10 August 1973, Volume 181, Number 4099 SCIENCE

Homogeneous Catalysis

Modern spectroscopic techniques are applied to the elucidation of reaction mechanisms.

C. A. Tolman and J. P. Jesson

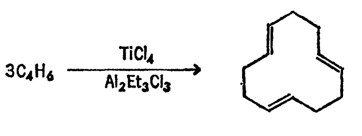
The last 5 to 10 years have witnessed an extremely rapid growth in the organometallic chemistry of the transition metals. The effort has been justified in large measure by the finding and understanding of homogeneous catalytic systems which are capable of rapid and selective organic synthesis under mild conditions. A number of these reactions have important industrial applications; examples are the Wacker oxidation of ethylene to acetaldehyde

$$2CH_2 = CH_2 + O_2 \xrightarrow[CuCl]{PdCl_4^{2-}} 2CH_3CHO \tag{1}$$

the hydroformylation of olefins to aldehydes and alcohols

$$RCH = CH_2 + CO + H_2 \xrightarrow{Co_2(CO)_8} RCH_2CH_2CHO,\ RCH_2CH_2CH_2OH \tag{2}$$

and the cyclotrimerization of butadiene.



(3)

Recently announced industrial processes include the conversion of methanol (*1*) to acetic acid

$$CH_3OH + CO \xrightarrow[RhCl_3 \cdot 3H_2O]{HI} CH_3COOH \tag{4}$$

and the hydrocyanation of butadiene (*2*) to adiponitrile

$$C_4H_6 + 2HCN \xrightarrow{Ni(0)} NC(CH_2)_4CN \tag{5}$$

Heterogeneous catalysis, employing solid catalysts, sometimes on a silica or alumina support, has been used for many years, especially in the petroleum industry. Because these reactions take place only at the surface of the solid, often under conditions of high temperature and pressure, they have been very difficult to study, and the character of the surface reactions and active surface species remains largely obscure.

Homogeneous catalysis occurs in solution and involves soluble transition metal complexes, usually containing one metal atom surrounded by a number of attached atoms or groups which are commonly referred to as ligands. Great advances in mechanistic studies have been made possible by the use of modern spectroscopic techniques; in many cases it has been possible to identify and characterize intermediates and to specify the individual steps of the overall reactions.

The purpose of this article is to review the present state of our understanding of reaction mechanisms in homogeneous catalysis, together with the generalizations that can be made on the basis of comprehensive investigations of a small number of catalytic systems and studies of stable model complexes.

Concept of a Catalytic System

Figure 1 shows a reaction scheme for the hydrogenation of olefins using $RhClL_3$ [L is a tertiary phosphine ligand such as triphenylphosphine, $P(C_6H_5)_3$] as the complex placed in or charged to the reactor. The scheme is oversimplified but can be used to illustrate most of the features involved in catalytic systems. A large number of discrete transition metal complexes exist which differ in the number, type, and mode of attachment of the ligands. The arrows represent the chemical reactions which convert one complex into another. Thus, the olefin $RCH = CH_2$ becomes coordinated to the metal in steps 7 and 3; hydrogen becomes coordinated in steps 1 and 9. The two loops containing steps 1 to 6 and 7 to 6 effect the catalytic conversion of the olefin to the alkane RCH_2CH_3. By cycling the loops again and again, a single metal atom can produce a large number of product molecules. Some complexes in catalytic systems may not be species on the loops (reactive intermediates) but may be connected to loop species by reversible (step 10) or irreversible reactions. Any loop species or any complex which can be converted to a loop species could be charged to the reaction to give an active system. Reactions that irreversibly remove metal from the loop will cause a gradual loss of activity and hence limit the usefulness of the catalyst. The number of catalyst cycles is dependent on the rate of loop cycling compared to the rate of irreversible loss. The complex present in highest concentration during a catalytic reaction may not be the one charged and may not even be a loop species. The reactive intermediates will generally be present in markedly different concentrations, depending on the rate constants for various steps and on the concentrations of the free ligands in solution. Some of the complexes which react rapidly may be present in such low concentrations as to be undetectable spectroscopically. This is why the common phrase "the reactive intermediate" is often misused. If a chemist is able to identify a reactive intermediate under catalytic conditions, the chances are good that he has found one of the less reactive intermediates in the system.

In a mechanistic study one hopes to establish the nature of the organo-

---

Dr. Tolman is a research chemist and Dr. Jesson is a research supervisor at the Central Research Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Delaware 19898.

metallic species present in solution, and the rates and equilibrium constants for their reactions. It should be borne in mind that the rate constants depend strongly on the type of metal and ancillary ligands and the reactants involved, and may also depend on the solvent and the temperature.

In the following section we examine in detail a number of catalytic systems, including the one mentioned above, to demonstrate the depth of our present understanding and to illustrate how the experimental information is obtained.

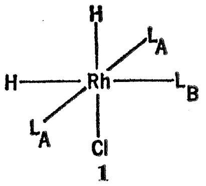
Olefin Hydrogenation by $RhCl[P(C_6H_5)_3]_3$

The hydrogenation of olefins to alkanes proceeds smoothly under mild conditions in the presence of $RhClL_3$ complexes (*3*), but not at all in their absence. The x-ray crystal structure of $RhCl[P(C_6H_5)_3]_3$ has been determined (*4*). One chlorine and three phosphorus atoms are attached to the central metal atom. There is a great deal of steric crowding due to the bulky phosphine ligand, and as a result the complex reacts readily with small molecules such as H_2 or C_2H_4, but cannot accommodate an additional large ligand such as $P(C_6H_5)_3$. X-ray crystallography can determine interbond angles and bond distances with high precision provided that single crystals are available and the complex does not decompose in the x-ray beam. In catalytic work the method has been applied to relatively stable complexes such as $RhCl[P(C_6H_5)_3]_3$ and to unstable intermediates where crystals are grown and examined at low temperatures.

The overall reaction for olefin hydrogenation can be written as

$$RCH = CH_2 + H_2 \xrightarrow{RhClL_3} RCH_2CH_3 \quad (6)$$

Nuclear magnetic resonance (NMR) studies (on ^1H and ^{31}P nuclei) at moderate rhodium concentrations (0.1 to 0.01 molar) show that the $RhClL_3$ present in solution reacts with H_2 to form H_2RhClL_3 (*5*). The spectrum in Fig. 2 shows that the stereochemistry of the hydride is that in configuration **1**.



1

The structure can be established from the spin-spin coupling pattern. The upper portion of Fig. 2 shows a ^{31}P NMR pattern consisting of two doublets and two triplets (the four lines in the middle are due to unreacted starting material). The two doublets arise from the two phosphorus ligands L_A (configuration **1**), the major splitting being due to coupling to the rhodium nucleus (^{103}Rh, nuclear spin $I = 1/2$) and the minor splitting arising from the phosphorus ligand L_B. Similarly, the doublet of triplets pattern arises from the phosphorus nucleus in the ligand L_B, the doublet splitting from coupling to the ^{103}Rh nucleus and the triplet from the two equivalent phosphorus nuclei in the ligands L_A. In general, if a nucleus A is coupled to n other equivalent nuclei B, each with $I = 1/2$, the resonance of A is split into $n + 1$ components with a symmetrical distribution of intensity.

Nuclear magnetic resonance has proved to be the most useful spectroscopic technique for determining the structure and dynamics of organometallic complexes in solution (*6*). Modern Fourier transform techniques greatly enhance the sensitivity of the method and will undoubtedly make it even more important. High-resolution spectra can be observed for atomic nuclei with $I = 1/2$, such as ^1H, ^{31}P, ^{19}F, and ^{13}C. The resonance frequency depends on the type of nucleus, its chemical environment, and the strength of the strong magnetic field in which the sample is placed. For a magnetic field of known strength, the frequency [usually expressed as a chemical shift in parts per million (ppm) from some internal standard] gives additional information about the kinds of atoms to which the nucleus in question is bound.

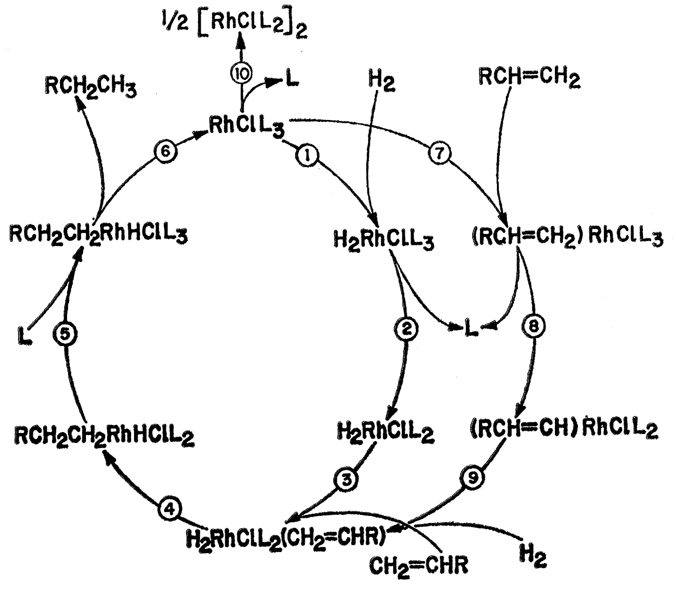
Line shape effects in NMR can be used to obtain kinetic, thermodynamic, and mechanistic information. These effects are observed when a nucleus changes its chemical environment at a rate comparable to the difference in chemical shift between the two environments (about 1 to 10^6 times per second). Both intramolecular and intermolecular exchange may occur. In the former case no bonds are broken —the ligands merely exchange positions in the coordination sphere. A complex that undergoes intermolecular exchange is H_2RhClL_3. When the temperature is raised the spin-spin coupling between rhodium and phosphorus is lost for the phosphorus *trans* to a hydrogen atom, and this is reflected in the ^{31}P spectrum (Fig. 2). This indicates that the bond between Rh and L_B is being rapidly broken and reformed. Preliminary line shape studies indicate that the rate constant for dissociation of the unique ligand is about 400 sec^{-1} at 30°C (*5*). Olefin coordination in step 3 of Fig. 1 undoubtedly occurs at the position vacated by L_B. The possibility of exchange behavior means that great care must be exercised in interpreting NMR spectra since rapid exchange effects can give a deceptively simple spectrum. Infrared spectra of solutions of the hydride show a broad absorption centered at 2050 reciprocal centimeters caused by the Rh–H stretching vibration. From spectrophotometry (Fig. 3) the equilibrium constant for reaction 7

$$H_2 + RhClL_3 \rightleftharpoons H_2RhClL_3 \quad (7)$$

has been determined as 9.6 ± 1.6 reciprocal atmospheres in CH_2Cl_2 at 26°C (*5*).

Visible and near-ultraviolet spectroscopy, or spectrophotometry, is useful because transition metal complexes invariably show intense absorption of light in the wavelength range of about 200 to 700 nanometers, and the electronic absorption spectrum changes as the number and type of ligands change. Spectrophotometry can be employed on very dilute solutions (down to $10^{-4}M$ metal complex or lower) where most of the other techniques cannot be used. Precise temperature control and measurement are relatively easy, so that accurate thermodynamic data such as rate and equilibrium constants can be obtained.

Electronic transitions occur in very short times (approximately 10^{-15} second) so that each chromophore makes its own contribution to the spectrum. Although the resolution of electronic bands is not normally high, there are techniques for determining the number of absorbing species in solution as the composition changes (*7*). Isosbestic points are very useful. These are points where a series of spectra cross; that is, the absorbance at those wavelengths does not change as the composition of the solution is changed. The presence of an isosbestic point in the series of spectra in Fig. 3 indicates that the starting complex is being converted into only one other compound, in this case $H_2RhCl[P(C_6H_5)_3]_3$. In the absence of dissociation or association, the absorbance of a complex at a particular wavelength should be directly proportional to its concentration (Beer's law).



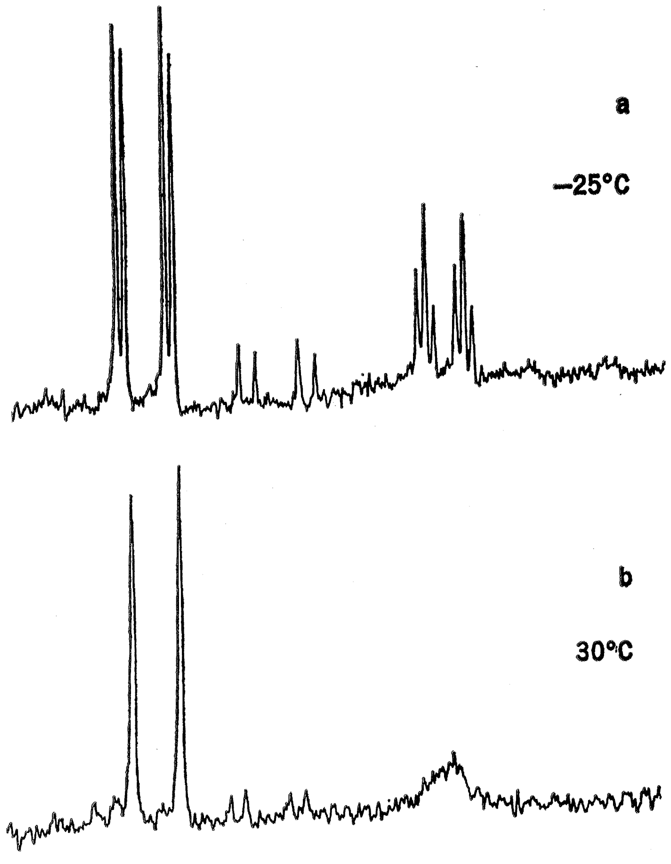
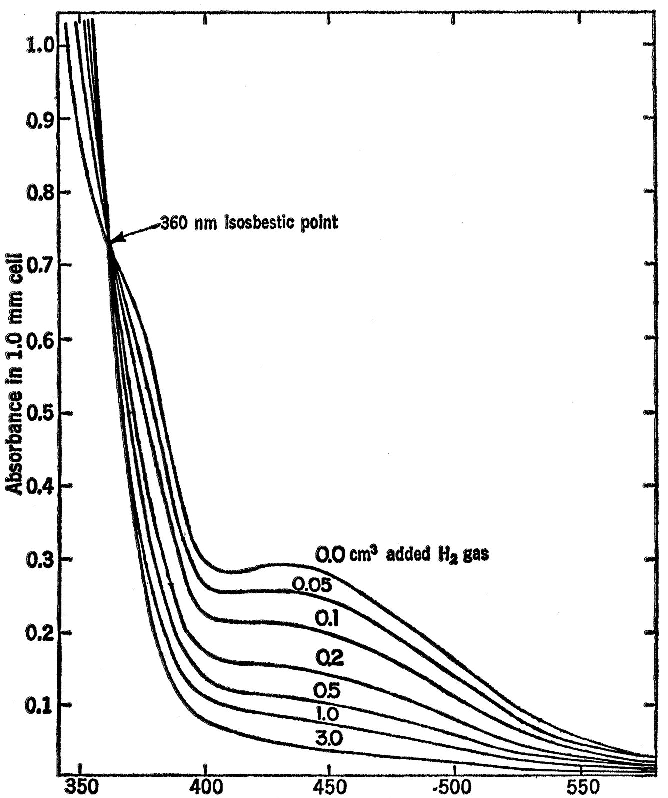


Fig. 1 (left). Simplified mechanism for olefin hydrogenation by RhClL$_3$. The ligand L is a phosphine such as P(C$_6$H$_5$)$_3$. Fig. 2 (right). Proton noise decoupled spectra of ^{31}P at 36.43 megahertz after H$_2$ was added to a 0.14*M* solution of RhCl[P(C$_6$H$_5$)$_3$]$_3$ in CH$_2$Cl$_2$. (a) At −25°C Rh–P and P–P coupling establishes the stereochemistry of the complex. (b) At 30°C the Rh coupling to the unique P collapses due to rapid ligand exchange [see (*5*)].



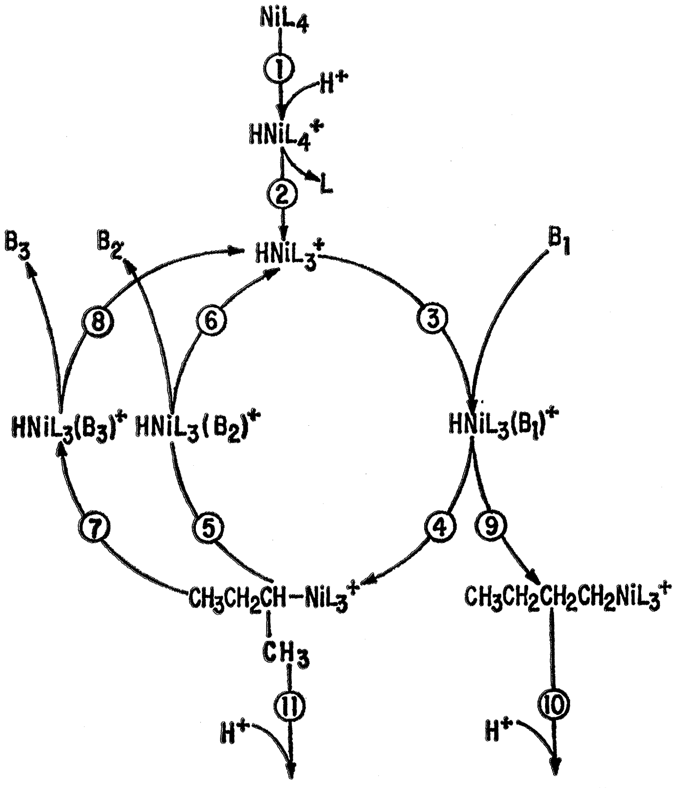


Fig. 3 (left). Ultraviolet-visible spectra obtained on addition of H$_2$ gas to a solution of 2.31 × 10^{-3}*M* RhCl[P(C$_6$H$_5$)$_3$]$_3$ and 0.1*M* P(C$_6$H$_5$) in CH$_2$Cl$_2$ at 26°C. [From (*5*)] Fig. 4 (right). Butene isomerization by Ni[P(OC$_2$H$_5$)$_3$]$_4$ in the presence of H$^+$; L, B$_1$, B$_2$, and B$_3$ represent P(OC$_2$H$_5$)$_3$, 1-butene, *cis*-2-butene, and *trans*-2-butene, respectively [see (*13*)].

Deviations from Beer's law indicate changes in coordination which might be difficult to detect by other means. Techniques have been developed for conveniently determining equilibrium (*8*) and rate constants (*9*) in reactions involving transition metal complexes and gases such as H_2 or C_2H_4 at pressures up to a few atmospheres.

Some of the intermediates shown in Fig. 1 have not been directly observed spectroscopically because their concentrations are so low. The existence of the reaction intermediate $H_2RhClL_2(CH_2{=}CHR)$ is based on kinetic evidence. The hydrogenation rate is first order in olefin concentration and inverse order in added ligand concentration under conditions where the principal complex in solution is H_2RhClL_3. Intermediates formed in steps 4 and 5 (Fig. 1) have likewise not been observed. Evidence for stepwise rather than concerted addition of the hydrogen atoms has been given by product analyses (*10*) and deuteration studies (*11*). An olefin complex $(C_2H_4)Rh[P(C_6H_5)_3]_2$ of the type formed in step 8 has been isolated (*3*).

Conventional kinetic studies (*12*) are an important part of the characterization of a catalytic system, and show how the reaction rate depends on the variables of concentration, temperature, and solvent. Great care must be exercised, however, to avoid too much speculation about the mechanistic details of catalytic systems based only on kinetic studies of rates of product formation. A rate law, which expresses the dependence of the rate on the concentrations of various species, gives information only on the difference between the composition of the transition state of the rate-determining step and the composition of the principal metal-containing species in solution. Suppose, for example, that the rate law for olefin hydrogenation by $RhClL_3$ over some range of concentration is

$$\text{Rate} = \frac{k[H_2][Rh][\text{olefin}]}{[L]}$$

where [Rh] and [L] represent the total concentrations of $RhClL_3$ and L charged. If the principal rhodium complex in solution under the conditions of the reaction is $RhClL_3$, the rate law indicates that the composition of the transition state for the rate-determining step is $H_2RhClL_2(\text{olefin})$. The rate law will change to

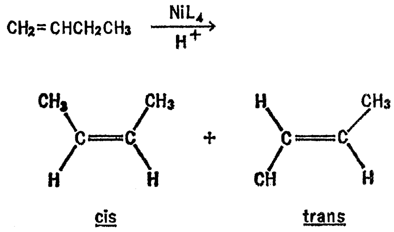
$$\text{Rate} = \frac{k'[Rh][\text{olefin}]}{[L]}$$

at a higher hydrogen pressure where H_2RhClL_3 becomes the principal rhodium complex. The principal metal species in solution must be known in order to fix the composition of the transition state of the rate-determining step.

The picture of the mechanism of olefin hydrogenation by $RhClL_3$ complexes outlined in this section has been somewhat oversimplified, but it is substantially correct at moderate catalyst concentrations, or in the presence of added phosphine, and for weakly coordinating olefins. In highly dilute solutions without added L a substantial fraction of the metal can be present as a chlorine bridged dimer, as shown by Fourier transform ^{31}P NMR and spectrophotometric studies (*5*).

Butene Isomerization by $Ni[P(OC_2H_5)_3]_4$ and H^+

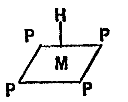
Another catalytic system that has been studied in some detail is the isomerization of 1-butene to *cis*- and *trans*-2-butenes in the presence of $Ni[P(OC_2H_5)_3]_4$ and acids such as H_2SO_4 (*13*).



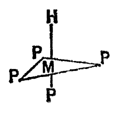
(8)

Figure 4 shows the details of the mechanism. The first step is the association of H^+ to give $HNiL_4^+$. The presence of a hydrogen and four phosphorus atoms on nickel is indicated by the quintet ^1H NMR resonance at +14.3 ppm from the tetramethylsilane resonance (*14*). The Ni–H stretching vibration occurs at 1970 cm^{-1} in the infrared and at 1980 cm^{-1} in the Raman spectrum (*15*).

The quintet in the proton NMR spectrum suggests that all four phosphorus ligands are equivalent, as in a square pyramidal structure **2**. X-ray crystal structures of a number of other complexes of the HML_4 type (M is metal) have shown that they all have the distorted trigonal bipyramidal structure **3** in the crystal (*16*).



2



3

If structure **3** were rigid in solution, one would have observed two quartets for the NMR pattern. Detailed NMR studies in which the temperature was varied (*17*) suggest that the pattern of five lines observed for $HNiL_4^+$ at ambient temperature is a consequence of rapid intramolecular exchange, which makes the phosphorus nuclei appear equivalent. In some studies of this type it is possible to extract detailed information regarding the actual mechanism of exchange (*18*).

The equilibrium and rate constants of $HNiL_4^+$ formation can be accurately determined spectrophotometrically, since adding H^+ gives a new absorption band in the ultraviolet at 325 nm. The reaction is so fast that a special stopped-flow technique, which mixes the NiL_4 and H^+ solutions very quickly, must be used to measure the rate. With 0.1*M* H^+, the half-life for $HNiL_4^+$ formation at 25°C is only 0.0045 second (*15*).

The second step in Fig. 4, dissociation of L to give $HNiL_3^+$, is based on kinetic evidence. Adding $P(OC_2H_5)_3$ to the solution has no effect on the concentration of $HNiL_4^+$ but markedly slows the isomerization reaction. The concentration of $HNiL_3^+$ must be very small, since it has not been detected spectroscopically. In fact, none of the loop species in this system are spectroscopically detectable; proton NMR and spectrophotometric experiments have only detected three nickel complexes in solution: NiL_4, $HNiL_4^+$, and Ni^{2+} (dead catalyst).

Evidence for the hydrido-olefin and alkyl intermediates in Fig. 4 is indirect. Isomerization of 1-butene by the use of $DNiL_4^+$ introduces deuterium into the 2-butene products and into the recovered unisomerized 1-butene. This suggests a series of reversible insertion and elimination steps. Analysis by microwave spectroscopy of the monodeutero propylenes produced by exposure of propylene to $DNiL_4^+$ shows that the location of the deuterium atoms is consistent with this proposal (*19*). The $CH_2{=}CDCH_3$ found must arise by insertion of propylene into a Ni–D bond to give $N{-}CH_2CHDCH_3$, followed by the elimination of Ni–H.

An analog of the proposed $HNiL_3(\text{olefin})^+$ intermediates is $HPt[P(C_2H_5)_3]_2(\text{ethylene})^+$; it has been isolated as the crystalline $B(C_6H_5)_4^-$ salt and was shown unambiguously to contain H and C_2H_4 is a *trans* square planar arrangement on platinum by proton NMR spectroscopy (*20*).

General Principles of Homogeneous Catalysis

We conclude by considering some of the generalizations that can be made concerning homogeneous catalysis on the basis of studies of model compounds and the relatively small number of catalytic systems which have been examined in detail.

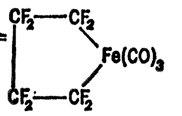
It has long been recognized that transition metals tend to form complexes in which the effective number of valence electrons on the metal is 18, corresponding to the configuration of the next higher inert gas in the periodic table. There are numerous exceptions to this rule, but if one restricts attention to the diamagnetic organometallic complexes of groups IVB through VIII of the periodic table, the vast majority of the well-characterized compounds have 16 or 18 metal valence electrons. We postulate that organometallic reactions, including catalytic ones, proceed by elementary steps involving only intermediates with 16 or 18 metal valence electrons (*21*). Complexes of the type $RhClL_3$ illustrate this point; it was once thought (*3*) that the 16-electron complex with $L = P(C_6H_5)_3$ dissociated extensively to a 14-electron complex according to

$$RhClL_3 \rightleftharpoons RhClL_2 + L \qquad (9)$$

Later experiments showed that ligand dissociation is very small indeed and that, to the extent it does take place, the 16-electron dimer forms (*22*).

The basic reactions that occur in homogeneous catalytic systems can be divided into five classes, each reaction with a microscopic reverse. These are shown in Table 1; most of the examples are taken from the earlier discussion. There are few well-defined examples of the last type of reaction in Table 1, oxidative coupling, but it presumably plays a key role in olefin oligomerization catalysis.

Table 1. Basic reactions in homogeneous catalytic systems; L = ligand.

Reaction	Example	Reverse
1. Lewis base dissociation	$H_2RhClL_3 \rightleftharpoons H_2RhClL_2 + L$	Lewis base association
2. Oxidative addition	$H_2 + RhClL_3 \rightleftharpoons H_2RhClL_3$	Reductive elimination
3. Insertion	$H_2RhClL_2(C_2H_4) \rightleftharpoons CH_3CH_2RhHClL_2$	Deinsertion
4. Lewis acid association	$H^+ + NiL_4 \rightleftharpoons HNiL_4^+$	Lewis acid dissociation
5. Oxidative coupling	$(C_2F_4)_2Fe(CO)_3 \rightleftharpoons$ 	Reductive decoupling

Both electronic and steric factors appear to be extremely important in catalytic systems. Increased electron density on the metal enhances the ability of a 16-electron complex to undergo oxidative addition (*23*); $RhClL_3$ complexes should add H_2 more easily with more electron donating phosphines. Increased electron density should also favor Lewis acid association (*24*) and oxidative coupling. Steric effects are important in aiding ligand dissociation from 18-electron complexes to give 16-electron species, as in the dissociation of H_2RhClL_3 to H_2RhClL_2.

Complementary studies have been undertaken to establish trends in electronic effects by using both infrared techniques on complexes of the form $Ni(CO)_3L$ (*25*) and by direct measurement of the binding energies of the $2p_{3/2}$ electrons of Ni in a series of NiL_4 complexes (*26*). The binding energies correlate well with both the carbonyl stretching frequencies and the equilibrium constants for reaction 10 (*27*)

$$H^+ + NiL_4 \rightleftharpoons HNiL_4^+ \qquad (10)$$

Steric effects of phosphorus ligands have been put on a semiquantitative basis by measurements of a ligand cone angle on molecular models (*28*). The angle is the apex angle of a minimum cone, centered on a metal atom, which just touches the outermost atoms of the phosphorus-containing ligand. Ligand size has been shown to account for the results of the exchange equilibria involving ligands L and L′

$$NiL_4 + 4L' \rightleftharpoons NiL_{4-n}L'_n + nL \qquad (11)$$

^{31}P nuclear magnetic resonance studies indicate that small ligands are more effective in competing for coordination sites than large ones (*28*).

Steric effects are far more important in determining catalytic activity than has generally been recognized. Measurements of the ligand dissociation equilibrium constant K_d for Eq. 12

$$NiL_4 \overset{K_d}{\rightleftharpoons} NiL_3 + L \qquad (12)$$

show that K_d increases by a factor of about 10^7 (10 million) when L is changed from tri(*para*-tolyl)phosphite to tri(*ortho*-tolyl)phosphite (*29*). These ligands are essentially identical electronically, but the ligand cone angle of the *ortho* isomer is larger by about 13 degrees (*29*).

Detailed physical and chemical studies employing modern spectroscopic techniques have now led to a reasonably clear picture of how homogeneous catalytic systems work and have produced some general principles to help guide future research. We expect that the guidelines will become more sharply defined and that homogeneous catalysis will become increasingly important as mechanistic studies become more extensive and sophisticated.

References

1. J. F. Roth, J. H. Craddock, A. Hershman, F. E. Paulik, *Chem. Technol.* (October 1971), p. 600.
2. *Chem. Eng. News* (26 April 1971), p. 30.
3. J. A. Osborn, F. H. Jardine, J. F. Young, G. Wilkinson, *J. Chem. Soc. A* (1966), p. 1711.
4. P. B. Hitchcock, M. McPartlin, R. Mason, *Chem. Commun.* (1969), p. 1367.
5. P. Meakin, J. P. Jesson, C. A. Tolman, *J. Amer. Chem. Soc.* **94**, 3240 (1972).
6. J. P. Jesson, in *Transition Metal Hydrides*, E. L. Muetterties, Ed. (Dekker, New York, 1971), pp. 75–201.
7. J. S. Coleman, L. P. Varga, S. H. Mastin, *Inorg. Chem.* **9**, 1015 (1970).
8. C. A. Tolman, W. C. Seidel, D. H. Gerlach, *J. Amer. Chem. Soc.* **94**, 2669 (1972).
9. M. F. Werneke, thesis, Clarkson College of Technology (1971).
10. G. C. Bond and R. A. Hillyard, *Discuss. Faraday Soc.* **46**, 20 (1968).
11. A. S. Hussey and Y. Takeuchi, *J. Amer. Chem. Soc.* **91**, 672 (1969).
12. See, for example, A. A. Frost and R. G. Pearson, *Kinetics and Mechanism* (Wiley, New York, 1953).
13. C. A. Tolman, *J. Amer. Chem. Soc.* **94**, 2994 (1972).
14. W. C. Drinkard, D. R. Eaton, J. P. Jesson, R. V. Lindsey, Jr., *Inorg. Chem.* **9**, 392 (1970).
15. C. A. Tolman, *J. Amer. Chem. Soc.* **92**, 4217 (1970).
16. B. A. Frenz and J. A. Ibers, in *Transition Metal Hydrides*, E. L. Muetterties, Ed. (Dekker, New York, 1971), pp. 33–74.
17. P. Meakin, E. L. Muetterties, J. P. Jesson, *J. Amer. Chem. Soc.* **94**, 5271 (1972).
18. P. Meakin, E. L. Muetterties, F. N. Tebbe, J. P. Jesson, *ibid.* **93**, 4701 (1971).
19. C. A. Tolman and L. H. Scharpen, *J. Chem. Soc. Dalton Trans.* (1973), p. 584.
20. A. J. Deeming, B. F. G. Johnson, J. Lewis, *Chem. Commun.* (1970), p. 598.
21. C. A. Tolman, *Chem. Soc. Rev.* **1**, 337 (1972).
22. See (*5*) and the references contained therein.
23. J. P. Collman, *Accounts Chem. Res.* **1**, 136 (1968).
24. D. F. Shriver, *ibid.* **3**, 231 (1970).
25. C. A. Tolman, *J. Amer. Chem. Soc.* **92**, 2953 (1970).
26. ———, W. M. Riggs, W. J. Linn, C. M. King, R. C. Wendt, *Inorg. Chem.*, in press.
27. C. A. Tolman, *ibid.* **11**, 3128 (1972).
28. ———, *J. Amer. Chem. Soc.* **92**, 2956 (1970).
29. ———, W. C. Seidel, L. W. Gosser, in preparation.