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Low valent metal clusters — an overview

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Abstract

Low valent transition metal cluster chemistry emerges as a major field in organometallic research. Metal clusters exhibit interesting structural, chemical and catalytic properties intermediate between those of mononuclear metal complexes and the multinuclear metals. The opportunities offered by these clusters such as cooperative effect, electron reservoir properties, storehouse of active fragments and heterosite reactivity features are briefly discussed. Other advantages such as mimics of metal surfaces and biomolecules, precursors to heterogeneous catalysts and materials, homogeneous catalysts, and stoichiometric and catalytic reagents in organic synthesis are highlighted. They provide problems of interest in connection with our understanding of structure and bonding. Examples of recent progress in this area show practical promise of preparing new complex organic molecules and inorganic materials by mild and selective methods using these molecules.

Keywords: Metal clusters; Catalysis; Properties; Structures

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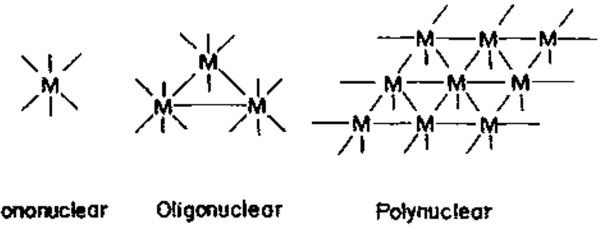
1. Introduction

Transition metal cluster chemistry has been a rapidly developing area of research in recent years with applications in the areas of catalysis, materials science and organic chemistry. Several excellent review articles (for recent reviews see [1a–1j]; for popular articles see [1k–1o]) and books [2] have appeared which emphasize the role of ligated clusters in these fields. The emerging popularity of clusters is also evident from the new periodical *Journal of Cluster Science* devoted to the current advances in basic and applied research. The scope of this paper consists of research highlights of the last two decades in low valent transition metal clusters with broad approach. The main emphasis is given to a general discussion of the important properties of clusters and the specific objective is to introduce the non-specialist reader to this active area of research with a few examples to illustrate important points. No attempt is made to cover the subject comprehensively and several important fundamental and practical cluster science issues have not been treated here.

According to the usual convention, the clusters are oligonuclear compounds with a framework of metal atoms held together by metal–metal (M$-$M) bonds and surrounded by a shell of ligands (M_mL_n) (Scheme 1). Their characteristics are intermediate between mononuclear complexes and polynuclear metal surfaces, i.e. they serve as bridge between molecular and solid state chemistry. Transition metal clusters are ideal candidates to study the M$-$M bonds stretching from the single bond to the collective behavior in a three-dimensional network of metals. As discrete molecules they react in homogeneous phases with substrates. They can be isolated and characterized like mononuclear complexes using various spectroscopic and crystallographic techniques and show typical phenomena known for polynuclear metal surfaces such as multimetal ligand binding and delocalized metal–metal bonds. In Table 1 we collect typical examples of clusters with nuclearity ranging from four to nine and their metal framework structures. Characterization of cluster compounds by single-crystal X-ray diffraction analysis shows a variety of polyhedral structural arrangements, both regular and semiregular [3]. In some cases their molecular structures in the solid state and in solution are different. Unusual reactivity features are thus expected and in fact observed because of this great diversity in molecular architectures.

The basic question is how large must a cluster be to have metal-like character or, in other words, how many metal atoms are required to form a bulk metal? The

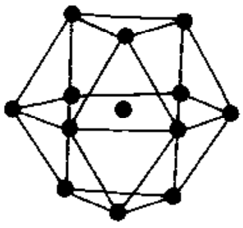


Scheme 1. Schematic representation of clusterification process [6a].

Table 1
Representative examples of medium nuclearity clusters together with their skeletal frameworks

Number of metals	Examples	Core structure
4	$Rh_4(CO)_{12}$	Tetrahedron
	$[Re_4(CO)_{16}]^{2-}$	Butterfly
	$Pt_4(CH_3CO_2)_8$	Square planar
	$Os_3Pt(CH_2)(CO)_{11}(PPh_3)_2$	Spiked triangular
5	$Os_5(CO)_{16}$	Trigonal bipyramid
	$Fe_5C(CO)_{15}$	Square pyramid
	$[Fe_4Pt(CO)_{16}]^{2-}$	Bow tie
	$H_2Os_5(CO)_{16}$	Edge-bridged tetrahedron
	$Ru_5(CO)_{14}(t\text{-}BuNC)_2$	Bi-edge-bridged triangle
6	$Ru_6C(CO)_{17}$	Octahedron
	$[Rh_6C(CO)_{15}]^{2-}$	Trigonal prism
	$Os_6(CO)_{18}$	Bicapped tetrahedron
	$H_2Os_6(CO)_{18}$	Capped square pyramid
	$H_2Os_6(CO)_{12}(CNMe_2)_2(SMe)_2$	Edge-sharing bi-tetrahedron
	$H_2Os_6(CO)_{18}(PPh)$	Triangular raft
	$HCuRu_5(CO)_8(PPh_3)$	Rhombic raft
7	$[Rh_7(CO)_{16}]^{3-}$	Capped octahedron
	$[H_2AuOs_6(CO)_{20}]^-$	Vertex-sharing butterfly
8	$[Os_8(CO)_{22}]^{2-}$	Bicapped octahedron
	$Ni_8(CO)_8(PPh)_6$	Cubic
	$[Co_8C(CO)_{18}]^{2-}$	Square antiprism
	$Cu_2Rh_6C(CO)_{15}(NCMe)_2$	Bicapped trigonal prism
9	$[Co_9Si(CO)_{21}]^2$	Capped square antiprism
	$[Rh_9(CO)_{19}]^{3-}$	Face-sharing octahedron

answer is certainly still highly speculative. However, in some known examples of ligated clusters, the arrangement of metal atoms corresponds to the packing commonly found for bulk metals, i.e. h.c.p., c.c.p. or b.c.c. For example, the rhodium framework in $[Rh_{13}(CO)_{24}H_3]^{2-}$ cluster corresponds to an h.c.p. structure (Fig. 1) [4]. In this molecule the central rhodium atom is coordinated to nothing except the other 12 metal atoms. In a sense, the cluster is a microscopic chunk of rhodium with



$[H_2Rh_{13}(CO)_{24}]^{3-}$

Fig. 1. The metal core structure of $[HRh_{13}(CO)_{24}]^{3-}$ showing the fragment of h.c.p. array [4]. (Note the ABA layer arrangement.)

carbon monoxide chemisorbed at its surface. Similarly, in the $[Pt_{38}(CO)_{44}]^{2-}$ cluster the metal atoms adopt the c.c.p. structure found in the bulk platinum. Moreover, the metal–metal bond distances in this type of zero-valent metal carbonyl cluster are similar to those in the corresponding bulk metal [5]. Estimated average M−M bond energies in metal clusters and the respective metals are very similar. The observed deviation in the structures of certain clusters from the idealized arrangement of the metal atoms in the respective bulk metal (e.g. $[Pt_{26}(CO)_{32}]^{2-}$, h.c.p.) may have an origin in the crystal packing forces and the nature of the ligand binding.

In low nuclearity clusters with polyhedral structures, the wide range of metal–metal bond distances may correspond to malleability in metals. Redox activity indicates a relationship to metallic conductivity. It is observed that very often high nuclearity clusters are somewhat darker than the low nuclearity clusters. This gradation in color would indicate that with increasing nuclearity the separation between the highest bonding and lowest antibonding skeletal molecular orbital decreases, and that high nuclearity clusters have many closely spaced energy levels. Then the connection between the d–d bandwidth of the bulk metal system (band gap) and the separation of bonding and antibonding orbitals of clusters (highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap) becomes obvious (Fig. 2). Similarly, another solid state property of alloying is related to the formation of heteronuclear M−M′ bond in clusters [1e–1g].

In cluster chemistry, with increasing nuclearity we can see the gradual evolution of properties such as structure, magnetic behavior and ionization potential. In principle, these properties should approach those of the bulk metal as the cluster size increases. For example, we can see the gradual growth of the tetrahedron on going from four to ten to 20 metal atoms (Fig. 3) [6]. The $[Os_{20}(CO)_{40}]^{2-}$ dianion has a metal framework consisting of 20 c.c.p. osmium atoms arranged to form a perfect tetrahedron. On the way from the atom to the bulk, one can see the typical hierarchy in the degree of metal aggregation, i.e. mononuclear complex→low nuclearity cluster→high nuclearity cluster→particulate metal→bulk metal. Mononuclear complexes and low nuclearity clusters have a discrete energy level structure with well-defined bonding and antibonding molecular orbitals. As we move towards

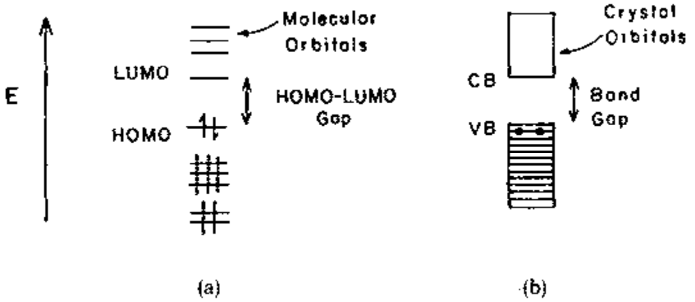
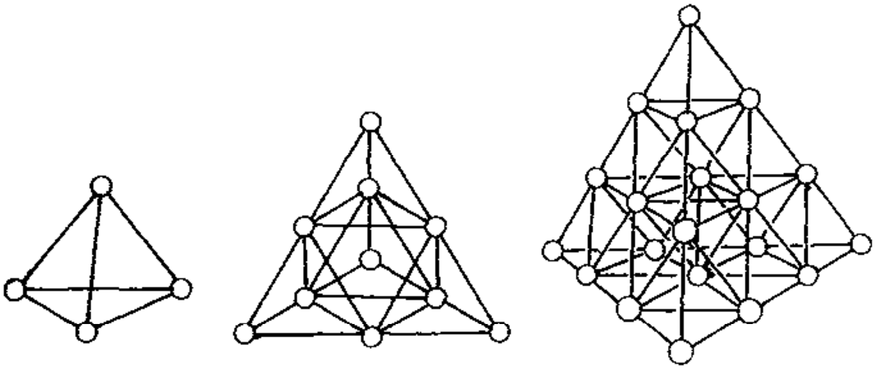


Fig. 2. The energy level and band diagram for the molecular clusters M_n and solid state metals M_∞ showing their interrelationships. E, energy; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; CB, conduction band; VB, valence band.



$[H_2Os_4(CO)_{12}]^{2-}$ $[Os_{10}C(CO)_{24}]^{2-}$ $[Os_{20}(CO)_{40}]^{2-}$

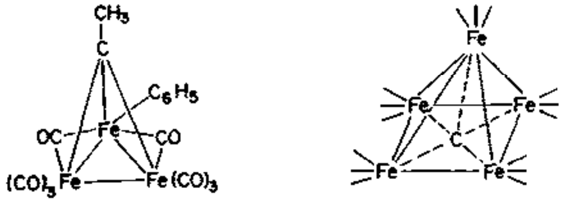
Fig. 3. Tetrahedral cluster growth pattern with increasing nuclearity [6a].

higher nuclearity clusters, quantum size effects come into picture. In a bulk metal we see a quasi-continuum of energy states with delocalized electrons (band structure).

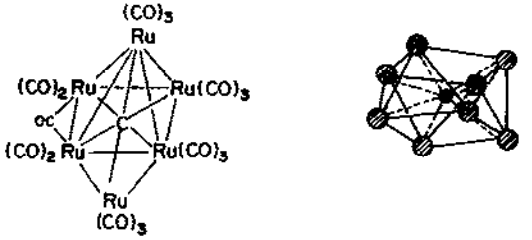
Another similarity between the structures of clusters and those of metals is the incorporation of interstitial non-metallic atoms such as H, C, N, B, S, Si, Sb, As and P in the framework [7]. The environment of main group elements in interstitial clusters is mainly octahedral, tetrahedral, trigonal prismatic, tetragonal antiprismatic and icosahedral. For example, the hydride occupies the tetrahedral cavity whereas the octahedral cavity is occupied by a carbide in the anionic cluster $[(\mu_4\text{-H})Os_{10}(\mu_6\text{-C})(CO)_{24}]^-$. As a consequence, we have different coordination numbers of carbon in clusters from those found in classical organic structures (Fig. 4). In the cluster $Fe_3(CO)_8(CH_3C)(C_6H_5)$, the apical carbon atom bonded to a methyl group is normal four coordinated whereas the carbon atom at the center of the $Fe_5C(CO)_{15}$ cluster has a coordination number of five. In the hexanuclear ruthenium cluster $Ru_6(CO)_{17}(\mu_6\text{-C})$ the carbon is six coordinated and the cobalt cluster $[Co_8(\mu_8\text{-C})(CO)_{18}]^{2-}$ has the interstitial carbon atom with a coordination number of eight. The encapsulated atom donates all its valence electrons to the cluster. Here again the metal–metal and metal–main group element bond lengths in discrete and solid state interstitial compounds are similar. Although subtle electronic effects and steric crowding of the stabilizing ligands cannot be neglected, geometrical systematics emerge by considering metal clusters as valid structural intermediates between discrete complex and extended solid metals [8].

2. Opportunities offered by clusters

Here the focus question is: why do we need to study polymetallic clusters? Let us first look at the opportunities offered by these clusters (Scheme 2) and then we shall consider some known applications in a later section.

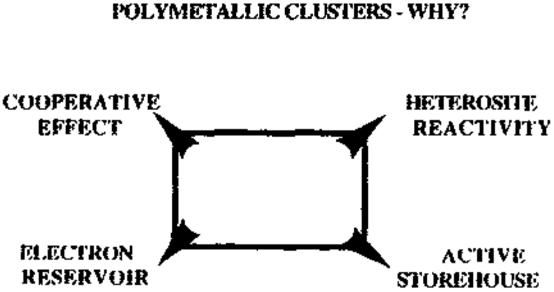


$Fe_3(CO)_8(CH_3C)(C_6H_5)$ $Fe_5C(CO)_{15}$



$Ru_6(CO)_{17}(\mu_6-C)$ $[Co_8(\mu_8-C)(CO)_{18}]^{2-}$

Fig. 4. Coordination numbers of carbon in metal clusters.



Scheme 2. Schematic representation of the opportunities offered by metal clusters.

2.1. Cooperative effect

Firstly, there is a possibility that the substrate binds to more than one metal atom simultaneously. This cooperative effect is quite common in clusters, and the ligands adopt the bridging rather than the terminal sites. Multimetal substrate binding will modify the reactivity in a way not possible in mononuclear complexes. So we can have multicenter activation as well as multicenter reaction (Fig. 5). Electronic effects can be adjusted anywhere between adjacent metals and the active center in a cluster. Studying the fundamental transformation of ligands on a cluster polyhedron allows

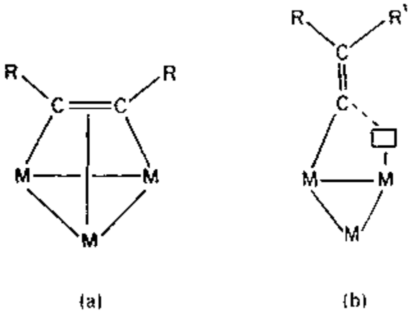


Fig. 5. Illustration of (a) multimetal activation and (b) multicenter reaction in polynuclear clusters.

us to draw an analogy between metal clusters and metal surfaces, and to predict the steps involved in heterogeneous catalysis.

Clusters also permit the migration of coordinated ligands from one metal atom to another. For instance, hydrogen and carbon monoxide scrambling is very common in many molecular clusters (e.g. $H_2FeRuOs_2(CO)_{13}$). This mobility is important in catalytic reactions because it allows atoms or molecules to approach each other and is similar to the thermal motion of substrate (CO, H etc.) on the metal surface [9]. Metal framework rearrangements within the ligand envelope model another type of surface dynamic process (e.g. $[Pt_9(CO)_{18}]^{2-}$). A third type of dynamic behavior is ligand migration within the metallic cluster unit (e.g. $[H_2Rh_{13}(CO)_{24}]^{3-}$). All these three types of fluxional process help to elucidate catalytically relevant mechanistic pathways [10]. Since both CO and H are common ligands on clusters, opportunities exist for the development of selective catalysts for synthesis gas conversion. Clusters could offer selectivity in catalysis by virtue of their discrete structures, providing uniformity.

Coordination of a ligand to more than one metal atom will result in unusual coordination modes (Fig. 6). The catalytic activation of carbon monoxide on a metal surface depends on the mode of coordination of CO [11]. Recently discovered rare bonding modes include the quadruply bridging CO group [12] in the mixed metal Mo—Ru cluster $Mo_2Ru_5(CO)_{14}(\mu_4\text{-}\eta^2\text{-}CO)_2Cp_2(\mu_4\text{-}S)$ where the C—O bond is inclined towards the metal atoms. In fact, the cluster contains two such carbonyl ligands each of which interact with four metal atoms using both carbon and oxygen (Fig. 6(a)). In another cluster $Cp_4Mo_2Ni_2S_2(\eta^1,\mu_4\text{-}CO)$, the carbonyl group is attached to all four metal atoms and the C—O bond is projected away from the metal atoms so that there is no significant metal–oxygen interactions (Fig. 6(b)) [13]. Similarly, other recently discovered examples [14] include (i) $\mu_4\text{-}\eta^2\text{-}NO$ coordinated to the Mo_2Co_2 core (Fig. 6(c)), (ii) the new triply bridging mode for the CO group bridging the Ru spike in the Ru–Pt cluster, $Ru_8Pt_2(CO)_{23}(Ph_2PCH_2CH_2PPh_2)(\mu\text{-}H)_2$, (iii) the benzene in the face capping bonding mode in $[Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ (Fig. 6(d)) and (iv) μ_4-oxo atoms capping the square faces of the trigonal prism of osmium atoms in the cluster $[Os_{11}(\mu_4\text{-}O)_3(CO)_{30}]$. A wide variety of hydrocarbon fragments (CH, CH_2, CH_3,

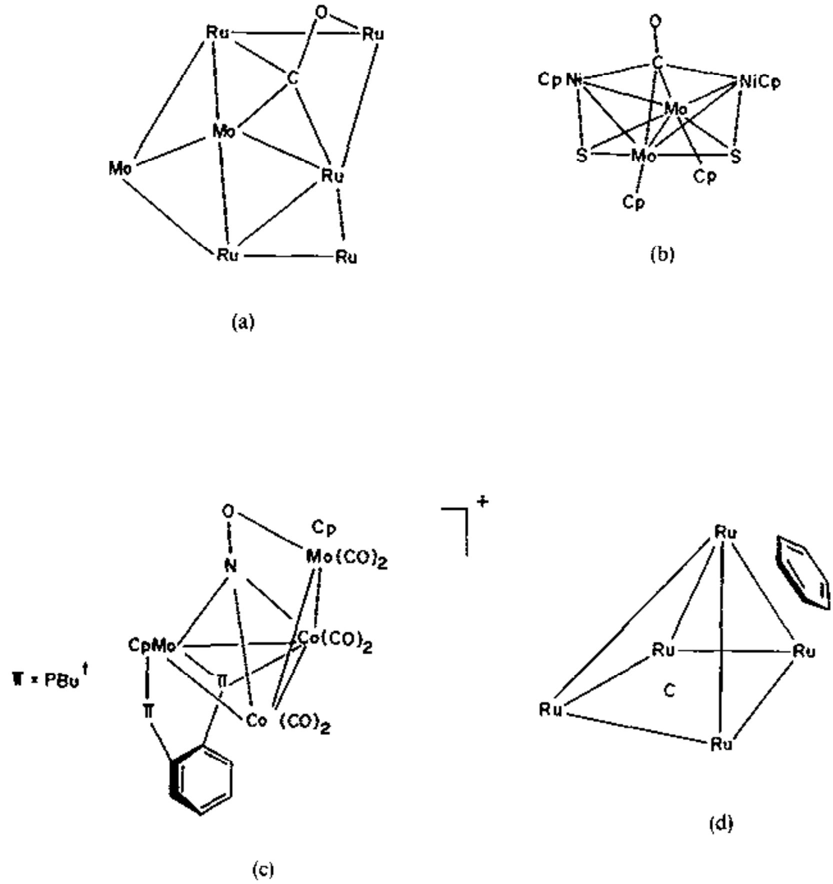
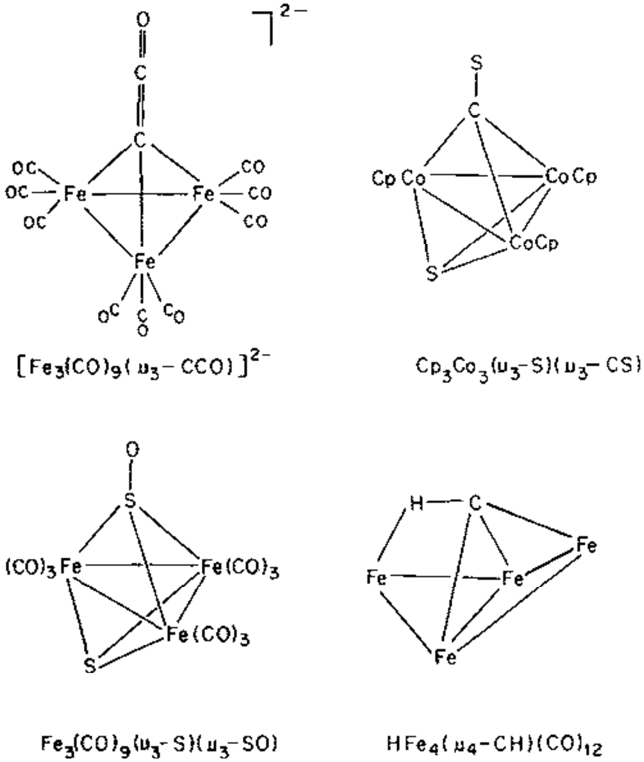


Fig. 6. Unusual coordination modes of ligands in organometallic clusters.

CCH, CCH_2, CCH_3 etc.), often in rare bonding modes, are found in clusters owing to close cooperation among the adjacent metal atoms. It is worth noting that the structural features of these molecules provide an important database for understanding unusual chemical and catalytic properties of metal atom clusters [10d,15].

Some ligands are mostly found in clusters because they need stabilization by bonding to several metal atoms (Fig. 7) [16]. For example, several important small substrates such as CCO, BCO, CS, SO, CH, $\overline{C{\equiv}CCH_2C}H_2$ and PO are found to be stable when attached to a cluster framework. Typical examples include $[Fe_3(CO)_9(\mu_3\text{-}CCO)]^{2-}$, $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}BCO)$, $Co_3Cp_3(\mu_3\text{-}S)(\mu_3\text{-}CS)$, $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}SO)$, $HFe_4(\mu_4\text{-}CH)(CO)_{12}Os_3(CO)_9(\mu\text{-}\eta^2\text{-}C_2CH_2CH_2)(\mu\text{-}\eta^2\text{-}\overline{C_2CH_2C}H_2)(\mu\text{-}SPh)(\mu\text{-}H)$ and $WNi_2Cp_2(CO)_4(\mu_3\text{-}PO)_2$. Therefore it is possible to stabilize unstable or highly reactive intermediate species in solution by supporting them on a cluster. Their ability to activate by coordination of other small molecules such as CO, N_2, CO_2, H_2 and olefins is yet another advantage of polymetallic



$[Fe_3(CO)_9(\mu_3-CCO)]^{2-}$

$Cp_3Co_3(\mu_3-S)(\mu_3-CS)$

$Fe_3(CO)_9(\mu_3-S)(\mu_3-SO)$

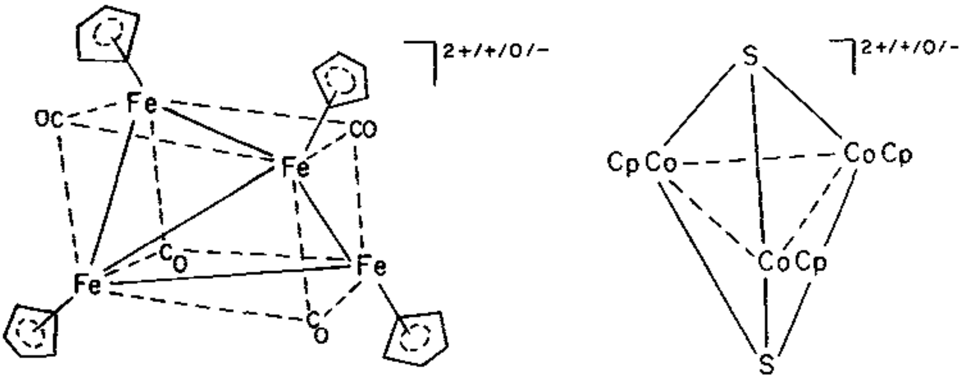
$HFe_4(\mu_4-CH)(CO)_{12}$

Fig. 7. Stabilization of unstable species supported on molecular clusters.

clusters over monomeric metal complexes. Isolation of such metal clusters containing rare ligands and common inert molecules, by multimetal attachment, help us to study the elementary reaction steps involved in catalysis [17]. Interestingly, as the metal nuclearity increases, the tendency to behave in a collective fashion becomes more significant while losing the individual character of the metal.

2.2. Electron reservoir

Secondly, clusters can act as electron reservoir compounds with charge-donating and charge-accepting properties [18]. Such clusters have a much lower ionization energy than that of an isolated atom and also have a high electron affinity. Multinuclear metal clusters contain a greater number of accessible redox states than their mononuclear counterparts, and many of them, in fact, reversibly change oxidation states. For instance, the iron cluster $[(\eta^5-C_5H_5)Fe(CO)]_4$ (Fig. 8(a)) remains intact in four oxidation states (+2, +1, 0 and −1). If we replace all the carbonyls in the above cluster by sulfur, then the resulting iron–sulfur cluster $[(\eta^5-C_5H_5)FeS]_4$ exists in five molecular oxidation states (+3, +2, +1, 0 and −1). This property is biologically significant because the required number of electrons can be supplied to



(a) (b)

Fig. 8. Multiple oxidation states in multimetallic clusters.

the substrate with less variation in the oxidation state of the metals involved. For example, the six electrons required for the reduction of dinitrogen to ammonia can be transferred from a suitably designed cluster. It has been demonstrated [19] by cyclic voltametry that the bicapped triangular cobalt cluster $Co_3Cp_3(\mu_3\text{-}S)_2$ (Fig. 8(b)) exists in four reversible oxidation states. Chemically stable multiple redox states between −1 and +5 have also been reported for analogous cluster $Ni_3Cp_3(\mu_3\text{-}S)_2$. Metal–metal bond making and breaking acts as an electron source and sink in the oxidation–reduction process. Depending on the metal(s), the ligand(s) and redox stabilities, the metal framework either remains intact or undergoes a declustering process. In general, cluster compounds with strong M—M bonds, those having a greater number of electrons and those containing ligands with delocalized electrons show multiple-oxidation-state properties.

2.3. *Active storehouse*

Thirdly, metal clusters may function as storehouses for the release and uptake of catalytically active fragments [20]. The breaking of M—M bonds can provide coordination sites for the activation of incoming organic substrates. Some clusters are known to be efficient catalyst precursors for different types of reaction such as isomerization, hydrogenation, hydroformylation and oligomerization. For example, $Fe_3(CO)_{12}$ reacts with alkenes at 80 °C to generate a catalytically active intermediate complex $[Fe(CO)_4(\eta^2\text{-alkene})]$ that initiates alkene isomerization. Recently, it has been shown [21] that hydroformylation of 3,3-dimethylbut-1-ene using $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ as catalyst precursors leads to the selective formation of $RCORh(CO)_4$ ($R = -CH_2CH_2(CH_3)_3$). In homogeneous systems, several high nuclearity rhodium carbonyl clusters such as $[Rh_{12}(CO)_{30}]^{2-}$ and $[Rh_6(CO)_{15}]^{2-}$ generate $[Rh_5(CO)_{15}]^-$ and $[Rh(CO)_4]^-$ [22]. In some cases, because of the competition between M—M and M—L interactions according to the stereoelectronic requirements, a particular organometallic fragment may be stabilized for a moment and then the labile behavior necessary in homogeneous catalytic reactions will be exhibited. Since it is often difficult to predict or to detect such intermediates, the trial-and-error testing of different clusters seems to be the obvious choice here. For a more complete account of the cluster-mediated catalytic reactions where active fragments are generated during the course, the reader is referred to recent review articles [20]. Industrial interest in metal clusters is obviously centered around their application as catalysts, either directly or indirectly as precursors. Most industrial, academic and government research laboratories are now making major efforts in cluster research with emphasis on developing selective catalysts for C_1 chemistry.

2.4. *Heterosite reactivity*

Then comes their ability to activate different substrates at different metal atoms, i.e. heterosite reactivity. The mixed-metal cluster $Ru_2Co_2(CO)_{13}$ reacts with hydrogen under mild conditions at the ruthenium atoms to form $H_2Ru_2Co_2(CO)_{12}$ and with acetylenes at the cobalt atoms to give $Ru_2Co_2(CO)_{11}(R_2C_2)$ (Fig. 9) [23]. It is known that individual clusters of ruthenium and cobalt would prefer to react with hydrogen and acetylenes respectively. It is often observed that mixed-metal clusters containing a Co—Rh bond react with PEt_3 and CH_3CN preferentially at the rhodium atoms whereas they interact with alkynes at the cobalt sites. The influence of ligand size and basicity on substitution site preference has been observed [24] in the reaction of $H_2FeRu_3(CO)_{13}$ with tertiary phosphines. Of the two isomers (C_1 and C_s) of monosubstituted cluster products, large ligands give only the C_s isomer whereas, with the smaller ligands, the more basic ligands prefer the C_1 isomer. This ability to activate more than one substrate would be useful in designing specific

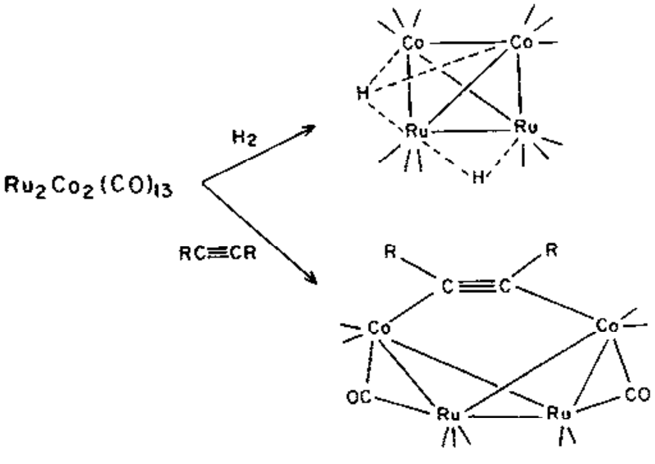
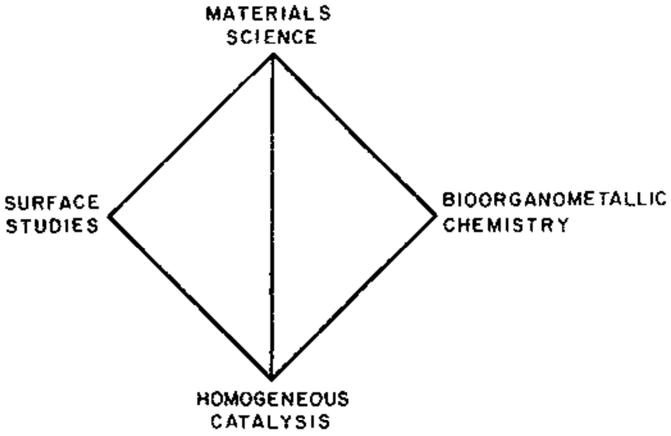


Fig. 9. Heterosite reactivity of the heterometallic cluster $Ru_2Co_2(CO)_{13}$ [23].



Scheme 3. Schematic representation of some dimensions of cluster chemistry.

catalysts with site-specific properties for complicated organic reactions. The key questions in all these studies are as follows.

(i) What is the nature of the M—M bond?

(ii) How does this bond formation affect the properties of metal clusters?

(iii) Which factor, the nature of the metal(s), the ligand(s) or the structural geometry, is dominant?

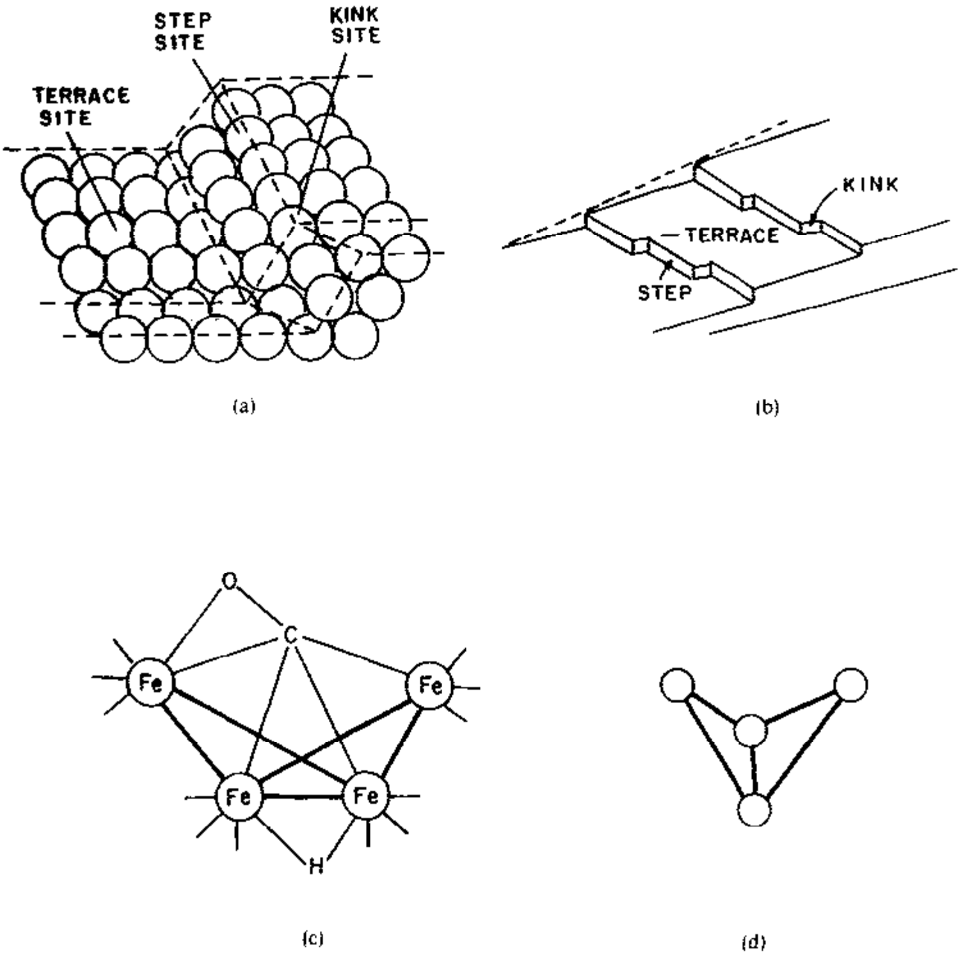
3. Areas of current application

Now let us take a look at some of the applications of clusters in surface studies, homogeneous catalysis, bio-organometallic chemistry and materials science (Scheme 3).

3.1. Cluster models

First of all, transition metal clusters can serve as models of metal surfaces [5,25]. Clusters are amenable to complete characterization by various physical methods whereas metal surfaces are not easily structurally characterizable by the tools of surface chemistry. As already mentioned in the previous section, larger clusters whose structure corresponds to those in bulk metals such as $[Rh_{13}(CO)_{24}H]^{4-}$ and $[Pt_{38}(CO)_{44}]^{2-}$ can be considered as small bits of metals with CO adsorbed on their cores. Metal surfaces show a distribution of structural and chemical defects such as steps, kinks, vacancies and heteroatoms, as sketched in Fig. 10(a) and 10(b) [26]. Metal atoms in such positions are much more reactive because of their coordinative unsaturation and accessibility. The butterfly framework shown in Figs. 10(c) and 10(d) may represent the kink on the surface of a catalyst. In fact, the clusters can offer vertices, edges or faces as catalytically active sites.

They can also serve as models of chemisorbed species on surfaces of metals. For



(a) (b) (c) (d)

Fig. 10. Types of active site on a metal surface and a cluster model of the kink [26]; (b), (d) simplified representations.

example, in Fischer–Tropsch chemistry, the proposed surface bound intermediates are shown in Fig. 11(a), and Fig. 11(b) shows the isolated cluster analogs which are well characterized [27]. One can clearly see the structural similarities between the corresponding pairs. The hexanuclear ruthenium cluster [28] $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ contains benzene in two different bonding modes, i.e. conventional η^6-terminal and face-capping $\eta^2:\eta^2:\eta^2$. This cluster species could serve as a model for chemisorption of benzene at a threefold site on metal surfaces. A more extensive list of model molecular clusters in organometallic transformations on metal, metal oxide and metal sulfides can be found in a recent review article [1a].

The structure of $[Pt_6Ni_{38}(CO)_{48}]^{6-}$ (Fig. 12) represents a very good model of a bimetallic particle that is surface enriched with a heterometallic counterpart [29]. In this cluster the metallic lattice represents an octahedral section of an overall c.c.p.

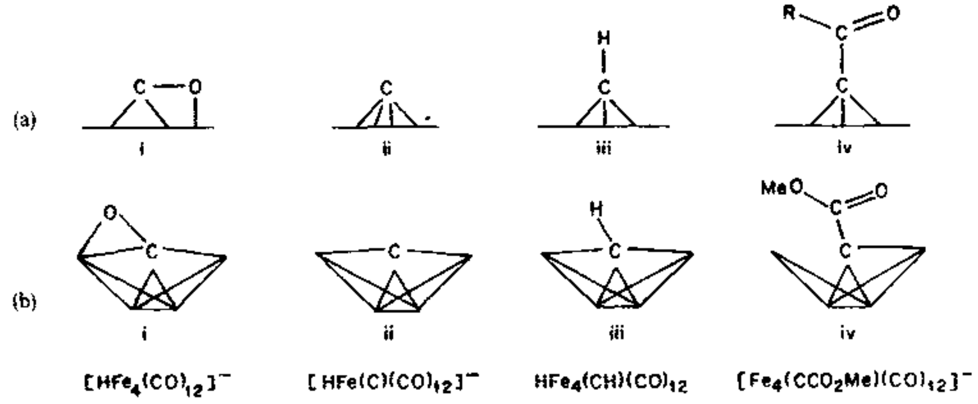


Fig. 11. (a) Proposed surface bound intermediates; (b) their isolated cluster analogs [27].

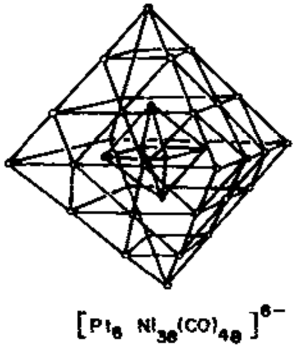


Fig. 12. The skeletal metal structure of $[Pt_6Ni_{38}(CO)_{48}]^{6-}$.

array. This is still the largest cluster to be characterized by single-crystal X-ray diffraction techniques. The heteronuclear planar clusters such as $HCuRu_5(CO)_8(PPh_3)$ represent a two-dimensional equivalent of this 'cherry' model. The cluster-bound exposed carbide in the dianion $[Fe_4(\mu_4\text{-}C)(CO)_{12}]^{2-}$ reacts with the silver ion under hydrogen to form the methylidyne cluster $HFe_4(\mu_4\text{-}CH)(CO)_{12}$ [30]. This represents a reactivity model in solution which can be compared with the reaction of surface-bound carbon atoms with hydrogen on metallic catalysts. Recently, it has been demonstrated [31] that even C_2 can act as an interstitial unit (cage dicarbide) in $[Ni_{16}(CO)_{12}(\mu\text{-}CO)_{10}(\mu_3\text{-}CO)(C_2)_2]^{4-}$ and as an exposed moiety (peripheral dicarbide) in $Co_6(\mu_6\text{-}C_2)(\mu\text{-}CO)_6(CO)_8(\mu_4\text{-}S)$. In addition, clusters could serve as models of transient intermediates involved in a homogeneous catalytic cycle initiated by a cluster or mononuclear complex. These models will allow us to understand why a solid behaves the way that it does, and to predict the properties of macroscopic bulk materials [32].

3.2. Heterogeneous catalysis

Apart from this type of modeling study, clusters can be used in the formation of heterogeneous catalysts [1a]. Again there are two possibilities. One is to make a supported cluster together with the surrounding ligands (immobilized metal clusters) and the other is the generation of small metallic crystallites by thermal treatment (anchored metal aggregates). There are some advantages in using a cluster in heterogeneous catalysis.

(a) Non-aqueous methods of catalyst preparation can be utilized because they are soluble in organic solvents.

(b) Normally they do not contain halogen atoms so that the resulting catalyst can be halide free. Otherwise normally halide ions would contribute to poisoning of the catalyst.

(c) The high temperature reduction by hydrogen necessary to reduce the metal ions is not required because in many cases clusters have the metals formally in the zero-valent state. So we can activate the cluster-derived catalysts under mild conditions.

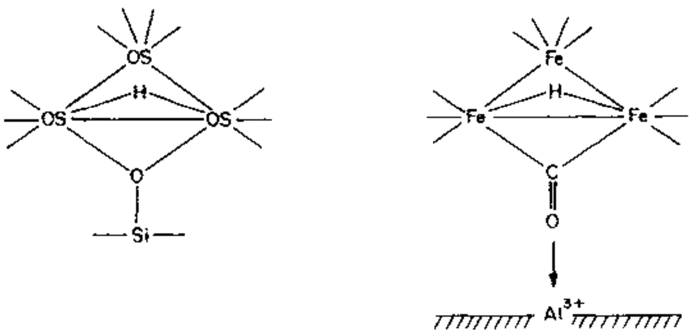
(d) Anchoring on a support prevents migration and sintering under reaction conditions.

(e) Homonuclear polymetallic clusters may lead to small skeletal assemblies to facilitate the binding of substrate to more than one metal atom.

(f) Already many mixed-metal clusters with different compositions are known [1e–1g]. Therefore we have the possibility of preparing bimetallics or alloys of predetermined composition in a controlled manner.

(g) The potential to decompose after adsorption on a support produces well-dispersed small metallic particles or even intact metal ensembles.

The molecular cluster grafted to the surface of silica, $(H)Os_3(CO)_{10}(OSi{\equiv})$ (Fig. 13(a) acts as a catalyst for ethylene hydrogenation at 353 K and the mechanism involving the intact metal framework has been proposed on the basis of IR spectroscopic evidence [33]. The adsorption of $Fe_3(CO)_{12}$ on hydrated η- and ν-Al_2O_3



(a) (b)

Fig. 13. Molecular clusters grafted to the surface: (a) $(H)Os_3(CO)_{10}(OSi{\equiv})$; (b) $[HFe_3(CO)_{11}]$ /Al_2O_3.

results in the formation of surface bound $[HFe_3(CO)_{11}]^-$ [34] (Fig. 13(b)). By using an alternative method of preparation, the silica-anchored tetraruthenium cluster $H_4Ru_4(CO)_8(PPh_2C_2H_4-SIL)_4$ has been prepared and found to be highly active in ethylene hydrogenation [35]. The supported ruthenium cluster $[H_4Ru_4(CO)_{12}]/Al_2O_3$ reacts with synthesis gas $(CO + H_2)$ and undergoes rearrangement to give $[Ru_6C(CO)_{16}]^{2-}$. This catalyst has been shown [36] to exhibit good selectivity towards oxygenated products (CH_3OH and C_2H_5OH) and this oxygenate selectivity is attributed to the presence of intact metal clusters on the surface. Of particular interest is the supported cluster $[Ru_6C(CO)_{16}Me]^- -SiO_2$ which in the presence of $CO + H_2$ shows high selectivity (77%) for acetaldehyde formation [37]. Many examples of clusters attached to polymer (phosphine functionalized poly(styrene-divinylbenzene), silica and magnesia can be found in the literature [10,38]. Preparation and properties of surface-anchored metal clusters with well-defined structure can give the necessary insight into the mechanism of certain industrial organic transformations.

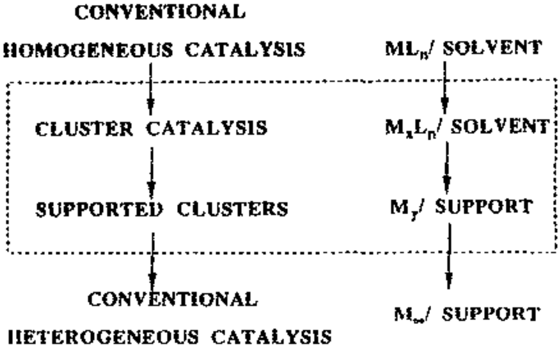
Typical particle size distributions for catalysts prepared by different methods show that the use of clusters as precursors leads to metal particles of smaller size than those obtained from conventional methods [39]. For example, we can generate ruthenium particles in the size range 1.5–2.0 nm from the cluster precursors $Ru_3(CO)_{12}$ and $Ru_6C(CO)_{17}$. If we use the mononuclear complex–metal salt, $[Ru(NH_3)_5N_2]Cl_2$ (ion exchange) and $RuCl_3.xH_2O$ (aqueous impregnation) in a heterogeneous catalyst preparation, particles of a larger size (2.5–4.5 nm) will result. Because of the smaller crystallite size in the former case, increased activity is of course observed. With cluster-derived catalysts, *n*-heptane is completely hydrogenolized to methane at 473–523 K whereas temperatures above 623 K are required to give 78% and 22% conversions over the catalysts based on the mononuclear compounds mentioned above. In another study [40] of carbon dioxide methanation, the cluster-derived catalysts have been found to be more active than those obtained from the corresponding metal salt. For example at 180 °C the catalyst derived from $Ru_6C(CO)_{17}$ was 22 times more active than that derived from $RuCl_3$. The activity of the supported neutral species has been observed to increase with the nuclearity of the precursor, i.e. $Ru(CO)_5 < Ru_3(CO)_{12} < H_4Ru_4(CO)_{12} < Ru_6C(CO)_{17}$. Increasing the number of metal atoms in the cluster framework may cause unusual core properties, providing the possibility of the development of novel industrial catalysts.

It has been shown [41] that bimetallic particles of precisely known composition can be obtained from bimetallic supported molecular clusters by thermal decomposition. For example, the surface-generated anionic clusters $[HFeOs_3(CO)_{13}]^-$, $[HFeRu_3(CO)_{13}]^-$ and $[FeCo_3(CO)_{12}]^-$ form small and highly dispersed bimetallic particles with $Fe:M = 1:3$. The cluster-derived bimetallic catalysts obtained from various SiO_2-supported mixed metal carbonyl clusters show high activities and selectivities for formation of C_1 and C_2 alcohols from synthesis gas [42]. Similarly, the bimetallic cluster $[PtRh_5(CO)_{15}]^-$ has been shown [43] to be an active catalyst precursor for ethylene glycol and methanol formation from CO hydrogenation. Catalysts composed of two different metals often function better than those containing one of the metal components or those obtained from mononuclear metal complexes. In such studies, suitable selection of metal combination may lead to the preparation of tailored bimetallic catalysts for specific transformations.

3.3. Homogeneous catalysis

Thirdly, clusters can act as homogeneous catalysts themselves [19a,44]. Typical cluster catalysis falls in between conventional homogeneous and conventional heterogeneous catalysis (Scheme 4). Because of this intermediate position, transition metal clusters have raised expectations about the possibility of performing unique catalytic reactions [45]. It is anticipated that clusters will be able to carry out catalytic reactions with a high activity typical of heterogeneous catalysts, and with a high selectivity which is characteristic of homogeneous catalysts. The high activity attributable to the cooperative nature of metal network and the high selectivity due to the limited number of active sites are apparent in metal clusters. This potential to combine advantages of both homogeneous and heterogeneous catalysis is one driving force for the active research efforts in the area. Secondly, a suitable combination of different metals with different sets of chemical properties in heteronuclear clusters may permit more efficient interactions with substrates than homometallic clusters or mononuclear metal complexes have. The tendency of some clusters to undergo fragmentation reaction can be prevented [46] (a) by using non-fluxional chelating ligands ($Ph_2PCH_2PPh_2$), (b) by capping by donor ligands (μ_3-PPh) or (c) by using main group elements acting as interstitial or bridging heteroelement clamps (μ_6-C or μ_3-S). One recent example demonstrates the application of such main-group-element-bridged clusters in catalysis. The sulfido bimetallic cluster $Cp'_2Mo_2Co_2(CO)_4S_3$ ($Cp' = CH_3C_5H_4$) can function as a homogeneous hydrodesulfurization catalyst [47].

It is indeed difficult to prove that the intact cluster and not a low nuclearity complex or a microscopic metal particles generated in solution is actually responsible for a catalytic reaction in question [41a,48]. Isotopic labeling experiments of hydroformylation of ethylene using the cluster anion $[HRu_3(CO)_{11}]^-$ clearly show the involvement of actual cluster intermediates during the course of the reaction (Fig. 14)



Scheme 4. Relations between metal clusters, homogeneous and heterogeneous catalysis [39].

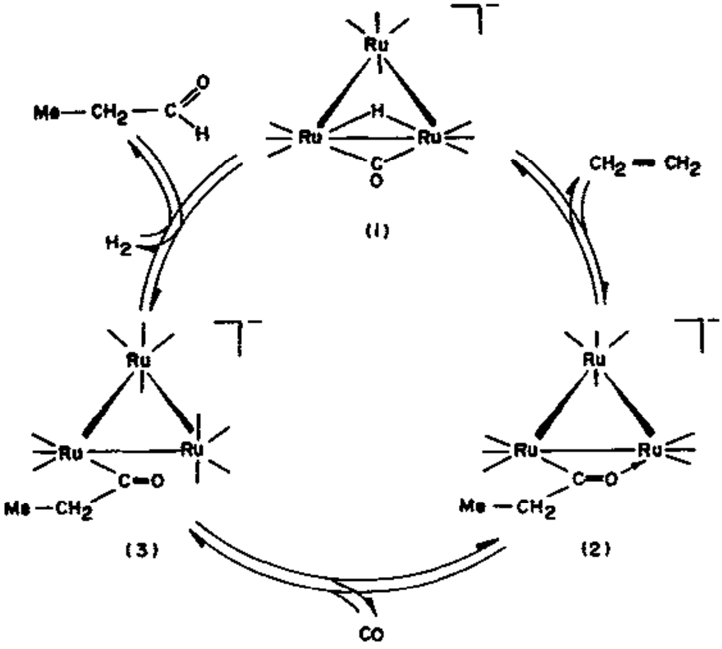


Fig. 14. Catalysis cycle for the cluster-catalyzed hydroformylation of ethylene [49].

[49]. Ethylene reacts with the electrophilic bridging carbon atom in **1** to give a μ_2-η^2(C,O) propionyl **2** which reacts with more CO to become η^1 in **3**. Hydrogenolysis of the acyl gives propionaldehyde, restoring the original cluster anion. Another good example of cluster catalysis [50] is the hydroformylation of terminal alkene to an aldehyde using the tetracobalt cluster $Co_4(\mu\text{-}CO)_2(CO)_8(\mu_4\text{-}PPh)_2$ (Fig. 15). This cluster is particularly stable because of the presence of the μ_4 bridging PPh groups. A total of five bonds to cobalt has to be broken to give a species of lower nuclearity. The original cluster has been recovered after long reaction times (60 h) with no other detectable organometallic products such as $[Co(CO)_4]^-$, $HCo(CO)_4$ or $HCo(CO)_3L$. Moreover, the turn-over frequency increases with increasing cluster concentration. These further support cluster catalysis. Another example [51] is the hydroformylation of 1-pentene using the mixed-metal cluster $Fe_2Co_2(CO)_{11}(\mu_4\text{-}PPh)_2$. Cluster catalysis is suggested on the basis of Fourier transform IR and high performance liquid chromatography analysis of the final reaction solutions and in-situ cylindrical internal reflectance measurements of the working catalyst solution.

The ability of metallic clusters to generate catalytically active mononuclear fragments (catalyst precursors) by breaking the metal–metal bond has already been mentioned in the preceding section 2.3, and several examples to demonstrate this point are available in the literature. It is interesting to note that clusters could generate catalytically active metal colloids in solution under appropriate conditions to prevent further aggregation of the metal, e.g. stabilization of colloidal transition metal particles in hydrocarbon solution in the presence of protective polymers. They

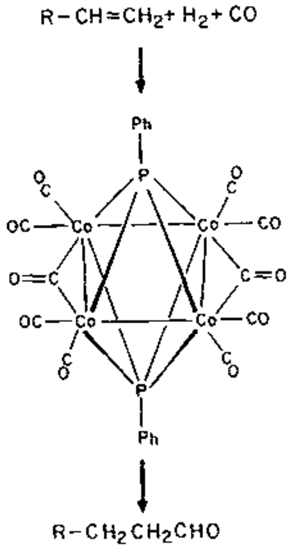


Fig. 15. Example of cluster catalysis using $Co_4(CO)_{10}(PPh)_2$ for the hydroformylation of a terminal alkene.

may also provide precursors of very small clusters (1–10 nm) with hybrid molecular solid state properties under suitable three-dimensional surface confinement. It is known that the properties of clusters change with cluster size. In order to minimize the electronic influence of the ligands, higher nuclearity clusters have to be synthesized and in fact, it is observed that the ligand-to-metal ratios decrease with increasing nuclearity. We have then the advantage of possessing the electronic properties of a metal and the solubility properties because of the ligand shell. In fact, the giant palladium clusters of approximate composition $Pd_{561}L_{60}(OAc)_{180}$ (L = 1,10-phenanthroline (Phen) or 2,2′-bipyridine) and $Pd_{561}(Phen)_{60}O_{60}X_{60}$ (X = PF_6, ClO_4, BF_4 or CF_3CO_2) contain close-packed metal cores [52]. They are soluble in water and polar organic solvents. This aspect is important with respect to homogeneous catalysis. These clusters have been shown to catalyze oxidative acetoxylation of ethylene into vinyl acetate, oxidation of primary aliphatic alcohols into esters and transformation of aldehydes to acetals.

3.4. Biological application

The fourth is their biological application. Here certain polynuclear clusters serve as models of biological compounds such as iron–sulfur proteins [53]. For example, the composition of the cluster $[MoFe_6S_6(CO)_{16}]^{2-}$ closely reflects the core stoichiometry of the FeMo cofactor of nitrogenase (Fig. 16). This synthetic analog also approximate the Mo—Fe bond length distribution of the cofactor. Although several types of Fe—S cluster have been structurally characterized, organometallic examples are relatively rare. Nevertheless, such synthetic approach to structural and functional models of native metalloproteins help to elucidate enzymatic reaction pathways

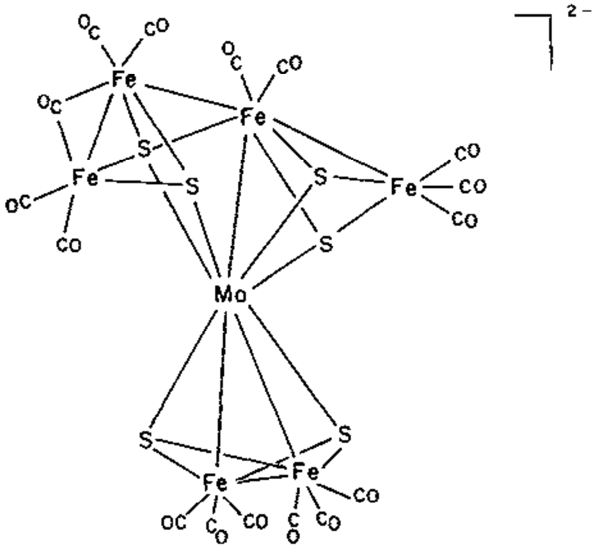


Fig. 16. Metal cluster model for FeMo cofactor of nitrogenase.

[54], and they may provide a vehicle for the development of effective catalysts for industrial nitrogen fixation at ambient conditions. Moreover, because of the relative simplicity of the synthetic clusters when compared with the complexity of natural clusters, the study of structure–reactivity correlations becomes easier. And the availability of physical techniques for full characterization of molecular clusters provide much better understanding of the reaction steps involved.

3.5. Precursors to materials

Another area where cluster chemistry could play an important role is in materials science [55]. Here the basic questions are as follows: what are the structural variations in the transition from molecules to macroscopic bulk materials and, how are the building blocks connected to the growing lattice? More importantly, at which size does the cluster lose its molecular properties? In Fig. 17 we can see the transformation of discrete molecules to solid state compound β-cobalt telluride and cluster intermediates that are identifiable fragments of the solid lattice [56]. The broken lines connect the four cobalt atoms in the solid which can be compared with the Co_4 core of the tetracobalt ditelluride cluster $(Et_3P)_4(CO)_6Co_4Te_2$. The CoTe fragment results from a 60° rotation of one face of the Co_6 octahedron of $(Et_3P)_6Co_6Te_8$ cluster, thereby generating a trigonal prism of six cobalt atoms. The stoichiometry of the starting cluster and the nature of the decomposition reaction determine the composition of the final solid product. Thus one can make use of clusters as building blocks for extended arrays.

Solid state thin films can be prepared by using single-source cluster precursors [57]. The practical technique commonly used for their deposition is known as

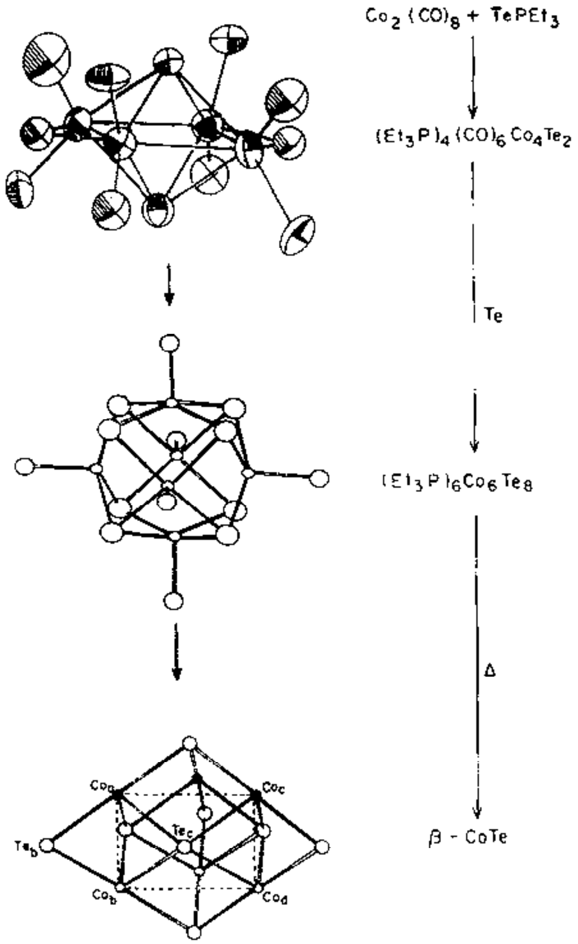


Fig. 17. Molecules-to-solid transformation showing cluster intermediates [56].

organometallic chemical vapor deposition [58]. In this molecular precursor approach, the aim is to synthesize clusters that are easy to handle, have low toxicity and intrinsically have the desired stoichiometry and low temperature decomposition pathway. In this sense, $HFe_3(CO)_9BH_4$ can act as a potential source of the well-known metallic glass $Fe_{75}B_{25}$. The pyrolysis of this cluster produces the basic geometric building block Fe_3B of the final amorphous alloy thin film material (Fig. 18) and the ligands are lost as carbon monoxide and dihydrogen [59]. Further, Mössbauer spectral analysis indicates that the film prepared by this method has different magnetic properties and the orientation of the magnetic moments is perpendicular rather than parallel to the film plane. By this method, we can prepare films of known stoichiometry with new properties and previously unknown metastable materials under substantially lower temperatures.

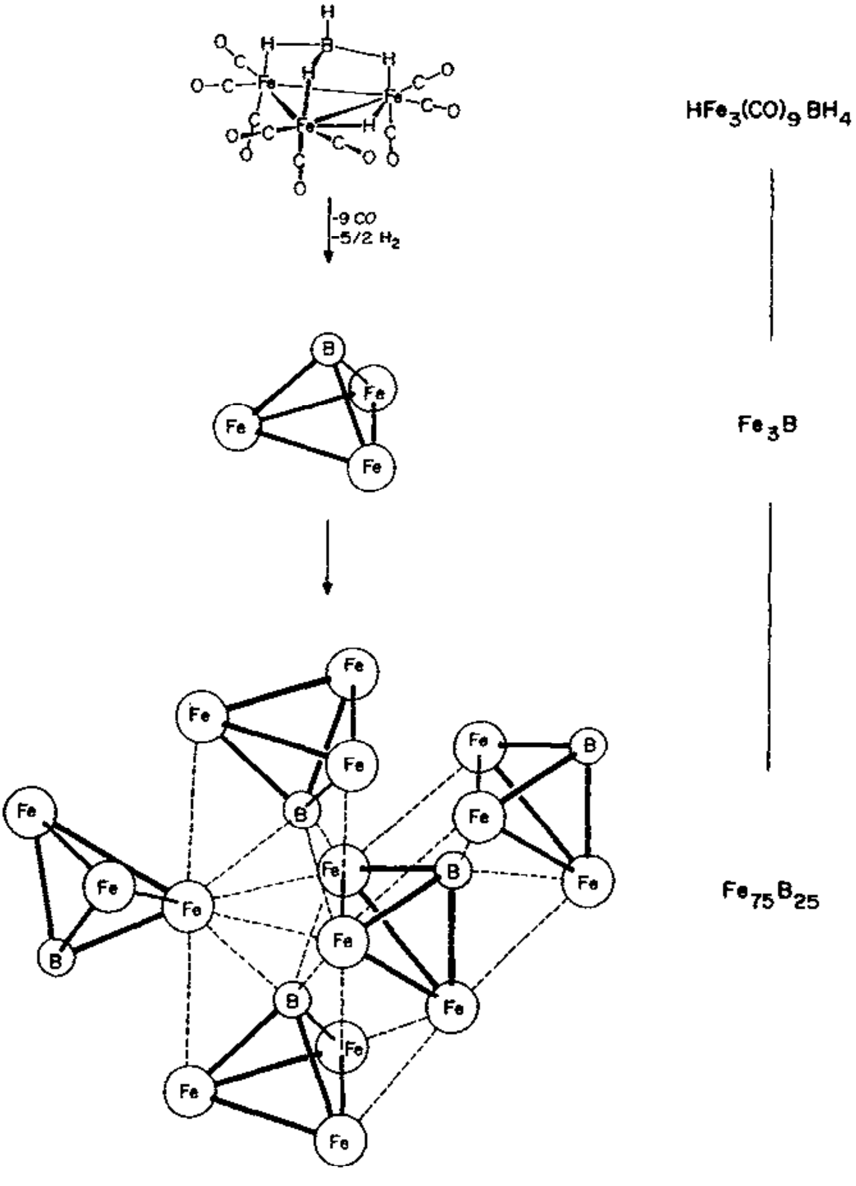


Fig. 18. Illustration of the cluster-to-solid transformation [57a].

3.6. Organic synthesis

One more application of transition metal clusters is in organic synthesis by making use of the unique catalytic properties which had not been observed with other catalysts before (Fig. 19) [20d,60]. For example, $HFeCo_3(CO)_{12}$ cluster catalyze the

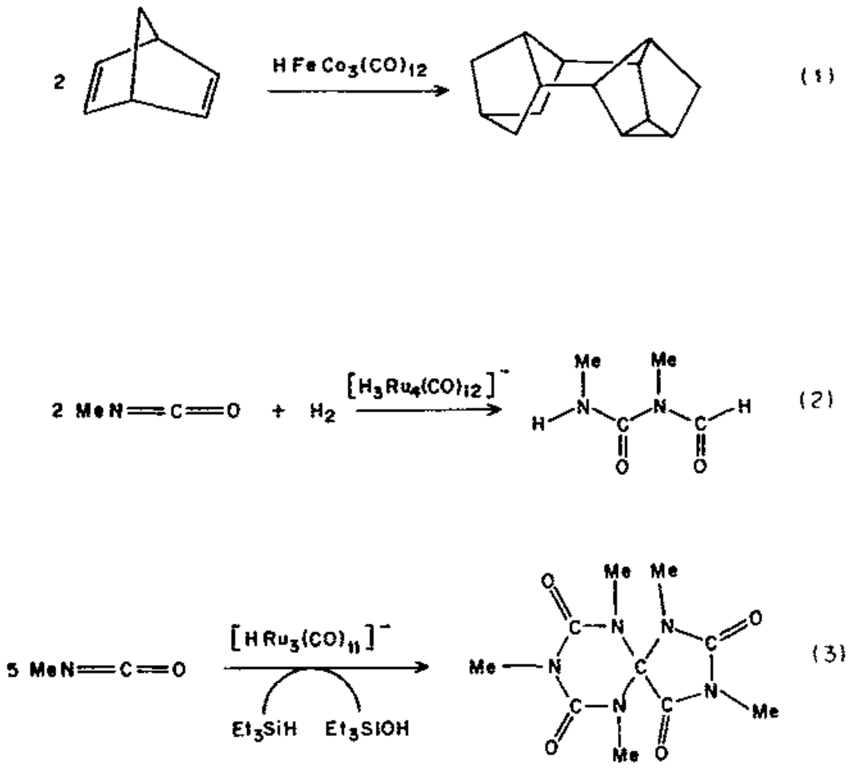


Fig. 19. Organic synthesis by cluster-initiated catalysis.

dimerization of norbornadiene by the stereospecific fusion of two molecules (Fig. 19, Eq. (1)). The tetranuclear cluster anion [$H_3Ru_4(CO)_{12}$]$^-$ has been found to catalyze coupling reaction of heterocumulenes to give carbamyl formamides of type shown in Fig. 19, Eq. (2). Another good example is spirocyclization of alkyl isocyanates catalyzed by [$HRu_3(CO)_{11}$]$^-$ in the presence of triethyl silane (Fig. 19, Eq. (3)). A catalytic cycle involving exclusively intact Ru_3 cluster anions has been proposed [61]. Currently, the design of better catalysts for desired organic transformations is being explored and the reaction trajectories are being studied.

Cluster-mediated synthesis of an organic molecule [62] is illustrated in Fig. 20. Oxidative fragmentation of the carbidocarbonyl cluster [$Fe_6C(CO)_{16}$]$^{2-}$ in methanol forms $Fe_4(CO)_{13}C$ containing an exposed cluster-bound carbon atom. One molecule of CO then probably reacts with the electrophilic carbon atom to give a ketenediyl cluster intermediate $Fe_4(CO)_{12}CCO$ which on further reaction with MeOH gives the carbomethoxymethylidyne cluster [$Fe_4(CO)_{12}CCO_2CH_3$]$^-$. The hydrogenation of

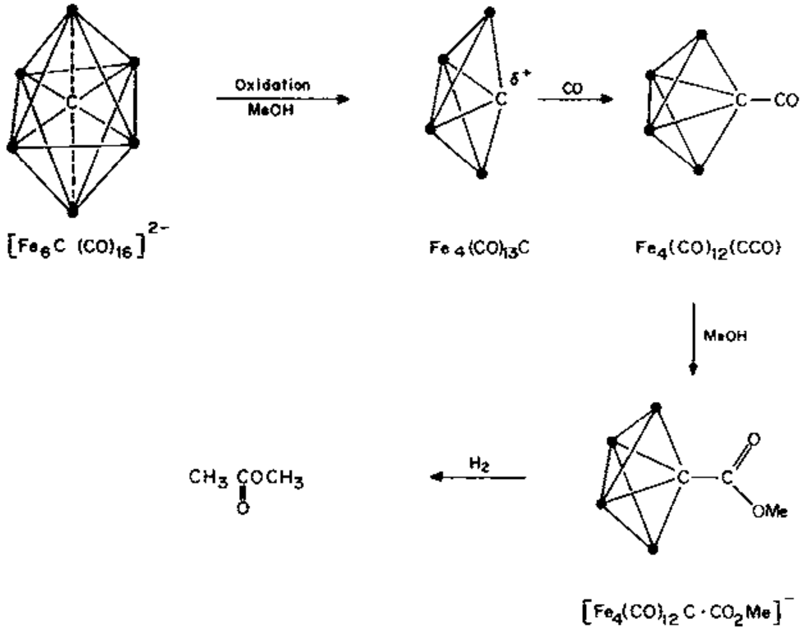


Fig. 20. Stoichiometric conversion of CO into CH_3COOMe using a metal cluster framework.

this butterfly cluster to methyl acetate provides a unique synthetic methodology for organic oxygenation from synthesis gas. The nitrene cluster $[Ru_3(CO)_{10}(\mu_3\text{-}NPh)]$ can be used in the synthesis of pentaphenylpyridone and 1,3,4-triphenyl maleimide (Fig. 21) [63]. The use of transition metal clusters in organic synthesis involving stoichiometric and catalytic reactions has been discussed in detail by Süss-Fink and Neumann [20d]. The reactions of clusters with organic molecules and a survey of C—H, C—C and C—O bond chemistry using clusters can be found elsewhere [64]. Chiral transition metal clusters may find applications in asymmetric syntheses of organic molecules [65]. Therefore we have the possibility of synthesizing some speciality and fine chemicals by using small amount of cluster compounds in the homogeneous liquid phase as well as of preparing previously unknown organic compounds.

4. Summary and outlook

An overview of the past progress and recent research results reveals that there is a spectrum of interest in transition metal cluster chemistry stretching from the very basic to the very applied and developmental. Analogies between metal clusters and bulk metals can be drawn by considering the overall structure, metal–metal distances, redox reaction and color criteria. Higher nuclearity transition metal clusters tend to adopt close-packed configurations because these structures maximize the intermet-

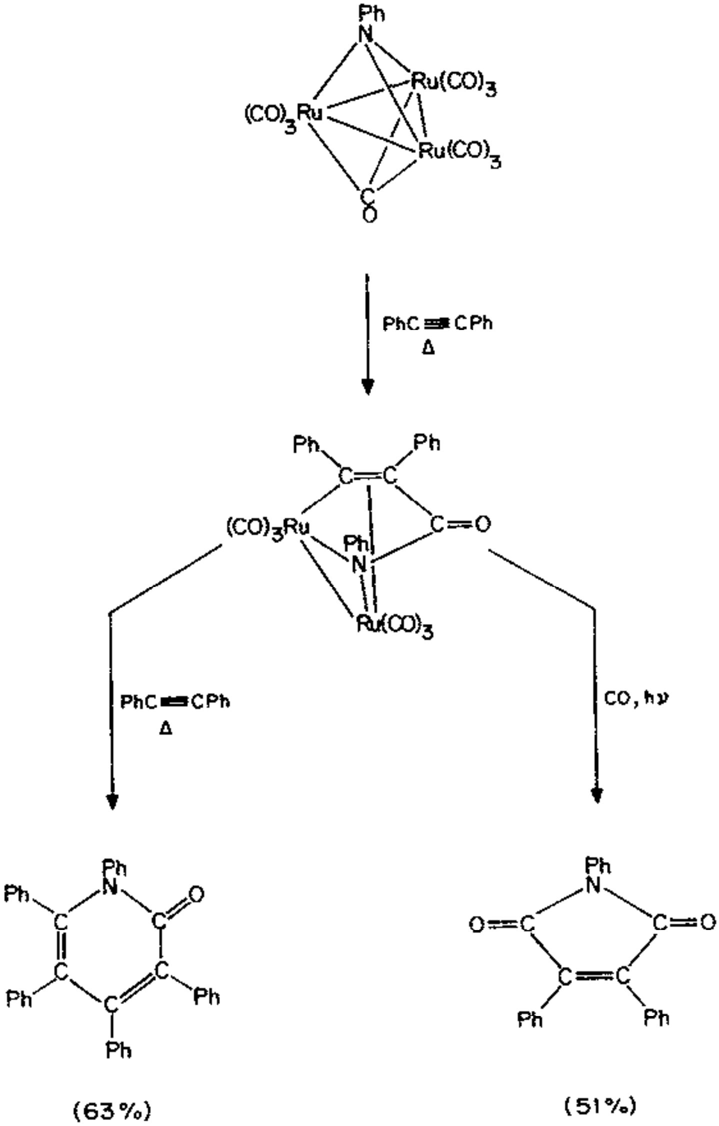
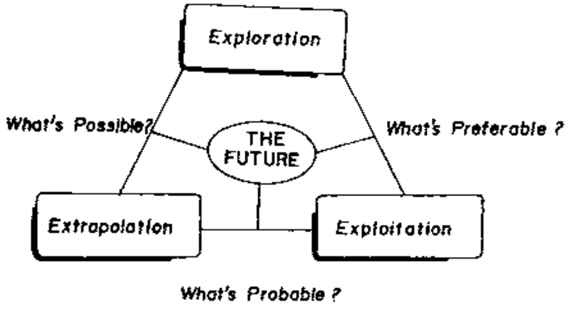


Fig. 21. Cluster-mediated synthesis of organic compounds.

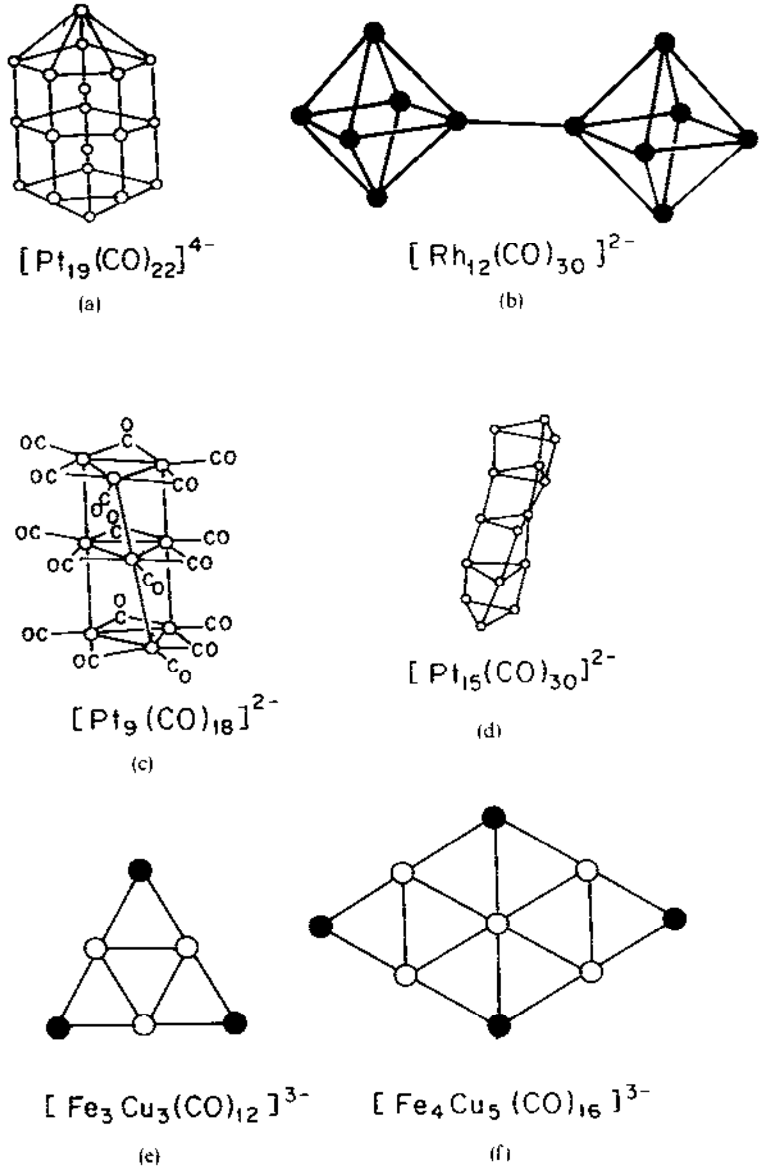
allic interactions and they are usually stabilized by the external ligands and the negative charges. Further, the geometries of discrete clusters mimic the interstitial sites found in the metallic lattice. The connection to heterogeneous catalysis is obvious when we consider ligated multimetallic clusters as the smallest metal crystal with ligands coordinated to its surface. The mobility of ligands and also the non-rigidity of the skeletal atoms themselves is yet another interesting property of these compounds. The study of cluster models aid understanding how metallic catalysts function at the molecular level. Two other major opportunities for clusters present in catalysis are to provide a source of organometallic reactive fragments and to effect catalytic cycles by retention of the skeletal framework. In the conversion of molecules to solids, structures of the isolable intermediate clusters can be rationalized in terms of the structure of the solid. Cluster-mediated catalysis often provides access to new organic products.

It is expected that both academic and practical studies of clusters will further reveal some of their peculiar properties with the promise of future commercial successes (Scheme 5). First is the exploration to obtain results of basic research (a) to gain some knowledge of the structural and reactivity patterns of clusters and (b) to obtain access to new organic molecules and inorganic materials. Current trends are stabilization of species which are intrinsically unstable or have high reactivities by multimetal coordination and generation of unusual structural patterns (Fig. 22). Although for symmetry reasons it is not possible to fill space with pentagons, a pentagonal prism of $[Pt_{19}(CO)_{22}]^{4-}$ cluster is possible [66]. The structure of $[Rh_{12}(CO)_{30}]^{2-}$ consisting of a linked octahedron would not be formed if we allow the 12 rhodium atoms to interact freely [67]. Other interesting twisted trigonal prismatic clusters such as $[Pt_9(CO)_{18}]^{2-}$ and $[Pt_{15}(CO)_{30}]^{2-}$ are worth noting here [68]. The molecular structure of the latter looks like a five-storey pagoda and both are not parts of the close-packed structures expected for pure platinum metal. Similarly, the planar structures are also known [69] for certain low valent metal clusters where the three-dimensional growth pattern is absent, e.g. $[Fe_3Cu_3(CO)_{12}]^{3-}$ and $[Fe_4Cu_5(CO)_{16}]^{3-}$. Asymmetric and symmetric star-shaped structures have been observed [70] for clusters containing three different metals, $Ni_2W_4Pt_2(\mu\text{-}CR)(\mu_3\text{-}CR)_3(\mu\text{-}CO)(CO)_7Cp_4$ and $Ni_2W_4Pt_2(\mu_3\text{-}CR)_4(CO)_8Cp_4$ respectively. Recently, boat and sofa configurations of the Ru_6 core has been observed [71] in $[Ru_6(CO)_{14}(\mu\text{-}CO)_2(\mu_4\text{-}S)(\mu_3\text{-}n^2\text{-}EtNCSNHEt)$ $(\mu_3\text{-}\eta^2\text{-}EtNCNHEt)]$ and $[Ru_6(CO)_{16}(\mu\text{-}H)(\mu_5\text{-}S)(\mu_3\text{-}\eta^2\text{-}PhNCSNHPh)]$ respectively. Probably, these chemically stabilized clusters are more exceptions than the rule in the direction of ordered structures of pure metals. This is evident by considering the number of such examples (particularly high nuclearity examples) known to date ($m > 10$).

Yet another recent trend is to synthesize medium nuclearity clusters inside zeolite



Scheme 5. General scheme for future prospects of research in cluster chemistry.



$[Pt_{19}(CO)_{22}]^{4-}$ (a)

$[Rh_{12}(CO)_{30}]^{2-}$ (b)

$[Pt_9(CO)_{18}]^{2-}$ (c)

$[Pt_{15}(CO)_{30}]^{2-}$ (d)

$[Fe_3Cu_3(CO)_{12}]^{3-}$ (e)

$[Fe_4Cu_5(CO)_{16}]^{3-}$ (f)

Fig. 22. Some uncommon structural patterns observed in cluster compounds.

supercages, particularly large pore supercages such as those in $AlPO_4$-8 (8.7 Å), Faujasite (7.4 Å) and VPI-5 (12.1 Å). Recently reported examples [1a,72] include triangular $M_3(CO)_{12}$, (M = Fe or Ru), octahedral $M_6(CO)_{16}$ (M = Rh or Ir) and the trigonal prismatic $[Pt_{12}(CO)_{24}]^{2-}$ cluster dianion, all encapsulated in an intracrystalline NaY cavity. The stability of such immobilized clusters is higher than that of the clusters bound to inorganic oxide supports such as alumina or silica. This holds good even the under high pressure and temperature conditions of synthesis gas conversion. The intercalation of clusters between the layers in certain interlayered clay minerals with spacings of molecular dimensions provide an interesting alternative research theme, e.g. $[HRu_3(CO)_{12}{}^+]$—APM (APM = alumina-pillared montmorillonite). The high selectivity for isomerized hydrocarbons observed in CO hydrogenation using the above Ru—APM catalyst has been attributed to the unique texture and bifunctional nature of Ru—APM [73]. Also, such an approach possibly helps to prevent aggregation and consequent changes in the nuclearity of metal clusters.

Second is the extrapolation of the bonding theories [3a,74] to explain the experimentally observed structures in many metal clusters (M_mL_n) in the light of the multicenter bonding concept. Unusual structures obviously provide benchmarks for the broad testing of theories. For lower nuclearity clusters ($m = 2$–4), the commonly employed electron counting rule is the 18-electron rule [75] whereas, for the medium nuclearity clusters ($m = 5$–9), the polyhedral skeletal electron pair theory [76], topological electron counting [77] and Lauher's [78] cluster model are useful. In these clusters, one can observe polyhedral structures and a more localized bonding picture. The band theory of solids is applicable in the case of high nuclearity clusters ($m > 10$) possessing fragments of close-packed metallic structures with a more delocalized nature of bonding. In smaller clusters, electronic factors are predominant whereas, in larger clusters, geometric factors dominate. Therefore, by developing intermediate level theories, correlation between condensed matter systems and molecular systems can be carried out and consequently the chemical behavior of the large majority of clusters can be explained. Alternatively, by varying the properties of the ligands such as basicity, steric hindrance, cone angle and chelating effects, unobserved metallic core structures can be chemically stabilized, thereby providing a challenge to existing theories. The ligand polyhedral model [79] developed by Johnson considers the structures of binary carbonyls $M_m(CO)_n$ as the reflection of the insertion of the metal core M_n within the ligand polyhedron $(CO)_n$.

Finally, exploitation of basic research results to end use is equally important. The structural and reactivity patterns of metal clusters, particularly those that are unavailable to mononuclear complexes, may be finely tuned to obtain tailor-made catalysts. In doing so, one has to consider the nature and number of metals, the oxidation state, the geometrical structure of the system and the nature of the ligands bonded to the metal(s). In the future, it may be possible (a) to develop new multimetallic catalysts active under mild conditions and with greater selectivity, (b) to create solid state materials that have controllable electrical conductivity, (c) to prepare multiclusters which in solution phase have properties that are intermediate between those of solid state materials and molecular metal clusters [1n], (d) to design clusters in which interconnected network of metal atoms lead to net multielectron redox processes useful in the activation of inert molecules and (e) to establish the relationship of such ligated transition metal clusters with their ligand-free counterparts [70d,80]. Construction of clusters with desired steric and electronic specifications is a challenge for the next decade. Research activities directed towards a range of actual and potential applications of clusters in quite different fields awaits various surprising observations to follow. Realizing the significance of research, development and design in this frontier area of cluster chemistry, it is necessary to address the basic problem regarding the particle size at which metallic character disappears, and the practical problem of preparation of very small particles [25b]. In short, organotransition metal cluster chemistry has a rich past and a bright future!

Acknowledgments

Thanks are due to the following: Dr. P. Mathur, Indian Institute of Technology, Bombay, who introduced me to the field of research in cluster chemistry, and Professor T.P. Fehlner and Professor E.E. Wolf, University of Notre Dame, who exposed me to the research involving applications of clusters in thin films and catalysis.

Addendum

A general survey of very recent publications related to the chemistry of cluster compounds that is of special interest is presented in this section. Chapter 2 in the new book by Gonzalez-Moragna [81] covers the mainstream research activities in the area with more general appeal. A critical review of the use of molecular clusters as models of metallic catalysts has been given [82]. It has been shown by ^{197}Au Mössbauer spectroscopy of the Pt_{309} cluster that the inner core exhibits metallic behavior [83]. A review article dealing with distinct examples of structural comparison of certain hydrocarbon species on metal clusters and on rhodium surfaces has appeared [84]. It has been demonstrated that an amphiphilic tricobalt cluster derivative can be used to form stable Langmuir–Blodgett films [85]. Surface-mediated synthesis of several neutral and anionic metal carbonyl clusters has been summarized elsewhere [86]. An extended array of clusters can be prepared from functionalized cluster building blocks [87]. Extensions of these investigations may lead to clusters that contain as many as several dozen metal atoms and materials with more complex structures. The use of transition metal clusters in homogeneous catalysis has been reviewed in a comprehensive fashion in [88]. There are available other more specialized review articles such as borane–osmium cluster chemistry [89], cluster and crystals of clusters [90], and acetylene–vinylidene transformation on mixed-metal clusters [91].

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