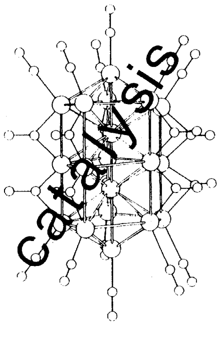
Clusters Provide Unusual Chemistry

Organometallic clusters provide models for the reactions at metal surfaces, and may be a way to produce new types of catalysts



They are beautiful to behold, stimulating to contemplate, challenging to work with, and, perhaps best of all, they can be put in a bottle. "They" are organometallic clusters, "small chunks of metal that you can handle in solution and study a little more effectively than you can a sheet of metal or a big glop of metal on the surface of some kind of support," in the words of George W. Parshall of the Du Pont Company. The study of these clusters is one of the fastest growing areas of chemistry.

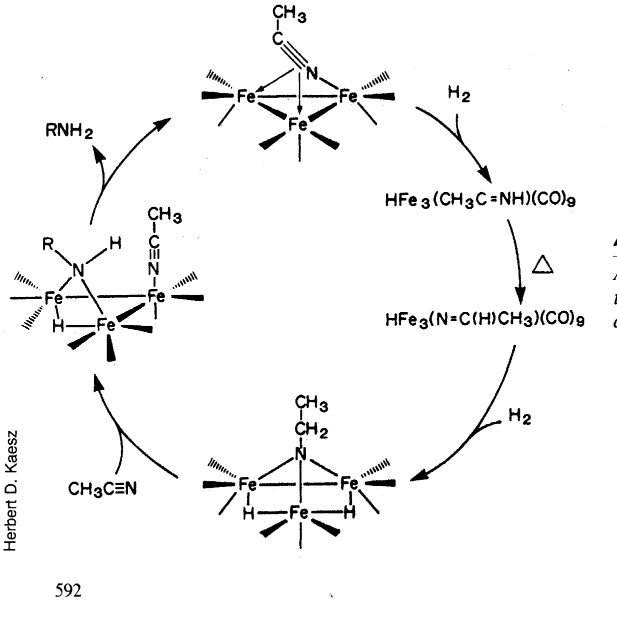
Because organometallic clusters can be synthesized relatively easily and their structures can be determined precisely, many investigators say that their study should provide crucial information about the nature of heterogeneous catalysis on those "big globs of metal," where reactions and intermediates are far more difficult to identify. Many investigators also believe that such study will open new avenues to the synthesis of more traditional types of catalysts, and perhaps to major new classes of catalysts that are more selective than existing ones.

Whether the clusters can fulfill these expectations is still an open question, however, and opinions are fairly sharply divided. One critic is Robert L. Burwell, Jr., of Northwestern University, who argues that the work on organometallic clusters "has led to nothing. It is like a promising young child—it keeps on promising, maybe for too long." Adds Alan Brenner of Wayne State University, "My general feeling is that there has been much overselling."

Such gloomy views seem to be held only by a minority, however. Parshall calls some of the new work by Earl L. Muetterties of the University of California, Berkeley, and John S. Bradley of Exxon Research and Engineering Company "quite a significant kind of chemistry and a major achievement." Bruce C. Gates of the Center for Catalytic Science and Technology at the University of Delaware, is particularly optimistic about the impact of clusters on studies of the interaction between catalysts and supports: "There have been many disappointments in the past, but the new clusters have reduced it to a chemistry problem and we can expect rapid progress now. I see clear sailing ahead."

Muetterties, who has become something of an unofficial spokesman for cluster chemistry, remains optimistic. Organometallic clusters, he says, "provide an excellent basis for understanding the metal-metal bond in a complete structural, electronic, and chemical sense. . . . These fundamental data are invaluable background information for interpretation of molecular details of surface chemistry."

The first synthesis of transition metal carbonyl clusters (those in which a carbon monoxide molecule is attached to the metal atom as a ligand) was performed in the late 1950's by Walter Hieber and his colleagues at the Technische Hochschule in Munich. Their discoveries were virtually ignored, says Muetterties, and related syntheses during the next decade "largely were accidents." Interest in the clusters did not pick up until the late 1960's, when organized programs to prepare transition metal clusters were initiated by the late Paolo Chini of the University of Milan and Lawrence F. Dahl of the University of Wisconsin. Their work was aided by the rapid development of computer procedures and hardware that made x-ray crystallographic analysis relatively quick and inexpensive. X-ray analysis of clusters is now routine at most of the laboratories where clusters are studied.



Herbert D. Kaesz

A potential cycle

A potential catalytic cycle for the reduction of acetonitrile by a triiron cluster.

The metal atom framework in these clusters is, in many cases, a fragment of a hexagonal or cubic close-packed crystal or of a body-centered cubic crystal, the same types of ordered arrangements that are found in bulk metal. These configurations maximize metal-metal interactions, making the structure more stable. One of the largest clusters known $[Pt_{38}(CO)_{44}H_x]^{2-}$ synthesized in Milan, has cubic close-packed structure.

In metal carbonyl clusters, as well as in most other clusters, the metal-metal bond lengths are similar to those in the bulk metal; in a few cases they may be as much as 10 percent longer. Also like bulk metals, the organometallic clusters can incorporate various atoms, including those of other metals, in their interstices, the spaces within the metal framework. In virtually all cases, the clusters have a design and symmetry that could qualify them for a spot in an art gallery.

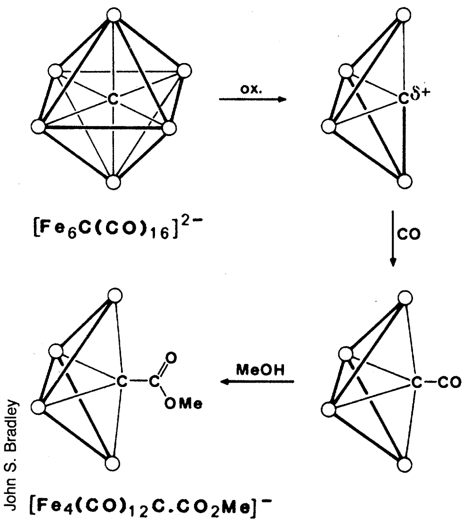
By far the largest class of organometallic clusters that have been investigated so far are the metal carbonyl clusters. Unfortunately, says Muetterties, "none of the known metal carbonyl clusters appears to possess high catalytic reactivity and most of the reported reactions that used these catalysts required relatively high temperatures"—a condition under which many of the clusters fragment into mononuclear species (complexes containing only one metal atom). That does not mean that the clusters are not useful. In fact, they provide good models for what happens at the surface of classical metal catalysts.

With the exception of a few very simple cases,* little is known about the nature of chemical intermediates at the surface of metals. "Most of what we know," says Parshall, "is by inference. The closest approximation to those intermediates that we have are the bonds in metal clusters." Adds Muetterties: "For the few surface cases where they have found how carbon monoxide or other carbon moieties are bonded to a metal surface, there is a model for every one in clusters. Even the C–O stretching frequencies for analogous species are similar in the two regimes. You can find a cluster model for any surface species that has been established."

One of the best examples of this, says John R. Shapley of the University of Illinois, is the bonding of ethylene to the (111) surface of platinum. Gabor A. Somorjai of the University of California, Berkeley, and Harold E. Ibach of the University of Jülich in West Germany have found that the molecule is bound as an ethylidyne moiety in which the terminal carbon is bound equidistant from three platinum atoms and the carbon-carbon bond is perpendicular to the metal surface. Norman Sheppard of the University of East Anglia and others have observed an identical geometry and similar vibrational spectra for the binding of ethylidyne to triosmium and tricobalt clusters.

Such findings give confidence that the intellectual process can be carried out in the reverse direction. "When scientists trying to establish structure and stereochemistry for a molecule bonded to a surface develop a set of data and postulate a model," says Muetterties, "very often they can go back to cluster chemistry, find that model, and make a comparison of the spectroscopic data. . . . If there is a close correspondence, then there is a good chance that their model is correct."

The low-temperature stability of the metal carbonyl clusters that makes it possible to isolate and characterize them is also their downfall when it comes to catalysis. The clusters are stable in large part because the metal atoms are coordinately saturated—that is, all possible binding sites of the metals are occupied. On the surface of a working metal catalyst, in contrast, a significant proportion of the metal atoms are coordinately unsaturated and can therefore bind reactants. The hydrogenation of a carbon monoxide molecule bound to a metal surface, for example, probably requires binding of a hydrogen molecule to an adjacent metal atom, and subsequent transfer of a liberated hydrogen atom to the carbon atom. Because there are no open binding sites on adjacent metal atoms in the clusters, this reaction does not occur easily.



John S. Bradley

"A reactive carbon indeed"

Carbide chemistry on the surface of a tetrairon cluster.

If one of the carbonyl ligands could be displaced easily to generate a coordinately unsaturated metal, catalysis might occur. Unfortunately, the metal-metal and metal-carbonyl bond energies are about the same in most metal carbonyl clusters, and the magnitudes of those energies are small compared to those of bonds between elements in the first and second rows of the periodic table—the C–C, C–H, C–O, and C–N bonds that are of most interest in catalytic chemistry.

The net effect is that conditions which might displace a carbonyl ligand from the cluster are just as likely to cleave a metal-metal bond, destroying the cluster. Metal-metal bond energies do increase going down any column in the periodic table; they are also highest in the center columns of each row. The confluence of these trends in iridium and osmium means that they exhibit the highest metal-metal bond energies in clusters. This is a major reason why many investigators study clusters based on these two metals despite their rarity and associated high cost.

The fragility of most clusters under potential reaction conditions introduces the problem, says M. Frederick Hawthorne of the University of California, Los Angeles, of determining "whether the cluster is actually catalyzing the reaction in question or whether it merely serves as a depot for a more reactive fragment." In many cases, adds Herbert D. Kaesz of the same school, "the clusters may be nature's little red herring."

The classic example of this problem involves the cluster $Ru_3(CO)_{12}$. In 1975, Christopher Masters of Shell Chemicals U.K., Ltd., thought that he observed Fischer-Tropsch chemistry—the production of hydrocarbons from a mixture of carbon monoxide and hydrogen (syngas)—catalyzed by the cluster in solution. This was surprising because no one had previously observed Fischer-Tropsch chemistry with a homogeneous catalyst. Closer study by Bradley and investigators at Shell, however, showed that, in an excess of hydrogen, the cluster dissociates and small crystallites of ruthenium are deposited on the walls of the reaction vessel. It was these crystallites that catalyzed the Fischer-Tropsch chemistry, not the cluster; if the metal is kept in solution, only methanol is produced. If iodide is added to the reaction medium as a promoter and the reaction is conducted in an acidic medium, the cluster catalyzes synthesis of ethylene glycol (a product not produced from syngas by heterogeneous catalysts) and ethanol in a ratio of 40:60. "If those proportions could be reversed," says Kaesz, "you would have a commercial process." Even in this case, however, the ruthenium cluster fragments and it is not clear which is the catalytic species. The second lesson from this episode, then, is that small clusters make it easier to define reaction mechanisms.

The coordinately saturated clusters can have some chemistry despite their lack of binding sites, Kaesz has found. The carbonyl moieties attached to the metal atoms are activated by the bonding and can be attacked by nucleophiles. Methyllithium, for example, attacks one of the carbonyl carbons in $Os_3(CO)_{12}$ to form an acyl group (CH_3CO–) that bridges a metal-metal bond; that is, the carbon is bonded to one metal atom and the oxygen to an adjacent atom. Similar reactions are observed with other nucleophiles, such as amines and alcohols, and with the corresponding ruthenium cluster $Ru_3(CO)_{12}$. When a second acyl group is formed, however, the cluster falls apart, indicating, Kaesz says, that "the clusters are not as robust as was thought." This type of reaction is "unique to condensed solution systems," he adds, and has not been observed with single metal centers.

Kaesz has also synthesized a series of triiron clusters (see figure) that illustrate the stepwise reduction of acetonitrile on the face of a triiron complex. These reactions are not catalytic, but the individual reactions, Kaesz argues, provide an insight into how the reactions occur on the surface of a metal.

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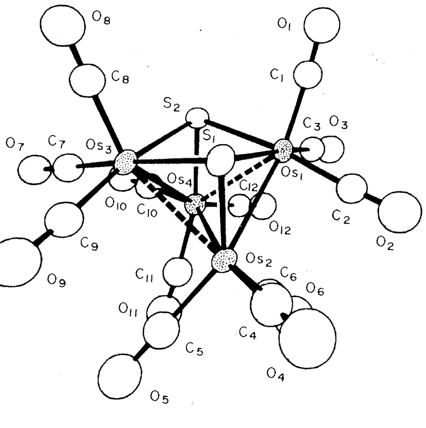
*Some are discussed in earlier articles in this series: 4 February, p. 474; 25 February, p. 944; and 25 March, p. 1413.

Many investigators have attempted to overcome the lack of reactivity of the clusters by producing coordinately unsaturated clusters, either by direct synthesis or by generating them in situ. This is not a simple task, says Muetterties, because the compounds "should be—and are—very reactive." One possible way to do this would be to replace one or more carbonyls with a ligand, such as acetonitrile, that binds more weakly than carbon monoxide so that a metal-ligand bond is broken in preference to a metal-metal bond. Both Shapley and Jack Lewis and B. F. G. Johnson of Cambridge University have succeeded in introducing two acetonitrile ligands into triiron and triosmium clusters, but the resultant clusters have displayed no unusual catalytic chemistry.

Another approach is to introduce ligands that bind to the metals more strongly and that can bridge metal-metal bonds. In this case, the bridging ligand holds the cluster together even when metal-metal bonds have been cleaved.

Muetterties has been working with dirhodium and trirhodium clusters that function according to this principle; each of the metal atoms in these clusters has an "open" coordination site. Typical examples are $\{(\mu\text{-H})Rh[P(OC_3H_7)_3]_2\}_2$ and $\{(\mu\text{-H})Rh[P(OCH_3)_3]_2\}_3$, which he characterizes as "exquisitely reactive."† These clusters catalyze the hydrogenation of both alkynes and alkenes at significant rates even at low temperatures, about −80°C. The dimer catalyzes alkene hydrogenation at a rate about an order of magnitude faster than the rate at which it catalyzes alkyne hydrogenation. Nevertheless, says Muetterties, "if the dimer is presented with hydrogen and a mixture of internal alkene and alkyne, the alkyne is hydrogenated first to give the corresponding alkene." Furthermore, the alkene is produced in the *trans*-configuration, "a unique catalytic result in that all other reported molecular and solid state systems produce *cis*-alkenes as the first product."

Muetterties believes that the catalysis is carried out by the cluster. "The data are consistent with a cluster-based catalytic reaction, but I can't say that we've proved that. . . . It is very difficult to establish unequivocally that a cluster is a catalyst. You can only disprove it." He also concedes that the catalyzed reactions are "not themselves useful, but they do show that the concept works." They also demonstrate that "unique catalytic reactions can be realized with clusters wherein more than one metal atom takes part in a catalytic reaction."



Richard D. Adams

An electronic flip-flop

This cluster has five metal-metal bonds and obeys the skeletal electron pair rule. When a carbonyl moiety is added, the two long bonds indicated by the dashed lines are broken and the cluster obeys the 18-electron rule.

Gregory L. Geoffroy and his colleagues at Pennsylvania State University have synthesized a series of bimetallic cluster compounds containing iron and rhodium or iron and iridium in which each metal atom is coordinately unsaturated. A typical compound is $FeRh[\mu\text{-}P(C_6H_5)_2](CO)_4[P(CH_2CH_3)_2]_2$, in which the phosphido group bridges the two metals so they cannot separate. These compounds undergo rapid and reversible ligand additions and oxidative-addition reactions, but these investigators have just begun seeking catalytic reactions.

Bradley has been working with iron clusters containing a bare carbon (carbide) atom. The parent compound is $[Fe_6(CO)_{16}]^{2-}$, in which the carbide is encapsulated within the octahedral metal cage and is therefore unreactive. Oxidation of the cluster with tropylium bromide splits off two of the iron atoms to expose the carbide; the resultant cluster can readily be converted to $Fe_4C(CO)_{13}$, in which, Bradley says, the carbide atom is "a very reactive carbon indeed." It reacts with gaseous hydrogen to form a methylidyne group, with carbon monoxide and alcohols to form esters, with carbon monoxide and amines to form amides, and with carbon monoxide and alkylating agents to form ketones. Many of these compounds can easily be further derivatized while bound to the cluster. The compounds can be split off by the addition of hydrogen, but the cluster cannot be forced through the cycle again, and therefore the reactions are not strictly catalytic.

But they are important, Bradley argues. "We've been able to see some unique carbon chemistry that takes place because the carbon is situated on a cluster. This chemistry has not been observed in mononuclear systems, so it is one of the relatively few examples of organometallic chemistry on clusters that is radically different from what goes on in mononuclear systems." The clusters, he continues, "are at least a structural and maybe a reactivity model for carbon atoms on surfaces. Now that is a very important thing because carbon atoms on iron, for example, are believed to be the initiation point for Fischer-Tropsch synthesis." Shapley has observed some related chemistry in the interconversion of methyl, methylene, and methylidyne ligands in clusters such as $HOs_3(CO)_{10}(CH_3)$, $H_2Os_3(CO)_{10}(CH_2)$, and $H_3Os_3(CO)_9(CH)$. The first cluster is unusual in that the methyl bridge involves not only an Os · · C · · Os interaction, but also an Os · · C–H · · Os bridge.

Richard D. Adams of Yale University and Heinrich Vahrenkamp of the University of Freiburg have independently synthesized organometallic clusters that, like Geoffroy's, show facile, reversible addition of carbon monoxide and other ligands, but apparently through a previously unsuspected process. Adams has worked with clusters such as $Os_4(CO)_{12}(\mu_3\text{-}S)_2$, and Vahrenkamp has worked with clusters like $Fe_4(CO)_{11}(PC_6H_5)$. In each case, the ability of the cluster to add ligands can be attributed to a change in the electronic structure of the metal cage.

In the tetraosmium cluster, for example, electron counting shows that the metal cage contains 64 electrons. If each metal atom were to obey the so-called "18-electron rule" that is generally accepted to govern the bonding of metal complexes, this cluster would contain only four metal-metal bonds. X-ray crystallography, however, shows that there are five such bonds. This particular configuration can be rationalized by an alternate hypothesis known as the skeletal electron pair theory. This theory says that a cluster with this structure should be stable with eight pairs of skeletal electrons; in fact, the tetraosmium cluster has eight pairs of electrons.

Several clusters that obey the skeletal electron pair rule have recently been found, which is "surprising," Adams says, because the rule was developed to explain bonding in electron-deficient boron hydride complexes and organometallic clusters are electron-rich.

The key point, he continues, is that when a carbonyl ligand is added to the tetraosmium cluster, two metal-metal bonds are broken, and the cluster then

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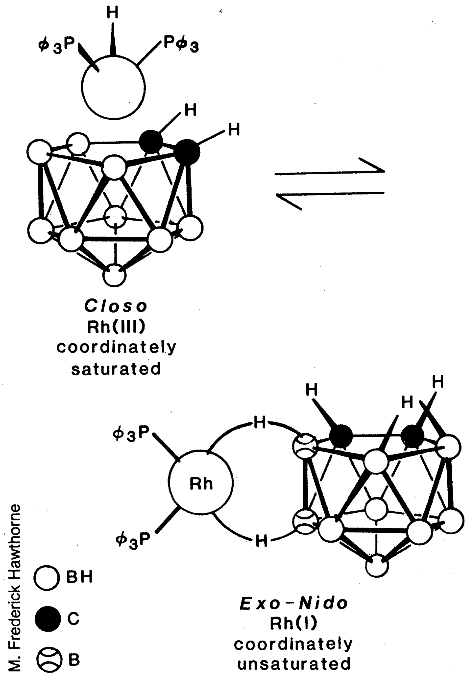
†The qualifier μ_x denotes a ligand that is bridge-bonded between x metal atoms; if there is no subscript, x is taken to equal 2. The qualifier η^x denotes that x ligand atoms are bonded to one metal atom.

obeys the 18-electron rule. When the new cluster is heated, the added carbon monoxide is expelled, and the metal cage reverts back to the structure that obeys the skeletal electron pair rule. A similar type of flip-flop is also observed in Vahrenkamp's tetrairon cluster. This ability to flip-flop between the two stable electronic configurations via addition and elimination of small molecules, Adams says, "could have major implications for catalysis."

Hawthorne has synthesized an 18-electron rhodium(III) cluster, *closo*-3,3,-$[P(C_6H_4)_3]_2$-3-H-3,1,2-$RhC_2B_9H_{11}$, and an extensive series of related species that exhibit an analogous behavior and that function as effective catalysts for alkene isomerization, hydrogenation, and other reactions under very mild conditions. The cluster "shouldn't be a catalyst," Hawthorne says, because of the stable electronic configuration of the rhodium center. He and his colleagues also observed, however, that substitution of alkyl groups on both carbon atoms of the carborane cage enabled them to isolate and characterize the corresponding 16-electron rhodium(I) *exo-nido* species (see illustration).

The *exo-nido* species are catalytically active and display all the kinetic characteristics of the *closo* species in alkene isomerization and hydrogenation reactions. This suggests, Hawthorne says, that the *closo* species is in equilibrium with a spectroscopically invisible and catalytically active *exo-nido* tautomer of similar structure. Says Hawthorne: "I like to think of it as a retractable catalytic center."

These novel rhodacarborane clusters catalyze a number of interesting reactions. In the absence of hydrogen, they convert 1-hexene to 2-hexene very rapidly, with *cis* and *trans* isomers occurring in the thermodynamically controlled ratio of 1:2. If bulky organic substrates are substituted on the carborane cage, however, the *cis:trans* ratio is changed to 6:1. The clusters will hydrogenate terminal olefins selectively. In a most unusual reaction, they will catalyze the hydrogenolysis of O–C bonds in alkenyl carboxylates. In the presence of hydrogen, vinyl acetate, for example, is converted to ethylene and acetic acid. Some metal hydrides can carry out this reaction stoichiometrically, Hawthorne says, but a catalyzed reaction has never been observed before.



M. Frederick Hawthorne

"A retractable catalytic center"

A small amount of the inactive closo *tautomer is converted to the catalytically active* exo-nido *tautomer in solution.*

Two final potential advantages of organometallic clusters deserve mention. First, it is possible to combine in a metal cluster two metals that do not form alloys and are thus difficult to combine in conventional catalysts. This may make it possible to observe unusual catalytic reactions. Second, the organometallic cluster can potentially be attached to a solid support to produce what Gates terms "a unique metal species." This may make it possible to create heterogeneous catalysts with precisely controlled composition; it also makes it possible to vary the composition systematically. The bonded cluster may remain intact or some of the ligands may be removed to create coordinately unsaturated sites.

Shapley has synthesized a series of clusters containing tungsten and iridium in various proportions. These include $(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}$, $(\eta^5\text{-}C_5H_5)_2W_2Ir_2(CO)_{10}$, and the known clusters $Ir_4(CO)_{12}$ and $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$. They have not been able to prepare the W_3Ir cluster. These clusters were deposited on alumina supports and heated to produce coordinately unsaturated sites. Their activities for the hydrogenolysis of butane were then compared.

Butane hydrogenolysis can take two courses. If the molecule is split in the middle, each butane molecule yields two ethane molecules; if it is split at one end, it yields one methane and one propane molecule. Iridium crystallites on a support produce about 75 percent ethane; tungsten does not catalyze the reaction. Catalysts prepared from Ir_4 and WIr_3 clusters also produce about 75 percent ethane. The catalyst prepared from the W_2Ir_2 cluster, however, produces only 45 to 50 percent ethanes, indicating that the selectivity has changed. Conventional catalysts produced from equimolar mixtures of tungsten and iridium, in contrast, produce 75 percent ethanes. These results, Shapley says, "support the idea that the overall approach of using a preformed organometallic to generate catalytic sites could have utility in terms of control of the nature of those sites."

Gates has been trying to stabilize clusters on the surfaces of oxide supports. In most cases, however, heating the cluster above about 120°C causes metal-metal bonds to rupture, leaving an ensemble of metal ions electrostatically bonded to the support. Usually, these metal ions sinter (aggregate) to form "globs" of traditional metal catalyst. The two exceptions Gates has observed are a triosmium carbonyl cluster on the surface of magnesium oxide and a ruthenium-triosmium carbonyl cluster on aluminum oxide. The first cluster is stable to at least 270°C in carbon monoxide and hydrogen, and catalyzes the Fischer-Tropsch production of hydrocarbons. "It's not a particularly interesting catalyst and the selectivity is not good," says Gates, "but it is a catalyst and that is what is important."

Gates and his colleagues have also studied ensembles of osmium atoms on supports produced from clusters containing different numbers of osmium atoms. They find, as they suspected, that catalytic activity does vary with the number of atoms. When they studied the hydrogenolysis of butane, for example, the catalyst derived from $H_2Os(CO)_4$ had very low activity and worked only at higher temperatures. Catalysts prepared from $Os_3(CO)_{12}$ and $Os_6(CO)_{18}$ had increasing activity with increasing size of the ensemble. Interestingly, a supported triosmium carbonyl cluster had two to four times as much activity as the ensembles in a different reaction, isomerization of 1-hexene, although it was less active than traditional catalysts.

The study of organometallic clusters is obviously still in its infancy and many questions remain to be resolved. Nonetheless, it would appear that the doubts of the naysayers are being overcome. For the moment, Gates says, the primary motivation for studying the clusters is intellectual, but it is becoming increasingly likely that the practical applications will follow.—**THOMAS H. MAUGH II**

Additional Readings

1. E. L. Muetterties, *Chem. Eng. News* (30 August 1982), p. 28.
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3. B. F. G. Johnson and J. Lewis, *Adv. Inorg. Chem. Radiochem.* **24**, 225 (1981).
4. B. F. G. Johnson, Ed., *Transition Metal Clusters* (Wiley, New York, 1980).