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Molecular Metal Clusters

Cluster chemistry may provide valuable insights to chemisorption and catalysis on surfaces

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With the increasing awareness that energy and natural resources are finite, there has been a significant upsurge in academic and industrial research in catalysis (*1*). This correlation has a logical basis because a catalyst may reduce substantially the activation energy for a reaction (*2*) as illustrated in Fig. 1. Also, there is a selectivity factor of considerable importance. A set of reactants may produce through different reaction paths different sets of products, and a catalyst may selectively reduce the activation energy for one reaction path, thereby producing solely or primarily one set of products. Hence, the ideal catalyst will conserve energy by reducing reaction activation energies and will conserve energy as well as resources by selectively promoting the desired reaction path. In addition, the selective feature will minimize disposal or pollution problems.

The discovery or design of ideal catalysts is a scientific and technological challenge before the nation and the world—be it in the production of fuels, food substitutes, fertilizers, gasoline, fibers, plastics, elastomers, or pharmaceuticals (*3*). For rational design of ideal catalysts, there must be an understanding of the catalytic reactions at a molecular level. This article describes a new and exciting area of scientific investigation that should provide considerable insight to these catalytic reactions.

Catalysis, a Science and a Technology

There are two types of catalytic reactions. One is the so-called homogeneous catalytic reaction, a solution phase reaction, wherein a discrete molecular compound (catalyst) like nickel carbonyl is dissolved in a solution containing reactants (*2, 4, 5*). These molecular compounds are referred to as homogeneous catalysts. The second type is a heterogeneous catalytic reaction where a solid-state catalyst, for example, a metal or metal oxide, is exposed to gaseous or liquid reactants with the catalytic reaction occurring between the chemisorbed reactants on the surface of the catalyst—here, the catalysts are called heterogeneous catalysts (*6, 7*). In a precise characterization, both types of catalytic reactions are homogeneous, and an accurate distinction would be between catalytic reactions in a solution phase and in a chemisorbed phase (*8*).

Differentiation of catalysts and catalysis goes well beyond an apparent phase distinction. Heterogeneous catalysts present significant advantages in an engineering and economic context: no costly (energy) separation of catalyst and products, typically good catalyst stability, and the possibility of high productivity (low capital investment). In contrast, homogeneous catalysts are often fragile compounds, unstable to oxygen, moisture, and temperature extremes, conditions all too common in many industrial processes. Accordingly, it is no surprise that most industrial processes are based on heterogeneous catalysts. However, new and important industrial processes for commodity chemicals such as acetic acid and adiponitrile, a nylon intermediate, actually employ homogeneous catalysts, complexes of rhodium and nickel, respectively (*9*). How do these developments arise in view of the aforementioned distinctions? The answer lies simply in one key performance factor, selectivity (*10*). The molecular catalyst, in principle, can be tailored to a specific (selective) reaction requirement in almost infinite detail, but the solid-state or heterogeneous catalyst is rather limited in modification. Furthermore, the tailoring of the homogeneous catalyst to a reaction can be achieved largely in a logical fashion, whereas the analogous modification of a heterogeneous catalyst is sometimes an exercise in art or intuition. Finally, a typical heterogeneous catalyst has an imperfect surface with sites of possibly different reactivity, a feature antithetical to selectivity.

An interesting distinction between catalysis "types" extends to recent times: heterogeneous catalysis is studied largely in academic departments of chemical engineering, homogeneous catalysis in chemistry departments; the two areas often have been administratively disjoint in industrial research laboratories, and scientists representing the two areas have not commonly communicated in an in-depth fashion. However, this partitioning of catalysis science is changing now in dramatic fashion. For example, in our Cornell Materials Science Center, we have an interdisciplinary surface science group that includes members from applied physics, chemistry, chemical engineering, and materials science departments. Interactions with these members have been important to my developing research (*11*) in this catalysis area.

How Does a Catalyst Function?

Aside from the selectivity advantage that may accrue to a homogeneous catalyst, there is a potential for understanding of how, on a molecular basis, a catalyst functions in solution. During the last two decades, mechanism studies of homogeneous catalytic reactions have provided great, although not complete, in-

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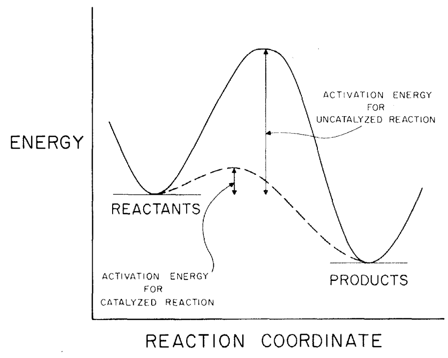


Fig. 1. A two-dimensional representation of a potential surface for a reaction system. The reaction coordinate, from left to right, represents some reaction path going from reactants to products as a function of potential energy. The catalyst does not affect the energy levels of the reactants or the products but "directs" the reaction along a pathway (dotted line) that is different and of lower energy than the uncatalyzed reaction.

sight to the molecular details of these catalytic reactions that occur in solution (*2, 4, 5*). This depth of understanding at a molecular level has not been realized for heterogeneous catalysts, and such an understanding is unlikely to be realized from surface physics and chemistry studies for years. This dichotomy in no way arises from different levels of research activity in the homogeneous and heterogeneous catalytic fields, but simply reflects the intrinsic ease with which diffraction and spectroscopic data can be interpreted in a relatively precise fashion to structurally define a molecular (homogeneous) catalyst and to characterize its interactions with other molecules, that is, the catalytic reactions. Analogous data for the structural details of a surface (heterogeneous catalyst) and of the molecular features of the surface interaction with molecules are far more difficult to interpret.

The geometric and stereochemical features of a molecular catalyst can be rapidly and accurately determined for the crystalline state by three-dimensional x-ray crystallographic analysis (*12*). Stereochemical and dynamic features for the catalyst molecule in the solution state can be quickly assessed by spectroscopic analysis, most notably by nuclear magnetic resonance (NMR) techniques; and the nature of the catalytic reaction, specifically the interaction of the catalyst and the reacting molecules, can be probed by the same techniques under conditions that precisely represent the catalytic conditions. Kinetic parameters of the solution-state catalytic reaction are readily established by standard procedures.

For the solid-state catalyst, the bulk structure also can be rigorously defined by crystallographic analysis, but it is only the surface that is relevant to the chemisorption and catalytic processes. Surface definition can be achieved by low-energy electron diffraction (LEED) and Auger spectroscopy; but the key issue of how the surface atoms interact and dynamically interact with molecules can be addressed realistically only with a battery of spectroscopic and diffraction techniques (*13, 14*). In addition, many of the surface physics techniques can be applied only if the reaction system is at extremely low pressures. The normal conditions under which catalytic reactions are effected cannot even be approximated for application of these techniques. The pressure differential between physical studies and the catalytic reaction is often from 4 to 12 orders of magnitude, a disparity of possible thermodynamic and mechanistic significance. However, there are intensive efforts to bridge this pressure gap between surface science and heterogeneous catalysis.

Since the mechanistic features of a solution phase catalytic reaction can be established, there understandably have been attempts to use this information to set up simple models of the surface processes of chemisorption and heterogeneous catalysis. One principle from homogeneous catalysis shows that the reacting molecules in a catalytic system typically first interact with (bond to) the metal atom (*15*) in the molecular catalyst. For example, in the simple catalytic reaction of olefin hydrogenation to give alkanes

$$H_2C{=}CH_2 + H_2 \rightarrow H_3CCH_3 \quad (1)$$

a hydrogen molecule must interact and add to the catalyst molecule to give a metal dihydride catalyst intermediate with which the olefin must then bind through the metal atom to give an olefin metal dihydride (*2, 4, 5*). This sequence is mechanistically limned in Fig. 2 for the specific catalyst, $ClRh[P(C_6H_5)_3]_3$ (*5, 16*). In the latter intermediate, hydrogen atom transfers from metal to the carbon atoms proceed stepwise to yield ultimately the alkane and the original catalyst molecule. All these sequences must often be accompanied by dissociation and association of other groups bound to the metal atom. In this conceptually very simple catalytic reaction of olefin hydrogenation, at least four or five steps are required as outlined in Fig. 2.

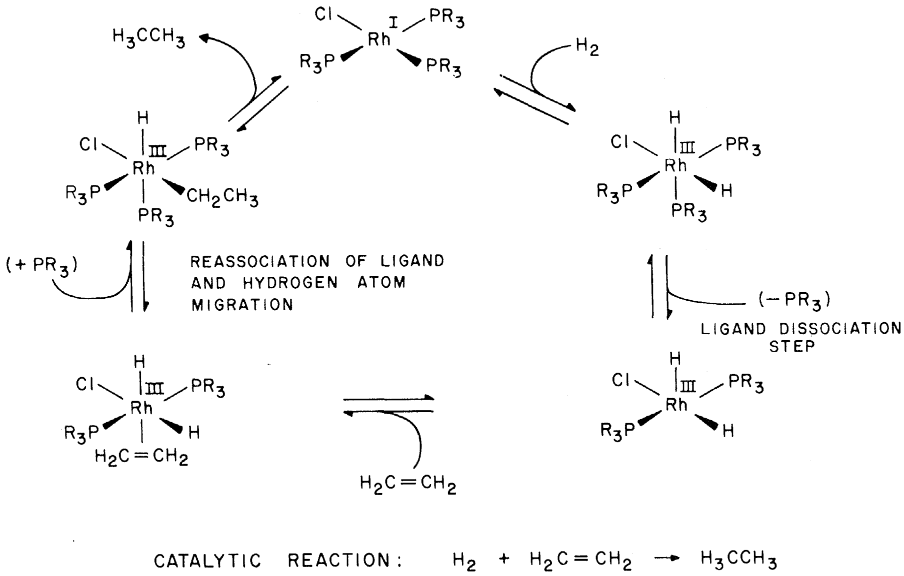
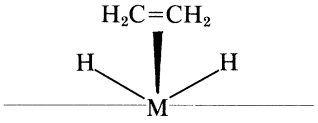


Fig. 2. A representation of discrete reaction steps in the hydrogenation of ethylene as catalyzed by the molecular coordination complex, $ClRh[P(C_6H_5)_3]_3$. This example was selected because the individual steps have been well defined through spectral and kinetic studies and because the stereochemistry of the hydrides have been established by NMR studies (*5, 16*). The sequence illustrated is one of three pathways operative in the catalytic cycle as shown from the kinetic studies. The most important (most rapid) pathway involves the species $ClRh[P(C_6H_5)_3]_2$ which follows the cycle illustrated above except that the ligand dissociation and association steps are missing; in this case, the minimum number of reaction steps in the catalytic cycle is four.

Now consider the catalytic olefin hydrogenation sequence in the context of a metal surface catalyst. Presume that reactants must initially bind to the metal atoms at the surface (*17*). If a sequence analogous to that outlined in Fig. 2 were the paradigm, then substantial problems would arise when this is imposed on a single metal atom on a surface. A metal atom at the surface is bound to metal atoms below and minimally to four other metal atoms at the surface. There remains insufficient space and available orbitals for this metal atom (M) to form an intermediate, analogous to one shown in Fig. 2, namely



An obvious modification of the model would involve adjacent metal atoms at the surface. Such an alternative, based on a plausible extension of the olefin hydrogenation scheme with a molecular catalyst to a surface catalyst, is outlined in Fig. 3 where M represents a metal atom. The scheme is plausible, but further questions arise. Is a hydrogen atom at the surface bonded simply to one metal atom or to two or more metal atoms? Is the ethylene molecule bonded to one metal atom or to several metal atoms? Possible interactions at the surface of a close-packed array are depicted in Fig. 4. Further, as shown in the hypothetical scheme in Fig. 3 for the second hydrogen migration step, a hydrogen atom "moves" directly from one metal atom to an adjacent one. This feature, not possible in a molecular catalyst which has only one metal atom, addresses the important issue of mobility in chemisorbed species on a surface. Thus, although concepts and principles derived from solution reactions with molecular or homogeneous catalysts are of value in synthesizing schemes for surface reactions, these applications have substantial limitations simply because the molecular catalysts studied have, with but few exceptions, comprised a single metal atom bonded to a set of ligands as in $ClRh[P(C_6H_5)_3]_3$, the catalyst for mechanistic illustration in Fig. 2. Fortunately, there is another large class of inorganic molecules and ions whose members might present far more meritorious models of surfaces in chemisorption and heterogeneous catalytic processes (*18–20*). This is the cluster class.

Metal Clusters

Clusters are discrete molecular species in which three or more atoms interact (bond) to form triangular or polyhedral arrays, and typically, the center position of the clusters is vacant although there are a few metal clusters that have a central atom such as carbon, rhodium, or gold (*21*). In most clusters, the periphery is enveloped by a set of ligands; ligand is the term used by chemists to describe atoms, groups of atoms, and molecules that are bonded to some core—in this case cluster—atom. Common cluster ligands are halogen, sulfur, and hydrogen atoms, alkyl groups, carbon monoxide, nitric oxide, phosphines, olefins, acetylenes, dienes, benzene, isonitriles, and nitriles. The actual range of ligands in clusters rather fully encompasses the

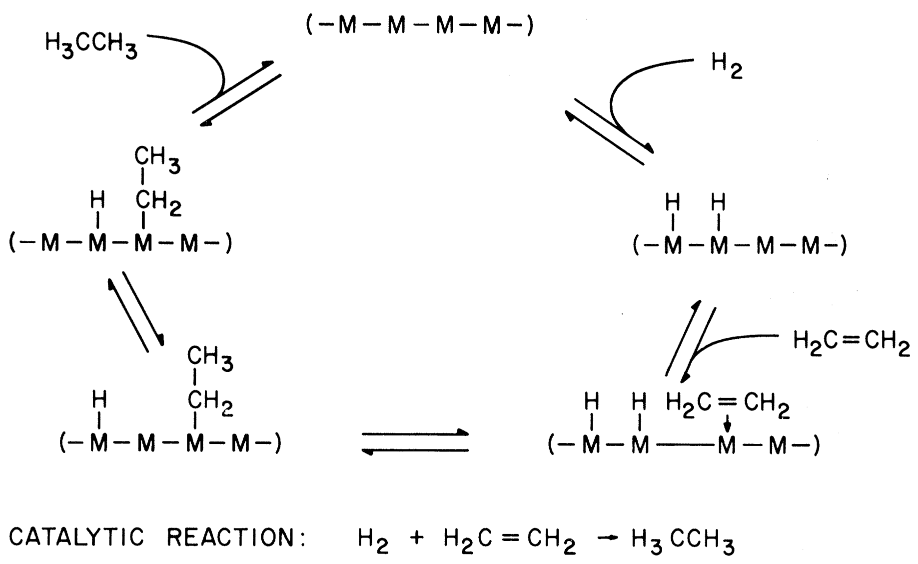


Fig. 3. A speculative sequence of reaction steps for the catalytic hydrogenation of ethylene at a metal surface (the M–M–M–M set is a partial one-dimensional representation of a metal surface). The long M–M separation at the lower right arises only from a tactical drafting problem and should not be construed as a long M–M separation.

Table I. Metal clusters.

TRIANGLES (3)	TETRAHEDRA (4)	FIVE-ATOM
$Os_3(CO)_{12}$	$Ni_4(C_5H_5)_4H_3$	$Pt_3Sn_2(1,5\text{-}C_8H_{12})_3Cl_6$
$Pd_3(CNR)_6$	$Ir_4(CO)_{12}$	Bi_5^{3+}
$Re_3Cl_{12}^{2-}$	$Li_4(CH_3)_4$	$Fe_5\underline{C}(CO)_{15}$*
$Fe_3(CO)_9(RC{\equiv}CR)$	$Ni_4[CNR]_7$	$Ni_5(CO)_{12}^{2-}$
OCTAHEDRA (6)	SEVEN-ATOM	EIGHT-ATOM
$Co_6(CO)_{14}^{2-}$	$Rh_7(CO)_{16}^{3-}$	$Os_8(CO)_{23}$
$Mo_6Cl_{14}^{2-}$	$Rh_7(CO)_{16}I^{2-}$	$Au_8\underline{Au}[PR_3]_8^{3+}$*
$Ru_6\underline{C}(C_6H_6)(CO)_{14}$*		Bi_8^{2+}
$Au_6[PR_3]_6^{2+}$		$Co_4B_4H_4(C_5H_5)_4$
NINE-ATOM	TEN-ATOM	TWELVE-ATOM
Bi_9^{5+}	$Au_{10}Au[SCN]_3[PR_3]_7$	$Pt_{12}(CO)_{24}^{2-}$
Sn_9^{4-}		$Rh_{12}Rh(CO)_{24}H_3^{2-}$*
$Pt_9(CO)_{18}^{2-}$		
	FIFTEEN-ATOM	
	$Pt_{15}(CO)_{30}^{2-}$	
	$Rh_{15}\underline{C_2}(CO)_{28}^{-}$*	

*Metal cages. An atom, underlined, is at the center of the polyhedron.

range of atoms, groups of atoms, and molecules that are encountered in catalytic chemistry and in surface chemisorption phenomena. There is also a small subclass of naked metal cluster ions (*22*) that have no ligands; these include B_5^{3+}, Te_6^{2+}, Sb_7^{3-}, Se_8^{2+}, Bi_8^{2+}, Bi_9^{5+}, and Sn_9^{4-}. An exemplary set of clusters is presented in Table 1. Only one example in the listing is drawn from the largest known cluster subclass (*23, 24*), the polyhedral boranes, which comprise clusters of boron atoms and of boron atoms with other atoms. These polyhedral boranes, with the exception of the embryonic subset (*25*) that are clusters with large numbers of transition metal atoms in combination with boron atoms, are not especially relevant to this particular discussion of catalysis chemistry.

The metal cluster class has an extraordinary potential for providing simple models of surfaces in the chemisorption and catalytic processes (*18–20*). Metal clusters, because they are discrete molecular entities soluble in a variety of nonreactive solvents, retain all the experimentally desirable features of simple mononuclear homogeneous catalysts for the definition of structure, stereochemistry, dynamic stereochemistry (ligand mobility), and the mechanistic details of catalytic chemistry. These specific aspects are discussed, with respect to surface chemistry, from established cluster chemistry and new developments from our research group.

Clusters—Little Pieces of Metal

Clusters have triangular or polyhedral arrays of metal atoms with most polyhedral arrays being deltahedra, polyhedra with all triangular faces as in tetrahedra (four), trigonal bipyramids (five), octahedra (six), and symmetrically tricapped trigonal prisms (nine) with triangular, tetrahedral, and octahedral arrays most common. The pervasive triangular facial structure of clusters is also found in metals which have close-packed structures (*26*). An especially notable cluster ion is $Rh_{12}Rh(CO)_{24}H_3^{2-}$ in which the arrangement (*27*) of rhodium atoms is precisely that of a hexagonal close-packed metal, as is schematically shown in Fig. 5. In contrast, the square metal array found for example in the 100 face of close-packed metals is only occasionally found in metal clusters—a serious but not fatal flaw in this developing analogy between surfaces and clusters. Thus, with some qualification, these clusters are like very small pieces of metal. But are they? How do the metal-metal bond energies compare in the two limiting cases? How can a metal cluster be an analog of a metal surface when the metal cluster surface typically is enveloped by ligands?

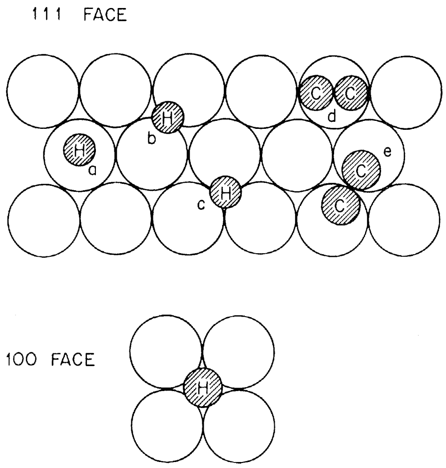


Fig. 4. The stereochemistry of several possible interactions of the hydrogen atom and the ethylene molecule with a metal surface is illustrated for the 111 and 100 faces of a metal crystal with a close-packed arrangement of metal atoms. The hydrogen atoms of the ethylene molecule have been omitted for simplification. The two ethylene modes shown are far from a complete set but do illustrate possible interactions with one and with two metal atoms.

Metal-metal bond energies for metal clusters and for metal surface atoms cannot be directly compared simply because the requisite data are nonexistent for either limiting case. A crude comparison can and has been made (*19, 28*) through data available for dinuclear metal complexes (cluster prototypes) and the bulk metal phase. The values for identical metals are in the limiting cases similar, with dinuclear metal-metal bond energies usually 0.5 to 0.8 those for the "bonds" in the bulk metal. In both metals and metal clusters, the metal-metal bond energy increases within a group as the size or atomic weight of the metal increases, and parallel changes in bond energy are found with variation in the electronic character of the metal (*19*).

Clusters—Little Pieces of Metal with Chemisorbed Species on the Periphery

In no realistic fashion is a metal cluster like $Rh_4(CO)_{12}$ or $Co_6(CO)_{14}^{4-}$ a model of a clean metal surface, but the cluster may be a reasonable approximation of chemisorbed species on a metal surface, in this case, chemisorbed carbon monoxide molecules. To precisely pursue this analogy, we look to the stereochemistry of the clusters, the spatial manner in which the ligands are bound or arranged, and then to a comparison of the cluster arrangements with those of analogous species chemisorbed on metal surfaces. In $Rh_4(CO)_{12}$, the carbon monoxide ligands are bound both in terminal 2-center and edge bridging 3-center modes (*29*), while in $Co_6(CO)_{14}^{4-}$ the ligands are in 2-center and face bridging 4-center modes (*30*) as is illustrated in Fig. 6. One sees in these two clusters three of the four modes of ligand binding to a surface that were postulated in Fig. 4 for the specific case of the hydrogen atom ligand. Terminal edge bridging and face bridging binding for the hydrogen atom are also established in metal cluster hydrides like $H_2Os_3(CO)_{11}$, $H_4Ru_4(CO)_{12}$, and $H_3Ni_4(C_5H_5)_4$. Analogous binding for other ligands like isonitriles, halide ions, sulfide ion, and nitric oxide is a relatively common stereochemical feature of clusters. Truly, clusters exhibit a full range of ligand binding as would seem necessary for a valid cluster-surface analogy since both terminal and bridge bonding have been reasonably defined for hydrogen atoms and carbon monoxide ligands on some metal surfaces (*19, 31, 32*).

Analysis of thermodynamic and calorimetric data shows a close correspondence between bond energies for the metal-ligand bond in the limiting cases of molecular complexes and the metal surface chemisorbed species (*19, 28*). Although these data are largely limited to the carbon monoxide ligand, the analysis suggests no sharp thermodynamic differentiation between ligand binding on surfaces and in molecular complexes. Perhaps, then, a localized model of bonding will prove to be a reasonable, first approximation for the surface chemisorbed state. In the localized model, nonadjacent and long-distance metal-metal interactions are ignored (*33*). This approximation, which is not valid for a "clean" metal surface nor for bulk metal properties, greatly simplifies theoretical attempts (*34*) to describe chemisorbed species on a metal surface. Recent surface physics studies suggest that such an approximation for the chemisorbed state may be acceptable.

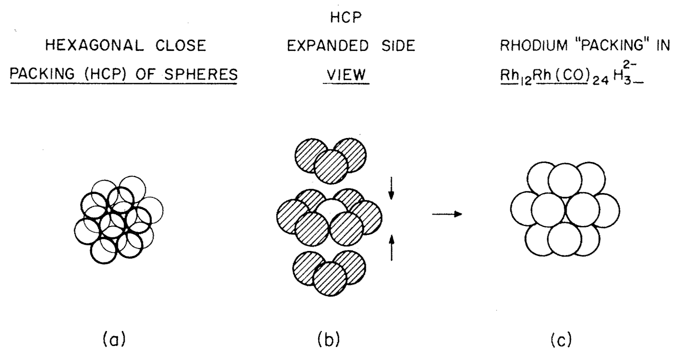
A quite different ligand binding on surfaces and clusters and one of probable great significance in certain catalytic hydrogenation reactions, for example, hydrogenation of nitrogen and of carbon monoxide, may be found in the interaction of molecules or ions that have triple bonds, with an array of metal atoms (*20*). The exemplary molecule is an acetylene. Interaction of the π and π^* orbitals of an acetylene, $RC{\equiv}CR$, with orbitals associated with two metal atoms may occur with the acetylenic C-C axis aligned with the M-M axis, or more probably with the two axes orthogonal. The latter arrangement can lead to a substantial increase in the C-C bond distance, that is, reduction of the C-C bond order (*35*). Additional acetylene-metal interactions, as are feasible on a metal surface or cluster, should and do further reduce bond order. Structurally defined two- (*36*), three- (*37*), and four- (*38*) metal interactions with acetylene molecules in discrete metal clusters are illustrated in Fig. 7; and here the C-C bond distances, direct but nonlinear measures of bond orders, are respectively 1.36, 1.41, and 1.44 Å for the two-, three-, and four-metal interactions in these clusters as compared with distances of 1.20, 1.344, and 1.54 Å for a C-C triple, double, and single bond, respectively. For the chemisorbed surface state, the acetylene binding seems to be analogous to the four-metal-atom interaction in metal clusters at least for the 111 face of platinum shown in Fig. 8 (*39*), although binding modes of acetylenes to a metal surface will probably vary as a function of the metal electronic configuration, crystal face, and metal-metal separation (*40*).

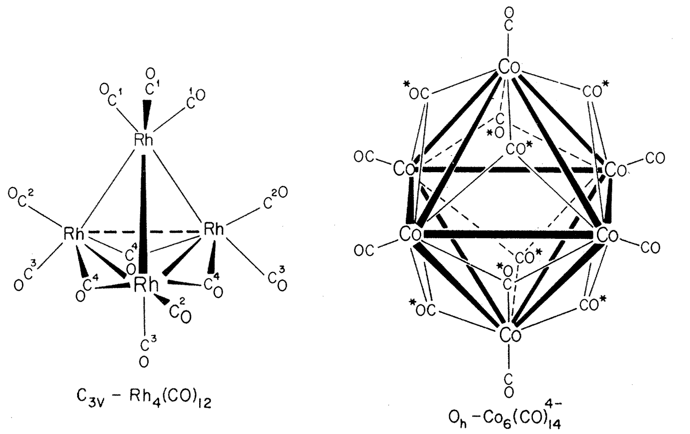
The ground-state structure of these bound acetylenes draws close to the fully reduced state found in ethane, H_3CCH_3, at least with respect to the observed C-C bond distance; hence, these structural data suggest a partial explanation for the experimentally observed facile hydrogenation of acetylenes when catalyzed by metal clusters or metal surfaces.

Mobility—Ligands on Clusters and Chemisorbed Species on Metal Surfaces

Mobility of chemisorbed species seems absolutely essential in order to account mechanistically for reactions catalyzed by surface metal atoms. Experimental evidence, although largely indirect, indicates that chemisorbed atoms like hydrogen and molecules like carbon monoxide are mobile on a metal surface (*6, 19, 41*). We would then expect a similar phenomenon for the ligands in clusters if the cluster-surface analogy is valid. Actually, ligand mobility on clusters is experimentally well defined for hydrogen, carbon monoxide, and isonitriles; ligand "walks" about the cluster periphery have been monitored by the nuclear (^1H and ^{13}C) magnetic resonances of the ligand atoms as a function of temperature (*9*). Accurate activation parameters and information about the mechanism of ligand mobility easily can be derived from the NMR measurements, whereas no such definitive and mechanistically informative technique is available for study of mobility on surfaces.

The ease with which ligand mobility can be definitively probed bodes well for an illuminating analogy in the cluster-surface comparison, at least for this important aspect of surface chemistry. One example should suffice to incisively document this claim. The metal carbonyl cluster, $Rh_4(CO)_{12}$, whose structure is shown in Fig. 6, yields a ^{13}C NMR spectrum for the solution state at low temperatures; this spectrum is fully consistent with the structure established for the crystalline state (*42*). In the ^{13}C NMR experiment, the carbonyl (carbon monoxide) carbon atoms directly bonded to rhodium exhibit a fine structure due to spin-spin coupling of ^{13}C and ^{103}Rh nuclei, each of which has a nuclear spin quantum number, *I*, of one-half. Thus, there are four sets of multiplets that represent the four types of carbonyl environments: three are doublets due to ^{13}C-^{103}Rh spin-spin coupling, and these represent the three types of terminal carbonyl groups; the fourth is a triplet due to coupling of ^{13}C with two ^{103}Rh nuclei, and this represents the three bridging carbonyl groups, each of which is bonded to two rhodium atoms. The ^{13}C spectrum is temperature dependent; as the temperature is raised from −65°C, the multiplets broaden and merge, a feature characteristic of dynamic exchange and at +60°C, the spectrum is a binomial quintet. Interpretation of the spectral data is unambiguous; there is a rapid intramolecular exchange of carbonyl groups such that, on this NMR time scale of approximately 10^{-2} second, all carbonyl groups sense an equivalent environment. The limiting high temperature (+60°C) spectrum of a quintet shows that on a time-averaged basis all carbonyl carbon atoms are spin coupled with all four rhodium atoms [$2nI + 1 = 2(4 \times 1/2) + 1 = 5$]. Retention of ^{13}C-^{103}Rh spin-spin coupling in the limiting spectrum unequivocally establishes that the averaging of carbonyl environments does not occur through a dissociative or





$C_{3v} - Rh_4(CO)_{12}$

$O_h - Co_6(CO)_{14}^{4-}$

Fig. 5 (left). In the cluster ion $Rh_{12}Rh(CO)_{24}H_3^{2-}$, the rhodium atom positions are those of a "piece" of a hexagonal close-packed metal. There is a central rhodium atom bonded to 12 rhodium atoms to form a polyhedron of idealized D_{3h} symmetry. This polyhedral section of a hexagonal close-packed array of metal atoms is shown in three illustrations. (a) An overview of the layer sequencing for the hexagonal close-packing. There is a *repeating* two-layer sequence; the third-layer spheres are then positioned directly over those in the first layer, the fourth layer over the second, and so forth. (b) The 13-atom polyhedron is shown with a separation between the three layers so that all atoms and their relative positions can be seen. The central rhodium atom is evident as an unshaded sphere. (c) The actual 13-atom array. Not depicted for clarity reasons are the 24 carbonyl atoms (12 terminally bonded and 12 bridge bonded to two metal atoms) and the three hydrogen atoms whose precise positions were not established in the crystallographic study (*27*). This remarkable cluster is only one of many large metal clusters prepared in the elegant studies by Chini and co-workers (see *21*). Fig. 6 (right). The structures of two metal carbonyl clusters $Rh_4(CO)_{12}$ and $Co_6(CO)_{14}^{4-}$. The rhodium cluster is a tetrahedron with three of the edges bridged by carbonyl groups. There are four different types of carbon monoxide environments, which are indicated by number superscripts at each carbon atom (*29*). In idealized form, the cobalt cluster has regular octahedral symmetry. The six cobalt atoms describe the vertices of regular octahedron with 6 of the 14 carbon monoxide ligands terminally bound, one to each cobalt atom. The remaining eight carbonyl groups lie over faces of the Co_6 octahedron with each carbon atom interacting with three cobalt atoms (*30*). All three types of metal-carbon monoxide bonding shown above for the two clusters have been established for carbon monoxide chemisorbed on a metal surface.

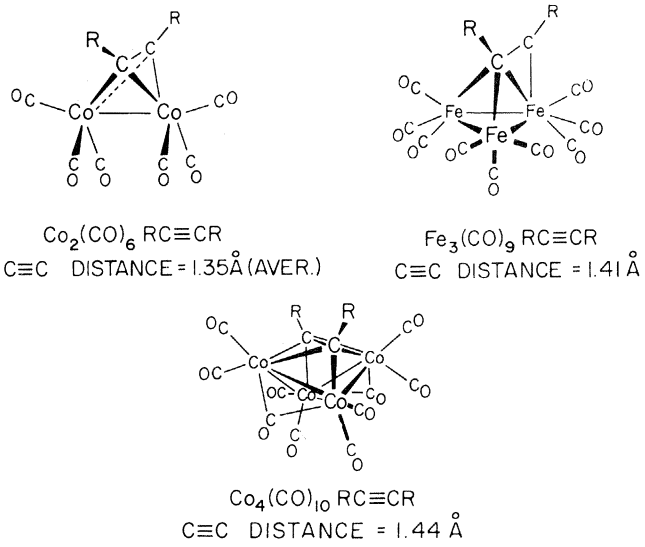
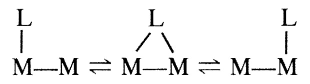


Fig. 7. Three classes of acetylene interactions with metal atoms in a metal cluster have been established. Specific examples are illustrated. As the number of metal atom-acetylenic carbon atom interactions increases, the extent of electron transfer to the acetylenic C-C bond increases with concomitant C-C bond distance increase (*36–38*).

bond-breaking process, for example, $Rh_4(CO)_{12} \rightleftharpoons Rh_4(CO)_{11} + CO$.

The extensive nuclear magnetic resonance programs on metal clusters by a number of research groups (*19*, p. 974; *43*) should ultimately provide a quite detailed mechanistic delineation of just how ligands "walk" around a cluster. Undoubtedly, the low-energy bending modes (*44*) that can readily interconvert terminal and bridge binding of ligands



$$\overset{L}{\overset{|}{M}}\text{—}M \rightleftharpoons M\overset{L}{\overset{/\backslash}{\text{—}}}M \rightleftharpoons M\text{—}\overset{L}{\overset{|}{M}} \qquad (2)$$

will prove a common mechanistic element for ligands like hydrogen, alkyl groups, carbon monoxide, and isonitriles. Stereochemical features (ligand spatial arrangement) seem to contribute substantially to the magnitude of the activation energy for ligand migration in clusters. A "stereochemically degenerate" form, which has a symmetry, imposed by ligands, lower than T_d for a tetrahedral cluster or lower than T_d or O_h for an octahedral cluster, generally has a low activation energy. These "degenerate" forms, formally analogous to chemisorbed species at incomplete surface coverages or on an imperfect surface, have open sites for terminal to edge or terminal to face ligand migrations (*19*, p. 974; *43, 44*).

Cluster Chemistry

The range of ligands in metal clusters is sufficiently large that it presents a complete structural definition of possible chemisorbed species on a metal surface. The next step in the development of the analogy is identification of cluster chemical reactions that parallels metal surface reactions. Although the registry of cluster chemical reactions is not very large (*21*), the extensive studies of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ have established an important capability of these clusters, namely, the scission of C-H and C-C bonds, a reaction common to metal surfaces.

Mononuclear metal complexes or catalysts exhibit no activity for the scission of C-C bonds in hydrocarbons unless presented with a highly strained cyclic hydrocarbon like cyclopropane but $Ru_3(CO)_{12}$ reacts with cyclohexadiene with C-C bond cleavage to yield an acyclic allyl ruthenium complex (*45*). Activation of C-H bonds is a more facile and common phenomenon. Particularly illuminating is the reaction sequence observed for ethylene with the $Os_3(CO)_{12}$ cluster where the net effect is dehydrogenation of ethylene through formation of metal-hydrogen and metal-carbon bonds (*46, 47*). The cluster reaction product $H_2Os_3(CO)_9(C{=}CH_2)$ is structurally represented in skeletal detail in Fig. 9. This cluster reaction is formally analogous to the chemisorption of ethylene on metal surfaces which also occurs with dehydrogenation to initially give metal-hydrogen and metal-acetylene (C_2H_2) chemisorbed species (*6*, p. 229; *19*). For the latter, the bound species has been thought to be acetylene, HC≡CH, rather than $C{=}CH_2$ as in the cluster; this cluster reaction raises the possibility that ethylene chemisorption on some metal surfaces will yield a $C{=}CH_2$ chemisorbed species. Some substituted ethylenes do react with $Os_3(CO)_{12}$ to give RC≡CR complexes, and benzene undergoes a similar reaction (*48*) which may model the initial stages of metal surface-benzene reactions. This alternative binding mode of the unsaturated species to the metal atoms of a cluster is presented in Fig. 9.

Cluster Catalysis Chemistry

When our research on metal clusters was initiated several years ago, there were only fragmentary reports of metal cluster catalysis chemistry, and these were primarily publications of patents (*19*). Accordingly, it has been essential to establish a metal cluster catalysis chemistry with a scope comparable to that of metal surfaces. Because most known metal clusters had been synthesized under rather severe reaction conditions and were thereby rather stable and unreactive (*21*), it also has been necessary to devise synthesis procedures for new, highly reactive metal clusters that would be active catalysts under relatively mild reaction conditions. We considered this activity factor important in the developing analogy between clusters and surfaces because the catalytic activity of metal surfaces is extremely high (*6*). The ultimate experimental and theoretical issue is the elucidation of mechanistic features in the cluster-catalyzed reactions for a comparison with analogous heterogeneous catalysis reaction.

The present scope of the very young area of cluster catalysis includes olefin isomerization and hydrogenation (*49, 50*), acetylene hydrogenation (*51–54*), oxidation reactions (*55*), hydroformylation of olefins (formation of aldehydes and ketones) (*56*), cyclization and polymerization reactions (*51, 53, 54, 57*), dehydrogenation of cyclic dienes (*45, 49*), selective hydrogenation of α,β-unsaturated carbonyl and nitrile compounds (*58*), and reduction of aldehydes to alcohols (*59*). Three basic and technologically important catalytic reactions demonstrated for solid-state but not for homogeneous catalysts were, in our view, important objectives in cluster catalysis; it seemed essential to demonstrate that these difficult reactions could be catalyzed by discrete metal clusters if the cluster-surface analogy were to have validity. These three basic reactions are the hydrogenation of nitrogen to give ammonia

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad (3)$$

the hydrogenation of carbon monoxide to give methanol

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad (4)$$

or methane

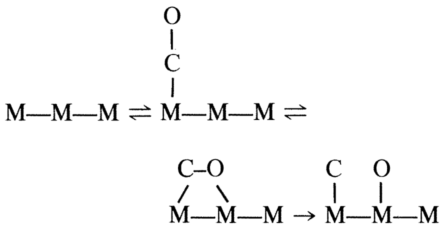
$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad (5)$$

and the rearrangement and dehydrogenation of saturated hydrocarbons

$$n\text{-}C_6H_{14} \rightarrow \text{mixtures of alkanes and cycloalkanes} \qquad (6)$$

To date, we have successfully demonstrated solution phase, cluster-catalyzed hydrogenation of carbon monoxide, and rearrangement of saturated hydrocarbons.

Hydrogenation of carbon monoxide with solid zinc chromite catalyst (*60*) at about 250°C and 150 atmospheres to give methanol (Eq. 4) is a very large-scale industrial process of great technological significance. Methanation, a related reaction (Eq. 5) that can be easily effected with a nickel catalyst, is not at present operated in industry. Until recently, neither reaction had been demonstrated with a homogeneous catalyst. In the methanation reaction, the carbon-oxygen bond which thermochemically (*61*) is very strong must be cleaved. Nevertheless, this reaction is thermodynamically (*61*) very favorable. The primary difficulties in effecting this reaction are the activation of the carbon monoxide molecule for the reduction reaction and an available mechanistic pathway for the cleavage of the carbon-oxygen bond. Some clean metal surfaces, for example, iron, chemisorb carbon monoxide in a dissociative fashion, and the carbon-oxygen bond is cleaved. Presumably, this type of chemisorption process proceeds through intermediates or transition states (*62*) of the type



$$\mathrm{M{-}M{-}M} \rightleftharpoons \mathrm{M{-}}\overset{\mathrm{O}}{\overset{|}{\overset{\mathrm{C}}{\overset{|}{\mathrm{M}}}}}\mathrm{{-}M} \rightleftharpoons \overset{\mathrm{C{-}O}}{\overset{/\quad\backslash}{\mathrm{M{-}M{-}M}}} \rightarrow \overset{\mathrm{C}}{\overset{|}{\mathrm{M}}}\mathrm{{-}}\overset{\mathrm{O}}{\overset{|}{\mathrm{M}}}\mathrm{{-}M}$$

where M represents surface metal atoms. This type of process simply is not available to a molecular complex with a single metal atom, but it is for a metal cluster (*63*). Thus, we thought that scission of the robust carbon-oxygen bond in a catalytic reaction would be more facile with a molecular catalyst that had minimally two metal atoms (*64*). Interaction of both the carbon and the oxygen atoms of carbon monoxide with metal atoms, at least in a transition state (*62*), should lead to a reduction in bond order, that is, increase in bond length, and thereby lower the energy required for bond scission.

Experimentally, we found no mononuclear metal compound that would catalyze the hydrogenation of carbon monoxide (*65*). However, two metal carbonyl clusters, $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$, yielded methane (*66*). The reactions were homogeneous as the clusters were dissolved in an inert solvent, toluene. Unfortunately, the reaction rates at approximately 160°C and 1 to 3 atmosphere pressure were so low as to preclude the possibility of mechanistic studies. Recently, we have found that solvent substitution of toluene by molten (*67*) $NaCl \cdot 2AlCl_3$ changes reaction rate by orders of magnitude, and mechanistic studies are now feasible and under way. Most interestingly, the reaction product is not just methane but a mixture of methane, ethane, and propane. In fact, there is evidence that ethane is the primary initial product (*68*). This reaction system now more closely resembles the Fischer-Tropsch synthesis reaction (*69*) which typically yields a mixture of hydrocarbons, olefins, and alcohols with solid-state catalysts such as iron oxide. A selective Fischer-Tropsch reaction probably will be a source of our petrochemicals at that time when world oil reserves are severely depleted.

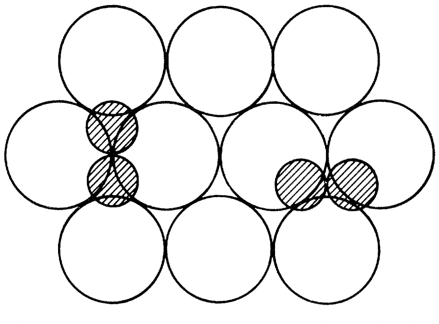


Fig. 8. Two possible cluster-like binding modes for acetylene on the 111 face of platinum. The model on the right is consistent with experimental LEED data for the "stable" chemisorbed form of acetylene on this surface (*39*).

Catalysis of carbon-carbon and carbon-hydrogen scission is a key element in the present-day petrochemical industry, with all such operations based on heterogeneous catalysts (*70*). These catalytic transformations have never been and are unlikely to be demonstrated with the typical transition metal complex or organometallic compound because the associated ligands are most apt to react in a degradative fashion with the metal atom before the saturated hydrocarbon reacts. Metal carbonyl clusters, which have only the relatively inert carbon monoxide ligand, have not exhibited catalytic activity toward saturated hydrocarbons to temperatures of 180°C (*49*). Fortunately, there is the subclass of metal cluster ions that have no ligands (Table 1), and we have found one of these, Bi_5^{3+}, to catalyze the conversion of *n*-hexane to a mixture of C_4 to C_8 alkanes. It now appears that the scope of cluster catalytic reactions will be comparable to that of solid-state or heterogeneous catalysts.

Mechanistic Insights to Cluster Catalytic Reactions

In the course of our early research directed to the development of synthesis techniques for reactive metal clusters, we were fortunate to discover a quite remarkable and extraordinarily reactive nickel cluster (*51*) whose structure,

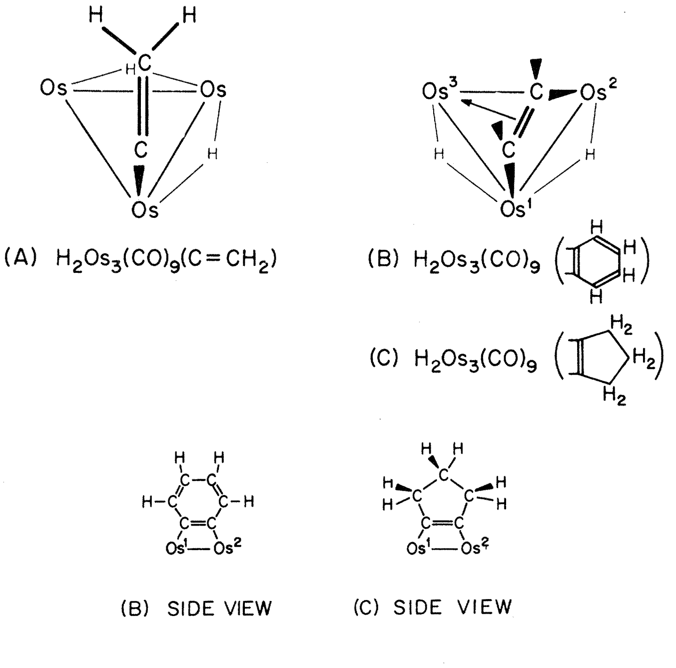
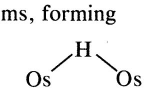


Fig. 9. Ethylene, benzene, and cyclopentene react with $Os_3(CO)_{12}$ or $H_2Os_3(CO)_{10}$ with two hydrogen atom transfers to the osmium atoms, forming



bridging hydrides. The skeletal arrangements in these reaction products are shown in the two upper figures. Not shown in the drawings are the nine carbonyl ligands which are terminally attached to the osmium atoms, three carbonyls for each osmium atom. At the bottom of the figure are side-view illustrations of the organic molecule bound to osmium atoms 1 and 2 in the benzene (B) and cyclopentene (C) reaction products (*46–48*).

mode of ligand bonding, ligand mobility, and catalytic chemistry have provided an incisive documentation of our purported metal cluster–metal surface analogy.

Reaction of bis-1,5-cyclooctadiene nickel(0) with a limited amount of a sterically large isonitrile, like cyclohexyl or tertiary butyl isonitrite, leads to the formation

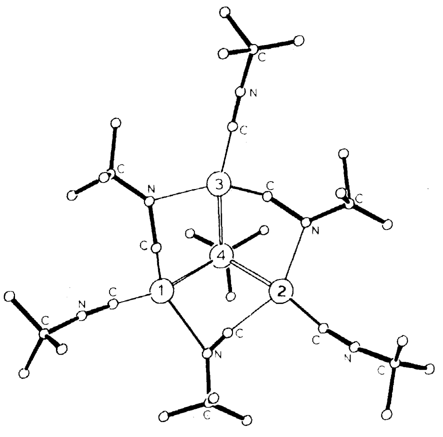
$$4Ni(C_8H_{12})_2 + 7(CH_3)_3CNC \rightarrow Ni_4[CNC(CH_3)_3]_7 + 8C_8H_{12} \qquad (7)$$

of $Ni_4[CNR]_7$, a tetrahedral nickel cluster (*51, 54, 71*). Crystallographic analysis of the tertiary butylisonitrile derivative established a compressed tetrahedral cluster structure of idealized C_3 symmetry. A unique feature of this tetrahedral nickel cluster is the isonitrile ligands that are effectively four electron donors and bridge the basal edges of the compressed tetrahedron as illustrated in Fig. 10 (*51*). This cluster structure has three different isonitrile ligand environments, one apical terminal site and three basal terminal sites and three basal bridging sites. In solution, the cluster produces a complex proton NMR spectrum fully consistent with the solid-state structure but only at low temperatures, below 10°C. At higher temperatures the complex NMR spectrum merges and collapses in a two-step process to a single resonance line signifying equivalence of ligand environments on a time-averaged (about 10^{-1} second) basis (*51, 54*). The bridging isonitrile ligands are highly mobile on the cluster surface, and the activation energy for their migration about tetrahedral edges is approximately 14 kcal/mole (*54, 71, 72*). In the second of the two-step exchange process, ligand exchange between terminal and bridge sites occurs along with another process that involves ligand dissociation

$$Ni_4(CNR)_7 \rightleftharpoons Ni_4(CNR)_6 + RNC \qquad (8)$$

a reaction key to the cluster catalytic properties (*54, 71*).

The reactivity of the nickel clusters has been both a delight, in the analogy to a reactive metal surface, and a frustration, with respect to experimental difficulties (the clusters literally can be used to titrate traces of oxygen in our "inert" atmosphere glove boxes). Small donor molecules like oxygen and carbon monoxide irreversibly destroy the cluster molecules but fortunately other catalytically important molecules like olefins, acetylenes, and hydrogen do not destroy the cluster. We have found that $Ni_4[CNC(CH_3)_3]_7$ is an active catalyst at room temperature for a variety of chemical reactions (*51, 54*) of which the hydrogenation of acetylenes is the one most informative in a mechanistic context (*54, 71, 72*).



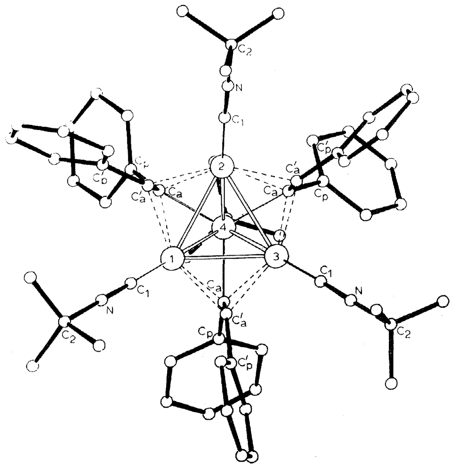


Fig. 10 (left). A representation of the structure of $Ni_4[CNC(CH_3)_3]_7$ looking down the threefold axis of the compressed tetrahedron. The unique apical nickel atom is labeled 4, and the basal nickel atoms are numbered 1 through 3. Hydrogen atoms of the tertiary butyl groups are not depicted. The three isonitrile ligands that bridge the basal edges of the tetrahedron are effectively four-electron donors whereas the four terminally bound isonitrile ligands are two-electron donors. Because there was a disorder in the crystal used in the crystallographic study, a precise characterization of the unique bridging isonitrile ligand atom positions was not feasible (*51*). The apical to basal nickel-nickel distances are very short, ~ 2.34 Å. Fig. 11 (right). The tetrahedral $Ni_4[CNC(CH_3)_3]_4[C_6H_5C{\equiv}CC_6H_5]_3$ structure (*52*). The nickel atoms lie nearly at the vertices of a regular tetrahedron, and each has a terminally bound isonitrile ligand. In this view, the unique nickel atom, labeled 4, is in the center and lies on a threefold axis. Each of the unique basal edges of the Ni_4 tetrahedron are symmetrically bridged by diphenylacetylene molecules. In these acetylene ligands, the acetylenic carbon atoms, C_a and $C_{a'}$, are bonded to basal and apical nickel atoms. The $C_{a'}$ carbon atom, nearer the reader, is bound to two basal nickel atoms, and the C_a carbon atom, farther away, is bound to two basal nickel atoms and to the apical nickel atom. Here, the acetylene formally is a four-electron donor ligand. The acetylenic carbon-carbon distance is 1.344 Å. Hydrogen atoms associated with the ligands are not shown.

Dialkylacetylenes and hydrogen are cleanly converted to *cis*-olefins by the $Ni_4(CNR)_7$ catalyst and the catalyst is completely recovered from the reactions (*54, 71*). Hydrogen alone does not react with $Ni_4[CNC(CH_3)_3]_7$ but the acetylenes react directly with the nickel cluster as evidenced by the solubilization of the cluster by acetylene interaction in nonpolar solvents and by NMR spectra studies. The nature of this reversible interaction is best illustrated for a related system based on diarylacetylenes, which also are catalytically hydrogenated to *cis*-olefins. Diphenylacetylene alone reacts with $Ni_4[CNC(CH_3)_3]_7$ to form as shown in Eq. 9

$$4Ni_4(CNR)_7 + 15C_6H_5C{\equiv}CC_6H_5 \rightarrow 12(RNC)_2Ni(C_6H_5C{\equiv}CC_6H_5) + Ni_4(CNR)_4(C_6H_5C{\equiv}CC_6H_5)_3 \qquad (9)$$

$$(R{=}C(CH_3)_3 = \text{tertiary butyl})$$

a monometal acetylene complex and a tetrahedral tetrametal tris-acetylene cluster (*52*). The mononuclear nickel acetylene complex is unreactive toward hydrogen from 0°C to approximately 80°C, and above this temperature the complex decomposes to form what appears to be a tetranuclear cluster,

$$Ni_4(CNR)_6(C_6H_5C{\equiv}CC_6H_5)$$

which then reacts with hydrogen to yield the olefin *cis*-stilbene,

$$C_6H_5CH{=}CHC_6H_5$$

(*71*). In sharp contrast, the cluster product of Eq. 9

$$Ni_4(CNR)_4(C_6H_5C{\equiv}CC_6H_5)_3$$

reacts with hydrogen at 20°C to give *cis*-stilbene. Crystallographic analysis (*52*) of this tetranuclear nickel-acetylene cluster provided a rather illuminating snapshot of acetylene activation mediated through multimetal atom interaction. There is a tetrahedral array of nickel atoms with the acetylene molecules bound in a three-metal centered π^2 fashion analogous to that in Fig. 7 for an iron complex, $Fe_3(CO)_9(RC{\equiv}CR)$. In this acetylene cluster structure (Fig. 11), the acetylenic carbon-carbon bond distance has been increased to 1.344 Å. Thus, the poly(three)metal interaction of an acetylene should substantially increase the susceptibility of the acetylene toward reduction (hydrogenation). Since the $Ni_4(CNR)_4(C_6H_5C{\equiv}CC_6H_5)_3$ cluster is directly reduced by hydrogen to give *cis*-stilbene and since it can be used as a catalyst for acetylene hydrogenation, the cluster is properly described as a catalyst intermediate.

This very simple nickel cluster system

is beginning to reveal some mechanistic details of a catalytic reduction of a molecule with a triple bond and the general outlines may set a reasonable scenario for analogous metal surface reactions.

Problems in the Analogy

Like the above nickel clusters, nickel and other metals are effective catalysts for the hydrogenation of acetylenes although they are not selective to the formation of *cis*-olefins unless the surface is modified by prior reaction with nitrogen or sulfur compounds. However, in the reaction of a clean metal surface, for example a clean platinum surface, with acetylene, HC≡CH, there is an initial and irreversible reaction. Further reaction of acetylene and hydrogen at the surface does lead to catalytic hydrogenation, but that first layer of chemisorbed acetylene remains untouched (*73*). In fact, all metal and even metal oxide catalysts seem to retain a superstructure of carbon atoms in many catalytic reactions of organic molecules. Perhaps catalysis occurs at defect (in the overlayer) sites where there may be metal-molecule reactions unimpeded by the overlayer. In the dehydrogenation of hydrocarbons and cycloalkenes, like cyclohexene, over a platinum metal surface, a carbonaceous or graphitic overlayer develops, but "islands" of platinum clusters obtrude and these may be the active sites as suggested by Somorjai (*74*). In any case, these overlayers or superstructures seem to have no analogs in our cluster catalysts. If the overlayers themselves should prove to be the active sites, our analogy may be seriously flawed.

Metal clusters may fragment at some step in a catalytic cycle to give reactive mononuclear intermediates (*57*). Such a process, which has no precise analog in surface chemistry, may be based on very short-lived intermediates. In this case, experimental delineation of the mononuclear intermediates may be difficult.

Summary and Conclusions

Discrete metal clusters would appear to provide reasonable approximations of the chemisorbed state for metal or metal oxide surfaces in the full molecular regime of structure, stereochemistry, ligand (chemisorbed molecule) mobility, and chemistry. Cluster chemistry has a great potential in modeling the chemisorption and catalytic processes at a metal surface. However, it is neither a panacea nor a substitute to the ongoing studies of surface physics and chemistry, but, rather, it is a valuable adjunct to the latter. Modeling of this character is only an approximation, albeit a valuable and insightful one. Future research, strongly collaborative with surface scientists so as to achieve close correspondence between the cluster and surface studies, should establish the boundary conditions of validity for the cluster-surface analogy.

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60. Alternatively, copper-zinc oxide-on-alumina is used.
61. The triple bond in carbon monoxide is thermodynamically the strongest known chemical bond. The hydrogenation reactions which produce methanol (Eq. 4) and methane (Eq. 5) are both thermodynamically favorable.
62. A transition state, unlike an intermediate, is represented by a maximum in the potential energy surface for the reaction system, and it has no significant lifetime.
63. Interaction of the oxygen atom, of the carbon monoxide molecule, with a second metal atom seems to be a necessary step in methane formation, whether it occurs before or after addition of hydrogen to the complexed carbon monoxide molecule commences.
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Science in the White House: A New Start

Lewis M. Branscomb

The story is told that young King Solomon was given the choice between wealth and wisdom. When he chose wisdom, God was so pleased that he gave Solomon not only wisdom but wealth also. So it is with science.—ARTHUR HOLLY COMPTON (*1*)

Many scientists believe that all society should expect from science is access to the knowledge and understanding that comes from searching for truth. Certainly science has been given too much credit—and too much blame—for the uses of technology and their effects on the well-being of mankind. To be true to its own principles and promise, the world scientific community must sustain its commitment to the fullest possible understanding of man and nature. But what assurance can we have of the continued commitment of the public and its political leadership to the health of the scientific and technical enterprise?

The commitment of science to the search for truth does not free the scientist from the obligation to participate in the process through which scientific knowledge is applied. Scientists should, of course, be wary of imposing their values on others, of assuming that they know the right path for mankind to follow. But we scientists must realize that hope for a better life for future generations depends on public conviction that this hope is realistic, that there are alternatives to a Malthusian destiny. Thus the values of contemporary society are as much a consequence as a source of the commitment of science to human betterment.

American science continues to have much to contribute to the well-being of humanity. The challenges of energy, raw materials, environment, health, jobs, and improving the quality of life call for imaginative new solutions. Our industrialized trading partners pay us the compliment of emulating our tradition for innovation. The Japanese and West Germans have been particularly successful, and this success is a matter of great national pride. Communist nations place a high value on developing relationships through which they may share in American technological experience. The developing nations are particularly insistent on accelerating their own ability to ab-

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