

8

Homogeneous Hydrogenation by Defined Metal Clusters

Roberto A. Sánchez-Delgado

8.1

Introduction

The catalytic potential of well-defined transition-metal clusters in homogeneous reactions has attracted a great deal of attention over the years, as they represent a natural bridge between mononuclear complexes, metal nanoparticles, and metal-oxide, -sulfide and related surfaces used in heterogeneous catalysis. The molecular nature of metal clusters, together with their solubility properties, provides the advantages of classical mononuclear homogeneous catalysts (high activity, high selectivity, moderate operating conditions, possibility of catalyst design and modification), while the polynuclear framework can offer the possibility of multi-metallic cooperative effects often identified as a key element in the desirable properties of solid heterogeneous catalysts. Therefore, metal clusters can be expected, in principle, to combine the positive aspects of homogeneous and heterogeneous catalytic reactions and, perhaps more importantly, they may react through unique pathways associated with the cluster structures and thereby catalyze reactions not accessible by mononuclear or heterogeneous catalysts. Nevertheless, despite the impressive amount of work that has been devoted to develop these concepts over several decades, the great expectations first advanced during the mid-1970s have not yet been fully accomplished [1–6].

From a different perspective, well-defined metal clusters have served as useful models for discerning the complex mechanisms of heterogeneous catalytic systems. The structural trends for metal clusters are now well understood, and their reactions in solution can be studied in detail by relatively simple chemical and spectroscopic methods, thereby producing important information at the molecular level – something that is very difficult to achieve on solid catalysts. The knowledge thus gained from studying metal cluster chemistry can be extrapolated, with adequate caution, to heterogeneous reactions [1–6].

Another trend that has received considerable recent attention is the decomposition of metal clusters under controlled conditions on solid supports or on liquid suspensions, which generates small metallic particles of specific size, struc-

ture or composition, displaying interesting catalytic features [7]. Although this is perhaps the area in which cluster chemistry has had the highest impact, such methods lead unambiguously to *heterogeneous* systems, and therefore it falls beyond the scope of this book.

Homogeneous hydrogenation has been one of the most frequently studied classes of reactions in an effort to demonstrate the principles of cluster catalysis and its links to heterogeneous catalysis. A good number of well-defined metal clusters have been claimed to promote hydrogen addition to C=C, C≡C, C=O bonds and aromatic rings, and a number of detailed mechanistic studies have been conducted. Many of these catalysts have later been shown to be mononuclear or heterogeneous in nature, but some others have proved to induce truly homogeneous cluster-catalyzed reactions. For the purpose of the discussion that follows, the classical definition of a cluster as a compound containing at least three metal atoms [8] will be adopted. Also, the concept of *cluster catalysis* is associated here to reaction mechanisms involving only polynuclear intermediates, regardless of whether the important interactions take place at only one or at several metal atoms.

8.1.1

Is a Cluster the Real Catalyst? Fragmentation and Aggregation Phenomena

One of the key points in discussing cluster catalysis is to determine whether a cluster is actually catalyzing the hydrogenation reaction, or if instead a mononuclear entity derived from cluster fragmentation, or metallic nanoparticles resulting from decomposition and aggregation are responsible for the catalytic transformation. An ideal model reaction would involve bonding of the substrate to more than one metal atom, so that if the cluster becomes degraded in the process, the catalytic activity would be lost. Nevertheless, sensible hydrogenation cycles have been proposed in which the cluster framework is maintained but the substrate does not need to bind to more than one metal atom in order to be transformed. In such cases it is difficult to ascertain which is the true catalytically active species. Several methods have been used to address the two questions that need to be answered:

- Is the catalyst truly homogeneous?
- If so, is the catalyst really a cluster?

Finke and coworkers have extensively addressed the question of homogeneous versus heterogeneous catalysis, and have provided a rather complex (but extremely reliable) set of experiments that allow the distinction of a molecular catalyst in solution from a suspended nanostructured metallic material [9]. The generation of metallic particles from metal complexes under a highly reducing hydrogen atmosphere is now recognized as a frequent phenomenon, particularly in arene hydrogenation studies [9, 10].

Once the homogeneity of a reaction has been established, it is never easy to determine the precise nuclearity of the active species, and a series of indicators or qualitative tests has been proposed [11]. Many publications provide as evi-

dence for cluster catalysis simple statements such as "... the cluster was quantitatively recovered at the end of the reaction" or "... the cluster was the only species observed by IR or NMR spectroscopy". This type of assumption can be very misleading; it suffices to have 1% or less of the cluster transform into highly active mononuclear fragments or metallic particles in order to develop a high hydrogenation activity. Such small amounts of very reactive species easily go unnoticed in *in-situ* spectroscopic studies, and would certainly not be accounted for in a "quantitative" recovery of the cluster at the end of the reaction.

In order to establish the participation of a cluster, the best approach is to use a combination of experiments:

- Kinetic measurements, particularly the study of the rate-dependence on *cluster* concentration can be very informative; cluster-catalyzed reactions often display a first-order rate dependence on *cluster* concentration, whereas fractional or complex orders of reaction are associated with fragmentation processes.
- Reactions that are much faster than the analogous one catalyzed by a mononuclear complex, or that lead to different products or selectivities, are more likely to involve cluster intermediates.
- Heterobimetallic complexes that induce reactions at significantly faster rates than (or notably different product selectivities from) monometallic derivatives are probably genuine cluster catalysts.
- Edge- and face-capping chelating ligands have been proposed as a method to guarantee the stability of the cluster framework.
- Another interesting idea that has been explored without much success so far is the use of clusters with a chiral metal framework as catalysts for asymmetric hydrogenation, since only the intact cluster would induce enantioselectivity.
- NMR studies involving *para*-hydrogen has recently been introduced as a powerful tool to obtain direct evidence for cluster catalysis (*vide infra*).

This chapter reviews the literature involving well-defined molecular metal clusters as hydrogenation catalysts or catalyst precursors, with particular emphasis being placed on those systems that are likely to involve only or predominantly cluster intermediates throughout the hydrogenation cycle. The mechanisms in cases where cluster catalysis is strongly supported by experimental evidence are discussed in more detail.

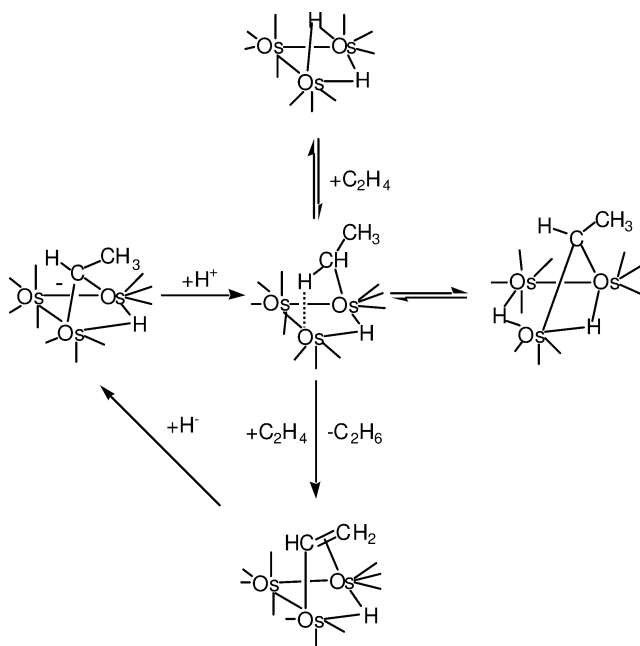
8.2

Hydrogenation of C=C Bonds

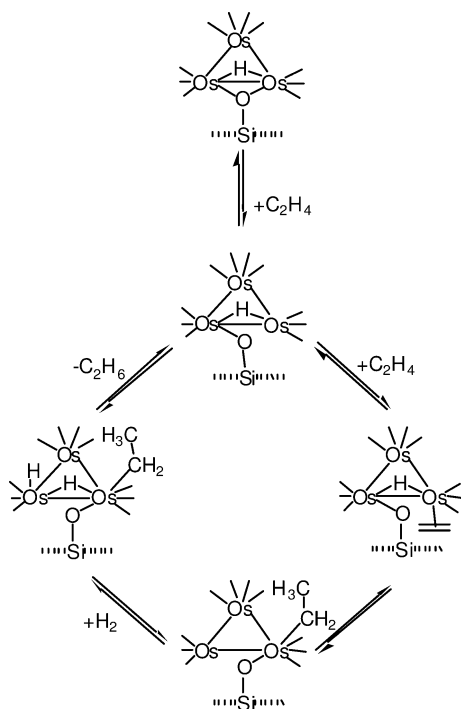
Early investigations by Shapley [12], Basset [13], and Gladfelter [14] provided the first convincing examples of C=C bond hydrogenation cycles involving metal clusters; these are shown in Schemes 8.1–8.3. Shapley's mechanisms for $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ was based on experiments performed under noncatalytic conditions, involving the isolation and/or NMR observation of all the species implicated in the cycle depicted in Scheme 8.1, as well as the pathways for their interconversion.

Basset's proposal for the silica-supported cluster $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi}\equiv)]$ was made on the basis of surface IR spectroscopy studies, kinetic and gas uptake measurements, and reactions of the soluble analogue $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-OSi-Ph})]$; the supported catalyst hydrogenated ethylene at 90°C and atmospheric pressure in a flow reactor at a TOF of 144h^{-1} for extended periods of time, achieving up to 24000 turnovers overall. Gladfelter also used kinetic measurements and IR spectroscopy to deduce the mechanism of alkene hydrogenation by anionic clusters containing isocyanate ligands $[\text{Ru}_3(\mu\text{-NCO})(\text{CO})_{10}]^-$; this catalyst reduced 3,3-dimethylbutene at rates of about 300 to 360 turnovers h^{-1} under ambient conditions. The same group also characterized intermediates and individual reactions of the more stable, but catalytically less active, osmium analogue $[\text{Os}_3(\mu\text{-NCO})(\text{CO})_{10}]^-$ (eight turnovers after 24 h at 78°C and 3.3 bar H_2 for 3,3-dimethylbutene hydrogenation). Although these are important pioneering cases from a fundamental point of view, they are of no practical use because catalytic activities were low and the scope of the reactions was limited.

Sánchez-Delgado et al. reported a comparative study of the hydrogenation of 1-hexene by use of $[\text{Ru}_3(\text{CO})_{12}]$ in solution and supported on silica; IR evidence pointed to cluster catalysis in solution [turnover frequency (TOF) ca. 200h^{-1} at 90°C and 40 bar H_2] and to the formation of mononuclear species on the silica surface (TOF ca. 600h^{-1} at 90°C and 40 bar H_2) [15]. Another early proposal for a cluster-catalyzed reaction was provided by Doi et al. for $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ in the

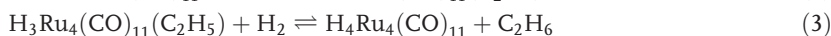
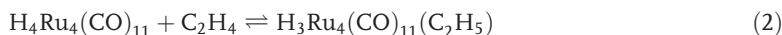
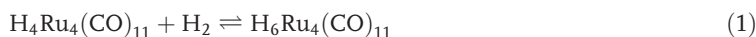


Scheme 8.1 Mechanism for the hydrogenation of alkenes catalyzed by $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ (CO ligands omitted for clarity).



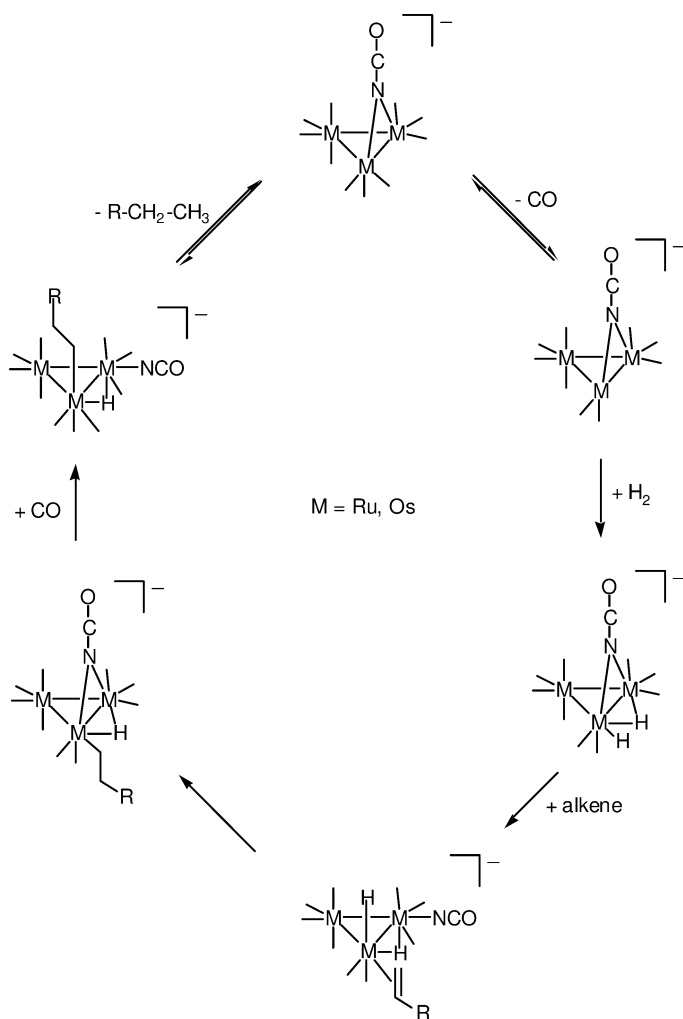
Scheme 8.2 Mechanism for the hydrogenation of ethylene catalyzed by silica-supported osmium clusters (CO ligands omitted for clarity).

hydrogenation of ethylene (TOF 40 h^{-1} at 72°C , 0.13 bar H_2 , and $0.26 \text{ atm ethylene}$). Kinetic measurements were in agreement with a mechanism involving Eqs. (1)–(3); in particular, a first-order dependence of the reaction rate on cluster concentration was taken as evidence of cluster catalysis, although the hydrogenation cycle involved a single Ru atom [16].



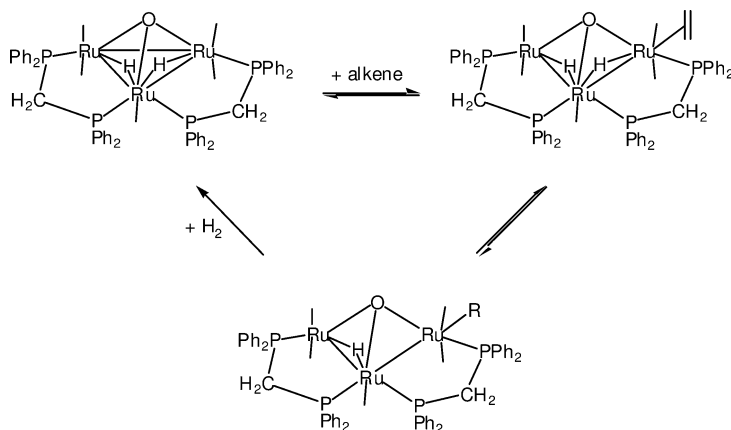
Related studies by Sánchez-Delgado and coworkers on the kinetics of the hydrogenation of styrene (140°C , 1.05 bar H_2) catalyzed by the tetranuclear Os clusters $[\text{H}_4\text{Os}_4(\text{CO})_{12}]$ (TOF 87 h^{-1}), $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$ (TOF 52 h^{-1}), $[\text{H}_3\text{Os}_4(\text{CO})_{12}\text{I}]$ (TOF 583 h^{-1}), and $[\text{H}_2\text{Os}_4(\text{CO})_{12}\text{I}]^-$ (TOF 63 h^{-1}), pointed to cluster fragmentation as being responsible for the catalytic activity of these systems, which conclusion was based on a complex rate-dependence on cluster concentration and the similarity of the hydrogenation rate when a mononuclear Os complex was employed [17].

Phosphine-substituted complexes have shown promise for cluster catalysis, especially in the case of chelating ligands, because of the added stability that might help avoid cluster fragmentation. Bergounhou et al. reported a detailed study of the hy-



Scheme 8.3 Mechanism for the hydrogenation of alkenes catalyzed by anion-promoted osmium clusters (CO ligands omitted for clarity).

drogenation of 1-hexene by $[\text{Ru}_3(\mu\text{-H})_2(\mu^3\text{-O})(\text{CO})_5(\text{dppm})_2]$ (TOF ca. $25\,200\text{ h}^{-1}$), and provided kinetic and spectroscopic evidence for the cycle depicted in Scheme 8.4, in which a Ru–Ru bond is broken but the cluster integrity is maintained by the oxo and diphosphine ligands [18]. Further catalytic studies with $[\text{Ru}_3(\text{CO})_{12}]$ substituted with chelating diphosphines were provided by Fontal et al. [19], and with PPh_3 by Dallmann and Buffon [20]. The suggestion was that the reactions proceed through cluster intermediates, although C=C bond hydrogenation was accompanied by extensive isomerization and no details of reaction mechanisms were provided. Clusters derived from $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ by substitution with *chiral* diphosphines



Scheme 8.4 Mechanism for the hydrogenation of alkenes catalyzed by ruthenium clusters stabilized by edge-bridging diphosphine ligands (CO ligands omitted for clarity).

sphines exhibited reasonable activities (TOF up to $60\,000\text{ h}^{-1}$) and moderate enantioselectivities (6 to 46% ee) in the hydrogenation of α , β -unsaturated carboxylic acids. Although the clusters were generally “recovered intact” at the end of the reactions, the participation of mononuclear species cannot be ruled out [21, 22].

Moura et al. recently reported the first example of the use of Ir clusters in homogeneous diene hydrogenation [23]. $[\text{Ir}_4(\text{CO})_{11}(\text{PPh}_2\text{H})]$, $[\text{Ir}_4(\text{CO})_8(\mu^3\text{-}\eta^2\text{-HCCPh})(\mu\text{-PPh}_2)_2]$, $[\text{Ir}_4(\text{CO})_9(\mu^3\text{-}\eta^3\text{-Ph}_2\text{PC}(\text{H})\text{CPh})(\mu\text{-PPh}_2)]$, and $[\text{Ir}_4(\text{CO})_{12}]$ selectively reduce 1,5-cyclooctadiene to cyclooctene with high activities [average turnover number (TON) 2816], in contrast with mononuclear or metallic Ir catalysts, which quickly yielded the fully reduced product cyclooctane; this is strongly indicative of a cluster-catalyzed reaction. All the complexes lose the phosphine ligands during the course of the reactions to produce a common active species likely related to $[\text{Ir}_4(\text{CO})_5(\text{C}_8\text{H}_{12})_2(\text{C}_8\text{H}_{10})]$; an “anchor-type” interaction between the two C=C bonds of the diene to one Ir atom allows the activation and hydrogenation of only one of those bonds by the cluster.

Much emphasis has been placed in recent times on easily recoverable liquid biphasic catalysts, including metal clusters in nonconventional solvents. For instance, aqueous solutions of the complexes $[\text{Ru}_3(\text{CO})_{12-x}(\text{TPPTS})_x]$ ($x=1, 2, 3$; TPPTS=triphenylphosphine-trisulfonate, $\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3$) catalyze the hydrogenation of simple alkenes (1-octene, cyclohexene, styrene) at 60°C and 60 bar H_2 at TOF up to 500 h^{-1} [24], while $[\text{Ru}_3(\text{CO})_9(\text{TPPMS})_3]$ (TPPMS=triphenylphosphine-monosulfonate, $\text{PPh}_2(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})$) is an efficient catalyst precursor for the aqueous hydrogenation of the C=C bond of acrylic acid (TOF 780 h^{-1} at 40°C and 3 bar H_2) and other activated alkenes [25]. The same catalysts proved to be poorly active in room temperature ionic liquids such as $[\text{bmim}][\text{BF}_4]$ (bmim=1-butyl-3-methylimidazolium). No details about the active species involved are known at this point.

Well-known anionic clusters such as $[\text{HFe}_3(\text{CO})_{11}]^-$, $[\text{HWOs}_3(\text{CO})_{14}]^-$, $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$, and $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ have also been tested as catalyst precursors in the hydrogenation of styrene in $[\text{bmim}][\text{BF}_4]$, and in organic solvents such as octane and methanol [26]. The activity of the Fe cluster is the lowest of the series, and that for Ru is the highest, but the robust Ru_6 cluster was found to decompose under the reaction conditions to metallic particles, which are responsible for the catalytic activity. The WO_3 and Os_4 clusters are much more active in the ionic liquid than in octane or methanol, and the improvement in activities ($\text{TOF } 30\,000 \text{ h}^{-1}$) was associated with increased stability of the clusters in the ionic medium, although no detailed mechanistic studies were conducted.

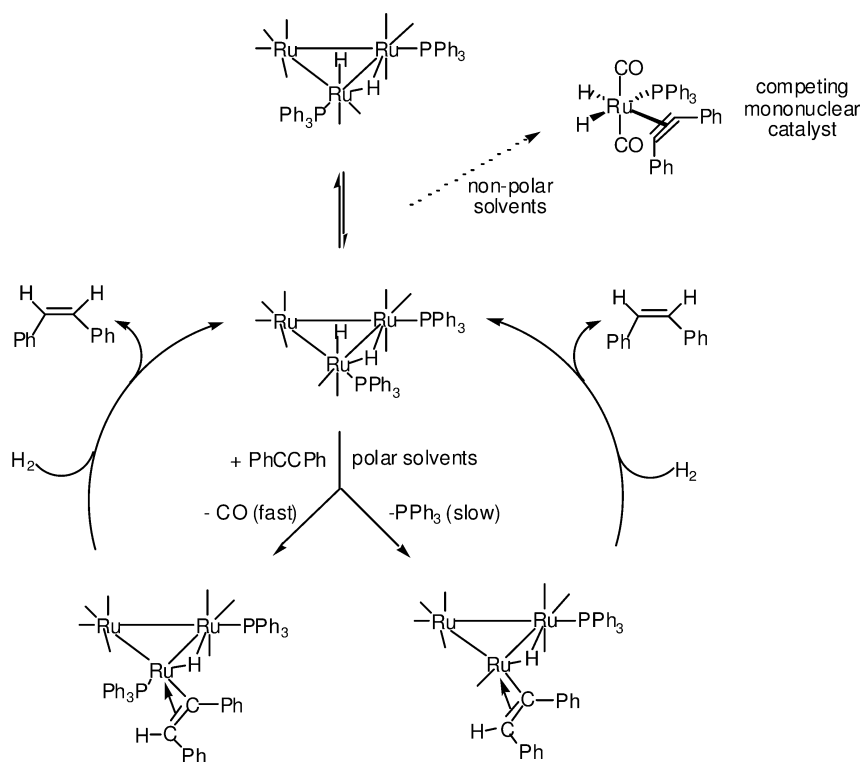
8.3

Hydrogenation of $\text{C}\equiv\text{C}$ Bonds

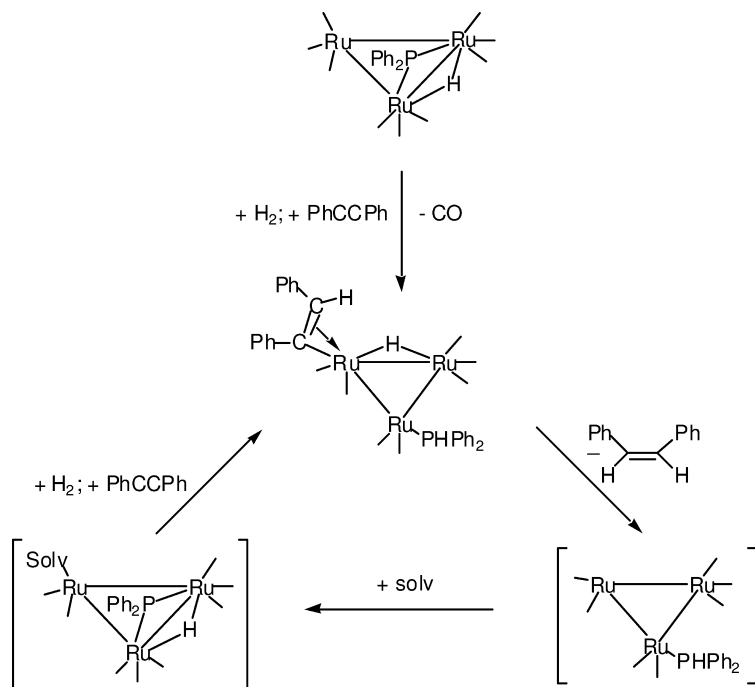
The hydrogenation of alkynes is a very interesting reaction, since the selectivity toward the partially or the fully reduced product allows the *in-situ* comparison of the ability of a catalyst to reduce $\text{C}\equiv\text{C}$ versus $\text{C}=\text{C}$ bonds. This is perhaps the area in which cluster catalysis has been most extensively developed, as recently reviewed by Cabeza [27], Adams and Captain [4], and Dyson [28]. A good number of metal clusters have been employed as catalyst precursors in alkyne hydrogenation, the majority of them containing ruthenium.

Early studies by Valle and coworkers showed that $[\text{Ru}_3(\text{CO})_{12}]$ [29], $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ [30], and the phosphine- and phosphite-substituted derivatives $[\text{H}_4\text{Ru}_4(\text{CO})_{12-n}(\text{PR}_3)_n]$ ($\text{R} = \text{Bu}^n, \text{Ph}, \text{OEt}, \text{OPh}$) ($n = 1-3$) [31] hydrogenate 1-pentyne and 2-pentyne efficiently at 80°C and 1 atm H_2 to the corresponding alkenes; the internal $\text{C}\equiv\text{C}$ bond is reduced more rapidly than the terminal one. Reaction rates increased with increasing number of P-donor ligands for the hydrogenation of 1-pentyne and decreased for 2-pentyne; rates were also increased with increasing basicity of the phosphine or phosphite. The complexes also promote $\text{C}=\text{C}$ bond migration, and therefore 1-pentene, *cis*-2-pentene and *trans*-2-pentene are observed during the course of the reaction. Consecutive hydrogenation of the alkenes to *n*-pentane takes place only after the alkyne has been completely consumed. No attempt was made then to identify reaction intermediates or the catalytic mechanism, although common pathways were presumed for both complexes. The same clusters $[\text{Ru}_3(\text{CO})_{12}]$, $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ [32], the related complex $[\text{H}_2\text{Ru}_4(\text{CO})_{13}]$ [33, 34], and the diphenylphosphine and diphenylphosphido derivatives $[\text{H}_4\text{Ru}_4(\text{CO})_{12-n}(\text{PPh}_2\text{H})_n]$ ($n = 1-3$), $[\text{Ru}_3(\mu\text{-H})(\mu\text{-PPh}_2)_n(\text{CO})_{11-n}]$ ($n = 1, 3$), $[\text{Ru}_3(\mu\text{-H})_{2-n}(\mu\text{-PPh}_2)_{2+n}(\text{CO})_{8-n}]$ ($n = 0, 1$), and $[\text{Ru}_4(\mu^3\text{-PPh})(\text{CO})_{13}]$ [33-38] were evaluated by the group of Sappa and found to hydrogenate *tert*-butylacetylene and diphenylacetylene at 120°C and 1 atm H_2 ($\text{TOF } 200\text{--}400 \text{ h}^{-1}$) to a mixture of *cis*- and *trans*-stilbene; complete hydrogenation to the alkane was not observed in this case, and the dihydride displayed the slowest rate. The direct participation of cluster structures in the catalytic cycle was suggested by the isolation of some intermediates that could be used as catalyst precursors with essentially the same activity.

Long-awaited direct evidence for cluster catalysis has recently been provided using *para* hydrogen induced polarization (PHIP) NMR techniques (see Chapter 12); hydride transfer to coordinated organic fragments and fluxional processes were shown to occur on metal clusters [39, 40]. When such methods were applied to the hydrogenation of alkenes and alkynes by $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$, $\text{Ru}_3(\text{CO})_{10}\text{L}_2$ ($\text{L} = \text{PPh}_3$, PMe_2Ph , dppe), several active intermediates could be identified, including clusters and mononuclear species. It was further demonstrated that the catalytic route is dependent on the solvent; cluster catalysis is preferred in polar media and in that case, the active species are produced either by CO dissociation or, more slowly, by phosphine dissociation, which generates the vacant coordination site required for the alkene or alkyne to bind. In nonpolar media, fragmentation to a mononuclear complex was observed, and this complex actually competes with the clusters in the hydrogenation cycle (Scheme 8.5). Interestingly, for the phosphido-bridged cluster $[\text{Ru}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-PPh}_2)]$, similar experiments show that, independently of the solvent used, only cluster catalysis takes place, according to Scheme 8.6 [41].



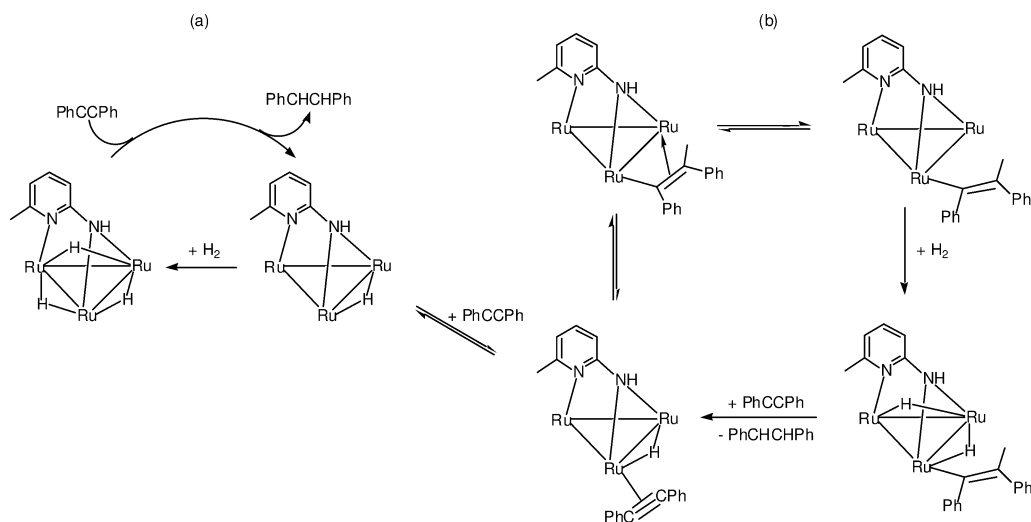
Scheme 8.5 Main species involved in the hydrogenation of diphenylacetylene catalyzed by ruthenium clusters, as determined by PHIP methods (CO ligands omitted for clarity).



Scheme 8.6 Mechanism for the hydrogenation of diphenylacetylene catalyzed by ruthenium clusters containing phosphido bridging ligands, as determined by PHIP methods (CO ligands omitted for clarity).

The Cp derivative $[\text{Ru}_3\text{Cp}_2(\mu^3\text{-Ph}_2\text{C}_2)(\text{CO})_5]$ [42] also hydrogenates diphenylacetylene and 3-hexyne, but fragmentation probably takes place in this case to an important extent.

Cabeza and coworkers have extensively investigated the catalytic hydrogenation of alkynes by metal clusters substituted with N-donor ligands. Diphenylacetylene hydrogenation is induced by $[\text{Ru}_3(\mu\text{-H})(\mu\text{-dmdab})(\text{CO})_9]$ (Hdmdab = 3,5-dimethyl-1,2-diaminobenzene), but the catalytic activity is thought to be due to an unidentified mononuclear fragment [43]. This indicates that edge-bridging bidentate N-donor ligands do not stabilize the cluster structure sufficiently to avoid fragmentation. On the other hand, face-bridging N-donor ligands derived from 2-amino-6-methylpyridine (Hampy) do seem to stabilize clusters enough to maintain the polynuclear structure throughout a catalytic cycle. The complexes $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-ampy})(\text{CO})_9]$, $[\text{Ru}_6(\mu\text{-H})_6(\mu^3\text{-ampy})(\text{CO})_{14}]$, and their acetylene and phosphine derivatives [44–50], hydrogenate diphenylacetylene selectively to mixtures of *E*- and *Z*-stilbene readily at 80 °C and sub-atmospheric H₂ pressure (TOF 27 h⁻¹), as well as phenylacetylene to styrene under more forcing conditions (100 °C, 15 bar H₂). A related cluster containing the 2-anilinopyridine ligand has also been reported to hydrogenate phenyl-1-propyne [51]. Scheme 8.7

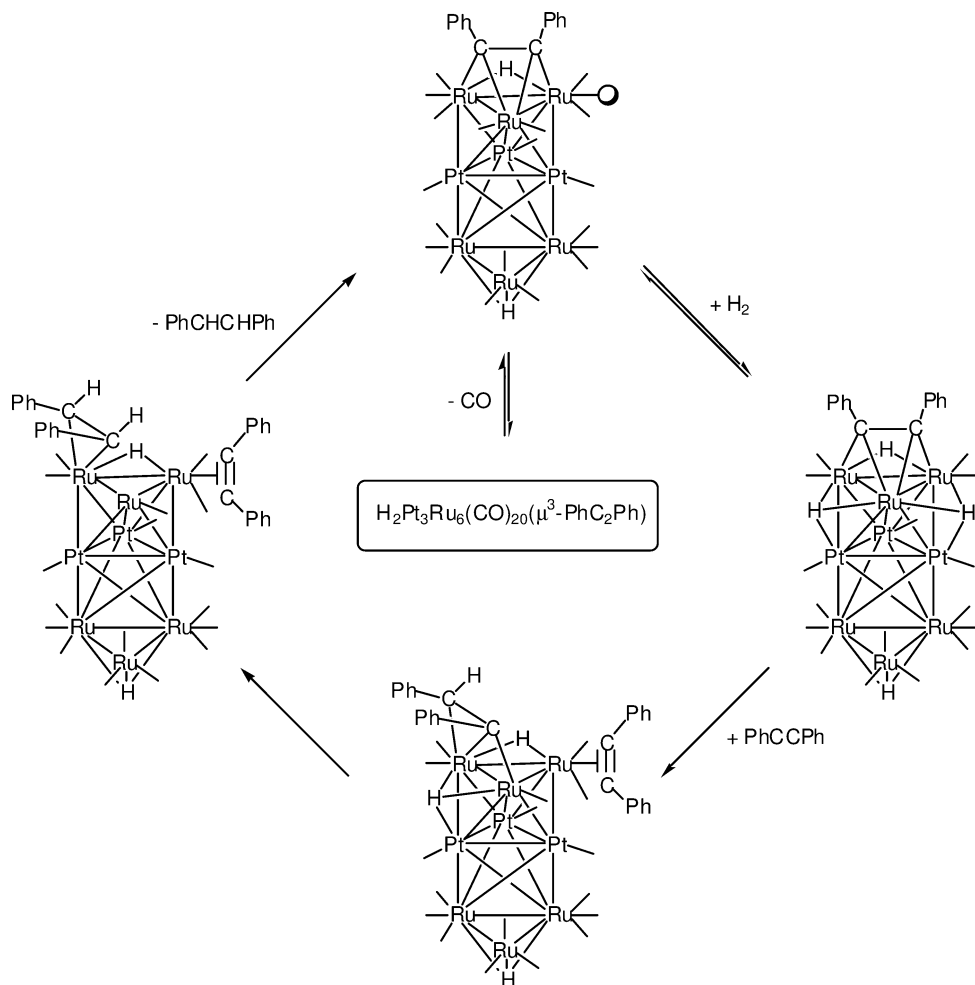


Scheme 8.7 Mechanism for the hydrogenation of diphenylacetylene catalyzed by ruthenium clusters containing face-capping ampy ligands at: (a) low [substrate]:[cat] ratios; and (b) high [substrate]:[cat] ratios (CO ligands omitted for clarity).

shows the main features of the diphenylacetylene hydrogenation mechanism for $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-ampy})(\text{CO})_9]$, where the active species is the alkenyl derivative $[\text{Ru}_3(\mu_3\text{-ampy})(\mu\text{-PhC=CHPh})(\text{CO})_8]$, readily formed by reaction of the hydride with the alkyne. If the latter complex is used as the catalyst precursor, the activity of diphenylacetylene hydrogenation is increased to TOF ca. 40 h^{-1} at 60°C and 0.8 bar H_2 . The catalytic cycle in Scheme 8.7 is supported by detailed kinetic studies, together with isolation and identification of a number of intermediates, and the independent study of various elementary steps included in the cycle. Phosphine-substituted ampy clusters also catalyze the hydrogenation of alkynes, albeit at lower rates (TOF $< 11 \text{ h}^{-1}$ at 80°C and 0.8 bar H_2), but probably through very similar mechanisms.

Heteronuclear clusters have also been used in homogeneous hydrogenation with some success. Early studies by Ugo and Braunstein led to low-activity bimetallic catalysts [52]. $[\text{RuFe}_2(\text{CO})_{12}]$, $[\text{Ru}_2\text{Fe}(\text{CO})_{12}]$ and $[\text{Ru}_3\text{FeH}_2(\text{CO})_{13}]$ were studied by Giordano and Sappa [32]; these promote the hydrogenation of diphenylacetylene at lower rates than the homonuclear Ru clusters, and the nature of the active species was not established. Süss-Fink and coworkers reported the use of $[\text{IrRu}_3(\text{CO})_{13}(\mu\text{-H})]$ in the hydrogenation of diphenylacetylene, curiously to *E*-stilbene (TOF 3900 h^{-1}), and proposed a cycle involving cluster intermediates [53].

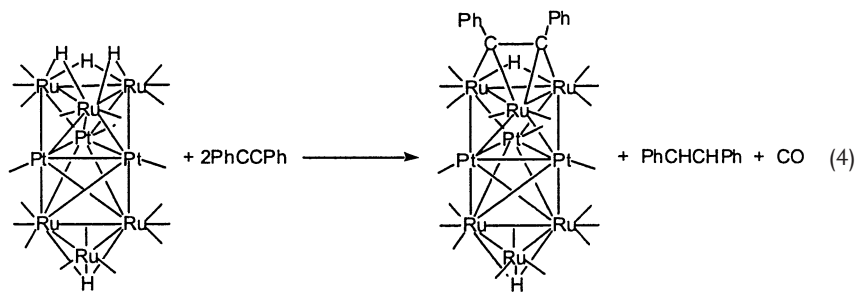
More recently, Adams and coworkers have provided a very interesting case of heteronuclear clusters that are very active for the hydrogenation of alkynes [4, 54, 55]. The high-nuclearity layer-segregated Pt–Ru complex $[\text{Pt}_3\text{Ru}_6(\text{CO})_{21}(\mu^3\text{-H})(\mu\text{-H})_3]$, consisting of three stacked triangular layers of metal atoms with an



Scheme 8.8 Mechanism for the hydrogenation of diphenylacetylene catalyzed by layer-segregated Pt_3Ru_6 clusters (CO ligands omitted for clarity).

alternating arrangement $\text{Ru}_3\text{Pt}_3\text{Ru}_3$, readily reacts with diphenylacetylene to yield an alkyne complex, according to Eq. (4). In the process, two of the hydrides are transferred to a second diphenylacetylene molecule to yield 1 equiv. Z-stilbene, and one CO ligand is lost.

The resulting alkyne complex is capable of catalytically hydrogenating diphenylacetylene at 50°C and 1 bar of H_2 with TOF close to 50 h^{-1} . The hydrogenation rate is first order in cluster concentration, indicating the participation of polynuclear species in the cycle, and it is also first order in substrate and hydrogen concentrations, while it is inhibited by CO. Labeling studies involving D_2



and $\text{ToIc}\equiv\text{CTol}$ further pointed to cluster catalysis, according to the mechanism depicted in Scheme 8.8. The catalytic activity is high, but catalyst life is short, the cluster being degraded into various species after a few hundred turnovers. A related homonuclear cluster $[\text{Ru}_3(\text{CO})_9(\mu^3\text{-PhCCPh})(\mu\text{-H})_2]$ was shown to hydrogenate the alkyne at considerably lower rates than those observed for the heteronuclear complex, showing that the presence of platinum in the vicinity of the “working” ruthenium triangle enhances the catalytic activity. Even though there is no evidence for any direct participation of platinum in the catalytic cycle, the activation of H_2 is thought to occur on Ru_2Pt triangular units (see Scheme 8.8). The same Pt_3Ru_6 cluster has also been found to catalyze the hydrosilylation of diphenylacetylene with triethylsilane [56].

8.4 Hydrogenation of Other Substrates

The anionic cluster $[\text{Ru}_4\text{H}_3(\text{CO})_{12}]^-$ is a catalyst precursor for the transfer hydrogenation of simple and α,β -unsaturated ketones in boiling Pr^iOH , with reasonable rates (TOF up to 100 h^{-1}) and, in the latter case, with moderate diastereoselectivity (up to 77%). Although a detailed kinetic modeling was performed, the identity or nuclearity of the active species could not be ascertained, and a radical mechanism was proposed [57]. $[\text{Ru}_3(\text{CO})_{12}]$, in combination with chiral tetradentate diimino phosphines (P_2N_2), catalyzes the transfer hydrogenation of prochiral ketones in boiling $\text{Pr}^i\text{OH}/\text{KOPr}^i$, with enantioselectivities up to 81% at 91% yield (TOF ca. 40 h^{-1}). Evidence pointing to a cluster-catalyzed reaction include the fact that an anionic cluster $[\text{HRu}_3(\text{CO})_{12}(\text{P}_2\text{N}_2)]^-$ could be isolated at the end of the hydrogenation runs, and it was shown to catalyze the reaction in the absence of added base. The reaction rate was also first order in cluster concentration, and a related mononuclear complex containing the same ligand was inactive [58].

The ligand-stabilized cluster $[\text{Ru}_3(\text{CO})_7(\mu^3, \eta^5: \eta^5\text{-4,6,8-trimethylazulene})]$ reacts with $\text{PhMe}_2\text{Si-H}$ to yield a new cluster containing a partially hydrogenated azulene ligand $[\text{Ru}_3(\text{CO})_7(\mu^3, \eta^5: \eta^5\text{-4,5-dihydro-4,6,8-trimethylazulene})]$. Both of these complexes are efficient catalyst precursors for the hydrosilylation of aceto-

phenone with moderate activities (TOF ca. 10 h^{-1}). Cluster participation is proposed on the basis of observed intermediates by NMR, and the fact that lower nuclearity-related complexes were not active in catalysis [59].

A series of tri- and tetra-nuclear Ru clusters previously reported by the groups of Süss-Fink [60] and of Dyson [61] as catalysts for the hydrogenation of benzene and other simple aromatics in biphasic media have later been shown to consist predominantly of active metallic particles [9, 10, 62].

8.5

Concluding Remarks

Despite the fact that the great expectations produced by cluster chemistry over two decades ago as a means of discovering novel catalysts with unique properties have not yet been realized, cluster catalysis continues to attract attention both as a conceptual issue and as a potential method to achieve unusual catalytic features. A number of catalysts originally thought to operate through cluster intermediates have subsequently been shown to owe their activity to the formation of mononuclear complexes or of metallic aggregates. Other systems do provide strong cases for catalytic cycles involving well-defined polynuclear intermediates, and a number of thorough kinetic and mechanistic studies have been performed which shed light on this fundamental question. The introduction of PHIP as a means of obtaining direct evidence for cluster catalysis is a most welcome development, and it is expected that further studies involving this technique will either corroborate or contradict the participation of polynuclear species in other catalytic systems. Although it is difficult to predict accurately whether fragmentation will occur when a given cluster is placed under catalytic hydrogenation conditions, some indicators are available to orient the search for polynuclear active species; in particular, the use of polydentate edge-bridging or face-capping ligands provides a good probability of obtaining cluster catalysis.

To date, there are no examples available of well-defined clusters that are of practical use, or that offer any advantages over mononuclear complexes in homogeneous hydrogenation reactions. The promising approach to enantioselective hydrogenation by use of chiral metal frameworks or of chiral polydentate ligands on clusters has been explored with limited success, but developments of possible utility are yet to be realized; continued efforts in that direction are certainly worthwhile. Heterobimetallic clusters appear as good candidates for promoting reactions not catalyzed by a single metal through synergistic enhancement of the properties of individual components; some interesting examples are now available where bimetallic high-nuclearity cluster catalysis has been demonstrated, and applications to unusual reactions are to be expected [4, 53–56]. The use of defined clusters as precursors of nanostructured materials is also of great interest, even if it falls outside the field of homogeneous hydrogenation. For example, applications to the synthesis of active catalysts for the important arene hydrogenation reaction are very appealing.

Until now, most studies on homogeneous hydrogenation by clusters have concentrated on alkenes and alkynes, though hopefully other substrates such as aldehydes, ketones, imines, and others will be further investigated, particularly using those systems that are now known to be genuine cluster catalysts.

Although the field of homogeneous hydrogenation by use of well-defined metal clusters has risen and fallen in popularity over the years, it has never been abandoned, most likely because the basic concept of a limited number of metal atoms in a well-defined structural and electronic molecular unit performing unique catalytic reactions still appears very seductive, and its realization poses exciting challenges in molecular design and synthetic chemistry. Hopefully, the expected breakthroughs toward distinctive catalytic properties in hydrogenation reactions by metal clusters will “see the light” before too long.

Abbreviations

bmim	1-butyl-3-methylimidazolium
ee	enantiomeric excess
IR	infra-red
NMR	nuclear magnetic resonance
PHIP	<i>para</i> hydrogen-induced polarization
TOF	turnover frequency
TON	turnover number
TPPMS	triphenylphosphine-monosulfonate
TPPTS	triphenylphosphine-trisulfonate

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