no immediate answer to this question, but there is a clear progression towards the clusters taking on metal-

lic properties as the nuclearity increases, although different sizes of cluster exhibit different types of metal-like properties under different conditions (2).

One of the main thrusts of cluster chemistry at Cambridge has been to prepare ever larger transition metal clusters and to investigate their physical and chemical properties. A range of clusters containing more than ten metal atoms has now been prepared and crystallographically characterised (3) and examples in which the metal atoms “condense” to form structures corresponding to the hexagonal, cubic and body-centred cubic packings found in bulk metal have been observed, as well as other clusters, such as $[\text{Pt}_{19}(\text{CO})_{22}]^{4-}$ (4), which exhibit five-fold symmetry packing.

The diameters of the metal cores in the largest of these clusters, such as $[\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}\text{H}_{6-n}]^{n-}$ ($n = 5, 4$) are of the order of 2 nm (5). Even larger clusters containing copper and selenium



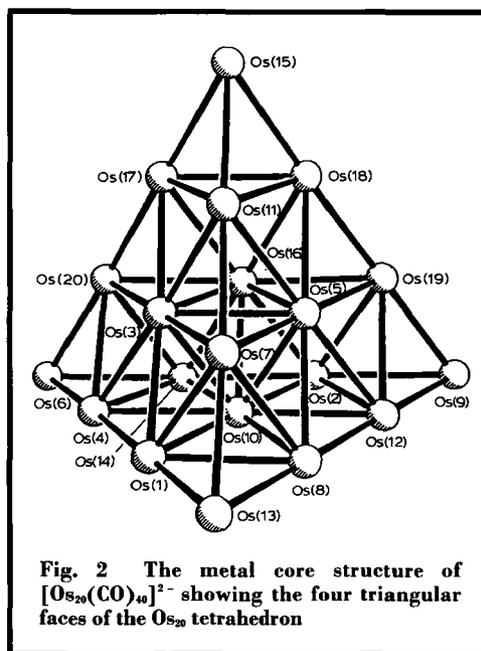
have been prepared, and the largest of these to have been crystallographically characterised is $[\text{Cu}_{146}\text{Se}_{73}(\text{PPh}_3)_{30}]$ in which the selenium atoms exhibit “ABA” stacking and the copper atoms occupy interstitial sites (6). There are also reports of transition metal clusters, for instance those containing Au_{55} (7) and Rh_{55} (8), Pt_{309} (9) and Pd_{561} (10) units, and a series of palladium clusters containing up to 2000 metal atoms (11), which have not yet been crystallographically characterised, but which must have dimensions of the order of 4 nm.

Several research groups have proposed that clusters can act as good building blocks in nanoscale architecture and thus will find application in the fabrication of single electron devices (12). Small metal particles and other transition metal clusters have also been clearly shown to form densely packed monolayers on electron microscope grids when they are ligated by organic surfactant molecules (13).

From the viewpoint of catalysis, metal clusters can be considered as fragments of a metal surface surrounded by a layer of “adsorbed” ligand molecules. Even the largest osmium cluster carbonyl so far characterised, $[\text{Os}_{20}(\text{CO})_{40}]^{2-}$, where the metal framework is approximately $0.9 \times 0.9 \times 0.9$ nm in size, contains only surface atoms, with each osmium atom being bonded to at least one carbonyl ligand, see Figure 2, (14).

However, can clusters be regarded as good models of metal surfaces in heterogeneous catalytic reactions? The “cluster/surface” analogy was pointed out quite early in the development of cluster chemistry (15), and ever since then clusters have been used as models for catalytic systems (16).

Certainly, organic molecules bond to catalytically active metal surfaces in the same way as to metal clusters, and analysis of cluster systems is easier because they can be subjected to the full range of solution spectroscopic techniques, such as IR and multinuclear NMR spectroscopies, mass spectrometry and, in the solid state, single crystal X-ray crystallography, whereas analysing the bonding modes of co-ordinated molecules on a metal surface



under catalytic conditions is rather more challenging. However, for the majority of cluster models, for example $[\text{Os}_{20}(\text{CO})_{40}]^{2-}$ (14), only “surface” atoms are present, and since the sub-layers of the bulk metal influence the chemistry of the surface atoms on a catalytic surface, some aspects of the model are not valid, so the “analogy” should be treated with caution.

Therefore, the simple answer to the question of whether clusters are good models for heterogeneous catalysts would be “no”.

“Rational” Synthesis of High Nuclearity Mixed-Metal Clusters

With a view to preparing precursor materials that could have applications in catalysis and nanoparticle technology, the “cluster” group in Cambridge has been developing strategies for synthesising high nuclearity mixed-metal clusters containing ten or more metal atoms in their cluster cores. Even the smallest of these clusters should have a core diameter in excess of 0.5 nm and have the advantage, unlike bimetallic particles prepared by other routes, that the exact ratio of the two metallic elements is known. As much of the early cluster synthesis work

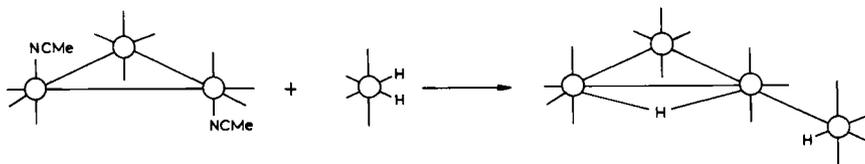


Fig. 3 The formation of the "spiked"-triangular cluster $[\text{Os}_4\text{H}_2(\text{CO})_{15}]$ from the reaction of the activated cluster $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ with $[\text{OsH}_2(\text{CO})_4]$

involved pyrolysis or thermolysis techniques and resulted in a range of products, all in low yields, from a single reaction, it has been necessary to develop synthetic strategies where one target cluster molecule can be obtained in good yield (17).

In order to achieve this, two fairly straightforward synthetic routes are available, given that the starting materials for the production of high nuclearity clusters are usually low nuclearity carbonyl clusters.

The first route, illustrated in Figure 3 by the formation of $[\text{Os}_4\text{H}_2(\text{CO})_{15}]$, involves the activation of the binary carbonyl $[\text{Os}_3(\text{CO})_{12}]$ with Me_3NO , in the presence of MeCN and results in the oxidation of carbonyl ligands to carbon dioxide and the occupation of the vacant coordination sites with labile MeCN ligands. The subsequent addition of the neutral mononuclear complex $[\text{OsH}_2(\text{CO})_4]$ displaces the MeCN groups and affords the "spiked"-triangular cluster $[\text{Os}_4\text{H}_2(\text{CO})_{15}]$ (18). In this method the cluster nuclearity is increased by one, by the reaction of a neutral, activated, low nuclearity

cluster with a neutral monometal complex.

The second route involves the ionic coupling reaction between a carbonyl cluster anion and a monometal cationic species, again to increase the cluster nuclearity by one. In Figure 4, the tetranuclear osmium cluster $[\text{Os}_4\text{H}_4(\text{CO})_{12}]$ is initially reduced with $\text{K}/\text{Ph}_2\text{CO}$ to form the dianion $[\text{Os}_4\text{H}_4(\text{CO})_{11}]^{2-}$, and then treated immediately with the labile cation $[\text{M}(\eta^6\text{-C}_6\text{H}_6)(\text{MeCN})_3]^{2+}$ ($\text{M} = \text{Ru}, \text{Os}$) to form the pentanuclear, neutral cluster $[\text{Os}_4\text{MH}_4(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_6)]$ (19). By choosing appropriate cation and anion charges and ratios, the cluster nuclearity can be increased by two units, as in the reaction of $[\text{Os}_3(\text{CO})_{11}]^{2-}$ with two equivalents of $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{MeCN})_3]^+$ to give the pentanuclear cluster $[\text{Os}_3\text{Ru}_2(\text{CO})_{11}(\eta^5\text{-C}_5\text{H}_5)_2]$ (20). This latter ionic coupling route has been particularly successful, and has been extensively exploited to prepare a wide range of higher nuclearity clusters containing carbocyclic ligand groups (21).

The method has also been used by a number of research teams for synthesising mixed-metal

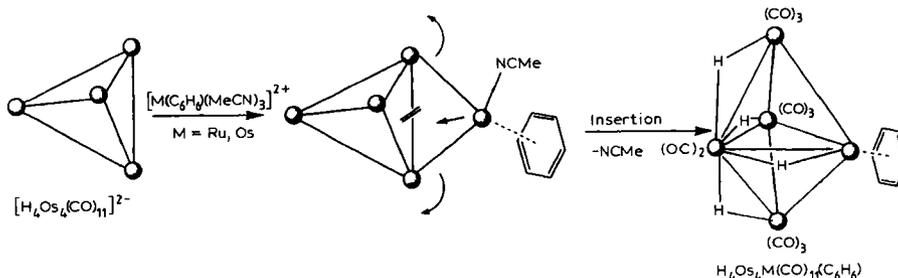
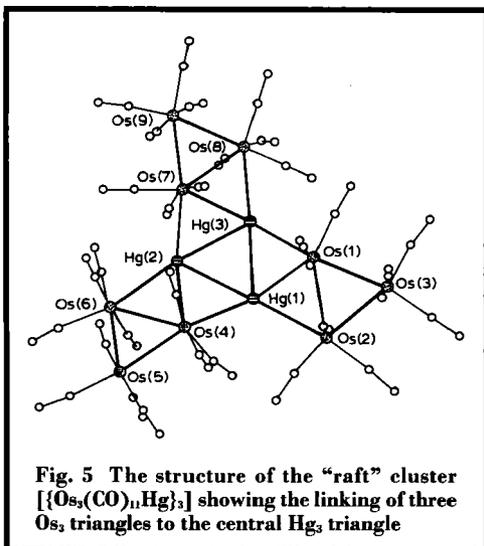


Fig. 4 The synthesis of $[\text{Os}_4\text{MH}_4(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_6)]$ ($\text{M} = \text{Ru}, \text{Os}$) from the coupling of $[\text{Os}_4\text{H}_4(\text{CO})_{11}]^{2-}$ with $[\text{M}(\eta^6\text{-C}_6\text{H}_6)(\text{MeCN})_3]^{2+}$ ($\text{M} = \text{Ru}, \text{Os}$)



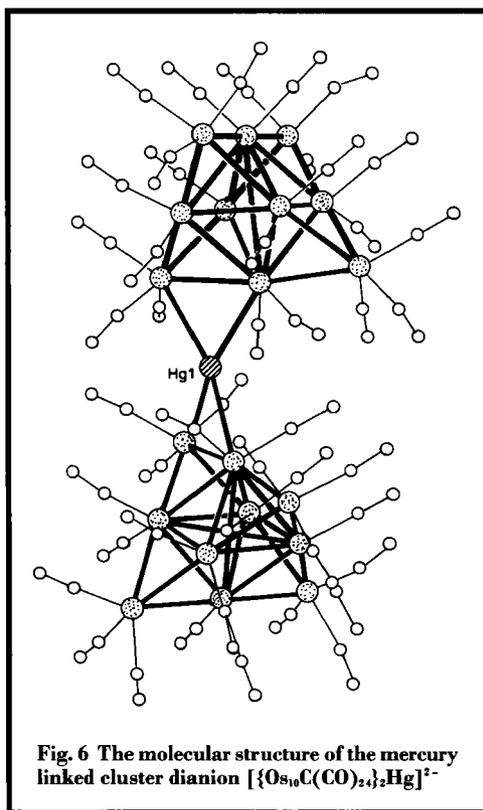
clusters containing the coinage metals by the reaction of carbonyl cluster anions with cationic copper, silver and gold complexes (22).

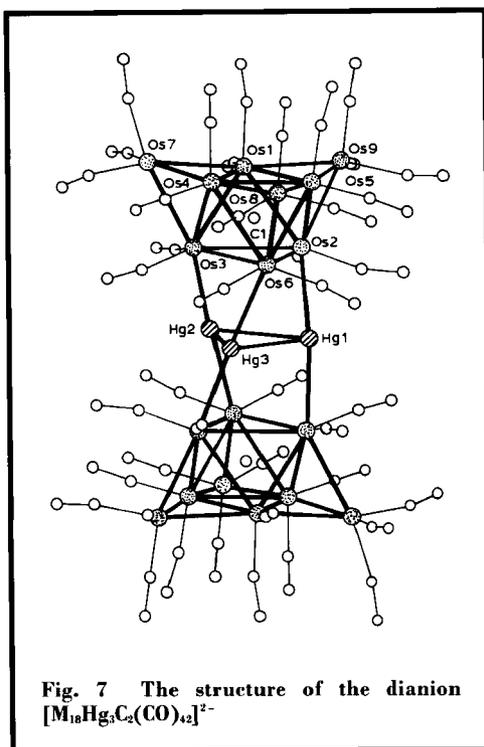
Osmium-Mercury Clusters

So far, our most extensive series of studies into the formation of mixed-metal clusters containing ten or more metal atoms have also involved the reaction of a range of ruthenium and osmium cluster carbonyl anions with late transition metal cations, such as $[HgX]^+$ ($X = Cl, CF_3$), $[AuPR_3]^+$ ($R = \text{alkyl, aryl}$) and $[Cu(NCMe)_4]^+$. The first indication that cluster build-up could occur to produce higher nuclearity clusters came from the metathesis reaction of $[Os_3H(CO)_{11}]^-$ with mercury(II) salts. The product of the reaction was the extremely photolabile, dodecanuclear "raft" cluster $[\{Os_3(CO)_{11}Hg\}_3]^{2-}$ shown in Figure 5 (23). It is significant that the three mercury atoms form a central triangle with Hg-Hg distances in the range 3.08–3.12 Å. The " $Os_3(CO)_{11}$ " fragments bridge this central triangle, with each " $Os_3(CO)_3$ " group forming bonds to two mercury atoms (Os-Hg in the range 2.71–2.76 Å); the co-ordinated " $Os(CO)_4$ " groups each form one bond to a mercury atom (Os-Hg in the range 2.98–3.05 Å). This cluster can be viewed as a model for a bimetallic surface, and while being only one layer thick

has a core diameter in the surface plane of approximately 1.2 nm (12 Å).

This coupling process, more correctly called redox condensation, resulting in cluster build-up, can also be achieved between the carbido-stabilised, decanuclear cluster anion $[Os_{10}C(CO)_{24}]^{2-}$ and $[Hg(O_3SCF_3)_2]$ to afford the anion $[\{Os_{10}C(CO)_{24}\}_2Hg]^{2-}$, Figure 6. Here the mercury atom links the two decanuclear clusters by bridging an edge of each Os_{10} unit, forming a cluster containing 21 metal atoms (24). In this reaction, the appropriate choice of the mercury(II) salt, $[Hg(O_3SCF_3)_2]$, is the key to the formation of the higher nuclearity mixed-metal cluster. This is partly because the decaosmium dianion precursor has low nucleophilicity (the negative charge being delocalised over the ten metal centres) and because there is an increased propensity for the reaction to follow alternative pathways involving partial degradation or rearrangement of the metal





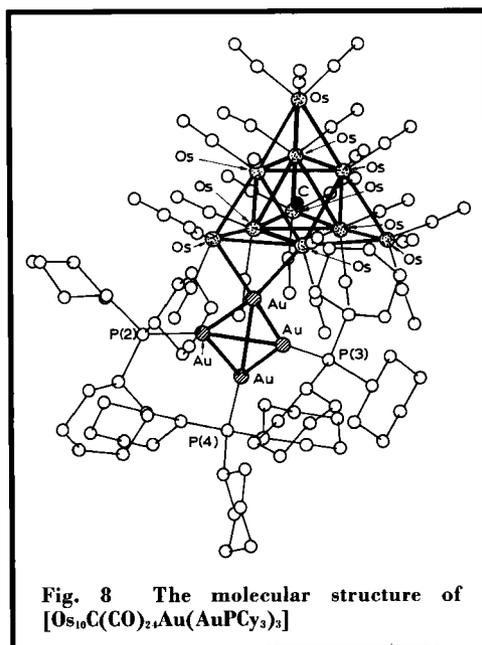
framework. Again, the metal core in this cluster is somewhat asymmetric but has a maximum dimension of approximately 1.6 nm.

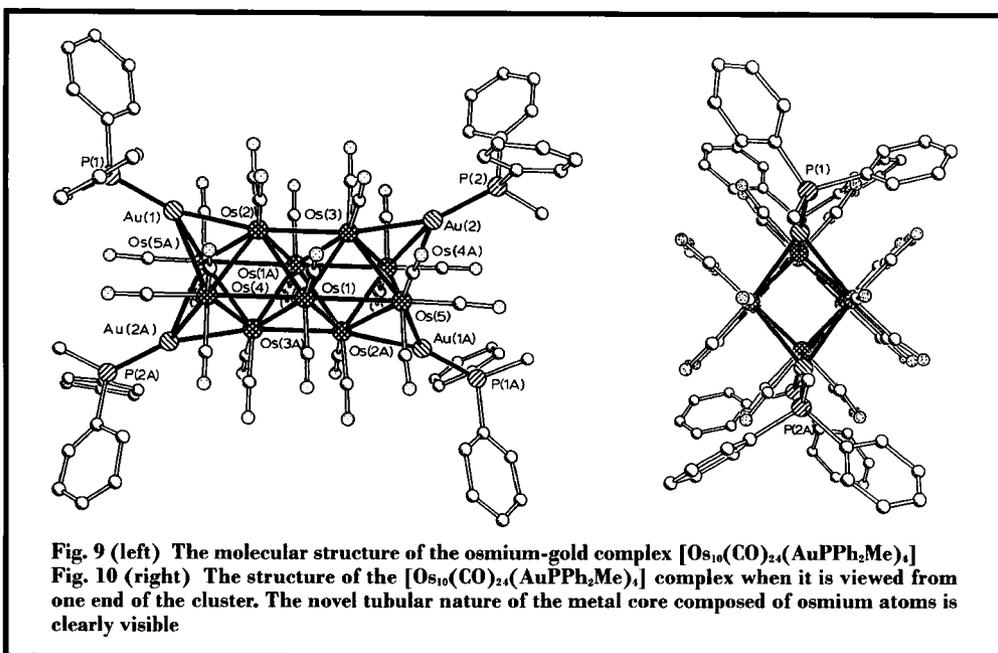
When a similar reaction occurs between $[M_{10}C(CO)_{24}]^{2-}$ ($M = Os, Ru$) and the mercury salt $[Hg(O_2CCF_3)_2]$, a different type of product, $[M_{18}Hg_3C_2(CO)_{42}]^{2-}$, is obtained (24, 25), although the metal core still contains 21 metal atoms. This also contains a central Hg_3 triangle, Figure 7, linking two " $M_9C(CO)_{21}$ " units, derived from the framework of the tetrapped octahedral starting materials $[M_{10}C(CO)_{24}]^{2-}$ by the loss of an " $Os(CO)_3$ " vertex. As in $\{Os_3(CO)_{11}Hg\}_3$ it is of interest that the mercury atoms have linked together between two osmium/ruthenium cores forming, in metallurgical terms, a mercury domain. Another fascinating feature of the cluster dianion $[Os_{18}Hg_3C_2(CO)_{42}]^{2-}$ is that it undergoes reversible photochemical and redox extrusion of mercury atoms to give a complete series of high nuclearity clusters with general formula $[Os_{18}Hg_nC_2(CO)_{42}]^{m-}$ ($n = 1-3, m = 1-4$) (26).

The Hg-Hg bonds in the Hg_3 dianion are an average 2.927 Å long, but in the Hg_2 dianion $[Os_{18}Hg_2C_2(CO)_{42}]^{2-}$, which has also been crystallographically characterised and found to have a pair of mercury atoms linking the two Os_9 units, the Hg-Hg bond is significantly shorter at 2.745 Å long.

Osmium-Gold Clusters

A wide range of reactions which form high nuclearity osmium-gold clusters has been carried out (27), but this discussion will be restricted to two key syntheses which yield important information about the build-up processes in high nuclearity clusters. The first reaction is that between $[Os_{10}C(CO)_{24}]^{2-}$ and the polygold cation $[(AuPR_3)_3O]^+$ ($PR_3 = PCy_3, PPh_3, PMe_2Ph$) which affords the fourteen atom cluster $[Os_{10}C(CO)_{24}Au(AuPR_3)_3]$ (28). The structure of the PCy_3 derivative has been characterised crystallographically and is shown in Figure 8. The tetrapped octahedral geometry of the parent Os_{10} dianion is retained, and the four gold atoms form a tetrahedral cluster which is linked to the osmium core via one gold atom that bridges an Os-Os edge of one of the





tetrahedral caps. The mean Au-Au distance within the Au₄ tetrahedron is only 2.71 Å, which suggests that the Au-Au bonds are relatively strong. As also observed for the osmium-mercury clusters, the gold atoms have a tendency to “cluster” together to form a domain, and do not become incorporated into the osmium atom framework.

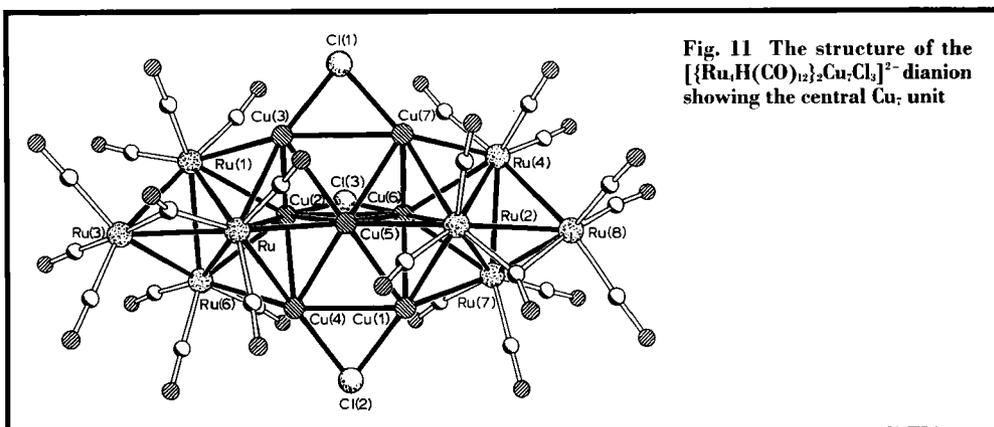
In the second key reaction the non-carbido decaosmium cluster dianion $[\text{Os}_{10}(\text{CO})_{26}]^{2-}$ is further reduced with $\text{K/Ph}_2\text{CO}$, presumably to give a tetra-anion, that is treated *in situ* with $[\text{AuPPh}_2\text{Me}]^+$ to give a new type of high nuclearity cluster $[\text{Os}_{10}(\text{CO})_{24}(\text{AuPPh}_2\text{Me})_4]$, see Figure 9 (29).

At first sight, from the structure of this fourteen atom cluster, it appears that the four $[\text{AuPPh}_2\text{Me}]^+$ cations merely cap the four end faces of a biocuboctahedral osmium core, but the view looking from one end of the cluster to the other, Figure 10, shows that the octahedra are distorted and that a novel tubular structure has formed. The Os-Os equatorial edges [Os(4)-Os(5a), Os(1)-Os(1a), Os(5)-Os(4a)] have expanded to lie in the range 3.29–3.32 Å, a distance that is significantly longer than is judged

to indicate a bonding interaction, while the *trans* axial osmium atoms [Os(2)...Os(3a) and Os(3)...Os(2a)] have moved closer together than would be expected in an octahedron, to an average distance of 3.3 Å. The pairs of gold atoms are separated by 4.43 Å, and the length of the tube including the gold phosphine groups exceeds 1 nm. In order to support this type of geometry the metal bonding must be delocalised in character.

Ruthenium-Copper Clusters

Of all the cations discussed above, $[\text{Cu}(\text{NCMe})_4]^+$ is the most versatile for use in cluster build-up reactions. It has been used in combination with a number of ruthenium cluster anions to produce a range of novel, high nuclearity, mixed copper-ruthenium clusters. For example, in dichloromethane, the reaction of the octahedral ruthenium anion $[\text{Ru}_6(\mu_6\text{-H})(\text{CO})_{18}]^-$ with an excess of $[\text{Cu}(\text{NCMe})_4]^+$ affords the dianionic cluster $[\{\text{Ru}_4\text{H}(\text{CO})_{12}\}_2\text{Cu}_7\text{Cl}_3]^{2-}$, see Figure 11 (30). The fifteen-atom cluster core contains two Ru₄ tetrahedra linked through a Cu₇ unit which may be described as two fused square-based



pyramids sharing a common triangular face. Three chloro ligands each symmetrically bridge pairs of copper atoms, while the remaining copper atom, Cu(5), forms no bonds with ligands but has eight metal contacts. Thus, the immediate environment around Cu(5) is similar to that in metallic copper and, overall, again it is seen that the element with the formal d^{10} electron configuration has formed the central domain, and the transition metal units are fused to its periphery.

The product of this reaction is very sensitive to the nature of the solvent used. In the presence of $[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in MeCN, when $[\text{Ru}_6\text{H}(\text{CO})_{18}]^-$ is treated with a large excess of $[\text{Cu}(\text{NCMe})_4]^+$, a different product, $[\{\text{Ru}_6\text{H}(\text{CO})_{17}\}_2\text{Cu}_6\text{Cl}_2]^{2-}$, is obtained in good yield, see Figure 12 (30). In this case degrada-

tion of the original Ru_6 octahedron has not occurred, and the two octahedra are linked through two Cu₂ tetrahedra which share a common edge, generating two butterfly arrangements which bond to the ruthenium units. Overall, the eighteen-atom cluster can be viewed as a linear condensation of four octahedra. Two edges of the Cu_6 unit are symmetrically bridged by chloride ions.

For both reactions, the presence of chloride ions is apparently necessary, even if, in the first case, they are abstracted from the solvent. However, by simply altering the solvent, from dichloromethane to $[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ in MeCN, good yields of high nuclearity clusters with ruthenium:copper ratios of 8:7 (approximately 1:1) and 2:1, respectively, are obtained from a room temperature reaction.

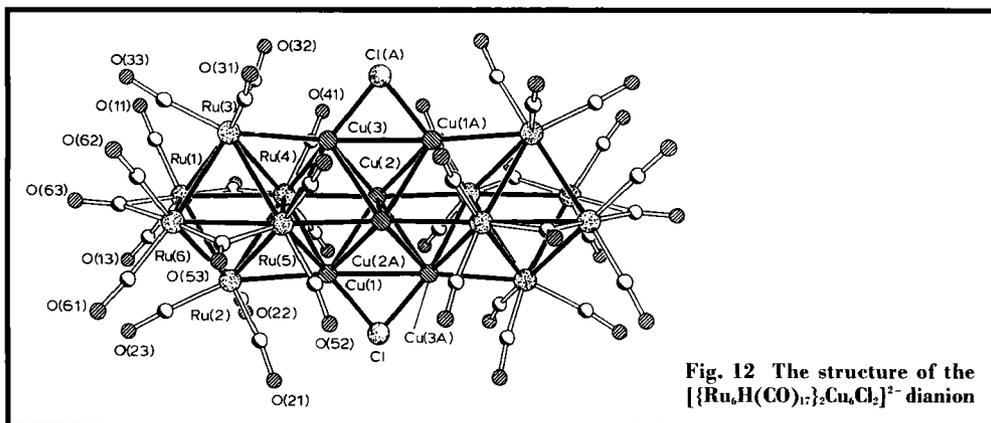
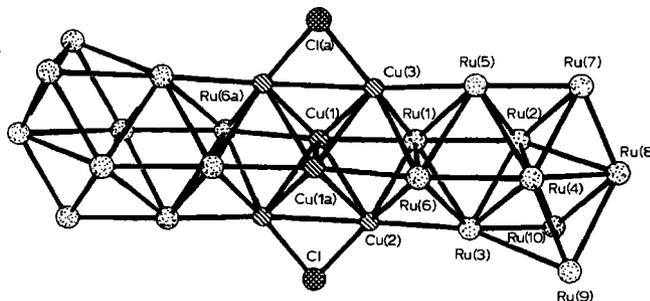


Fig. 13 The core geometry in the $[\{\text{Ru}_{10}\text{H}_2(\text{CO})_{24}\}_2\text{Cu}_6\text{Cl}_2]^{2-}$ dianion



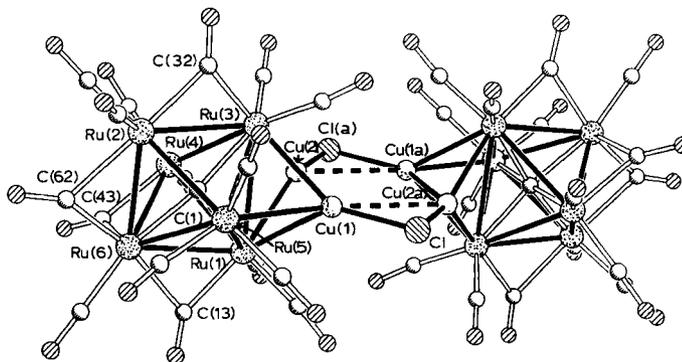
This synthetic methodology can be expanded further. The reaction of the decanuclear dianion $[\text{Ru}_{10}\text{H}_2(\text{CO})_{25}]^{2-}$ with excess $[\text{Cu}(\text{NCMe})_4]^+$, in dichloromethane, in the presence of chloride ions, affords the twenty-six-atom cluster $[\{\text{Ru}_{10}\text{H}_2(\text{CO})_{24}\}_2\text{Cu}_6\text{Cl}_2]^{2-}$ with a 70 per cent yield and a ruthenium:copper ratio of 10:3 (31). Here, the two Ru_{10} units are fused on either side of a Cu_6 unit which adopts the same geometry as that found in $[\{\text{Ru}_6\text{H}(\text{CO})_{17}\}_2\text{Cu}_6\text{Cl}_2]^{2-}$ (Figure 12). The overall core geometry can be described as six fused octahedra with an additional ruthenium atom at each end capping a butterfly face to form a trigonal bipyramid, Figure 13; this metal framework is over 1.6 nm long.

In order to investigate the role of the chloride ions in these reactions, the carbido dianion $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ was treated with CuCl , instead of the $[\text{Cu}(\text{NCMe})_4]^+$ cation, and $[\{\text{Ru}_6\text{C}(\text{CO})_{16}\}_2\text{Cu}_6\text{Cl}_2]^{2-}$, another high

nuclearity cluster, was obtained in quantitative yield, see Figure 14 (32). The two Ru_6 octahedra are linked by a rectangular planar arrangement of four copper atoms, opposite edges of which are bridged by chloride ions. Thus, with chloride ions present in the starting material the cluster build-up is not so efficient, resulting in a sixteen-atom cluster with a ruthenium:copper ratio of 3:1, but the yields of the product are improved.

In all of the copper-ruthenium clusters investigated, the copper atoms condense to form a central domain and the ruthenium cluster units condense around the periphery to produce nanosized particles based on the fusion of octahedral or tetrahedral units, just as is observed in other high nuclearity clusters and in close packed metals (3). The advantage of the strategy employed in the synthesis of these copper-ruthenium clusters is that by carefully controlling the reaction conditions, nanosized particles with

Fig. 14 The structure of the dianion $[\{\text{Ru}_6\text{C}(\text{CO})_{16}\}_2\text{Cu}_6\text{Cl}_2]^{2-}$

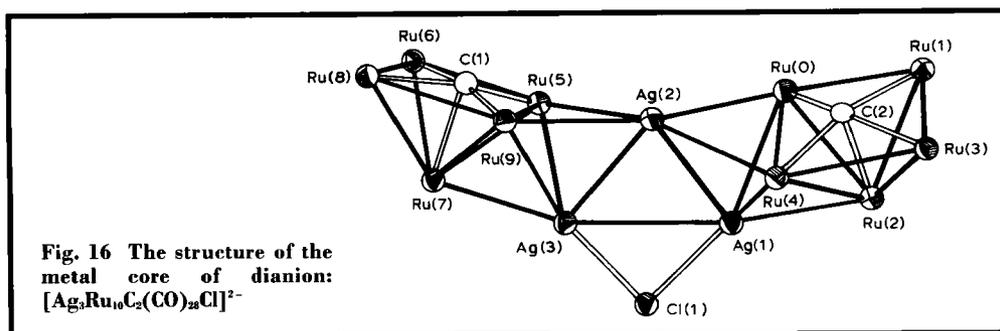


or $[\text{N}(\text{PPh}_3)_2]^+$. Interpretation of EXAFS data has enabled specific models to be developed for the catalyst particle nanostructures which correlate with their catalytic activities. The more active catalysts are modelled by a hemisphere of close packed metal atoms, with an average diameter of 1 nm, with iridium at the core. In a series of related studies, Shapley has also shown that $[\text{PtRu}_5\text{C}(\text{CO})_{10}]$ can be used as a neutral cluster precursor for the formation of carbon-supported platinum-ruthenium nanoparticles with exceptionally narrow size and composition distributions (36). The bimetallic particles are obtained by reduction of the carbido cluster with hydrogen. A detailed structural model of the nanoparticles was deduced on the basis of *in situ* EXAFS, scanning transmission electron microscopy, microprobe energy-dispersive X-ray analysis and electron microdiffraction studies. These experiments show that the nanoparticles have a Ru:Pt ratio of 5:1, an average diameter of approximately 1.5 nm and adopt a face centred cubic close packed structure. This is in contrast to the stable phase of the bulk alloy which is hexagonal close packed. The EXAFS studies also show that there is a non-statistical distribution of different metal atoms in the nanoparticles: the platinum atoms exhibit preferential migration to the surface of the particles under an atmosphere of dihydrogen.

Of particular interest is a recent report by Johnson, Thomas and colleagues that a cluster anion $[\text{Ag}_3\text{Ru}_{10}\text{C}_2(\text{CO})_{28}\text{Cl}]^{2-}$ (Figure 16) with a structure in which a central Ag_3 triangle links two Ru_5 square based pyramids, closely related to the copper-ruthenium systems

described above, had been successfully anchored inside mesoporous silica (37). Activation and anchoring of the adsorbed cluster on the MCM-41 silica support was achieved by heating the sample under dynamic vacuum. EXAFS spectroscopy confirmed the presence of a bimetallic particle anchored to the silica oxygen atoms through the silver atoms of the cluster. High-resolution electron microscopy of the heat-treated material shows a uniform distribution of the bimetallic nanoparticles aligned along the zeolite channels. The catalytic performance of the activated, supported bimetallic particles was tested for hydrogenation of hex-1-ene to hexane. Initial experiments showed a high selectivity (in excess of 99 per cent) and a turnover frequency of at least 6300 mol hexane per mol $[\text{Ag}_3\text{Ru}_{10}]$ per hour.

The success of these studies led to the incorporation of the copper-ruthenium cluster anion, $[\{\text{Ru}_6\text{C}(\text{CO})_{10}\}_2\text{Cu}_4\text{Cl}_2]^{2-}$, described previously (Figure 14) (32), into the mesoporous channels of silica (38). Gentle thermolysis of the anchored clusters gives the bimetallic nanoparticles, characterised by X-ray absorption and FT-IR spectroscopies, and high-resolution scanning transmission electron microscopy. The copper and ruthenium *K*-edge X-ray absorption spectra show that these catalytically active particles have diameters of approximately 1.5 nm and display a rosette-shaped structure with 12 exposed ruthenium atoms that are connected to a square base composed of relatively concealed copper atoms. In turn, these are anchored by four oxygen bridges to four silicon atoms of the mesopore. The nanoparticles are



active catalysts for the hydrogenation of hex-1-ene, diphenylacetylene, phenylacetylene, stilbene, *cis*-cyclooctene and D-limonene, with turnover frequencies of 22400, 17610, 70, 150 and 360, respectively, at 373 K and 65 bar of dihydrogen. The catalysts showed no tendency to sinter, aggregate or fragment into their component metals during these experiments.

Conclusions

In this review it has been shown that synthetic strategies to prepare high nuclearity, bimetallic clusters in good yields have been developed. The metal cores of these clusters have dimensions in excess of 1 nm. By careful control of reaction conditions it is possible to obtain specific target molecules with known ratios of the two metallic components, and the methodology may be extended further to encompass the majority of the late transition elements. In the "condensed" clusters obtained, for the major-

ity of the osmium/mercury, ruthenium/mercury, osmium/gold and copper/ruthenium systems investigated, the mercury, gold or copper atoms form a central domain and the osmium or ruthenium cluster units are fused onto the periphery of these central units. In no case did the two metallic components become dispersed throughout the metal core. Lastly, evidence is beginning to emerge that nanoparticles derived from these and related clusters may prove to be active catalysts when anchored on silica or alumina supports.

Acknowledgements

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Construction of Miniature Organo-Rhodium Boxes

Many types of molecular cages exist in which ions, atoms or molecules can be trapped. These cages are usually held in suspension and are typically constructed from bifunctional ligands, with square planar or tetrahedral metal centres at the vertices. Until now there have been no cubic shaped organometallic cages. However, if octahedral transition metal building blocks could be constructed, then the assembly of cubic-shaped structures should be possible.

Now, researchers from the University of Illinois have succeeded in constructing a molecular box from a cubic array of cyano-linked rhodium and cobalt octahedra (K. K. Klausmeyer, T. B. Rauchfuss and S. R. Wilson, *Angew. Chem. Int. Ed.*, 1998, **37**, (12), 1694–1696).

Tricyanometalates $\text{Et}_4\text{N}[\text{Cp}^*\text{Rh}(\text{CN})_3]$ and $\text{K}[\text{CpCo}(\text{CN})_3]$ (where $\text{Cp}^* = \text{C}_5\text{Me}_5$, $\text{Cp} =$

C_5H_5) were used to prepare a series of molecular "squares", by reaction with $[\text{Cp}^*\text{RhCl}_2]_2$ or $[(\text{cymene})\text{RuCl}_2]_2$ (cymene = 4-isopropyltoluene). To assemble the box from the "squares" the chloride ligands were removed by AgPF_6 . The "molecular boxes" of most interest have the structure $[(\text{C}_5\text{R}_5)_8\text{M}_8(\mu\text{-CN})_{12}]$ ($\text{M} = \text{Rh}$ or Co) and are a subunit of hexacyanometalates, of which Prussian blue is one example.

The most interesting box has alternate rhodium and cobalt atoms at the vertices, linked by CN groups. Each metal atom can adopt its preferred octahedral position. The box has edges 5.1 Å long with a volume of $\sim 132 \text{ \AA}^3$, giving enough space inside to encapsulate a caesium atom. The box is also soluble so it could therefore be used for trapping molecules in solution.