Homogeneous Catalysis

Industrial Applications and Implications

A symposium sponsored by the
Division of Industrial and
Engineering Chemistry at the
152nd Meeting of the American
Chemical Society, New York,
N. Y. Sept. 13-14, 1966.

B. J. Luberoff, *Symposium Chairman*

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FOREWORD

ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are refereed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Papers published in ADVANCES IN CHEMISTRY SERIES are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

PREFACE

Catalysis, according to the dictionary, derives from the same classic root as catastrophe and implies destruction or ruin. It, therefore, does not seem worthwhile to pursue this definition except to excuse it by noting that the word catalysis was first used by Berzelius in 1836 in discussing decomposition. The fact that catalysis of decomposition should be recognized before that of synthesis is quite reasonable in view of our present understanding of catalysis. Thus, if catalyzed synthesis implies a three-body collision, it is far less probable than the simple collision of a decomposing species with a catalytic center. This line of reasoning leads to the heart of catalysis which is primarily a probabilistic or thermodynamic phenomenon. Hence, a catalyst is an entity that alters the rate of a reaction by becoming intimately involved in the reaction sequence but without becoming a product. It must, therefore, be close to the reactants and usually in a well-defined geometric relationship to them. Such a relationship implies an unfavorable entropic transition on forming the activated complex. This transition must be more than offset by enthalpic considerations—*i.e.*, bond making—in order for catalysis to be effected. Thus, a catalyst alters the free energy of activation by becoming part of an activated complex which could not form in its absence. Hence, catalysis makes available an otherwise unavailable reaction path. Furthermore, a true catalyst must, on collapse of the activated complex, be returned to a state in which it can function again. This frequently is not the same state in which the catalyst was introduced.

A *homogeneous* catalyst is one so dispersed in the reactants that no gross interface exists between it and the reactants. This does not necessarily mean that catalyst and reactant, when alone under reaction conditions, must be in the same physical state. However, when they are not, some agent—*e.g.*, a solvent—must be present to bring them into the same phase, but the solvent is often more than a simple mutualizing agent. It is part, at least a thermodynamic part, of the reactants, of the catalyst, of the products, and of the activated complex. The lattice of heterogeneous catalysts can thus be thought of as a special case of solvent effect. Broadly speaking, solvents themselves are often homogeneous catalysts. Sometimes, if a transition state is less polar than its initial state, the reaction can be catalyzed by the entropy gain arising from the liberation of solvent when the transition state forms.

Working in a liquid medium involves not only heat and mass transfer problems that are different from those of heterogeneously catalyzed gas phase reactions, but also introduces solvent recovery and pollution problems. Since the catalysts are expensive and fugitive (because they are molecularly dispersed), their conservation also becomes important. Finally, in trying to contain the system, whole new areas of corrosion control are opened. Probably the largest titanium fabrication job ever done was recently done for a plant based on a homogeneously catalyzed oxidation. These problems notwithstanding, it does seem that most "breakthrough type" industrial processes developed during the last decade are homogeneously catalyzed ones; although industrial applications of homogeneous catalysts are young, these catalysts often seem better understood, more predictable—and if we include enzymes—more versatile than heterogeneous catalysts.

This volume concentrates on reactions in solution. In the first chapter, Halpern reviews the kinds of substances which can be used as homogeneous catalysts and the ways in which they function. In Chapter 2, Bond contrasts phenomena of homogeneous catalysis with those of heterogeneous catalysis. Gessner examines some of the implications of replacing the gross interface between catalyst and reactant, of heterogeneous catalysis, with the interfaces of homogeneous catalysis. Although the phenomena he discusses usually fall in the realm of the engineer, they should be thoroughly understood by chemists whose research must be tempered by economic considerations. Using the open literature, Szonyi has documented some of the industrial applications of homogeneous catalysis. The remaining papers treat specific subjects in depth; they are roughly grouped in terms of oxidation, reduction, and finally polymerization.

The papers in this volume were sponsored by the Division of Industrial and Engineering Chemistry with the exception of Tsuji's paper, which was read before the Petroleum Division.

Sincere appreciation is extended to each of the authors and particularly to Jack Halpern, and to Dolores Olson, whose help in organizing this symposium was invaluable.

B. J. LUBEROFF

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Homogeneous Catalysis by Coordination Compounds

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Two classes of catalytic reactions of transition metal ions and coordination compounds are considered—i.e., *those involving catalytic activation of inert saturated molecules and those involving addition to unsaturated molecules. Among the factors contributing to the catalytic activity are the existence of relatively stable but highly reactive complexes of transition metals which exhibit reactivities closely related to those of the "reactive intermediates" of organic chemistry; the ability of transition metal atoms to stabilize by coordination various reaction intermediates as relatively stable, but reactive complexes; and the ability of a transition metal atom to assemble and to orient appropriately within the framework of its coordination shell, several components of a reaction. The underlying principles of coordination chemistry which govern catalytic activity are developed and illustrated.*

Among the most significant developments in the field of catalysis in recent years have been the discovery and elucidation of various new, and often novel, catalytic reactions of transition metal ions and coordination compounds (*13, 34*). Examples of such reactions are the hydrogenation of olefins catalyzed by complexes of ruthenium (*36*), rhodium (*61*), cobalt (*52*), platinum (*3, 26, 81*), and other metals; the hydroformylation of olefins catalyzed by complexes of cobalt or rhodium (Oxo process) (*6, 46, 62*); the dimerization of ethylene (*1, 23*) and polymerization of dienes (*15, 64, 65*) catalyzed by complexes of rhodium; double-bond migration in olefins catalyzed by complexes of rhodium (*24, 42*), palladium (*42*), cobalt (*67*), platinum (*3, 5, 26, 81*), and other metals (*27*); the oxidation of olefins to aldehydes, ketones, and vinyl esters, catalyzed by palladium chloride (Wacker process) (*47, 48, 49,*

Table I. Some Homogeneous Reactions of Olefins

Reaction	*Typical Catalysts*		
	d^6	d^7	d^8
	Ru^{II}	Co^{II}	Fe^0
Hydrogenation	$RuCl_6^{4-}$	$Co(CN)_5^{3-}$	$Fe(CO)_5$
Hydroformylation	[a]$RuCl_2L_4$		
Double-bond migration			$FeH(CO)_4^-$
Dimerization			
Oxidation			

[a] Active form of catalyst uncertain.

76, 79, 82); the hydration of acetylenes catalyzed by ruthenium chloride (*38*); and many others. The catalytic reactions listed in Table I are illustrative of the subject but fall short of conveying its full scope.

This article will be concerned with the mechanisms of some of these reactions and with some of the general principles that underly this relatively new and rapidly developing field of chemistry. The subject in question has attracted much interest in recent years both because of the novelty of much of the chemistry it reveals and because of its potential practical applications, exemplified by at least two processes (the Oxo and Wacker processes) which have already achieved considerable industrial importance. The possible relevance of many of the catalytic reactions in this field as model systems for related heterogeneous and enzymic process also lends interest to the subject although attempts to exploit this theme have thus far met with only limited success.

Structure and Reactivity of Transition Metal Complexes

The majority of catalytic reactions to be considered (Table I) involve as catalysts coordination compounds of the metals near the end of each transition series—notably the platinum groups comprising Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, and Pt. The electron configurations of the metal atoms in question are generally in the range d^6 to d^{10}, with the configuration d^8 being especially widely represented. Furthermore, the catalytic complexes of interest are generally (although not invariably) of the spin-paired or low-spin type—*i.e.*, complexes in which the ligand field splittings are sufficiently large so that the d electrons first fill up (with pairing if necessary) the most stable orbitals available to them before occupying those of higher energy. Because of the relevance of this subject to an understanding of the catalytic properties of interest, some aspects of the electronic structures and chemical reactivities of this general class of complexes will first be considered.

Catalyzed by Transition Metal Complexes

(L = PPh$_3$)

		d^8		
Co^I	Rh^I	Ir^I	Pd^{II}	Pt^{II}
$CoH(CO)_4$	$RhClL_3$	$IrI(CO)L_2$		[a]$Pt(SnCl_3)_5^{3-}$
$CoH(CO)_4$	$RhCl(CO)L_2$			
$CoH(CO)_4$	$RhCl_3(olefin)^{2-}$		$PdCl_4^{2-}$	[a]$Pt(SnCl_3)_5^{3-}$
	$RhCl_2(C_2H_4)_2^-$			
			$PdCl_4^{2-}$	

The stable coordination numbers of spin-paired complexes of transition metals range from 8 to 2 and exhibit a systematic inverse dependence on the number of *d* electrons of the metal atom, which is illustrated by Table II.

Table II. Coordination Numbers of Some Transition Metal Complexes

Coordination Number	*Examples*	*Electron Configuration*	*Total Number of Valence Electrons*
8	$Mo(CN)_8^{3-}$, $Mo(CN)_8^{4-}$	d^1, d^2	17, 18
6	$M(CN)_6^{3-}$ (M=Cr, Mn, Fe, Co)	d^3, d^4, d^5, d^6	15–18
5	$Co(CN)_5^{3-}$, $Ni(CN)_5^{3-}$	d^7, d^8	17, 18
4 (square planar)	$Ni(CN)_4^{2-}$	d^8	16
4 (tetrahedral)	$Cu(CN)_4^{3-}$, $Ni(CO)_4$	d^{10}	18
2	$Ag(CN)_2^-$, $Au(CN)_2^-$	d^{10}	14

This trend has its origin in the fact that in general, the higher the coordination number, the fewer the *d* electrons that can be accommodated in stable (bonding or near nonbonding) orbitals of the complex. Configurations in which the valence shell of the metal atom contains 18 electrons tend to be particularly stable (inert gas rule), whereas those configurations in which this number is exceeded are generally unstable. For an octahedral complex, for example, reference to the simplified molecular orbital diagram in Figure 1 reveals that the three stable t_{2g} orbitals (non-σ-bonding or possibly slightly π-bonding in the case of π-acceptor ligands such as CO or CN$^-$) can accommodate up to six *d* electrons, any additional electrons being forced to occupy the $e_g{}^*$ orbitals which are strongly anti-σ-bonding in the complexes of interest. This generally results in the destabilization of the coordination number 6, in favor of a lower coordination number which permits a larger number of *d* electrons to be accommodated in stable orbitals (*see* Figure 2). Taking account of ligand π-orbitals leads to some modification of this molecular orbital

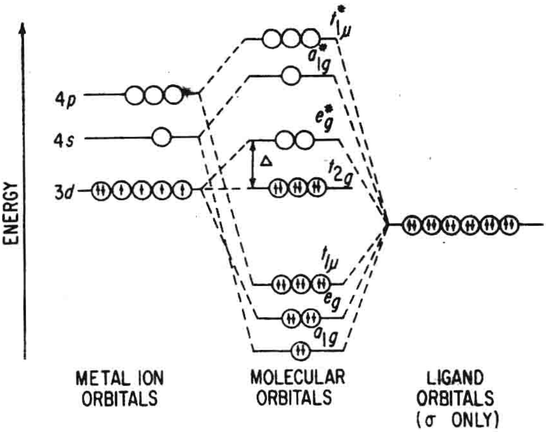


Figure 1. Molecular orbital (ligand field) diagram for octahedral complex (schematic)

scheme, but essentially the same conclusion is generally reached. (The symbols a_{1g}, e_g, and the like in the energy level diagrams in this article refer to the group theoretical designations of the orbital symmetries; starred orbitals, *i.e.*, e_g^*, a_{1g}^* etc., are antibonding.)

The loss of a CN^- ligand when an electron is added to the very stable d^6 complex, $Co(CN)_6^{3-}$, to give the pentacoordinated spin-paired cobalt(II) complex, $Co(CN)_5^{3-}$, can be understood in these terms,

$$\underset{\substack{d^6\\ \text{very stable}}}{Co(CN)_6^{3-}} \overset{+e^-}{\rightarrow} \underset{\substack{d^7\\ \text{unstable}}}{[Co(CN)_6^{4-}]} \rightarrow \underset{\substack{d^7\\ \text{stable}}}{Co(CN)_5^{3-}} + CN^- \qquad (1)$$

This process is analogous to that which accompanies the addition of an electron to a saturated carbon compound CX_4 (*e.g.*, CCl_4), represented by the simplified molecular orbital diagram in Figure 3. Here, again, because all the stable bonding orbitals are filled, the extra electron is forced into a strongly antibonding orbital, with the result that the coordination number 4 is destabilized and a species of lower coordination number (a free radical or, in some cases, a carbanion depending on the relative electron affinities of X and CX_3) is generated,

$$\underset{\text{very stable}}{CX_4} \overset{+e^-}{\rightarrow} \underset{\text{unstable}}{[CX_4^-]} \rightarrow \underset{\text{stable}}{CX_3\cdot + X^-} \qquad (2)$$

The purpose of developing this analogy is to provide a basis for the expectation that the chemical reactivities of $Co(CN)_5^{3-}$ and related pentacoordinated d^7 complexes will resemble those of typical organic free radicals, and indeed this is found to be the case. This is illustrated, for example, by the general reaction which $Co(CN)_5^{3-}$ undergoes with organic halides to form stable organocobalt complexes (*39, 40, 51, 54*).

$$Co(CN)_5^{3-} + RX \rightarrow Co(CN)_5X^{3-} + R^{\cdot} \quad (3)$$

$$Co(CN)_5^{3-} + R^{\cdot} \rightarrow Co(CN)_5R^{3-} \quad (4)$$

$$2Co(CN)_5^{3-} + RX \rightarrow Co(CN)_5X^{3-} + Co(CN)_5R^{3-} \quad (5)$$

With respect to this and many other reactions such as Reactions 6–12,

$$2Co(CN)_5^{3-} \rightleftarrows Co_2(CN)_{10}^{6-} \quad (6)$$

$$2Co(CN)_5^{3-} + H_2 \rightleftarrows 2Co(CN)_5H^{3-} \quad (7)$$

$$2Co(CN)_5^{3-} + H_2O_2 \rightleftarrows 2Co(CN)_5OH^{3-} \quad (8)$$

$$2Co(CN)_5^{3-} + Br_2 \rightleftarrows 2Co(CN)_5Br^{3-} \quad (9)$$

$$2Co(CN)_5^{3-} + O_2 \rightleftarrows [(CN)_5CoOOCo(CN)_5]^{6-} \quad (10)$$

$$2Co(CN)_5^{3-} + HC{\equiv}CH \rightleftarrows [(CN)_5CoCH{=}CHCo(CN)_5]^{6-} \quad (11)$$

$$2Co(CN)_5^{3-} + CF_2{=}CF_2 \rightleftarrows [(CN)_5CoCF_2CF_2Co(CN)_5]^{6-} \quad (12)$$

the reactivity of $Co(CN)_5^{3-}$ resembles, to a remarkable degree, that of a typical reactive organic free radical. The basis for this marked parallelism is that in each case the characteristic reactivity pattern is dominated by the tendency to go from the open-shell configuration of the species in question to the more stable closed-shell configuration (CX_4 for the organic compound and the octahedral d^6 configuration for the coordination compound). The types of reactions which achieve this are the same in both cases. One such reaction which is of particular importance for the catalytic applications to be considered is that involving the reductive homolytic cleavage of covalent single bonds—*i.e.*,

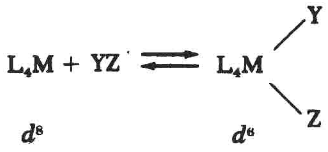
$$2Co^{II}(CN)_5^{3-} + Y{-}Z \rightarrow Co^{III}(CN)_5Y^{3-} + Co^{III}(CN)_5Z^{3-} \quad (13)$$

where YZ = H—H, HO–H, HO—OH, CH_3—I, etc.

The analogy developed above between pentacoordinated d^7 complexes and organic free radicals is capable of meaningful extension to coordination compounds of other electron configurations and coordination numbers (*see* Table III). Thus, similar reasoning leads to the expectation of similarities between the reactivity patterns of tetracoordinated d^8 complexes and carbenes, pentacoordinated d^8 complexes and carbanions, and pentacoordinated d^6 complexes and carbonium ions. In each case the stoichiometries of the reactions which restore the stable closed-shell configurations are the same for both species; hence the similarity of reactivity patterns.

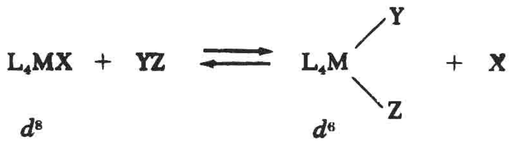
Many of the novel reactions of d^7 and d^8 complexes which contribute to the widespread roles of these complexes in homogeneous catalysis and which reflect reactivity patterns that are relatively unfamiliar in inorganic chemistry, are thus seen to be closely related to reactivity patterns that have in fact long been familiar in organic chemistry. For d^8 complexes in particular, the following general classes of reactions generally should be recognized:

$$\underset{d^8}{L_4M} + X \rightleftarrows \underset{d^8}{L_4MX} \quad (\text{where } X = \text{CO or olefin}) \tag{14}$$



$$\underset{d^8}{L_4M} + YZ \rightleftarrows \underset{d^6}{L_4M}\langle{}^{Y}_{Z}$$

(where YZ = H_2, CH_3—I, Br_2, etc.) (15)



$$\underset{d^8}{L_4MX} + YZ \rightleftarrows \underset{d^6}{L_4M}\langle{}^{Y}_{Z} + X$$

(16)

The first two reactions—namely the addition to an unsaturated molecule and the insertion into a single bond—are also generally characteristic of carbenes. The last reaction is essentially a combination of the first two. The following specific reactions of $Ir^{I}Cl(CO)(PPh_3)_2$ (*84, 87*), and $Ru^{0}(CO)_3(PPh_3)_2$ (*21*), are illustrative.

$$Ir^{I}Cl(CO)(PPh_3)_2 + CO \rightleftarrows Ir^{I}Cl(CO)_2(PPh_3)_2 \tag{17}$$

$$Ir^{I}Cl(CO)(PPh_3)_2 + H_2 \rightleftarrows Ir^{III}H_2Cl(CO)(PPh_3)_2 \tag{18}$$

$$Ru^{0}(CO)_3(PPh_3)_2 + HCl \rightleftarrows Ru^{II}HCl(CO)_2(PPh_3)_2 + CO \tag{19}$$

Catalytic Activation of Hydrogen and Other Saturated Molecules

The ability to catalyze certain reactions of molecular hydrogen homogeneously in solution has been demonstrated for many transition metal ions and complexes (*34*)—among them complexes of Cu^{II}, Cu^{I}, Ag^{I}, Hg^{II}, Hg^{I}, Co^{I}, Co^{II}, Pd^{II}, Pt^{II}, Rh^{I}, Rh^{III}, Ru^{II}, Ru^{III}, and Ir^{I}. In each case it appears that H_2 is split by the catalyst with the formation of a reactive transition metal hydride complex (which may or may not be detected) as an intermediate. Three distinct mechanisms by which this can occur have been recognized (*34*), which are exemplified by the following reactions.

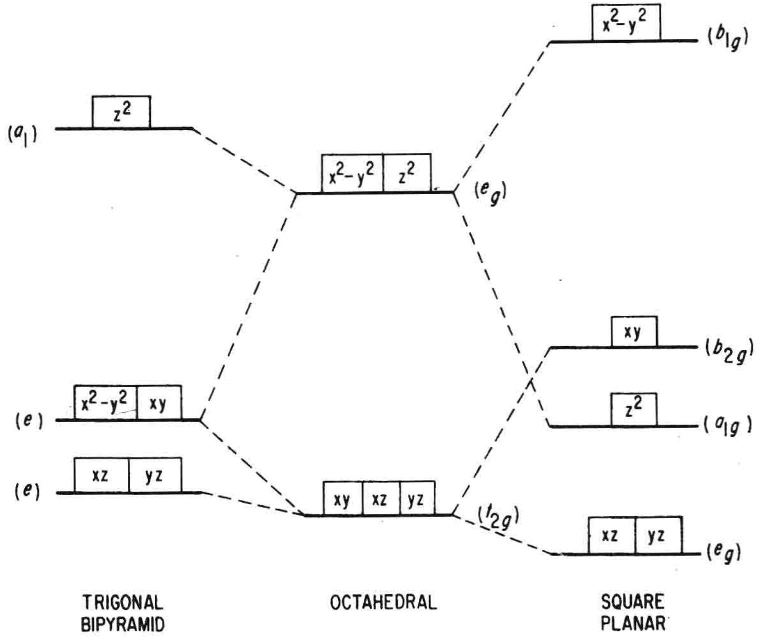


Figure 2. Energy level diagrams depicting orbital splitting in complexes of various symmetries. Only the orbitals involved in accommodating the d *electrons of the metal are depicted. Note that the octahedral configuration with only three stable (t_{2g}) orbitals is most favorable for accommodating six* d *electrons, whereas the two configurations of lower coordination number, each with four stable orbitals, are more favorable for accommodating seven or eight* d *electrons. The orbital symmetries are described by the symbols xz, yz, x^2-y^2 . . . , as well as by the group theoretical designations* a, e, t_{2g}

I. Heterolytic Splitting (*37*)
$Ru^{III}Cl_6^{3-} + H_2 \rightleftarrows Ru^{III}HCl_5^{3-} + H^+ + Cl^-$ (20)

II. Homolytic Splitting (*11, 29, 50, 52*)
$2Co^{II}(CN)_5^{3-} + H_2 \rightleftarrows 2Co^{III}H(CN)_5^{3-}$ (7)

III. Insertion (formation of dihydride) (*18, 87*)
$Ir^{I}Cl(CO)(PPh_3)_2 + \rightleftarrows Ir^{III}H_2Cl(CO)(PPh_3)_2$ (21)

The assignment of oxidation numbers to the metal atoms in these and other hydride complexes is based on the generally accepted convention which assigns the oxidation number (-1) to the hydride ligand.

The characteristic reactivities of hexa-, penta- and tetracoordinated complexes exemplified by these reactions follow readily from the general principles developed above. The first mechanism (heterolytic splitting), which is of widespread occurrence, involves essentially a substitutional process (replacement of a chloride ligand by a hydride derived from H_2) without change in the formal oxidation number of the metal. Reactivity is thus governed by the substitution lability of the complex, by the stability of the hydride formed, and by the presence of a suitable base (which may be the solvent or the displaced ligand) to stabilize the released proton (*41*).

In the other two mechanisms (homolytic splitting and insertion) hydride formation is accompanied by formal oxidation of the metal, and reactivity is closely linked to the susceptibility of the latter to oxidation. Thus, the high reactivity of $Co(CN)_5^{3-}$ toward H_2, compared with that of $Co(CNCH_3)^{2+}$, reflects the tendency of CN^- to stabilize preferentially the higher oxidation state, and $CNCH_3$ the lower oxidation state, of cobalt. For square planar d^8 complexes the expected order of the tendency toward oxidation, and hence of reactivity toward H_2, is (subject to some modification by ligand variation),

$$\mathrm{Os^0 > Ru^0 > Fe^0, Ir^I > Rh^I > Co^I, Pt^{II} > Pd^{II} >> Ni^{II}, Au^{III}}$$

Analogous mechanisms are applicable to the splitting of other saturated molecules and are realized in the following examples involving the reductive cleavage of carbon-halogen bonds (*39, 40, 45, 51, 54*).

$$\mathrm{2Co^{II}(CN)_5{}^{3-} + CH_3I \rightarrow Co^{III}(CN)_5CH_3{}^{3-} + Co^{III}(CN)_5I^{3-}} \tag{22}$$

$$\mathrm{Ir^{I}I(CO)(PPh_3)_2 + CH_3I \rightarrow Ir^{III}I_2(CH_3)(CO)(PPh_3)_2} \tag{23}$$

In principle it should also be possible to accomplish the reductive cleavage of C—H and C—C bonds by similar mechanisms, but this has not yet been realized except in a few special cases such as the tautomeric equilibrium described by Chatt and Davidson (*17*) (Reaction 24).

$$\mathrm{Ru^0(C_{10}H_8)(PP)_2 \rightleftarrows Ru^{II}H(2\text{-}C_{10}H_7)(PP)_2} \tag{24}$$

$$\mathrm{[PP = (CH_3)_2PCH_2CH_2P(CH_3)_2]}$$

The reactive nature of the hydrido complexes formed in many of the above reactions permits them to function as intermediates in homogeneous catalytic hydrogenation reactions. Thus, the reversible reaction,

$$\mathrm{RuCl_6{}^{3-} + H_2 \rightleftarrows RuHCl_5{}^{3-} + H^+ + Cl^-} \tag{20}$$

provides a mechanism for the homogeneous exchange of H_2 with D_2O (*37*) and for the homogeneous catalytic oxidation of H_2 by $FeCl_3$ since the latter oxidizes $RuHCl_5{}^{3-}$ rapidly (*43*) according to Reaction 25.

$$\mathrm{RuHCl_5{}^{3-} + 2FeCl_3 \rightarrow RuCl_6{}^{3-} + 2FeCl_2 + H^+ + Cl^-} \tag{25}$$

The reactivity of the hydride intermediate in such reactions is generally high so that its formation is the rate-determining step in the over-all catalytic reaction.