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Review

Catalysis by low oxidation state transition metal (carbonyl) clusters

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Contents

Abstract

This review seeks to evaluate the role of low oxidation state transition metal clusters (metal carbonyl clusters) in catalysis. The review commences with a discussion of the cluster surface analogy and then proceeds to discuss whether catalysis takes place by intact molecular clusters or mononuclear fragments; both these topic have been fiercely contested in the literature. Next, the application of clusters in organic transformations is briefly reviewed with an emphasis given to reactions that cannot be conducted using other catalysts (or pre-catalysts); areas for future studies are also highlighted. The latest developments in cluster immobilisation using alternative solvents such as water, ionic liquids and supercritical fluids, and the use of clusters as precursors to heterogeneous nanocluster catalysts are reviewed. Finally, the possibility of using materials at the cluster–colloid interface in catalytic applications is discussed.

Keywords: Cluster; Transition metal; Catalysis; Biphasic catalysis; Immobilisation; Nanocluster

1. Introduction

The discovery of the first discrete molecular compounds with metal–metal bonds, which lead to the burgeoning field of low oxidation state transition metal cluster chemistry (typified by metal carbonyl compounds), presented chemists with an opportunity to explore compounds that might exhibit different properties and have different applications to well characterised and explored mononuclear compounds. Early expectations were high, and Muetterties, amongst others, postulated that clusters might act as reasonable models for heterogeneous catalysts [1]. Since characterisation of surface species and mechanistic studies of reactions that take place on metal surfaces are considerably more difficult to conduct than those of molecular species in solution, the hypothesis that molecular clusters might serve as models for heterogeneous catalysts was extremely attractive [2]. Furthermore, it was suggested that clusters might prove to be effective catalysts in their own right, and may even catalyse certain reactions that could not be catalysed by mononuclear complexes. In other words, clusters might fill the void between mononuclear species and colloidal (or heterogeneous) catalysts and open up new possibilities in catalysis and organic synthesis (for example see [3]).

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0010-8545/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
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Of course, studying the fundamental properties of clusters is extremely important regardless of their applications, and today structure and bonding in cluster compounds is reasonably well understood [4]. Cluster reactivity is also becoming clearer, but the multitude of available substitution sites, the possibility of skeletal transformations and different ways in which ligands can interact with clusters, means that rational synthesis and elucidating reactions mechanisms remains problematic. However, with respect to the catalytic properties of clusters, much data is available which has allowed some basic trends and protocols to emerge [5]. The main areas where clusters have had an impact in catalysis are as follows.

1. Their ability to model heterogeneous catalysts—termed the cluster surface analogy.
2. Their ability to act as intact homogeneous catalysts, which has only been proven very recently.
3. Their use as precursors to active mononuclear catalysts, with applications in organic synthesis.
4. Their use as precursors to well defined nanoparticle catalysts.

This review will commence with a discussion of the current status of the cluster surface analogy and then explore the concept of cluster catalysis and the evidence for catalysis by intact clusters. Following this discussion the application of clusters in catalysis, including biphasic liquid–liquid and solid–liquid systems, will be examined.

2. The cluster surface analogy

Clusters have traditionally occupied a special position between mononuclear complexes and the bulk solid state and while the lower end of the cluster spectrum is easy to define, i.e. three metal atoms based on Johnson's early definition [6], the upper end remains unknown. Low oxidation state clusters with up to 145 metals have been structurally characterised by single crystal X-ray diffraction however, even the largest homonuclear osmium cluster which has only 20 osmium centres [7] has been shown by mass spectrometry to comprise a mixture of different species in solution, and this behaviour is colloid-like in that a colloidal solution does not consist of a pure compound, but a mixture of compounds [8]. The famous Au_{55} compound of Schmid, $Au_{55}(PPh_3)_{12}Cl_6$ [9] remains at the interface of cluster and colloid science [10], although if an X-ray structure is ever obtained, it may be viewed as a true cluster—at least in a traditional sense. Gas phase clusters are seldom prepared as pure species, and while they are considered clusters, they cannot be isolated on a synthetic scale and are beyond the scope of this review, as are the many other types of materials that are also referred to as clusters.

There are many qualitative features which support the cluster surface analogy. For example, the metal packing in clusters often resembles that of the bulk metallic state, and ligand interactions with clusters often involve bonding to more than one metal centre, and many related bonding modes have been established on metal surfaces. Much has been made of the osmium clusters $[Os_4(CO)_{13}]^{2-}$, $[Os_{10}C(CO)_{24}]^{2-}$ and $[Os_{20}(CO)_{40}]^{2-}$ (Fig. 1), which can be viewed as segments of a cubic close-packing (CCP) lattice, but it should be noted that metallic osmium is not CCP. As the size of the cluster increases, the properties progress towards those of the bulk metallic state. For example, $[H_{6-n}Ni_{38}Pt_6(CO)_{48}]^{n-}$ ($n = 5$ or 6), in which all six platinum atoms are bulk metal atoms, act as electron reservoirs undergoing six reversible redox changes with almost constant amounts of energy (ΔE) [11]. Such behaviour implies the absence of a well-defined HOMO-LUMO gap, which is indicative of semiconductor rather than metallic character. A plot of the average ΔE exhibited by the known carbonyl clusters displaying electrochemically reversible multiple redox changes versus their nuclearity, suggests that the transition from semiconductor to metallic behaviour might occur with cluster nuclearities greater than 65. This work goes a long way towards quantifying, 'when does a cluster become metal-like?' Although the actual answer to such a question is dependant on the property under question, since low oxidation state clusters are getting bigger all the time, $Pd_{54}(CO)_{40}(PEt_3)_{14}$ [12], $Pd_{69}(CO)_{36}(PMe_3)_{18}$ [13] and $Pd_{145}(CO)_x(PEt_3)_{30}$ [14] have recently been reported, it should not be long before this hypothesis is tested more fully. Dynamic rearrangements of metal cluster cores have also been observed which closely resemble the hopping mechanism of adatom diffusion on metal surfaces [15].

In terms of ligand bonding modes observed on clusters and surfaces there are many structural similarities. As an illustrative example, benzene can coordinate to a cluster in several ways and these are shown in Fig. 2 [16]. Studies on well defined metal surfaces have revealed the presence of related modes [17]. The face-capping bonding mode is perhaps the most interesting from a structural viewpoint in that the C–C bonding lengths around the benzene alternate long and short; the short bonds are supposedly the double bonds and lie directly above the metals [18]. It would also appear that the additional metal atoms affect the nature of the μ_3-interaction. In the trinuclear cluster $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ the long and short C–C bonds average 1.45(1) and 1.40(2) Å ($\Delta = 0.04$ Å), respectively, which increases to $\Delta = 0.08$ Å in $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ [19], and for the hexaruthenium cluster, $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$, $\Delta = 0.09$ Å [18a]. In the related surface structure [Rh(111)/C_6H_6/CO] the long and short C–C bonds average 1.81(15) and 1.33(15) Å ($\Delta = 0.48$ Å) [17]. The difference between long and short bonds are much larger in the surface structure than in the clusters, but the larger standard deviations associated with the surface structure bond distances could mean that the differences are equivalent to those in the cluster, despite the increase in Δ as the nuclearity of the cluster increases. In clusters, a number

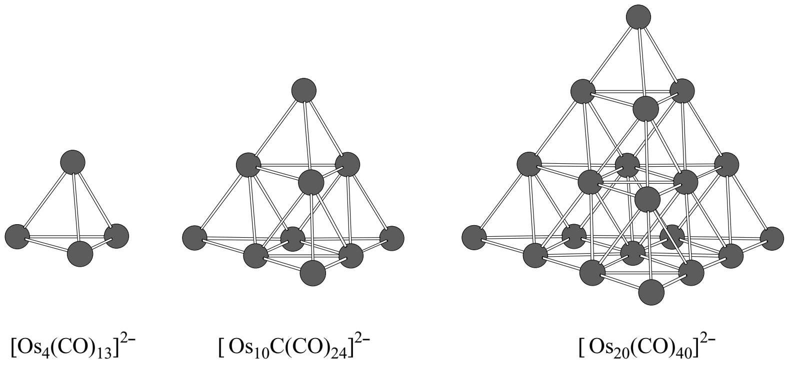


Fig. 1. A series of osmium clusters that can be viewed as segments of cubic close-packing.

of skewed structures of μ_3-$\eta^2:\eta^2:\eta^2$ arenes have also been observed, tending to a μ_3-$\eta^1:\eta^1:\eta^1$ bonding mode in which alternate C-atoms of the arene ring sit directly over the metal atoms [20]. Other clusters with polyaromatic [21] or vinyl substituted arenes [22] have been characterised where all the unsaturated bonds interact with the cluster.

The mean Rh(surface)–C(benzene) bond distance of 2.35(5) Å is the same as the mean Ru–C bond length of 2.33(1) found in $Ru_3(CO)_9(\mu_3$-$\eta^2:\eta^2:\eta^2$-$C_6H_6)$. Furthermore, theoretical modelling of the Rh(1 1 1) surface predicts that a major adsorption effect involves the symmetrical bending of the hydrogen atoms out of the plane of the benzene ring, away from the metal [23]. This is precisely the behaviour observed in the cluster species; an out of plane bending angle of 20° was predicted for the Rh(1 1 1) surface which is in excellent agreement with the value of 21.5° observed for the Ru_3 cluster. Calculations have shown that a rehybridisation of the benzene π molecular orbitals ($sp^2 \rightarrow sp^3$) is necessary for maximised overlap with metal orbitals and gives rise to the C–H bending [24]. Buckminsterfullerene and other related carbon clusters also coordinate to clusters in the μ_3-$\eta^2:\eta^2:\eta^2$ face capping bonding mode and it would appear that the slight curvature of the C_6-face in these systems increases the tendency for such a coordination mode [25].

The cluster-surface analogy appears to be valid from a structural perspective, and there is also good evidence to suggest that the analogy holds for reactivity, as indicated in a recent review [26]. However, reactivity between the two regimes is less easily compared. For example, cyclohexadiene has been shown to dehydrogenate when coordinated to a cluster to give a face-capping benzene [19,27] and the benzene can subsequently be converted to benzyne [28]. These reactions involve the use of a chemical reagent and photolysis, respectively, and while both reactions also take place on metal surfaces, they do so under very different conditions. Heterogeneous catalysts, including relatively well defined soluble colloidal particles, are widely used to reduce arenes to cyclohexanes, however, while clusters have been used to promote such transformations, there remains some doubts concerning the identity of the catalyst [29], which may well be heterogeneous, although similar mechanisms could be involved for both systems [30]. Furthermore, the bonding modes are not static and migration from one to another is facile [31], which makes comparisons of reactivity problematic.

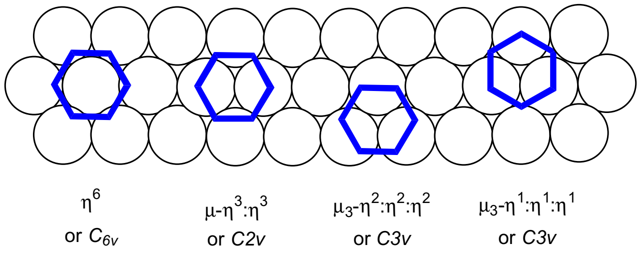
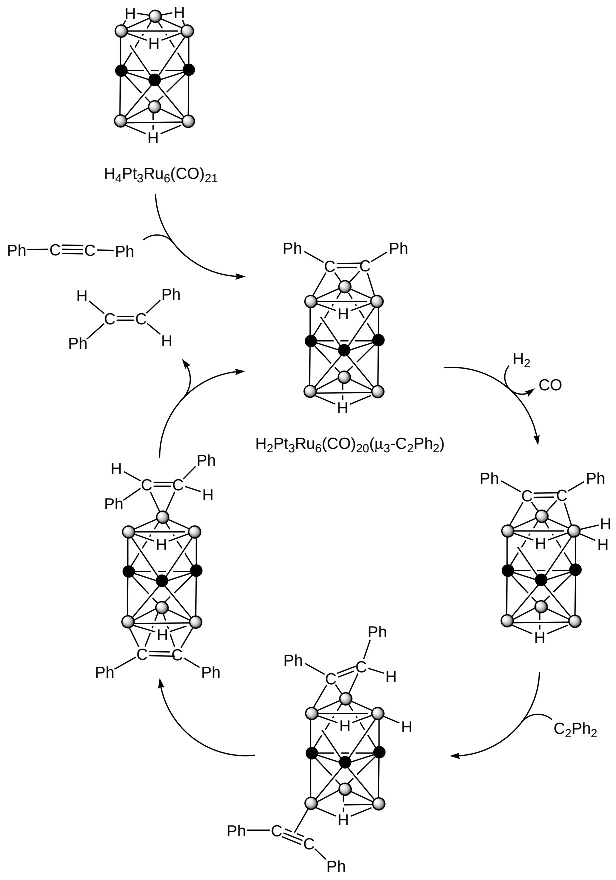


Fig. 2. Representations of four recognised ways in which arenes interact with metal clusters and metal surfaces (others are known).

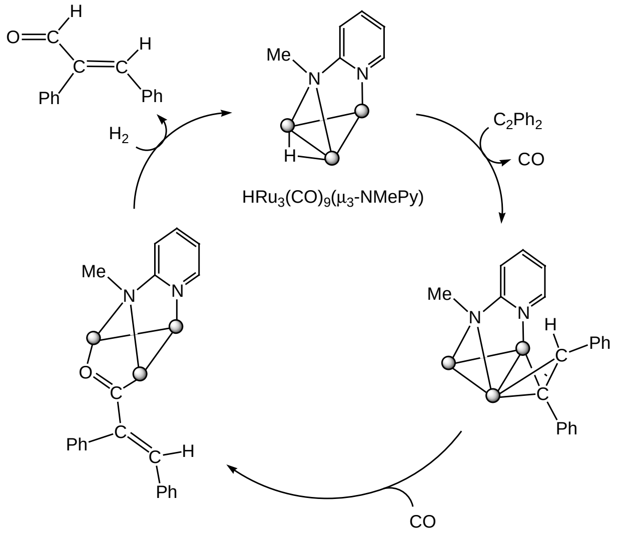
3. Evidence for cluster catalysis

In a sense, if a cluster is merely a precursor to a catalyst that is either mononuclear or colloidal in nature it does not matter, assuming the active catalyst cannot be isolated and used in its place. However, knowing the identity of the active catalyst is essential if more efficient and effective catalysts are to be developed. Not surprisingly, considerable effort has been devoted towards determining whether intact cluster catalysis takes place, but despite these efforts, a great deal of confusion has surrounded this topic.

Over the years there has been much debate as to whether clusters fragment to form mononuclear species, aggregate to form nanoparticles, or remain as intact molecular clusters during catalysis. It is now known that examples involving all three possibilities exist and in the same reaction more than one catalyst can operate simultaneously. Differentiating between mononuclear and cluster catalysis is considerably more involved that distinguishing cluster catalysis from colloidal (or heterogeneous) catalysis. Various tests are used to establish whether a reaction is catalysed by a homogeneous or heterogeneous species, and although one test on its own



Scheme 1. Proposed catalytic cycle for the hydrogenation of diphenylacetylene to *trans*-stilbene using $H_4Pt_3Ru_6(CO)_{21}$.



Scheme 2. Proposed catalytic cycle for the hydroformylation of diphenylacetylene to α-phenylcinnamaldehyde using $HRu_3(CO)_9(\mu_3$-η^2-NMePy).

is not satisfactory, a ‘toolkit’ is available, which includes kinetic measurements, poisoning experiments and spectroscopic tests, allowing assignment of the type of catalysis [32].

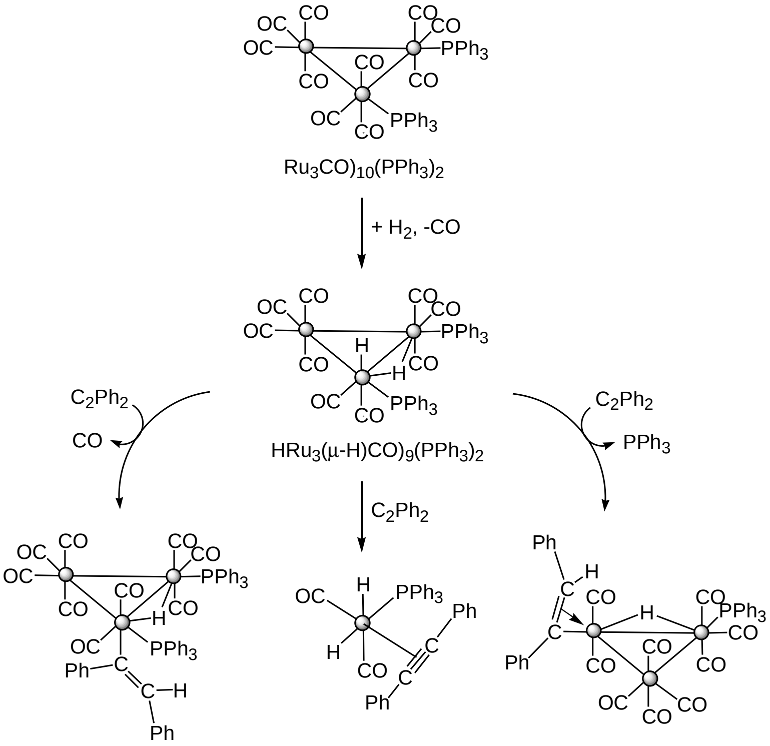
Once homogeneous catalysis has been confirmed, the next step is to determine whether catalysis is by the intact cluster or by mononuclear fragments. This is not an easy task, but several qualitative tests have been proposed [33], and a number of convincing examples of homogeneous cluster catalysis have been reported, although based on indirect evidence. For example, the heteronuclear cluster $H_4Pt_3Ru_6(CO)_{21}$ catalyses various alkyne transformations without appearing to undergo fragmentation (Scheme 1) [34]. The structure of $H_4Pt_3Ru_6(CO)_{21}$ comprises of a Pt_3 triangle sandwiched between two Ru_3 layers. Reaction with PhC≡CPh affords $H_2Pt_3Ru_6(CO)_{20}(\mu_3$-$C_2Ph_2)$, which catalyses alkyne hydrogenation and hydrosilation. The cluster is superior to homonuclear analogues for the hydrogenation of diphenylacetylene to *trans*-stilbene, although catalyst recovery is not quantitative, and the catalyst lifetime is limited.

Catalytic transformations involving $H_2Pt_3Ru_6(CO)_{20}$ $(\mu_3$-$C_2Ph_2)$ appear to occur at the Ru_3 faces, with the platinum metals not actively involved, although they seem to have a pronounced effect transmitted to the ruthenium layers to give what has been described as a ‘synergistic enhancement’. It is unlikely that such a synergistic enhancement would take place if the cluster underwent fragmentation to afford a mononuclear catalyst.

Heteronuclear clusters have proven very useful in making a case for intact cluster catalysis, with some examples giving activities indicative of cluster catalysis, and others showing that catalysis results from mononuclear fragments [5].

A number of trinuclear clusters with face-capping ligands also appear to act as intact cluster catalysts, with the face-capping ligand conferring stability to the metal core. This does not mean that metal–metal bonds remain unperturbed throughout the catalytic cycle, but if a metal–metal bond is cleaved, the metals remain in proximity to one another, and the bond can reform at an appropriate stage of the reaction. For example, $HRu_3(CO)_9(\mu_3$-η^2-NMePy) catalyses the hydroformylation of diphenylacetylene to α-phenylcinnamaldehyde by what is most likely by an intact cluster species (Scheme 2) [35].

All the species shown in the scheme have been isolated and structurally characterised. In the migratory insertion step a 50-electron cluster is formed in which one Ru−Ru bond has broken, but the μ_3-η^2-NMePy ligand prevents further metal–metal bond cleavage and fragmentation, at least in part. The hydroformylation reaction is not without problems and depending upon the conditions employed the active catalyst can be poisoned. Conversion of $HRu_3(CO)_9(\mu_3$-η^2-NMePy) to the catalytically inactive dinuclear species $Ru_2(CO)_6(\eta^3$-NMePyCO) takes place after several cycles, formed by insertion of CO into the Ru−amide bond. Such a process points towards a catalyst that can operate as an intact cluster, but also perhaps as a fragment, with both mechanisms possibly taking place at the same time.



Scheme 3. Proposed hydrogenation paths for $Ru_3(CO)_{10}(PPh_3)_2$.

One criteria for identifying intact cluster catalysis is the observation of asymmetric induction in a reaction catalysed by a chiral cluster, with the chirality in the cluster frame, rather than from a chiral ligand [36]. As far as we are aware, such a goal has yet to be realised, despite various attempts [37]. Recently, however, $H_4Ru_4(CO)_{12}$ derivatised with a chiral bis-phosphine has been found to exhibit some chiral induction in the hydrogenation of tiglic acid, and while catalysis by fragmentation products cannot be excluded, the starting clusters were recovered unaltered after reaction [38].

Direct evidence for intact cluster catalysis has finally been provided using parahydrogen (p-H_2) NMR methods. Fluxional processes and transfer of hydrides into organic groups coordinated to clusters were initially demonstrated with p-H_2 [39]. Subsequent studies employing $Os_3(\mu\text{-}H)_2(CO)_{10}$ [40] and $Ru_3(CO)_{10}(L)_2$, where L = PMe_2Ph or PPh_3 [41], previously shown to be homogeneous hydrogenation catalysts [42], provided direct evidence for intact cluster catalysis. The active catalyst intermediates that have been identified by p-H_2 NMR are derived from the dihydride derivative $HRu_3(\mu\text{-}H)(CO)_9(L)_2$ and are shown in Scheme 3 for the triphenylphosphine compound [43]. Each of the intermediates releases *cis*-stilbene and reacts with further hydrogen and substrate to continue the catalytic process. The route taken depends on the substrate *and* the solvent, with intact cluster catalysis preferred in polar solvents and fragmentation to the mononuclear intermediate being facilitated by non-polar solvents. If the cluster stays intact, CO loss or slower phosphine loss leads to hydrogenation, with the substrate binding to the vacant site. This process shows a first order dependence on the hydrogen concentration, which requires H_2 to coordinate before the product is eliminated. In all cases, catalysis by a route involving an intact cluster showed greater activity than that involving a mononuclear counterpart. However, both intact cluster catalysis and catalysis by a fragmentation product occur simultaneously, albeit at different rates. The strong dependence of the solvent on the type of catalyst generated may have led to confusion in the literature regarding the identity of the active catalysts in other systems. However, under similar conditions the cluster $Ru_3(\mu\text{-}H)CO)_9(\mu_2\text{-}PPh_2)$ does not fragment and all catalytic activity stems from the intact trinuclear cluster, indicating the importance of the ligands on the catalytic mechanism [44].

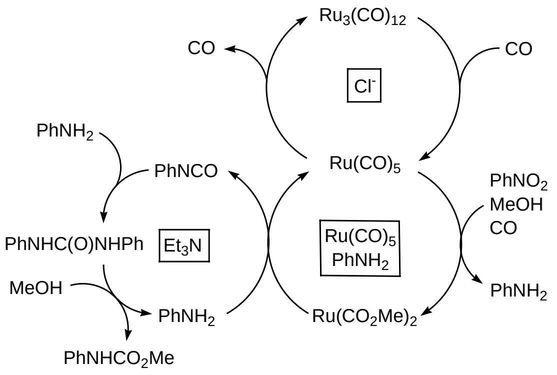
Although most discussions centre on clusters fragmenting to form active mononuclear catalysts, the reverse process is also possible, i.e. mononuclear complexes form catalytically active clusters under certain reaction conditions. For example, rhodium clusters generated from mononuclear species have been proposed as the active catalysts in the reduction of nitro compounds under phase transfer conditions [45], although it is possible that subsequently the clusters could have transformed to colloids that were responsible for the catalysis.

4. Application of clusters in organic transformations

The application of clusters for large scale industrial processes such as hydrogenation and hydroformylation has been extensively studied, and while polynuclear intermediates may be involved in certain processes, clusters appear to offer little advantage over other types of catalysts. However, interesting results continue to appear, and recent examples include the use of clusters as catalyst precursors for the carbonylation of methanol [46] and ammonia [47]. It has become apparent that clusters (or at least cluster catalyst precursors) catalyse a number of highly selective organic transformations where other types of catalysts are less effecient. Table 1 lists a number of reactions catalysed by metal carbonyls clusters, the majority of which cannot be catalysed by other types of compounds.

From the table it is clear that the majority of the cluster precursors used are simple homoleptic species. In a few cases a co-ligand, typically a phosphine, is added, but in general the reactions have not been optimised in terms of finding a more active cluster catalyst. The regioselective acylation of aromatic heterocycles using CO and alkenes was evaluated in the presence of a number of different homoleptic compounds including $Re_2(CO)_{10}$, $M_3(CO)_{12}$ (M = Fe, Ru and Os) and $Rh_4(CO)_{12}$ with $Ru_3(CO)_{12}$ proving most effective, but no other cluster derivatives were tested. A rare example of a more elaborate cluster catalyst is the acenaphthalene derivative $Ru_3(CO)_7(\mu_3\text{-}C_{12}H_8)$ which catalyses the reduction of esters, carboxylic acids and amides by trialkylsilanes.

It is likely that the majority of the reactions listed in Table 1 are not catalysed by intact clusters and a number of mononuclear complexes have been isolated during mechanistic studies. For example, the $Ru_3(CO)_{12}$/tetraalkylammonium chloride catalysed carbonylation of nitroamines to carbamates and ureas was originally believed to be catalysed by the capped-cluster $Ru_3(CO)_{10}(\mu_3\text{-NPh})$ [66]. It has since been shown that the active catalyst is a monoruthenium complex derived from $Ru(CO)_5$ and that the formation of the monomer is accelerated by chloride as shown in Scheme 4 [96]. What is clear is that these simple catalysts (or catalyst precursors) that have been known for many years are finding more and more uses in organic synthesis and have made a significant contribution to the recent growth in metal-catalysed reactions [97].



Scheme 4.

In general, those clusters evaluated in synthetically useful organic transformations are those that are commercially available. However, based on the vast number of known clusters, incorporating a huge range of different ligands, it seems likely that more effective cluster catalysts will emerge and a combined high-throughput screening-rational design approach might lead to the discovery of many more effective cluster catalysts.

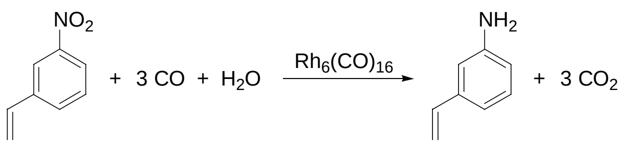
5. Immobilised cluster catalysts

In recent years one of the major directions in homogeneous catalysis has been to find ways to immobilise catalysts so that their separation from reaction products is facile like in heterogeneous catalysis. Many ingenious protocols have been developed including the use of biphasic liquid supports and attaching molecular catalysts to solid supports.

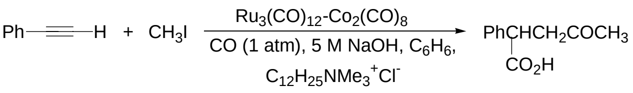
The liquid immobilisation media used in biphasic or multiphasic processes that are under most intensive investigation include water, ionic liquids, supercritical fluids and fluorocarbons. As far as we are aware, cluster catalysts have been evaluated in the former three solvents, but not in fluorous biphases. Aqueous-organic biphasic catalysis represents the most mature of these methods [98] and it is not surprising that clusters have been most extensively studied in water.

Water can be used not only as an immobilisation solvent in biphasic catalysis, but also as a source of hydrogen in the water gas shift reaction, and the use of clusters to catalyse the conversion of CO and H_2O to CO_2 and H_2 has been reviewed [99]. If the water gas shift reaction is conducted in the presence of an alkene then hydroformylation or hydrohydroxylmethylation can take place, the former being the dominant reaction. Clusters have also been used to catalyse hydrogenation reactions using water as a substrate. For example, $Rh_6(CO)_{16}$ catalyses the chemoselective reduction of nitro groups in high yield as shown in Scheme 5 [100].

Clusters have also been used as catalysts in phase transfer reactions. For example, a mixture of $Ru_3(CO)_{12}$ and $Co_2(CO)_8$ catalyses the carbonylation of alkynes with methyl iodide under phase transfer conditions as shown in Scheme 6 [101]. The solvent system composed of benzene and 5 M aqueous NaOH with an ammonium salt used as the phase transfer catalyst.



Scheme 5.



Scheme 6.

Table 1
Key organic transformations catalysed by cluster compounds

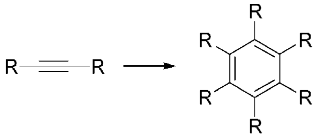
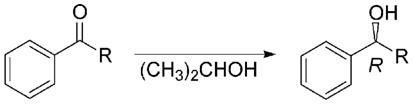
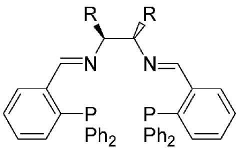
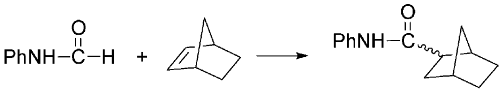
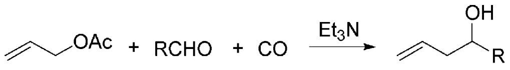
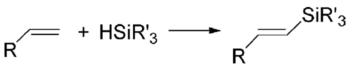
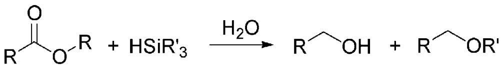
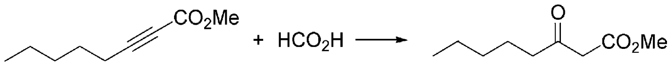
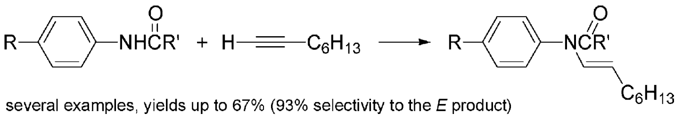
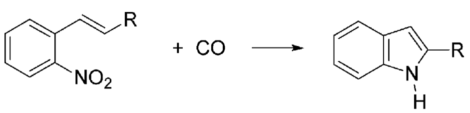
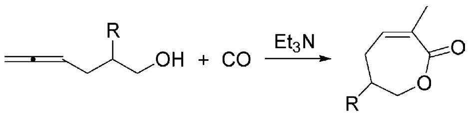
Catalyst	Reaction[a]	Ref.
$Co_3(CO)_9(\mu_3\text{-CR})$	 several examples and related examples, yields up to 96%	[48]
$M_3(CO)_{12}$ (M = Ru and Os)	$Et_3N + Pr_3N \longrightarrow Et_2PrN + Pr_2EtN$ yields up to 60%	[49]
$Ru_3(CO)_{12}$ + chiral ligand	 several examples, yields up to 98% Typical chiral ligand = 	[50]
$Ru_3(CO)_{12}$ or $[HRu_3(CO)_{11}]^-$ + phosphine	 several examples, yields up to 97%	[51]
$Ru_3(CO)_{12}$	 several examples, yields up to 91%	[52]
$Ru_3(CO)_{12}$	 many examples, yields up to 100%	[53]
$Ru_3(CO)_7(\mu_3\text{-}C_{12}H_8)$	 many examples, yields/selectivities up to 100%	[54]
$Ru_3(CO)_{12}$	 several examples and related examples, yields up to 100%	[55]
$Ru_3(CO)_{12}$ + PCy_3	 several examples, yields up to 67% (93% selectivity to the *E* product)	[56]
$Ru_3(CO)_{12}$ or $Rh_6(CO)_{16}$	 several examples, yields up to 75%	[57]
$Ru_3(CO)_{12}$	 several examples, yields up to 85%	[58]

Table 1 (*Continued*)

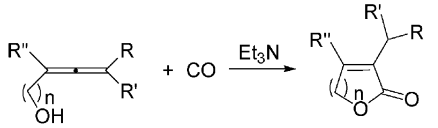
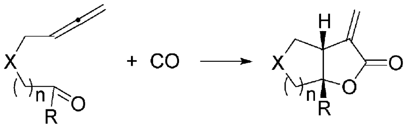
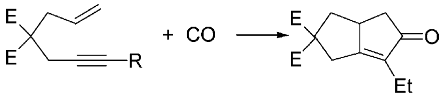
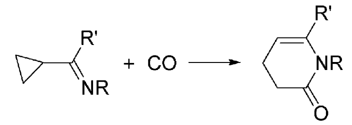
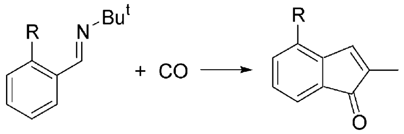
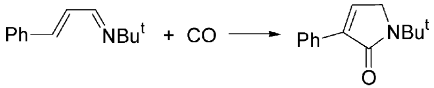
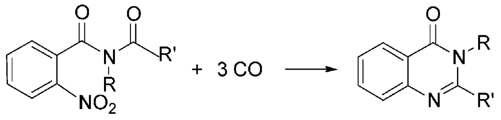
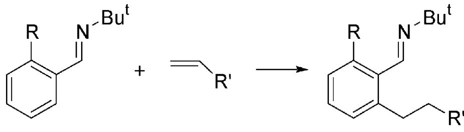
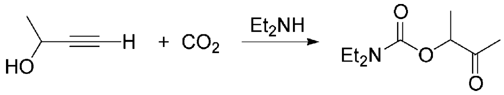
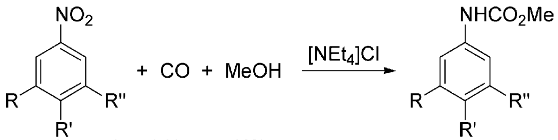
Catalyst	Reaction[a]	Ref.
$Ru_3(CO)_{12}$	 many examples, yields greater than 90%	[59]
$Ru_3(CO)_{12}$	 many examples and related reactions, yields up to 82%	[60]
$Ru_3(CO)_{12}$	 many examples, yields up to 89%	[61]
$Ru_3(CO)_{12}$	 many examples, yields typically around 60%	[62]
$Ru_3(CO)_{12}$	 many examples and related reactions, yields up to 85%	[63]
$Ru_3(CO)_{12}$	 several examples, yields up to 96%	[64]
$Ru_3(CO)_{12}$	 several examples, yields up to 98%	[65]
$Ru_3(CO)_{12}$	 many examples and related reactions, yields up to 97%	[66]
$Ru_3(CO)_{12}$	 several examples and related examples, yields up to 65%	[67]
$Ru_3(CO)_{12}$	 several examples, yields up to 93%	[68]

Table 1 (*Continued*)

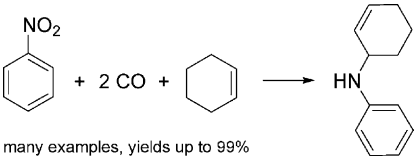
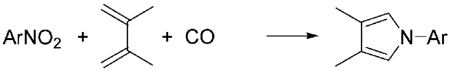
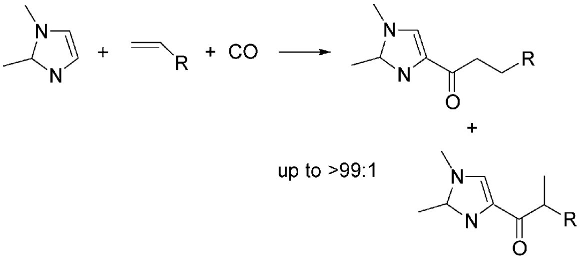
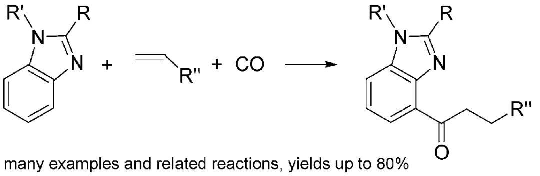
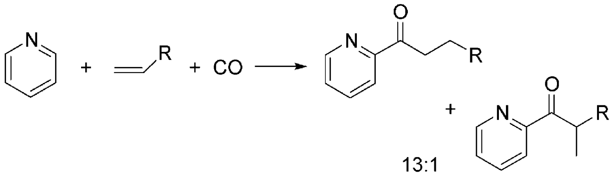
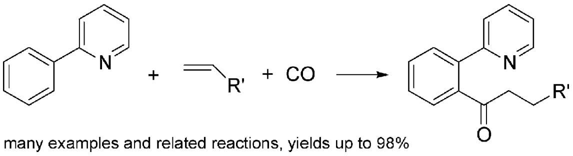
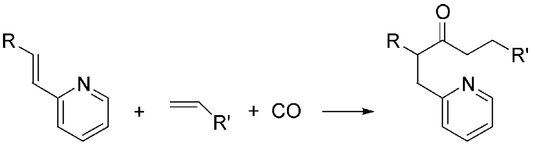
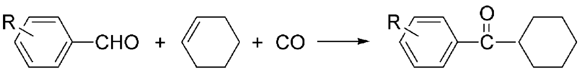
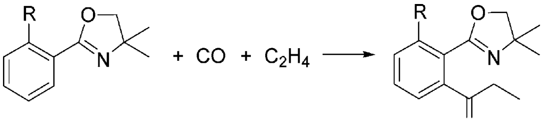
Catalyst	Reaction[a]	Ref.
$Ru_3(CO)_{12}$ + Ar-BIAN	 many examples, yields up to 99%	[69]
$Ru_3(CO)_{12}$ + Ar-BIAN	 many examples, selectivity up to 56%	[70]
$Ru_3(CO)_{12}$	 up to >99:1	[71]
$Ru_3(CO)_{12}$	 many examples and related reactions, yields up to 80%	[72]
$Ru_3(CO)_{12}$ (other clusters were tested, but all were less active)	 13:1	[73]
$Ru_3(CO)_{12}$	 many examples and related reactions, yields up to 98%	[74]
$Ru_3(CO)_{12}$ or $Rh_4(CO)_{12}$	 many examples and related reactions, yields up to 95%	[75]
$Ru_3(CO)_{12}$	 many examples, yields typically around 50%	[76]
$Ru_3(CO)_{12}$	 many examples, yields up to 98%	[77]

Table 1 (*Continued*)

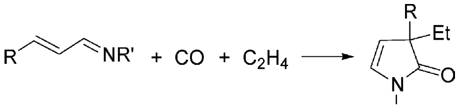
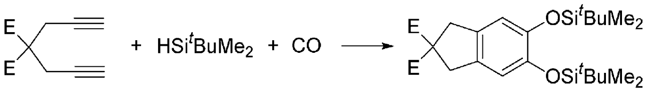
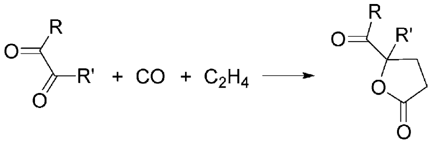
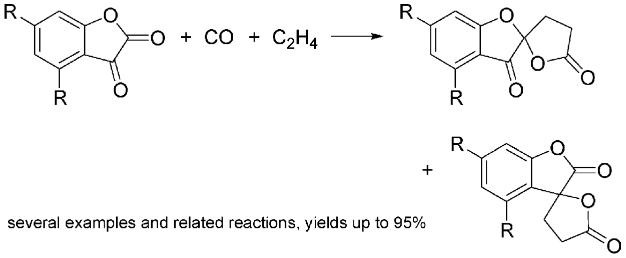
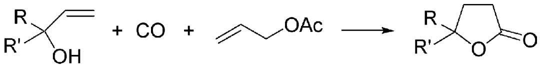
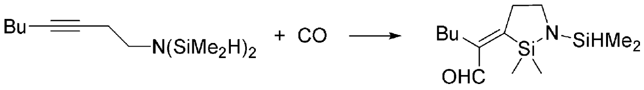
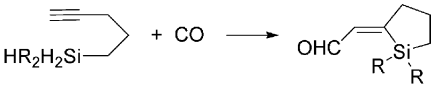
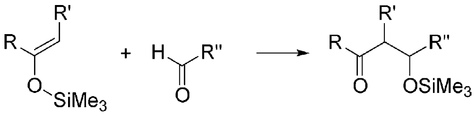
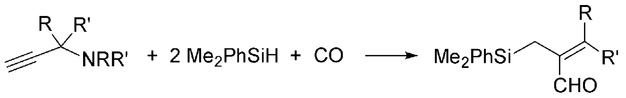
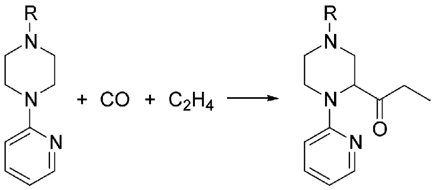
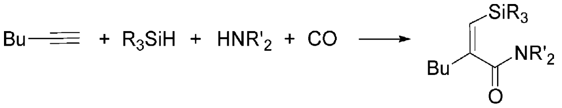
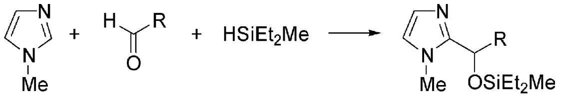
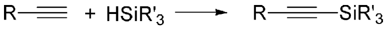
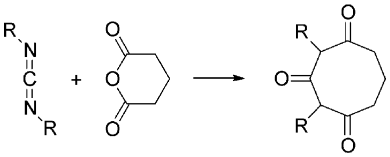
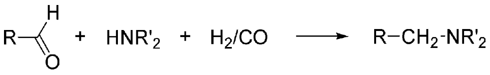
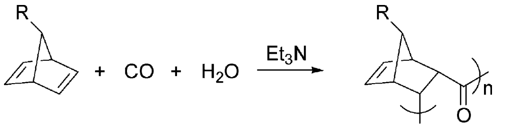
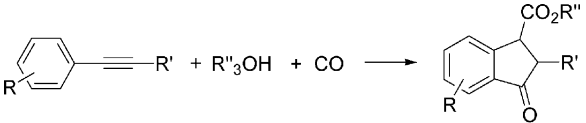
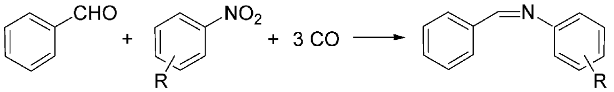
Catalyst	Reaction[a]	Ref.
$Ru_3(CO)_{12}$	 several examples, yields up to 95%	[78]
$Ru_3(CO)_{12} + PCy_3$	 many examples, yields up to 73%	[79]
$Ru_3(CO)_{12} + P(C_6H_4\text{-}p\text{-}CF_3)_3$ (other metal carbonyls and phosphines tested, but all were less active)	 several examples and related reactions, yields up to 98%	[80]
$Ru_3(CO)_{12} + P(C_6H_4\text{-}p\text{-}CF_3)_3$	 several examples and related reactions, yields up to 95%	[81]
$Ru_3(CO)_{12} + PPh_3$ + base	 several examples and related reactions, yields up to 99%	[82]
$Co_2Rh_2(CO)_{12}$	 several examples and related examples, yields up to 75%	[83]
$Rh_4(CO)_{12}$	 several examples and related examples, yields up to 83%	[84]
$Rh_4(CO)_{12}$	 several examples, yields up to 83%	[85]
$Rh_4(CO)_{12}$	 several examples and related examples, yields up to 94%	[86]
$Rh_4(CO)_{12}$	 many examples, yields up to 95%	[87]

Table 1 (*Continued*)

Catalyst	Reaction[a]	Ref.
$Rh_4(CO)_{12}$	 several examples and related examples, yields up to 90%	[88]
$Ir_4(CO)_{12}$	 several examples, yields up to 94%	[89]
$Ir_4(CO)_{12}$ + PPh_3 + base	 several examples, yields up to 96%	[90]
$[H_3Ru_4(C_6H_6)_4(OH)]^{2+}$	 several examples, yields up to 70%	[91]
$Rh_6(CO)_{16}$	 several examples, yields up to 100% by GLC	[92]
$Rh_6(CO)_{16}$	 several examples, yields up to 95%	[93]
$Rh_6(CO)_{16}$	 many examples, yields up to 93%	[94]
$Rh_6(CO)_{16}$	 a reinvestigation	[95]

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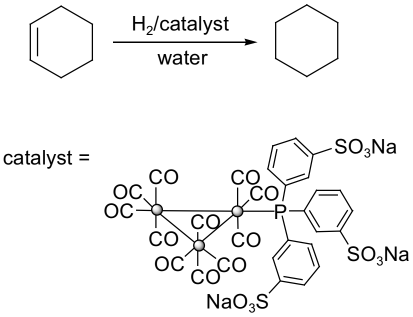
[a] In some of the reactions illustrated only the main product is shown.

While many examples of reactions utilising water as a hydrogen source are known, the vast majority are catalysed by clusters that are not naturally water soluble, but take place in the presence of CO and a base or phase transfer reagent [102]. It would seem that cluster anions often form, and that these are moderately soluble in water, but the cluster may also be a source of colloids or nanoparticles. However, some cluster-carbonyl compounds have been derivatised with hydrophilic phosphines in order to provide high water solubility. The first clusters prepared in such a way included $P(m\text{-}C_6H_4SO_3Na)_3$ derivatives of $M_3(CO)_{12}$ (M = Ru and Os) and $Ir_4(CO)_{12}$ [103]. The range of compounds was subsequently extended to include derivatives of $Ru_6C(CO)_{17}$ and $H_4Ru_4(CO)_{12}$ and some of the clusters were shown to act as catalyst precursors in the water–gas shift reaction [104] and hydrogenation reactions [105]. The water-catalyst solution employing $Ru_3(CO)_{11}\{P(m\text{-}C_6H_4SO_3Na)_3\}$ as the catalyst precursor was used five times for the hydrogenation of cyclohexene, 1-octene and styrene without any decrease in activity (see Scheme 7). In addition, the cluster $Ru_3(CO)_9\{PPh_2(m\text{-}C_6H_4SO_3Na)\}_3$ is a catalyst precursor for the hydrogenation of acrylic acid and the hydroformylation of propylene under water–gas shift conditions [106]. The $P(m\text{-}C_6H_4SO_3Na)_3$ derivatised clusters were also evaluated for activity in the ionic liquid [bmim][BF_4] (bmim = the 1-butyl-3-methylimidazolium cation), but their solubility was low and catalytic activity was very low. Similarly, the ruthenium cubane cluster $[Ru_4(\eta^6\text{-}C_6H_6)_4(OH)_4]^{4+}$ is an active pre-catalyst for the hydrogenation of benzene in aqueous solution, but in [bmim][BF_4] it is almost inactive, which is thought to be due to activation of the compound by reaction with water [107]. Other water soluble clusters



Scheme 7.

have been made by attaching the water soluble ligand pta (pta = 1,3,5-triaza-7-phosphaadamantane), but these have not been evaluated as catalysts, instead their ability to damage DNA was assessed [108].

While not a cluster-carbonyl compound, $[H_4Ru_4(\eta^6\text{-arene})_4]^{2+}$ and some related clusters, catalyse the hydrogenation of arenes under biphasic aqueous-organic [109] and ionic liquid-organic conditions [110]. It was found the purity of the ionic liquid was critical with chloride impurities often present impeding activity [111].

Ionic liquids provide a polar, non-nucleophilic environment which can increase catalyst lifetimes in certain biphasic processes [112]. Such an observation is important as biphasic catalysis has been criticised since homogeneous catalyst lifetime is often short and it is possibly not worth finding ways to recycle and reuse them [113]. Only very few clusters have been screened in ionic liquids, but since charged compounds are generally highly soluble and well retained in the ionic liquid during product separation [114], there is considerable potential for cluster catalysis using ionic liquids as immobilisation media. Clusters can also be prepared in ionic liquids due to their large temperature ranges, which can accelerate reactions by allowing temperatures usually only accessible to solid-state pyrolysis reactions to be achieved in solution [115]. Some nascent results show that considerable improvements in activity of clusters immobilised in ionic liquids compared to organic solvents for hydrogenation of simple alkene substrates [116]. The ionic liquid also appears to influence the selectivity of the reaction and the mechanism of cluster catalysis. In addition, a strategy for making liquid metal carbonyl anions has been reported and the same protocol might be applicable to cluster-carbonyls as well [117].

Metal carbonyl compounds are highly soluble in supercritical fluids [118], and although supercritical fluids are under intensive evaluation as solvents in which to conduct

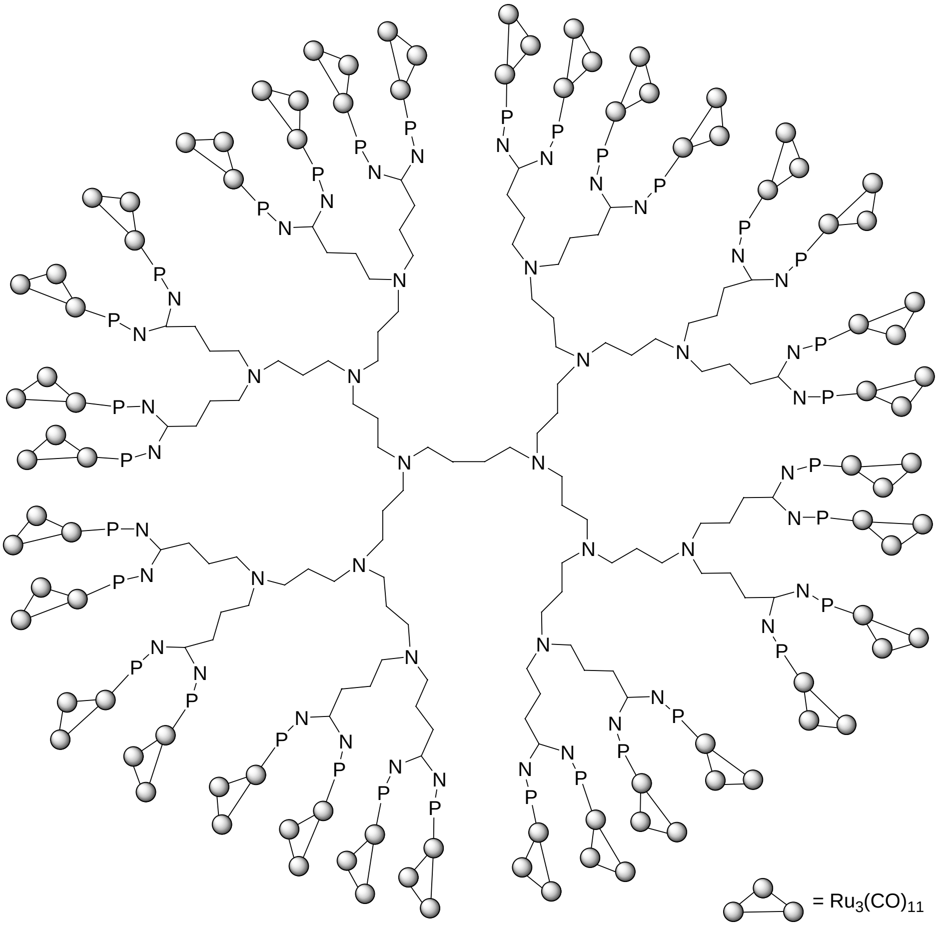


Fig. 3. An example of a cluster derivatised dendrimer currently undergoing catalytic evaluation.

catalysis, very little catalysis using clusters has been undertaken in them. $Fe_3(CO)_{12}$ has been shown to catalyse the isomerisation of 1-hexene to 2-hexene in supercritical CO_2 at 190 atm and 90 °C (mentioned in [119]). The same reaction takes place in the neat alkene, but a higher reaction temperature is required. The hydroformylation of ethylene using $Ru_3(CO)_{12}$ as the catalyst precursor has been conducted in supercritical CO_2 [120]. The reaction was conducted at pressures ranging from 224 to 408 atm, with turnover frequencies increasing rapidly with pressure. The same catalyst precursor was found to be only slightly active for hydrogenation reactions under similar conditions [121]. Supercritical water at 220 atm and 374 °C has also been used as a solvent for the water–gas shift reaction using $Rh_6(CO)_{16}$ as a catalyst precursor [122].

Clusters immobilised on solid supports is a considerably more developed field than that involving liquid supports, and only an outline, together with some significant recent developments will be described here. Various solid supports have been used to immobilise clusters including silica, alumina, clays and nanotubes and the resulting catalytic activity of the resulting materials have been extensively studied and reviewed [123]. Perhaps the most recent advance in this field concerns the use of heteronuclear clusters anchored to silica, then decomposed, to give very small (1–1.5 nm diameter) nanoparticles which often result in highly selective catalysts [124], although a similar approach has been used previously involving alumina supports [125]. The clusters, for example, $Ru_6C(CO)_{16}SnCl_2$, $[Ru_6C(CO)_{16}SnCl_3]^-$, $[Ru_6C(CO)_{16}Cu_2Cl]^{2-}$, $[Ru_{12}C_2(CO)_{32}Cu_4Cl_2]^{2-}$ and $[Ru_5PtC(CO)_{15}]^{2-}$ may be deposited onto MCM-41 (a nanoporous silica with a surface area typically of 500–900 $m^2\,g^{-1}$) without any change in the characteristic carbonyl stretching frequencies, implying that they remain intact. Following pyrolysis, all the carbonyls are driven off, leaving behind the bimetallic nanoparticles. It is worth pointing out that carbide centred ruthenium compounds and their heteronuclear derivatives are not known for their catalytic activity as molecular species [126]. The main application of these MCM-41 supported heteronuclear cluster derived nanoparticles is in hydrogenation reactions of alkenes, polyenes and arenes, ideally under solvent free conditions. Clusters have also been anchored inside nanoporous alumina membranes in a controlled fashion and then thermalised to give nanoparticles [127]. In addition, heterogeneous clusters entrapped in sol-gel matrices and bound to silica afford nanoparticles under hydrogenation conditions [128]. Subsequently, the nanoparticles were shown to catalyse C–C bond forming reactions. The homonuclear cluster $[Ru_6C(CO)_{16}]^{2-}$ has also been supported on TiO_2 which affords a supported particle catalyst that is highly active for the reduction of SO_2 with H_2 to give elemental sulphur [129]. Clusters have also been attached to more flexible supports such as polymers, which have been evaluated in catalysis [130], and dendrimers [131]. For example, dendrimers derivatised with phosphines on the periphery form stable compounds with clusters (see Fig. 3), but as yet, their catalytic applications have not been reported.

6. Giant cluster/colloid catalysis

Clusters are often viewed as the intermediate species between mononuclear complexes and colloids. However, colloids may be viewed as bridging the gap between clusters and metal surfaces. But when does a cluster become a colloid and vice versa. Certain compounds such as $Au_{55}(PPh_3)_{12}Cl_6$ remain at the cluster/colloid interface because its size is nearer to that of clusters, but at the same time the number of metal atoms in the structure can vary, which is a feature typical of colloids. At the time $Au_{55}(PPh_3)_{12}Cl_6$ was first reported, it contained many more metal atoms than the largest known cluster, but now many clusters with around 50 metal atoms are known such as $Pd_{54}(CO)_{40}(PEt_3)_{14}$ [12] and $Pd_{69}(CO)_{36}(PMe_3)_{18}$ [13] and a much larger cluster, viz. $Pd_{145}(CO)_x(PEt_3)_{30}$ [14], has also been reported (see Fig. 4). In addition, matrix assisted laser desorption ionisation mass spectrometry can be used to generate very large clusters which contain in excess of 100 metal atoms [132], but unfortunately while the small clusters formed mirror those that can be isolated in the laboratory [133], macroscopic syn-

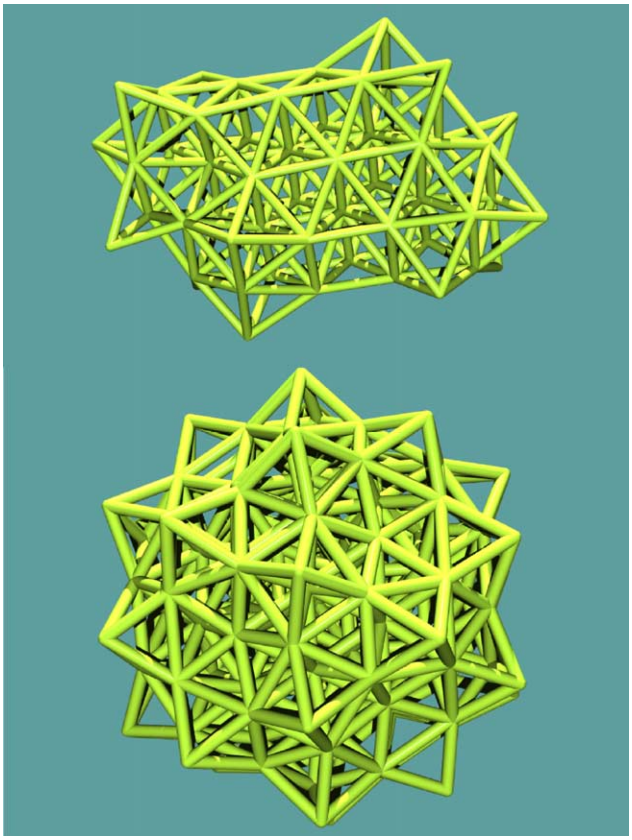


Fig. 4. The structure of the metal core in $Pd_{54}(CO)_{40}(PEt_3)_{14}$ (top) and $Pd_{145}(CO)_x(PEt_3)_{30}$ (bottom). The ligands have been omitted revealing the complexity of the metal cores.

thetic routes to the larger clusters have yet to be developed (could $Ru_{60}(CO)_{60}$ correspond to a C_{60} analogue—a ruckyball).

One goal in cluster chemistry is to prepare and characterise increasingly large clusters and while the catalytic properties of the largest have yet to be determined it is likely that the presence of internal metal atoms (bulk metal atoms) will lead to colloid-like properties. In contrast, one of the main goals in colloid/nanoparticle science is to reduce their size so that more atoms are exposed to the surface to increase reaction sites. In fact, many small so called soluble colloids are more active than true homogeneous counterparts which contrasts with the usual view that homogeneous catalysts are more active than heterogeneous catalysts [134]. Already, clusters and colloids have exchanged sides, and it is likely that in the future the two fields will become increasingly blurred and may eventually merge.

7. Concluding remarks

After nearly half a century of cluster chemistry the subject remains intensely studied, despite initial expectations having not been fully realised. There is no doubt that one of the chief reasons for this sustained activity is the ability of clusters to model heterogeneous catalysts and also to act as catalysts in their own right, and only recently has direct evidence for catalysis by intact clusters been provided. However, it would appear that many of the most efficient catalyst systems do not involve cluster catalysts, but mononuclear fragments generated from them in situ, or nanoclusters, deliberately prepared from molecular clusters. There also seems to be considerable potential for cluster catalysis in ionic liquids and supercritical fluids. Anionic clusters are highly soluble in ionic liquids and metal carbonyl compounds more generally have high solubilities in supercritical solvents. As such, there are considerable opportunities available as an extensive range of compounds can be screened in these solvents without the need to modify them in any way. Finally, a giant palladium cluster containing in excess of 500 metal centres, although not a low oxidation state cluster, catalyses the isomerisation and dimerisation of lower alkenes [135] and other reactions [136], and although this cluster could also be categorised as a colloid, it paves the way for catalytic studies on massive, but well defined and soluble, metal systems, which may lead to new activities and other possibilities.

Acknowledgements

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References

[1] (a) E.L. Muetterties, Bull. Soc. Chim. Belg. 84 (1975) 959;
(b) E.L. Muetterties, T.N. Rhodin, E. Band, C. Brucker, H. Pretzer, Chem. Rev. 79 (1979) 91.
[2] B.F.G. Johnson, J. Lewis, M. Gallup, M. Martinelli, Faraday Dis. 92 (1991) 241.
[3] (a) P. Braunstein, L.A. Oro, P.R. Raithby (Eds.), Metal Clusters in Chemistry, Wiley-VCH, New York, 1999;
(b) P.J. Dyson, J.S. McIndoe (Eds.), Transition Metal Carbonyl Cluster Chemistry, Gordon and Breach, Amsterdam, 2000.
[4] (a) D.M.P. Mingos, R.L. Johnston, Struct. Bonding 68 (1987) 29;
(b) D.M.P. Mingos, Pure Appl. Chem. 63 (1991) 807.
[5] R.D. Adams, F.A. Cotton (Eds.), Catalysis by Di- and Polynuclear Metal Cluster Complexes, Wiley-VCH, New York, 1998.
[6] B.F.G. Johnson (Ed.), Transition Metal Clusters, Wiley, Chichester, 1980.
[7] A.J. Amoroso, L.H. Gade, B.F.G. Johnson, J. Lewis, P.R. Raithby, W.T. Wong, Angew. Chem. Int. Ed. Engl. 30 (1991) 107.
[8] P.J. Dyson, B.F.G. Johnson, J.S. McIndoe, P.R.R. Langridge-Smith, Inorg. Chem. 39 (2000) 2430.
[9] G. Schmid, R. Pfeil, R. Boese, F. Bandermann, S. Meyer, G.H.M. Calis, W.A. Vandervelden, Chem. Ber.-Recl. 114 (1981) 3634.
[10] D.H. Rapoport, W. Vogel, H. Colfen, R. Schlogl, J. Phys. Chem. B 101 (1997) 4175.
[11] F.F. de Biani, C. Femoni, M.C. Iapalucci, G. Longoni, P. Zanello, A. Ceriotti, Inorg. Chem. 38 (1999) 3721.
[12] N.T. Tran, M. Kawano, D.R. Powell, L.F. Dahl, J. Am. Chem. Soc. 120 (1998) 10986.
[13] T. Tran, L.F. Dahl, Angew. Chem. Int. Ed. 42 (2003) 3533.
[14] N.T. Tran, D.R. Powell, L.F. Dahl, Angew. Chem. Int. Ed. 39 (2000) 4121.
[15] R.D. Adams, B. Captain, W. Fu, P.J. Pellechia, M.D. Smith, Angew. Chem. Int. Ed. 41 (2002) 1951.
[16] (a) H. Wadepohl, Angew. Chem. Int. Ed. 31 (1992) 247;
(b) B.F.G. Johnson, P.J. Dyson, Tansit. Metal Chem. 18 (1993) 539;
(c) D. Braga, P.J. Dyson, F. Grepioni, B.F.G. Johnson, Chem. Rev. 94 (1994) 1585.
[17] (a) M. Neumann, J.U. Mack, E. Bertel, F.P. Netzer, Surf. Sci. 155 (1985) 629;
(b) F.P. Netzer, G. Rosina, E. Bertel, Surf. Sci. 184 (1987) L397;
(c) F.P. Netzer, H.H. Graen, H. Kuhlenbeck, M. Neumann, Chem. Phys. Lett. 133 (1987) 49;
(d) M.A. Van Hove, R.F. Van Hove Lin, G.A. Somorjai, J. Am. Chem. Soc. 108 (1986) 2532;
(e) A. Barbieri, M.A. Van Hove, G.A. Somorjai, Surf. Sci. 306 (1994) 261.
[18] (a) M.P. Gomez-Sal, B.F.G. Johnson, J. Lewis, P.R. Raithby, A.H. Wright, J. Chem. Soc. Chem. Commun. (1985) 1682;
(b) B.F.G. Johnson, J. Lewis, M. Martinelli, A.H. Wright, D. Braga, F. Grepioni, J. Chem. Soc. Chem. Commun. (1990) 364.
[19] (a) P.J. Bailey, D. Braga, P.J. Dyson, F. Grepioni, B.F.G. Johnson, J. Lewis, P. Sabatino, J. Chem. Soc. Chem. Commun. (1992) 177;
(b) D. Braga, P. Sabatino, P.J. Dyson, A.J. Blake, B.F.G. Johnson, J. Chem. Soc., Dalton Trans. (1994) 393.
[20] (a) P.J. Dyson, B.F.G. Johnson, D. Reed, D. Braga, F. Grepioni, E. Parisini, J. Chem. Soc., Dalton Trans. (1993) 2817;
(b) P.J. Dyson, B.F.G. Johnson, C.M. Martin, A.J. Blake, D. Braga, F. Grepioni, Organometallics 13 (1994) 2113;
(c) A.J. Blake, P.J. Dyson, B.F.G. Johnson, S.L. Ingham, C.M. Martin, Organometallics 14 (1995) 862;

(d) A.J. Blake, P.J. Dyson, S.L. Ingham, B.F.G. Johnson, C.M. Martin, J. Chem. Soc., Dalton Trans. (1995) 1063;
(e) J.P.-K. Lau, Z.-Y. Lin, W.-T. Wong, Angew. Chem. Int. Ed. 42 (2003) 1935.
[21] H. Nagashima, T. Fukahori, K. Aoki, K. Itoh, J. Am. Chem. Soc. 115 (1993) 10430.
[22] (a) D. Braga, F. Grepioni, E. Parisini, P.J. Dyson, S.L. Ingham, B.F.G. Johnson, A.J. Blake, J. Chem. Soc. Chem. Commun. (1995) 537;
(b) A.J. Blake, P.J. Dyson, P.E. Gaede, B.F.G. Johnson, D. Braga, E. Parasini, J. Chem. Soc., Dalton Trans. (1995) 3431.
[23] E.L. Garfunkel, C. Minot, A. Gavezzotti, M. Simonetta, Surf. Sci. 176 (1986) 177.
[24] M. Elian, M.M.L. Chen, D.M.P. Mingos, R. Hoffmann, Inorg. Chem. 15 (1976) 1148.
[25] K. Lee, H. Song, J.T. Park, Acc. Chem. Res. 36 (2003) 78.
[26] S. Brait, S. Deabate, S.A.R. Knox, E. Sappa, J. Cluster Sci. 12 (2001) 139.
[27] (a) P.J. Dyson, B.F.G. Johnson, J. Lewis, D. Braga, P. Sabatino, J. Chem Soc. Chem. Commun. (1993) 301;
(b) A.J. Blake, P.J. Dyson, B.F.G. Johnson, C.M. Martin, J.G.M. Nairn, E. Parisini, J. Lewis, J. Chem. Soc., Dalton Trans. (1993) 981;
(c) P.J. Dyson, B.F.G. Johnson, D. Reed, D. Braga, P. Sabatino, Inorg. Chim. Acta 213 (1993) 191.
[28] B.F.G. Johnson, J.G.M. Nairn, D.B. Brown, J. Lewis, M. Gallop, D.G. Parker, Chem. Eur. J. 1 (1995) 252.
[29] J.A. Widegren, R.G. Finke, J. Mol. Catal. A: Chem. 191 (2003) 187.
[30] P.J. Dyson, Dalton Trans. (2003) 2964.
[31] P.J. Dyson, B.F.G. Johnson, D. Braga, Inorg. Chim. Acta 222 (1994) 299.
[32] J.A. Widegren, R.G. Finke, J. Mol. Catal. A: Chem. 198 (2003) 317.
[33] (a) R.M. Laine, J. Mol. Catal. 14 (1982) 137;
(b) E. Rosenberg, R.M. Laine, in: R.D. Adams, F.A. Cotton (Eds.), Catalysis by Di- and Polynuclear Metal Cluster Complexes, Wiley-VCH, New York, 1998.
[34] (a) R.D. Adams, T.S. Barnard, Organometallics 17 (1998) 2567;
(b) R.D. Adams, T.S. Barnard, Organometallics 17 (1998) 2885;
(c) R.D. Adams, J. Organomet. Chem. 600 (2000) 1.
[35] P. Nombel, N. Lugan, B. Donnadieu, G. Lavigne, Organometallics 18 (1999) 187.
[36] J.R. Norton, in: Tsutsui (Ed.), Fundamental Research in Homogeneous Catalysis, Plenum Press, New York, 1977.
[37] J. Collin, C. Jossart, G. Balavione, Organometallics 5 (1986) 203.
[38] P. Homanen, R. Persson, M. Haukka, T.A. Pakkanen, E. Nordlander, Organometallics 19 (2000) 5568.
[39] (a) S. Aime, R. Gobetto, D. Canet, J. Am. Chem. Soc. 120 (1998) 6770;
(b) S. Aime, W. Dastru, R. Gobetto, A. Russo, A. Viale, D. Canet, J. Phys. Chem. A 103 (1999) 9702;
(c) B. Bergman, E. Rosenberg, R. Gobetto, S. Aime, L. Milone, F. Reineri, Organometallics 21 (2002) 1508.
[40] R. Gobetto, L. Milone, F. Reineri, L. Salassa, A. Viale, E. Rosenberg, Organometallics 21 (2002) 1919.
[41] D. Blazina, S.B. Duckett, P.J. Dyson, B.F.G. Johnson, J.A.B. Lohman, C.J. Sleigh, J. Am. Chem. Soc. 123 (2001) 9760.
[42] (a) G. Gervasio, R. Giordano, D. Marabello, E. Sappa, J. Organomet. Chem. 588 (1999) 83;
(b) B. Fontal, M. Reyes, T. Suárez, F. Bellandi, J.C. Díaz, J. Mol. Catal. A: Chem. 149 (1999) 75.
[43] (a) D. Blazina, S.B. Duckett, P.J. Dyson, J.A.B. Lohman, Chem. Eur. J. 9 (2003) 1045;
(b) D. Blazina, S.B. Duckett, P.J. Dyson, J.A.B. Lohman, Angew. Chem. Int. Ed. 40 (2001) 3874.
[44] D. Blazina, Ph.D. thesis, University of York, 2003.
[45] F. Joó, H. Alper, Can. J. Chem. 63 (1985) 1157.
[46] G. Süss Fink, S. Haak, V. Ferrand, H. Stoeckli-Evans, J. Mol. Catal. A: Chem. 143 (1999) 163.
[47] D.C.D. Butler, D.J. Cole-Hamilton, Inorg. Chem. Commun. 2 (1999) 305.
[48] T. Sugihara, A. Wakabayashi, Y. Nagai, H. Takao, H. Imagawa, M. Nishizawa, Chem. Commun. (2002) 576.
[49] R.M. Laine, D.W. Thomas, L.W. Cary, J. Am. Chem. Soc. 104 (1982) 1763.
[50] H. Zhang, C.-B. Yang, Y.-Y. Li, Z.-R. Donga, J.-X. Gao, H. Nakamura, K. Murata, T. Ikariya, Chem. Commun. (2003) 142.
[51] T. Kondo, T. Okada, T.-a. Mitsudo, Organometallics 18 (1999) 4123.
[52] Y. Tsuji, T. Mukai, T. Kondo, Y. Watanabe, J. Organomet. Chem. 369 (1989) C51.
[53] (a) Y. Seki, K. Takeshita, K. Kawamoto, S. Murai, N. Sonoda, J. Org. Chem. 51 (1986) 3890;
(b) N. Furukawa, N. Kourogi, Y. Seki, F. Kakiuchi, S. Murai, Organometallics 18 (1999) 3767.
[54] K. Matsubara, T. Iura, T. Maki, H. Nagashima, J. Org. Chem. 67 (2002) 4985.
[55] N. Menashe, Y. Shvo, J. Org. Chem. 58 (1993) 7434.
[56] T. Kondo, A. Tanaka, S. Kotachi, Y. Watanabe, J. Chem. Soc. Chem. Commun. (1995) 413.
[57] C. Crottoi, S. Cenini, B. Rindone, S. Tollaris, F. Demartin, J. Chem. Soc. Chem. Commun. (1986) 784.
[58] E. Yoneda, S.-W. Zhang, K. Onitsuka, S. Takahashi, Tetrahedron Lett. 42 (2001) 5459.
[59] E. Yoneda, T. Kaneko, S.-W. Zhang, K. Onitsuka, S. Takahashi, Org. Lett. 2 (2000) 441.
[60] S-K. Kang, K.-J. Kim, Y.-T. Homg, Angew. Chem. Int. Ed. 41 (2002) 1584.
[61] T. Kondo, N. Suzuki, T. Okada, T.-a. Mitsudo, J. Am. Chem. Soc. 119 (1997) 6187.
[62] A. Kamitani, N. Chatani, T. Morimoto, S. Murai, J. Org. Chem. 65 (2000) 9230.
[63] T. Fukuyama, N. Chatani, F. Kakiuchi, S. Murai, J. Org. Chem. 62 (1997) 5647.
[64] T. Morimoto, N. Chatani, S. Murai, J. Am. Chem. Soc. 121 (1999) 1758.
[65] M. Akazome, T. Kondo, Y. Watanabe, J. Org. Chem. 58 (1993) 310.
[66] F. Kakiuchi, M. Yamauchi, N. Chatani, S. Murai, Chem. Lett. (1996) 111.
[67] Y. Sasaki, P.H. Dixneuf, J. Org. Chem. 52 (1987) 4389.
[68] S. Cenini, C. Crotti, M. Pizzotti, F. Porta, J. Org. Chem. 53 (1988) 1243.
[69] F. Ragaini, S. Cenini, S. Tollari, G. Tummolillo, R. Beltrami, Organometallics 18 (1999) 928.
[70] F. Ragaini, S. Cenini, E. Borsani, M. Dompé, E. Gallo, M. Moret, Organometallics 20 (2001) 3390.
[71] N. Chatani, T. Fukuyama, F. Kakiuchi, S. Murai, J. Org. Chem. 52 (1987) 2714.
[72] T. Fukuyama, N. Chatani, J. Tatsumi, F. Kakiuchi, S. Murai, J. Am. Chem. Soc. 120 (1998) 11522.
[73] E.J. Moore, W.R. Pretzer, T.J. O’Connell, J. Harris, L. LaBounty, L. Chou, S.S. Grimmer, J. Am. Chem. Soc. 114 (1992) 5888.
[74] N. Chatani, Y. Ie, F. Kakiuchi, S. Murai, J. Org. Chem. 62 (1997) 2604.
[75] N. Chatani, Y. Ishii, Y. Ie, F. Kakiuchi, S. Murai, J. Org. Chem. 63 (1998) 5129.
[76] T. Kondo, M. Akazome, Y. Tsuji, Y. Wantanabe, J. Org. Chem. 55 (1990) 1286.
[77] Y. Ie, N. Chatani, T. Ogo, D.R. Marshall, T. Fukuyama, F. Kakiuchi, S. Murai, J. Org. Chem. 65 (2000) 1475.
[78] D. Berger, W. Imhof, Chem. Commun. (1999) 1457.
[79] N. Chatani, Y. Fukumoto, T. Ida, S. Murai, J. Am. Chem. Soc. 115 (1993) 11614.

[80] N. Chatani, M. Tobisu, T. Asaumi, Y. Fukumoto, S. Murai, J. Am. Chem. Soc. 121 (1999) 7160.
[81] N. Chatani, K. Amako, M. Tobisu, T. Asaumi, Y. Fukumoto, S. Murai, J. Org. Chem. 68 (2003) 1591.
[82] T. Kondo, F. Tsunawaki, R. Sato, Y. Ura, K. Wada, T.-a. Mitsudo, Chem. Lett. 32 (2003) 24.
[83] I. Ojima, E.S. Vidal, Organometallics 18 (1999) 5103.
[84] F. Monteil, I. Matsuda, H. Alper, J. Am. Chem. Soc. 117 (1995) 4419.
[85] S. Sato, I. Matsuda, Y. Izumi, Tetrahedron Lett. 27 (1986) 5517.
[86] I. Matsuda, J. Sakakibara, H. Inoue, H. Nagashima, Tetrahedron Lett. 33 (1992) 5799.
[87] Y. Ishii, N. Chatani, F. Kakiuchi, S. Murai, Organometallics 16 (1997) 3615.
[88] I. Matsuda, K. Takeuchi, K. Itoh, Tetrahedron Lett. 40 (1999) 2553.
[89] Y. Fukumoto, K. Sawada, M. Hagihara, N. Chatani, S. Murai, Angew. Chem. Int. Ed. 41 (2002) 2779.
[90] R. Shimizu, T. Fukuyama, Tetrahedron Lett. 41 (2000) 907.
[91] F. Chérioux, G. Süss-Fink, Tetrahedron Lett. 43 (2002) 6653.
[92] L. Markó, J. Bakos, J. Organomet. Chem. 81 (1974) 411.
[93] S.-W. Zhang, S. Takahashi, Chem. Commun. (2000) 315.
[94] E. Yoneda, T. Kaneko, S.-W. Zhang, K. Onitsuka, S. Takahashi, Tetrahedron Lett. 40 (1999) 7811.
[95] F. Ragaini, S. Cenini, J. Mol. Catal. A: Chem. 144 (1999) 405.
[96] F. Ragaini, A. Ghitti, S. Cenini, Organometallics 18 (1999) 4925.
[97] T. Naota, H. Takaya, S.-I. Murahashi, Chem. Rev. 98 (1998) 2599.
[98] B. Cornils, W.A. Hermann (Eds.), Aqueous-Phase Organometallic Catalysis, Concepts and Applications, Wiley-VCH, Weinheim, 1998.
[99] G. Süss-Fink, G. Meister, Adv. Organomet. Chem. 35 (1993) 41.
[100] K. Kaneda, H. Kuwahara, T. Imanaka, J. Mol. Catal. 88 (1994) L267.
[101] H. Alper, J.-F. Petrignani, J. Chem. Soc. Chem. Commun. (1983) 1154.
[102] K. Nomura, J. Mol. Catal. A: Chem. 130 (1998) 1.
[103] J. Orlewski, C.C. Santini, J.M. Basset, Inorg. Chem. 25 (1986) 4320.
[104] D.J.F. Bryce, P.J. Dyson, B.K. Nicholson, D.G. Parker, Polyhedron 17 (1998) 2899.
[105] P.J. Dyson, D.J. Ellis, D.G. Parker, T. Welton, J. Mol. Catal. A: Chem. 150 (1999) 71.
[106] J.-x. Gao, P.-p. Xu, X.-d. Yi, H.-l. Wan, K.-r. Tsai, J. Mol. Catal. A: Chem. 147 (1999) 99.
[107] P.J. Dyson, K. Russell, T. Welton, Inorg. Chem. Commun. 4 (2001) 571.
[108] C.S. Allardyce, P.J. Dyson, J. Cluster Sci. 12 (2001) 563.
[109] (a) G. Süss Fink, L. Plasseraud, A. Maisse-François, H. Stoeckli-Evans, H. Berke, T. Fox, R. Gautier, J.Y. Saillard, J. Organomet. Chem. 609 (2000) 196;
(b) L. Plasseraud, G. Süss Fink, J. Organomet. Chem. 539 (1997) 163.
[110] P.J. Dyson, D.J. Ellis, D.G. Parker, T. Welton, Chem. Commun. (1999) 25.
[111] P.J. Dyson, D.J. Ellis, W. Henderson, G. Laurenczy, Adv. Synth. Catal. 345 (2003) 216.
[112] J. Dupont, R.F. de Souza, P.A.Z. Suarez, Chem. Rev. 102 (2002) 3667.
[113] P.M. Maitlis, H.C. Long, R. Quyoum, M.L. Turner, Z.Q. Wang, Chem. Commun. (1996) 1.
[114] P.J. Dyson, Appl. Organometal. Chem. 16 (2002) 495.
[115] P.J. Dyson, Trans. Met. Chem. 27 (2002) 353.
[116] D. Zhao, G. Laurenczy, J.S. McIndoe, P.J. Dyson, J. Mol. Catal. A: Chem. 214 (2004) 19.
[117] (a) R.J.C. Brown, P.J. Dyson, D.J. Ellis, T. Welton, Chem. Commun. (2001) 1862;
(b) P.J. Dyson, J.S. McIndoe, D. Zhao, Chem. Commun. (2003) 508.
[118] J.A. Darr, M. Poliakoff, Chem. Rev. 99 (1999) 495.
[119] P.G. Jessop, T. Ikariya, R. Noyori, Chem. Rev. 99 (1999) 475.
[120] C. Erkey, E. Lozano Diz, G. Süss Fink, X. Dong, Catal. Commun. 3 (2002) 213.
[121] P.G. Jessop, Y. Hsiao, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 118 (1996) 344.
[122] F. Ungváry, Coord. Chem. Rev. 213 (2001) 1.
[123] For a recent review see, J. Guzman, B.C. Gates, Dalton Trans. (2003) 3303.
[124] J.M. Thomas, B.F.G. Johnson, R. Raja, G. Sankar, P.A. Midgley, Acc. Chem. Res. 36 (2003) 20.
[125] (a) P. Braunstein, R. Bender, J. Kervennal, Organometallics 1 (1982) 1236;
(b) P. Braunstein, J. Kervennal, J.-L. Richert, Angew. Chem. Int. Ed. Engl. 24 (1985) 768.
[126] P.J. Dyson, Adv. Organomet. Chem. 43 (1999) 43.
[127] P. Braunstein, H.-P. Kormann, W. Meyer-Zaika, R. Pugin, G. Schmid, Chem. Eur. J. 6 (2000) 4637.
[128] J. Blum, F. Gelman, R. Anu-Reziq, I. Miloslavski, H. Schumann, D. Avnir, Polyhedron 19 (2000) 509.
[129] A. Ishiguro, T. Nakajima, T. Iwata, M. Fujita, T. Minato, F. Kiyotaki, Y. Izumi, K.-i. Aika, M. Uchida, K. Kimoto, Y. Matsui, Y. Wakatsuki, Chem. Eur. J. 8 (2002) 3260.
[130] (a) K. Kaneda, T. Takemoto, K. Kitaoka, T. Imanaka, Organometallics 10 (1991) 846;
(b) K. Kaneda, K. Morioka, T. Imanaka, Macromolecules 28 (1995) 876;
(c) T. Mizugaki, K. Ebitani, K. Kaneda, App. Surf. Sci. 121–122 (1997) 360.
[131] (a) E. Alonso, D. Astruc, J. Am. Chem. Soc. 122 (2000) 3222;
(b) N. Feeder, J. Geng, P.G. Goh, B.F.G. Johnson, C.M. Martin, D.S. Shephard, W. Zhou, Angew. Chem. Int. Ed. Engl. 39 (2000) 1661.
[132] (a) M.J. Dale, P.J. Dyson, B.F.G. Johnson, C.M. Martin, P.R.R. Langridge-Smith, R. Zenobi, J. Chem. Soc. Chem. Commun. (1995) 1689;
(b) M.J. Dale, P.J. Dyson, B.F.G. Johnson, P.R.R. Langridge-Smith, H.T. Yates, J. Chem. Soc., Dalton Trans. (1996) 771.
[133] G. Critchley, P.J. Dyson, B.F.G. Johnson, J.S. McIndoe, R.K. O'Reilly, P.R.R. Langridge-Smith, Organometallics 18 (1999) 4090.
[134] A. Roucoux, J. Schulz, H. Patin, Chem. Rev. 102 (2002) 3757.
[135] M.N. Vargaftik, V.P. Zagorodnikov, I.P. Stolarov, I.I. Moiseev, D.I. Kochubey, V.A. Likholobov, A.L. Chuvilin, K.I. Zamaraev, J. Mol. Catal. 53 (1989) 315.
[136] G. Kovtun, T. Kameneva, S. Hladyi, M. Starchevsky, Y. Pazdersky, I. Stolarov, M. Vargaftik, I. Moiseev, Adv. Synth. Catal. 344 (2002) 957.