Hydrogenation of Organic Compounds Using Homogeneous Catalysts

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Contents

I. Introduction

In this review article the literature dealing with homogeneous catalytic hydrogenation of organic compounds has been reviewed through January 1972. Applications of this technique originated perhaps with the work of Roelen[1] in 1948 when it was observed that olefins in the presence of a soluble cobalt carbonyl complex react with carbon monoxide and hydrogen to form aldehydes (the "oxo process"). Since then many other reactions have been discovered including the polymerization[2] and oligomerization[3] of olefins on soluble Ziegler–Natta catalysts[4] and the cyclooligomerization of acetylenes[5] and conjugated diolefins on nickel.[6]

This review is primarily concerned with recent developments in the design and use of homogeneous catalysts for the hydrogenation of organic compounds. Organic chemists have shown great interest in these developments because of the high degree of selectivity in the reduction of functional groups afforded by the new catalysts. Variation of the nature of the ligands, geometry of the complex, and valence state of the metal has been termed "catalyst tailoring" by Henrici-Olive[2] in an apt description of the versatility which is developing. In many cases hydrogenation catalysts have been complexes of group VIII metals: Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, and Pt. Especially effective combinations have resulted from d^8 spin-paired (low-spin) configurations arising from strong ligand fields or electron delocalizing (π-acceptor) ligands. Frequently it is possible to identify the mechanism by which the homogeneous catalyst activates molecular hydrogen, activates the substrate, and transfers activated hydrogen to the substrate, often with considerable stereospecificity. Excellent review articles on the catalytic properties of metal complexes, their electronic structures, and chemical reactivities have been written by Collman,[7] Halpern,[8] Heck,[9] and others.[10]

A. Diversity of Metal Ions and Complexes Exhibiting Catalysis

A considerable variety of metal ions in aqueous and other solvent systems exhibit the ability to activate hydrogen. For instance, Ag(I), Cu(II), and Hg(II) catalyze hydrogen isotopic exchange, ortho–para conversion, and hydrogen reduction of inorganic, but not organic, compounds in aqueous solution. Hg(I), MnO_4^-, MoO_4^{2-}, and salts of the platinum group metals are active in aqueous

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(1) O. Roelen, *Angew. Chem.*, **60**, 62 (1948).

(2) G. Henrici-Olive, *Advan. Polym. Sci.*, **6**, 421 (1969).

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(4) L. Reich and A. Schindler, "Polymerization by Organometallic Compounds," Wiley, New York, N. Y., 1966, pp 243–402.

(5) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Justus Liebigs Ann. Chem.*, **560**, 1 (1948).

(6) G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Deim, M. Droner, W. Oberkirch, K. Tanaka, E. Steinrucke, D. Walter, and H. Zimmerman, *Angew. Chem.*, **78**, 157 (1966); *Angew Chem., Int. Ed. Engl.*, **5**, 151 (1966).

(7) J. P. Collman, *Accounts Chem. Res.*, 1, 136(1968).

(8) J. Halpern, *Advan. Chem. Ser.*, No. **70**, (1967).

(9) R. F. Heck, *Accounts Chem. Res.*, **2**, 10 (1969).

(10) (a) J. E. Lyons, L. E. Rennick, and J. L. Burmeister, *Ind. Eng. Chem., Prod. Res. Develop.*, **9** (1), 2 (1970); (b) W. Strohmeier, *Fortschr. Chem. Forsch.*, **25**, 71 (1972).

solution. Simple ions are also active in nonaqueous media as in the case of Ni(II) in DMF or DMA, copper and silver salts dissolved in amines, and copper, silver, and mercury salts in heptanoic acid and in biphenyl. In ethanol, liquid paraffin, and *n*-heptane, the stearates and adipates of Ni(II), Fe(III), Co(II), Mn(II), Cr(III), and Zn(II) function as hydrogenation catalysts. Rhodium(II) chloride in alcohol and $Co^{II}(CN)_5^{3-}$ in aqueous solution are also simple catalytic systems.

A more complicated group of hydrogenation catalysts is the Ziegler–Natta type. Here catalytic reactivity is found to follow the sequence $Ni \gg Co \geq Cu \gg Fe \geq Cr > V$ for transition metal compounds such as acetylacetonates combined with organometallic reducing agents of the type Alk_3Al, Et_3B, or RMgBr.

An extensive list of ternary or more complex systems could be developed, *e.g.*, $CrH_2(CO)_3$, $Cp_2Ti(CO)_2$, $CoH(CO)_4$, and species where Ph_3P replaces CO as in $CoH_2(Ph_3P)_3$ and $OsHCl(CO)(Ph_3P)_3$. Rhodium compounds include the derivatives of $RhCl_3$ such as $RhCl_3(Ph_3P)$, $RhHX(CO)(Ph_3P)_2$, $RhH(CO)(Ph_3P)_3$, $RhX(Ph_3P)_3$, etc., where X is Cl, Br, or I. Among the iridium compounds one finds Vaska's compound $IrCl(CO)(Ph_3P)_2$, $IrH(CO)(Ph_3P)_3$, $IrH_3(Ph_3P)_3$, and the series $IrHX_2L_2$ where X = halogen and L = Ph_3P, Ph_3As, or Ph_3Sb. Active ruthenium compounds are $RuHCl(Ph_3P)_3$, $RuCl_2(Ph_3P)_4$, and $RuCl_2(Ph_3P)_3$. In some cases a trichlorostannate(II) ligand is present as in the system (K_2PtCl_4 + $SnCl_2$)-alcohol. The system $[PtHCl(Ph_3P)_2 + SnCl_2]$ is active as is the series $[MX_2L_2 + SnCl_2]$, where X = halogen, L = R_3P, R_3As, etc., and M = Ni, Pd, Pt, etc.

B. Scope of the Catalysis Reactions

Hydrogenation of olefins has been catalyzed by complexes of ruthenium, rhodium, cobalt, and platinum as well as other cations.[11] The Oxo process[1] involves hydroformylation of olefins using cobalt or rhodium catalysts. Rhodium also catalyzes the dimerization of ethylene and polymerization of dienes. Complexes of rhodium, palladium, cobalt, platinum, and other metals catalyze double-bond migration in olefins. The Wacker process utilizes palladium chloride to catalyze the oxidation of olefins to aldehydes, ketones, and vinyl esters. Acetylene is catalytically hydrated in the presence of ruthenium chloride. Additional examples may be found in ref 8 and articles cited therein. Several of these applications will be discussed subsequently.

C. Mechanisms of Hydrogen Activation

In all cases of catalytic hydrogenation, molecular hydrogen is activated or split by the catalyst. Frequently, although not always, the formation of specific reactive transition metal hydride complexes can be demonstrated. Three mechanisms of hydrogen activation may be distinguished.

1. Heterolytic Cleavage.[12,13] The covalent bond of the H_2 molecule is split heterolytically with the hydride moiety becoming bonded to the transition metal catalyst and the hydrogen ion becoming associated with a suitable Lewis base. Examples are as follows.

$$Rh^{III}(PAr'Ar''Ar''')_2Cl_3S + 2H_2 \rightleftharpoons Rh^{III}H_2(PAr'Ar''Ar''')_2ClS + 2HCl \quad (1)$$

$$Ru^{III}Cl_6^{3-} + H_2 \rightleftharpoons Ru^{III}HCl_5^{3-} + HCl \quad (2)$$

2. Homolytic Cleavage.[13,14] Both atoms from the hydrogen molecule become incorporated equivalently into the catalyst structure.

$$2Co^{II}(CN)_5^{3-} + H_2 \rightleftharpoons 2Co^{III}H(CN)_5^{3-} \quad (3)$$

In an insertion-type reaction both hydrogens are bonded to the same metal forming a dihydride.[15,16]

$$Ir^{I}ClCO(Ph_3P)_2 + H_2 \rightleftharpoons Ir^{III}H_2Cl(CO)(Ph_3P)_2 \quad (4)$$

3. Electron Transfer.[17] A simple redox process may occur without formation of a stable hydride.

$$Hg^{2+} + H_2 \rightarrow Hg^0 + 2H^+ \quad (5)$$

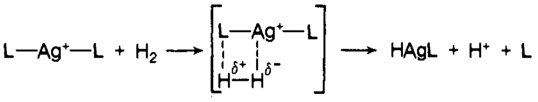
Some insertion reactions constitute a preliminary step which is followed by hydrogen redistribution,[10] for example

$$MXL_n + H_2 \rightarrow M(H_2)XL_n \rightarrow MHL_n + HX \quad (6)$$

$$RuCl_2(Ph_3P)_4 + H_2 \rightarrow Ph_3P + [Ru(H_2)Cl_2(Ph_3P)_3] \rightarrow RuHCl(Ph_3P)_3 + HCl \quad (7)$$

Instances have been cited in the literature where activation of hydrogen occurs at more than one catalytic center. The metal atoms may be the same as in $Co_2(CO)_8$[18] or different as in complexes with a Pt–Ge bond.[19] An unusually low activation energy for splitting the H–H bond was found in the latter case (9 kcal mol^{-1}).

Ligand assisted heterolysis has been proposed in some instances. This is presumed to be the case for some amine complexes of silver(I)[20,21] (eq 8).



$$L{-}Ag^+{-}L + H_2 \rightarrow \left[\begin{array}{ccc} L & {-}Ag^+{-} & L \\ \vdots & \vdots & \\ H^{\delta+} & {-}H^{\delta-} & \end{array}\right] \rightarrow HAgL + H^+ + L \quad (8)$$

D. Characteristics of an Active Catalyst

Out of the considerable body of literature on homogeneous hydrogenation catalysis it is possible to abstract a number of features which contribute to active catalysis. These will be considered briefly.

1. Available Coordination Sites on the Transition Metal

This is undoubtedly the single most important attribute of the transition metal catalyst.[22] The ability to bind hydrogen is essential to its activation and in those cases where substrate activation has been demonstrated it also must be held within the coordination sphere. In this con-

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[11] J. Halpern, *Annu. Rev. Phys. Chem.*, **16**, 103 (1965).

[12] (a) R. E. Harmon, J. L. Parsons, and S. K. Gupta, *Chem. Commun.*, 1865 (1969); (b) L. Horner, H. Buthe, and H. Siegel, *Tetrahedron Lett.*, 4023 (1968).

[13] M. G. Burnett, P. J. Connolly, and C. J. Kemball, *J. Chem. Soc. A*, 800 (1967).

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[15] P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **88**, 3511 (1966).

[16] L. Vaska and J. W. DiLuzio, *J. Amer. Chem. Soc.*, **84**, 670 (1962).

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[18] M. Orchin, *Advan. Catal. Relat. Subj.*, **9**, 385 (1953).

[19] R. I. Kross and F. Glocking, *J. Chem. Soc. A*, 5422 (1965).

[20] L. Wright, S. Weller, and G. A. Mills, *J. Phys. Chem.*, **59**, 1060 (1955).

[21] W. K. Wilmarth and A. J. Kapaun, *J. Amer. Chem. Soc.*, **78**, 1308 (1956).

[22] J. P. Collman, *Trans. N. Y. Acad. Sci.*, **30**, 479 (1968).

Table I[8]

Coordination no.	Examples	Electronic confign	Total no. 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

text the poisoning of a catalyst by species which bind strongly such as sulfur compounds, amines, phosphines, and carbon monoxide is readily envisioned. Thus, complexes which are stable and coordinately saturated such as $Rh(NH_3)_6Cl_3$ and $Rh(en)_3Cl_3$ do not catalyze hydrogen reduction of Fe^{3+} or organic substrates.[23] On the other hand, complexes such as $[Rh(NH_3)_5H_2OCl_3]$, $[Rh(NH_3)_4Cl_2]Cl$, $RhCl_3$, and anionic chlororuthenate(III) ions in general have readily replaceable ligands and are catalytically active.[24] The occurrence of induction periods and the requirement of thermal or photochemical stimulation usually indicate the need to expell a ligand in order to provide a catalytically active site. Bridging by ligands such as halide, hydroxide, and various sulfur ligands frequently blocks sites which might appear to be available from the stoichiometry of the complex.

Collman[25] emphasized the relationship between various d^n electronic configurations and the maximum coordination possible. Since, for any metal ion only a limited number of low energy orbitals exist, an inverse relationship between the number occupied by its own electron pairs and that involved in coordination to ligands is exhibited. Thus spin-paired d^6, d^8, and d^{10} are coordinately saturated with six, five, and four ligands, respectively. Some important coordination tendencies are illustrated in Table I.[8] Lower coordination numbers would leave the possibility for further coordination open. The tendency to use all low energy orbitals found its early expression in the rule of 18 (effective inert gas concept) but has its modern counterpart in molecular orbital energy level diagrams.

The orbital splittings associated with complexes of the more common coordination geometries are illustrated by Figure 1.[8] In most complexes of catalytic importance the ligands represent strong field cases. That is to say, the splitting is so large that electrons spin-pair in the relatively low-energy orbitals rather than remain spin-free and occupy higher energy orbitals singly. When the number of d electrons to be accommodated exceeds six, the advantage of octahedral geometry (a low-energy orbital triplet and high-energy orbital doublet) diminishes, and coordination geometries involving lower coordination numbers (five or four) may become favored. The crystal field stabilization energy associated with the specific distribution of electrons (preferentially in low energy orbitals) is a significant (often 10-20%) part of the total electronic energy of the complex. However, it must be borne in mind that the crystal field levels correlate with antibonding levels in a molecular orbital scheme, and the number and strength of covalent bonds formed are the dominant energy factors. In a simplified molecular orbital diagram[8] for an octahedral complex (Figure 2), the σ-bonding a_{1g}, e_g, and t_{1u} levels are filled; the t_{2g} level may be nonbonding and accommodate metal d electrons or π bonding and accommodate ligand electrons. In the latter case a t_{2g} π* level is present (not shown in Figure 2) in which d electrons are accommodated. This level may become involved in metal to ligand "back-bonding" if the ligand has vacant π or π* levels of suitable energy. The e_g* level is σ antibonding and accommodates any remaining d electrons while the a_{1g}* and t_{1u}* levels are generally vacant.

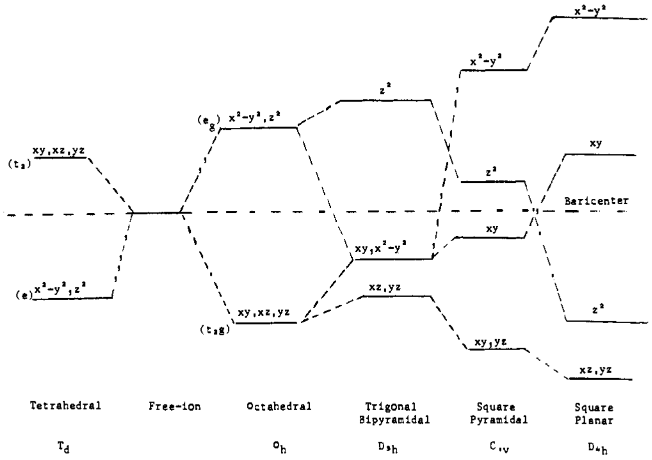

Figure 1. Relative one-electron d-orbital splittings for crystal fields of several different symmetries.

2. Facile Rearrangement

The possibility of different coordination numbers with differing bond strengths and different utilization of stable bonding or nonbonding levels and antibonding levels frequently produces different complexes of similar energies. Hence interconversion is readily accomplished. This leads to low energy catalytic mechanisms. For example, $Co(CN)_6^{3-}$ (d^6 low-spin configuration) is a very stable octahedral complex. However, if an electron were to be added (reduction), it would have to occupy a high energy σ* e_g level. Stabilization of the O_h geometry is diminished and the Co(II) complex readily loses cyanide and becomes pentacoordinate (eq 9). The pentacoordinate

$$\underset{\text{stable}}{\underset{d^6}{Co(CN)_6^{3-}}} \xrightarrow{+e^-} \underset{\text{unstable}}{\underset{d^7}{[Co(CN)_6^{4-}]}} \rightarrow \underset{\text{stable}}{\underset{d^7}{Co(CN)_5^{3-}}} + CN^- \quad (9)$$

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(23) M. Iguti, *J. Chem. Soc. Jap.*, **60**, 1787 (1939).

(24) (a) J. N. Harrod and J. Halpern, *Can. J. Chem.*, **37**, 1933 (1959); (b) B. R. James and G. J. Rempel, *ibid.*, 44, 233 (1966); (c) W. C. Wolsey, C. A. Reynolds, and J. Kleinberg, *Inorg. Chem.*, **2**, 463 (1963); (d) J. N. Harrod, S. Ciccone, and J. Halpern, *Can. J. Chem.*, **39**, 1372 (1961).

(25) J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, **87**, 4008 (1965).

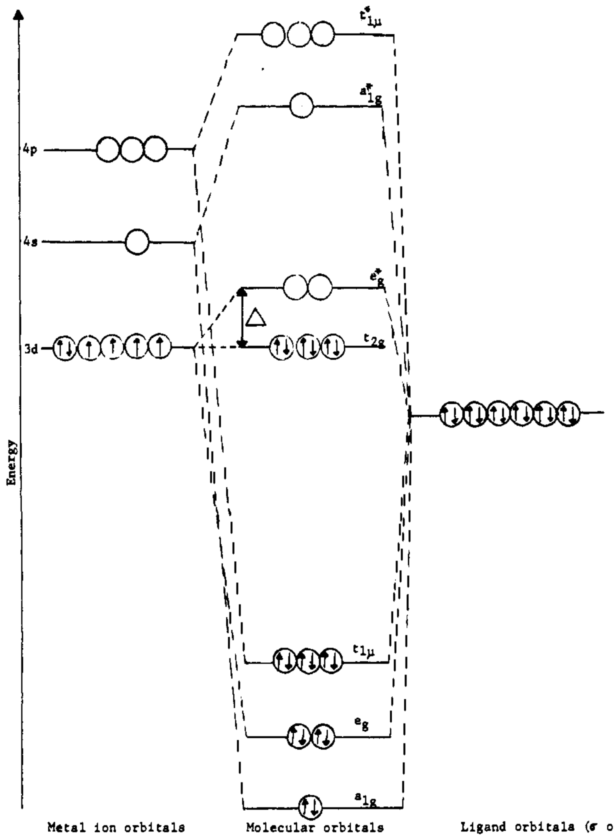

Figure 2. Molecular orbital (ligand field) diagram for octahedral complex (schematic).

complex can then be oxidized to a stable six-coordinate complex or dimerize *via* reactions analogous to organic free radical systems, as shown below.

$$2\mathrm{Co(CN)_5}^{3-} + \mathrm{Br_2} \rightarrow 2\mathrm{Co(CN)_5Br}^{3-} \qquad (10)$$

$$2\mathrm{Co(CN)_5}^{3-} + \mathrm{H_2} \rightarrow 2\mathrm{Co(CN)_5H}^{3-} \qquad (11)$$

$$2\mathrm{Co(CN)_5}^{3-} \rightarrow \mathrm{Co_2(CN)_{10}}^{6-} \qquad (12)$$

3. Stabilization of Intermediates

By virtue of their varied bonding capabilities, transition metals may stabilize, through coordination, a variety of otherwise very reactive intermediates. These complexes are stable enough to have significant lifetimes, yet they are very reactive with suitable reactants. σ-Bonded ligands such as hydride and alkyl groups and π-bonded ligands such as allyl and cyclobutadiene are cases in point.

4. Template Effect

An attribute of great importance in stereospecific synthesis is the ability of certain catalysts to assemble and/or to orient several components of a reaction within their coordination spheres. Subsequent reaction yields asymmetric reduction in the case of dissymmetric hydrogenation catalysts and various stereospecific reactions of other systems. Several examples will be discussed in a later section.

E. Analogies to Organic Reactions

Many of the reactions of d^6, d^7, and d^8 complexes which make them suitable hydrogenation catalysts bear a close formal relationship to familiar organic reactions. The organic chemist may find these relations quite helpful in visualizing the reactions of transition metal complexes in catalytic processes. Several important analogies are illustrated in Table II.

II. Mechanisms of Homogeneous Hydrogenation Reactions

A. Isotopic Exchange and Conversion of Hydrogen

The isotopic exchange of molecular hydrogen and the conversion of ortho-hydrogen into para-hydrogen can be used to study the activation of hydrogen. A significant advantage of these reactions, as compared with hydrogenation, is their convenience for kinetic studies and their relative simplicity since there is no need for activation of a substrate, and the chemical changes in the system are minimal.

1. Systems Containing Salts of Transition Metals

The homogeneous isotopic exchange and ortho-para conversion of hydrogen was first observed by Calvin[26] in the presence of salts of transition metals. To explain these results the following scheme, involving the intermediate formation of a transition metal hydride, was postulated.

$$n\mathrm{Cu^I} + \mathrm{H_2} \rightleftharpoons \mathrm{Cu^I \cdot H_2} \qquad (13)$$

$$\mathrm{Cu^I}_n\cdot\mathrm{H_2} + 2\mathrm{Cu^{2+}} \rightleftharpoons (n+2)\mathrm{Cu^I} + 2\mathrm{H^+} \qquad (14)$$

It was found that in the presence of copper(II) acetate neither conversion nor isotopic exchange of hydrogen takes place and the molecular hydrogen is used up only in the reduction of the bivalent copper acetate. It is only when this reaction is complete that the Cu(I) acetate formed begins to catalyze the exchange and conversion of hydrogen. It has also been reported,[27] however, that the competing reactions of reduction and isotopic exchange (or conversion) of hydrogen takes place under these conditions.

The rate of ortho-para conversion is greater than the rate of isotopic exchange of hydrogen. This is due to the fact that the conversion of hydrogen generally involves the recombination of two hydrogen atoms on a single metallic center, whereas the exchange of hydrogen also requires interaction between the metal-hydrogen bond and the solvent. The isotope exchange and ortho-para conversion of hydrogen are catalyzed not only by copper salts but also by salts of silver, ruthenium, cobalt, etc., as well as by complexes of these compounds which may be charged or neutral species. Both heterolytic and homolytic rupture of the H-H bond may take place.

2. Systems Containing Transition Metal Complexes

The distinction between simple transition metal salts and complexes is not entirely rigorous since the metal ion is always enclosed in some coordination sphere even if it is only solvent or labile anion association. In the case of stable complexes, however, the ligand may significantly modify the activity of the metal ion.

The mechanism of hydrogen activation will be considered in detail for a number of catalysts subsequently;

(26) M. Calvin, *Trans. Faraday Soc.*, **34**, 1181 (1938).

(27) S. Weller and G. A. Mills, *J. Amer. Chem. Soc.*, **75**, 769 (1953).

TABLE II.[a] **Comparison of Reactions in Organic and Coordination Chemistry**

Organic Reactions				Transition Metal Reactions			
Compound	Coordination no.	Nonbonding electrons	Characteristic reactions	Coordination no.	Nonbonding electrons	Examples	Reactions
Saturated	4	0	Nucleophilic substitution (SN2)	6	6	$RhCl_3(Ar_3P)_3$	$RhCl_3(Ar_3P)_3 + H_2 \rightleftharpoons RhHCl_2(Ar_3P)_3 + HCl$
Free radical ($R_3C\cdot$)	3	1	Dimerization Abstraction Addition	5	7	$Co(CN)_5^{3-}$	$2Co(CN)_5^{3-} \rightleftharpoons Co_2(CN)_{10}^{6-}$ $Co(CN)_5^{3-} + H_2 \rightarrow Co(CN)_5H^{3-}$ $2Co(CN)_5^{3-} + HC{\equiv}CH \rightarrow [(NC)_5CoCH{=}CHCo(CN)_5]^{6-}$
Carbene	2	2	Addition	4	8	$IrI(CO)(PPh_3)_2$	$IrICO(PPh_3)_2 + C_2H_4 \rightleftharpoons IrI(CO)(C_2H_4)(PPh_3)_2$
			Insertion				$IrI(CO)(PPh_3)_2 + H_2 \rightleftharpoons IrH_2I(CO)(PPh_3)_2$
Carbonium ion (R_3C^+)	3	0	Nucleophilic substitution (SN1)	5	6	$Co(CN)_5^{2-}$	$Co(CN)_5^{2-} + I^- \rightarrow Co(CN)_5I^{3-}$
Carbanion (R_3C^-)	3	2	Electrophilic substitution	5	8	$Mn(CO)_5^-$	$Mn(CO)_5^- + H^+ \rightleftharpoons Mn(CO)_5H$

[a] The change in coordination number and nonbonding electrons in going from one species to the next is the same in each series. This results in corresponding changes in reactivity patterns of the organic and inorganic series of compounds since the reactivity in each case is dominated by the tendency to return to the stable closed-shell configuration of the first member of the series.

however, the interaction of a few catalysts with molecular hydrogen is described briefly in this section. Homolytic rupture of the H-H bond takes place when the $CoCl_2$–KCN catalyst system is used, and also in the presence of copper acetate in quinoline. These reactions are analogous to free radical reactions in organic chemistry. On the other hand, detailed studies of the kinetics of exchange and conversion of hydrogen in the presence of $RuCl_3$-HCl-H_2O[28-30] showed that the hydrogen in this system undergoes heterolytic splitting according to the following scheme (analogous to a substitution reaction in organic chemistry) in which $Ru^{III}Cl^-$ represents the active chloro complex of ruthenium. According to this scheme, the exchange and conversion of hydrogen are accompanied by the intermediate formation of hydride and deuteride complexes of ruthenium.

$$Ru^{III}Cl^- + D_2 \rightarrow Ru^{III}D^- + D^+ + Cl^- \qquad (15)$$

$$Ru^{III}D \;-\!\!\left\{\begin{array}{l} \xrightarrow{HCl} Ru^{III}Cl^- + HD \\ \xrightarrow{H_2O} Ru^{III}H^- + HOD \end{array}\right. \qquad (16)$$

$$Ru^{III}H^- \xrightarrow{HCl} Ru^{III}Cl^- + H_2 \qquad (17)$$

Of particular interest is the recently prepared iridium complex, $IrHD(CO)(PPh_3)_3$, which contains H and D attached to the same metal atom and is active in catalytic hydrogenation reactions.[31] The properties of these mixed hydrides make it possible not only to reach a deeper understanding of the individual stages in the exchange, but also to arrive at definite conclusions regarding the structures of intermediate hydride complexes. Jardine, *et al.*,[32] studied the homogeneous hydrogenation of olefins using Wilkinson's catalyst,[33] $Rh^IX(PPh_3)_3$ (where X = Cl, Br, and I), in the presence of HD[34] and obtained monodeuterated alkanes. They suggested that the dihydride intermediate is formed as follows

$$Rh^ICl(PPh_3)_2(S_n) + DH \rightleftharpoons Rh^{III}ClDH(PPh_3)_2(S) + (S_{n-1}) \qquad (18)$$

where S is solvent used (usually ethanol). Note that this involves an oxidative addition of H–D to a coordinatively unsaturated d^8 complex to yield a coordinatively saturated d^8 complex. This is analogous to a carbene insertion or addition reaction in organic chemistry.

B. Mechanism of Activation of Hydrogen and Homogeneous Hydrogenation

As has been pointed out by Collman,[25] the single most important property of a homogeneous catalyst is a vacant coordination site. This site must be nascent in some complexes; *i.e.*, it may be occupied by a readily displaceable ligand. Various features of homogeneous catalytic hydrogenation are the activation of hydrogen in the presence of transition metal complexes, the part played by the transition metal and ligands, the influence of solvents, and the stereospecificity and selectivity of the catalysts.

Activation of Molecular Hydrogen by Transition Metal Complexes. Because of its closed electron cloud, the H_2 molecule is fairly inert and its dissociation energy is 104 kcal mol^{-1}. There are two possible ways by which the activation of hydrogen can take place. The first involves H_2 acting as an electron donor; *i.e.*, the bonding electrons of the hydrogen molecule are partly transferred to vacant orbitals of the metal ion (donor-acceptor bond).[33] The second possibility involves the transfer of an electron from the metal atom to an antibonding orbital of the hydrogen molecule (dative bond); *i.e.* H_2 acts as an electron acceptor (in Halpern's opinion,[35] this process may involve the 2p orbitals of hydrogen).

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(28) U. Shindewolf, *Ber. Bunsenges. Physik. Chem.*, **67**, 219 (1963).

(29) J. Halpern, *Can. J. Chem.*, **39**, 1372 (1961).

(30) J. Halpern, *Can. J. Chem.*, **44**, 671 (1966).

(31) L. Vaska, *Chem. Commun.*, 614 (1966).

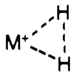
(32) F. H. Jardine, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1574 (1967).

(33) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

(34) I. Wender, R. A. Friedel, and M. Orchin, *J. Amer. Chem. Soc.*, **71**, 1140 (1949).

(35) (a) J. Halpern, *Advan. Catal. Relat. Subj.*, **11**, 301 (1959); (b) J. Halpern and R. S. Nyholm, *Proc. Int. Congr. Catal., 3rd*, **1**, 25, 146 (1965).

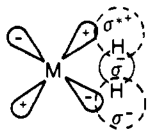
Thus the transition states (or intermediate compounds) of these two extreme types (depending on whether hydrogen acts as an electron donor or electron acceptor) can be represented as $M{-}{-}{-}H_2^+$ and $M{-}{-}{-}H_2^-$. The energies of rupture of the H–H bonds in the corresponding molecular ions H_2^+ and H_2^- are not the same and have the values of 62 and 3.4 kcal mol^{-1} (or 18.6 kcal mol^{-1} according to other data), respectively.[36] Syrkin[37] has suggested that in the activation of H_2 by the formation of a bond of the donor-acceptor type, a three-center transition state with two electrons in the field or three nuclei may be realized.



For a transition state of the type $M{-}{-}{-}H_2^+$ to be realized, the M atom must have suitable vacant orbitals with sufficiently low energies. For transition metals these are primarily d orbitals.

In an earlier review[35a] it was noted that the active species are primarily transition metal ions with filled or almost filled d electron levels: Cu(II), $3d^9$; Cu(I), $3d^{10}$; Pd(II), $4d^8$; Ag(I), $4d^{10}$; Hg(II), $5d^{10}$.

It is significant that for ions with a filled d level the difference in the energies of the d and the next vacant s and p orbitals is comparatively small and the ease of the d → s → p transitions leads to the formation of vacant d orbitals. It is interesting to note that although Zn(II), Cd(II), and Hg(II) have similar d^{10} configurations, only Hg(II) is effective in the activation of hydrogen, since the difference in the energies of the d and the higher s orbitals is much smaller for this ion than for other ions of this series.[38] On the other hand, the formation of a dative $M{-}{-}{-}H_2^-$ bond, which involves the transfer of electrons from the M atom to an antibonding molecular orbital of hydrogen, is favored by a minimal positive charge on the metal (see structure **1**). This explains the higher activating power of Cu(I) as compared to Cu(II) in the reaction with hydrogen. A large proportion of the known catalysts for homogeneous hydrogenation are complexes of transition metals with low oxidation states.



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Another factor facilitating the formation of dative bonds is the presence of electron-donating ligands on the metal atom. Thus the activation of hydrogen may be favored by the presence of vacant orbitals and by a low oxidation state of the metal in the complex.

C. Influence of Ligands and Solvents on the Activity and Specificity of Catalysts

Interest in preparative coordination chemistry has advanced rapidly in the last few years, and many new and interesting complexes have been reported. But this area of chemistry is still at a very early stage in its development because it is still not possible to design a catalyst in advance for a specific purpose (*e.g.*, to add molecular hydrogen to olefins). This long-term objective cannot be achieved without precise knowledge of the kinetic and thermodynamic principles underlying every step of the catalytic reactions. Though research on these principles is being carried out by various groups,[39-42] procedures in practical catalysis are still semiempirical at best.

1. Activation of Substrate and Transfer of Hydrogen

In hydrogenation it is possible to distinguish between the stages involving the activation of hydrogen, the activation of substrate, and the transfer of hydrogen to the substrate. The general sequence of these stages can be represented by the following schemes (M represents the transition metal complex and S the substrate).[43]

SCHEME I

$$M + H_2 \rightleftharpoons M{\cdot}H_2 \tag{19}$$

$$M{\cdot}H_2 + S \rightleftharpoons S{\cdot}M{\cdot}H_2 \tag{20}$$

$$S{\cdot}M{\cdot}H_2 \rightarrow SH_2 + M \tag{21}$$

According to Scheme I, first the activation of hydrogen takes place to form a hydride, which then reacts with the substrate and hydrogen is transferred to the substrate.

SCHEME II

$$M + S \rightleftharpoons M{\cdot}S \tag{22}$$

$$M{\cdot}S + H_2 \rightleftharpoons H_2{\cdot}M{\cdot}S \tag{23}$$

$$H_2{\cdot}M{\cdot}S{\cdot} \rightarrow S{\cdot}H_2 + M \tag{24}$$

According to Scheme II, the complex with the substrate is formed first, and this complex then activates hydrogen.

SCHEME III

$$M + S \rightleftharpoons M{\cdot}S \tag{25}$$

$$M + H_2 \rightleftharpoons M{\cdot}H_2 \tag{26}$$

$$M{\cdot}S + M{\cdot}H_2 \rightleftharpoons M + S{\cdot}H_2 + M \tag{27}$$

According to Scheme III, the activation of hydrogen and the substrate is effected separately, by one or more complexes. Examples of reactions of this kind are provided by various enzymatic catalysis, in which the substrate and hydrogen are activated by different centers.[44]

Activation of the substrate has been studied, in detail, for the hydrogenation of alkenes and alkynes.[33] In most cases of homogeneous hydrogenation using metal complexes, the reaction takes place on covalently σ-bonded hydrogen and a substrate molecule (alkene or alkyne) coordinated to the metal M. The substrate is inserted between the metal and hydrogen by a four-center reaction (concerted reaction) as shown below for an alkene. L_n stands for all the other ligands in the complex. The catalyst is restored to its original condition by hydrogenolysis or homolysis. The transition metal, the stability of M–H and M–olefin bonds, and the possibility of influencing these bonds through other ligands are, therefore, of the utmost importance.

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(37) Ya. K. Syrkin, *Usp. Khim.*, **28**, 903 (1959).

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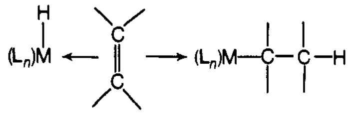


2. The Transition Metal

As was stated previously the transition metals are characterized in that the (n − 1) d orbitals have energies similar to those of the ns and np orbitals of the valence shell, and so participate in bond formation. The spatial symmetry of these d orbitals is responsible for a particular type of bond between the transition metal and the ligand. This does not occur with other metals. For symmetry reasons, some of the five d orbitals cannot participate in normal σ bonds between the metal and the ligands. In an octahedral complex, for example, the d_{z^2} and $d_{x^2-y^2}$ orbitals point in the directions of the six bonds, but the "loops" of maximum electron density in the d_{xy}, d_{xz}, and d_{yz} orbitals lie between these directions. However, these orbitals can overlap with empty antibonding orbitals of suitable symmetry. This may be illustrated by the following well-known Dewar-Chatt-Duncanson model of the metal-olefin bond (Figure 3).[45]

The bonding π orbital of the alkene which contains two electrons has σ symmetry with respect to the axis of the metal-olefin bond. This type of symmetry is characterized by the fact that underlying wave functions retain their sign on rotation about the axis of the bond through 180°. The π orbital of the alkene can overlap with an empty dσ orbital of the metal with the formation of a coordinate σ bond. The empty antibonding π orbital of the alkene has π symmetry with respect to the axis of the bond. In π symmetry a change in sign does occur in the underlying wave function when it is rotated about the axis of the bond by 180°. If the dπ orbital of the metal that lies in the same plane is occupied, a π bond is also formed. The metal and the alkene can thus form a sort of double bond between them *via* the σ bond electron density passing from the alkene to the metal, while the π bond electron density passes from the metal into the antibonding π^* orbital of the alkene. Both effects lead to destabilization of the double bond of the alkene. This is equivalent to activation of the molecule. Its relevance to catalysis is obvious.

The preparations of a fairly large number of alkene and alkyne complexes have been described.[46,47] Homogeneous hydrogenation is usually undergone only by those alkenes which react reversibly with the transition metal catalyst in solution.[33] Attempts to correlate the tendency of alkenes to undergo hydrogenation with the stability constants of the complex formed by the transition metal with these alkenes are extremely interesting.[33] According to Osborn and coworkers,[33] the equilibrium constant for the reaction of propene with the rhodium complex, $RhCl(Ph_3P)_3$, is smaller by a factor of 2000 than that for ethylene, so that propene unlike ethylene is hydrogenated by means of this catalyst. The higher activity of $RhBr(Ph_3P)_3$ and $RhI(Ph_3P)_3$ compared with the corresponding chloro complex is in agreement with low stability of the complexes formed by alkenes with iodide- and bromide-containing catalysts.

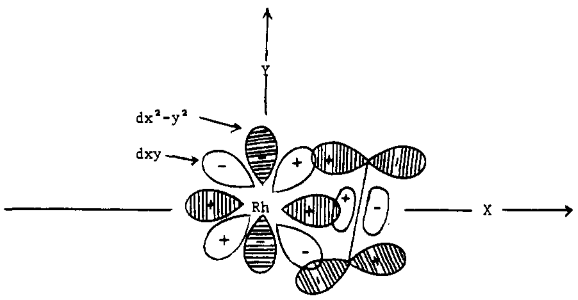
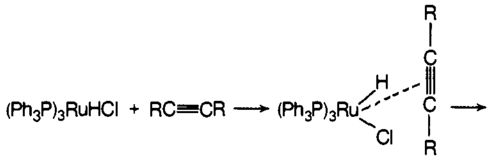


Figure 3. Coordination of ethylene to a transition metal (rhodium); schematic representation of the relevant orbitals in the X–Y plane of an octahedral complex. Shaded area represents empty (acceptor) orbitals.

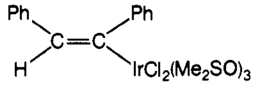
In many organometallic compounds of transition metals the metal-carbon bonds are not very strong, and such compounds can be isolated only at low temperatures. However, it was recognized as early as the 1950's that ligands that build up a strong ligand field around the central metal atom can stabilize alkyl and aryl compounds of the transition metals. For instance, using phosphines as ligands, it was possible to isolate stable complexes of the type $(PR_3)_2PtCH_3X$ (where R = alkyl or aryl and X = halogen) at room temperature.[48] Carbonyl and π-cyclopentadienyl ligands have also been found to have a stabilizing effect,[49] and a whole new series of stable organotransition metal complexes is now known.

In the stage involving activation of alkenes and alkynes, both π and σ complexes of the transition metal may be formed. Under the influence of basic ligands (σ donors, *e.g.*, phosphines), the configuration of π-bonding ligands can change with the formation of a localized σ bond between the metal and the carbon,[50] whereas, the "π complex" is favored by the presence of acceptor ligands (*e.g.*, Cl). According to eq 28 the hydride formed by the reaction of hydrogen with transition metal complex may give a π complex with the alkene (or alkyne), which is then converted into a σ complex. This scheme was adopted by Jardine and McQuillan.[49]



$$(Ph_3P)_3RuHCl + RC{\equiv}CR \longrightarrow (Ph_3P)_3Ru(H)(Cl)(RC{\equiv}CR) \longrightarrow (Ph_3P)_3Ru(CR{=}CRH)Cl \qquad (28)$$

Examples of complexes containing both the hydrogen and a π-bonded alkene on the same metallic center are provided by the recently prepared complexes of iridium,[50] $[IrHCl_2(C_8H_{12})]_2$, and rhodium,[51] $RhH_2Cl(C_2H_4)(Ph_3P)_2$. The organometallic σ complex **2**, whose existence was proposed by Jardine and McQuillan, has recently been prepared.[52]



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On acidification this compound gives *cis*-stilbene. On the

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(45) (a) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C71 (1951); (b) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

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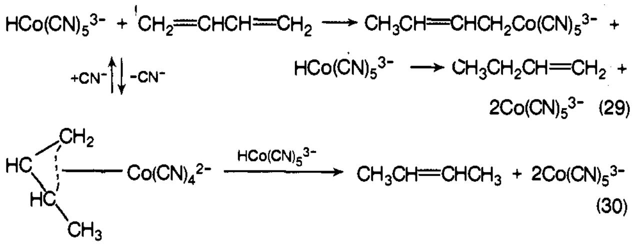
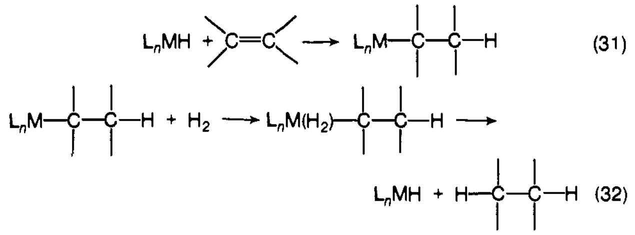
other hand, the reaction of the hydride with the substrate may involve the initial formation of a σ complex which is subsequently converted into a π complex. Thus the sequence of reactions in eq 29 and 30 was proposed to explain isomerization during hydrogenation.[53]


(29)

(30)

The organometallic σ compound may subsequently react with the transition metal hydride or undergo hydrogenolysis or hydrolysis (alcoholysis) depending on the reaction conditions. The hydrogenolysis of metal-carbon bonds is a fairly common phenomenon. Gilman[54] described the splitting of alkali metal compounds by hydrogen. Clauss and Bestain[55] have described hydrogenolysis of organometallic compounds of Mn and Ti, and Hein and Weiss[56,57] reported the hydrogenolysis of the compounds of chromium (the formation and properties of these derivatives have been reviewed).[58,59]

In a sense, the hydrogenolysis of a metal-carbon bond represents the activation of hydrogen by an intermediate organometallic compound as shown in eq 31 and 32.


(31)

(32)

A mechanism involving the formation of a σ-alkyl complex was assumed for an iridium complex by Vaska.[60] It has also been proposed for Ziegler-Natta catalysts.[61]

Although the formation of a σ-alkyl bond is widely encountered, this stage cannot always be observed in homogeneous hydrogenation. Thus, during the hydrogenation of alkenes by rhodium hydride, Osborn and coworkers[33] were unable to detect the formation of a σ C–Rh bond using nmr. In this case (on the basis of the available experimental data), they postulated a hydrogenation scheme involving the simultaneous transfer of two hydrogens to the alkene.

The form (ionic or radical) in which the hydrogen is transferred to the compound being hydrogenated depends to a large extent on the nature of the transition metal hydride, the substrate, the presence of a hydrogen carrier, the participation of solvent, and several other factors.

3. *Influences of the Ligands L (σ-Donor Ability).*

The ligands L involved in transition metal catalysts[1] may be ions (Cl^-, CN^-, H^-, etc.) or neutral molecules (phosphines, phosphites, amines, CO, NO, etc.). A number of concepts have been used to interpret the influence of such ligands[2,6,62] on the stability of the M–R and M–olefin bonds, and hence on catalytic activity. These include the σ-donor ability or basicity of the ligands,[42] the trans effect,[33] the inductive effect,[63] the resonance effect,[64] the electron density on the metal,[2,42] and the influence on the energies of orbitals.[65-67] The concepts stem, in part, from different theories of chemical bonding (the valence bond theory, the MO theory, ligand field theory), but they are all basically descriptions of the same thing, *i.e.*, a change in the electronic structure, or a decrease in electron density in a certain region of the complex, and increase in others, and a consequent change in the bonding.

Any attempt to depict catalytic activity as a monotonous function of a variable ligand property such as σ-bonding ability is doomed by its naiveté. We already have characterized homogeneous catalytic hydrogenation as a multistage process operating within narrow energy restrictions. A progressive change in ligand properties of sufficient magnitude to modify one effect may completely unbalance another (*e.g.*, the σ-bonding, π-back-bonding synergism). Thus if hydride formation is augmented, substrate activation or hydride transfer may be disrupted. Consequently clear trends based on ligand variation will not be anticipated in general. For instance, ligand basicity for phosphines[62] and phosphites[63] or alkyl ligands[2] does not relate in a simple way to catalytic activity. If ligand dissociation is required to provide a vacant site for hydrogen or substrate coordination, the metal ligand bond energy will be an important property but not the only property affected by changes in the other ligands.

In considering the bonding effects in the metal complexes of interest, it must be borne in mind that the formal assignment of oxidation states within the complex may bear little relation to the actual accumulation of positive or negative charge on specific atoms. For instance, the hydrides are conveniently thought of as precisely that, a complex of H^- analogous to chloride and other anionic ligands, yet the extreme trans effect and other physical characteristics of hydride complexes demonstrate their covalence. Likewise, the formal accumulation of negative charge on the metal by bonding to several σ donor ligands is often relieved by considerable π delocalization of electrons back over the ligands (CO, CN^-, π-acceptor organic ligands). In general Pauling's principle of essential electroneutrality is applicable. Clearly then, a change in the σ-bonding ability of one ligand must be reflected in changes in the polarity and strengths of the remaining metal-ligand bonds. Complexes containing organometallic bonds are particularly sensitive to this effect in view of the rapid variation in metal-carbon bond reactivity as a function of polarity.

The susceptibility of metal-ligand bonds to weakening in the presence of strong σ donors has been demonstrated by extended Hückel MO calculations on square-

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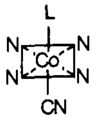
planar Pt(II) complexes of the type $PtCl_2(L)(NH_3)$.[68] Both cis and trans effects were noted and the σ bonding ability of the ligand L ($H > PH_3 > CH_3 > H_2S > Cl > NH_3 > H_2O$) was reflected in a lower electron density in the overlap region with the other ligands. Experimental evidence based on infrared studies leading to bond force constants has been reported supporting these effects.[69] Infrared studies of cobalt(III) corrinoids (complexes related to vitamin B_{12}) show analogous effects in these hexacoordinated complexes.[70,71]



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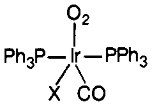
The four nitrogens of the corrin system (represented by structure **3**) are cis to the ligand, L, varied in the study, and cyanide is trans to it. Donor strength of L varies in the order ($CH_3CH_2 > CH_3 > CH_2{=}CH > HC{\equiv}C > CN > OH$). Concurrent weakening of M–N bonding and especially M–(trans)CN bonding is observed with increasing L donor strength. Phosphines and related donors have been ranked in the following sequences:[62,63,72,73] $(C_2H_5)_3P > (CH_3)_3P > (C_2H_5)_2PC_6H_5 > (C_2H_5)P(C_6H_5)_2 > (C_6H_5)_3P$, R_3P; $(CH_3OC_6H_4O)_3P > (C_6H_5O)_3P > (ClC_6H_4O)_3P$; $R_3P > R_3As > R_3Sb$.

The coordinative mobility of complexes in undergoing ligand positional rearrangements to accomodate additional incoming ligands can play an important role. This is especially significant in the oxidative addition of H_2 to square-planar complexes, an important step in many catalytic hydrogenation reactions. It was found that for *trans*-$IrL(CO)[(C_6H_5)_3P]_2$ (L = halogen), the rate of oxidative addition decreased in the order $I > Br > Cl$.[41]

Similar observations have been made by Osborn, *et al.*,[33] for the square-planar rhodium complex $RhX(Ph_3P)_3$ where X = Cl, Br, I. In the case of uptake of molecular oxygen, Vaska's complex forms a five-coordinate complex[74] **4**, which is reversibly oxygenated when X = Cl but irreversibly oxygenated if X = I.[75]



4

In the oxidative addition of hydrogen, a cis dihydride six-coordinate species seems to be involved. Cis–trans relations in the original square-planar complex are in part replaced by new relations in the octahedral complex. Thus the increased rate of hydrogenation corresponds to increased trans effect ($Cl < Br < I$) in the square-planar complex $RhX(Ph_3P)_3$. The trans effect should continue to influence the lability of hydrogen in the cis dihydride complex produced (**5**). Operation of the trans effect in catalytic activity is not always observed. For example, the complex $Rh(SnCl_3)(Ph_3P)_3$[76] has catalytic activity well below that of $RhCl(Ph_3P)_3$ despite the known[77] large trans effect of $SnCl_3$. Here again the change in catalytic activity must be the result of more than a single controlling factor.

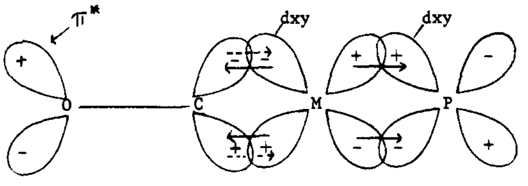
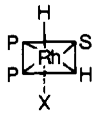


Figure 4. Retrodative π bonding between metal and CO, on one hand, and between metal and phosphine, on the other. The π bond to the CO is weakened by the presence of the phosphine (σ orbitals, not shown).



5, P = Ph_3P; X = halide; S = solvent

4. Ligand Effects (π-Bonding Ability)

In the case of ligands that have available orbitals of the appropriate symmetry (antibonding π^* orbitals in olefins and CO, d orbitals of phosphorus in phosphines, etc.), the influence of the π electrons is superimposed on the action *via* the σ-electron system. A ligand that can act as a π acceptor can withdraw electron density from the π bonds involving other ligands; the $d\pi$ orbitals of the metal act as a "conductor" for electrons. This is schematically illustrated in Figure 4.

The extent of retrodative π bonding is determined by ir spectroscopy. The CO stretching frequency, ν_{CO}, depends on the electron density passing into its antibonding π orbital by retrodative π bonding from the metal to CO; the greater this quantity, the weaker is the bond between C and O and the lower is the value of ν_{CO}. The costretching frequency ν_{CO} is also affected *via* σ bonding. The contributions of these two effects to the measured result has not been ascertained yet.[78] If electron density is withdrawn from π^*(CO) by a π acceptor at another point in the complex, ν_{CO} is increased. NO can be used as a "diagnostic ligand" in a similar manner. By investigating the complexes of the type $ML(CO)X_n$ and $ML(NO)X_n$ in which the metal (M) and other ligands (X_n) are kept constant, while L is varied, it is possible to arrange the ligands L in order of their π-acceptor strength as follows:[42,78-81] $NO \approx CO > PF_3 > PCl_3 > PCl_2C_6H_5 > PCl(C_6H_5)_2 > P(C_6H_5)_3 > P(C_2H_5)_3$; $PCl_2(OC_2H_5) > P(OC_6H_5)_3 > P(OC_2H_5)_3 \approx P(OCH_3)_3 > P(CH_3)_3 > P(C_2H_5)_3$; $PR_3 \approx AsR_3 \approx SbR_3$. Halide ions have no appreciable influence on ν_{CO}. They do not appear to act either as π acceptors or π donors.[78] Their influence on catalytic reactions is probably due to the interaction *via* the σ-electron systems.

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5. *Bond Strength of Ligand L*

Reactions in which the vacant coordination site must be formed by dissociation of a ligand also depend on the bond strength of the ligand. The bond strength of a series of ligands has been estimated by measuring the rate of replacement of L by CO.[82]

$$\text{(phen)Cr(CO)}_3\text{L} + \text{CO} \rightarrow \text{(phen)Cr(CO)}_4 + \text{L} \quad (33)$$

(phen = o-phenanthroline, a bidentate ligand)

Since this reaction may be assumed to proceed by dissociation, the rate may be taken as a measure of the bond strength. The stability was found to decrease in the following order: L = $(n\text{-C}_4\text{H}_9)_3\text{P} > \text{P(OC}_2\text{H}_5)_3 > \text{CO} > \text{P(OC}_6\text{H}_5)_3 > \text{P(C}_6\text{H}_5)_3 > \text{PH}_2\text{(C}_6\text{H}_5)$.

6. *Steric Effects*

Bulky ligands can influence a catalytic process by allowing coordinative addition of the substrate only in certain orientation; the result may be a stereospecific catalysis. In reactions involving the dissociation of ligands to creat a vacant coordination site, bulky ligands have been found to be facilitative.[12a,83] Steric considerations have also been used to explain the formation of the products when certain alkenes were hydrogenated using homogeneous catalysts containing asymmetric ligands. This will be discussed in detail later.

D. Organic Synthesis Using Homogeneous Hydrogenation

1. *Experimental Methodology*

In general, the homogeneous hydrogenation of relatively unhindered "electron rich" alkenes and alkynes (*e.g.*, terminal alkene and alkynes) or "electron poor" alkenes and alkynes (*e.g.*, α,β-unsaturated carbonyl compounds) can be accomplished using relatively mild conditions.[33,84] It is usually necessary to rigorously exclude oxygen from the reaction mixture. The solvents (*e.g.*, benzene, toluene, alcohol, substituted amides, etc.) must be deoxygenated before the catalyst is added. One method of degassing the solvents is to bubble argon or helium through the solvents as they are heated under reflux. Another method involves the introduction of the catalyst after hydrogen has been bubbled several times through the solvent containing the substrate. Peroxides may be removed from the solvents by passing them over alumina. Augustine and Van Peppen[85] have found that in the case of Wilkinson's catalyst the presence of peroxides caused excessive isomerization of alkenes. Lyons[86] also found that the presence of peroxides greatly accelerated the isomerization of alkenes by the homogeneous catalyst, $\text{RuCl}_2(\text{Ph}_3\text{P})_3$. The usual procedure used by organic chemists to exclude oxygen from a reaction mixture by using nitrogen gas is not useful in some cases because certain complexes tend to react with nitrogen, yielding less active hydrogenation catalysts.[87] $(\text{NH}_3)_5\text{RuN}_2^{2+}$ and $\text{HCo(PPh}_3)_3\text{N}_2$ are notable examples.

2. *Preparation of Catalysts*

a. Rhodium Catalysts

Square-planar (coordinatively unsaturated) complexes of rhodium(I) can be prepared by using the procedure described by Osborn, *et al.*[33] This involves treating $\text{RhCl}_3\cdot3\text{H}_2\text{O}$ with an excess of triphenylphosphine in aqueous ethanol. If insufficient ethanol is used, an orange crystalline material is first precipitated which turns red upon heating. The orange complex gives the same analyses as the red complex and may be a different crystalline form.[88] The above reaction of triphenylphosphine appears to be unique, because the reaction of other tertiary arylalkylphosphines and arsines with hot ethanolic solutions of $\text{RhCl}_3\cdot3\text{H}_2\text{O}$ gives mono- or binuclear complexes.[89] Although the reaction of triphenylphosphine in stoichiometric amount with $\text{RhCl}_3\cdot3\text{H}_2\text{O}$ has been reported[90] to give an octahedral complex $\text{RhCl}_3(\text{PPh}_3)_3$, Osborn and coworkers[33] had some difficulty reproducing this preparation. The only compound having a structure similar to Wilkinson's catalyst, which had been reported previously, was the diphenylphosphine complex,[91] $\text{RhCl(PHPh}_2)_3$, obtained by the interaction of PHPh_2 with $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$. The molecular weight of this complex in solution was reported to be normal. A number of phosphite complexes were obtained[91] from $[(\text{CO})_2\text{RhCl}]_2$. The five-coordinate complexes of rhodium seem to be unstable for alkyl or aryl phosphines, despite the existence of five-coordinate species such as $\text{Rh(CO)H(PPh}_3)_3$,[92] $\text{Rh(C}_8\text{H}_{10})(\text{SnCl}_3)(\text{PPh}_3)_2$,[93] and $\text{RhH(PF}_3)_4$.

Some confusion as to the structure of Wilkinson's catalyst in solution arose from initial osmometric studies of benzene and chloroform solutions. These were interpreted as indicating extensive dissociation presumed to be

$$\text{RhCl(PPh}_3)_3 \underset{\text{PPh}_3}{\overset{\text{solvent}}{\rightleftharpoons}} \text{RhCl(PPh}_3)_2 + \text{PPh}_3 \quad (34)$$

Subsequent nmr studies,[94] however, showed that dissociation was less than 5% at 10^{-2} *M* concentration. Cryoscopic studies[95] carefully excluding oxygen showed no evidence of dissociation, while introduction of a trace of oxygen yielded a lower molecular weight. Likewise added BF_3 showed no evidence of free PPh_3 since the stable complex Ph_3PBF_3 failed to form in oxygen free solutions. The fact that the rate of cis–trans phosphine isomerization of these rhodium(I) chlorotrisphosphines is greater than the rate of phosphine ligand exchange has been cited as evidence for an intermediate involving one

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loosely coordinated phosphine. This possibility is very significant in catalytic processes.

Using an absorption band at about 410 nm characteristic of the rhodium(I) complexes with phosphine (but not of free phosphine), Arai and Halpern[96a] established an equilibrium constant of $(1.4 \pm 0.4) \times 10^{-4}\ M$ for the dissociation of Wilkinson's catalyst.

$$\mathrm{RhCl(Ph_3P)_3 \rightarrow RhCl(Ph_3P)_2 + Ph_3P} \qquad (35)$$

Preliminary results indicated that $RhBr(Ph_3P)_3$ and $RhI(Ph_3P)_3$ behave similarly with $K = 10^{-4}\ M$. Hence, dissociation is not extensive but certainly sufficient to be of catalytic importance.

On the basis of spectrophotometric studies, Jesson, *et al.*,[96b] showed that $RhCl(PPh_3)_3$ and $RhH_2Cl(PPh_3)_3$ are the major species present in solutions of tris(triphenylphosphine)rhodium chloride and hydrogen.

In contrast to triphenylphosphine, other phosphines such as dialkylarylphosphines,[97] alkyldiarylphosphines,[98] and bulky diarylphosphines[99] tend to yield octahedral complexes rather than square-planar complexes when the procedure[33] used for the preparation of Wilkinson's catalyst is employed. A more versatile method for the preparation of square-planar complexes was introduced by Djerassi and Gutzwiller.[100] They treated μ-dichlorotetraethylenedirhodium[101] with the tertiary phosphine in benzene. The preparations of other coordinatively unsaturated rhodium and iridium complexes, *e.g.*, $Rh(CO)Cl(PPh_3)_3$,[102] $Rh(CO)Cl(P(C_6H_{11})_3)_2$,[103] $Ir(CO)Br(PPh_3)_2$,[104] etc., have been described.

b. Iridium Catalysts

In 1961 Vaska and DiLuzio[105] reported the reaction of iridium(III) salts $[IrCl_3\cdot(H_2O)_x]$ and haloiridates $[(NH_4)_2IrCl_6]$ with excess triphenylphosphine in alcohol to yield species such as $IrHX_2L_3$ at low temperatures and IrH_2XL_3 at higher temperatures (X = halide, L = the phosphine ligand). Solvents, temperatures, times, and per cent conversion to iridium complexes were as follows: aqueous 2-(β-methoxyethanol)-ethanol, 190°, 2 hr, 86%; ethylene glycol, 190°, 7 hr, 75%; diethylene glycol, 270°, 4 hr, 83%.

The compounds reported were $IrCl(CO)(Ph_3P)_2$, $IrBr(CO)(Ph_3P)_2$, $IrHCl_2(CO)(Ph_3P)_2$, $IrHBr_2(CO)(Ph_3P)_2$, and the arsine analog $IrHCl_2(CO)(Ph_3As)_2$. $IrHCl_2(CO)(Ph_3P)_3$ was formed rapidly and quantitatively by reaction of $IrCl(CO)(Ph_3P)_2$ with dry HCl in ether. $IrHBr(CO)(Ph_3P)_2$ was formed from the analogous $IrBr(CO)(Ph_3P)_2$ and HBr. $IrHCl_2(CO)(Ph_3As)_2$ forms readily in ethylene glycol at 170° from the reaction of an Ir(III) chloro compound and excess Ph_3As.

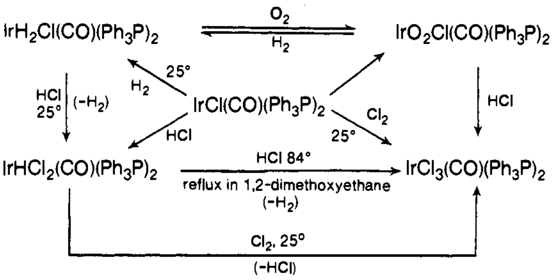
Examination of X-ray diffraction patterns showed the iridium carbonyl hydrides to be isomorphous with one another. Likewise, the carbonyl halides were isomorphous with one another and isomorphous with the rhodium complex $RhCl(CO)(Ph_3P)_2$ which is known to have the trans configuration.

In a subsequent study, Vaska and DiLuzio[106] clarified the solution chemistry of these complexes by showing that the iridium(I) chloro carbonyl readily took up hydrogen (or deuterium).

$$\mathrm{IrCl(CO)(Ph_3P)_2 + H_2 \xrightarrow[25^\circ]{benzene} IrH_2Cl(CO)(Ph_3P)_2} \qquad (36)$$

The analogous reactions with HCl and Cl_2 were reported as well as certain interconversions among the Ir(III) products. These reactions (plus the separately reported reaction with O_2) are conveniently summarized in Scheme IV.

SCHEME IV



Vaska reported[107] another complex, $IrH(CO)(Ph_3P)_3$, to be of superior catalytic ability compared to $IrCl(CO)(Ph_3P)_2$. It is prepared[108] by reaction of the chloro carbonyl with 95% aqueous hydrazine (eq 37). Rhodium behaves analogously and the structure of the rhodium analog is known[109] to be a trigonal bipyramid with equatorial phosphines and the H and CO axial.

$$\mathrm{2[IrCl(CO)(Ph_3P)_2]\,cryst} + n.5\,\mathrm{N_2H_4} \xrightarrow{\text{ethanol}}$$
$$\mathrm{[IrH(CO)(Ph_3P)_3]_{cryst}} +$$
$$\mathrm{\{IrCl(CO)(Ph_3P)(N_2H_4)_{\mathit{n}-1}\ldots\}_{soln} + N_2H_5Cl + 0.5N_2} \qquad (37)$$

c. Ruthenium Catalysts

The simplest of ruthenium catalysts are its aqueous solutions. Halpern, *et al.*,[110] reported in 1961 that aqueous ruthenium(III) chloride was an effective catalyst for the hydration of acetylenic compounds. Harrod, *et al.*,[24d] described the preparation of such solutions by reduction of $RuCl_4$ with hydrogen. Later Halpern[111] used reduction with excess of Ti(III) chloride in aqueous HCl(>1 *M* HCl) to yield catalyst solutions of chlororuthenium(II). These solutions were stable up to several days when stored under N_2 with rigorous exclusion of O_2. More recently Adamson[112] studied chloride exchange among various chloroanions of Ru(II), -(III), and -(IV). Ruthenium(II) chloride was prepared by reduction of a concentrated HCl solution of ruthenium tetroxide by vigorous shaking

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with mercury. Excess mercury and Hg_2Cl_2 were removed by filtration. Ru(II) changes to Ru(III) on standing in contact with air for several days.

Catalytically active ruthenium(II) phosphine complexes were formed by reaction of Ph_3P with $RuCl_3$ in methanol. Jardine *et al.*,[49] found a 1:6 ratio of $RuCl{\cdot}3H_2O$ (10^{-2} mol) to Ph_3P (6×10^{-2} mol) to be most effective and assumed the active agent to be $RuClH(Ph_3P)_3$. Similar solutions had been studied previously[113] and were known to contain $(PH_3P)_nRu(II)Cl_2$ where $n = 2, 3, 4$. Evans, *et al.*,[113] also had shown that $RuCl_2(Ph_3P)_4$ resulted from reaction of a cold methanol solution of hydrated ruthenium(III) chloride with excess Ph_3P while refluxing methanol solution yielded $RuCl_2(Ph_3P)_3$. Solutions of these two in benzene–ethanol reacted with hydrogen to form $RuClH(Ph_3P)_3$.

$RuClH(Ph_3P)_3$ is readily prepared *in situ*[114] in benzene by quantitative base-promoted hydrogenolysis at 25° and 1 atm pressure (H_2) using solid bases such as sodium phenoxide or organic bases such as triethylamine.

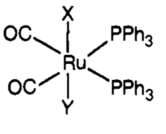
$$RuCl_2(Ph_3P)_3 + H_2 + Et_3N \rightarrow RuClH(Ph_3P)_3 + Et_3NHCl \qquad (38)$$

In a later paper Hallman[115] described further reactions along these lines. In a preparative scale (6 g/l.) reaction, hydrogen bubbled through a solution of $RuCl_2(Ph_3P)_3$ in benzene–ethanol (1:1) resulted in a color change from brown to red violet over several hours. If continued several days violet black crystals of $RuClH(Ph_3P)_3$ formed. At 100 atm hydrogen pressure, a concentrated (25 g/l.) solution reacted completely in about 12 hr. Alternatively benzene containing an equivalent amount of Et_3N could be used. The bromo analog formed similarly. A most convenient preparation was found to be refluxing a benzene solution of $RuCl_2(Ph_3P)_3$ and $NaBH_4$ in the presence of a little water or THF. Less than 1 hr of reflux was required. If solvents from which CO can be abstracted were used, the colorless $RuH_2(CO)(Ph_3P)_3$ resulted.

$Ru(CO)_3(Ph_3P)_2$ was found to be a very effective catalyst for hydroformylation. Collman[25] presented its preparation as in eq 39 and 40. By similar means, $Ru(CO)_3(Ph_3As)_2$ is obtained. $Ru(CO)_3(Ph_3P)_2$ undergoes oxidative addition reactions accompanied by the loss of one CO when the following reagents are used: I_2, Br_2, HCl, HBr, $2CF_3CO_2^-$. The structure of $Ru(CO)_3(Ph_3P)_2$ is trigonal bipyramidal with axial phosphines. Its oxidation addition products are pseudooctahedral of the form in **6**.

$$RuCl_3{\cdot}xH_2O \xrightarrow[\text{methanol, 30 hr}]{\text{CO(80.psi)}} [RuCl_2(CO)_2]_n \xrightarrow[\text{65°; methanol}]{\text{2Ph}_3\text{P}} \qquad (39)$$

$$RuCl_2(CO)_2(Ph_3P)_2 \xrightarrow[\substack{\text{hot DMF}\\ \text{100°, 24 hr}\\ \text{80 psi, CO}}]{\text{Zn}} \begin{array}{c} Ru(CO)_3(Ph_3P)_2 \\ \text{(yellow crystals in high yield)} \end{array} \qquad (40)$$



6

A series of complexes bearing a formal relationship to $RuCl_2(Ph_3P)_3$ are those in which the tris(triphenylphosphine) is replaced by an aromatic π ligand. Avilov, *et al.*,[116] reported their use in catalytic hydrogenation of olefins in DMF. In studying the catalytic ability of $[Ru(C_6H_6)Cl_2]_n$, Ogata, *et al.*,[117] observed that olefin hydrogenation and the competing isomerization reaction exhibited strong solvent dependence (benzene, CH_3CN, DMSO, and DMF were studied). Three μ-dichloro π complexes were prepared by Winkhaus:[118] $[Ru(C_7H_8)Cl_2]_x$, $[Ru(C_6H_6)Cl_2]_x$, and $\{Ru(C_6H_6)[P(C_4H_9)_3]Cl_2\}_2$. The first two were prepared by reaction of $RuCl_3{\cdot}xH_2O$ with cycloheptatriene and 1,3-cyclohexadiene, respectively (in ethanol), and the third was prepared by further reaction of the latter complex with tributylphosphine. In all cases the products precipitate and are readily purified. They are considered to be extended μ-dichloro (bridged) complexes. Ogata's study added two DMSO adduct complexes which were incompletely characterized but seem to be $Ru(C_6H_6)Cl_2{\cdot}DMSO$ and $[RuClH(C_6H_6){\cdot}DMSO]_2$.

Chloro complexes of Ru(II) with 1,1-difluoroethylene and vinyl fluoride were studied by James and Louie[119] with regard to their homogeneous catalytic hydrogenation. Acetic acid and acetaldehyde were produced by a competing catalytic hydration process. The kinetics were rather complex, but a plausible hydration scheme was proposed.

An extensive series of hydridocarboxylatotris(triphenylphosphine)ruthenium(II) complexes was prepared by Rose, *et al.*,[120] and found to be catalysts for homogeneous hydrogenation of 1-alkenes. They are formed by reaction of $RuCl_2(Ph_3P)_3$ with the sodium salt of the carboxylic acid in methanol solution under an atmosphere of hydrogen. Alternatively H_2 may be omitted and an equivalent of sodium hypophosphite used as the hydride source. The solids are quite stable in air, but their solutions readily react with traces of oxygen. Complexes prepared were of the general formula $RuHR(Ph_3P)_3$, where R is the carboxylate: CH_3CO_2, CH_2ClCO_2, CF_3CO_2, $EtCO_2$, Pr^nCO_2, Pr^iCO_2, Me_3CCO_2, $PhCO_2$, and $[o\text{-}(OH)C_6H_4CO_2]$.

A great many homogeneous hydrogenation catalysts are not isolated; they are used *in situ*. Catalysts in this category are those of the Ziegler–Natta type used by Breslow and coworkers[121] and also those prepared from cobalt halides and potassium or sodium cyanide in aqueous solution. In addition many of the rhodium phosphine complexes have been prepared *in situ*.

3. Stereochemical and Kinetic Aspects

The transition metal complexes which have been successfully used in the asymmetric reduction of alkenes have all been derived from rhodium. Before considering the introduction of an asymmetric center into a previously achiral unsaturated organic molecule, it is important to examine some of the mechanistic studies which have been reported by various investigators using soluble com-

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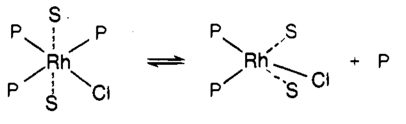
plexes of rhodium as hydrogenation catalysts. The introduction of molecular hydrogen into an unsaturated organic molecule using Wilkinson's catalyst [$RhX(PPh_3)_3$, where X = Cl, Br, and I] can be considered to involve the following steps: (1) dissociation of one of the triphenylphosphine ligands from the "square-planar" complex, (2) hydrogen activation, (3) substrate activation, (4) hydrogen transfer, and (5) catalyst regeneration. It is necessary to discuss these steps more fully in order to understand their importance and how they interact with each other.

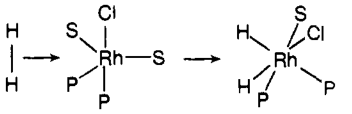
The studies of Eaton and Stuart[122] and Lehman, *et al.*,[95] both indicate that Osborn's initial evidence for extensive dissociation resulted from failure to exclude oxygen from the system. Augustine and Van Peppen[85] felt that the effect of oxygen on double isomerization during alkene hydrogenations was related to this problem. Using thin layer chromatography, they found that oxygen and hydrogen promoted the dissociation of Wilkinson's catalyst in ethanol and benzene.

Eaton and Stuart[122] proposed an "outer-sphere" complex in which the dissociated phosphine ligand might be retained within the solvent cage. Formation of such a five-coordinate (including solvent) intermediate is readily visualized starting from a pseudooctahedral complex (square planar with weak solvent coordination) (eq 41).



(41)

Addition of hydrogen with synchronous displacement of weakly held solvent would produce a six-coordinate oxidative addition product (eq 42). These processes are speculative but have the merit of proceeding along low-energy pathways related to known mechanisms.[123] Aside from the cis addition of H_2, particular isomers are not meant to be specified since isomerization through five-coordinate intermediates generally is facile.



(42)

The hydrogen activation process depends on a number of factors, each of which is related to the other.[35] For a d^8 complex to be oxidized by hydrogen to give a d^6 species, $H_2 + ML_4 \rightarrow H_2ML_4$, it would appear that $2E_{M-H} > E_{H-H} + P$, where E_{M-H} is the energy of formation of the metal-hydrogen bond, E_{H-H} is the bond strength for molecular hydrogen, and P is the promotional energy of the metal.[33] Therefore, if the hydrogen activation is to be reversible, $2E_{M-H}$ must be approximately equal to $E_{H-H} + P$. The electronic and ligational conditions for a reversible system are quite critical. For $RhCl(PPh_3)_2L$, where L is a ligand of low π-acidic nature, *e.g.*, chloroform, benzene, acetic acid, ethyl acetate, pyridine, or acetonitrile, activation of hydrogen proceeds rapidly. If, however, L is a strong π acid, *viz.*, carbon monoxide, tetrafluoroethylene, ethylene, or perfluorobutyne, no activation occurs at atmospheric pressure. E_{H-H} remains constant and E_{M-H} is not significantly changed (as verified by infrared spectral data; *e.g.*, the M-H stretching frequencies of *cis*-$H_2IrCl(CO)(PPh_3)_2$ are 2190 and 2100 cm^{-1} as compared with those of *cis*-$H_2RhCl(py)(PPh_3)_2$, which are 2143 and 2075 cm^{-1}). Therefore, the principal factor in reversible hydrogen activation is promotional energy, including energies of reorientation of ligands. Thus any ligand which withdraws electron density from the metal increases the promotional energy and reduces the ability of the species to activate molecular hydrogen. Osborn, *et al.*,[33] believe that the interaction of molecular hydrogen and a homogeneous catalyst in solution involves the feeding-in of electron density from filled metal orbitals to an acceptor orbital on one hydrogen atom of the hydrogen molecule. A tentative suggestion has been made by Halpern and Nyholm[35b] that an antibonding orbital could be used as an acceptor. Another mechanism has been proposed by Halpern[35] who suggested that the bonding electrons of hydrogen could attack a vacant metal orbital. Osborn, *et al.*,[33] thought that the former concept seems more likely, especially since hydrogen activators are, in general, electron-rich systems. The precise mechanism for this type of activation is highly speculative. Such an electron flow would induce a charge separation in the H-H bond and lead to a bond weakening, lengthening, and synchronous formation of two metal-hydrogen bonds. At least initially, these should be mutually cis but, depending on the nature of the metal species, rearrangement may occur. Thus if the configuration of the complex is such that no cis site is immediately available [*e.g.*, $(Ph_3P)_2RhCl_2Rh(PPh_3)_2$] then some sort of reorganization by edge displacement and/or dissociation is required; trans dihydrides could then result, depending on the nature of the metal and its ligands. Alternatively, solvation by polar solvents could remove the more positively charged hydrogen atom, so that the heterolytic fission in eq 43 may occur. Undoubtedly this is what happens when octahedral species like $Rh(py)_3Cl_3$,[124] $Rh(PhPr^nMeP)_3Cl_3$,[125] $Rh[\alpha\text{-naphthyl-4-biphenylylphenyl})P]_3Cl_3$,[12a] $Rh(PAr_3)_3Cl_3$,[12b] etc., activate hydrogen; hydrogen chloride is in fact eliminated with the formation of $RhHI_3Cl_2$.[12b,124]

$$M^+ + H_2 \rightarrow MH + H^+ \tag{43}$$

The failure of $RhClCO(PPh_3)_2$ to activate hydrogen under mild conditions is in contrast to the ability of the iridium analog to give reversible hydrogen activation and a cis dihydride. From their kinetic studies Chock and Halpern[41] have found that Vaska's catalyst, $IrXCO(PPh_3)_2$, behaves similar to Wilkinson's catalyst, $RhX(Ph_3P)_3$. The rate of addition of hydrogen was markedly dependent on X (increasing in the order Cl > Br > I) and also on the solvent used, increasing when more polar solvents replaced benzene. The very small deuterium isotope effect observed in this case ($k(H_2)/k(D_2)$ = 1.22) could also mean that bond breaking in the hydrogen molecule was accompanied by a synchronous metal hydrogen bond formation, possibly through a triangular transition state. This difference in reactivity between $RhCl(CO)(PPh_3)_2$ and $IrCl(CO)(PPh_3)_2$ can be ascribed to the greater nonbonding d electron density and the lower promotional energy in the large third transition series atoms and partly to the somewhat increased strength of the Ir-H bonds as compared to Rh-H bonds.

The failure of the square-planar phosphite complex,

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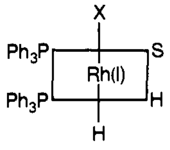
(124) W. S. Knowles and M. J. Sabacky, *Chem. Commun.*, 1445 (1968).

(125) (a) J. T. Mague and G. Wilkinson, *J. Chem. Soc. A*, 1736 (1966); (b) W. D. Hurrocks and R. C. Taylor, *Inorg. Chem.*, **2**, 723 (1963).

$RhCl(P(OPH)_3)_3$, to activate hydrogen at 1 atm pressure may be attributed, in part, to the higher π acidity of triphenyl phosphite as compared to triphenylphosphine,[125] which lowers the nonbonding electron density on the metal. However, the main difference is that the phosphite complex does not dissociate in solution, thereby failing to provide a vacant site. Finally, the unexpected inability of $RhCl(PPh_3)_2(S)$ to catalytically hydrogenate ethylene has an explanation analogous to that for the effect of carbon monoxide in $RhCl(CO)(PPh_3)_2$. From the trans effect and other studies, it is known that ethylene stands high in the π-acid and trans-effect sequence and is comparable to carbon monoxide as a π-acid ligand. Thus, $RhCl(C_2H_4)(PPh_3)_2$ cannot be expected to activate hydrogen at 1 atm. The complex $RhCl(PPh_3)_2H_2$ will transfer hydrogen to ethylene, but once the ethylene complex is formed, hydrogen activation ceases. The formation of the intermediate, $RhCl(PPh_3)_2H_2$(olefins), in the substrate activation step, cannot be readily ascertained. There is evidence that the lifetime of the hydrido species is quite long, and this fact, together with the evidence mentioned earlier, strongly indicates that the alkene attacks the hydrido species. The alternative pathway has a further contradiction, since there is evidence that an olefin complex would not be able to activate molecular hydrogen. There is a clear indication that there must be an intermediate species or at least an activated complex in which both molecular hydrogen (as *cis*-MH_2) and an alkene are coordinated to the metal atom.

Various poisoning and competition experiments have indicated that a vacant site on the hydrido species, at which the substrate alkene can be activated, is necessary for efficient catalysis. Those substrates which cannot approach the activating site because of steric factors are not readily reduced. In view of the very rapid and stereospecific cis reduction, it is reasonable to assume that the vacant site is cis to the two M–H bonds as in Wilkinson's catayst (**7**).



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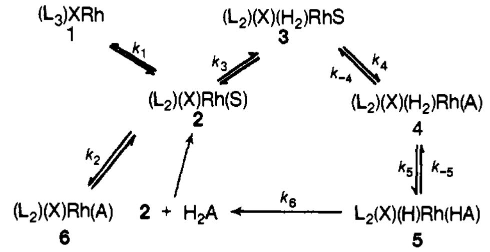
In the case of simple alkenes, the intramolecular transfer of hydrogen in $RhH_2(PPh_3)_2$(alkene) probably occurs in a stereospecific cis manner since cis alkenes are reduced more rapidly than trans alkenes. However, while studying the amounts of isomerization and formation of cis and trans isomers during the hydrogenation (using D_2 or H_2) of substituted cyclohexenes using a variety of rhodium complexes in different solvents, Hussey and Takeuchi[126] found that in the case of $RhCl(PPh_3)_3$ in ethanol–benzene the amount of cis isomer ranged from 30 to 67%. The amounts of cis isomers obtained using Adam's catalyst (PtO_2) ranged from 43 to 74%. The results are given in Table III. In addition the investigators found that when deuterium is used the thermodynamically less stable isomers obtained from homogeneous hydrogenation reactions are exchanged appreciably more than their more stable counterparts. The results obtained by Odell, *et al.*,[129] Biellman and Jung,[130] and Osborn, *et al.*,[33] led Hussey and Takeushi to formulate Scheme V.[126] The influence of the solvent (S), the ligand (L), and the ligand/rhodium ratio on the dissociation of the catalyst **1** to catalyst **2** is outlined in this scheme. Concentrations of the dihydro complex **3** and the complex **4** are shown to be functions of the hydrogen tension and the coordination potential of A *vs.* S. The two-step (**4** → **5** → H_2A) transfer of hydrogen becomes noticeable as k_{-5} approaches k_6 in magnitude.

TABLE III.[127,128] **Per Cent Cis Isomers Using Homogeneous Rhodium and Heterogeneous Platinum Catalysts**

Substrate Cyclohexene	Catalyst $(Ph_3P)_3ClRh$[a]	Catalyst Pt
1,4-Dimethyl	50	57
2,3-Dimethyl	50	77
2,4-Dimethyl	48	47
1-Methyl-4-isopropyl	30	43
4,4-Dimethyl	67	74

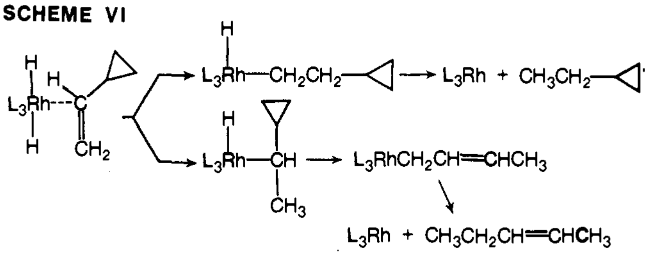
[a] Using benzene–ethanol as solvent.

SCHEME V



Further evidence for a nonconcerted two-step transfer of hydrogen can be found in the work reported by Heathcock and Poulter[131] as shown in Scheme VI. Hartwell and Clark[132] studied the hydrogenation and isomerization of unsaturated tertiary phosphine complexes of Rh(I), *e.g.*, $RhCl(CO)[Ph_2P(CH_2)_nCH{=}CH_2]_2$, where $n = 0$, 1, 2, or 3, and found the hydrogenation to be a two-step process and that the interactions are most favorable when $n = 2$.

SCHEME VI



L = triphenylphosphine or Cl

Using the steady-state treatment,[133] Hussey and Takeuchi[126] arrived at the following rate equation (44), for their hydrogenation Scheme V, where $[H_2][A]$, and [cat.] are the molar concentrations of hydrogen, alkene, and catalyst (added as **1**), respectively. Notice that if k_{-4} is

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(126) A. S. Hussey and Y. Takeuchi, *J. Amer. Chem. Soc.*, **91**, 672 (1969); *J. Org. Chem.*, **35**, 643 (1970).

(127) S. Siegel and C. V. Smith, *J. Amer. Chem. Soc.*, **82**, 6080 (1960).

(128) J. F. Savvage, R. H. Baker, and A. S. Hussey, *J. Amer. Chem. Soc.*, **82**, 6090 (1960).

(129) A. L. Odell, J. B. Richardson, and M. J. Jung, *J. Catal.*, **8**, 393 (1967).

(130) J. B. Biellman and M. J. Jung, *J. Amer. Chem. Soc.*, **90**, 1673 (1968).

(131) C. H. Heathcock and S. R. Poulter, *Tetrahedron Lett.*, 2755 (1969).

(132) G. E. Hartwell and P. W. Clark, *Chem. Commun.*, 1115 (1970).

(133) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y.

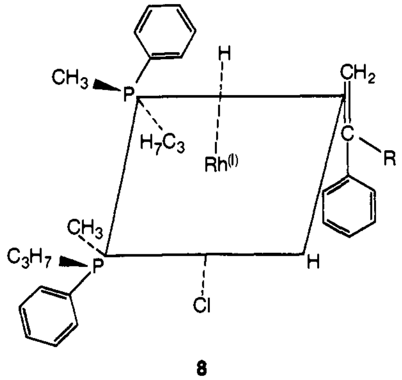
very small, the above equation becomes equivalent to Wilkinson's rate expression for cyclohexene[33] except for the additonal term in the denominator for the reassociation of **1**.

$$\text{rate} = \frac{k_4k_5k_6k_3[\mathrm{H_2}][\mathrm{A}][\mathrm{cat.}]}{(1 + [\mathrm{L}]/k_1 + K_2\mathrm{A} + K_3[\mathrm{H_2}](k_{-4}k_{-5} + k_{-4}k_6 + k_5k_6)} \quad (44)$$

4. *Asymmetric Synthesis*

The early reports of stereoselective reduction of alkenes using homogeneous catalysis by transition metal complexes suggested that asymmetric syntheses might be carried out using optically active catalyst systems. In 1968, Knowles and Sabacky[97] and Horner, et al.,[134] reported the first examples of homogeneous catalytic asymmetric hydrogenation of an optically inactive compound. When catalysts having the general formula $\mathrm{RhCl_3L_3}$ which have optically active ligands [L = P*PhMePr or $\mathrm{PhP(CH_2C^*MeEt)_2}$] were used to catalyze the addition of hydrogen to α-phenylacrylic acid, the resulting product was optically active [15% optical yield or 15% enantiomeric excess (ee)]. Knowles and Sabacky[97] suggested that the octahedral d^6 Rh(III) complexes might yield a square-planar d^8 Rh(I) complex which would be coordinatively unsaturated and would behave in a manner similar to Wilkinson's catalyst in the above reductions.

Horner, *et al.*,[134] used the catalyst formed *in situ* from (*S*)-(+)-methylphenyl-*n*-propylphosphine and Rh(1,5-hexadiene)$\mathrm{Cl_2}$ in benzene (a procedure known to give square-planar rhodium(I) complexes). The ground-state model **8** has been constructed by Horner, *et al.*,[134] to explain the (*S*)-(+)-2-phenylbutane (7–8% ee) obtained from α-ethylstryrene and the (*R*)-(+)-1-methoxy-1-phenylethane (3–4% ee) obtained from 1-methoxystyrene.



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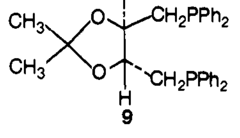
Recent reports by Morrison, *et al.*,[135] and by Dang and Kagan[136] indicate that in order to obtain asymmetric reduction using rhodium phosphine complexes the chiral center does not have to be on phosphorus. Morrison, *et al.*,[135] prepared their catalyst *in situ* by the reaction of neomenthyldiphenylphosphine with Rh(I) μ complexes of ethylene or dienes in ethanol–benzene. This catalyst [tris(neomenthyldiphenylphosphine)rhodium(I) chloride] in the presence of molecular hydrogen was used to reduce (*E*)-β-methylcinnamic acid. The resulting 3-phenylbutanoic acid contained a 61% enantiomeric excess of the *S* isomer. The reduction of α-ethylstyrene, where no bifunctional interactions are possible, led to a 7% enantiomeric excess of (*R*)-2-phenylbutane. Dang and Kagan[136] used the diphosphine (P–P) **9** derived from (+)-ethyl tartrate to prepare 1,1-dimethyl-(1*S*,2*R*)-bis(diphenylphosphinomethyl)dioxolane (P–P) *in situ*, a complex represented by $[\mathrm{Rh^I(P{-}P)ClS}]$, where S is the solvent. These solutions catalyzed the reduction of alkenes at room temperature and atmospheric pressure. Thus α-acetamidocinnamic acid was reduced to (*R*)-*N*-acetylphenylalanine with an optical yield of 72%, the chemical yield being 95%. They attributed the high stereoselectivity of this reduction to the conformational rigidity of the diphosphine chelating the rhodium together with the participation of the acid function of the substrate.



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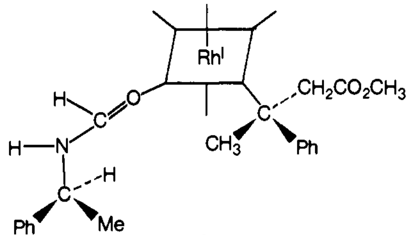
We also found that the participation of the acid functions of highly substituted cinnamic acids greatly aid in the homogeneous hydrogenation of these compounds by rhodium–phosphine complexes under similar conditions.[87] The esters of these acids were not reduced.[87] We also attempted the asymmetric reduction of various α-acetamidocinnamic acids using the catalyst tris(phenyl-α-naphthyl - 4 - biphenylphosphine)trichlororhodium(III).[87] The phenyl-α-naphthyl-4-biphenylylphosphine was obtained in 50% optical purity using the kinetic resolution method of Wittig.[12a,137] We found that even though this catalyst was quite effective in reducing α-acylaminocinnamic acids to substituted *N*-acylphenylalanines, no optical activity was detected in the products. These results are similar to the results obtained by other investigators who found that a *p*-phenyl group[138] exerted no steric influence on the asymmetric induction reactions since such a group is too far away from the reaction site.

Recently Abley and McQuillan[139] reported the homogeneous hydrogenation of methyl 3-phenylbut-2-enoate to methyl 3-phenylbutanoate in better than 50% optical yield. The catalyst used for this reaction was prepared by reducing $\mathrm{py_3RhCl_3}$ with sodium borohydride in (+)- or (−)-PhCHMeNHCHO as solvent. The induced asymmetry observed in the hydrogenation product was explained by the complementary arrangement of ligands in the half-hydrogenated state as shown in **10.**



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In a later report[140] Abley and McQuillan used many other optically active formamides, oxamides, and lactam-

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(134) L. Horner, H. Siegel, and H. Buthe, *Angew. Chem., Int. Ed. Engl.*, **7**, 942 (1968).

(135) J. D. Morrison, R. E. Burnett, A. M. Aguiar, C. J. Morrow, and C. Phillips, *J. Amer. Chem. Soc.*, **93**, 1301 (1971).

(136) T. P. Dang and H. B. Kagan, *Chem. Commun.*, 481 (1971); H. B. Kagan and T. P. Dang, *J. Amer. Chem. Soc.*, **94**, 6429 (1972).

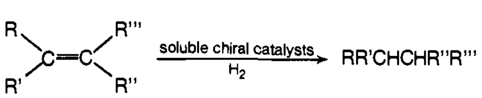
(137) G. Wittig, H. J. Cristau, and H. Brown, *Angew. Chem., Int. Ed. Engl.*, **6**, 700 (1967).

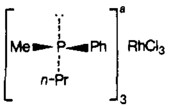
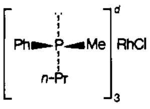
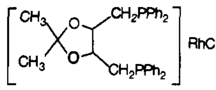
(138) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1971, p 190.

(139) P. Abley and F. J. McQuillan, *Chem. Commun.*, 477 (1969).

(140) P. Abley and F. J. McQuillan, *J. Chem. Soc. C*, 844 (1971).

TABLE IV. Asymmetric Reduction with Soluble Rhodium Catalysts



No.	Alkene R	R'	R''	R'''	Catalyst	Product % ee	Ref
1	Ph	CO_2H	H	H		22^b S-(+)	97
2	CH_2CO_2H	CO_2H	H	H		4^c	97
3	Ph	Et	H	H		7–8 S-(+)	134
4	Ph	OCH_3	H	H		3–4 R-(+)	134
5	Ph	CO_2H	H	H	$[PhP(CH_2C^*HMeEt)_2]_3RhCl^e$	1	97
6	Ph	CH_3	H	CO_2CH_3	$(py)_2Rh[(-)\text{-}PhMeC^*HNHCHO]Cl_2BH_4{}^f$	47 R-(−)	139
7	Ph	CH_3	H	CO_2CH_3	$(py)_2Rh[(+)\text{-}PhMeC^*HNHCHO]Cl_2BH_4{}^g$	54 S-(+)	139
8	Ph	CH_3	H	CO_2CH_3	$(py)_2Rh[(+)\text{-}PhMeC^*HNHCHO]Cl_2BH_4{}^h$	54 S-(+)	139
9	Ph	CH_3	H	CO_2CH_3	$(py)_2Rh[(-)\text{-}MeC^*HOHCONMe_2]Cl_2BH_4$	16 R-(−)	140
10	Ph	CH_3	H	CO_2CH_3	$(py)_2Rh[(+)\text{-}PhMeCHN(CO)_2]Cl_2BH_4{}^i$	14	140
11	Ph	CH_3	H	CO_2CH_3	$(py)_2Rh[(+)$-*N*-acetylglucoseamine$]Cl_2BH_4{}^i$	14 S-(+)	140
12	Ph	CH_3	H	CO_2CH_3	$(py)_2Rh[(-)$-bornyl-NHCHO$]Cl_2BH_4{}^h$	45 S-(+)	140
13	Ph	CH_3	H	CO_2CH_3	$(py)_2Rh[(-)$-isobornyl-NHCHO$]Cl_2BH_4{}^j$	36 S-(+)	140
14	Ph	CH_3	H	CO_2CH_3	$(py)_2Rh[(-)$-isobornyl-NHCHO$]Cl_2BH_4{}^k$	29 S-(+)	140
15	Ph	CH_3	H	CO_2H	Tris(neomenthyldiphenylphosphine)$RhCl^l$	61 S-(+)	135
16	Ph	H	CH_3	CO_2H	Tris(neomenthyldiphenylphosphine)RhCl	52^1 R	135
17	H	H	Ph	CO_2H	Tris(neomenthyldiphenylphosphine)RhCl	28^1 S	135
18	CH_3	H	Ph	CO_2H	Tris(neomenthyldiphenylphosphine)RhCl	8^1 R	135
19	H	H	Ph	CO_2H		63 S	136
20	Ph	H	NHAc	CO_2H		72 R	136
21	Ph	H	NHCO-CH_2	$PhCO_2H$		68 R	136

[a] The structure of the catalyst prepared *in situ* is uncertain although it is probably octahedral. [b] Corrected for % ee of phosphine. [c] Configuration not reported. [d] The catalyst was prepared *in situ* from $[Rh(1,5\text{-hexadiene})Cl]_2$ and (*S*)-(+)-methylphenyl-*n*-propylphosphine in benzene. Hydrogenation was carried out at room temperature and 1 atm pressure of hydrogen. The % ee of the phosphine was not reported. [e] Neither the configuration nor the enantiomer purity was reported. [f] Catalyst was prepared by the reduction of $(py)_3RhCl_3$ with $NaBH_4$ using (*S*)-(−)-PhMeCHNHCHO ($[\alpha]_D$ −172°) as solvent. [g] The catalyst was prepared in the same way as that given in footnote *f*, but with (*R*)-(+)-amide, $[\alpha]_D$ +180°. [h] The reaction was run with 5% solution of the (+)-amide in $EtOCH_2CH_2OCH_2CH_2OH$. [i] The reaction was run with 5% solution of (+)-amide in $EtOCH_2CH_2OCH_2CH_2OH$-water (10:1). [j] Reaction conditions same as those in footnote *h*; cis ester was used. [k] Reactions conditions same as those in footnote *h*; trans ester was used. [l] The catalyst was prepared by reacting neomenthyldiphenylphosphine with $[(ethylene)_2RhCl]_2$ in ethanol–benzene to give $(NMDPP)_3RhCl$. Reaction was run at 60° and 300 psi of hydrogen gas for 24 hr. [m] Catalyst was prepared by the reaction of chiral diphosphine with $[(cyclooctene)_2RhCl]_2$ in benzene–ethanol solution. Hydrogenations were carried out at room temperature and 1 atm pressure.

ides in the preparation of rhodium catalysts for asymmetric homogeneous hydrogenations. They used the ground state model of their catalyst systems to predict the configuration of methyl 3-phenylbutanoate which should be obtained from the reduction of methyl 3-phenylbut-2-enoate. The *N,N'*-(+)- or -(−)-di-α-phenylethyloxamides, *N,N*-dimethyllactamide derived from (+)-lactic acid, *N*-formyl derivatives of bornylamine and isobornylamine, and *N*-acetyl-D-glucosamine were used to prepare rhodium complexes which gave asymmetric reductions. A few examples of asymmetric reductions using soluble rhodium catalysts are given in Table IV.

Recently Knowles, *et al.*,[141] reported an efficient direct route to optically active α-amino acids by catalytic asymmetric reduction of α-acylaminoacrylic acids. Table V shows the results with various chiral phosphines and substrates.

The considerable variation of yields with phosphine structure clearly shows the need for a match of catalyst and substrate. Of particular interest are the high optical purities obtained with *o*-anisylmethylcyclohexylphosphine when applied to various acylphenylalanine precursors. These yields in the 85–90% range, and the probability that their phosphine was only 95% optically pure shows that they have achieved almost complete stereospecificity.

With acylaminocinnamic acids their catalyst system was very active, the results (Table V) being obtained in 3 hr at 25° with 500 mm of H_2 and 0.05% metal. A successful catalyst can be made in a variety of ways. Rhodium(I)-diene complexes of the type $[Rh(1,5\text{-hexadiene})Cl]_2$ mixed with two chiral ligands and prehydrogenated for 5 min at 1 atm of H_2 work well; $RhCl_3 \cdot 3H_2O$

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(141) W. S. Knowles, J. J. Sabacky, and B. D. Vineyard, *Chem. Commun.*, 10 (1972).

TABLE V. Hydrogenation of α-Acylaminoacrylic Acids[141]

Chiral phosphine, $R^1PR^2R^3$			Approx. optical purity, %	Substrate $R^4CH{=}C(NHCOR^5)CO_2H$		Product R^4CH_2-CH-$(NHCOR^5)$-CO_2H Optical purity, %[a]
R^1	R^2	R^3		R^4	R^5	
o-Anisyl	Me	Ph	95	3-MeO-4-(OH)C_6H_3	Ph	58[b]
Me	Ph	Pr^n	90	3-MeO-4-(OH)C_6H_3	Ph	28[c]
Me	Ph	Pr^i	90	3-MeO-4-(OH)C_6H_3	Ph	28[c]
m-Anisyl	Me	Ph	80	3-MeO-4-(OH)C_6H_3	Ph	1[c]
o-Anisyl	Cyclohexyl	Me	95	3-MeO-4-(OH)C_6H_3	Ph	87[d]
o-Anisyl	Cyclohexyl	Me	95	3-MeO-4-(OH)C_6H_3	Ph	90[e]
Cyclohexyl	Me	Ph	75	3-MeO-4-(OH)C_6H_3	Ph	32[c]
o-Anisyl	Ph	Pr^i	80	3-MeO-4-(OH)C_6H_3	Ph	1[c]
o-Anisyl	Me	Ph	95	3-MeO-4-(AcO)C_6H_3	Me	55[b]
o-Anisyl	Me	Pr^n	95	3-MeO-4-(AcO)C_6H_3	Me	20[c]
o-Anisyl	Cyclohexyl	Me	90	3-MeO-4-(AcO)C_6H_3	Me	77[f]
o-Anisyl	Cyclohexyl	Me	95	3-MeO-4-(AcO)C_6H_3	Me	85[d]
o-Anisyl	Cyclohexyl	Me	95	3-MeO-4-(AcO)C_6H_3	Me	88[e]
o-Anisyl	Cyclohexyl	Me	95	Ph	Me	85[d]
o-Anisyl	Cyclohexyl	Me	95	Ph	Ph	85[d]
o-Anisyl	Cyclohexyl	Me	95	H	Me	60[d]

[a] All optical purities were determined by direct comparison of the total reaction mixture with a blank made from authentic acylated amino acid in order to avoid any enrichment from work-up or slight contribution from the catalyst. [b] In a stirred autoclave in methanol at 55 psi (abs) of hydrogen at 50° with 1 equiv of NaOH added. The molar ratio of substrate to catalyst was 3000:1. [c] In a Parr shaker in methanol at 55 psi (abs) at 25°. [d] As in footnote c in 95% ethanol at 10 psi (abs). [e] As in footnote *d* in propan-2-ol. [f] As in footnote *b* using 0–05% triethylamine instead of NaOH.

TABLE VI.[142] Hydrogenation of α,β-Unsaturated Carboxylic Acids and Esters

Reactant	Product	Yield, %	Reduction based on nmr and ir spectral analyses, %
Cinnamic acid	Hydrocinnamic acid	85	100
p-Methylcinnamic acid	p-Methylhydrocinnamic acid	90	100
α-Methylcinnamic acid	α-Methylhydrocinnamic acid	83	100
α-Phenylcinnamic acid	2,3-Diphenylpropionic acid	85	100
Itaconic acid	α-Methylsuccinic acid	92	100
Citraconic acid	α-Methylsuccinic acid	90	80
Ethyl cinnamate	Ethyl hydrocinnamate	93	100
1-Menthyl α-phenylcinnamate	No reduction		

and two ligands with a more vigorous prehydrogenation are also quite effective.

III. Scope of Homogeneous Hydrogenation Reactions

A. Rhodium and Iridium Catalysts

Harmon, *et al.*,[142] and Jardine and Wilkinson[143] have shown that unsaturated organic substrates containing a variety of potentially reducible functional groups (in addition to double and triple bonds) may easily be hydrogenated in the presence of $RhCl(PPh_3)_3$ without alteration of the functional groups; *e.g.*, α,β-unsaturated carbonyl compounds yield saturated carbonyl compounds, etc. The pertinent examples are given in Tables VI and VII.

Unsaturated compounds which contain functional groups which tend to form very stable complexes may not easily be reduced. Allylamine and acrylic acid, for example, are not reduced as easily as allyl alcohol and allyl cyanide. Conjugated double bonds are not always more readily reduced than monoalkenes.[144] Cyclohexene is hydrogenated over six times faster than 1,3-cyclohexadiene. Terminal double bonds react more readily than internal double bonds and the rate of hydrogenation of *cis*-alkenes exceeds that of *trans*-alkenes.[145] The difference in rates of hydrogenation between terminal, substituted alkenes, cycloalkenes, etc., has been attributed to the effect of stereochemistry on the formation constant of $RhClH_2P_2$(alkene) where P = phosphine. A recent study by O'Connor and Wilkinson[145] has shown that the rate of hydrogenation is sensitive to the nature of the substituents on the phenyl groups in the triarylphosphine ligand (P). Harmon, *et al.*,[12a] and Horner, *et al.*,[12b] have shown that bulky aryl groups on the phosphine ligand (P) also affect the rate of hydrogenation but do not affect the selectivity toward various alkenes. The results are contained in Tables VIII–X.

A terminal carbon-carbon triple bond is more readily reduced than a double bond as has been shown by the stepwise reduction of alkynes (eq 45).[145] O'Connor and

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(142) R. E. Harmon, J. L. Parsons, D. W. Cooke, S. K. Gupta, and J. Schoolenberg, *J. Org. Chem.*, **34**, 3684 (1969).

(143) F. H. Jardine and G. Wilkinson, *J. Chem. Soc. C*, 270 (1967).

(144) F. H. Jardine, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1574 (1967).

(145) C. O'Connor and G. Wilkinson, *Tetrahedron Lett.*, 1375 (1969).

TABLE VII.[142] **Hydrogenation of α,β-Unsaturated Nitro Compounds, Nitriles, Ketones, and Aldehydes**

Reactant	Product	Yield, %	Reduction based on nmr and ir spectral analyses, %
p-Nitro-β-nitrostyrene	2-(*p*-Nitrophenyl)-nitroethane	60	100
3,4-Methylenedioxy-β-nitrostyrene	2-(3,4-Methylene-dioxyphenyl)nitroethane	84	100
3-Methoxy-4-benzyl-oxy-β-nitrostyrene	2-(3-Methoxy-4-benzyloxyphenyl)-nitroethane	90	100
Cinnamonitrile	Hydrocinnamonitrile	86	100
2,3-Diphenylacrylonitrile	No reduction		
Benzal acetone	4-Phenyl-2-butanone	80	100
3,4-Diphenyl-3-buten-2-one	No reduction		
Cinnamaldehyde	60% hydrocinnamal-dehyde and 40% ethylbenzene[a]	90	
o-Nitrocinnamaldehyde	60% *o*-nitrohydro-cinnamaldehyde and 40% *o*-nitro-ethylbenzene[a]	70	
α-Methylcinnamaldehyde	No reduction		
p-Dimethylamino-cinnamaldehyde	No reduction		

[a] Based on mnr spectral analyses.

TABLE VIII.[145] **Hydrogenation of Hex-1-ene with $[Rh(1,5\text{-}C_8H_{16})Cl]_2$**

No.	Phosphine	Rh:P	Uptake of H_2, ml/min
1	Triphenyl	1:3.0	16
2	Tri(*p*-tolyl)	1:4.5	21
3	Tri(*p*-tolyl)	1:3.0	29
4	Tri(*p*-tolyl)	1:2.4	38
5	Diphenyl-*p*-dimethylaminophenyl	1:2.7	56
6	Tri(*p*-methoxyphenyl)	1:3.0	33
7	Tri(*p*-methoxyphenyl)	1:2.5	47
8	Tri(*p*-chlorophenyl)	1:2.2	1.7
9	Diphenyl-*p*-acetylphenyl	1:2.2	~6
10	Phenylbis(*p*-diphenylyl)	1:2.2	~1
11	Tri(α-naphthyl)	1:2.2	0.1
12	Diphenylethyl	1:2.0	10
13	Diphenylethyl	1:3.0	0.2
14	Tris(morpholino)	1:2.2	~1
15	Tri-*n*-butyl	1:2.2	2.5
16	Tri-*n*-butyl	1:3.0	0.2

TABLE IX.[12a] **Hydrogenation of α,β-Unsaturated Carboxylic Acids**

Reactant	Product	Reduction (%)[a]		Yield (%)	
α-Acetamidocinnamic acid	*N*-Acetyl-β-phenylalanine	100[b]	100[c]	75[b]	83[c]
Atropic acid	Hydrotropic acid	100	100	90	87
Cinnamic acid	Hydrocinnamic acid	100	80	85	85
Itaconic acid	α-Methylsuccinic acid	100	100	70	92
p-Methylcinnamic acid	*p*-Methylhydrocinnamic acid	100	100	80	85

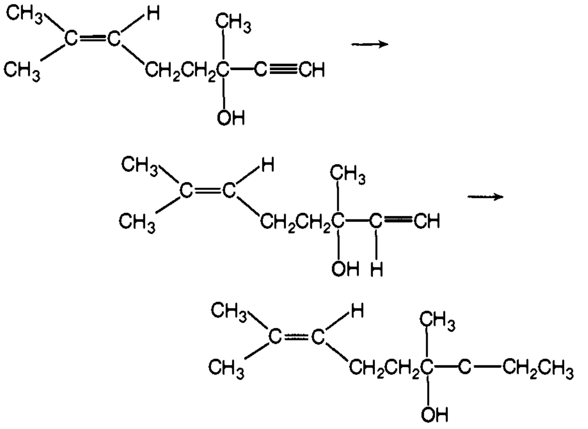
[a] Based on nmr and ir spectral analyses. [b] Using Wilkinson's catalyst. [c] Using trichlorotris(4-biphenylyl-1-naphthylphenylphosphine)rhodium(III) as the catalyst.

TABLE X.[12b] **Hydrogenation of Alkenes Using $RhCl(PPh_3)_3$**[a]

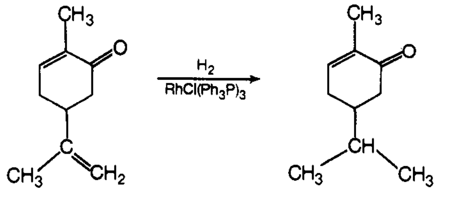
Phosphine ligand	Hex-1-ene	Cyclohexene	*cis*-4-Methyl-pent-2-ene	*trans*-4-Methyl-pent-2-ene
Tri-*p*-methoxyphenyl	99.5	68.0	34.7	8.23
Tri-*p*-methylphenyl	85.3	58.8	29.0	6.85
Triphenyl	38.9	28.1	14.1	3.12
Ethyldiphenyl	17.5			
Tri-*p*-fluorophenyl	5.78	3.93	1.75	0.35
Tri-*p*-chlorophenyl	1.58	1.20	0.44	0.10
Tri-2-phenylethyl	1.39			
Tri-*o*-methylphenyl	0.11			
Tri-2,3-dimethylphenyl	0.12			
Tri-2,4,6-trimethylphenyl	0.09			

[a] Relative rates of hydrogen uptake in ml min^{-1} at 50 cm partial pressure of H_2 and 25°. Catalyst 1.25 m*M*, substrate 0.6 *M*, in benzene.

Wilkinson[146] found that the catalyst $RhCOCl(PPh_3)_2$ was selective for terminal alkenes and certain nonconjugated terminal dienes.

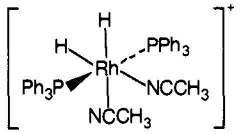

(45)

It is also interesting to note that among the unsaturated centers which may be present in an organic molecule, the least substituted double bond may not be the one which is reduced. However, Birch and Walker[147] found the high degree of selectivity of the coordinated substrate to its steric and electronic environments (during hydrogenation) to be of particular interest in natural product chemistry; *e.g.*, carvone is readily reduced to carvolactone (eq 46) as might be expected. The effect of conjugation in a hindered system has been found to be beneficial.[144] In other instances, however, the double bond in the 1 position of a steroidal 1,4-diene-3-one could only be slowly hydrogenated. 1,4-Naphthoquinone can be reduced to yield the 2,3-dihydro derivative. Using homogeneous catalysts the carbon-halogen bond in allylic halides is reduced to a lesser extent than it is over heterogeneous catalysts, making it possible to obtain reasonable yields of 3-phenyl-1-chloropropane from cinnamoyl chlorides.[145]



(46)

It is apparent from the foregoing reactions that Wilkinson's catalyst cannot be used to reduce a wide variety of functional groups including ketones. Schrock and Osborn[147] found that certain cationic complexes of rhodium, *e.g.*, $[RhH_2(PPhMe_3)_2L_2]^+$ (as PF_6^-, ClO_4^- salts), where L = solvent, can function as homogeneous catalysts for the hydrogenation of ketones. There is appreciable D_2/H_2O exchange using these cationic catalysts containing basic phosphines (PPh_2Me, PMe_3, etc.) as ligands even in the absence of ketones. Shapley, Schrock, and Osborn[148] had previously reported that dimeric d^8 complexes $[M(diene)Cl]_2$, where M = Rh, Ir, underwent cleavage by triphenylphosphine in polar solvents such as alcohols or nitromethane to give cationic species $[M(diene)(PPh_3)_2]^+$ which can be isolated as their tetraphenylborate or perchlorate salts. A deep red acetone solution of the iridium cation $[Ir(COD)(PPh_3)_2]^+$ undergoes immediate decolorization when treated with molecular hydrogen, and from the resultant solution crystals of the cationic complex $\{IrH_2(PPh_3)_2[(CH_3)_2CO]_2\}^+$ can be isolated in good yield. On the addition of excess of triphenylphosphine to the acetone solution the known cation,[149] $[IrH_2(PPh_3)_4]^+$ can be isolated. Complexes with coordinated solvents such as acetonitrile, 2-butanone, dimethylacetamide, and ethyl alcohol are also readily isolated. The complex formed by rhodium in acetonitrile is believed to have structure **11**.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These complexes function as homogeneous hydrogenation catalysts under mild conditions; *e.g.*, 5 m*M* acetone solutions of the Ir(III) cation, $[IrH_2(PPh_3)_2[(CH_3)_2CO]_2]^+$, catalytically hydrogenate 1,5-cyclooctadiene at an initial rate of *ca.* 0.1 M^{-1} hr^{-1} at 25°. Stepwise reduction occurs; cyclooctene being the initial product is more slowly reduced to the saturated hydrocarbon. Small amounts of 1,3- and 1,4-cyclooctadiene are also formed during this hydrogenation, possibly indicating that hydride transfer to this system is stepwise and not synchronous.

The analogous rhodium(III) cation $\{RhH_2(PPh_3)S_2]^+$ (S = solvent) can be prepared by treating a solution of

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(146) C. O'Connor and G. Wilkinson, *J. Chem Soc. A*, 2665 (1968).

(147) (a) A. J. Birch and K. A. M. Walker, *J. Chem. Soc. C*, 1894 (1966); (b) R. R. Schrock and J. A. Osborn, *Chem. Commun.*, 567 (1970).

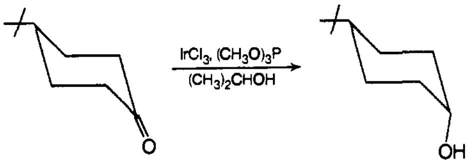
(148) J. R. Shapley, R. R. Schrock, and J. A. Osborn, *J. Amer. Chem. Soc.*, 91, 2816 (1969).

(149) M. Angoletta, *Gazz. Chim. Ital.*, 92, 811 (1962).

the rhodium(I) species, $[Rh(NBD)(PPh_3)_2]^+$, with hydrogen in the requisite solvent. The complexes [S = $(CH_3)_2CO$, C_2H_5OH] dissolve in solvents such as tetrahydrofuran, dioxane, 2-methoxyethanol, dimethylacetamide, or acetone, and very effectively catalyze the hydrogenation of double and triple bonds. The rate of hydrogenation of monoalkenes decreases in the sequence: 1-hexene > cyclohexene ~ *cis*-2-hexene > *trans*-2-hexene ≫ 1-methylcyclohexene. Norbornadiene is reduced very rapidly whereas 1,5- and 1,3-cyclooctadienes are reduced more slowly. Again as in the iridium catalysis, intermediate formation of a monoalkene is observed. Alkynes are hydrogenated faster than the corresponding alkenes: 1-hexyne > 2-hexyne > 1-hexene. Unsaturated ketones and esters are reduced without reduction of the carbonyl function. When dioxane is used as a solvent, the complex $[IrH_2(PPh_3)_2[(CH_3)_2CO]_2]^+$ reduced 1-butyraldehyde to 1-butanol slowly. The hydrogenation process is inhibited by an excess of triphenylphosphine or good donor solvents such as acetonitrile.

More recently Schrock and Osborn[150] reported a wide variety of coordinatively unsaturated species $[ML_2]^+$ from the readily accessible chloro-bridged dimeric complexes of the type $[ML_2Cl]$ where M = Pd, Pt, Ir, and Rh. These investigators mentioned that it is sometimes difficult to differentiate between a vacant and a solvent occupied site on a metal complex.

The complex $IrCl_3[P(OCH_3)_3]_3$ has been found by Eliel, *et al.*,[151] to reduce ketones *via* a hydrogen transfer reaction. 4-*tert*-Butylcyclohexanone was reduced to *cis*-4-*tert*-butylcyclohexanol (eq 47).



(47)

Nashiguchi and Fukuzumi[152] have found that complexes of the type of $MX_2(PPh_3)_2$ (where M = Ni^{2+} or Co^{2+} and X = halogen) promote the homogeneous transfer of hydrogen from o- and *p*-dihydroxybenzenes to 1,5-cyclooctadiene and 1,3-cyclooctadiene yielding cyclooctene and cyclooctane, respectively. The complexes $FeCl_2(PPh_3)_2$ and $FeBr_2(PPh_3)_2$ were found to be the most active.

Mestroni, *et al.*,[153] found that complexes of the type of $[CoH_2(chel)_3(PR_3)_2]^+ClO_4^-$ (where chel = 2,2-bipyridyl or 1,10-phenanthroline; R_3P = triethylphosphine, tri-*n*-propylphosphine, tri-*n*-butylphosphine, and diethylphenylphosphine) reduced 1,3-butadiene and isoprene to butene and methylbutene, respectively.

Abley and McQuillan[140] reported that bis(pyridine)-dimethylformamidedichlororhodium borohydride could be used as a catalyst for homogeneous hydrogenation to reduce -N=N-, -N=C, and NO_2 groups in addition to carbon-carbon double and triple bonds.

Strohmeier and coworkers[42] reported that $Ir(CO)Br[P(C_6H_{11})_3]_2$, $Ir(CO)Cl[P(CH_2Ph)_3]_2$, $Ir(CO)Cl[P(C_6H_5)_3]_2$, and $Ir(CO)I[P(C_6H_5)_3]_2$ could be used as homogeneous catalysts for the hydrogenation of ethylene under mild conditions.

Bailar and Itatani[154] made a systematic study on the effects of the central metal atom and the ligands about it on the rate and selectivity of homogeneous hydrogenations. The hydrogenation of methyl lineolate was investigated in the presence of catalysts of the general formula $(R_3Z)_3MX_2$ (where R = alkyl or aryl; Z = P, As, or Sb; M = Ni, Pd, or Pt) with or without the addition of $M'X_2$ or $M'X_4$ (where M′ = Si, Ge, Sn, or Pb). In most instances, $M'X_2$ or $M'X_4$ was converted to the $-M'X_3$ ligand which modified the M–H bond formed during hydrogenation so that the reaction with the double bond of an alkene was enhanced.[154,155] Thus, the addition of $SnCl_2$ enhances the catalytic activity of $(Ph_3P)_2PtCl_2$ or $(Ph_3P)_2PdCl_2$; however, it does not affect the activity of the corresponding nickel catalyst. As in the related ruthenium complexes, the first step in the course of hydrogenation is believed to be the formation of a hydride complex. In the presence of excess of $SnCl_2$, the hydrido(trichlorostannate)bis(triphenylphosphine)platinum(II) complex was formed. The reactivity of this hydride complex is enhanced by π-acceptor ligands such as $-SnCl_3$ and $-SnBr_3$.[154]

These catalysts are quite selective since in a compound containing two or more double bonds only one is reduced.[154-156] Although terminal alkenes undergo hydrogenation, substituted olefins do not. Hence, when reduction of internally conjugated diene occurs, the unreactive internal alkene[157] is produced. This selectivity is illustrated by the products obtained by the reduction of isomeric hexadienes. Hydrogenation of 1,5-hexadiene yields mainly the isomeric hexenes (20%); however, since both double bonds of the hexadiene were originally terminal, some of the 1-hexene initially formed undergoes further reduction to yield hexane (2.5%). In contrast, the hydrogenation of 1,4- and 1,3-hexadienes yield only 2-hexene and 3-hexene, respectively. Isomerization as in the case of other homogeneous hydrogenations has been found to accompany hydrogenation with the platinum–tin phosphine system; however, complete isomerization to conjugated system does not occur before reduction takes place.[157] Substituted conjugated dienes are also reduced but slowly; *e.g.*, 2,4-hexadiene yields 2-hexene in low yield. The results of the hydrogenation of isomeric hexadienes are summarized in Table XI.[157-158]

When $PtCl_2(PPh_3)_2$ was used as a catalyst without the cocatalyst, no hydrogenation occurred. On the other hand, a similar nickel complex, $NiCl_2(PPh_3)_2$, is an effective catalyst for the isomerization and hydrogenation of methyl lineolate.[159] In fact, some reduction of methyl lineolate catalyzed by the nickel complex occurred even in the absence of molecular hydrogen.

B. Ruthenium Complexes

In 1961 Halpern[160] established that aqueous solutions of ruthenium(II) chloride are effective catalysts for the

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(150) R. R. Schrock and J. A. Osborn, *J. Amer. Chem. Soc.*, **93**, 3089 (1971).

(151) E. L. Eliel, T. W. Doyle, R. O. Hutchins, and E. C. Gilbert, *Org. Syn.*, **50**, 13 (1970); Y. M. Y. Haddad, H. B. Henbest, J. Husbands, and T. R. B. Mitchell, *Proc. Chem. Soc., London*, 361 (1964).

(152) T. Nashiguchi and K. Fukuzumi, *Chem. Commun.*, 139 (1971).

(153) G. Mestroni, A. Camus, and E. Mestroni, *J. Organometal. Chem.*, **24**, 755 (1970).

(154) J. C. Bailar, Jr., and H. Itatani, *J. Amer. Chem. Soc.*, **89**, 1592 (1967).

(155) E. N. Frankel, H. M. Peters, E. P. Jones, and H. J. Dutton, *J. Amer. Oil Chem. Soc.*, **44**, 186 (1967).

(156) H. A. Tayim and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **89**, 4300 (1967).

(157) R. W. Adams, G. E. Batley, and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **90**, 6051 (1968).

(158) R. W. Adams, G. E. Batley, and J. C. Bailar, Jr., *Nucl. Chem. Lett.*, **4**, 455 (1968).

(159) H. Itatani and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **89**, 1600 (1967).

(160) J. Halpern, J. N. Harrod, and B. R. James, *J. Amer. Chem. Soc.*, **83**, 753 (1961).

TABLE XI.[157] **Catalytic Hydrogenation of Isomeric Hexadienes (10 mmol) with $PtCl_2(PPh_3)_2$ (0.25 mmol) and $SnCl_2.2H_2O$ (2.5 mmol) in Benzene-Methanol (50 ml, 3:2)**[a]

	Glpc analysis, %								
		2-Hexene				Hexadiene			
Diene	1-Hexene	*cis*	*trans*	3-Hexene	*n*-Hexane	1,5	1,4	1,3	2,4
1,5	0.8	5.8	12.2	1.0	2.5	0	17.0	2.0	58.7
1,4	0	5.0	12.5	0	0	0	5.7	3.6	73.2
1,3	0	0	0	7.5	0	0	0	73.1	19.4
2,4	0	0.9		0	0	0	1.3	1.8	96.0

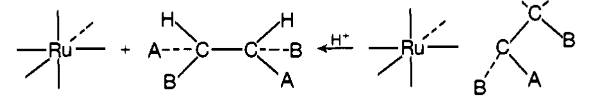
[a] Under 34 atm of hydrogen at 90° for 3 hr.

TABLE XII.[162] **Examples of Transfer Hydrogenation by $RuCl_2(PPh_3)_3$**

Hydrogen donor	Hydrogen acceptor	Yield of saturated carbonyl compound after 4 hr, %
$PhCH_2OH$	$PhCH{=}CHOCH_3$	94
$PhCH_2OH$	$PhCH{=}CHCOCH_3$	55
$PhCH_2CH_2OH$	$PhCH{=}CHCOCH_3$	94
$PhCH(OH)CH_3$	$PhCH{=}CHCOCH_3$	93
$CH_3(CH_2)_6CH_2OH$	$PhCH{=}CHCOCH_3$	82
$PhCH_2OH$	$PhCH{=}CHCOPh$	98
$PhCH_2OH$	$\underline{CH_2C(CH_3)_2CH_2C(CH_3){=}CHCO}$	41
$PhCH_2OH$	$PhCH{=}CHCOC(CH_3)_3$	89
$PhCH_2OH$	$PhCH{=}C(CH_3)CHO$	61
$PhCH_2OH$	$PhCH{=}CHCOOC_2H_5$	53

hydrogenation of ethylenic compounds. The various chloro anions of Ru(II), -(III), and -(IV) were thoroughly studied by Adamson,[112] and some of the more effective catalytic species have been identified as $Ru(H_2O)_2Cl_4^-$, $Ru(H_2O)Cl_5^{2-}$ and $RuCl_6^{3-}$. Activated olefin compounds such as maleic and fumaric acids are hydrogenated in the presence of Ru(II) in HCl solution. First the ruthenium-olefin complex is formed and then it is hydrogenated in a slow step. Reduction with H_2 or D_2 in D_2O yields chiefly (±)-2,3-dideuteriosuccinic acid (*i.e.*, addition is stereospecifically cis). Halpern, *et al.*,[161] studied the system and proposed the mechanism in Scheme VII.

SCHEME VII



$RuCl_2(Ph_3P)_3$ has been reported by Sasson and Blum[162] as well as other workers[163] to be a homogeneous catalyst for hydrogen transfer in several organic reactions. In the presence of primary alcohols this catalyst readily catalyzes the reduction of α,β-unsaturated ketones to saturated ketones. By using $C_6H_5CD_2OH$ it was shown that the hydroxylic hydrogen is incorporated in the transfer reaction, probably as a result of initial intramolecular hydrogen migration catalyzed by the ruthenium complex. Examples are given in Table XII.

In the presence of hydrogen some of the hydrido complex may be formed and account for the activity of the catalyst. It is more highly specific than the related $RhCl(Ph_3P)_3$ and catalyzes the hydrogenation of 3-oxo-1,4-diene steroids selectively at the 4 position.

Tris(triphenylphosphine)hydridochlororuthenium(II), $RuClH(Ph_2P)_3$, has been described as the most active catalyst known for hydrogenation of terminal monosubstituted olefins.[114,115] Other olefins are hydrogenated slowly or not at all; *viz.* internal and cyclic alkenes have rates slower than those of 1-alkenes by a factor of 10^3 to 10^4. Acetylenic compounds react very slowly to give low yields of alkenes. Conjugated dienes are hydrogenated slowly in the presence of catalytic amounts of $RuClH(Ph_3P)_2$ with about 90% retention of steric configuration. With 4-vinyl-1-cyclohexene reduction occurred mainly at the vinyl group and was not accompanied by migration of the internal double bond.

The active catalyst is readily prepared *in situ* in benzene by quantitative base-assisted hydrogenolysis of $RuCl_2(Ph_3P)_3$ at 25° and 1 atm of hydrogen pressure. If the starting material is $RuBr_2(Ph_3P)_3$, the analogous bromo product, $RuBrH(Ph_3P)_3(C_6H_6)$, is formed.

$$RuCl_2(Ph_3P)_3 + H_2 + Et_3N \rightarrow RuClH(Ph_3P)_3 + Et_3NCl \quad (48)$$

$$RuClH(Ph_3P)_3 + C_6H_6 \rightarrow RuClH(Ph_3P)_3(C_6H_6) \quad (49)$$

The superior effectiveness of the hydridochloro complex over $RhCl(Ph_3P)_3$ in benzene or $RuCl_2(Ph_3P)_3$ in ethanol-benzene is demonstrated by a hydrogenation rate of over 100 ml min^{-1} at subatmospheric pressure and catalyst concentration of 8.3 × 10^{-4} *M* while

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(161) J. Halpern, J. N. Harrod, and B. R. James, *J. Amer. Chem. Soc.*, **88**, 5150 (1966).

(162) L. Vaska, *Z. Naturforsch. B*, 15, 56 (1960).

(163) J. Chatt and B. L. Shaw, *Chem. Ind. (London)*, 931 (1960); 290 (1961).

TABLE XIII.[114] **Homogeneous Catalytic Hydrogenation of Olefins**^{a}

Substrate	Rate, ml min^{-1}	Product
Pent-1-ene	99	Pentane
Hex-1-ene	109	Hexane
Hex-2-ene	0.1	
Hept-1-ene	69^b	Heptane
Hept-3-ene	0.1	
Oct-2-ene	0.1^c	
Dec-1-ene	86	Decane
Cyclohexene	0.3	
Penta-1,3-diene	3	Pent-2-ene

^{a}RuCl(H)(PPh$_3$)$_3$, 5 × 10^{-5} mol; olefin, 7.1 × 10^{-2} mol in benzene to total volume 60 ml. Rate at 50 cm, partial pressure hydrogen at 25°. ^{b}Under same conditions, RhCl(PPh$_3$)$_3$ gives 14 ml min^{-1}. ^{c}Noncompetitive to hept-1-ene at same concentration.

TABLE XIV.[115] **Initial Rates of Hydrogenation of Alkenes, Relative to That of Hept-1-ene under Standard Conditions**^{a}

Alkene	Rate	Product^b
Hept-1-ene	1.0^c	Heptane
Pent-1-ene	1.4	Pentane
Hex-1-ene	1.6	Hexane
Dec-1-ene	1.3	Decane
cis + *trans*-hex-2-ene	$<3 \times 10^{-4}$	
cis + *trans*-oct-2-ene	$<3 \times 10^{-4d}$	
Hept-3-ene	$<3 \times 10^{-4}$	
Cyclohexene	$<1 \times 10^{-3}$	
2-Methylpent-1-ene	$<3 \times 10^{-4}$	

^{a}Catalyst, 5 × 10^{-5} mol; alkene, 7.1 × 10^{-2} mol; benzene to total volume, 60 ml; hydrogen pressure, 50 cm, 25°. ^{b}By glc; no evidence for isomerization of unconverted alk-1-ene. ^{c}Rates under comparable conditions for RuClH(PPh$_3$)$_3$, RhCl(PPh$_3$)$_3$, and RhH(CO)(PPh$_3$)$_3$, respectively, are *ca.* 260, 15, and 8 ml min^{-1}. ^{d}Subsequent addition (5 min) of hept-1-ene gave rate 0.94.

TABLE XV.[115] **Hydrogenation of Dienes by RuCl(H)(PPh$_3$)$_3$**^{a}

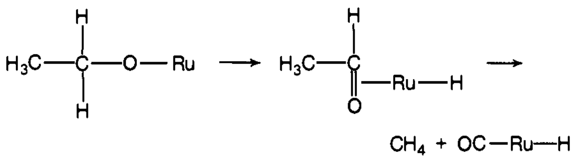
Alkene	Product	Yield, %			
		1 hr	2 hr	3 hr	15 hr
trans-Hexa-1,4-diene	*trans*-Hexa-1,4-diene	58.2	44.6		18.3
	trans-Hex-2-ene	28.6	37.9		52.7
	cis-Hex-2-ene	3.4	5.3		9.2
	Hexane	0.7	1.5		3.6
	Unidentified (3 peaks)	9.1	10.7		16.2
cis-Hexa-1,4-diene	*cis*-Hexa-1,4-diene	52			
	cis-Hex-2-ene	31			
	trans-Hex-2-ene	3			
	Hexane	<1			
	Other	13			
2-Methylhexa-1,5-diene	2-Methylhexa-1,5-diene			60.7	
	2-Methylhex-1-ene			29.1	
	5-Methylhex-1-ene			7.9	
	2-Methylhexane			2.1	

^{a}Catalyst: 5 × 10^{-5} mol; alkene, 10 ml; benzene, 50 ml, at 25°, 60 cm pressure.

RuCl$_2$(Ph$_3$P)$_3$ under similar conditions yields a rate of less than 0.1 ml min^{-1}.[49] The specificity for terminal olefins is not exhibited by Rh catalysts. Several factors may be noted with regard to catalysis by RuClH(Ph$_3$P)$_3$. The catalyst exchanges not only with terminal olefins ($t_{1/2}$ ~ 30 sec) but also with internal olefins ($t_{1/2}$ ~ 5 min) even though the latter are not readily hydrogenated. Isomerism of olefins, *e.g.*, conversion of *cis*-hept-2-ene to the trans isomer or hex-l-ene into hex-2-ene, is not detectable in 24 hr. The rhodium catalyst exchanges terminal olefins exceedingly rapidly, *e.g.*, for pent-1-ene $t_{1/2}$ ~ 20 sec, whereas internal olefins are exchanged very slowly, *e.g.*, *cis*-pent-2-ene has $t_{1/2}$ ~ 60 min. Also, using 10^{-2} *M* catalyst and 2 *M* olefin in benzene at 25° pent-1-ene gives 50% conversion to *cis*- and *trans*-pent-2-enes in an hour (excess Ph$_3$P inhibits both reactions). The direct involvement of a transition metal–hydrogen bond in exchange and isomerization reactions is shown in these reactions which must proceed *via* the reversible formation of an alkyl intermediate. Nmr spectra in fact show the reversible formation of a Ru–C$_2$H$_5$ bond under ethylene at 25°. Since RuCl(H)(Ph$_3$P)$_3$ readily exchanges with internal olefins, the failure to hydrogenate them may be attributable to steric hindrance in the hydrogenolysis of the metal-to-carbon bond in the alkyl intermediate. Representative catalytic hydrogenations are presented in Tables XIII–XV.

Jardine, *et al.*,[49] obtained data on a number of the less reactive olefins using RuCl$_3$·3H$_2$O (10^{-2} mol), Ph$_3$P (6 × 10^{-2} mol) in methanol, together with 10^{-2} mol of substrate. The rates of hydrogen uptake produced by the substrate and product are given in Tables XVI and XVII.

A number of reactions have been studied which relate to the formation of ruthenium alkyls and the process of ligand migration. Vaska[105,162] noted that ruthenium(III) chloride (or the Os counterpart) reacted with triphenylphosphine and various alcohols to give RuClH(CO)(PhP)$_3$. Since base assists the reaction, it was postulated that the initial step may be the formation of an alkoxide complex which rearranges. Chatt, *et al.*,[163,164] suggested that hydride transfer from alkoxide to the metal produces an aldehyde which is the source of the carbonyl group. When the alkoxide is from ethanol, the overall reaction 51 takes place. It is not clear whether the methane comes directly from the aldehyde or from a RuCH$_3$ species which is first formed and then cleaved.


(50)

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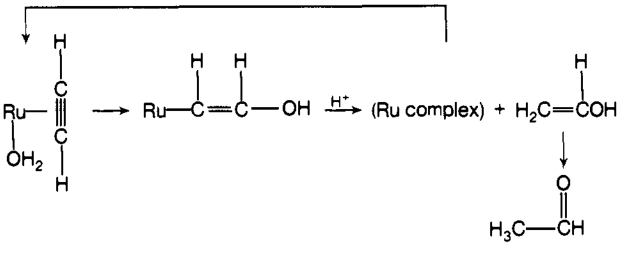
(164) J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 3466 (1960).

$$[Ru_2Cl_3(PR_3)_6]Cl + 2KOH + 2C_2H_5OH \rightarrow 2RuHCl(CO)(PR_3)_3 + 2CH_4 + 2KCl + 2H_2O \quad (51)$$

Migration also occurs in the catalytic hydration of acetylenic compounds by ruthenium(III) chloride in aqueous HCl solution. The active species seem to be $Ru(H_2O)_2Cl_4^-$ and $Ru(H_2O)Cl_5^{2-}$. $RuCl_6^{3-}$ is not a catalyst (eq 52). The subsequent migration is rapid (eq 53). A

$$Ru(H_2O)Cl_5^{2-} + C_2H_2 \longrightarrow Ru(C_2H_2)(H_2O)Cl_4^- + Cl^- \quad (52)$$



(53)

TABLE XVI[49a]

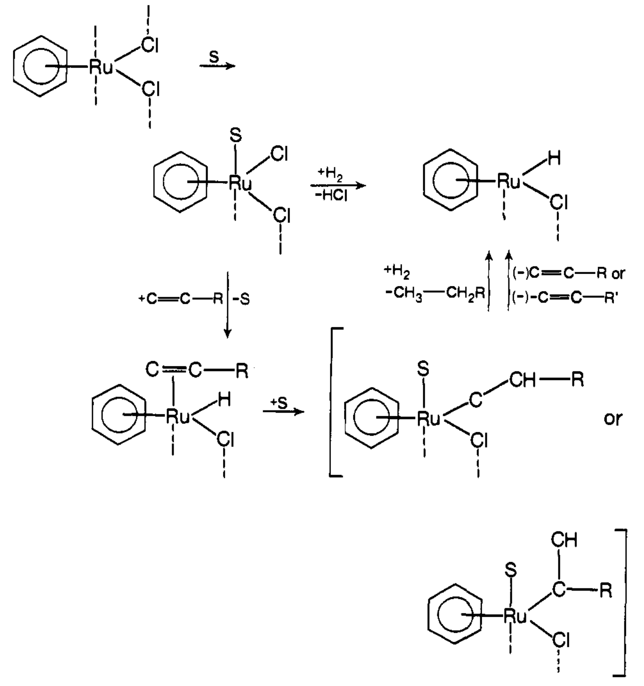
Substrate	Product	Rate, cm³ of H_2 min⁻¹
Cyclopentene	Cyclopentane	5.9×10^{-2}
Cyclohexene	Cyclohexane	15×10^{-2}
Cyclooctene	Cyclooctane	6×10^{-2}
3,5-Dimethylhex-1-yn-3-ol	3,5-Dimethylhexan-1-ol	
Diphenylacetylene	*cis*-Stilbene	

TABLE XVII[49]

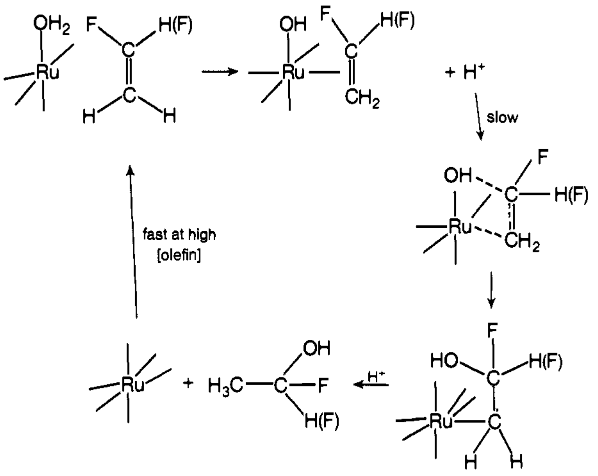
Substrate	Product	Rate, cm³ of H_2 min⁻¹
Norbornadiene	Norbornane	5.3×10^{-2}
Diphenylacetylene	*cis*-Stilbene	7.6×10^{-2}
Stearolic acid	Oleic acid	2.2×10^{-2}
2,5-Dimethyl-hex-3-yn-2,5-diol	*cis*-2,5-Dimethylhex-3-ene-2,5-diol	3×10^{-2}

polymeric complex, $[Ru(C_6H_6)Cl_2]_n$, μ-dichloro-π-benzeneruthenium(II), was studied by Ogata, *et al.*,[117] with regard to its ability to catalyze the hydrogenation of olefins. The complex is soluble in DMSO and partially soluble in DMF but functions heterogeneously in other organic solvents in which it is substantially insoluble. Addition of an organic base markedly improved catalysis in a number of cases presumably due to promotion of heterolytic splitting of hydrogen and formation of hydride complex. With strongly coordinating solvents (acetonitrile and DMSO) olefin presumably can not compete successfully and is not activated. In DMF olefin isomerization greatly exceeds hydrogenation. Unlike $RuCl_2(Ph_3P)_3$ to which these dichloro-π-benzene complexes bear some formal relation, $[(RuC_6H_6)Cl_2]_n$ hydrogenates internal olefins (although more slowly than terminal olefins). The hydrogenation mechanism proposed is similar to that for the phosphines (Scheme VIII). Typical hydrogenations are shown in Table XVIII. $Ru(C_6H_6)Cl_2 \cdot DMSO$ seemed to be a derivative isolated and shown to catalyze the hydrogenation of maleic acid to succinic acid in aqueous solution at room temperature under 20 kg/cm² of hydrogen pressure. James and Louie[119] attempted to study the hydrogenation of halogen-substituted (activated) olefins catalyzed by chlororuthenate(II) ions in aqueous HCl. It was anticipated that electron-withdrawing substituents would favor hydride transfer to the olefin. Instead, the competing process of catalytic hydration converted 1,1-difluoroethylene to acetic acid and vinyl fluoride to acetaldehyde. Initial steps in the process are similar to hydrogenation catalysis, *i.e.*, loss of Cl^- and addition of olefin. However, it was clearly shown that the adduct was incapable of reduction by hydrogen. Rather, in the presence of water, hydration of the olefin is catalyzed by this Ru catalyst. The hydroxyfluoro intermediate hydrolyzes to acetaldehyde or acetic acid depending on whether one or two fluoro groups are present (Scheme IX).

SCHEME VIII



SCHEME IX



A very interesting class of ruthenium catalysts, the hydrido carbonates, was reported by Rose, *et al.*[120] They are good catalysts for hydrogenation of alk-1-enes although of limited solubility and sensitive to air oxidation in solution. Some results for benzene solutions are presented in Tables XIX and XX. The mechanism is presumed to involve dissociation of a phosphine group from $RuH(OCOCF_3)(Ph_3P)_3$ to give $RuH(OCOCF_3)(Ph_3P)_2$, attack by alkene to give the alkyl complex, followed by the

TABLE XVIII.[117] **Results of Hydrogenation**

				Products composition, %			
Olefin (0.5 ml)	Solvent (3 ml)	Additive	(ml)	Pentane	Pentene-1	Pentene-2 (*trans*)	Pentene-2 (*cis*)
Pentene-1	Benzene			5	91		4
		C_4H_8NH[b]	(0.007)	91		7	2
		C_4H_8NH[b]	(1.0)	1	99		
		Et_3N	(0.01)	22	46	20	12
		Et_3N	(1.0)	2	98		
	CH_3CN			1	99		
	DMSO			1	99		
	DMF			14	1	71	14
Pentene-2[a]	Benzene	C_4H_8NH[b]	0.007	47		42	11

[a]trans 54%, cis 46%. $[RuCl_2(C_6H_6)]_n$, 10 mg; H_2, 20 kg/cm^2; temp 30 ± 0.1°; reaction time, 4 hr. [b]Pyrrolidine.

TABLE XIX.[120] **Initial Rates of Hydrogenation of Hex-1-ene**[a]

Catalyst	Rate, mmol min^{-1}
$RuH(MeCO_2)(PPh_3)_3$	2.45
$RuH(EtCO_2)(PPh_3)_3$	1.16
$RuH(Pr^iCO_2)(PPh_3)_3$	2.41
$RuH(CF_3CO_2)(PPh_3)_3$	0.97
$RuH(PhCO_2)(PPh_3)_3$	2.25
$RuH[o\text{-}HOC_6H_4CO_2](PPh_3)_3$	2.46

[a]Catalyst, 1.25 mmol, hex-1-ene (7.9 ml), benzene to total volume 50 ml; hydrogen pressure, 50 cm, 25°.

TABLE XX.[120] **Relative Rates of Hydrogen Consumption (ml min^{-1}) at 50 cm of Hydrogen Partial Pressure for Substrates under Standard Conditions**[a]

Substrate[b]	Rate	Substrate[b]	Rate
Hex-1-ene	21.70	*trans*-Hexa-1,4-diene	1.26
Undec-1-ene	20.90	Cyclohexene	1.24
Hept-1-ene	16.38	Penta-1,3-diene	0.71
Allybenzene	7.14	Cyclooctene	0.54
Hexa-1,5-diene	4.45	Allyl alcohol	0.53

[a]Catalyst $RuH(CF_3CO_2)(PPh_3)_3$, 0.625 m*M* in benzene, substrate concentration 1.25 *M*. [b]Not reduced or reduced extremely slowly (<0.1) under the conditions: 1-methylcyclohexene, *cis*- + *trans*-hex-2-enes, *cis*- + *trans*-hex-3-enes, *cis*-hept-2-ene, 2-methyl-pent-1-ene, hex-1-yne.

rate-determining attack of hydrogen. Isomerism is also catalyzed in some cases, as with hex-l-ene, which at 25° under nitrogen undergoes about 12% conversion to *cis*-hex-2-ene and 3% conversion to *trans*-hex-2-ene in 4 hr.

Another group of ruthenium catalysts showing a high degree of specificity for terminal alkenes is generated by the protonation of $Ru_2(OAc)_4 \cdot 2PPh_3$.[165] Protonation is accomplished by fluoroboric acid in methanol solution, and the exact nature of the catalyst is not certain. Methanolic fluoroboric acid solutions of Rh(II) and Ru(II) acetates and of $Ru_2(OAc)_4Cl$ in the presence of triphenylphosphine are active catalysts for the homogeneous hydrogenation of alkenes, alkynes, and other unsaturated substances. Some rates are given in Table XXI.

TABLE XXI.[165] **Relative Rates of Hydrogenation of Substrates by Rhodium and Ruthenium Catalysts**[a]

	H_2 uptake/ml min^{-1}, at 450 mm		
Substrate	Rh	Ru[b]	Ru[c]
3-Methylbut-1-yn-3-ol	44.8	14.1	
Hexa-1,5-diene	36.6	46.2	
Hex-1-yne	34.2		0.4[f]
Propargyl alcohol	17.6[d]		...[g]
Allyl phenyl ether	14.1	1.3	...[g]
Hex-1-ene	10.9	30.5[e]	41.8
Diethyl maleate	4.8		
cis- and *trans*-hex-2-ene	3.3	0.5	
cis-Hept-2-ene	2.2		
Cyclohexene	1.1		...[g]
cis-Pent-2-ene			...[g]
Acetylenedicarboxylic acid	<0.1[d]		
Cycloocta-1,5-diene	0.6[f]		48.7
Cycloocta-1,3-diene			...[g]
Bicyclo[2.2.1]hepta-2,5-diene			1.1

[a]Metal concentration 2.5 m*M*; substrate concentration 1 *M*; triphenylphosphine concentration 5 m*M*; temp 25°; solvent methanol. [b]Ruthenium catalyst, made by the protonation of $Ru_2(OAc)_4Cl$. [c]Ruthenium catalyst, made by the protonation of $Ru_2(OAc)_4$, $2PPh_3$ under hydrogen; temp 30°. [d]$[PPh_3]$ = 20 m*M*. [e]Red-brown chloride-free solution with hex-1-ene gives a rate of 30 ml min^{-1}. [f]$[H_2]$pressure = 50 mm. [g]No hydrogenation was observed.

Obviously a considerable variety of ruthenium catalysts is now available. The varying degrees of specificity of these systems and the rhodium and iridium systems previously described are quite dramatic.

C. Cyanide-Containing Cobalt Catalysts

Homogeneous hydrogenations using cobalt catalyts have been reviewed by Kwiatek.[14] The first studies of the activation of molecular hydrogen by aqueous solutions of cobalt(II) salts and cyanide ion were first reported by Iguchi,[166] although Descamps[167] had noted over a century ago that solutions of cobaltous salts evolved hydrogen in the presence of cyanide ion.

Solutions of $Co(CN)_5^{3-}$ are prepared[168] by addition of cyanide ion to solutions of cobaltous salts in an inert atmosphere. The light brown cobaltous cyanide precipitate initially formed is redissolved forming an olive-green solution of $Co(CN)_5^{3-}$. Evidence for tri- and tetracyano intermediates has been obtained recently.[169]

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(165) P. Legzdins, R. W. Mitchell, G. L. Rempel, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc. A*, 3322 (1970).

(166) M. Iguchi, *J. Chem. Soc. Jap.*, **63**, 634, 1752 (1942).

(167) A. Descamps, *C. R. Acad. Sci.*, **67**, 330 (1968).

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(169) T. Suzuki and T. Kwan, *Nippon Kagaku Zasshi*, **87**, 395 (1966); *Chem. Abstr.*, **65**, 13190c (1966).

TABLE XXII.[173] **Effect of Alcohols on the Selectivity of the Hydrogenation of Butadiene by Pentacyanocobaltate(II)**[a]

No.	Alcohol (ml)	H_2O, ml	Butenes, mol %[b] 1-	trans-2-	cis-2-	Yield,[c] mmol
1	0	50	89	5	6	1.19
2	MeOH (5)	45	84	6	10	0.99
3	MeOH (10)	40	80	6	14	1.18
4	MeOH (15)	35	69	7	24	1.14
5	MeOH (20)	30	56	5	39	0.47[d]
6	EtOH (5)	45	90	6	4	0.93
7	EtOH (10)	40	88	6	6	1.06
8	EtOH (15)	35	85	7	8	0.39[d]
9	*n*-PrOH (10)	40	91	5	4	1.11
10	*i*-PrOH (10)	40	91	5	4	1.12
11	Ethylene glycol (10)	40	77	6	18	1.28
12	Ethylene glycol (15)	35	71	7	22	0.95
13	Ethylene glycol (20)	30	60	7	33	0.95
14	Ethylene glycol (30)	20	45	6	49	1.22
15	Ethylene glycol (40)	10	39	5	56	1.55
16	Glycerol (10)	40	85	5	10	1.78
17	Glycerol (20)	30	82	5	13	2.55
18	Glycerol (30)	20	79	6	15	2.91
19	Glycerol (40)	10	85	8	7	2.73

[a] CN/Co = 6.0, 20°, $CoCl_2$ = 10 mmol, in the absence of hydrogen. [b] Composition of after 3 hr from the start of the hydrogenation. [c] Relative yield of after 3 hr from the start of the hydrogenation. [d] Precipitate was formed.

Various alkali metal or alkaline earth cyanides, as well as various cobaltous salts, may be employed. Practically all the work with this complex has been carried out in aqueous solution owing to the limited solubility of the complex in organic solvents. This fact limits the utility of this complex somewhat. However, methanol[170-172] and methanol-glycerol[173] mixtures as well as other alcohol-water mixtures[173] have been used.

Funabiki and Tarama[173] have studied the ratio of 1-butene to *cis*- and *trans*-2-butene when different alcohols were used in combination with water in the pentacyanocobaltate(II) catalyzed reduction of 1,3-butadiene. Their results are summarized in Tables XXII and XXIII.

Freshly prepared solutions of this complex have a magnetic moment of 1.72 BM/cobalt, corresponding to one unpaired electron.[168] The paramagnetism decreases with time[174] owing to the extreme reactivity of the complex which is readily oxidized even by water (eq 54).

$$2[Co(CN)_5]^{3-} + 2H_2O \rightleftharpoons [Co(CN)_5H]^{3-} + [Co(CN)_5OH_2]^{2-} + OH^- \quad (54)$$

Pentacyanocobaltate(II) reacts with hydrogen and absorbs 0.5 mol of hydrogen per mole of complex to yield the same hydride that is formed with water (eq 55). The hydrido complex $[Co(CN)_5H]^{3-}$ has been isolated by Banks and Pratt.[175]

$$2[Co(CN)_5]^{3-} + H_2 \rightleftharpoons 2[Co(CN)_5H]^{3-} \quad (55)$$

TABLE XXIII.[173] **Effect of Ethylene Glycol on the Selectivity of the Hydrogenation of Butadiene by Pentacyanocobaltate(II)**[a]

No.	Ethylene glycol, ml	H_2O, ml	H_2,[b] ml	Butenes, mol %[c] 1-	trans-2-	cis-2-	Yield, mmol
1	0	50	74	95	4	1	11.14
2	10	40	72	93	5	2	12.50
3	20	30	69	69	7	8	7.56
4	30	20	64	65	10	25	5.10
5	40	10	60	46	9	45	2.81

[a] CN/Co = 6.0, 20°, $CoCl_2$ = 10 mmol; hydrogen was absorbed prior to the introduction of butadiene. [b] Volume of hydrogen absorbed by pentacyanocobaltate(II) before the introduction of butadiene. [c] Composition of after 3 hr from the start of the hydrogenation. [d] Relative yield of after 3 hr from the start of the hydrogenation.

TABLE XXIV.[177] **Deuterium Distributions in Saturated Products from Deuterogenations of $CH_2{=}C(A)X$**

Catalyst	X	A	α[a]	β[a]	β/α
$[Co(CN)_5]^{3-}$[b]	C_6H_5	H	0.85	2.42	2.85
Pd/C	C_6H_5	H	0.58	1.41	2.43
$[Co(CN)_5]^{3-}$[b]	C_6H_5	CH_3	0.79	4.72	6.00
Pd/C	C_6H_5	CH_3	0.63	1.47	2.34
$[Co(CN)_5]^{3-}$[b]	CH_3O_2C	CH_3	0.08	1.22	14.7
Pd/C	CH_3O_2C	CH_3	0.15	1.82	12.1
$[Co(CN)_5]^{3-}$[b]	α-C_5H_4N	H	0.79	1.93	2.45

[a] Indicates average number of deuterium atoms found in α and β positions relative to X in the product. [b] D_2 and D_2O employed.

The structures of stable organocobalt complexes show that the hydrido complex adds to α,β-unsaturated acids, ketones, and nitriles as though the cobalt-hydrogen bond were polarized, $Co^+{-}H^-$. Whether such additions are cis or trans has not been determined unequivocally.[176] Activated olefins which are catalytically hydrogenated generally form unstable organocobalt complexes or none at all. Evidence for direction of addition must be obtained indirectly in these cases.

The use of deuterium in the reduction of butadiene[177] and sorbate has been reported. Additions of $Co(CN)_5D^{3-}$ to these compounds as well as to styrene, α-methylstyrene, α-vinylpyridine, methyl methacrylate, and cinnamate are reversible, as indicated by the quantity of deuterium incorporated in the products and the recovered olefins.[177] Product incorporation of one deuterium β and one deuterium α to the activating group reveals that initial addition of deuterium must be to the β-carbon atom. This direction of addition is also found with olefins forming stable organocarbon complexes. In Table XXIV, the results obtained by homogeneous hydrogenations using $CO(CN)_5{}^{3-}$ as catalyst are compared with those catalyzed by palladium on charcoal in heterogeneous hydrogenations.

It may be seen that the highest ratio of β to α deuterium incorporation in the product is obtained with methyl methacrylate for either type of catalyst. Especially striking is the small amount of deuterium incorporated at the α position in methyl methacrylate as compared to the styrenes. This difference has been noticed in a number of

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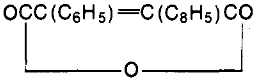
TABLE XXV.[179] **$[Co(CN)_5]^{3-}$-Catalyzed Reductions by Hydrogen**

Compound	Products
C_6H_5CHO	$C_6H_5CH_2OH$
$CH_3COCOCH_3$	$CH_3CH(OH)COCH_3$ 2,5-Dimethylhydroquinone
$C_6H_5COCOC_6H_5$	$C_6H_5CH(OH)COC_6H_5$
Isatin	Dioxindole
Methylcyclohexanones + NH_3	Methylcyclohexylamines
$CH_3COCOO^- + NH_3$	$CH_3CH(NH_2)COO^-$
$C_6H_5CH_2COCOO^- + RNH_2$	$C_6H_5CH_2CH(NHR)COO^-$
$C_6H_5CH{=}CHCOR + NH_3$	$C_6H_5CH_2CH_2CH(NH_2)R$
$C_6H_5COCOC_6H_5 + NH_3$	$C_6H_5CH(OH)CH(NH_2)C_6H_5$, $C_6H_5CH(NH_2)CH(NH_2)C_6H_5$
$(CH_3)_2C{=}NOH$	$(CH_3)_2CHNH_2$
$C_6H_5C(CH_3){=}NOH$	$C_6H_5CH(CH_3)NH_2$
$C_6H_5CH_2C(COO^-){=}NOH$	$C_6H_5CH_2CH(COO^-)NH_2$
$C_6H_5C(CN){=}NOH$	$C_6H_5CH(COO^-)NH_2$
$C_6H_5CH_2C(CN){=}NNHC_6H_5$	$C_6H_5CH_2CH(COO^-)NHNHC_6H_5$
Dimethylfurazone	Tetramethylpiperazine
$C_6H_5NO_2$	$C_6H_5N{=}NC_6H_5$ $C_6H_5NHNHC_6H_5$, $C_6H_5NH_2$
o-$CH_3C_6H_4NO_2$	*o*-$CH_3C_6H_4NO{=}NC_6H_4CH_3$-*o* *o*-$CH_3C_6H_4N{=}NC_6H_4CH_3$-*o*
p-$CH_3C_6H_4NO_2$	*p*-$CH_3C_6H_4NO{=}NC_6H_4CH_3$-*p*, *p*-$CH_3C_6H_4NHOH$
o-$ClC_6H_4NO_2$	o-$ClC_6H_4NO{=}NC_6H_4Cl$-*o*, o-$ClC_6H_4N{=}NC_6H_4Cl$-*o*, *o*-$ClC_6H_4NHNHC_6H_4Cl$-*o*
o-$HOC_6H_4NO_2$	*o*-$HOC_6H_4NH_2$
p-$HOC_6H_4NO_2$	*p*-$HOC_6H_4NH_2$
$C_2H_5NO_2$	$C_2H_5NH_2$
$(CH_3)_3CNO_2$	$(CH_3)_3CNH_2$
$(CH_3)_2NNO$	$(CH_3)_2NH$, $(CH_3)_2NNH_2$
$(C_6H_5)_2NNO$	$(C_6H_5)_2NH$
Cyclohexene oxide	Cyclohexanol
Styrene oxide	$C_6H_5CH_2CH_2OH$

TABLE XXVI.[179] **$Co(CN)_5{}^{3-}$-Catalyzed Hydrogenation of Activated Olefins**

Olefin	Product
$CH_2{=}CHCH{=}CH_2$	C_4H_8
$CH_2{=}C(CH_3)CH{=}CH_2$	C_5H_{10}
$CH_2{=}CHCH{=}CHCH_3$	C_5H_{10}
$CH_2{=}C(CH_3)C(CH_3){=}CH_2$	C_6H_{12}
$CH_3CH{=}CHCH{=}CHCH_3$	C_6H_{12}
$CH_2{=}CHCH{=}CHCH_2CH_2$-$CH{=}CH_2$	C_8H_{14}
Cyclopentadiene-1,3	Cyclopentene
Cyclohexadiene-1,3	Cyclohexene
3-Methylenecyclohexene	1- and 3-methylcyclohexenes
1,2-Dimethylenecyclohexane	Dimethylcyclohexenes, methylmethylenecyclohexane
Cyclooctatetraene	A bicyclooctadiene
Norbornadiene	Nortricyclene, norbornene
$C_6H_5CH{=}CH_2$	$C_6H_5C_2H_5$
$C_6H_5CH{=}CHCH_2OH$	$C_6H_5CH_2CH_2CH_2OH$
$C_6H_5C(CH_3){=}CH_2$	$C_6H_5CH(CH_3)_2$
$C_6H_5C(OCH_3){=}CH_2$	$C_6H_5CH(OCH_3)CH_3$
$(C_6H_5)_2C{=}CH_2$	$(C_6H_5)_2CHCH_3$
p-$NCC_6H_4CH{=}CH_2$	*p*-$NCC_6H_4C_2H_5$
α-Vinylpyridine	α-Ethylpyridine
$CH_2{=}C(CH_3)CHO$	$(CH_3)_2CHCHO$
$CH_3CH{=}CHCHO$	$CH_3CH_2CH_2CHO$
$CH_3CH{=}C(CH_3)CHO$	$CH_3CH_2CH(CH_3)CHO$
$CH_2{=}C(CH_3)COCH_3$	$(CH_3)_2CHCOCH_3$
$CH_2{=}C(CH_3)COC_6H_5$	$(CH_3)_2CHCOC_6H_5$
$CH_2{=}CHCOC_6H_5$	$C_2H_5COC_6H_5$
$C_6H_5CH{=}CHCOCH_3$	$C_6H_5CH_2CH_2COCH_3$
$C_6H_5COCH{=}CHCOC_6H_5$	$C_6H_5COCH_2CH_2COC_6H_5$
p-Benzoquinone	*p*-Hydroquinone
Anthraquinone	Hydranthraquinone
Indigo	Indigo white
$CH_2{=}CHCOO^-$	$CH_3CH_2COO^-$
$CH_2{=}C(CH_3)COO^-$	$(CH_3)_2CHCOO^-$
$CH_2{=}C(CH_3)COOCH_3$	$(CH_3)_2CHCOOCH_3$, $(CH_3)_2CHCOO^-$
$CH_2{=}C(CH_2COO^-)COO^-$	$CH_3CH(CH_2COO^-)COO^-$
$CH_2{=}C(C_6H_5)COO^-$	$CH_3CH(C_6H_5)COO^-$
$CH_3CH{=}CHCH{=}CHCOO^-$	Hexenoates
$C_6H_5CH{=}CHCOO^-$	$C_6H_5CH_2CH_2COO^-$
cis-$OOCCH{=}CHCOO^-$	$^-OOCCH_2CH_2COO^-$
 $OCC(C_6H_5){=}C(C_8H_5)CO$	$^-OOCCH(C_6H_5)CH$-$(C_6H_5)COO^-$
$^-OOCC{\equiv}CCOO^-$	$^-OOCCH_2CH_2COO^-$, *trans* $^-OOCCH{=}CHCOO^-$
$CH_2{=}C(C_6H_5)CN$	$CH_3CH(OC_2H_5)CN$
$CH_2{=}C{=}CHCN$	$CH_3CH{=}CHCN$

reductions over palladium and is one of the features of the so-called "phenyl effect."[176] It has been suggested that styrenes hydrogenate over palladium *via* a route different from that of α,β-unsaturated esters owing to π-complexing of the phenyl group to the metal surface.[176] Although similarities in mechanisms involving π-allylic complexes for homogeneous and heterogeneous hydrogenation of dienes have been indicated,[177,178] there is no evidence for an arene cyanocobaltate. This observed difference in deuterogenation studies may be due to the semihydrogenated organometallic species. The species containing highly electronegative groups would be expected to form stronger carbon–metal bonds.[179] This hypothesis is substantiated by the deuterium distributions obtained from palladium-catalyzed deuterogenation of $C_6F_5CH{=}CH_2$ and $C_6F_5C(CH_3){=}CH_2$ which resemble those obtained for $CH_2{=}CHCO_2CH_3$ and $CH_2{=}C(CH_3)CO_2CH_3$ but not those obtained for $C_6H_5CH{=}CH_2$ and $C_6H_5C(CH_3){=}CH_2$.[176] Unfortunately, these substrates have not been deuterogenated in the presence of $Co(CN_5)^{3-}$. Similar distribution patterns might be expected for α-vinylpyridine and methyl methacrylate since unstable $[Co(CN_5)H]^{3-}$ adducts were isolated from each of these olefins. However, $[Co(CH)_5]^{3-}$ catalyzed deuterogenations revealed a distribution pattern for α-vinylpyridine which resembled the one obtained from styrene (see Table XXIV). Further investigations along these lines should help to point out common features of homogeneous and heterogeneous hydrogenations.

A general mechanistic scheme can be written for reductions catalyzed by $[Co(CN)_5]^{3-}$. Scheme X incorporates the observations made in $[Co(CN)_5]^{3-}$ catalyzed hydrogenations of butadiene, ethyl cinnamate, and α,β-unsaturated nitriles. The hydrogen of the hydrido complex approaches the positive β-carbon of an activated double bond. The four-center transiton state thus formed may collapse to a radical or an organocobalt complex. There is evidence that in the reduction of butadiene the σ-bonded butenylcobalt complex is in equilibrium with the π-bonded butenyl complex.[179] This equilibrium is believed to be dependent on the cyanide ion concentration. This is

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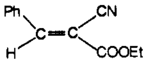
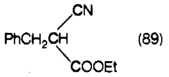
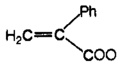
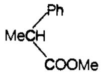
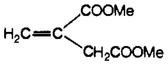
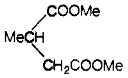
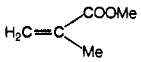
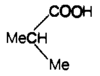
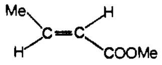
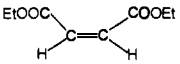
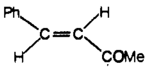
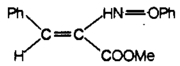
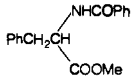
(178) J. Kwiatek and J. K. Seyler, *Advan. Chem. Ser.*, **No. 70**, 207 (1967).

(179) J. Kwiatek and J. K. Seyler, *J. Organometal. Chem.*, **3**, 421 (1965).

TABLE XXVII.[184] **Hydrogenation of Unsaturated Compounds Containing Heteroatoms Catalyzed by Bis(dimethylglyoximato)cobalt(II)**

Run	Substrate	S/Co[a]	Reaction time[b]	Products (yield, %)
1		2	7 hr	 (89)
2		1	1 hr	 (69)
3		4	1 hr	 (100)
4		10	2 hr	 (98.5)
5		10	4 days	Recovered
6		4	3 days	EtOOCCH$_2$CH$_2$COOEt (69)
7		7	4 days	Recovered
8		1	2 days	 (7.3) MBAC (3)

[a] S/Co: molar ratio of substrate to catalyst (Co). [b] Time required for the completion of reaction mixture to be left standing.

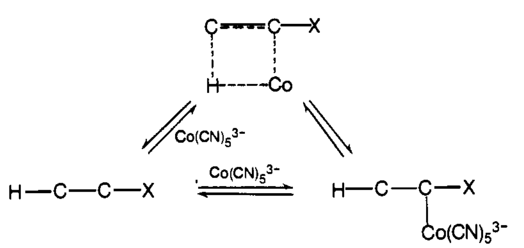
TABLE XXVIII.[184] **Hydrogenation of Olefins Catalyzed by Bis(dimethylglyoximato)cobalt**

Run	Substrate	S/Co[a]	Reaction time[b]	Products (yield, %)
16	$O_2NC_6H_4CH{=}CHCOOMe$ *(trans)*	2	1hr	$H_2NC_6H_4CH{=}CHCOOMe$ *(trans)* (78) PhNHNHPh (1.5 g)
17	$PhNO_2$ (2.4 g)	7	5 days	$PhNH_2$
18	$PhN{=}N(\rightarrow O)Ph$	3	45 min	$PhN{=}NPh$ (76)
19	$PhN{=}NPh$	5	29 min	PhNHNHPh (99)
20	PhCOCOOEt	10	80 min	PhC(OH)HCOOEt (98)
21	PhCOCOPh	10	35 min	PhC(OH)HCOPh (99.5)
22	$CH_3COCOCH_3$	10	24 hr	$CH_3C(OH)HCOCH_3$[c]

[a] S/Co: molar ratio of substrate to catalyst (Co). [b] Time required for the completion of reaction or for the reaction mixture to be left standing. [c] Biacetyl absorbed a theoretical amount of hydrogen, but only a small amount of acetoin was obtained because of an unsuitable isolation procedure.

the reason why more 1-butene is formed at high cyanide concentration.

SCHEME X



Tables XXV and XXVI summarize the reductions of a variety of organic compounds which may be accomplished using pentacyanocobaltate(II) in various aqueous alcoholic media. Ligands other than the cyanide ion have been used, *e.g.*, 2,2-bipyridine, used in dicyano(2,2-bipyridine)cobaltate(II).[180-183] As in the case of $Co(CN)_5^{3-}$ activation is necessary for reduction of carbon multiple bonds. Although initial hydrogenation rates are generally faster with this system thean with $Co(CN)_5^{3-}$, catalyst lifetimes are usually shorter.[183] Although only limited data are available, selectivity appears to be generally the same in the two systems. Schwab and Mandre[183] found that o-phenanthroline could not be used as a ligand in place of 2,2-bipyridine since it gave dicyanobis(o-phenanthroline)cobaltate(II), a coordinatively saturated complex which reacted very slowly with hydrogen. Ohgo, *et al.*,[184] studied the homogeneous hydrogenation of unsaturated compounds catalyzed by bis(dimethylglyoximato)cobalt(II). The results are shown in Tables XXVII and XXVIII.

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(180) C. E. Wymore, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., 1968, No. M53.

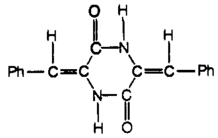
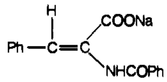
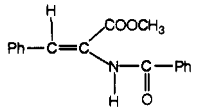
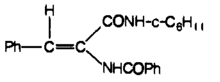
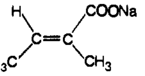
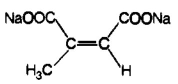
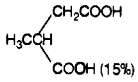
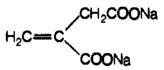
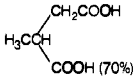
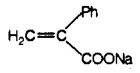
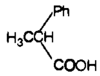
(181) A. Farcas, U. Luca, and O. Piringer, "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier, New York, N. Y., 1968, p 29.

(182) G. Mandre, ref 181, p 35.

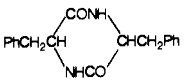
(183) G. M. Schwab and G. Mandre, *J. Catal.*, **12**, 103 (1968).

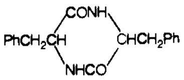
(184) Y. Ohgo, S. Takeuchi, and J. Yoshimura, *Bull. Chem. Soc. Jap.*, **44**, 283 (1971).

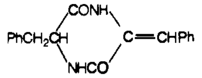
TABLE XXIX.[185] **Hydrogenation of Monoenes**

Substrate	Solvent	Complex	Product (yield)
	Pyridine and water	$[Co(CN)_5H]^{3-}$ [a] Co-Gly[b]	*c* *d*
	Water	$[Co(CN)_5H]^{3-}$ Co-Gly	*e*
	Pyridine and water	$[Co(CN)_5H]^{3-}$ Co-Gly	e
	Ethanol and water	$[Co(CN)_5H]^{3-}$ Co-Gly	*e*
	Water	$[Co(CN)_5H]^{3-}$ Co-Gly	e
	Water	Co-Gly	
	Water	Co-Gly	
	Water	Co-Gly Co-L-Isol[b]	 Quantitatively *g* *g*

[a] Reaction time of catalytic hydrogenation by $[Co(CN)_5H]^{3-}$ was 4 to 5 days at room temperature. [b] Co-Gly or Co-L-Isol represents the solution of $[Co(CN)_5]^{3-}$ and glycine or L-isoleucine. Reaction time was 1 day at room temperature. [c] Both double bonds were reduced quantitatively (see structure i).


i

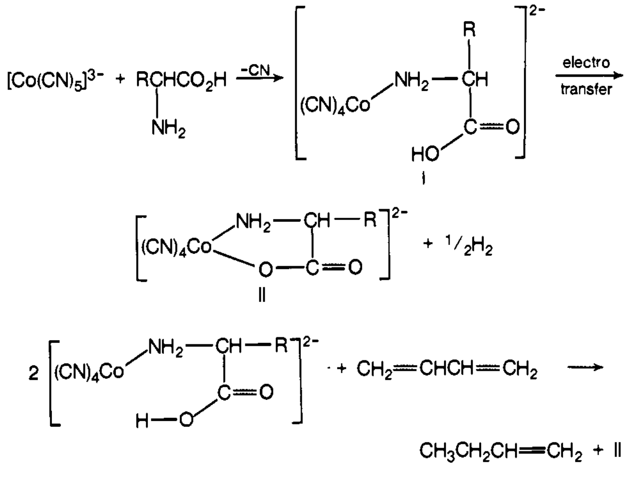

ii


iii

[d] Mixture of fully and partially hydrogenated products was obtained (ii and iii). [e] The starting material was recorded quantitatively. [f] These materials were known to be reduced by $[Co(CN)_5H]^{3-}$ [g] Raw product had $[\alpha]_D$ +0.2° but distillate had slightly negative rotation which was converted to acylthiourea derivative ($[\alpha]_{436}$ −0.2°).

Ohgo, *et al.*,[185] attempted an asymmetric reduction using a solution of $[Co(CN)_5]^{3-}$ and an optically active amino acid in the presence of hydrogen. It was found that the ability of $[Co(CN)_5]^{3-}$ to catalyze the reduction of olefins was not effected by the presence of an amino acid. Similar observations had been made by Suzuki and Kwan.[186] Atropic acid was reduced with a solution containing L-isoleucine and $[Co(CN)_5]^{3-}$ to give slightly optically active hydratropic acid.[185] It was found that the main reactive species in a solution of $[Co(CN)_5]^{3-}$ and an α-amino acid was $[Co(CN)_5H]^{3-}$ (this might be the reason for asymmetric reduction not taking place effectively), and the reversible change between $[Co(CN)_5]^{3-}$ and $[Co(CN)_5H]^{3-}$ was observed depending on the pH of the solution. The postulated mechanism of this reaction is given in Scheme XI. The asymmetric reductions attempted by Ohgo, *et al.*,[185] using the above catalyst system are given in Table XXIX.

SCHEME XI



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(185) Y. Ohgo, S. Takeuchi, and J. Yoshimura, *Bull. Chem. Soc. Jap.*, **43**, 505 (1970).

(186) T. Suzuki and T. Kwan, *Nippon Kagaku Zasshi*, **88**, 395, 400 (1967).

TABLE XXX.[181] **Hydrogenation of Olefins with Soluble Hydrogenation Catalysts**[a]

Expt	Transition metal compound	Catalyst alkylating agent	Ratio[b]	Concn,[c] m*M*	Olefin	Temp, °C	Time, hr	Conversion, %
1	$Ti(O\text{-}i\text{-}C_3H_7)_4$	$(i\text{-}C_4H_9)_3Al$	3.3	16.5	Cyclohexene	25	<20	100
2	$Ti(O\text{-}i\text{-}C_3H_7)_4$	$(i\text{-}C_4H_9)_3Al$	3.3	16.5	1-Octene	25	<20	94
3	$Ti(O\text{-}i\text{-}C_3H_7)_4$	$(i\text{-}C_4H_9)_3Al$	3.3	18.5	*trans*-Stilbene	25	<22	50
4	$Ti(O\text{-}i\text{-}C_3H_7)_4$	$n\text{-}C_4H_9Li$	9.9	15.5	Cyclohexene	50	22	6
5	$(C_5H_5)_2TiCl_2$	$(C_2H_5)_3Al$	1.2	23.2	1-Octene	25	16	70
6	$(C_5H_5)_2ZrCl_2$	$(i\text{-}C_4H_9)_3Al$	2.9	16.8	Cyclohexene	25	17	24.5
7	$VO(OC_2H_5)_3$	$(i\text{-}C_4H_9)_3Al$	4.2	17.3	Cyclohexene	30	1.08	50
8	$VO(O\text{-}n\text{-}C_4H_9)_3$	$(i\text{-}C_4H_9)_3Al$	3.9	19.3	Cyclohexene	40	<20	100
9	$VO(O\text{-}n\text{-}C_4H_9)_3$	$(i\text{-}C_4H_9)_3Al$	3.9	19.3	1-Octene	40	<20	100
10	$VO(OC_2H_5)_3$	$(C_2H_5)_3Al$	4.0	17.9	Cyclohexene	30	1.08	46.5
11	$VO(OC_2H_5)_3$	$(i\text{-}C_4H_9)_2AlH$	4.1	18.3	Cyclohexene	30	1.08	43.5
12	Cr(acac)$_3$	$(i\text{-}C_4H_9)_3Al$	6.0	9.5	Cyclohexene	31.5	2	100
13	Cr(acac)$_3$	$(i\text{-}C_4H_9)_3Al$	6.0	4.0	1-Octene	30	1.17	55
14	Cr(acac)$_3$	$(i\text{-}C_4H_9)_3Al$	6.0	7.7	2-Methyl-2-butene	30	0.83	16.5
15	Cr(acac)$_3$	$(i\text{-}C_4H_9)_3Al$	6.0	4.0	*trans*-2-pentene	30	0.83	50
16	Cr(acac)$_3$	$(i\text{-}C_4H_9)_3Al$	6.3	12.4	Tetramethylethylene	50	18	75
17	MoO_2(acac)$_2$	$(i\text{-}C_4H_9)_3Al$	7.1	15.7	Cyclohexene	30	<16	100
18	MoO_2(acac)$_2$	$(i\text{-}C_4H_9)_3Al$	7.1	14.9	1-Octene	30	<21	100
19	Mn(acac)$_3$	$(i\text{-}C_4H_9)_3Al$	6.0	15.9	Cyclohexene	30	<16	100
20	Mn(acac)$_2$	$(i\text{-}C_4H_9)_3Al$	6.0	21.8	Cyclohexene	31	0.45	12.5
21	Fe(acac)$_3$	$(i\text{-}C_4H_9)_3Al$	6.2	5.6	1-Hexene	30	5[d]	100
22	Co(acac)$_3$	$(i\text{-}C_4H_9)_3Al$	6.0	5.7	1-Hexene	30	2[d]	100
23	Co(acac)$_3$	$(i\text{-}C_4H_9)_3Al$	6.0	4.0	Cyclohexene	30	0.33	100
24	Co(acac)$_3$	$n\text{-}C_4H_9Li$	12.6	16.3	Cyclohexene	50	22	69
25	$Co[(C_6H_5)_3P]_2Cl_2$	$(i\text{-}C_4H_9)_3Al$	3.5	12.5	Cyclohexene	25	16	33.5
26	$Ni[(n\text{-}C_4H_9)_3P]_2Cl_2$	$(i\text{-}C_4H_9)_3Al$	4.3	12.6	1-Hexene	25	19	57.5
27	$Pd[(n\text{-}C_4H_9)_3P]_2Cl_2$	$(i\text{-}C_4H_9)_3Al$	4.2	13.0	1-Hexene	25	19	25.5
28	Ru(acac)$_3$	$(i\text{-}C_4H_9)_3Al$	7.1	15.5	1-Octene	40	<16	100

[a] Reactions were generally carried out with 20 mmol of olefin in 20–25 ml of *n*-heptane or toluene solution in a vessel having a void volume of 230–240 ml under an initial hydrogen pressure of 3.5–3.7 atm, except where indicated. [b] Ratio of organometallic to transition metal concentration. [c] Based on transition metal. [d] Time to reduce 0.2 mol of olefin in the absence of solvent under a constant hydrogen pressure of 2.4 atm.

D. Ziegler-Type Systems as Hydrogenation Catalysts

Ziegler-type systems also function as homogeneous catalysts. Catalysts derived from cobalt(II), cobalt(III), chromium(III), copper(II), iron(III), manganese(II), manganese(III), molybdenum(VI), nickel(II), palladium(II), ruthenium(III), titanium(IV), and vanadium(V) have been examined usually as acetylacetonates or alkoxides since halides give poorer catalysts. All but copper(II) give effective catalyst systems. Bis(π-cyclopentadienyl) dichloride derivatives of titanium and zirconium also yield satisfactory catalyst systems.[187-188] From a wide range of alkylmetal derivatives examined by Sloan, *et al.*,[187] the best were found to be triisobutylaluminum, triethylaluminum, and diisobutylaluminum hydride.[187] According to another report[188] zinc and aluminum alkyls are unsatisfactory with bis(π-cyclopentadienyl)titanium chloride. The most active catalysts were provided by cobalt(III), iron(III), and chromium(III) acetylacetonates in decreasing order of activity. The observed lower reactivities of cobalt(II), nickel(II), and palladium(II) derivatives may arise from the use of bis(triphenylphosphine) complexes, as triphenylphosphine is reported to inhibit the activity of catalyst systems derived from nickel 2-ethylhexanoate and triethylaluminum.[181] Table XXX shows that cyclohexene, 1-hexene, 1-octene, 2 methyl-2-butene, 2-pentene, tetramethylethylene, and stilbene are all reduced at 25-40° and a hydrogen pressure of 3.7 atm. The rate of hydrogenation of alkenes decreases in the following order: disubstituted > trisubstituted > tetrasubstituted. In contrast to the results with heterogeneous catalysts, cyclohexene is hydrogenated faster than 1-octene. Phenylacetylene is reduced to ethylbenzene, but the reduction of 3-hexyne is accompanied by cyclotrimerization to hexaethylbenzene. Functional groups not reduced include aldehydes, ketones, esters, nitriles, nitro, and azo compounds. Similar to other homogeneous hydrogenation catalysts, metal hydride species are probably involved in these reductions. Direct one-step addition of molecular hydrogen is excluded by the observation that reduction of 2-methyl-2-butene yields mono-, di-, and trideuterated products showing that hydrogen exchange occurs.

Aromatic nuclei are reduced under more vigorous conditions, 150-210° and 70 atm, using the catalyst derived from nickel(II) ethylhexanoate and triethylaluminum[187] (Table XXXI). This catalyst system is more reactive than Raney nickel, and in contrast to normal experience it fails to hydrogenate either nitrobenzene or nitrophenol. A comparison of analogous catalyst systems derived from other transition metal carboxylates shows that the order of activity for the hydrogenation of benzene is nickel > cobalt > iron > chromium > copper.

E. Group VIII Metal Carbonyl Hydrogenation Catalysts

Metal carbonyls have been widely used in hydroformylation reactions. Cobalt octacarbonyl was discovered by

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(187) M. F. Sloan, A. S. Matlock, and D. S. Breslow, *J. Amer. Chem. Soc.*, **85**, 4014 (1963).

(188) K. Shikata, K. Nishino, K. Azuma, and Y. Takegami, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, **68**, 358 (1965).

TABLE XXXI.[187] **Hydrogenation of Aromatic Compounds Using a Ziegler-Type Nickel Catalyst**

Substrate	Products	Yield, %
Benzene	Cyclohexane	100
o-Xylene	*cis*-1,2-Dimethylcyclohexane	65.5
	trans-1,2-Dimethylcyclohexane	34.5
Naphthalene	Tetralin	84
	Decalin	13
Phenol	Cyclohexanol	92
	Cyclohexanone	5
Dimethyl phthalate	Dimethyl hexahydrophthalate	100
Dimethyl terephthalate	Dimethyl hexahydroterephthalate	100
Pyridine	Piperidine	98

TABLE XXXII.[196] **Hydrogenations Catalyzed by Cobalt Hydrotetracarbonyl**

Substrate	Product	Yield, %
Stilbene	Bibenzyl	
Diphenylacetylene	Bibenzyl	80
Naphthalene	Tetralin	16
2-Methylnaphthalene	Methyltetralins	43
Acenaphthene	2a-3,4,5-Tetrahydroacenaphthene	45
Fluorene	No reaction	
Anthracene	9,10-Dihydroanthracene	99
Phenanthrene	Mostly unchanged, small amounts of di- and tetrahydrophenanthrenes	
Fluoranthene	1,2,3,10b-Tetrahydrofluoranthene	54
Pyrene	4,5-Dihydropyrene	69
Triphenylene	No reaction	
Naphthacene	5,12-Dihydronaphthacene	70
Chrysene	5,6-Dihydrochrysene	24
1,1-Binaphthyl	No reaction	
Perylene	1,2,3,10,11,12-Hexahydroperylene	72
Coronene	No reaction	
Benzyl alcohol	Toluene	63
1-Phenylethanol	Ethylbenzene	70
1-Napthalenemethanol	1-Methylnapthalene	72
Benzhydrol	Diphenylmethane	95
Triphenylcarbinol	Triphenylmethane	94
Benzopinacol	Diphenylmethane	89
Propionaldehyde	1-Propanol	57
n-Heptylaldehyde	1-Heptanol	50
Cyclohexylaldehyde	Cyclohexylcarbinol (46%) and formate (20%)	
Benzaldehyde	Benzyl alcohol (24%), dibenzyl ether (54%)	
2-Phenylpropionaldehyde	2-Phenylpropan-1-ol	38
Diphenylacetaldehyde	2,2-Diphenylethanol	88
Acrolein	Propionaldehyde	40–50
Crotonaldehyde	Butyraldehyde Butanol	40–50
Diethyl ketone	Limited reduction	
Cyclohexanone	Limited reduction	
Benzyl methyl ketone	Limited reduction	
Acetophenone	Ethylbenzene	67
p-Methoxyacetophenone	*p*-Ethylanisole	91
2-Acetylnaphthalene	2-Ethylnaphthalene	
Benzophenone	Diphenylmethane	86
Fluorenone	Fluorene	95
Benzanthrone	1,10-Trimethylenephenanthrene	59
Methyl vinyl ketone	Methyl ethyl ketone	70–90
Mesityl oxide	Methyl isobutyl ketone	70–90
Ethyl cinnamate	Ethyl β-phenylpropionate	70–90
Ethyl β-(2-furanyl)acrylate	Ethyl β-(2-furanyl)-propionate	70–90
Thiophene	Thiolane	66
2-Methylthiophene	2-Methylthiolane	77
2-Ethylthiophene	2-Ethylthiolane	82
2,5-Dimethylthiophene	2,5-Dimethylthiolane	22
2-Thenyl alcohol	2-Methylthiophene (24%), 2-methylthiolane (57%)	
2-Acetylthiophene	2-Ethylthiophene (52%), 2-ethylthiolane (26%)	

Roelen in 1943[189] to be an effective hydroformylating agent. The active species in these hydroformylating reactions was found to be cobalt hydrotetracarbonyl.[190] The observation that cobalt hydrotetracarbonyl must dissociate into the hydrotricarbonyl species before reaction with an alkene can occur explains the inhibitory effect of high concentrations of carbon monoxide.[191] It is also in keeping with the mechanisms of related substitution reactions.[192] The formation of alkyl cobalt tetracarbonyl compounds is well authenticated.[192] Similar complexes may be prepared from sodium tetracarbonyl cobaltate and alkyl halides.[193–195] Among the functional groups which may be reduced by cobalt hydrotetracarbonyl are ketonic carbonyl, nitro, and imino groups. Attempts to hydroformylate aromatic compounds led to the discovery that while phenanthrene is only slightly reduced to 9,10-dihydrophenanthrene at 200°, anthracene is quantitatively reduced to 9,10-dihydroanthracene at 135°.[196] Further work in this area has shown that a number of polycylic hydrocarbons can be partially hydrogenated under these conditions, isolated benzene rings and phenanthrenoid systems being exceptionally resistant to reduction. The thiophene ring is also reduced under these conditions. In contrast to heterogeneous catalysts, this catalyst system is much less susceptible to poisoning by sulfur-containing compounds.[197] Indoles[198] and pyridines[199] are also sometimes reduced. A few examples are given in Table XXXII. Iron carbonyls function as catalysts at temperatures around 200° and hydrogen pressures of 200 to 350 atm. Using these catalysts the hydrogenation of methyl esters of unsaturated fatty acids yields the corresponding saturated and monosaturated esters.[200–202] The formation of π complexes between the substrates and the iron carbonyls does not diminish their catalytic activity. In comparison with dicobalt octacarbonyl it has been shown that iron pentacarbonyl effects a fast reduction of conjugated

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(189) O. Roelen, U. S. Patent 2,327,066 (1943).

(190) D. S. Breslow and R. F. Heck, *Chem. Ind. (London)*, 467 (1960).

(191) G. L. Karopinka and M. Orchin, *J. Org. Chem.*, **26**, 4187 (1961).

(192) R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, **83**, 4023 (1961).

(193) R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, **82**, 750 (1960).

(194) R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, **82**, 4438 (1960).

(195) R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, **83**, 1097 (1961).

(196) S. Friedman, S. Metlin, A. Svedi, and I. Winder, *J. Org. Chem.*, **24**, 1287 (1959).

(197) J. Laky, P. Szabo, and L. Marko, *Acta Chim. Acad. Sci. Hung.*, **46**, 247 (1965).

(198) J. T. Shaw and F. T. Ryson, *J. Amer. Chem. Soc.*, **78**, 2538 (1956).

(199) P. Pino and R. Ercoli, *Ric. Sci.*, **23**, 1231 (1953).

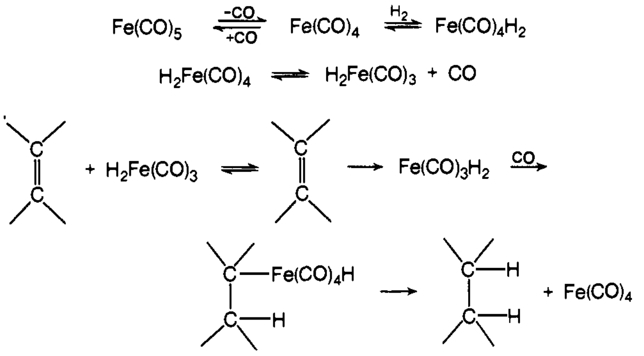
(200) E. N. Frankel, E. A. Emken, H. M. Peters, V. L. Davison, and R. O. Butterfield, *J. Org. Chem.*, **29**, 3299 (1964).

(201) E. N. Frankel, E. A. Emken, H. M. Peters, V. L. Davison, and R. O. Butterfield, *J. Org. Chem.*, **29**, 3292 (1964).

(202) I. Ogata and A. Misono, *Yukagaku*, **13**, 644 (1964); *Chem. Abstr.*, **63**, 17828 (1965).

and unconjugated double bonds, but the reduction stops at the monounsaturated stage. The high activation energy of 60 kcal suggests that the rate-determining step is thermal dissociation of the iron carbonyl.[202] A similar activation energy is found with the iron tricarbonyl complex with methyl linoleate.[203-204] It seems that a reaction sequence (Scheme XII) analogous to that formulated for cobalt hydrotetracarbonyl catalyzed hydrogenation occurs in this case also.

SCHEME XII



Iron carbonyls catalyze the reduction of nitriles to a mixture of primary and secondary amines.[205] The secondary amine is formed *via* the reaction sequence shown in Scheme XIII. Nickel carbonyl also catalyzes this reduction.

SCHEME XIII

$$R{-}C{\equiv}N \rightarrow R{-}CH{=}NH \rightarrow RCH_2NH_2$$

$$RCH{=}NCH_2R \rightarrow RCH_2NHCH_2R$$

A potentially useful catalytic specificity is shown by bis(π-cyclopentadienyl)titanium dicarbonyl.[196] In general, it seems to be a fairly selective catalyst for the hydrogenation of terminal acetylenes (Table XXXIII). The hydrogenations are performed in hydrocarbon solvents at 50–60° and 50 atm. Conjugated dienes and dialkylacetylenes are not reduced. The relative activating effects of substituents in terminal acetylenes is phenyl > *tert*-butyl > alkyl.

F. Arene Complexes of Group IV to VI Metals

Recently it has been found that arene complexes are capable of selectively hydrogenating unsaturated compounds containing more than one double bond.[206-209] Tricarbonyl(arene)chromium complexes catalyze the selective hydrogenation of methyl sorbate[207] (*trans*-2-*trans*-4 hexadienoate) to methyl 3-hexenoate as shown.

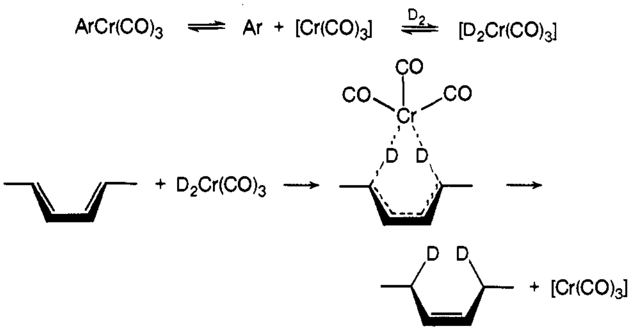
$$CH_3CH{=}CH{-}CH{=}CHCO_2CH_3 \xrightarrow[(PhCO_2CH_3)Cr(CO)_3]{H_2} CH_3CH_2CH{=}CHCH_2CO_2CH_3$$

Apparently this reduction proceeds by 1,4 addition of hydrogen to the diene. The mechanism suggested for this reaction involves the formation of a dihydrido species which reacts with methyl sorbate and transfers hydrogen in the second step. Deuterium tracer studies (Scheme XIV) substantiate this mechanism.

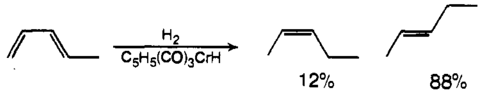
TABLE XXXIII.[196] **Hydrogenations Catalyzed by (π-C_5H_5)$_2$Ti(CO)$_2$**

Substrate	Products (yield, %)
Styrene	Ethylbenzene
trans-Stilbene	Not reduced
Butadiene	Not reduced
Cycloocta-1,3-diene	Not reduced
Acetylene	Not reduced
Pent-1-yne	Pent-1-ene (95)
Hex-1-yne	Hex-1-ene (90)
tert-Butylacetylene	*tert*-Butylethylene (40) 2,2-Dimethylbutane (60)
Hept-3-yne	Not reduced
Phenylacetylene	Ethylbenzene (95)
Diphenylacetylene	Bibenzyl (90)

SCHEME XIV



The selective hydrogenation of conjugated olefins was found to be of general utility with complexes having a variety of arene ligands.[207] When a mixture of fatty acid esters obtained from dehydrated methyl recinolate was used, the conjugated dienes (71%) were completely reduced to the monolefins whereas the nonconjugated dienes (24%) were not hydrogenated. Furthermore, the products of reduction consisted of a mixture of methyl 9-*cis*- and 10-*cis*-octadecenoate, indicating a stereoselective reduction of the 11,12 trans double bond in the starting diene. Bis(cyclopentadienyl)chromium in the presence of hydrogen and carbon monoxide forms a complex $C_5H_5(CO)_3CrH$ which is an effective catalyst for the selective hydrogenation of double bonds.[209] Isolated double bonds are not hydrogenated by this catalyst. The double bond migration is also not observed. With the exception of sterically hindered dienes, hydrogen adds to the terminal double bond of a conjugated system preferentially as in eq 56–58. When brought into contact with a conjugated diene at room temperature, the hydride chromium complex is quantitatively converted to a dimer and at the same time gives up its hydrogen to the olefin (eq 59). The corresponding complexes of molybdenum and tungsten react in an analogous manner.



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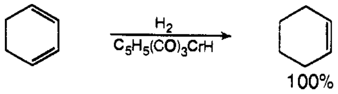
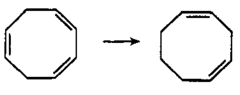


(57)



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(204) I. Ogata and A. Misono, *J. Chem. Soc. Jap.*, **85**, 753 (1964).

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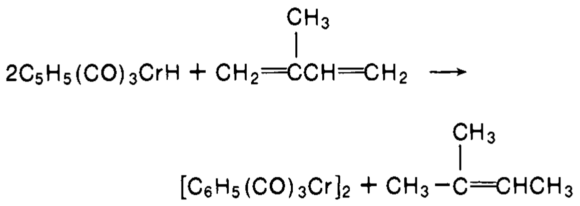

$$2C_5H_5(CO)_3CrH + CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}CH{=}CH_2 \longrightarrow [C_6H_5(CO)_3Cr]_2 + CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CHCH_3 \quad (59)$$

IV. Conclusions

We have endeavored to review the "state of the art" for the homogeneous hydrogenation area of inorganic and organic chemistry. It is apparent that although much progress has been made in this area many questions are still unanswered. It is possible to custom design a catalyst for almost every hydrogenation reaction. The amount of asymmetric synthesis achieved by the use of chiral hydrogenation catalysts has steadily increased since the first asymmetric reduction was reported. The use of difunctional chiral ligands in forming the complex or the use of chiral reagents both as ligands and solvents in the presence of transition metal salts lead to the highest asymmetric bias in a homogeneous hydrogenation reaction. The degree of stereoselectivity is much higher in the case of homogeneous hydrogenation catalysts than in the case of heterogeneous catalysis because the change of ligands greatly changes the activity of homogeneous catalysts.

In addition to asymmetric synthesis hydrogenation catalysts have been used for specific deuterations, selective reduction of double bonds in compounds containing multiple unsaturations, and the selective reduction of certain functional groups. Many of the problems encountered with heterogeneous catalysis, such as isomerization, disproportionation, hydrogenolysis, etc., can be entirely eliminated in many instances by the use of homogeneous catalysis. The reasons for the observed selectivity are becoming clear as more and more data become available. Steric factors seem to exert more influence on selectivity than electronic factors; however, the effect of both factors on reaction rate is significant. It is now possible for an organic chemist to find a catalyst to carry out selective reductions which were impossible to achieve a few years ago. The fact that soluble hydrogenation catalysts and their reactions have given some insight into analogous biochemical reactions has stimulated interest in this area of chemistry greatly and will continue to do so for some time to come.

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