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Using Metal Carbonyl Clusters To Develop a Molecular Approach towards Metal Nanoparticles

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This microreview aims at presenting a personal perspective on the possible contributions of molecular metal carbonyl clusters (MCCs) to a better understanding and development of metal nanoparticles. High-nuclearity molecular MCCs are perfectly (atomically) monodisperse, ligand-stabilised metal nanoparticles with nanometric dimensions. Thus, when the nuclearity of molecular clusters is increased and the dimensions of metal nanoparticles are reduced, these two worlds begin to overlap. Herein, the synthesis of larger MCCs is briefly outlined, together with the description of their structural features and physical properties. The use of molecular MCCs as nanometric or subnanometric building blocks for self-assembly of functional nanomaterials is also reported. Finally, the employment of MCCs as precursors for metal nanoparticles after decomposition of the molecular precursor is described. The purpose of this microreview is to discuss some representative examples of all these topics, showing that one of the most promising and fascinating aspects of molecular MCCs is their borderline nature between molecular chemistry and nanochemistry.

1. Introduction

Metal nanoparticles are one of the most widely studied topics, being the subject of thousands of papers every year. They play a fundamental role in both nanosciences and nanotechnology, with consequences and applications in chemistry, catalysis, optics, sensing, biology and medicine, among others.[1–5] Within this framework, the interest of many scientists has moved during the years towards smaller and smaller metal nanoparticles; obtaining atomically monodisperse ultrasmall metal nanoparticles (smaller than 5 or even 3 nm) is one of the major current goals of nanochemistry.[6]

As well exemplified for gold nanoparticles, when the diameter approaches the de Broglie wavelength of the conduction electrons (ca. 1 nm), the quasi-continuous electronic bands in bulk metals or large nanoparticles (> 5 nm) evolve to discrete levels.[7] Thus, ultrasmall nanoparticles (< 3 nm) should display peculiar and unique physical properties. For instance, it has been demonstrated that Au nanoparticles become catalytically active in several processes when their diameter is below 5 nm, whereas above this threshold they are almost inert.[8]

At the same time, within this size regime, the chemistry of ultrasmall metal nanoparticles overlaps with that of ligand-protected molecular metal clusters.[9] Actually, ultrasmall metal nanoparticles are nothing but mixtures of more or less polydisperse large molecular clusters. Alternatively, higher-nuclearity molecular clusters may be viewed as perfectly monodisperse and atomically defined metal nanoparticles. Thus, all the knowledge, experimental techniques and methods developed along the years for the preparation, purification and characterisation of large molecular metal clusters may play a major role in a better understanding of ultrasmall metal nanoparticles and metal nanoparticles in general.

For instance, the general model adopted for many years for thiol-stabilised Au nanoparticles has been based on a close-packed core of Au atoms protected by an innocent shell of ligands. Then, after the structural characterisation

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of the molecular cluster $Au_{102}(p\text{-MBA})_{44}$ (p-MBA = *para*-mercaptobenzoic acid)[10] by means of single-crystal X-ray crystallography, a completely different model has been proposed, on the basis of icosahedral or poly-icosahedral metal cores decorated by $[Au_n(SR)_{n+1}]^-$ fragments (the so-called "staple motives" or "staples").[11–13] This point well exemplifies the great impact that molecular techniques, and X-ray crystallography in particular, may have in nanochemistry.

Different examples of nanometric molecular clusters are known, including semiconductor molecular nanoclusters such as $Ag_{490}S_{188}(SR)_{114}$,[14] metalloid molecular nanoclusters such as $[Al_{77}\{N(SiMe_3)_2\}_{20}]^{2-}$[15] and $[Ga_{84}\{N(SiMe_3)_2\}_{20}]^{4-}$,[16] as well as low-valent transition metal molecular nanoclusters such as $Pd_{145}(PR_3)_{30}(CO)_{60}$.[17] Within the last category, homoleptic molecular metal carbonyl clusters (MCCs) represent one of the most widely studied classes of molecular clusters.[9,18–22] The largest MCC characterised up to now is $[Ni_{32}Pt_{24}(CO)_{56}]^{6-}$ (with a maximum length of ca. 2.1 nm), which already enters the domain of ultrasmall metal nanoparticles (Figure 1).[23] The topic of MCCs has been largely investigated throughout the 1970s and 1980s, with a marked decline in the literature during the 1990s. However, due to the recent explosion of interest in nanochemistry, there has been a gradual revival in this area over the past decade, as summarised in a few comprehensive reviews that appeared recently on the subject.[18,19]

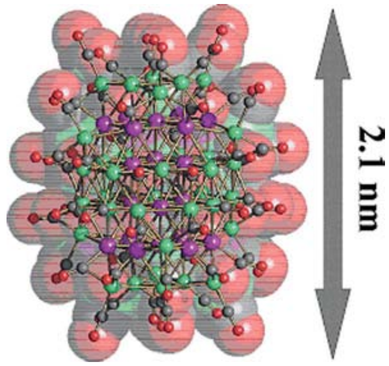


Figure 1. Structure of $[Ni_{32}Pt_{24}(CO)_{56}]^{6-}$ (Ni, green; Pt, purple; C, grey; O, red).[23]

This microreview aims at presenting a personal perspective on the possible contributions that molecular MCCs may make to a better understanding and overall development of metal nanoparticles. The synthesis of larger MCCs is briefly described in Section 2, which, far from being comprehensive, aims at showing some general guidelines to follow for inducing the growth of MCCs. Then, Sections 3 and 4 are dedicated to the description of the structural features and physical properties of large MCCs, respectively. In fact, in order to develop a molecular and functional approach towards large clusters, it is fundamental to characterise them structurally as well as studying their physical behaviour. In Section 5, the use of molecular MCCs as nanometric or subnanometric building blocks for self-assembly is reported, suggesting further applications of molecular clusters for the development of functional nanomaterials. Finally, Section 6 describes the use of MCCs as precursors for metal nanoparticles after decomposition of the molecular precursor.

The aim of this microreview is to discuss some representative examples of all these topics, showing that one of the most promising and fascinating aspects of molecular MCCs is their borderline nature between molecular chemistry and nanochemistry.

2. Synthesis

Large MCCs display a rich variety of structures and even species with very similar compositions can adopt rather different geometries. This is, probably, the result of the fact that M–M interactions are not very strong and are nondirectional, as compared, for instance, to C–C bonds. Moreover, only occasionally does a given product represent a relatively deep potential well along the reaction coordinate, and therefore only supposedly minor changes in the reagents or in the experimental conditions can result in completely different products.[24] Thus, even though our knowledge on the synthesis of high-nuclearity MCCs has incredibly grown over the years, it is not yet possible to design a priori the preparation of a species with a predefined structure. Nonetheless, we can outline some general guidelines to follow in order to induce the growth of MCCs. The yields of the reactions vary from case to case, but several large MCCs can nowadays be obtained in the scale of hundreds of milligrams or even grams. Experimental conditions must be carefully chosen in order to selectively obtain a single species as major product, and IR spectroscopic monitoring of the reactions were revealed to be very useful for seeking the best operative conditions. Side products may be other MCCs, small carbonyl species {e.g. $Ni(CO)_4$, $[Co(CO)_4]^-$, $Ni(CO)_3(PPh_3)$, $[Rh(CO)_4]^-$}, bulk metals and metal salts. Purification is usually achieved on the basis of their different solubility in water and organic solvents, and, since most of the MCCs studied are anionic, further differentiation of the solubility of the products may be achieved by using suitable tetraalkylammonium or phosphonium cations. The reader may notice that sometimes larger MCCs contain hydride ligands. These may arise from the solvent, from water (traces present in the solvents or added in the workup) or may be directly added in the form of free acids. It must be remarked that hydrides in MCCs are usually slightly acidic and may thus be removed with bases or added as H^+ (see Section 4.2). Further details on the syntheses are given in the original papers cited.

The possible methods for the preparation of large MCCs can be classified as follows: (1) direct (reductive) carbonylation; (2) thermal methods; (3) redox methods; (4) other chemically induced methods.

2.1 Direct (Reductive) Carbonylation

Direct (reductive) carbonylation represents the main entry to the chemistry of metal carbonyls, as described in many textbooks.[25] Actually, direct carbonylation (i.e. the reaction between a finely divided metal and CO) works only with Ni and Fe, whereas all other metal carbonyls are obtained by reductive carbonylation (i.e. metal salt + CO + reducing agent). These reactions usually result in the formation of low-nuclearity neutral metal carbonyls, such as $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$, $Mn_2(CO)_{10}$, $Ru_3(CO)_{12}$, $Co_2(CO)_8$ and $Rh_4(CO)_{12}$, which can then be converted into higher-nuclearity species (see below).

A rather fascinating exception is represented by the reductive carbonylation of Pt^{IV} salts developed by Chini and Longoni[26,27] (Scheme 1), which operates at room temperature and ambient CO pressure. In this case, the reducing agent is CO itself under basic conditions according to Equation (1).

$$CO + 2OH^- \rightarrow CO_2 + H_2O + 2e^- \qquad (1)$$

By employing methanol as solvent and a weak base such as CH_3COONa, Na_2PtCl_6 is quantitatively converted into the insoluble "platinum carbonyl" with a formula of $Na_2[Pt_{3n}(CO)_{6n}]$ ($n \approx 10$) based on elemental analysis. When the amount of CH_3COONa is increased or a stronger base such as NaOH is used, soluble $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 2–6) oligomers, the so-called "Chini clusters", are obtained. These clusters can also be prepared by the radiolysis of Pt salts in alcoholic media[28] or directly in water by room-temperature carbonylation of M_2PtCl_6 (M = Na, K).[29] The latter procedure (operating with high yields also in the gram scale) represents a considerable simplification for the synthesis of platinum carbonyl clusters. Moreover, by performing the carbonylation in water with different CO pressures, both $[Pt_{3n}(CO)_{6n}]^{2-}$ ($n > 6$; 900 Torr CO) and $[Pt_{38}(CO)_{44}]^{2-}$ (760 Torr CO) can be obtained in a single step.

Apart from solutions, reductive carbonylation can also be used in the solid state after impregnation of a suitable metal salt on supports such as metal oxides or zeolites.[30] In particular, the so-called "ship-in-a-bottle" technique has allowed the preparation of several homometallic Pt, Rh and Ir clusters, as well as bimetallic clusters, in the microporous cavities of zeolites.[30,31]

Reductive carbonylation in the presence of PR_3 ligands has been extensively employed by Dahl and Mednikov for the preparation of phosphane-substituted Pd–CO clusters according to Equation (2).[32]

$$n\mathrm{Pd(OAc)_2} + (x + n)\mathrm{CO} + y\mathrm{PR_3} + n\mathrm{H_2O} \rightarrow \mathrm{Pd}_n(\mathrm{CO})_x(\mathrm{PR_3})_y + n\mathrm{Co_2} + 2n\mathrm{HOAc} \qquad (2)$$

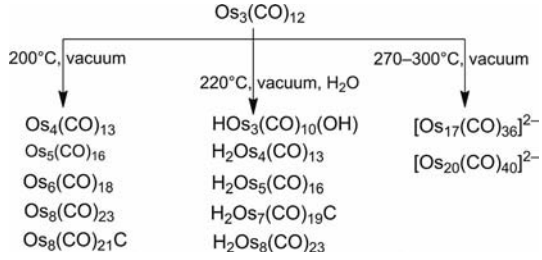
2.2 Thermal Methods

The simplest thermal reaction for the preparation of larger MCCs is based on partial decarbonylation of the precursor after heating followed by condensation of the resulting unsaturated species with formation of new M–M bonds, as in Equation (3).[33]

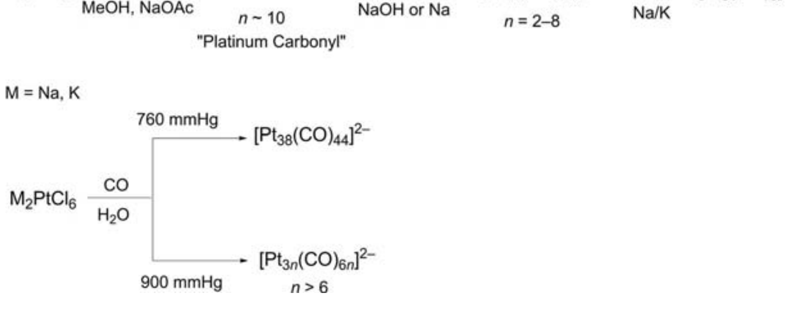
$$3Rh_4(CO)_{12} \rightleftarrows 2Rh_6(CO)_{16} + 4CO \qquad (3)$$

In a few cases, removal of CO ligands from the precursor results only in an intramolecular rearrangement of the cluster cage without an increase in the nuclearity. For instance, thermal removal of two CO molecules from trigonal prismatic $[Rh_6C(CO)_{15}]^{2-}$ yields the octahedral $[Rh_6C(CO)_{13}]^{2-}$ anion.[34] Recently, we have also described a peculiar case in which the $[Rh_{12}Sn(CO)_{27}]^{4-}$ cluster undergoes sequential loss of two CO ligands without any major change in the icosahedral cage.[35]

Pyrolysis of neutral $M_3(CO)_{12}$ (M = Os, Ru) carbonyls was extensively used by Lewis and Johnson for the preparation of large MCCs (Scheme 2).[36] Apart from decarbonylation followed by condensation to higher-nuclearity homometallic species such as $Os_8(CO)_{23}$, $[Os_{17}(CO)_{36}]^{2-}$ and $[Os_{20}(CO)_{40}]^{2-}$, carbido clusters, for example $Os_8C(CO)_{21}$ and $H_2Os_7C(CO)_{19}$, were formed after the dismutation of CO to C and CO_2 due to the severe conditions



Scheme 2. Preparation of Os clusters by thermal methods.[36]



Scheme 1. Preparation of Pt clusters by reductive carbonylation.

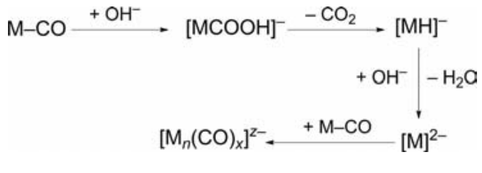
adopted. The main drawback of pyrolytic methods is their scarce selectivity.

Nonetheless, Chini and Martinengo demonstrated that carefully monitoring the dosage of sodium hydroxide while performing the thermolysis of $Rh_4(CO)_{12}$ under different atmospheres enables the more or less selective preparation of several high-nuclearity rhodium carbonyl clusters.[22a,22c,37] This anionic selectivity enhancement can be nearly quantitative, as in the preparation of $[Pt_{19}(CO)_{22}]^{4-}$[38] and $[Pt_{15}(CO)_{19}]^{4-}$[39] by heating appropriate mixtures of Chini clusters.

2.3 Redox Methods

All kinds of redox reactions (i.e. reduction, oxidation, redox condensation and disproportionation) can be used for the preparation of MCCs. It must be remarked that in some cases MCCs are multivalent in the sense that they undergo reversible redox reactions without any major structural rearrangement. For these species, the stoichiometric addition of a reducing and/or oxidising agent simply results in the formation of an isostructural cluster with increased or decreased negative charge, for example $[Ag_{13}Fe_8(CO)_{32}]^{n-}$ (n = 3–5),[40] $[Ni_{13}Sb_2(CO)_{24}]^{n-}$ (n = 2–4)[41] and $[Co_8Pt_4C(CO)_{24}]^{n-}$ (n = 1–4).[42] More often, the redox reaction is followed by irreversible processes yielding new MCCs or by complete decomposition.

Reduction of a MCC often results in cleavage of M–M bonds or CO loss as a consequence of electrons added to an antibonding orbital. For instance, reduction of Chini clusters $[Pt_{3n}(CO)_{6n}]^{2-}$ affords analogous species each having an n value one lower than the previous, which are obtained by the breaking of Pt–Pt bonds,[26,27] up to complete depolymerisation to $[Pt_3(CO)_6]^{2-}$ (n = 1). Alternatively, addition of reducing agents such as alkali metals can result in the replacement of a CO ligand with two negative charges with or without structural rearrangement, as in the reduction of $Rh_{12}C_2(CO)_{25}$ to $[Rh_{12}C_2(CO)_{24}]^{2-}$ and $[Rh_{12}C_2(CO)_{23}]^{4-}$.[43] Reduction and CO loss can also be promoted by OH^- ions; the resulting unsaturated species may undergo condensation processes to yield higher-nuclearity MCCs (Scheme 3). This approach was first developed by Hieber for the synthesis of iron carbonyl anions after treatment of $Fe(CO)_5$ with bases such as NaOH and amines,[44] and then also applied to the preparation of $[Ni_6(CO)_{12}]^{2-}$ and other Ni carbonylates starting from $Ni(CO)_4$.[25a,45]



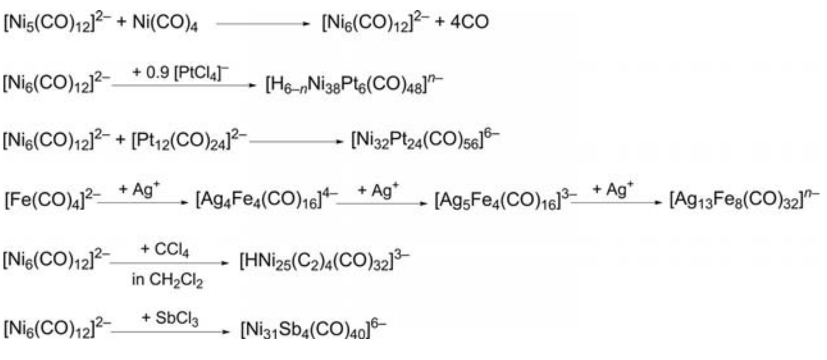
Scheme 3. Condensation induced by reduction.

Oxidation of MCCs with innocent (noncoordinating) reagents, such as tropylium, tetrafluoroborate or ferricinium ions, may result in the formation of new M–M bonds with or without CO loss, as in the dimerisation of $[Ir_6(CO)_{15}]^{2-}$ to $[Ir_{12}(CO)_{26}]^{2-}$,[46] or $[Pt_{19}(CO)_{22}]^{4-}$ to $[Pt_{38}(CO)_{44}]^{2-}$.[47] Conversely, when using coordinating oxidants such as H^+ and isolobal $[ML]^+$ (M = Cu, Ag, Au; L = neutral ligand) and $[HgR]^+$, the reactions are more complex, since these reagents can act as oxidants or coordinate to the cluster, which results in acid–base adducts. The latter process has been widely used to increase the nuclearity of clusters having 1–2 units by the stepwise addition of $[ML]^+$ fragments. The reaction of MCCs with metal salts or complexes can also afford bimetallic clusters by redox condensation (vide infra).

In the case of acids, several MCCs can add H^+ ions reversibly, affording hydrido clusters. On the contrary, if the resulting hydride is not stable, it can condense to larger species with H_2 evolution, as shown in Equation (4). The H^+ ions necessary for these reactions can alternatively be provided by the hydrolysis of $[M(H_2O)_x]^{n+}$ ions.[48]

$$2[Rh_6C(CO)_{15}]^{2-} + 2H^+ \rightarrow [Rh_{12}C_2(CO)_{24}]^{2-} + 6CO + H_2 \qquad (4)$$

Redox condensation is probably the most useful procedure for the preparation of higher-nuclearity MCCs.[22a] It consists of the reaction between a reduced metal carbonyl anion and a more oxidised species. The latter can be another (more oxidised) carbonyl species, a metal salt or complex, or even a main group compound. In this way homometallic, bimetallic and heteronuclear MCCs can be prepared (Scheme 4). Bimetallic Fe–Co, Rh–Pt, Ni–Co, Ni–Pt and so on can be easily prepared by starting from reduced carbonyls of either metals or salts of the second element.



Scheme 4. Some examples of redox condensation reactions.

Conversely, when one of the two metals does not form carbonyls, as, for example, in the Fe–Au, Fe–Ag, Ni–Pd and Ni–Au systems, the choice of the reagents is more limited.

By employing main group compounds such as CCl_4, $SbCl_3$, $SnCl_4$, $GaCl_3$ and $GeCl_4$, heteronuclear clusters such as $[Ni_9C(CO)_{17}]^{2-}$,[49] $[HNi_{25}(C_2)_4(CO)_{32}]^{3-}$,[50] $[Ni_{31}Sb_4(CO)_{40}]^{6-}$,[51] $[Rh_{12}Sn(CO)_{27}]^{4-}$,[52] $[Ni_{12}Ga(CO)_{22}]^{3-}$[53] and $[Ni_{12}Ge(CO)_{22}]^{2-}$[54] can be easily obtained from reduced homometallic anions such as $[Ni_6(CO)_{12}]^{2-}$ and $[Rh_7(CO)_{16}]^{3-}$. Similarly, bimetallic MCCs containing interstitial main group elements can be obtained by reacting a suitable heteronuclear anion with a metal salt; for example, $[Ni_{10}Rh_2C(CO)_{20}]^{2-}$ is obtained from $[Ni_9C(CO)_{17}]^{2-}$ and $[Rh(cod)Cl]_2$.[55]

Disproportionation is the reverse of redox condensation and is favoured in the case of neutral $M_x(CO)_y$ carbonyls in polar solvents. Depending on the reagents and experimental conditions, it can result in (a) $[ML_6]^{2+}[M_a(CO)_b]^{2-}$ ionic couples, (b) isocarbonyl adducts or (c) xenophilic clusters. An example of (a) is represented by the formation of $[Fe(dmf)_6][Fe_4(CO)_{13}]$ after heating $Fe(CO)_5$ in dmf. Xenophilic clusters[56] contain a direct M–M bond between a metal centre in a formal negative oxidation state and a second metal in a positive oxidation state, for example $Fe_4(CO)_8(py)_4$[57] and $[Mn][Mn_7(thf)_6(CO)_{12}]_2$.[58]

2.4 Other Chemically Induced Methods

Once formed, MCCs can be modified in several ways, and they can therefore be used for the preparation of new species. Apart from the use of acids, bases, oxidants and reducing agents that have been described above, both anionic (e.g. OH^-, I^-) and neutral (PR_3, CO, amines) nucleophiles can be employed. They can result in addition to the cluster, its degradation or even condensation to yield larger species. Nucleophilic addition, very often followed by removal of ML_x fragments, is the more usual reaction [Equations (5) and (6)]. In this way, higher-nuclearity MCCs are degraded to smaller species.[54,59]

$$[Ni_{12}Ge(CO)_{22}]^{2-} + 6CO \rightarrow [Ni_{10}Ge(CO)_{20}]^{2-} + 2Ni(CO)_4 \qquad (5)$$

$$[Ni_{38}C_6(CO)_{42}]^{6-} + 18CO \rightarrow [Ni_{32}C_6(CO)_{36}]^{6-} + 6Ni(CO)_4 \qquad (6)$$

In a few cases, nucleophilic attack promotes condensation and results in higher-nuclearity clusters, as exemplified by the conversion of $[Ni_{10}C_2(CO)_{16}]^{2-}$ into $[Ni_{16}(C_2)_2(CO)_{23}]^{4-}$ promoted by PPh_3,[60] the synthesis of $[Ni_{42}C_8(CO)_{44}(CdCl)]^{7-}$ after nucleophilic attack by OH^- on $[Ni_{36}C_8(CO)_{36}(Cd_2Cl_3)]^{5-}$[61] and the CO-induced condensation of $[Ni_{10}Rh_2C(CO)_{20}]^{2-}$ to give $[Ni_6Rh_8(C_2)_2(CO)_{24}]^{4-}$.[55]

3. Structural Features

Single-crystal X-ray crystallography is the ultimate technique in order to fully determine the complete structure of MCCs. Nonetheless, there are several IR and NMR spectroscopic and ESI-MS data, which point out that the structures displayed in the solid state are usually retained in solution.

High-nuclearity homo- and bimetallic MCCs very often adopt structures that closely resemble those of bulk metals, that is, body-centred cubic (bcc), hexagonal close-packed (hcp) and cubic close-packed (ccp) (Figure 2). In a few cases, combinations of two of these packing motives are also found within the same cluster.[18] These structural resemblances fuelled the cluster-surface analogy,[62] with potential implications in heterogeneous catalysis and surface science, particularly regarding our interpretation of the adsorption, coordination and activation of small molecules (e.g. CO) over metal surfaces.

Two-dimensional growth is well exemplified in low-nuclearity MCCs, but it is very rare for larger clusters, the dodecanuclear CO/diphos $Au_8Fe_4(CO)_{16}(P^\wedge P)_2$, $Au_6Cu_2Fe_4(CO)_{16}(P^\wedge P)_2$ and $Au_4Ag_4Fe_4(CO)_{16}(P^\wedge P)_2$ being the largest species characterised so far.[66]

In addition to close-packed structures, MCCs may adopt prismatic or antiprismatic cages. Chini clusters $[Pt_{3n}(CO)_{6n}]^{2-}$ ($n = 2$–8 for the species structurally characterised up to date)[26] are the largest trigonal prismatic clusters displaying nuclearities up to 24 as molecular species and basically infinite in the solid state, since they very often crystallise into infinite molecular wires.[67] All these species are based on triangular $[Pt_3(\mu\text{-}CO)_3(CO)_3]$ units stacked along a common C_3 axis and held together by two additional electrons (see Section 5.2).

Square antiprismatic cages and more complex structures are usually displayed by heteronuclear clusters, as a consequence of the inclusion of main group elements. Simple square antiprismatic structures are, for instance, adopted by the carbides $[Co_8C(CO)_{18}]^{2-}$[68] and $[Ni_8C(CO)_{16}]^{2-}$,[49] whereas $[Co_9Si(CO)_{21}]^-$,[69] $[Rh_9P(CO)_{21}]^-$, $[Rh_{10}P(CO)_{22}]^{3-}$[70] and $[Rh_{10}As(CO)_{22}]^{3-}$[71] provide examples of heavier main group elements encapsulated within mono- and bicapped square antiprismatic cavities. More complex structures may result from the fusion of two or more E-centred square antiprismatic cages, as in $[Rh_{17}S_2(CO)_{32}]^{3-}$[72] and $[Ni_{32}C_6(CO)_{36}]^{6-}$.[59] Furthermore, in some cases, such as $[Ni_{42}C_8(CO)_{44}(CdCl)]^{7-}$ and $[Ni_{36}C_8(CO)_{36}(Cd_2Cl_3)]^{5-}$,[61] the interstitial main group elements are present within different types of cavities (e.g. trigonal prismatic, square antiprismatic, octahedral) fused together, which results in even more complex M_xE_y cages.

The importance of noncrystallographic C_5 symmetry in the chemistry of clusters and colloids has considerably grown over the years, with important representatives also among MCCs. Probably, the first examples of icosahedral and poly-icosahedral structures in cluster chemistry are represented by Au and Ag species stabilised by phosphane ligands, such as $[Au_{13}(PMe_2Ph)_{10}Cl_2]^{3+}$ (icosahedral), $[Au_{13}Ag_{12}(PPh_3)_{10}Br_8]^+$ (biicosahedral), $Au_{18}Ag_{20}(PTol_3)_{12}Cl_{14}$ (triicosahedral) and $Au_{22}Ag_{24}(PPh_3)_{12}Cl_{10}$ (tetraicosahedral).[73,74] The tendency of gold to form structures with local C_5 symmetry has also been confirmed by the so far characterised Au thiolate nanoclusters, that is, [Au$_{25}$(S–

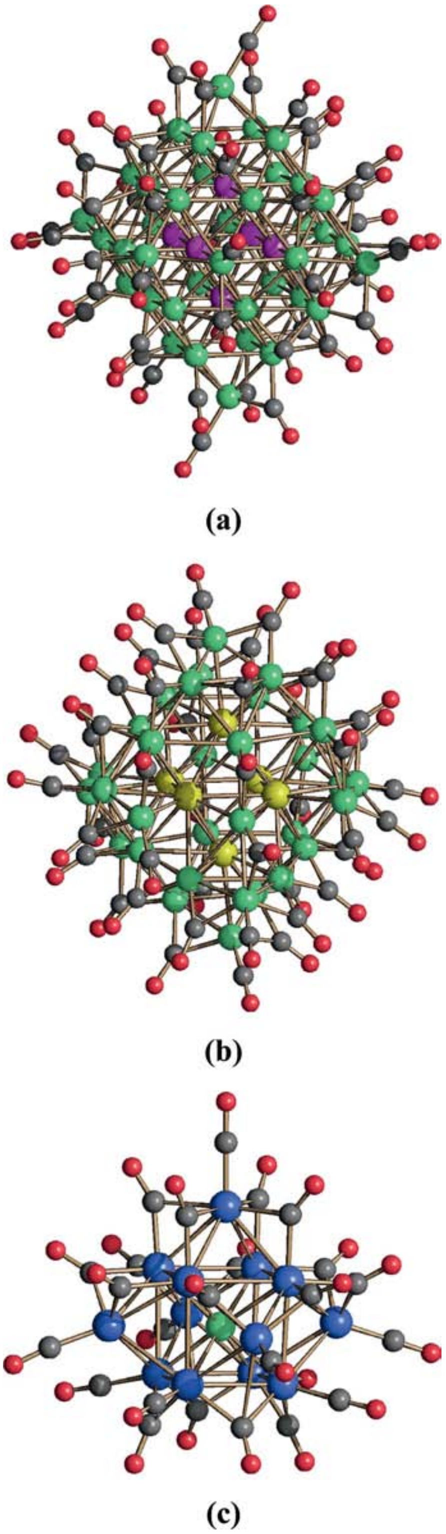


Figure 2. Some examples of MCCs with close-packed or body-centred structures (Ni, green; Pt, purple; Rh, blue; C, grey; O, red): (a) $[HNi_{38}Pt_6(CO)_{48}]^{5-}$ (ccp);[63] (b) $[Ni_{32}Au_6(CO)_{44}]^{6-}$ (hcp);[64] (c) $[NiRh_{13}(CO)_{25}]^{5-}$ (bcc).[65]

$CH_2CH_2Ph)_{18}]^{0/-}$,[7c,75] $Au_{38}(S–CH_2CH_2Ph)_{24}$[76] and $Au_{102}(p\text{-MBA})_{44}$.[10] Indeed, they all contain *ico* and *poly-ico* Au kernels, comprising much fewer Au atoms than indicated by their formula (13, 23 and 79, respectively), because their kernels are decorated by $[Au(SR)_2]^-$ and/or $[Au_2(SR)_3]^-$ moieties (so-called staples). This discrepancy between the apparent and real nuclearity of the metal cores of these nanoclusters might be the explanation for their delayed metallisation.[18]

Pseudo-I_h icosahedral symmetry was found by Dahl in miscellaneous Pd clusters stabilised by a mixture of carbonyl and phosphane ligands, up to the giant $Pd_{145}(CO)_{60}(PEt_3)_{30}$ and $PtPd_{164-x}Pt_x(CO)_{72}(PPh_3)_{20}$ ($x \approx 7$).[32] For homoleptic MCCs, D_{5h} $[Pt_{19}(CO)_{22}]^{4-}$ represents a rare example of a MCC whose structure is based on fused centred pentagonal prisms.[38]

Conversely, several examples of icosahedral MCCs are known, comprising (A) noncentred icosahedral clusters such as $[Ni_{10}(PR)_2(CO)_{18}]^{2-}$,[77] (B) E-centred clusters such as $[Ni_{12}Ga(CO)_{22}]^{3-}$ (Figure 3),[53] and (C) M-centred species such as $[Ni_{11}Sb_2(CO)_{18}]^{n-}$.[78] MCCs belonging to categories A and B are electron-precise, displaying 170 cluster valence electrons (CVEs) as required by the cluster-borane analogy,[79] whereas species in class C are electron-rich and multivalent (see Section 4.1). However, the recently reported $[Rh_{12}Sn(CO)_{26}]^{4-}$ and $[Rh_{12}Sn(CO)_{25}]^{4-}$ (class B) presented the first exceptions to the above rule by featuring 168 and 166 CVEs, respectively.[35]

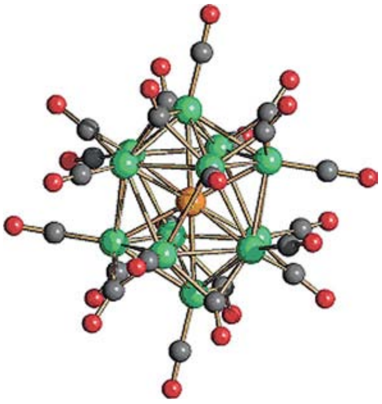


Figure 3. Structure of $[Ni_{12}Ga(CO)_{22}]^{3-}$ (Ni, green; Ga, orange; C, grey; O, red).[53]

The possibility that icosahedral MCCs could be electron-deficient was further confirmed by the structural characterisation of $[Pt_{13}(CO)_{12}\{Cd_5(\mu\text{-Br})_5Br_2(dmf)_3\}_2]^{2-}$ (Figure 4), obtained by reacting $[Pt_{12}(CO)_{24}]^{2-}$ with $CdBr_2$ in hot dmf.[80] This cluster possesses a $[Pt_{13}(CO)_{12}]^{8-}$ core featuring 162 CVEs, as found in $Pt_{13}[Au_2(PPh_3)_2]_2(CO)_{10}(PPh_3)_4$[81] as well as in structurally related Au_{13} clusters.[82] The electron deficiency of such clusters comprising heavier elements has been explained by Mingos as arising from the predominance of radial over tangential bonding[83] and further supported by relativistic DFT calculations on the hypothetical $WAu_{12}(CO)_{12}$.[84]

The $[Pt_{13}(CO)_{12}]^{8-}$ core of the above cluster is decorated by two $\{Cd_5(\mu\text{-Br})_5Br_2(dmf)_3\}^{3+}$ moieties that are reminiscent of the staple motives decorating gold thiolate nanoclu-

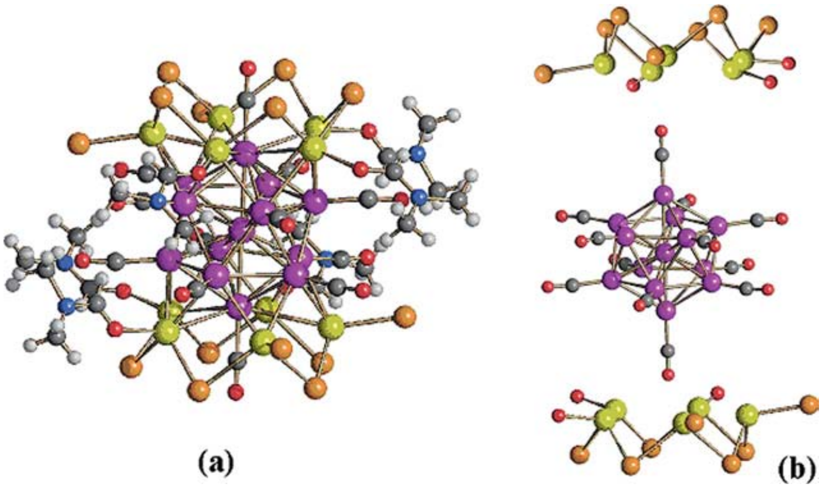


Figure 4. Structure of $[Pt_{13}(CO)_{12}\{Cd_5(\mu\text{-}Br)_5Br_2(dmf)_3\}_2]^{2-}$ (a), and representation of its fragments (b) (Pt, purple; Cd, yellow; Br, orange C, grey; O, red).[80]

sters.[10] It is rather interesting to find that pseudo-C_5 symmetry, electron deficiency and staple motives are common features among these very different polymetallic species at the border between molecular clusters and small metal nanoparticles. To further unravel similarities and analogies in this borderline region is one of the major goals and most fascinating aspects of the chemistry of MCCs to be addressed in the near future.

In this regard, we have recently demonstrated that brown solutions of Au–Fe–CO colloids are obtained by reacting $[Fe_3(CO)_{11}]^{2-}$ with $[AuCl_4]^-$ (Scheme 5). Fractional crystallisation allowed us to separate and structurally identify some of the components of these colloids, that is, $[Au_{22}Fe_{12}(CO)_{48}]^{6-}$, $[Au_{21}Fe_{10}(CO)_{40}]^{5-}$, $[Au_{28}Fe_{14}(CO)_{52}]^{8-}$ and $[Au_{34}Fe_{14}(CO)_{50}]^{10-}$.[85] All these species, apart from the first, display fivefold local symmetry and a metal core decorated by Au–Fe–CO staples (Figure 5), further supporting the above analogies between low-valent molecular clusters and ligand-protected nanoparticles.

At the same time, the reasons for which a molecular MCC adopts a bulk-like structure (bcc, ccp, hcp) rather than an icosahedral one or a prismatic cage are quite complex, depending on the nature and number of metal atoms, the metal/CO ratio and the presence of ancillary ligands. Shedding light on this point might also lead to a better understanding of the structures adopted by ultrasmall metal nanoparticles.

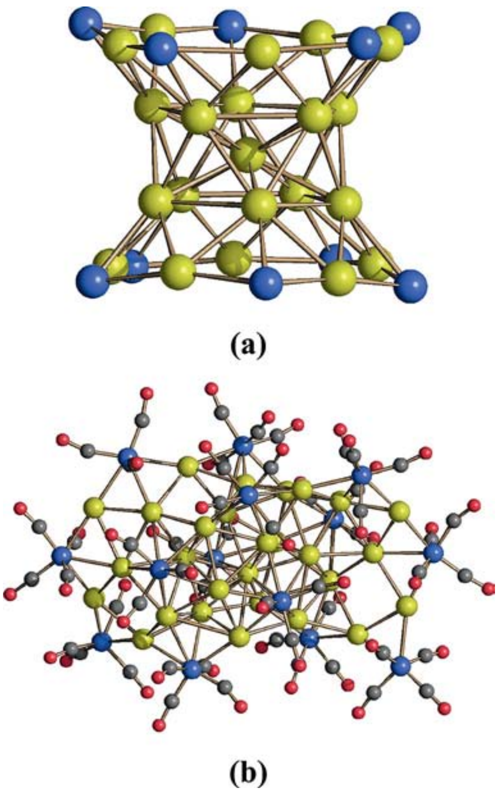
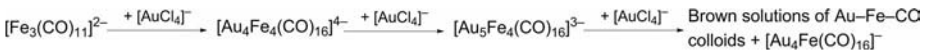


Figure 5. Metal core of $[Au_{21}Fe_{10}(CO)_{40}]^{5-}$ (a), and full structure of $[Au_{28}Fe_{14}(CO)_{52}]^{8-}$ (b) (Au, yellow; Fe, blue; C, grey; O, red).[85]

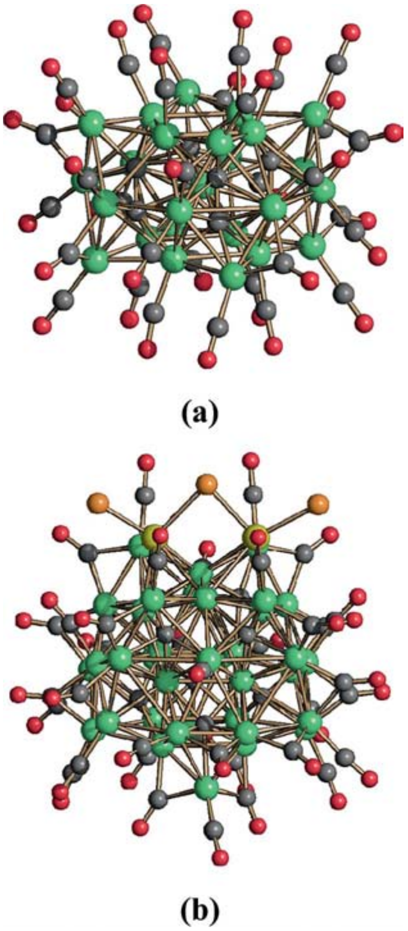
The structural variety of MCCs is further extended by considering heteronuclear clusters. In fact, inclusion of main group elements such as C, N, Si, P, S, Ga, Ge, As, Sn, Sb or Bi within the metal cage of MCCs induces massive rearrangements of the clusters due to steric and electronic requirements of the main group element.[24,86] This is well exemplified by the chemistry of carbido MCCs, probably the class of heteronuclear MCCs most extensively studied up to now.[18,50,61,87–90] The number as well as the relative size of the interstitial carbide atoms and the metals composing the cluster are of paramount importance; with the notable exception of $[Os_{10}C(CO)_{24}]^{2-}$, $[Ru_{10}C(CO)_{24}]^{2-}$ and



$$[Fe_3(CO)_{11}]^{2-} \xrightarrow{+ [AuCl_4]^-} [Au_4Fe_4(CO)_{16}]^{4-} \xrightarrow{+ [AuCl_4]^-} [Au_5Fe_4(CO)_{16}]^{3-} \xrightarrow{+ [AuCl_4]^-} \text{Brown solutions of Au–Fe–CO colloids} + [Au_4Fe(CO)_{16}]^-$$

Scheme 5.

$[Os_{11}C(CO)_{27}]^{2-}$,[91] the metal cage very usually displays large deformations to generate cavities of suitable dimensions to allocate the carbon atoms. Species containing from one up to eight isolated carbon atoms are known as well as polyacetylide clusters, which contain one, two or four tightly bound C_2 units. All these species display very complex and irregular metal cages, which are required to accommodate the interstitial carbon atoms (a few examples are shown in Figure 6). This behaviour confirms that the metal core in ligand-stabilised clusters is rather deformable and soft. It behaves more like a liquid metal drop that adapts itself to the surface and/or interstitial ligands rather than a solid close-packed metal chunk. It is, therefore, not surprising that the diffusion and mobility of carbon atoms into "nearly liquid" Fe, Co and Ni nanoparticles have been claimed as the basis of the growth of carbon nanotubes and other graphitic nanomaterials promoted by these catalysts.[92]


(a)

(b)

Figure 6. Molecular structures of (a) $[HNi_{25}(C_2)_4(CO)_{32}]^{3-}$[50] and (b) $[H_{5-n}Ni_{36}C_8(CO)_{36}(Cd_2Cl_3)]^{n-}$ (n = 3–5)[61] (Ni, green; Cd, yellow; Br, orange; C, grey; O, red).

4. Physical Properties

As briefly outlined in the previous section, the structures of several thousands of MCCs are already available. Their systematic analysis reveals that the CO/M ratio decreases as the nuclearity increases, and therefore the M–M bonds become more and more relevant and eventually predominant over M–CO interactions, approaching the coordination of bulk metals (Figure 7).[18,22] As the number of metallic M–M interactions increases, metallisation of the metal core of the cluster should occur, independently of the actual structure adopted. From a theoretical point of view, this corresponds to a transition of the electronic state of the cluster from discrete molecular eigenstates (localised electrons) at lower nuclearities to highly delocalised electrons subject to quantum size effects at higher nuclearities.[93] In other words, small MCCs display large HOMO–LUMO gaps and are thus usually electron-precise. As the nuclearity increases, the HOMO–LUMO gap decreases, and eventually a continuum of energy levels should appear as the bulk state is reached. As soon as this gap is of the order of kT, quantum size effects should appear. Thus, higher-nuclearity MCCs might have open-shell electronic structures.

All these considerations suggest that molecular clusters should undergo insulator-to-metal transitions with increasing nuclearity, passing through a semiconductor regime.[18] Theoretical calculations indicate that ligand coordination to the surface of bare metal clusters partially quenches the metallisation process. Nonetheless, the presence of surface ligands as well as staple motives described in Section 3 should only delay metallisation, but, eventually, this transition may occur.

The morphological approach based on X-ray crystallography is not able to answer the fundamental question "How many atoms maketh metal";[93] for instance, even though there are close structural analogies between adamantane and diamond, or between benzene and graphite,

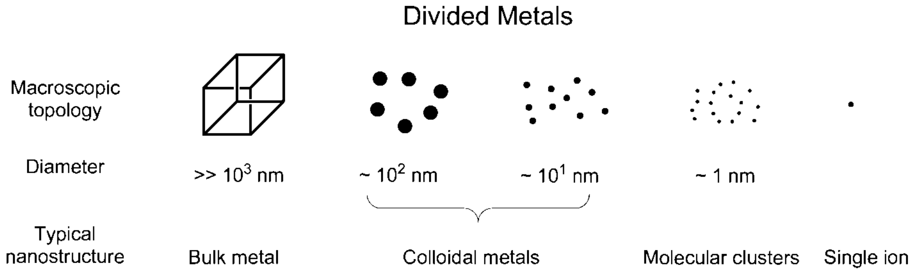


Figure 7. The divided states of metals.[22e]

their physical properties are completely different. Therefore, to unravel the electronic state of larger MCCs, a functional approach based on the determination of their physical properties is needed.

In performing physical measurements on large molecular MCCs we must pay great attention to the purity of the samples (by using crystalline samples), double check the results (when possible) with at least two independent techniques and, in the case of samples in solution, demonstrate that the solid-state structure is retained in solution by using suitable spectroscopic techniques.

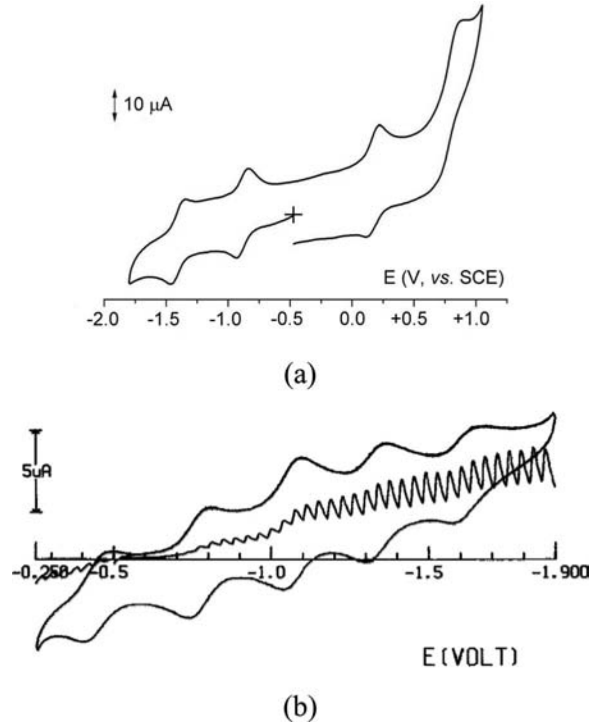
Various physical measurements (e.g. magnetisation, susceptibility, electric conduction, specific heat, photoelectron spectroscopy, redox properties) on various classes of molecular clusters (among which are also MCCs) and ligand-protected, quasi-monodisperse nanoparticles were reported along the years.[94] Our present increased ability of preparing larger MCCs makes these molecular clusters suitable candidates for a systematic functional approach toward the understanding of the size-induced transition of physical properties in polymetallic aggregates. This point will be exemplified below for electrochemical properties, NMR spectroscopic behaviour and magnetic measurements.

4.1 Electrochemistry and Multivalence in High-Nuclearity MCCs

Multivalence in high-nuclearity MCCs has been recently reviewed, and the reader can find a detailed description in these publications.[18,95] A molecular cluster is defined as multivalent if it can undergo several reversible redox processes without any major structural rearrangement. It has been shown that redox properties of MCCs can be due either to ad hoc conditions or incipient metallisation of the metal core.

Ad hoc conditions are at the origin of the redox behaviour of some low-nuclearity MCCs, which, in the absence of those conditions, are usually electron-precise and non-redox-active.[18,95] Ad hoc conditions arise from the presence of a nonbonding or weakly antibonding molecular orbital (MO) within an otherwise large HOMO–LUMO gap. Usually, these electronic conditions are supported by steric protection from the ligands or the presence of interstitial main group elements reinforcing the metal cage, which hamper intermolecular reactions or fragmentation. Extended Hückel molecular orbital (EHMO) calculations clearly point out the presence of discrete energy levels in these clusters. As an example, the bimetallic dodecanuclear dicarbide $[Co_8Pt_4C_2(CO)_{24}]^{2-}$ undergoes one oxidation and two reduction processes, all displaying features of chemical reversibility (Figure 8a). Both of the isostructural mono- and dianions have been structurally characterised.[42]

As the nuclearity increases, multivalence becomes very common, and larger MCCs often display a certain redox propensity. The structures of these large clusters usually include at least one metal atom with high connectivity, suggesting incipient metallisation.[18] This is confirmed by EHMO calculations, which indicate that HOMO–LUMO gaps of high-nuclearity MCCs are considerably reduced relative to those of lower-nuclearity MCCs. Thus, larger MCCs very often display two or more reversible redox processes as a consequence of the fact that they can reversibly release or accept several electrons in their frontier orbitals. The incipient metallisation of these high-nuclearity clusters is further corroborated by the fact that voltammetric profiles of the largest species display almost equally spaced redox waves, as in the case of $[Ni_{32}C_6(CO)_{36}]^{6-}$ (Figure 8b).[59] This means that in such high-nuclearity MCCs, the pairing energy within a single MO is very similar to the energy gap between two consecutive MOs.



(a)

(b)

Figure 8. Typical voltammetric profiles of redox-active MCCs: (a) a low-nuclearity cluster, for example $[Co_8Pt_4C_2(CO)_{24}]^{n-}$ (n = 1–4), and (b) a high-nuclearity cluster, for example $[Ni_{32}C_6(CO)_{36}]^{n-}$ (n = 5–10). Reprinted with permission from ref.[42] Copyright 2010 American Chemical Society (a) and ref.[59a] Copyright 1999 Wiley-VCH Verlag GmbH & Co. KGaA (b).

A systematic analysis of the electrochemical data available for several multivalent high-nuclearity MCCs has shown that the gap between the pairs of redox waves decreases as the MCC nuclearity increases and, by extrapolation, it should be almost zero at a nuclearity of approximately 70,[18] indicating that complete metallisation should occur at this nuclearity. In doing this analysis, it is of paramount importance to consider the real nuclearity of the metal core and not the nominal one, which is sometimes affected by staple motives and conjuncto structures.

Multivalence properties of larger MCCs makes them feasible candidates for molecular nanocapacitors, and applications can be envisioned in nanolithography and information storage.[18] In this regard, it is interesting to note that mixed Langmuir–Blodgett films consisting of an inert molecular stearic acid matrix and embedded MCCs, such as $Pt_4(CO)_5(PEt_3)_4$, $Pt_5(CO)_6(PR_3)_4$ (R = Et, Ph), $Pt_{17}(CO)_{12}(PEt_3)_8$ and $Pd_{23}(CO)_{20}(PEt_3)_8$, were prepared some years ago, and they were studied as possible high-temperature single-electron tunnelling (SET) devices.[96] More recently, a gold–cluster–gold junction has been fabricated by depositing a molecular Pt cluster on a gold surface and employing a Au STM tip.[97] With this approach, single-molecule MCCs can be electrically characterised.

Multivalence may also have some important chemical consequences on the behaviour of larger MCCs. For instance, we can speculate that, as the metallisation limit is reached and the energy difference between consecutive redox couples approaches the order of the thermal energy, *RT*, such large MCCs should undergo spontaneous auto-disproportionation equilibria in solution. Above this limit, even a single atomically monodisperse molecular MCC would be "ionically" polydisperse, in the sense that in solution there would be a mixture of species with exactly the same size and structure but with different ionic charges.

At the actual size (20–50 metal atoms), the charge of multivalent MCCs can be selected and controlled by means of chemical redox reactions or by electrochemical methods. This has allowed, in certain cases, the isolation and structural characterisation of redox-related species. At the same time, complications may arise, because high-nuclearity MCCs sometimes display a polyhydride nature. Hydrides in MCCs are usually slightly acidic, and therefore hydride atoms can be added or removed by protonation–deprotonation (acid–base) reactions.[90,98] As a consequence, the charge in a molecular MCC might change as a result of a redox or acid–base reaction. By considering both multivalence and polyhydride behaviour in high-nuclearity MCCs, four cases may be distinguished: (a) MCCs with neither redox nor polyhydride nature (fixed charge); (b) multivalent MCCs without polyhydride nature; (c) polyhydride MCCs without redox properties; (d) MCCs with both multivalent and polyhydride properties. Below a nuclearity of 22–30, these four cases can be easily distinguished by ^1H NMR spectroscopic studies. Conversely, as discussed in the next section, larger MCCs become NMR-silent, and their polyhydride nature can thus be confirmed only by means of indirect chemical and electrochemical studies.[88–90,98]

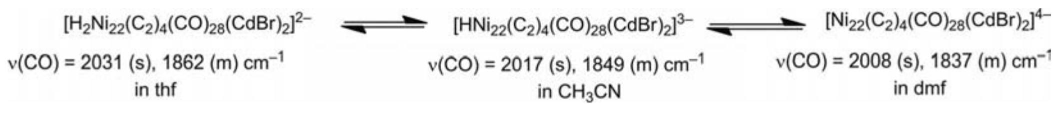
4.2 NMR Spectroscopy and the Problems of Detecting Hydrides in High-Nuclearity MCCs

As discussed in the previous section, several MCCs display a polyhydride nature. ^1H NMR spectroscopy would be the technique of choice to unravel this point, but, as already mentioned, it seems that above a certain nuclearity MCCs become NMR-silent. This is the case not only for ^1H NMR spectroscopy, but basically for investigations of all nuclei for large MCCs (e.g. ^1H, ^{13}C, ^{195}Pt).[90] At present, it seems that the limit for detecting hydrides (and other nuclei) by means of NMR spectroscopy is a nuclearity of approximately 22–30. This point is quite puzzling, and a conclusive explanation is not yet available.

Multinuclear NMR spectroscopy has been widely used to characterise low-nuclearity MCCs in solution and in the solid state. For instance, ^1H NMR spectra of low-nuclearity cluster species, for example $[H_{4-n}Ni_{12}(CO)_{21}]^{n-}$,[99] $[H_{4-n}Ni_9Pt_3(CO)_{21}]^{n-}$[100] and $[H_{5-n}Rh_{13}(CO)_{24}]^{n-}$,[101] are diagnostic of the presence of hydride atoms and support IR spectroscopic evidence in demonstrating the occurrence of protonation–deprotonation equilibria in solution. Furthermore, in favourable cases, multinuclear and bidimensional NMR (^{13}C, ^{31}P, ^{103}Rh, ^{195}Pt) spectroscopic studies have enabled the assignment of all the different resonances to each single atom, resulting in a detailed description of the structure of these clusters in solution as well as their dynamic behaviour.[102]

Unfortunately, beyond a nuclearity of approximately 22–30,[90] several spin-active nuclei (e.g. ^1H, ^{13}C, ^{195}Pt) in MCCs become partially or completely silent in NMR spectroscopic experiments. To the best of our knowledge, the most remarkable exception is represented by the neutral $H_{12}Pd_{28}Pt_{13}(PPh_3)_{12}(PMe_3)(CO)_{27}$.[103] Apart from providing a solution to the serious problems in the complete characterisation of MCCs as discussed in the previous section, a satisfactory explanation of this behaviour is needed for fundamental purposes.

The case of polyhydride $[H_{4-n}Ni_{22}(C_2)_4(CO)_{28}(CdBr)_2]^{n-}$ (*n* = 2–4) is rather significant in this regard.[90] ^1H NMR spectra in different solvents (Scheme 6 and Figure 9) clearly confirm the sequential deprotonation of $[H_2Ni_{22}(C_2)_4(CO)_{28}(CdBr)_2]^{2-}$ when passing from acetone to CH_3CN and eventually to dmso, as indirectly inferred from chemical and electrochemical studies. More importantly, all hydride resonances are very broad (the half-height widths are in the 500–800 Hz range), whereas the resonances of lower-nuclearity species such as $[H_{4-n}Ni_{12}(CO)_{21}]^{n-}$[99] are relatively sharp (5–10 Hz). It seems reasonable to think that a progressively enhanced broadening upon a further increase in nuclearity could eventually hinder the direct observation of ^1H NMR resonances in higher-nuclearity MCCs, as systematically observed for anionic Ni and Ni–Pt carbonyl clusters. Moreover, variable-temperature ^1H NMR spectroscopic studies indicate the presence of complex dynamic processes in all $[H_{4-n}Ni_{22}(C_2)_4(CO)_{28}(CdBr)_2]^{n-}$ (*n* = 2–3) species as well as a large temperature drift of 0.17–0.21 ppm K^{-1} of the resonances. Even the effect of the solvent on the chemical shifts is rather large.



Scheme 6.

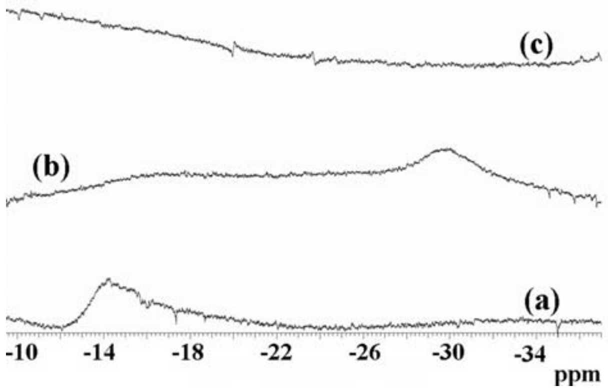


Figure 9. ^1H NMR spectra recorded at 298 K of $[H_{4-n}Ni_{22}(C_2)_4(CO)_{28}(CdBr)_2]^{n-}$ (n = 2–4) in solvents of different basicity.[90] Reproduced by permission of the Royal Society of Chemistry.

Dynamic site-exchange processes alone seem inadequate to justify both the great broadness of all peaks as well as their unprecedented drift in chemical shift with changes in solvent and temperature and, above all, the complete disappearance of all NMR resonances in larger MCCs. An explanation might be that incipient metallisation and emerging magnetism (Ni metal is magnetic), combined with ligand site-exchange, may cause this unprecedented broadening and temperature-drift of the hydride resonances.

A further piece of the puzzle is revealed by dynamic light scattering (DLS) studies, which systematically point out the presence of particles in solution with hydrodynamic diameters considerably greater than the free MCC ions in the case of $[HNi_{22}(C_2)_4(CO)_{28}(CdBr)_2]^{3-}$. Enormous particles have been detected by DLS also in the acetonitrile and dmso solutions of Au–Fe–CO nanoclusters[85] and Pt Chini clusters,[67] suggesting that this might be a general phenomenon. It seems conceivable that these enormous particles might arise by assembly in solution of fractal clusters or extensive chunks of ionic lattice by electrostatic interactions. The slow tumbling of these huge aggregates, with or without the contribution of dynamic hydride site-exchange processes, might account for the observed ^1H NMR spectroscopic behaviour of $[H_{4-n}Ni_{22}(C_2)_4(CO)_{28}(CdBr)_2]^{n-}$ (n = 2, 3) ions. Related difficulties in observing all expected NMR signals are also documented in the literature for colloidal metal nanoparticles stabilised in a ligand shell.[104]

4.3 Magnetic Properties in Odd- and Even-Electron MCCs

Odd-electron MCCs displaying one unpaired electron are paramagnetic species, as confirmed experimentally in several cases.[18] A notable case is $[Ag_{13}Fe_8(CO)_{32}]^{4-}$,[40] where coupling of the unpaired electron in its ESR spectrum with the different Ag atoms of the centred Ag_{13} cube-octahedral cage allowed an experimental mapping of electron density within the cluster by performing "experimental quantum mechanics" as originally envisioned by Dahl.

Conversely, the magnetic behaviour of even-electron MCCs is rather controversial.[105] The appearence of a temperature-dependent (Curie) paramagnetism resulting from quantum size effects was predicted as soon as the HOMO–LUMO gap was reduced to values close to kT.[93] In this sense, magnetic measurements might be of help to unravel metallisation of the metal core of the cluster. Magnetism was first discovered in osmium carbonyl clusters,[106] and then followed studies of magnetism in other MCCs, both by EPR spectroscopy[107] and magnetic susceptibility measurements.[105,108] Microcrystalline samples of several homometallic carbonyl clusters of Ru, Os, Ni, Pt, as well as bimetallic Ni–Pt carbonyl clusters[105,107,108] revealed weak Curie-type temperature-dependent paramagnetism (TDP) corresponding to magnetic moments in the range of 0.1–4 Bohr magnetons per cluster ion, in some cases also associated with a temperature-independent (van Vleck) paramagnetism (TIP), which was found to increase with cluster size.

However, SQUID measurements on a single crystal of $[HNi_{38}Pt_6(CO)_{48}]^{5-}$ failed to confirm the Curie-type TDP.[109] Moreover, combined magnetic susceptibility and EPR spectroscopic studies on single crystals of $[Fe_3Pt_3(CO)_{15}]^{2-}$ and $[Ag_{13}Fe_8(CO)_{32}]^{3-}$ salts unambiguously showed that their TDP was due to impurities of the oxidised and reduced $[Fe_3Pt_3(CO)_{15}]^{-\cdot}$ and $[Ag_{13}Fe_8(CO)_{32}]^{4-\cdot}$ species, respectively. This finding emphasised the necessity to investigate such behaviour by at least two complementary techniques.[110] Furthermore, DFT calculations on optimised model structures of highest-nuclearity Ni and Ni–Pt carbonyl clusters suggested that the surface carbonyl ligands should completely quench the magnetic moments of their corresponding bare metal kernels.[94]

The above experimental and theoretical observations led to the conclusion that TDP, as well as TIP, of even-electron MCCs systematically arises from adventitious contamination with odd-electron species or the presence of unidentified magnetic impurities. Consequently, studies aimed at proving that large MCCs could feature progressively vanishing HOMO–LUMO gaps and high-spin ground states as a function of size came to a rest for a while.

A somehow related controversy regarding the magnetic properties of ligand-stabilised gold nanoparticles and thiolated gold surfaces or thin films was raised later in the literature.[111] Assessment of the intrinsic magnetic properties of gold nanoparticles, rather than molecular MCCs, would be further complicated by their nonmolecular nature and ill-defined composition and structure.

As for electrochemical properties, the magnetic behaviour of even-electron MCCs may arise either from ad hoc conditions, stabilising two or more almost degenerate MOs, or from incipient metallisation of the metal core, reducing the energy gap of MOs to close to kT.

For instance, recent DFT calculations suggested that even low-nuclearity MCCs such as $[Fe_6Ni_6N_2(CO)_{24}]^{n-}$ (n = 2, 4),[112] $[Co_{11}RhN_2(CO)_{24}]^{2-}$ and $[Co_{10}Rh_2N_2(CO)_{24}]^{2-}$[113] could feature a triplet ground state, which was partially substantiated in the latter by EPR spectroscopic studies, as a result of the stabilising effect of the interstitial nitrogen atoms (ad hoc condition). This point was further corroborated by joined structural, NMR spectroscopic, electrochemical, variable-temperature EPR spectroscopic and SQUID studies on the structurally related dicarbides $[Co_8Pt_4C_2(CO)_{24}]^{n-}$ (n = 1,2) (Figure 10).[42] The paramagnetism of the odd-electron monoanion (n = 1) is due to the presence of one unpaired electron in the SOMO, resulting in a doublet state (S = 1/2). Conversely, the paramagnetic behaviour displayed by the even-electron species $[Co_8Pt_4C_2(CO)_{24}]^{2-}$ arises from triplet states (S = 1), as indisputably pointed out by its EPR spectrum. These indisputable examples of intrinsic magnetism of even-electron MCCs may lend support to the authenticity of some previously ascertained magnetism in highest-nuclearity MCCs and gold colloidal particles. At the same time, it points out that magnetic data on larger molecules must be carefully considered and cross-checked with at least two independent techniques.

This applies to $[Ni_{16}Pd_{16}(CO)_{40}]^{4-}$, whose magnetism has been confirmed by both SQUID magnetometry and muon spin rotation/relaxation (μSR) spectroscopy.[114] The susceptibility measurements show an exceptionally high magnetic moment corresponding to a total spin value of J = 2, suggesting a Hund filling of a quadruplet ground state and indicating incipient metallisation of the metal core of the cluster, as also confirmed by EHMO calculations.

It may be conjectured that a progressive tightening of the frontier energy levels by further increasing the size of the cluster could trigger magnetism in an increasing number of MCCs, regardless of even or odd numbers of electrons. Novel magnetic behaviour could be at hand, since the unpaired electrons reside in molecular orbitals delocalised over most atoms of the molecule, rather than being located in atomic orbitals, as for polynuclear compounds.[18,42,114]

The development of electronic and magnetic properties in molecular MCCs make them candidates for applications in nanosciences and nanotechnologies as molecular nanocapacitors, superparamagnetic quantum dots and nanomagnets,[18] as well as precursors of narrowly dispersed magnetic alloy and metal oxide nanoparticles of corresponding composition.[115]

5. Self-Assembly

MCCs can be used as nanometric or subnanometric building blocks for self-assembly. Self-assembly is a phenomenon of paramount importance in several chemical and biological systems, which may find applications in bottom-up nanotechnology.[1,2,116] Several types of organic, inorganic, organometallic and biological building blocks have already been studied, whereas MCCs have been so far scarcely investigated.

The fusion of two or more anionic clusters with a central core constituted by a single cation, such as $\{Hg[Os_{10}C(CO)_{24}]_2\}^{2-}$,[117] or cationic moieties, for example $[H_2Ru_{12}Cu_6Cl_2(CO)_{34}]^{2-}$,[118] $[H_4Ru_{20}Cu_6Cl_2(CO)_{48}]^{4-}$[119] and $[Ag_3Ru_{10}C_2(CO)_{28}Cl]^{2-}$,[120] has been used to prepare MCC aggregates close to or trespassing into the nanofield. This can be viewed as an alternative way to form larger molecular MCCs by assembling smaller clusters. Moreover, MCCs with different physical properties may be assembled together to yield polyfunctional MCC aggregates. In addition,

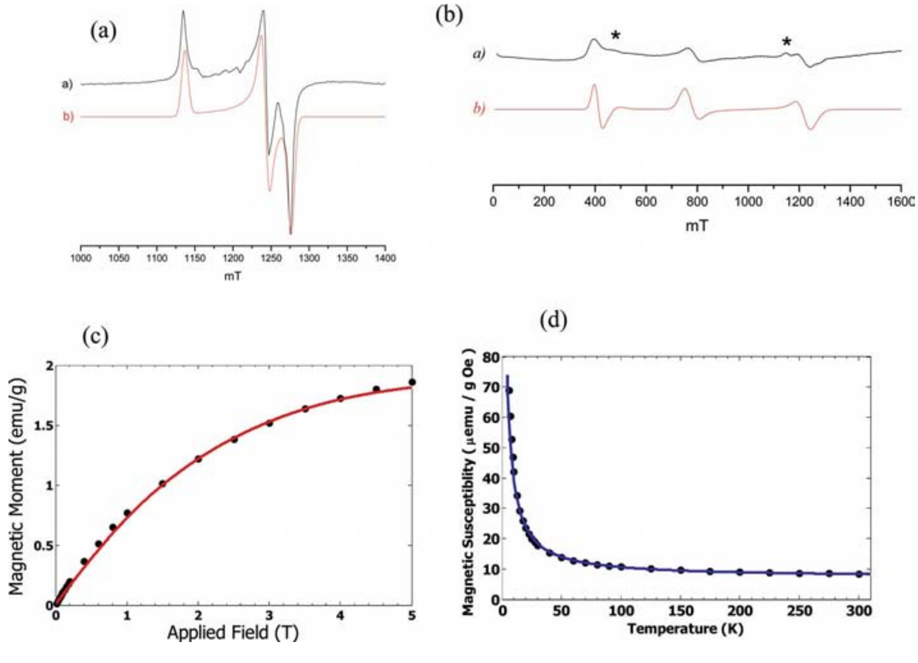


Figure 10. EPR spectra of solid $[Co_8Pt_4C_2(CO)_{24}]^{n-}$ at 5 K: (a) n = 1, S = 1/2; (b) n = 2, S = 1 (* background impurity). (c) First magnetisation curve and (d) temperature dependence of magnetisation of $[Co_8Pt_4C_2(CO)_{24}]^{2-}$. Reprinted with permission from ref.[42] Copyright 2010 American Chemical Society.

MCCs can be polymerised to produce infinite 1D molecular wires, or they can be assembled together into ordered 2D or 3D arrays as well as charge- and electron-transfer materials (see below). Therefore, MCCs might be used for the preparation of new functional and polyfunctional nanostructured materials.

We can envision six general strategies for self-assembly of MCCs:

(1) Formation of functionalised ionic materials (e.g. electron- and charge-transfer materials) by assembly of functional MCC anions with suitable cations (organic, coordination compounds, magnetic or redox-active clusters).

(2) Polymerisation of MCCs by the formation of homometallic M–M bonds with or without ligand dissociation.

(3) Aggregation of MCCs through heterometallic M–M′ bonds by using suitable M'^{n+} cations.

(4) Self-assembly through inorganic linkers, for example M_nX_m (X = halide or pseudohalide) units.

(5) Aggregation of clusters by polydentate organic linkers.

(6) Formation of isocarbonyl linkages.

5.1 Ionic Functionalised Materials Based on MCCs

Most MCCs are anionic, and therefore they are usually obtained as ionic solids in conjunction with alkali metal, tetraalkylammonium or phosphonium cations. Additional properties may be introduced by using suitable cations, for example redox-active, magnetic or luminescent species.

For instance, the combination of redox-active MCC anions with redox-active organic cations with similar redox potentials, such as viologens, allowed the preparation of charge- and electron-transfer materials, for example $[EtV]_5[Ag_{13}Fe_8(CO)_{32}]$, $[EtV]_2[Fe_4Pt(CO)_{16}]$, $[EtV][Fe_3Pt_3(CO)_{15}]\cdot$thf and $[EtV][Fe_4Au(CO)_{16}]_2$.[121] In particular, the mixed $[EtV][Fe_3Pt_3(CO)_{15}]\cdot$thf salt, containing both redox-active anions and cations, displays a resistivity in pressed pellet form ($6.6 \times 10^4\ \Omega$ cm) that is 3–4 orders of magnitude smaller than that of $[NMe_3CH_2Ph]_2[Fe_3Pt_3(CO)_{15}]$ ($1.5 \times 10^8\ \Omega$ cm) containing a nonredox ammonium cation.

Apart from applications as conductor and semiconductor materials, additional magnetic, optical or luminescence properties can be obtained by using suitable MCC anions and miscellaneous cations. For example, a long-bonded π-dimer of the $[EtV]^{\cdot+}$ radical ion displaying a significantly populated triplet state was demonstrated for the first time in the above-mentioned $[EtV]_2[Fe_4Pt(CO)_{16}]$ salt by solid-state EPR spectroscopy.[121] We can expect temperature-dependent magnetism for this material, and the field may be further developed by combining magnetic MCC anions and magnetic organic or coordination cations.

5.2 1D Molecular Wires by the Formation of Homometallic M–M Bonds

One-dimensional metal wires[122] and one- and two-dimensional superclusters that are assembled through M–M bonds[123] are interesting as low-dimensional molecular materials, and they may find applications in molecular electronics and nanolithography.

It has been known for a long time that stepwise oxidation of $[Pt_{3n}(CO)_{6n}]^{2-}$ Chini clusters results in 1D growth of the cluster by formal progressive addition of $Pt_3(CO)_3(\mu\text{-}CO)_3$ units along a common C_3 axis (Figure 11).[26] Thus, by pushing forward the oxidation process in a controlled manner, Pt wires based on an infinite stack of these units can eventually be obtained. The morphologies of the resulting $[M]_x[Pt_{3n}(CO)_{6n}]$ (M = mono- or bivalent cation; x = 1, 2; n = 2–8) materials depend on the nuclearity n of the cluster anions and the nature and size of the cations.[67]

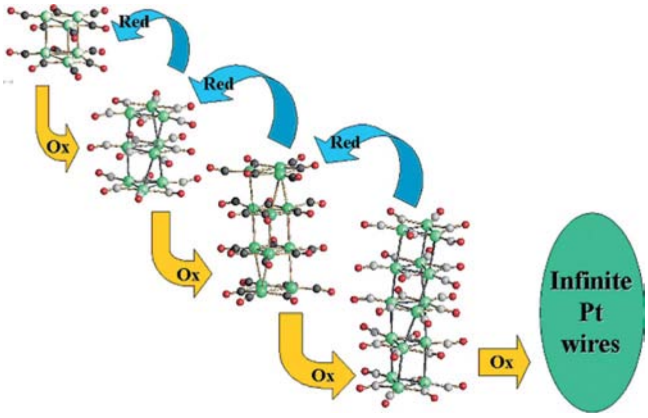


Figure 11. Stepwise oxidation of $[Pt_{3n}(CO)_{6n}]^{2-}$ clusters to form infinite wires (Pt, green; C, grey; O, red).

Lowest-nuclearity species ($n \leq 4$), independently of the cations employed, crystallise systematically by adopting ionic 0D packing, where anions and cations are separated by normal van der Waals contacts and do not show any supramolecular order of the anions.[67] This is probably due to electrostatic repulsions between these small and negatively charged anions. As the nuclearity of the cluster increases ($n \geq 5$) while the negative charge stays constant, electrostatic repulsions decrease and the cluster anions can approach each other and give rise to infinite chains, which can be discontinuous, semicontinuous or continuous, depending on the size of the cluster anion and the organic or inorganic cation (Figure 12).

The tendency of highest-nuclearity species (n = 5–8) to produce infinite wires at the molecular level is also macroscopically evidenced by the fact that they often afford crystals that look like whiskers (see, for instance, Figure 12d).[124] Moreover, a clear effect of the support on the self-assembly of Chini clusters was observed by STM imaging of highly ordered pyrolytic graphite (HOPG) impregnated with water/2-propanol solutions of $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 4–6) dianions, which demonstrated the preferential formation of nanowires over other morphologies.[125] As inferred from TEM images, well-defined Pt morphologies, including Pt nanowires, were also obtained by preparing $[Pt_{3n}(CO)_{6n}]^{2-}$ (n = 2–4) dianions in the micropores of zeolites, followed by thermal decomposition.[30b] This opens

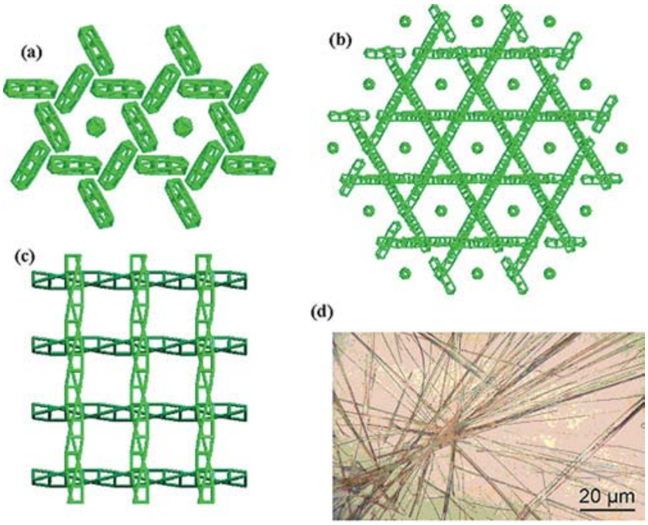


Figure 12. Crystal packing of (a) $[NBu_4]_2[Pt_{12}(CO)_{24}]$ (isolated ions, 0D packing), (b) $[NEt_4]_2[Pt_{15}(CO)_{30}]$ (discontinuous chains, 3D network) and (c) $[NEt_4]_2[Pt_{24}(CO)_{48}]$ (continuous chains, 2D network). Only Pt atoms are represented for clarity. (d) Optical micrographs (magnification 50 ×) of whisker-like crystals of $[NBu_4]_2[Pt_{15}(CO)_{30}]$.

the possibility to use such clusters as printable metals for the deposition of submicrometric Pt wires (see Section 6).[124]

As a further point of interest, the self-organised infinite chains morphologically and functionally resemble CO-sheathed Pt wires. In fact, electrical resistivity measurements on pressed pellets indicated that ionic 0D materials are electrical insulators, whereas the resistivity drops from approximately 10^5 to 10^3 and $10^2\ \Omega$ cm on passing from discontinuous to semicontinuous and continuous materials, respectively.[67] In this context, it is worth to mention that the typical resistivity of a continuous-chain salt of these Pt clusters is comparable to that of the doped Krogmann salt. For instance $K_2[Pt(CN)_4]\cdot 0.4Br$ displays a resistivity (as pressed pellets) of $10^3\ \Omega$ cm, which decreases to $10^{-2}\ \Omega$ cm in single crystals.[126]

Finally, DLS studies suggest that these aggregation phenomena might already be present in solution, which points the way for further developments for the self-assembly of MCCs. These aggregation phenomena in solution might also be related to some previous observations on the physical properties of MCCs in solution, such as their yet unexplained NMR spectroscopic behaviour.

5.3 Polymerisation and Copolymerisation of MCCs by the Formation of Heterometallic M–M′ Bonds

Oligomerisation as well as polymerisation of MCCs by the formation of heterometallic M–M′ bonds is well documented, and the basic approach consists of the reaction of a preformed cluster anion with M'^{n+} cations, such as Ag^+, Cu^+ and Hg^{2+}. The process can be described as a Lewis acid–base reaction where the metal cage of the cluster behaves as a soft Lewis base, alternative to redox condensation or attack on the hard-base sites represented by carbonyl oxygen atoms.

The existence in solution of several fused MCC moieties such as $\{Ag[Rh_6C(CO)_{15}]_2\}^{3-}$ and higher $\{Ag_{n-1}[Rh_6C(CO)_{15}]_n\}^{n-}$ oligomers was demonstrated several years ago by multinuclear NMR spectroscopy,[127] indicating the possibility to isolate MCC aggregates well beyond 2 nm. For instance, an infinite $\{[AgRu_6C(CO)_{16}]^-\}_\infty$ superwire was quantitatively assembled by reacting $[Ru_6C(CO)_{16}]^{2-}$ with Ag^+ ions.[123] In addition, semiconducting $[\{NEt_4\}\{TeFe_3(CO)_9Cu\}]_\infty$ tellurium–iron–copper carbonyl polymers were prepared from the reaction of $[TeFe_3(CO)_9]^{2-}$ with $[Cu(CH_3CN)_4]^+$ by the formation of heterometallic Cu–Fe bonds, with an extrapolated dc conductivity of $2 \times 10^{-2}\ (\Omega\ \mathrm{cm})^{-1}$.[128]

5.4 MCC Self-Assembly with Inorganic Linkers

Condensation of anionic MCCs with $M'X_n$ (M = metals of groups 11–12; X = halides or pseudohalides) salts with limited or no elimination of X counterions may result in the formation of dimeric, oligomeric or polymeric aggregates by $M–M'_nX_m–M$ interactions or through simultaneous heterometallic M–M′ interactions and M′–X–M′ bridges. Some representative examples are the $[H_2Ru_{12}Cu_6Cl_2(CO)_{34}]^{2-}$,[118] $[H_4Ru_{20}Cu_6Cl_2(CO)_{48}]^{4-}$,[119] $[Ag_3Ru_{10}C_2(CO)_{28}Cl]^{2-}$,[120] $[\{TeRu_5(CO)_{14}\}_2Cu_4X_2]^{2-}$ (X = Cl, Br),[129] $[\{TeFe_3(CO)_9\}_2Cu_4X_2]^{2-}$ (X = Cl, Br)[130] and $\{Cd_2Cl_3[Ni_6(CO)_{12}]_2\}^{3-}$ dimers[131] and the formation of the 1D $\{[Pt_9(CO)_{18}(\mu_3\text{-}CdCl_2)_2]^{2-}\}_\infty$ polymer (Figure 13) from the reaction of $[Pt_9(CO)_{18}]^{2-}$ with $CdCl_2$.[132] This approach is very flexible and applicable to almost all MCCs, once other reactions such as redox condensation are avoided. Its major limit is represented by the fact that it is very likely that the halide bridges interrupt electrical conduction, which results in insulating materials as in the case of $\{[Pt_9(CO)_{18}(\mu_3\text{-}CdCl_2)_2]^{2-}\}_\infty$.[132] Nonetheless, it might be

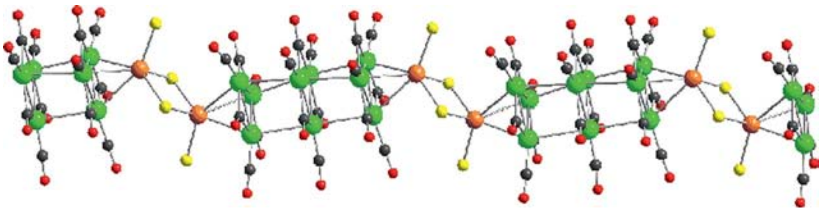


Figure 13. Chunk of the 1D $\{[Pt_9(CO)_{18}(\mu_3\text{-}CdCl_2)_2]^{2-}\}_\infty$ polymer[132] (Pt, green; Cd, orange; Cl, yellow; C, grey; O, red).

employed for other applications, such as, for instance, the assembly of clusters with magnetic or optical properties. A noticeable exception is represented by the $\{[PPh_4]_2[Te_2Ru_4(CO)_{10}Cu_4Br_2Cl_2]\cdot thf\}_\infty$ cluster chain polymer, which has a surprisingly low energy gap (ca. 0.37 eV) and exhibits semiconducting properties [extrapolated dc conductivity in the order of $(1–5)\times 10^{-2}$ $(\Omega\ cm)^{-1}$].[133]

5.5 MCC Self-Assembly with Organic Linkers

As an alternative, MCCs can be assembled by using organic linkers, such as bi- and polydentate ligands. In this case, the use of π-conjugated molecules may allow electronic communication, eventually resulting in conductive materials, although electrical conductivities of such materials have rarely been determined to date.

Dimeric units can be obtained by the formation of M–L–L–M bonds, as in the cases of $\{(H_2N(CH_2)_4NH_2)[Rh_5(CO)_{14}]_2\}^{2-}$,[134] $[\{Rh_6(CO)_{14}\}_2(dpbp)]$ and $[\{Ru_6C(CO)_{15}(dpbp)_3\}Ir_4(CO)_8]$ {dpbp = 2,2′-bis(diphenylphosphanyl)-4,4′-bipyridine}.[135] In this sense, the $[Fe_4Cu_2(CO)_{12}]$ moiety, readily available as the solvato cluster $[Fe_4Cu_2(CO)_{12}(CH_3CN)_2]$, is rather versatile, since, depending on the bidendate ligand employed, it can be assembled into dimers, tetramers or infinite polymeric chains.[136] Electronic conductivity along the superchains is likely when using aromatic bidentate ligands such as 4,4′-bipyridine, pyrazine and *p*-dicyanobenzene, as suggested by electrochemical studies. This point is confirmed in the case of the Cu–dipyridyl-linked Te–Fe carbonyl cluster polymer $[\{TeFe_3(CO)_9Cu_2\}(\mu\text{-}4,4'\text{-dipyridyl})_{1.5}]_\infty$ assembled from $[TeFe_3(CO)_9]^{2-}$, $[Cu(CH_3CN)_4]^+$ and 4,4′-dipyridyne, which displays semiconducting behaviour [extrapolated dc conductivity 5×10^{-2} $(\Omega\ cm)^{-1}$].[128]

Moreover, in the unit cells of the $[Fe_4Cu_2(\mu_6\text{-}C)(CO)_{12}(bipy)]_4\cdot 8thf$ tetramers and $[Fe_4Cu_2(\mu_6\text{-}C)(CO)_{12}(p\text{-}dcb)]_\infty\cdot 2thf$ polymeric structures there are clathrated thf molecules, which are readily lost by drying in vacuo. Thus, such materials are somehow related to metal organic frameworks (MOF) and provide the possibility to employ hybrid materials made up of MCCs and organic ligands for MOFs. This point has been further exemplified by the self-assembly of chains and nanochannels from carbido clusters, silver ions and heterocyclic ligands, resulting in 1D coordination polymers such as $[\{AgOC_4H_8\{Rh_6C(CO)_{15}\}AgOC_4H_8\}pyz]_\infty$ and $[bipy\{Ag_2Ru_6C(CO)_{16}\}(bipy)_2\ \{Ag_2Ru_6C(CO)_{16}\}\cdot 2thf]_\infty$.[137]

5.6 Ordered Materials by Isocarbonyl Linkages

The oxygen atoms of the carbonyl ligands in anionic MCCs are hard Lewis basic sites, and they therefore may interact with hard Lewis acids, such as alkali and lanthanide ions, resulting in the formation of isocarbonyl groups. These are often found in the alkali metal salts of MCC anions and can result in very beautiful 3D networks such as $[Cs(thf)_{0.33}]_3[\{Fe_3(CO)_9(\mu_3\text{-}O)\}_2H]$.[138]

Furthermore, miscellaneous 1- and 2D arrays assembled via η^2-carbonyl groups (isocarbonyl) of the previously unknown $[Co_4(CO)_{11}]^{2-}$ dianion with Yb^{II} or Eu^{II} cations have been obtained by the reaction of $Hg[Co(CO)_4]_2$ with Yb or Eu metals.[139]

Studies on these materials have been, up to now, limited to their structural aspects, but we can envision the possibility of using ordered salts based on isocarbonyl linkages as functional materials, for instance, by using magnetic or fluorescent metal ions or for the preparation of MOFs.

6. MCCs as Precursors for Metal Nanoparticles

As described in the previous sections, high-nuclearity MCCs may be viewed as molecular metal nanoparticles. In addition to being used intact, they can be also employed as molecular precursors for the preparation of metal nanoparticles, metal nanowires and other nanostructured materials. The advantage of using a molecular precursor containing an already well-defined metal core is that, by decomposing it under mild conditions, one is more likely to obtain very small metal nanoparticles (with sizes comparable to the original MCCs) with controlled dimensions and compositions. These points are of even greater importance in the case of bimetallic nanoparticles.

Nonetheless, data on applications of MCCs in the nanosciences are scarcely available in the literature, apart from their application as precursors for the preparation of supported metal nanoparticles to be used in catalysis.[140] This appears to be, up to now, the only field that has been quite extensively investigated, and it has revealed some interesting results. Apart from the preparation of catalytically active metal nanoparticles on conventional oxide supports, quite interesting studies have been performed on microporous and mesoporous supports. It is well established that homo- as well as bimetallic MCCs can be generated in cavities of zeolites (Faujasite, ZSM-5, ALPO-5) through “ship-in-a-bottle” syntheses and subsequently transformed into metal nanoparticles of controlled size (Figure 14).[30,141]

Further developments in this field were achieved in the last decade by using mesoporous silica supports (e.g. FSM-16, MCM-41, STAC-1, SBA-15).[142] The size of the pores (1.6–30 nm) of these supports should allow direct loading of most known homo- and heterometallic MCCs, which can then be decarbonylated under mild conditions, affording highly dispersed metal nanoparticles anchored to the support by M–O interactions; these should be sufficient in order to prevent metal migration and sintering. In this regard, a few examples of catalytic materials that are active for selective hydrogenation and that were prepared by introducing carbonyl clusters in mesoporous silica have recently appeared in the literature. The results obtained in terms of catalytic performance, selectivity, stability and recovery recommend these catalysts as new materials for clean technologies.[22e,140b,142,143] For instance, bimetallic nanoparticle catalysts supported on mesoporous silica can be prepared by using molecular bimetallic Ru–Cu,[143] Pt–Sn,[144] Ru–

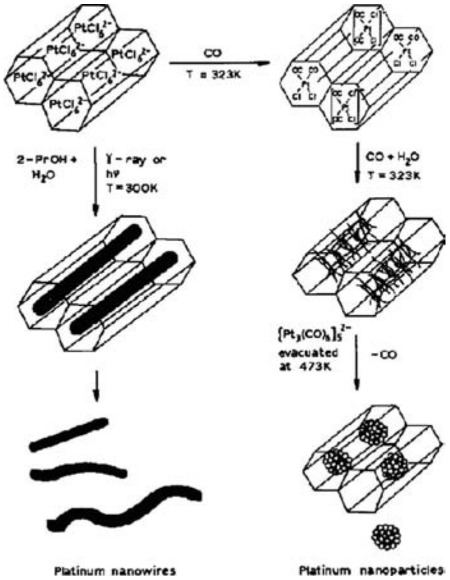


Figure 14. Ship-in-a-bottle fabrication of platinum nanowires and nanoparticles. Reprinted with permission from ref.[30b] Copyright 1999 Wiley-VCH Verlag GmbH & Co. KGaA.

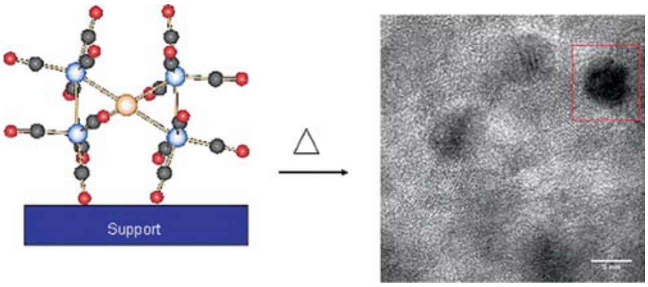


Figure 15. Preparation of Au–FeO$_x$ catalysts on TiO$_2$ from [Au-Fe$_4$(CO)$_{16}$]$^-$ clusters: the molecular precursor is adsorbed on the support (e.g. TiO$_2$, CeO$_2$, mesoporous silica) and then converted into the active phase by thermal decomposition. The TEM image on the right displays the presence of small (< 5 nm) Au nanoparticles well dispersed on the support and probably anchored to it through a FeO$_x$ layer. Reprinted from ref.[148b] with permission from Elsevier.

Pd[140b,145] and Ru–Sn[140a–140b,144,146] MCC precursors, among others. These materials are very active and selective for the hydrogenation of miscellaneous unsaturated organic molecules. Asymmetric hydrogenation can also be performed by introducing chiral modifiers on the support, as exemplified by the preparation of catalytic materials for the enantioselective hydrogenation of methyl pyruvate and acetophenone by depositing [H$_3$Ru$_4$(CO)$_{12}$]$^-$ on MCM-41 modified with (3-chloropropyl)trimethoxysilylcinchonidium.[147] In the case of bimetallic catalysts, the noble metal is mainly responsible for the catalytic performance, whereas the second metal acts as promoter and/or anchors the active nanoparticle on the oxide support. This point is further exemplified by the preparation of highly dispersed Au–FeO$_x$ nanoparticles on supports such as TiO$_2$, CeO$_2$ and mesoporous silica (SBA-15) starting from molecular bimetallic MCCs such as [AuFe$_4$(CO)$_{16}$]$^-$ and [Au$_4$Fe$_4$(CO)$_{16}$]$^{4-}$ (Figure 15).[148] The formation of a FeO$_x$ layer anchoring the Au nanoparticle on the support makes these catalysts very stable and active also for oxidation processes.

Furthermore, self-assembly phenomena described in Section 5 can be exploited together with soft lithography for fabricating submicrometric conductive metal wires on surfaces, and these might then be used to connect systems across length scales and for the fabrication of field effect transistor (FET) or submicrometric electrodes.[124] For instance, submicrometric stripes of [NBu$_4$]$_2$[Pt$_{15}$(CO)$_{30}$] have been prepared on glass by micro inject moulding in capillaries (MIMIC). Optical microscopy clearly demonstrates the crystalline nature of the deposited material; moreover, the crystalline domains (composed of infinite Pt molecular wires as discussed in Section 5.2) are mostly aligned along the direction of the channels used for MIMIC (Figure 16). Interestingly, already at the molecular level (prior to thermal decomposition), the aligned wires display a conductivity (2.1×10^{-2} S/cm) that is four orders of magnitude greater than that of the same material in pressed pellets (7.7×10^{-6} S/cm), which further increases to approximately 35 S/cm after thermal annealing.

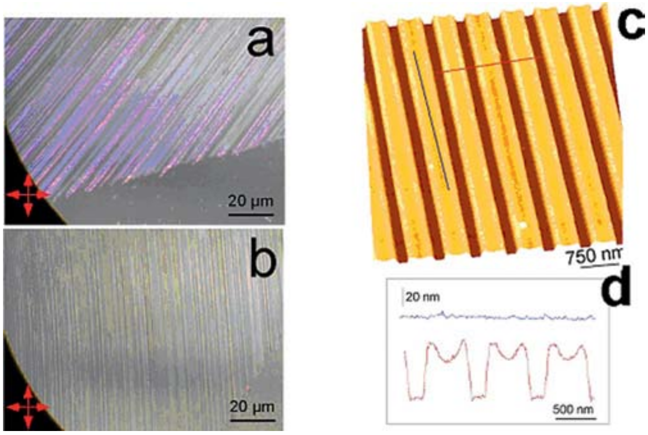


Figure 16. Optical micrographs of micrometric stripes fabricated on glass by MIMIC using [NBu$_4$]$_2$[Pt$_{15}$(CO)$_{30}$] with crossed polars (a) rotated ca. 30° and (b) parallel. (c) Corresponding AFM images and (d) profiles. Reprinted with permission from ref.[124a] Copyright 2008 American Chemical Society.

Bimetallic MCCs can be useful precursors for the preparation of magnetic bimetallic nanoparticles protected by ligands and dispersed in organic solvents or water as well as embedded in mesoporous matrices.[115,149] Thus, it has been demonstrated that the thermal decomposition of bimetallic Fe–Co, Fe–Ni and Fe–Pt MCCs in 1,2-dichlorobenzene solution in the presence of surfactants (e.g. oleic acid, myristic acid, oleylamine) results in the formation of magnetic nanoalloys with controlled size and composition (Figure 17).[115a] A similar approach might also be used for the preparation of nanoparticle–polymer nanocomposites.[150] Finally, the use of Pt carbonyl clusters for the preparation of modified electrodes employed in fuel cells has also been demonstrated.[151]

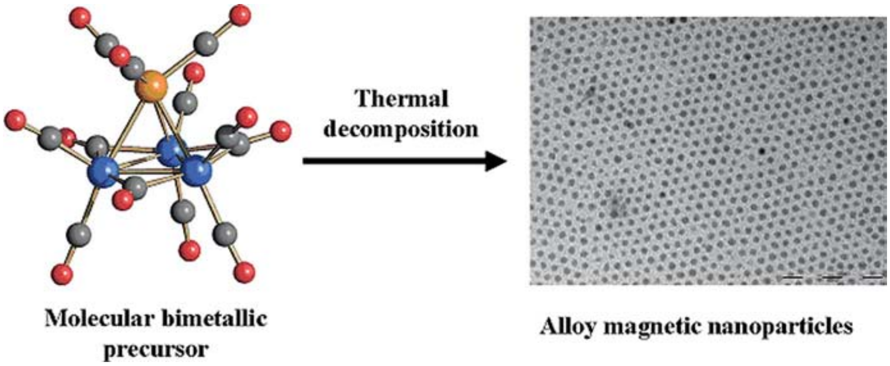


Figure 17. Preparation of bimetallic nanoparticles from MCCs. Reprinted with permission from ref.[115a] Copyright 2009 American Chemical Society.

7. Conclusions and Perspectives

As a major conclusion of this microreview, by considering all the examples reported herein, we can state that high-nuclearity molecular MCCs are perfectly (atomically) monodisperse, ligand-stabilised metal nanoparticles. In fact, the largest species studied to date already have nanometric dimensions, similar to those of ultrasmall metal nanoparticles. Thus, by increasing the nuclearity of molecular clusters and reducing the dimensions of metal nanoparticles, now these two worlds start to overlap.

The main remaining differences are semantic and historical. For a long time, scientists of these two communities have walked their ways independently, and it is now time to start communicating and exchanging ideas. Actually, ultrasmall metal nanoparticles are nothing but large molecular clusters or mixtures of some of them. It is now clear that it is only possible to fully understand their behaviour by knowing the structure of nanoclusters at the molecular level. In this regard, X-ray crystallography, which has been used for decades in order to elucidate the structures of molecular clusters, is becoming a key technique also for unravelling the structures of ultrasmall metal nanoparticles.[10]

Useful information on ultrasmall metal nanoparticles can be obtained by studying the electronic, magnetic, spectroscopic, structural and chemical properties of large molecular clusters and, among them, higher-nuclearity MCCs. Of particular interest is to understand how the physical properties of metal aggregates change with increasing size and when the molecular behaviour fades into bulk behaviour.

Major efforts must be made in order to prepare and characterise larger and larger MCCs with different compositions. We have demonstrated here that the structures of molecular MCCs with sizes of 1–2 nm are still heavily influenced by surface ligands and that their metal cores are rather deformable. This point has been confirmed also for the three examples of Au nanoclusters whose structures have been determined to date.[10,75,76] Further information might be obtained by investigating the structures of larger clusters.

Apart from morphological information obtained by X-ray crystallography, the molecular approach towards metal nanoparticles based on MCCs proposed herein also has some functional aspects, when physical properties are considered. The electrochemical behaviour of large MCCs is in keeping with the beginning metallisation of their metal cores as the nuclearity increases. In addition, to fully understand their NMR spectroscopic and magnetic behaviour is still a major goal, which might also shed some light on the physical properties of ultrasmall metal nanoparticles.

We have also shown that MCCs can be assembled into molecular wires, charge-transfer materials and nanostructured monolayers. Further applications in the field of molecular nanostructured materials may arise by systematically investigating their self-assembly properties.

Molecular MCCs are valuable precursors for the preparation of metal nanoparticles, conducting metal nanowires (“printable metals”) and nanostructured heterogeneous catalysts, after their controlled decomposition.

Overall, molecular MCCs may find applications as single-molecule metal nanoparticles with well-defined physical properties arising from their quantum size, as supramolecular aggregates in the field of molecular nanomaterials and as precursors of perfectly defined metal nanoparticles.

In conclusion, molecular metal clusters can have a substantial impact on nanoscience and nanotechnology by helping us to reach a better understanding of the chemical and physical phenomena occurring in the nanoworld.

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