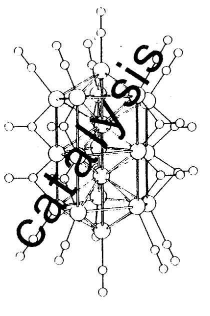
# Homogeneous Catalysis: Ultimate Selectivity

## *By using single metal atoms in solution, it is often possible to carry out specific reactions to the exclusion of all others*



It is rare when good analogies can be drawn between art and science. A good case can be made, however, for a relationship between the study of catalysis and Ravel's "Bolero." In the latter, an initial theme is laid down by flutes and then repeated, first by an oboe, then by a clarinet, then again and again by other woodwinds, separately and together. Eventually the melody is taken up by the strings, again individually and in various combinations, adding texture and definition. Meanwhile, the percussionists and, later, the horns hammer out a steady rhythm that binds the individual repetitions together until, finally, the whole orchestra joins in a thunderous conclusion.

So, too, with catalysis. In this case the theme is a simple one: selectivity, selectivity, selectivity. The theme was first laid down around the turn of the century when Friedrich Ostwald demonstrated that a platinum gauze could oxidize ammonia to nitric oxide selectively. That theme has been repeated many times as scientists have searched for agents that will enhance the rate of desired reactions without affecting competing ones. It was taken up first in heterogeneous catalysis by investigators who sought smaller, better defined aggregates of metal—progressing from metal particles to supported metal crystallites to supported microcrystallites—searching always for that elusive specificity that can spell the difference between academic curiosity and commercial viability.

That theme was taken up again and given counterpoint in studies of organometallic clusters, where still smaller numbers of metal atoms could be combined and manipulated in attempts to increase selectivity. These organometallic systems were also easier to study and provided insight into reactions occurring at the surface of metals. These clusters, like the horns and percussion, provided a bridge between heterogeneous and homogeneous catalysis.*

Homogeneous catalysts, then, are the string section of the piece, providing the ultimate definition of the theme by using complexes containing only one or two metal atoms to achieve the greatest selectivity possible. "The great thing about these catalysts," says George M. Whitesides of Harvard University, "is that you can tinker with the ligands to increase selectivity even more." Because some of these catalysts are relatively simple, furthermore, they are often the first choice for studying the mechanism of catalytic reactions. "The record of accomplishment in this field in recent years is quite impressive," says Jack Halpern of the University of Chicago.

Homogeneous catalysis, by definition, involves catalytic reactions in which all the participating species are in solution. "Prior to 1970," says Bruce C. Gates of the Center for Catalytic Science and Technology at the University of Delaware, "the term homogeneous catalysis usually denoted acid-base catalysis, and this [remains] the best understood kind of catalysis. Since then, however, homogeneous catalysis has come to connote primarily transition-metal-complex catalysis, which has been the object of intensive research." Strictly speaking, the term also includes the organometallic clusters, but many investigators prefer to consider clusters containing three or more metal atoms as belonging to a more or less separate category.

Hydrocarbation is a "new carbon-carbon bond-forming reaction unlike anything to date."

"There was a tremendous burst of activity around 1970, when five or six major new homogeneous processes were brought on stream," says George W. Parshall of the Du Pont Company. In most cases, the driving force for use of the new processes has been economic. When a reaction can be carried out either heterogeneously or homogeneously, says Halpern, the homogeneous version usually proceeds under less severe conditions—at lower temperatures and pressures. Lower temperatures usually lead to greater selectivity and lower pressures mean that less capital investment is required for construction of high pressure containment vessels.

Most catalytic reactions are exothermic, adds B. Duane Dombek of Union Carbide Corporation, "and it is easier to remove excess heat in a homogeneous system, reducing the need for expensive heat-exchangers." Counterbalancing these advantages, however, is the difficulty of separating the catalyst from the product. If the product cannot be distilled away from the catalyst or separated easily in some other fashion, the economic benefits of homogeneous catalysis may be lost in the added expense of product recovery and greater use of catalyst. To overcome this problem, many companies are investigating systems in which a homogeneous catalyst is linked to a support, bringing the wheel full circle back to heterogeneous catalysis.

The homogeneous systems commercialized during that period include:

- The use of Wilkinson's catalyst, $RhCl[P(C_6H_5)_3]_3$, to mediate the hydrogenation of olefins. This complex was first reported in 1966 by Sir Geoffrey Wilkinson and his colleagues at the University of London, and was the first successful homogeneous hydrogenation catalyst.
- The Shell higher olefin process, in which a proprietary nickel complex, among others, is used to convert ethylene to $\alpha$-olefins containing 10 to 14 carbon atoms.
- The Monsanto process for production of acetic acid from methanol and carbon monoxide, catalyzed by $RhCl_3$ and iodide.
- The Union Carbide "oxo" process for hydroformylation of alkenes, catalyzed by a proprietary rhodium complex. Propene, for example, is converted to *n*-butyraldehyde, a major source of four-carbon fragments in the chemical industry. The rhodium complex replaced a cobalt complex that required more rigorous conditions.
- The Du Pont process for hydrocyanation of butadiene to give adiponitrile, a precursor of the hexamethylenediamine used in nylon production; the reaction is catalyzed by a proprietary zerovalent nickel catalyst.
- The Monsanto process in which an asymmetric rhodium complex is used to

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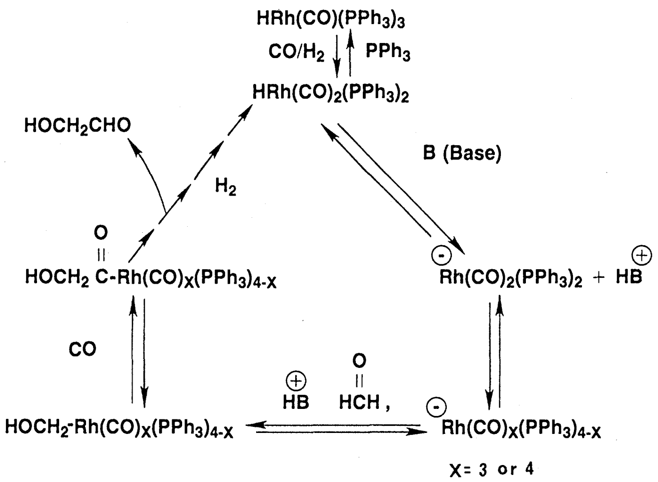
*Previous articles in this series appeared on 4 February, p. 474; 25 February, p. 944; 25 March, p. 1413; and 6 May, p. 592.

**Ethylene glycol**

*The proposed process for making a glycolaldehyde precursor of ethylene glycol, as developed by Albert S. C. Chan of the Monsanto Company.*



Monsanto Company

catalyze the asymmetric hydrogenation of an appropriately substituted olefin to give L-dopa, a drug used in treatment of Parkinson's disease. This accomplishment, says Gates, represents "perhaps the most sophisticated molecular design of a technological catalyst."

These and other homogeneous processes now account for between 15 and 20 percent of the dollar volume of the chemical industry, according to Parshall. But since the early 1970's, he adds, there has been "a definite lull." The one exception is the building of an Eastman Kodak Company plant, now under construction in Kingsport, Tennessee, where a proprietary homogeneous catalyst will be used to produce acetic anhydride and related products from syngas, a mixture of carbon monoxide and hydrogen produced by gasification of coal.

It is "something of a puzzle" why this slowdown has occurred, he continues. "It may just indicate that the field is maturing, but a more likely explanation is that the economics are not good right now." A good example of the latter possibility is a well-known Union Carbide process in which $Ru_3(CO)_{12}$ and iodide are the catalysts for production of ethylene glycol from syngas. At present, the declining cost of petroleum makes it cheaper to produce ethylene glycol (which is used for antifreeze and as a precursor for other chemicals) from oil. But when petroleum prices go back up, says Dombek, this process or a similar one will almost certainly be used to make ethylene glycol from less expensive coal. The new Eastman plant represents "a special case," says Stanley W. Polichnowski of that company, because it is situated near the coalfields, the products will be used on site, and the 1:1 ratio of carbon monoxide to hydrogen in the syngas represents the exact proportions needed in the process.

The problem may also be that many types of reactions of commercial interest may simply still be too difficult to do with homogeneous catalysts. Most of the processes now in use, as is apparent from the examples, involve reactions at an olefinic double bond—"a relatively simple reaction" that can be accomplished by many different heterogeneous and homogeneous catalysts, says Whitesides. Other types of reactions, particularly those that require cleavage of strong bonds, may require more selective catalysts or reaction conditions under which the homogeneous clusters are unstable.

Nonetheless, progress is being made in many areas. This progress can be roughly subdivided into three major groups of reactions, although there is a certain amount of overlap: (i) reactions involving formation or cleavage of carbon-carbon and carbon-oxygen bonds; (ii) activation of usually inert carbon-hydrogen bonds, such as those found in alkanes; and (iii) the synthesis of asymmetric compounds. The last two will be the topic of future articles in this series.

Most of the recent progress in the first group comes in two major areas, reactions of olefins and the production of chemicals from syngas. Many of the developments show potential either as commercial processes or for use in organic synthesis.

One interesting series of catalytic reactions was developed at Allied Corporation by Guido P. Pez, who is now at Air Products and Chemicals, Inc. He and Roger A. Grey, now at ARCO Chemical Development, prepared a ruthenium complex,

$$K^+\{[(C_6H_5)_3P](C_6H_5)_2\overline{PC_6H_4Ru}H_2\}^- \cdot C_{10}H_8 \cdot (C_2H_5)_2O,$$

that can perform reductions of polar organic compounds much like the well-known $LiAlH_4$. Lithium aluminum hydride is stoichiometric, however, while the ruthenium complex is catalytic with hydrogen being the reductant.

The ruthenium complex can transfer a hydride to the carbon atom of a polar group, such as a ketone or an aldehyde, reducing them to alcohols. It can also reduce nitriles to primary amines. Reaction with an ester produces two alcohols as the principal products: methyl acetate, for example, yields methanol and ethanol. This is the only case in which this type of reduction of an ester is seen for a homogeneous catalyst, Pez says; ruthenium metal does not catalyze the reaction and the best available metal oxide catalysts can do it only under much more severe conditions. The mechanism is still unknown, but it appears that the five-membered ring containing phosphorus and the metal atom opens up to produce a coordinately unsaturated metal atom, which can then bind the substrate. The potassium ion may facilitate the reaction by tying up the alkoxide ion produced by hydride transfer.

The complex can also selectively reduce one ring of polynuclear aromatics, "a remarkable selectivity," Pez says, that cannot be achieved with heterogeneous catalysts. Halpern studied the mechanism of this reaction and found that steric hindrance causes anthracene, for instance, to be bound end-on, preventing the ruthenium from transferring a hydride to the other two rings.

Pez also found a system for aminating olefins. It is not generally possible, for example, to add ammonia to ethylene because ammonia is too weak a nucleophile. He found, however, that cesium amide ($CsNH_2$) functions as a catalyst in liquid ammonia or molten salts at moderate pressures and temperatures. The amide anion appears to attack the double bond, and the new anion thus formed abstracts a proton from ammonia to produce ethylamine and regenerate amide ion. Finally, he discovered a titanium complex, $(C_5H_5)_3Ti_2(\mu\text{-}C_5H_4)$, that homogeneously catalyzes the polymerization of acetylene to polyacetylene.† Polyacetylene can be "doped" to make it an organic conductor (*Science*, 23 April 1982, p. 399) and has potential for use in electronics.

Charles P. Casey and his colleagues at the University of Wisconsin have synthesized a diiron complex that undergoes stoichiometric rather than catalytic reactions, but that provides what Parshall terms "an intriguing bit of synthetic chemistry." The complex is $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$, in which both the

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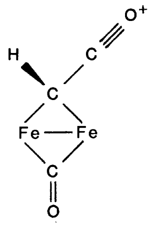
†The qualifier $\mu_x$ indicates that the ligand is bound to $x$ metal atoms. The absence of a subscript implies that $x = 2$.

carbonyl and the methylene moieties form bridges between the two iron atoms. $(C_6H_5)_3C^+PF_6^-$ abstracts a hydride from this complex to produce the cation $[(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH)]^+$, "the first methylidyne complex in which a CH unit bridges between [only] two metals." This cation reacts with carbon monoxide to produce a bridging acylium complex with the core structure



The acylium ion is readily attacked by nucleophiles; it reacts with water to give a carboxylic acid, with ammonia to give an amide, and with $K^+HB[OCH(CH_3)_2]_3^-$ to give an aldehyde. Casey suggests that investigators in heterogeneous catalysis should look for this type of acylium intermediate in Fischer-Tropsch chemistry on metal surfaces.

"But the most remarkable reactions of the bridging methylidyne complex are its reactions with alkenes," says Casey. There is a well-known reaction in synthetic organic chemistry, called hydroboration, in which a B–H group adds across the double bond of an olefin. The bridging methylidyne undergoes precisely the same reaction, adding a C–H group across the double bond; Casey calls this reaction hydrocarbation in analogy with the boron reaction. The methylidyne complex adds to ethylene, for example, to give the propylidyne complex $[(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_3)]^+$.

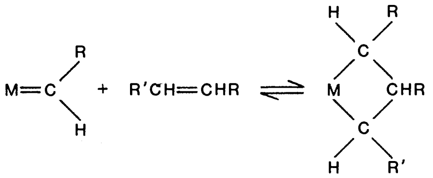
The mechanism of hydrocarbation is similar to that of hydroboration, says Casey, as are the regiochemistry and stereochemistry; "the difference is we can get some fancy rearrangements in the carbon system." Reaction of 1,2-disubstituted alkenes, for example, leads to the formation of equilibrating mixtures of bridging alkylidyne complexes and bridging vinyl complexes. Concludes Casey: "This is a new carbon-carbon bond-forming reaction unlike anything in organic chemistry to date."

One of the "really dramatic findings" of recent years, says Parshall, was the discovery that metathesis (dismutation) reactions can be accomplished by homogeneous catalysts. Metathesis is the redistribution of the side chains on an olefin

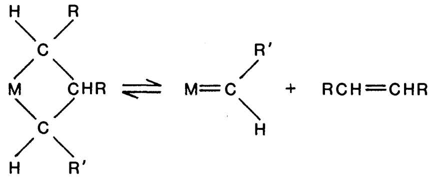
$$2\ RCH{=}CHR' \rightarrow RCH{=}CHR + R'CH{=}CHR'$$

This reaction, first discovered around 1964, is catalyzed by ill-defined homogeneous and heterogeneous molybdenum, tungsten, and rhenium catalysts.

Richard R. Schrock of the Massachusetts Institute of Technology has, over the last 5 years, synthesized a large number of complexes containing metal-carbon double and triple bonds that can carry out metathesis reactions and has studied the mechanism in detail. He has found, for instance, that octahedral complexes such as $W(O)[CHC(CH_3)_3]Cl_2[P(CH_3)_3]_2$ readily catalyze the metathesis of olefins. The first step is reaction of the complex with the olefin to form a metallacyclobutane

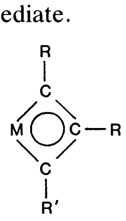


This intermediate can break down to reform the starting materials or to give the metathesized olefin



Schrock has observed that the reaction occurs only if the metal is in its highest oxidation state.

Metathesis of alkynes is more difficult, but it can be accomplished by alkylidyne complexes stabilized by alkoxide ligands, such as $W[CC(CH_3)_3][OC(CH_3)_3]_3$. This reaction proceeds in the same manner as olefin metathesis, but with the formation of a metallacyclobutadiene intermediate.



Similar reactions can be observed with imides and with nitriles; unfortunately, one of Schrock's original goals, breaking the nitrogen-nitrogen triple bond of nitrogen gas, cannot be achieved in this fashion. Schrock is now trying to find complexes that effect the same rearrangements with functionalized olefins; unfortunately, the metal center in the catalysts he has examined are so electrophilic that they attack the function rather than the olefin. The alkylidyne complexes, however, are much more tolerant of functional groups.

Robert H. Grubbs and his colleagues at the California Institute of Technology have observed similar reactions with titanium complexes. In his case, however, the metallacycles are the stable species and the species with a metal-carbon double bond, such as $(C_5H_5)_2Ti{=}CH_2$, are the reactive intermediates.

These complexes, says Grubbs, "allow us to make carbon-carbon bonds in special ways and are proving to be extremely useful in organic syntheses." Use of the titanium complex can result in an analog of the Wittig reaction, in which a phosphorus ylide replaces the oxygen in a ketone or aldehyde to form a new olefin. But where the Wittig reagent can react only with aldehydes and ketones, the titanium complex can react with esters, carbonates, and so forth. The complexes are also useful, he adds, for preparing allenes and metal enolates.

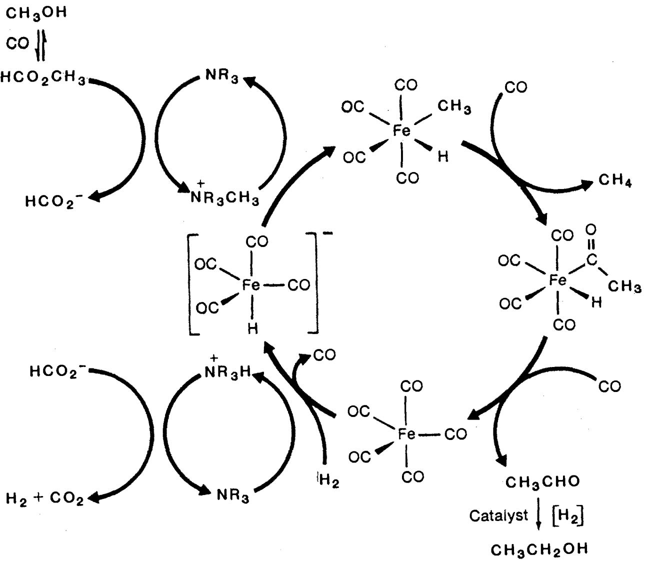
Many of the multiply bonded metal-carbon systems studied by Schrock, Grubbs, and Patricia Watson of Du Pont also catalyze the polymerization of olefins. Studies of these reactions, Schrock says, have resulted in a better understanding of the mechanisms of such well-known reactions as the Ziegler-Natta synthesis of polyethylene.

As has been the case for both heterogeneous catalysis and catalysis by organo-metallic clusters, many investigators are studying the potential of homogeneous complexes to selectively produce desired products from syngas. In many cases, the homogeneous approaches appear to be more successful.

At the recent American Chemical Society meeting in Seattle, Albert S. C. Chan of Monsanto revealed details of a new process for producing ethylene glycol from syngas. Methanol can be made from syngas relatively easily, Chan says, and it, in turn, can be converted to formaldehyde. The new Monsanto process hydroformylates formaldehyde to yield a glycolaldehyde that can be reduced to ethylene glycol.

The key is a mixture of anionic rhodium catalysts, such as $\{Rh(CO)_3[P(C_6H_5)_3]\}^-$ and $[Rh(CO)_4]^-$, that function effectively in many organic solvents in the presence of excess phosphine ligands. The catalysts react by a nucleophilic attack on a carbonyl to form a hydroxymethylrhodium species in the presence of a proton source. Insertion of a second carbonyl followed by hydrogenolysis gives the glycolaldehyde. Chan says the overall efficiency of formaldehyde conversion is greater than 95 percent.

There has been a lot of interest in the new Monsanto process, but also a fair amount of controversy. Du Pont produced ethylene glycol from formaldehyde in the 1950's, using a different process, but the approach was abandoned because of economics. Monsanto thinks the new approach could cost less but others are skeptical. The Monsanto process also operates under much less severe conditions than the Union Carbide process, but the latter has the advantage of requiring only one step, which makes it simpler. Meanwhile, at the same American Chemical Society meeting, Dan E. Hendrikson of Exxon Research and Engineering Company announced a new heterogeneous process for converting formaldehyde to ethylene glycol. Until petroleum prices rise again, however, the relative merits of the competing processes will be only of academic interest.



***Anhydrous ethanol***

*A proposed process for producing anhydrous ethanol from methanol, developed by Jerome W. Rathke and his colleagues at the Argonne National Laboratory.*

Argonne National Laboratory

Monsanto also has a new process for converting linear olefins into branched diolefins containing one more carbon atom, according to Denis Forster of that company. The process uses a rhodium catalyst, such as $HRh(CO)[P(C_6H_5)_3]_3$, to hydroformylate alkenes, such as 2-butene, regioselectively at the two-position. The resultant branched aldehyde is then dehydrated over a heterogeneous acidic silica or boron phosphate catalyst to produce a diolefin, in this case isoprene (2-methyl-1,3-butadiene). Dienes of this type can be readily polymerized to form rubbers, and the new process could be of interest if the relative costs of natural and synthetic rubbers change.

An unusual new process for producing two-carbon chemicals from syngas has been developed by John F. Knifton and his colleagues at Texaco Chemical Company. Knifton uses a catalyst such as $RuO_2 \cdot H_2O\text{-}[n\text{-}C_7H_{15}C_6H_4]_3PBr$ dissolved in the molten phosphine salt. In this system, carboxylic acids, such as propionic or butyric acid, are converted to their ethyl esters by syngas, probably in a two-step reaction:

$$C_2H_5COOH \xrightarrow{CO/H_2} C_2H_5COOCH_3 \xrightarrow{CO/H_2} C_2H_5COOCH_2CH_3$$

The ester can then be pyrolyzed to give ethylene and the carboxylic acid, or hydrolyzed to give ethanol and carboxylic acid; in either case, the acid is recycled through the system.

The Texaco process gives more than 50 percent selectivity for the two-carbon chemicals, a selectivity that is probably adequate for commercialization, and the principal by-products are ethanol and methanol. A similar homogeneous system that includes "halogen-free titanium or zirconium compounds" as cocatalysts can be used to produce one-, two-, and three-carbon alcohols and their acetate esters directly from syngas. Texaco is interested in these compounds as precursors for other chemicals and as octane enhancers to replace tetraethyl lead in gasoline.

Jerome W. Rathke and Michael J. Chen of Argonne National Laboratory have developed a new method for homologation of methanol to ethanol, which could supplant existing techniques. The best current technology depends on a cobalt complex to effect the reaction

$$CH_3OH + 2\ H_2 + CO \rightarrow CH_3CH_2OH + H_2O$$

This process, Rathke says, is not only inefficient in its use of hydrogen, but also produces water that must be separated from the ethanol by distillation, an energy-intensive process. The Argonne process depends on an iron complex, $Fe(CO)_5$, as the catalyst and trialkylamines as promoters to effect the reaction

$$CH_3OH + H_2 + 2\ CO \rightarrow CH_3CH_2OH + CO_2$$

This reaction produces anhydrous ethanol. Other complexes, including $RhI_3$ and $Mn_2(CO)_{10}$, may be used as cocatalysts to increase selectivity. The only significant by-product is methane, which may represent as much as 30 percent of the product mixture.

Rathke and Robert J. Klingler have also deveoped a new process for producing methanol from syngas. Syngas made by steam reforming of natural gas contains hydrogen and carbon monoxide in a 2:1 ratio, which is ideal for producing methanol with use of commercial copper-zinc chromite catalysts. But as mentioned previously, syngas from coal has a ratio of hydrogen to carbon monoxide of 1:1. Extra hydrogen for methanol production must be provided by means of the water-gas shift reaction

$$H_2O + CO \rightleftharpoons CO_2 + H_2$$

This is also an inefficient use of syngas, Rathke says, and the catalysts for the reaction are quickly poisoned by sulfur and nitrogen compounds from the coal. The Argonne group has developed a catalyst that produces methanol by the reaction

$$3\ CO + 2\ H_2O \rightarrow CH_3OH + 2\ CO_2$$

which Rathke says is a more thermodynamically favorable process.

For most of these processes, the summary is like a good news–bad news joke. The good news is that many of the potential syngas processes produce products selectively in high yield. The bad news is that the declining price of petroleum makes it unlikely that any of them will be used soon, possibly not until the next decade.

Meanwhile, the field of homogeneous catalysis itself is far from mature. "I don't think one can emphasize too much how far we have to go," says Halpern. "Even the simple olefin reactions are not as well understood as they should be." Adds Whitesides: "One of the hopes is that we will understand the homogeneous reactions well enough to design catalysts rationally. I anticipate another 20 years of trial and error before we reach that stage."—**Thomas H. Maugh II**

### References and Notes

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