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From clusters to nanoparticles and catalysis

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Contents

Abstract

Over the past two decades or so there has been sustained interest in the synthesis, characterisation and chemistry of transition metal clusters. In this paper we shall briefly review aspects of more recent advances in the chemistry of large metal clusters and go on to consider their application to nanoscale devices and as a precursors of stable and highly active, naked nanoparticles as catalysts. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Catalysts; Nanoparticles; Transition metal clusters

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1. Introduction

Over the past two decades or so there has been sustained interest in the synthesis, characterisation and chemistry of transition metal clusters [1]. Aside from the intrinsic interest in these compounds, which provide an opportunity to examine the evolution of properties associated with the bulk state, the continued high level of activity in this area is almost certainly due to:

1. the suggestion [2] that they might serve as good homogeneous catalysts with all the advantages of both the enhanced activity of a homogeneous system and the unique chemistry of a heterogeneous metallic system;
2. the proposition [3] that such clusters might serve as good building blocks in nanoscale architectures and as such find application in single electron device fabrication;
3. the recent observation [4] that many clusters may serve as precursors to highly active small particulates and catalysts, and;
4. the proposition [5] that clusters provide good models for chemistry occurring at the surface.

1.1. The metallic state(s)

Examination of the divided states of metals (Fig. 1) shows that between the extremes of the bulk on the one hand, and the single metal atom or ion on the other, there lies a complete spectrum of intermediate types ranging from small ligated (or naked) clusters falling in the size regime of 10–20 Å to colloidal particles falling in the regime 10^2–10^3 Å. Some years ago we posed the simple question:

> What would be the structural, electronic and chemical characteristics of these intermediate metallic types?

This led us to a long and sustained investigation of the synthesis, characterisation, and study of the chemistry and physics of metal clusters and small metal particles (colloids) and to an investigation of their use in 'new' nanoscale materials.

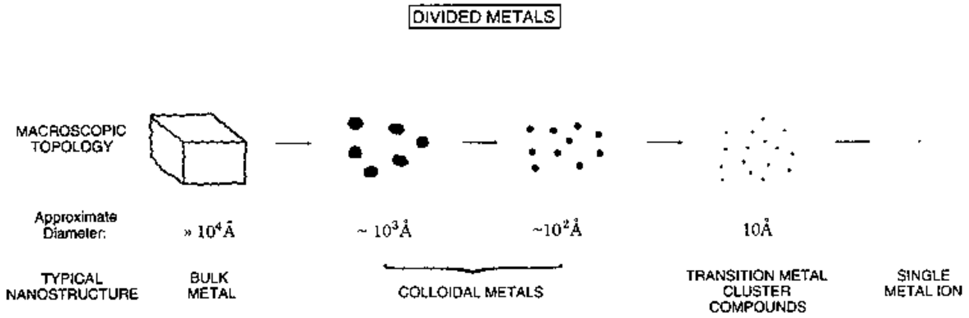
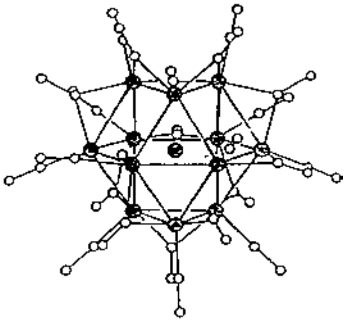


Fig. 1. The divided metals.



$[Rh_{13}(CO)_{24}H_3]^{2-}$

Fig. 2. The molecular structure of $[H_3Rh_{13}(CO)_{24}]^{2-}$.

1.2. Transition metal clusters

When we began our studies few metallic clusters were known and we developed our approach to these fascinating compounds on the back of our studies of the metal carbonyls and their use as synthetic organometallic reagents. Throughout, we have tended to restrict our attention to clusters containing the carbonyl or other related ligand types.

Many synthetic routes to ligated clusters have been employed; these may be divided broadly into two categories, namely either gas-phase or condensed-phase synthesis. The preparation of cluster complexes in the condensed-phase, via chemical synthesis using either thermal or photochemical activation to promote reaction, although historically the older approach, has been very successfully applied. To date, the formation of such fully coordinatively saturated clusters in the gas-phase remains an almost accidental affair, and few systematic routes appear to have been devised. The more recent developement of gas-phase techniques, such as laser vaporisation provides a route to high nuclearity refractory metal clusters which are ligand-free, although these have yet to be isolated or structurally characterised to any significant degree.

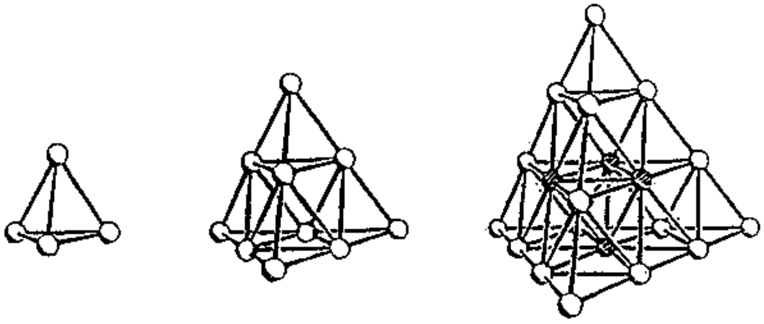
1.3. Larger metal clusters

Early work by Chini and his group [6] led to the synthesis and characterisation of the Rh_{13} cluster $[H_{5-n}Rh_{13}(CO)_{24}]^{n-}$ ($n = 2$ or 3) (Fig. 2) and the subsequent formation of the two related cluster anions $[Rh_{14}(CO)_{25}]^{4-}$ and $[Rh_{15}(CO)_{27}]^{3-}$. The Rh_{13} cluster is remarkable in that it possesses a molecular structure which closely approximates to the unit cell of a conventional hexagonal close-packed arrangement of metal atoms. This polyhedral unit is embraced within a sheath of 24 carbonyl ligands, while the H-ligands occupy the interstitial sites within the metal polyhedron mimicking the chemistry of the bulk. These observations lent credence to the view that clusters could serve as ideal homogeneous catalysts with the activity of the bulk. The Rh_{14} cluster approximated to the ccp arrangement, and for the first time the transformation of one metallic structural type (Rh_{13}-hcp) to another (Rh_{14}-ccp) had been demonstrated on the molecular scale.

In our work we have tended to concentrate on the chemistry of Ru and Os clusters, and about 10 years ago were able to prepare the Os_{20} cluster, $[Os_{20}(CO)_{48}]^{2-}$ (Fig. 3), with a perfect ccp arrangement of metal ions [7]. At the time we also found limited evidence for the next member of the tetrahedral growth sequence based on the Os_{35} unit. It is important to note that in the structure of the Os_{20} dianion the 48 carbonyl groups provide a protective sheath about the central metal core and their arrangement corresponds closely to that seen for the packing of such molecules on the metallic surface emphasising the usefulness of clusters as models for binding at the bulk surface.

1.4. Linked heteronuclear compounds

Complementing these studies has been our work on heteronuclear systems. Our initial intention was merely to develop good synthetic routes to linked metal clusters. The approach we adopted followed naturally from studies by us and others on the reactions of metal carbonyls or metal carbonyl anions with metal salts, for example, that of $[H_2Ru_{10}(CO)_{25}]^{2-}$ with $[Cu(MeCN)_4]^+$ to produce the mixed Ru–Cu cluster dianion $[H_4Ru_{20}Cu_6Cl_2(CO)_{48}]^{4-}$ (Fig. 4). We were particularly interested in cluster units linked by mercury since earlier work by others on simple systems, e.g. $Hg[Co_2(CO)_8]$ had shown that they were photosensitive liberating mercury and regenerating $[Co_2(CO)_8]$ on irradiation. In our work we were able to prepare the trimercury compound $Hg_3[Os_{18}C_2(CO)_{42}]$ from the reaction of the decaosmium anion $[Os_{10}C(CO)_{24}]^{2-}$ and $Hg(CF_3CO_2)_2$ (see Scheme 1). This compound which resembles a molecular wire with the central metal core surrounded by a sheath of CO ligands exhibits both photochemical and electrolytic behaviour (see Scheme 2).



$H_4Os_4(CO)_{12}$ $[Os_{10}(CO)_{24}]^{2-}$ $[Os_{20}(CO)_{48}]^{2-}$

Fig. 3. The molecular structure of the dianion $[Os_{20}(CO)_{48}]^{2-}$.

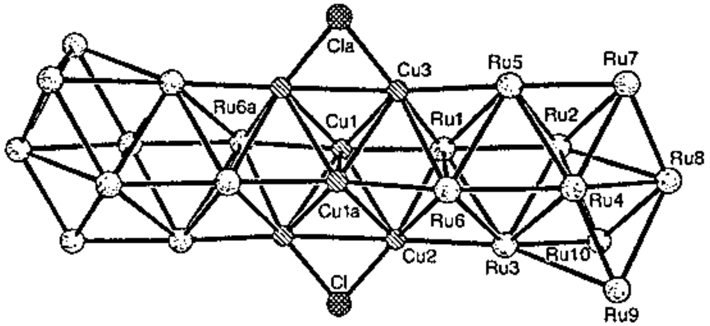
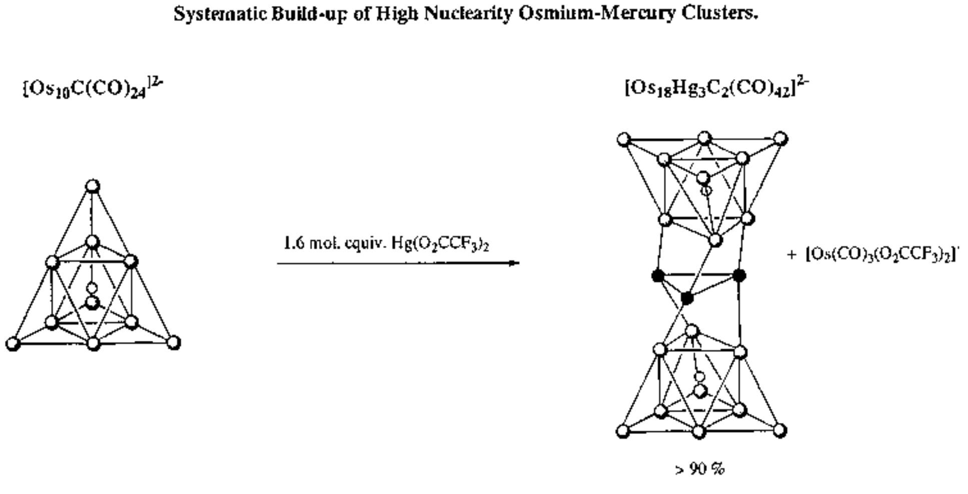


Fig. 4. The molecular structure of the heteronuclear cluster $[H_4Ru_{20}Cu_6Cl_2(CO)_{48}]^{2-}$.

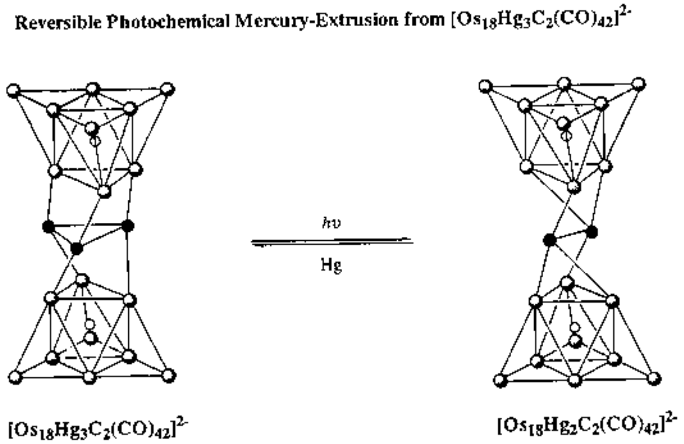
1.5. New synthetic approaches

We recently became interested in developing a new approach which involves laser desorption (see above) of preformed polynuclear transition metal complexes for the preparation of well-defined supramolecular metal clusters in sufficient concentration for isolation and subsequent characterisation by spectroscopic and diffraction methods. Previous attempts, involving laser photodissociation in the gas-phase of volatile transition metal carbonyls such as $[Ru_3(CO)_{12}]$, have not been successful, resulting only in ligand stripping and fragmentation [8]. However, in recent work [9], we have been able to show that it is possible to form very high nuclearity clusters by laser desorption of preformed polynuclear transition metal carbonyls.

These initial experiments were carried out on tetra- and hexaruthenium clusters carrying facially bonded arene ligands $\{[Ru_4(CO)_{12}(C_6H_6)]$ and $[Ru_6C(CO)_{14}(C_6H_6)]\}$ and which, on the basis of single-crystal X-ray diffraction



Scheme 1. Reaction of the dianion $[Os_{10}C(CO)_{24}]^{2-}$ with Hg salts.



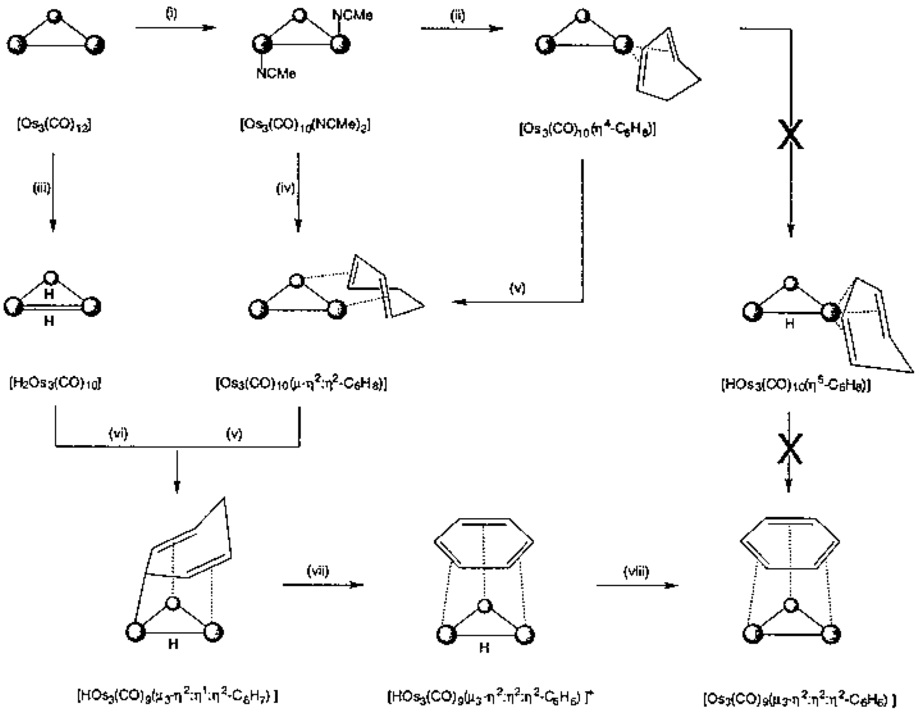
Scheme 2. Electrolytic and photochemical behaviour of $[Hg_3\{Os_{18}C_2(CO)_{38}]^{2-}$.

studies, appeared to form supraclusters in the solid through arene–arene (graphitic-like) interactions (see below). The samples, in the form of a solid target deposited from a suspension in dichloromethane, were irradiated with the focused output of a N_2 laser (337 nm). Ion production was monitored using time-of-flight mass spectrometry. For the tetraruthenium complex, the negative ion mass spectrum revealed a remarkably intense series of high mass ions, extending beyond 8000 Da, which correspond to 'supraclusters' of the original tetraruthenium complex. Similar, although less marked, behaviour was found for the hexaruthenium complex [11]. As yet, the precise mechanism for this novel aggregation mechanism remains unclear. The presence of the arene ligands was initially thought to be important for the self-assembly of these supraclusters but in subsequent work we were able to establish that this does not appear to be necessary. In very recent studies of the hexaruthenium complex, $[Ru_6C(CO)_{17}]$, we have observed supraclusters which extend to masses in excess of 35 000 Da. Again, the mechanism by which these species are produced is unclear, although the gas-phase ion-molecule chemistry which may be responsible for the formation of such high mass clusters seems to involve coalescence of the partially stripped polynuclear cores.

Although so far only the positive and negatively charged cluster ions have been observed, neutral clusters must also be formed. Laser vaporisation cluster sources, or oven-based versions, produce gas-phase samples having cluster densities of ca. 10^{10} cm^{-3}. This new technique promises to allow production of gas-phase densities exceeding ca. 10^{15} clusters cm^{-3}, which should be adequate for micro-synthetic and reactivity studies, or for film deposition.

1.6. Organometallic clusters

An aspect of cluster chemistry which has been particularly attractive to us, has been that of organometallic derivatives containing arene ligands [12]. The main impetus driving these studies was initially the comparative behaviour of benzene on the bulk surface and the cluster surface [10]. However, we were also keen, for purely 'artistic reasons', to produce the first cluster sandwich compounds analogous to *bis*(benzene)chromium. Work on triosmium dodecarbonyl [13] led us to the target molecule $[(C_6H_6)_2Os_3(CO)_6]$ (see Scheme 3). However, this proved-on the basis of single-crystal X-ray analysis-to have the *cis*- rather than the required *trans*-configuration of benzene groups [14]. Nevertheless, examination of the crystallographic structure by single-crystal X-ray analysis revealed significant graphitic-like interaction between the coordinated benzene ligands on adjacent molecules in the lattice (Fig. 5). In other related studies on $[Ru_6C(CO)_{17}]$, we were able to prepare and characterise the first cluster sandwich compound $[Ru_6C(CO)_{11}(C_6H_6)_2]$ (Fig. 6) entirely analogous to *bis*(benzene)chromium [15]. Significantly this compound and a whole host of related derivatives also exhibited the same type of arene–arene (graphitic interaction) in the solid. This cluster-unit–cluster-unit interaction is even more apparent when the clusters are subjected to pressure when a very marked change in colour is observed suggesting the possibility of electron transfer through the graphitic like bridges.



Typical synthetic routes to arene cluster complexes employing chemical activation. (i) $2.2Me_3NO$, MeCN; (ii) C_6H_8 in CH_2Cl_2 ; (iii) H_2 in CH_2Cl_2; (iv) C_6H_8, Δ in octane; (v) Δ in octane; (vi) C_6H_8, Δ in octane; (vii) $[Ph_3C][BF_4]$; and (vii) DBU.

Scheme 3. Synthesis of $\{Os_3(CO)_9(C_6H_6)]$.

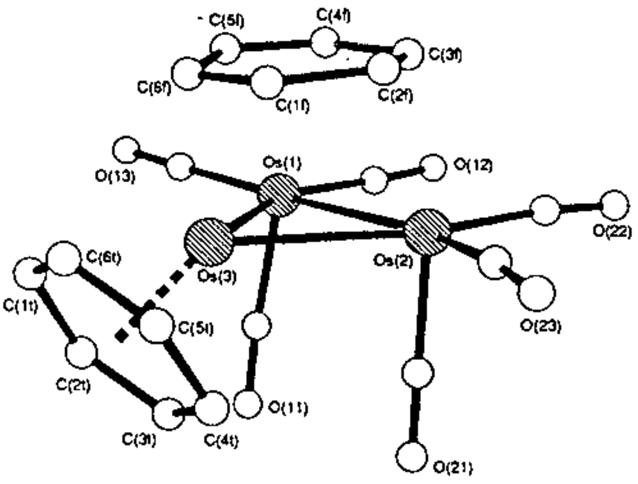


Fig. 5. The crystallographic structure of $[Os_3(CO)_9(C_6H_6)_2]$.

These observations led us to consider the possibility of generating materials with direct cluster-unit–cluster-unit interaction through organo-bridges. To us it seemed that the cyclophanes provided ideal templates with the possibility of 2-, 3, or 4-fold linking units (see Fig. 7). Using these ligands we have been able to design and produce a number of linked $[Co_4(CO)_n]$ cluster based materials (see Fig. 8) [16].

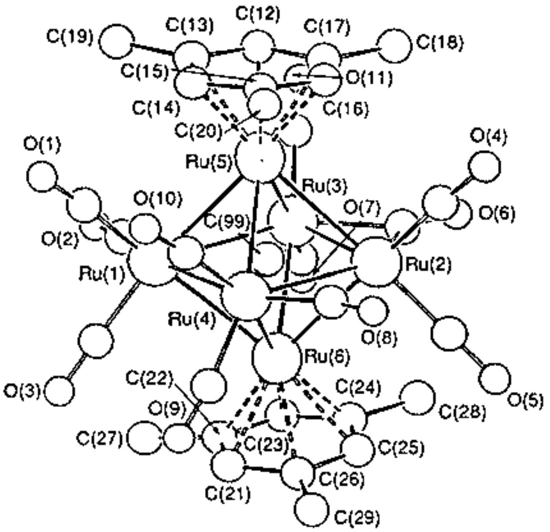


Fig. 6. The molecular structures of the first cluster sandwich compound $[Ru_6C(CO)_{11}(C_6H_6)_2]$.

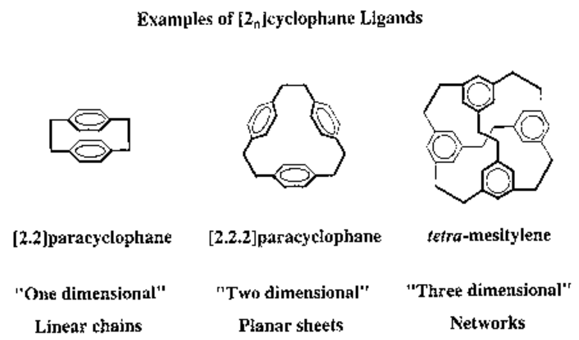
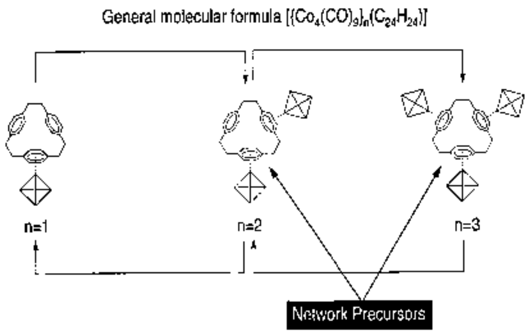


Fig. 7. Cyclophanes as linking units.

(a) *Tetra*-cobalt and [2.2.2]paracyclophane



(b) Connectors in organometallic networks

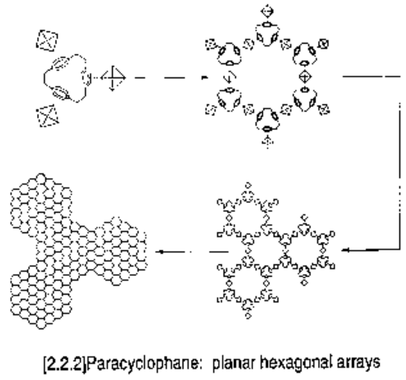


Fig. 8. Linked cobalt clusters.

2. Nucleation and growth of nanoparticle lattices and wires

The classic view of a carbonyl cluster is of a central metal core surrounded by essentially a non-conducting ligand envelope. However, an alternative view of a ligated cluster is shown in Fig. 9. Here we visualise the carbonyl cluster as a small metal island serving as an electron localised site surrounded by a carbonyl (or organometallic) sheath serving as an electron tunnel barrier. Viewed as such, these species provide ideal building blocks for the developement of nanoscale architectures in which one-, two or even three-dimensional arrays of small metallic islands are separated from each other by tunnel barriers. Electronic conduction in such structures can be varied from the metallic to the insulating limit by controlling the size of the metallic islands and the strength of the coupling between them.

Single electronics, among quantum functional device concepts, provides the strongest motive for advancing such nanofabrication technologies since the operating temperature of single electron devices is directly determined by the geometrical size of the electron localisation. The progress of lithography technology fails to satisfy the requirements arising from single electronics; a requirement which extends to a size range of a few nanometers or less. Clearly, ligated metal clusters or small colloidal particles satisfy these requirements.

In this work, methods of forming such architectures using clusters of the type described have been investigated and successful approaches to the formation of both a hexagonally-packed two-dimensional array, and linear chains of gold nanoparticles have been developed. In the gold work a sample of SiO_2 is reacted with the compound $[(MeO)_3Si(CH_2)_3NHCH_2CH_2NH_2]$; the OH functional groups remaining on the surface of the silica undergo a cross-linking reaction to produce the ligated surface shown in Fig. 10. This surface is then treated with a solution of a preformed gold colloid of the desired size to produce a submonolayer deposition of

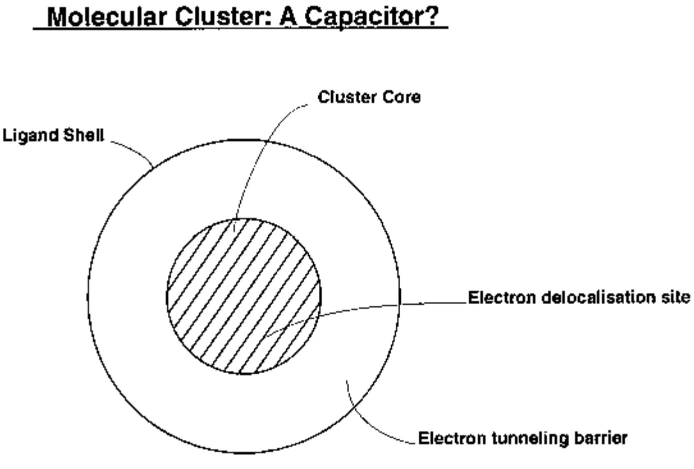


Fig. 9. The cluster as a capacitor.

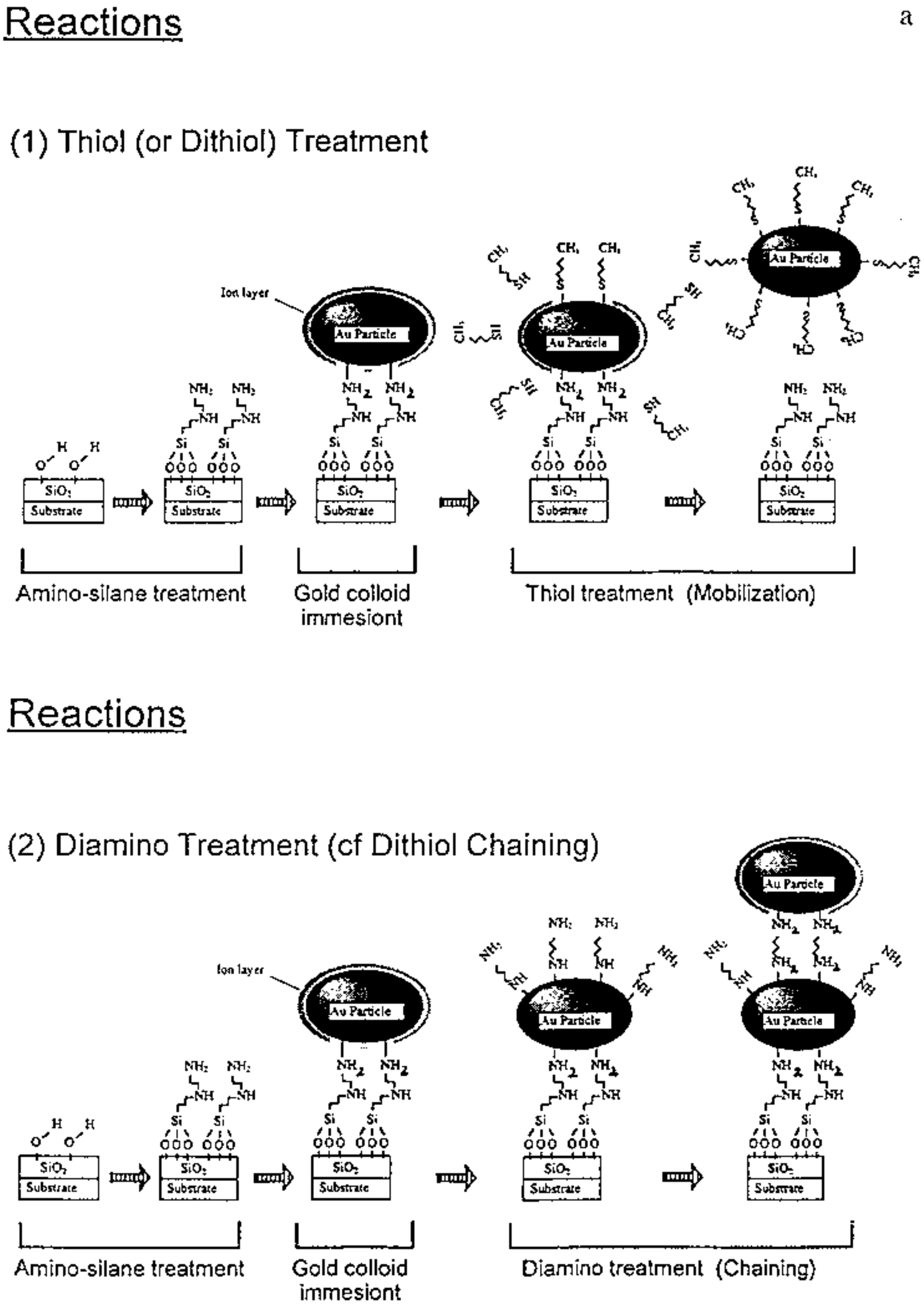


Fig. 10. Formation of a two-dimensiona1 lattice of gold particles.

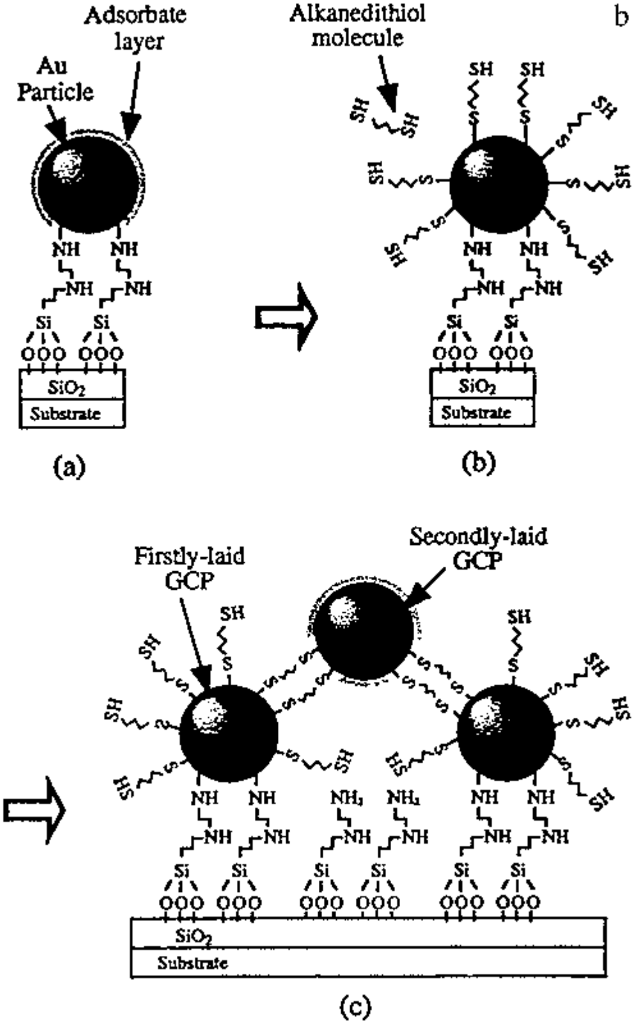


Fig. 10. (*Continued*)

gold particles which are bonded directly to the surface through the amine ligand. In turn, this material is treated with the monothiol [Me(CH$_2$)$_{11}$SH] which displaces the gold particles to bring about the nucleation of the gold colloidal crystal as shown in Fig. 10(a). Repetition of this process causes the vacancies in the array to be filled leading eventually to a highly ordered two-dimensional array of gold particles (see Fig. 11). Scanning electron microscopy of this highly ordered array shows that the average gap between the particles is about 2 nm which is about the same as twice the thickness of the dodecanethiol, confirming that the interparticle distances are determined by the size of the ligating substrate.

In a slightly modified procedure, the monothiol is replaced by the corresponding dithiol (Fig. 10). Here chains of gold particles are more readily

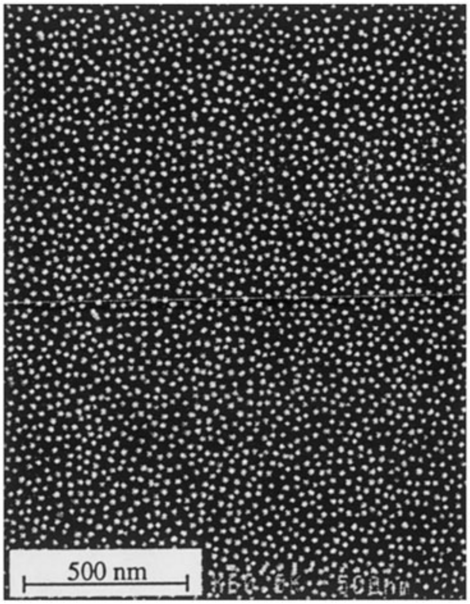


Fig. 11. Highly ordered two-dimensional array of gold particles.

produced. Under the correct experimental conditions these chains may be encouraged to form the source and drain metal electrodes defined by electron beam lithography (see Fig. 12); thus realising a quasi-one dimensional current path between source and drain. This device exhibits a clear Coulomb staircase at both 4.2 and 77 K.

3. Bimetallic nanoparticle catalysts anchored inside mesoporous silica

There has been considerable interest in the formation, structure and further exploitation of the catalytic activity of bimetallic particles ever since Sinfelt et al. [17] demonstrated the powerful, catalytic reforming properties of alumina-supported Ru–Cu, Pt–Ir, and Pt–Re ensembles. With the advent of readily preparable mesoporous solids possessing pore diameters in the range 25–100 Å and the feasibility of inserting ‘single-site’ centres that are catalytically active in atomically well-defined locations inside such mesopores, the incentive for extending such strategies to the insertion of bimetallic nanoparticles is high. One of the key aims of this work has been the design and production of discrete, supported bimetallic particles of well-defined and tuneable composition; another is to secure the clusters to the support in such away that they are prevented from sintering.

Over recent years we have successfully synthesised a whole range of bimetallic clusters containing, for example Ru–Cu and Ru–Ag units. In this report we shall concentrate, merely for convenience, on:

1. the novel, Ag_3Ru_{10} complex anion $[Ag_3Ru_{10}C_2(CO)_{28}Cl]^{2-}$ prepared from the simple reaction of Ag^+ with the dianion $[Ru_5C(CO)_{14}]^{2-}$;

2. the adsorption of this dianion onto the inner walls of the mesoporous silica (MCM-41), with a pore diameter of about 30 Å, together with spectroscopic proof that it retains its integrity;
3. the subsequent thermolytic conversion of the bound complex into discrete nanoparticles that have been shown (by bright-field and annular dark-field, high-resolution electron microscopy and EXAFS to be firmly anchored inside the siliceous mesopores, and finally;
4. the performance of the nanoparticles as a highly efficient catalyst for the hydrogenation of hex-1-ene.

The selected dianionic cluster was fully characterised before deposition inside the mesoporous silica. According to a single-crystal X-ray analysis (Fig. 13), the dianion is composed of two $Ru_5C(CO)_{14}$ units linked by three Ag atoms in a triangular arrangement which is in turn bridged by a Cl atom.

The chemical integrity of the cluster accommodate inside the MCM-41 was established by IR (Nujol mull) and extended X-ray absorption fine structure

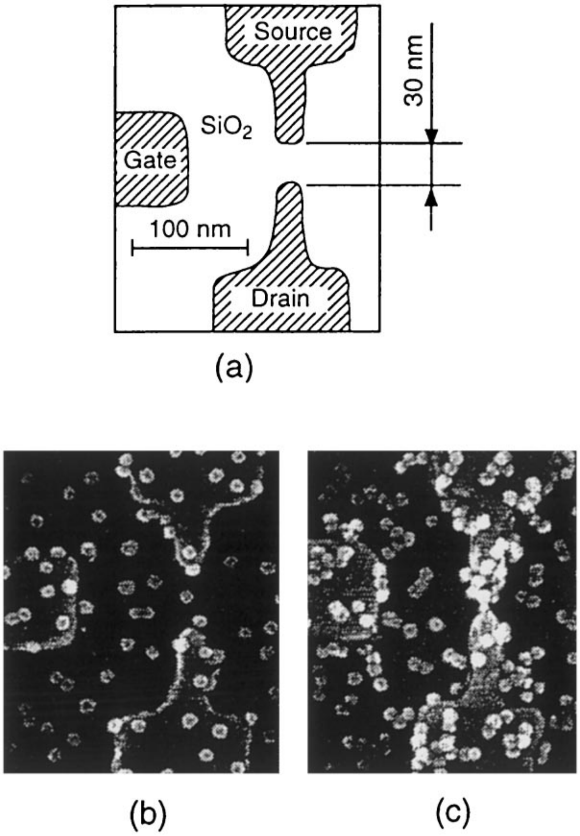


Fig. 12. Potential single-electron device.

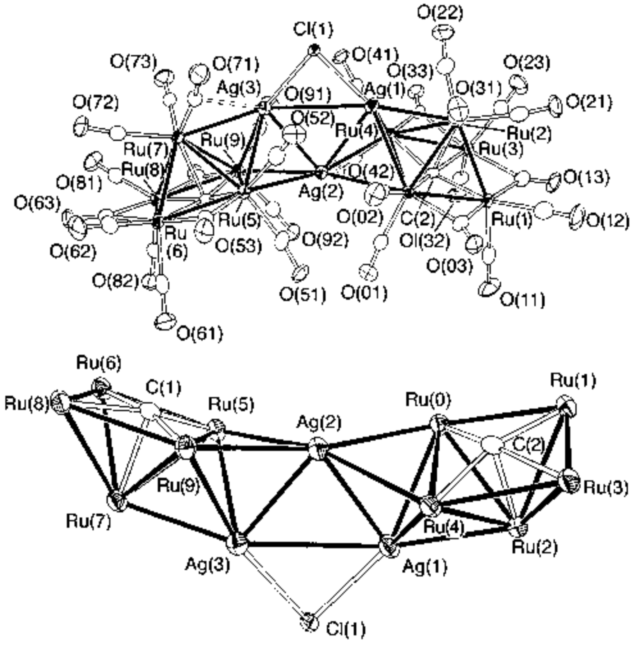


Fig. 13. The molecular structures of the heteronuclear dianionic cluster $[Ag_3Ru_{10}C_2(CO)_{28}Cl]^{2-}$.

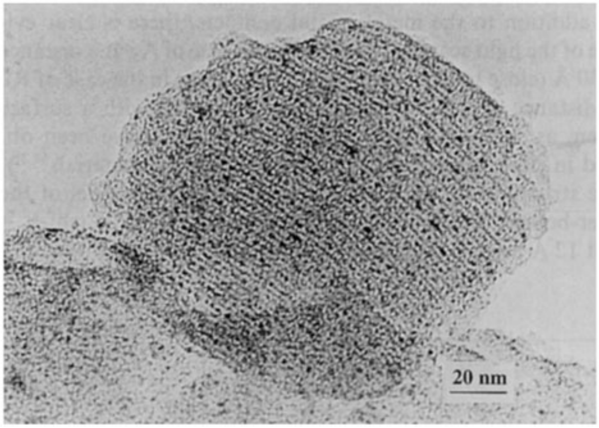


Fig. 14. The distribution of bimetallic nanoparticles in MCM-41.

(EXAFS) spectroscopies. The major bands in the IR spectrum were somewhat broader and shifted to lower frequencies (by about 3 cm^{-1}), which may be due to interaction with the pore wall. The structural parameters extracted from EXAFS analysis (Ru and AgK-edges) correspond well to those established from the single-crystal X-ray structure [18,19].

Activation and anchoring of the adsorbed cluster on the MCM-41 was achieved by heating the sample under dynamic vacuum for 1 h at 473 K. Upon thermolysis, the carbonyl region of the IR spectrum became featureless, and the interatomic distances as determined by EXAFS changed dramatically. The structural parameters established from analysis of the EXAFS data are consistent with the retention of a Ag_3Ru_{10} particle, and the even distribution of the particles throughout the mesopore. Conventional high-resolution electron microscopy of the heat treated material (Fig. 14) clearly indicated the uniform distribution of the bimetallic nanoparticles aligned along the channels of the mesopore. Electron-induced X-ray emission maps further confirm the spatial distribution of the nanoparticles.

The catalytic performance of the activated, supported bimetallic particles was tested for hydrogenation of hex-1-ene to hexane. Initial experiments show a high selectivity and a turnover frequency of at least 6300 mol hexane mol^{-1} $[Ag_3Ru_{10}]$ h^{-1}. In separate experiments we have been able to demonstrate that these highly active particles do not sinter under the conditions applied, and in our view must represent one of the rare examples of genuine cluster catalysis. The potential offered by these systems is enormous. We are able to synthesise directly a comprehensive range of bimetallic clusters containing for example different ratios of Ru to Cu which should permit the role of these bimetallic systems to be more fully explored and understood.

4. Conclusions

In this paper we have discussed the results of our successful application of clusters to nanoscale, single electron devices and to the successful use of clusters as tailored precursors to highly active small metal particles which exhibit good catalytic activity. We consider that these results offer considerable potential for the future.

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