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Invited Review

Homogeneous Hydrogenation of Organic Compounds Catalyzed by Transition Metal Complexes and Salts

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Contents

1. Introduction

In 1938 Calvin reported catalytic reduction of quinone to hydroquinone by a cuprous acetate–quinoline system,[1] the first example of a catalytic homogeneous hydrogenation of an organic compound by a transition metal complex. On the early 1950 investigators found that hydrogenation of olefins was a "side reaction" of the oxo process of hydroformylation of olefins by $HCo(CO)_4$[2–4] and that the product aldehyde itself could be reduced to alcohol in the same catalyst pot. On 1954 Flynn and Hulbuet discovered that at low temperatures ($\leqq 0°$C) the complex $[Pt(C_2H_4)Cl_2]_2$ catalyzes homogeneously the hydrogenation of ethylene.[5] The last decade has seen a virtually exponential growth in the number of papers on the subject of homogeneous hydrogenation by transition metal complexes, with large number of reviews in print.[6–32]

Why has this sudden interest in homogeneous hydrogenation resulted? The answer lies in three primary research motives. First, both academic and industrial chemists have been searching for new selective and stereospecific catalyst systems. Secondly, interest in hydrogenation has been part of a general investigation of organometallic patterns of reactions. Finally, chemists have hoped that the relatively easily studied homogeneous systems would provide clues to heterogeneous catalysts (but this hope appears to find merit only in the little explored metal cluster complexes and in the homogeneous supported catalysts). As listed by Volpin and Kolomnikov,[28] both industrial and academic researchers have noted distinct advantages of homogeneous hydrogenation catalysts over their heterogeneous counterparts: (1) mildness of conditions; (2) ease of catalyst regeneration; (3) high efficiency, selectivity, and stereospecificity; (4) convenience for kinetic study.

As in the case of the metals themselves, complexes of the group VIII elements have been found to be especially reactive. Such complexes have a number of properties which influence their ability to function as catalysts. Those properties which undergo gradual change from species to species (electron transferability, bond stability, ligand substitution) contribute to catalyst activity. Those features which change abruptly (number of transferable electrons, coordination sites available, electron configuration) contribute to catalyst selectivity. Both types of properties are further subject to steric effects.

In view of these variables meaningful comparisons of catalytic activity and selectivity can be made only between those complexes with isoelectronic structures and identical coordination numbers and modifying ligands. At the same time it must be recognized that the complexes employed in catalytic reactions are often, strictly speaking, catalyst precursors. They may undergo considerable modification (ligand dissociation and substitution, as well as metal valence changes) before being converted into the "active" species directly involved in the catalytic cycle. Such modification may be signalled by an induction period. Although any of the components of the catalytic cycle may be termed a catalyst, it is convenient to designate that component which does not contain the elements of either of the reactants as the active species.

The structure of the active species, as well as that of all other intermediates directly involved in the catalytic cycle, must be established in order to study the various factors influencing catalytic behavior. Unfortunately, such intermediates, by the very nature of the catalytic process, are often too unstable to isolate, and indirect evidence of their constitution must be relied on. Few systems have been so throughly investigated that the mechanisms proposed for them have been generally accepted. Nevertheless, the preliminary classification made here for those systems for which adequate data is available is useful.

This paper will be limited in scope to homogeneous hydrogenation of organic compounds by transition metal complexes and salts. Specifically excluded are reduction of inorganic compounds and hydrogenolysis of organic substances.

Three basic processes occur in the reduction of the substrate: (i) activation of H_2 by formation of M–N bonds; (ii) activation of substrate by its inclusion within the coordination sphere of the metal; (iii) hydride transfer from the central metal to the coordinated substrate. Generally these three processes occur on the same metal center (with the exception of radical type mechanisms).

A. Hydrogen Activation

A large number of reviews have examined hydrogen activation,[7,8,19,21,24,29–35] with special attention to the energetics of this process. To achieve the very delicate energy balance necessary for a significant rate of reaction, the M–H bond formed must be stable enough to be present in relatively large concentration, but it must not be stable that hydride transfer from metal to coordinated substrate is retarded. Thus it is obvious that the hydrogenation catalyst is quite sensitive to solvent, substrates, and ligand properties (both electronic and steric.).

Coordination number and electron configuration play an important role in hydrogen activation. Practically all metal complexes which are the best recognized hydrogenation catalysts have a d^6 to d^8 configuration. Coordinatively saturated complexes are unreactive to hydrogen unless the ligands present are labile. Where the complexes are stable in solution, the dissociation of ligands may be promoted by employing elevated temperatures or irradiation. Coordinatively unsaturated complexes have available vacant (active) sites which may react with hydrogen depending on the nature of the other ligands present and the metal.[36]

Several general possibilities exist for hydrogen activation by a metal center. Two of these involve "end–on" interaction of the H_2 molecule with the metal.[28] Interaction of filled $1s$ orbital of H_2 with empty metal p or d orbitals would yield a species described as $M–H_2^+$ which possesses a calculated H–H bond strength of 62 kcal mol^{-1}; or an empty $2p$ or $1s\sigma^*$ orbital of H_2 could combine with a filled metal orbital (p, d or hybrid) to give a complex described as $M–H_2$ with H–H bond strength calculated as 34 or 186 kcal mol^{-1}. A third possibility involves "sideways" interaction to form a three center intermediate[37] which may be pictured as shown in Diagram 1 below:

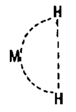
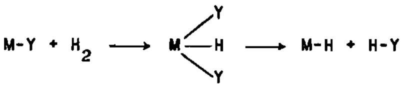


Diagram 1

Halpern[17] has noted three methods of activation of H_2 in homogeneous hydrogenation: (1) heterolytic splitting, (2) homolytic splitting, (3) dihydride formation by oxidative addition.

Homolytic splitting is known to involve a radical path (often by metal–metal bond, rupture) but details of the first and the third method are controversial. Heterolytic splitting may require entry of H_2 into the coordination sphere of an anion containing complex by oxidative addition with subsequent elimination of the protonated anion as represented below in Diagram 2:



$$M\text{-}Y + H_2 \longrightarrow M(H)(Y)_2 \longrightarrow M\text{-}H + H\text{-}Y$$

Diagram 2

Alternatively, it may involve reaction of an empty hydrogen orbital (end wise) with a filled metal orbital to form a polarized H_2 molecule–metal intermediate which can break down into a metal hydride by the removal of the positively polarizated end of the H_2 molecule as H^+ by some base (either externally as solvent or internally Y^-).

Diagram 3 illustrates possible mechanisms for this alternative:

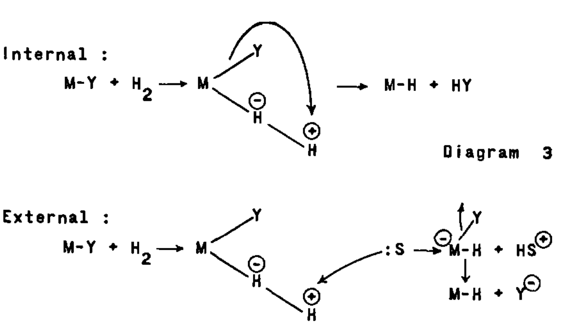


Diagram 3

Two mechanisms for oxidative addition of H_2 have been discussed. The first involved interaction of the $1s\sigma$ bonding H_2 orbital with a vacant metal d orbital. Support for this theory comes from the observation that no metal complex definitely known to have d^{10} configuration * adds H_2 or catalyzes the hydrogenation of any organic substrate. The second possibility is attach of an empty $1s\sigma^*$ H_2 orbital upon a filled metal orbital (d or hybrid), $[Rh(Ph_2PCH_2CH_2PPh_2)_2{}^+]\ Cl^-$ fails to add H_2 under conditions where the more basic complexes $[Ir(Ph_2PCH_2CH_2PPh_2)_2{}^+]Cl^-$[39] and $[Rh(Me_2PCH_2CH_2PMe)_2{}^+]Cl^-$ do.[39] The greater the basicity of the metal center the larger and more available are the d orbitals. This increasing tendency to add H_2 with basicity of the metal center supports this second mechanism. Nyholm[40] has discussed these two mechanistic alternatives in the addition of H_2 by $Ir(PPh_3)_2(CO)Cl$.

Of the three types of hydrogen activation, homolytic type 1 appears to be the most commonly encountered. The general order of reactivity toward the oxidative addition of hydrogen by d^8 complexes increases from nickel to iron, and from iron to osmium.[41] Ligands having both donor and acceptor properties (phosphines, carbon monoxide) stabilize the metal–hydrogen bond. Thus, for a given metal, the weaker the π-acidity of the ligand, the greater will be the electron density at the metal atom and its ability to interact with hydrogen. In this respect, the metal appears to behave as a nucleophile. The energy involved in oxidizing the metal is compensated for by the formation of the metal–hydrogen bond, the strength of which is particularly dependent on the ligand *trans* to it. The greater the *trans* effect of the ligand, the weaker the bond. The hydride ligand itself, in turn, serves to labilize the ligand *trans* to it.

It is generally recognized that a basic requirement for catalytic activity is that the hydrogen cleavage step be reversible. Not only must the hydrido complex be of sufficient stability that it is readily formed, it must also be labile enough that subsequent transfer of the hydride ligand to a substrate can occur. Nevertheless, many hydrido complexes which are catalytically active are stable enough to be isolated and characterized.

Homogeneous hydrogenation has previously been considered irreversible but several recent papers have produced evidence that casts doubt on this irreversibility.

Blum and Biger[42] have found that known homogeneous hydrogenation catalysts can dehydrogenate certain polynuclear aromatic compounds and have suggested a mechanism just the reverse of hydrogenation. Many low-valent metal phosphite or phosphine[43] complexes show insertion of the metal into alkyl and aryl C–H bonds by oxidative addition to give both M–C (alkyl or aryl) and M–H bonds in the same complex. This is the same arrangement found in the final intermediate postulated in hydrogenation before elimination of reduced substrate.

B. Substrate Activation

In the homogeneous hydrogenation process, it is generally accepted that coordination of the unsaturated compounds at a vacant site on the metal is necessary for their hydrogenation to proceed. This coordination usually goes through the formation of a π-olefin complex which serves both to lessen the double bond character of the substrate (activation) and to place it in a favourable position *(cis)* for interaction with a hydride ligand. The hydride ligand may be present in the active catalyst form, or may be introduced by hydrogen activation. The reaction takes place on a covalently σ-bonded hydrogen and a substrate molecule coordinated to the metal. Usually the catalyst is

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* The complexes $MNOL_3$, M = Rh, Ir; L = $P(C_6H_5)_3$, $P(CH_3)(C_6H_5)_2$, P(*o*-tolyl)$_3$, $P(F\text{–}C_6H_4)_3$, P(*p*-anisyl)$_3$, catalyze reduction of olefins and alkynes but may do so through a $NO^+ \rightarrow NO^-$ tautomer transition that causes the complex to assume an actual d^8 configuration.[200,376]

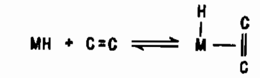


Diagram 4

restored to its original condition at the end of the hydrogenation cycle by hydrogenolysis or homolysis. The transition metal, the stability of M–H and M–substrate bonds, and the possibility of influencing these bonds through other ligands are factors of the upmost importance.[44] Although several π-olefin hydrido complexes, like those postulated as intermediates have been isolated,[45] there is just little direct evidence for their formation in actively idrogenating systems. Coordination substrate requirements may depend on the nature of the substrate itself. Olefins containing electron withdrawing (activating) substituents are most easily coordinated. Osborn *et al.* studied in detail the activation of the substrates for hydrogenation of alkenes and alkynes.[190–194]

C. Hydride Transfer

Insertion reactions are well known to occur. A similar mechanism has been proposed to occur for the transfer of hydride to a coordinate substrate.

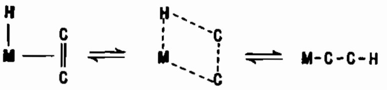


Diagram 5

Also if the direct evidence for the formation of metal alkyls is lacking for most hydrogenating systems, a metal–alkyl complex is postulate as intermediate during the reversible migration of a hydride to an olefin as represented in Diagram 5. Studies done on the decomposition of metal alkyls,[46] on the substrate–hydrogen atom exchange or isomerisation[47] give more evidences supporting the four center mechanism.

D. Discussion and Classification of Hydrogenation Catalysts

The simplest may to classify homogeneous hydrogenation catalysts in by their method of hydrogen activation. But since mechanistic studies have not been carried out on many systems the exact nature of the actual catalysts is often unclear. Thus has been set up an arbitrary classification system to discuss the catalysts, consisting of the four categories listed below:

Radical path (homolytic splitting)
Known monohydride (heterolytic splitting)
Known dihydride (oxidative addition)
Miscellaneous (unknown method of hydrogen activation)

2. Radical Path

All catalysts of the radical path type appear to utilize homolytic splitting of the H_2 molecule with conceptual one electron oxidation of the metal. On several cases, homolytic splitting of H_2 occurs with fissing of a metal–metal bond to yield two molecules of metal hydride.

A. Pentacyanocobaltate(II)

The most widely studied radycal type hydrogenation catalyst is $Co(CN)_5^{3-}$; two recent reviews[48,49] devoted exclusively to this system. Much work has gone into determination of the catalytically active form. A Co^I species was first proposed from proposed from the results of early H_2 uptake studies[50–52] but the reaction with N_2 has since been shown to involve the equilibrium

$$2\,Co(CN)_5^{3-} + H_2 \rightleftharpoons 2\,HCo(CN)_5^{3-}$$

(a conceptual oxidation from Co^{II} to Co^{III}).[53,54]

The activation of H_2 by $Co(CN)_5^{3-}$ follows a rate law[55] of the form $-d[Co(CN)_5^{3-}]/dt = k[H_2][Co(CN)_5^{3-}]$.

Hydrogen activation[54] may involve homolytic splitting of a metal–metal bonded dimer $[Co_2(CN)_{10}]^{6-}$ although activation through dimer–monomer equilibrium and through the alternative termolecular path are kinetically indistinguishable. Recent evidence has conclusively proven the nature of the catalytic species. Existence of a metal hydride has been shown by n.m.r.,[56,57] while cristals of formula $Na_3CoH(CN)_5$ have been isolated[58]. The active form can also be generated without H_2 in an "aging" process:[59] $2Co(CN)_5^{3-} + H_2O \rightleftharpoons HCo(CN)_5^{3-} + Co(CN)_5(OH)^{3-}$.

$Co(CN)_5^{3-}$ effectively catalyzes the hydrogenation of most activated olefins and the reduction of conjugated dienes to monoenes.

The mechanism is outlined below:[60]

1) Loss of CN^- ligand to give coordinatively unsaturated hydride complex;
2) Coordination of conjugated diene to metal;
3) Migration of hydride to diene to form allyl:
    a) at low CN^-/Co formation of π-allyl
    b) at higher CN^-/Co, formation of σ-allyl
4) Two-step radical transfer of H · from a second molecule of $HCo(CN)_5^{3-}$.

The involvement of the allyl complex has been confirmed by isolation of the σ-allyl[61] $Co(CN)_5[C(CH_3)H(CH = CH_2)]^{3-}$. The form of the allyl intermediate has been explored by Kwiatek *et al.*,[59] in an examination of the reduction products of butadiene (1 atm H_2, 25° C) as a function of the CN^-/Co ratio; since σ-allyl yields 1-butene and π-allyl leads to *trans*-2-butene, the composition of the allyl intermediate attached by $HCo(CN)_5^{3-}$ can be deduced from the product monoene composition. Table I shows how the product/monoene ratio changes with CN^-/Co ratio.

Funabiki and Tarama 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.[62] Their results are summarized in Tables II and III.

TABLE I. Effect of the Change of CN^-/Co Ratio in the Butenes % Total Product During the Hydrogenation of Butadiene by Pentacyanocobaltate(II).

CN^-/Co	% *trans*-2	% *cis*-2	% 1
4.5	86	1	13
5.5	70	1	29
6.0	12	3	85
8.5	19	1	80

A two-step radical transfer of $H^{\cdot}$ with significant concentration of radical intermediates has been postulated from detailed kinetic studies of the reduction of sorbic and cinnamic acids.[63–65] The reduction of styrene[66] (1 atm 25° C mixed solvents) studied by Strohmeier obeys the same rate law, $-d[\text{styrene}]/dt = k[Co(CN)_5 H^{3-}]$. Although the research of Bank *et al.*,[350] has purported to show certain discrepancies with regard to the previously established mechanism (their revised complex scheme involves Co^I complex formed by disproportion of Co^{II} kinetic data of Halpern and Pribancic in high pressure experiments, definitely support the older mechanism.[67]

TABLE II.[62] Effect of Alcohols on the Selectivity of the Hydrogenation of Butadiene by Pentacyanocobaltate(II).[a]

No	Alcohol (ml)	H_2O,	Butenes, mol %[b] *trans-*		*cis-*	Yield,[c]
		ml	1-	2-	2-	mmol
1	O	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° C, $CoCl_2$ = 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.

TABLE III.[62] 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]			Yield, mmol
				1-	*trans*- 2-	*cis*- 2-	
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° C, $CoCl_2$ = 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 start of the hydrogenation. [d] Relative yield of after 3 hr from the start of the hydrogenation.

The $Co(CN)_5^{3-}$ system selectively hydrogenates conjugated dienes (to monoene) no reduction to alkene. As previously mentioned, $Co(CN)_5^{3-}$ also reduces most styrenes and α,β-unsaturated aldehydes and acids, but fails to hydrogenate certain "activated" olefins (*e.g.*, acrolein and acrylic acid) for no obvious reason.[59]The catalyst reduces isoprene[68] and cinnamic acid[69], it also reduces benzil to benzoin[68] and aromatic and aliphatic nitro-compounds to the respective amines.[70] The rate of reduction of ciclopolyenes varies as the hybridization of the carbon atoms of the double bond.[71] Studies on the reduction of sorbic acid[72] and methyl sorbate[73] have shown that methanol as solvent makes the catalyst much faster and more specific (*versus* H_2O); use of gas–solvent combination

D_2–D_2O, D_2–H_2O and $H_2 + D_2O$ has yielded data supporting rapid exchange of solvent proton with complex hydride – 100% product with D_2–H_2O plus H–D exchange on δ-carbon (through reversibility of the allyl intermediate).

B. Modified Cobalt(II) Cyanide Systems

Two analogues of $Co(CN)_5^{3-}$ have been investigated. The first is $Co(bipy)(CN)_3^-$ which operates by the same mechanism as $Co(CN)_5^{3-}$ but reduced sorbate ion in three times as fast; however, sorbate slowly poisons this catalyst.[74] The other system[75] is the ethylenediamine-bridged dimer $[(CN)_4Co(H_2NCH_2CH_2NH_2)Co(CN)_4]^{4-}$, which is less stable than $Co(CN)_5^{3-}$; this catalyst reacts with H_2 (more slowly than does $Co(CN)_5^{3-}$) to produce the dimeric dihydride analogue of two $HCo(CN)_5^{3-}$, $[(CN)_4CoH(NH_2CH_2NH_2)HCo(CN)_4]^{6-}$.

Dimethylglyoxine ($dmgH_2$) complexes of cobalt(II) in which the metal is coplanar with nitrogen-containing ligands undergo a number of reactions[371] paralleling those exhibited by $Co(CN)_5^{3-}$. Those reactions involving the cleavage of molecular hydrogen differ, however, in that hydride ligand initially formed with "cobaloximes" is readily lost as a proton, the metal being reduced to the univalent state.[372]

Various activated olefins, as well as propylene, react with cobaloximes(II) in the presence of molecular hydrogen with formation of stable organocobaloximes(III) some of which undergo slow reductive cleavage of the organic moiety.[371] However, catalytic hydrogenolysis of disulfides[373] and reductive methylation of amines and thiols by formaldehyde have been demonstrated[374] (*cfr.* catalysis by rhodium analog).

Although vitamin B_{12} is not readily reduced by molecular hydrogen in the absence of a catalyst, its reactions, including catalysis of the reductive methylations mentioned above, are strikingly similar to those of the bis-dimethylglyoximato model compound. A bacterium extract containing a related complex has been observed to catalyze the formation of methane by hydrogenolysis of methylcobalamine or methylcobaloxime. Such reactions indicate possible pathways for hydrogen transfer in biological systems and are being studied as enzyme model.[375]

A cobalt–porphyrin system, *meso*-tetra(*p*-solfonatophenyl)-porphino cobalt(III) has been found to reduce acetylenes in presence of sodium borohydride.[370] The conversion of acetylene gives a mixture of ethylene/ethane depending on the pH at which the reaction is run; at a pH of 10 this ratio is >10.

C. Metal–Metal bonded Dimers

One system useful only for stoichiometric hydrogenation is $HMn(CO)_5$[76]which is known to reduce ethylene with the formation of $Mn_2(CO)_{10}$; since the Mn–Mn bond is too strong to be broken by H_2, the reaction cannot become catalytic.

In the case of $(\pi\text{-}C_5H_5)Cr(CO)_3H$, a similar reaction occurs (only with conjugated dienes), but hydrogenolysis of the weaker Cr–Cr bond of $[(\pi\text{-}C_5H_5)Cr(CO)_3]_2$ forms a catalytic cycle.[77] The same active hydride comes from the precursor $[(\pi\text{-}C_5H_5)M]^+[(\pi\text{-}C_5H_5)Cr(CO)_3]^-$ (M = V, Ti, Co, Cr).[78] These compounds produce the same activity as the dimer for M = V, Ti but much weaker with M = Co, Cr. The properties[77] of this system are listed below:

1) Isolated double bonds are not reduced; conjugated double bonds are hydrogenated by 1,4-addition.
2) Double bonds do not migrate.
3) Reduction is smooth above 70° C and 50 atm H_2 but slow at ambient temperature or 1 atm H_2.
4) H_2 adds preferentially at terminal ends of conjugated diene except for cases of great steric hindrance.

The molybdenum and tungsten analogues of $(\pi\text{-}C_5H_5)Cr(CO)_3H$ operate according to the same rules listed above with the restriction that they are useful only for a stoichiometric reduction since the dimers formed on reduction of diene contain metal–metal bonds too strong for H_2 to be broken.[79]

This property may actually be used to advantage in synthesis for step wise reduction of polyenes by control of the ratio of polyene to complex hydride; *e.g.*, a 1:2 ratio of 1,3,5,7-octatetraene and $(\pi\text{-}C_5H_5)Mo(CO)_3H$ yields only 2,4,6-octatriene.

3. Known Monohydrides

A considerable number of catalysts are known to operate by the monohydride path. Some systems of this type are quite stereospecific or stereoselective, but in general monohydride catalysts are noted for characteristically catalyzing isomerization as a side reaction. In systems where the monohydride is not the initial species, an induction period is usually observed during which the metal complex is converted by heterolytic splitting of H_2.

The mechanism illustrated below for reduction of olefins is similar to isomerization in that it involves olefin insertion into an M–N bond[80,81]

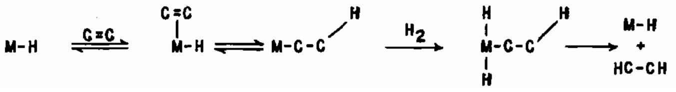


Diagram 6

TABLE IV. Hydrogenation of Organic Compounds by Monohydrides.

(1)	*trans*-$HPtCl(PEt_3)_2 + C_2H_4 \rightleftharpoons$ *trans*-$EtPtCl(PEt_3)_2$	Ref. 82
(2)	$IrH(CO)(PPh_3)_3 +$ *trans*-$(CN)HC=CH(CN) \rightarrow IrH(CO)(PPh_3)_2[(CN)HC=CH(CN)]$	Ref. 83
(3)	$IrH(CO)(PPh_3)_3 + CH_2=CHCN \rightarrow Ir(CO)(PPh_3)_2(CH_2=CHCN)(-CH_2CHCN)$	Ref. 83
(4)	$IrH(CO)(PPh_3)_3 + RC\equiv CR \rightarrow Ir(CO)PPh_3)_2(RC\equiv CR)(-CR=CRH)$	Ref. 83
(5)	*trans*-$HPt(CN)(PEt_3)_2 + (CN)_2C=C(CN)_2 \rightarrow HPt(CN)(PEt_3)_2[(CN)_2C=C(CN)_2]$	Ref. 84
(6)	$IrCl_6^{3-} + 1,5\text{-COD} \xrightarrow[H^+]{EtOH} [HIrCl_2(1,5\text{-COD})]_2$	Ref. 85

Isolation of stable complexes identical with postulated intermediates provides evidence for the existence of the mechanism shown in Diagram 4. Several of these compounds and reactions are listed in Table IV.

A. $HRu(PPh_3)_3X_2(X = Cl, O_2CR)$

The first catalyst[86] system of this type is $Ru(PPh_3)_3Cl_2$ reported to rapidly hydrogenate 1-heptene and 1-hexyne (1:1 C_6H_6/EtOH, 25° C, 1 atm H_2) after heterolytic splitting of H_2 for catalyst activation.[87] The rate of active catalyst formation can be increased in C_6H_6 solution by addition of alcohol or amine; reaction with $NaBH_4$ also produces $HRu(PPh_3)_3Cl$.[88]

In the absence of H_2, $HRu(PPh_3)_3X$ catalyzes extensive olefin isomerization. An n.m.r. experiment with a solution of $HRu(PPh_3)_3Cl$ under ethylene pressure has detected only the ethyl complex;[88] with $HRu(PPh_3)_3(O_2CCF_3)$ both the alkyl and M–H forms are observed.[89] With $DRu(PPh_3)_3Cl$ in another n.m.r. experiment, the half lives of the Ru–D species involved in H–D exchange with terminal and internal olefins have been measured as 0.5 and 5 min respectively (with no H–M(olefin) or M–alkyl intermediates detected[90]). With only D_2 present H–D exchange occurs at all *orto*-phenyl positions on the phosphine ligands.[88]

The system with X = Cl is a rapid and selective catalyst for reduction of terminal alkenes and alkynes. The failure of the catalyst to hydrogenate internal olefins (which do show H–D exchange) is attributed to severe hindrance from the three bulky phosphine ligands in the later stages of the reduction process (oxidative addition of H_2 to the alkyl complex and reductive elimination of the product alkane). Several groups have collected extensive data on H_2 uptake rates for varius substrates.[90,91] Jardine and McQuillin[92] have correlated reduction dates for substrates with respective K_{Ag^+} values (equilibrium constants for complexation with silver ion) and have concluded that the rate-controlling step for similar olefins is coordination of substrate with the metal hydride. This conclusion is supported by a kinetic study[89] which has found a rate law $-d[\text{substrate}]/dt = k[HRu(PPh_3)_3Cl][H_2][\text{Substrate}]$ (with inhibition by excess PPh_3). Another study has noted a similarity with heterogeneous hydrogenation for the reduction of norbornadiene at very large concentrations by the ruthenium hydride. The complexes $HRu(PPh_3)_3(O_2CR)$ differ somewhat from their chloride analogue.[89] For R = CH_3 the structure determined is six-coordinate with weakly bidentate acetate.[94] The more solubile carboxylates are less active than the halides (Cl:OAc ~10) so kinetic studies can be more easily done.[89]

TABLE V.[58] Homogeneous Catalytic Hydrogenation of Olefins[a] by $RuCl(H)(PPh_3)_3$.

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

[a] $RuCl(H)(PPh_3)_3$, 5×10^{-5} mol; olefin, 7.1×10^{-2} mol in bezene to total volume 60 ml.[6] Rate at 50 cm, partial pressure hydrogen at 25° C.

TABLE VI.[58] Hydrogenation of Dienes by $RuCl(H)(PPh_3)_3$.[a]

Alkene	Product	Yield %
trans-Hexa-1,4-diene	*trans*-Hexa-1,4-diene	18.3[b]
	trans-Hex-2-ene	52.7
	cis-Hex-2-ene	9.2
	Hexane	3.6
	Unidentified (3 peaks)	16.2
cis-Hexa-1,4-diene	*cis*-Hexa-1,4-diene	52[c]
	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[d]
	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° C, 60 cm pressure. [b] Data after 15 hr. [c] Data after 1 hr. [d] Data after 3 hr.

TABLE VII.[89] H_2 Uptake in mmole/min by $HRu(PPh_3)_3(O_2CR)$ for Reduction of 1-hexene in C_6H_6, 25° C, 50 cm H_2.

Carboxylate	Rate
CH_3CO_2	2.45
$C_2H_5CO_2$	1.16
i-$C_3H_7CO_2$	2.41
CF_3CO_2	0.97
$C_6H_5CO_2$	2.25
o-$C_6H_4(OH)CO_2$	2.46

TABLE VIII.[95] Rates of Hydrogenation of Hex-1-ene Using Different Sources of Ruthenium (Ruthenium concentration 7.5×10^{-4} mol l^{-1}; hexene, 1 mol l^{-1}; rates measured at 40 cmHg hydrogen pressure; methanol at 40° C using aqueous fluoroboric acid except noted).

Source	PPh_3:Ru	H^+:$MeCO_2^-$	Hydrogen Uptake in ml min^{-1} at S.T.P.
$Ru_3O(CO_2Me)_6(PPh_3)_3$[a]	2	4	36.0
	3	4	38.0
$Ru_2O(CO_2Me)_4(PPh_3)_2$[a]	2	4	53.2
	3	4	50.1
$RuH(CO_2Me)(PPh_3)_3$	3	4	48.0
	3	8[b]	56.8
	3	16[c]	17.2
	4	4	56.8
	10	4	56.8
$Ru(CO_2Me)_2(PPh_3)_2$	2	8	36.1
	2	8[b]	41.2
	3	8	31.0
$Ru(PPh_3)_3(CF_3SO_3)_2$	3	0	38.8[e]

[a] Catalyst solution made by electrolytic reduction. [b] CF_3SO_3H used. [c] CF_3SO_3H in t-butanol as solvent. [d] Solid complex used. [e] The red chloride free solution of $RuCl_2(PPh_3)_3$ under these conditions gave a rate for hex-1-ene of 39.8 ml min^{-1}.

The change in R has a relatively minor effect on catalytic activity (see Table VI). With 1-hexane at 25° C and 1 atm H_2, reduction is very greatly favored over isomerization.

The two electron reduction of the oxo-centred triangular acetato-complex, $Ru_3O(CO_2Me)_6(PPh_3)_3$, in which the metal has mean oxidation state $2\frac{2}{3}$, gives a yellow ruthenium(II) species, probably $Ru(CO_2Me)_2PPh_3$. In methanol containing a non-complexing strong acid and additional triphenylphosphine to give a minimum PPh_3:Ru ratio of 2:1, the complex acts as a catalyst for the hydrogenation of alkenes.[95] Similar catalyst solutions in methanol are obtained by the action of acids on the hydrido-acetate, $RuH(CO_2Me)(PPh_3)_3$, or the dihydride, $Ru(H)_2(PPh_3)_4$; aqueous fluoroboric acid, p-toluenesulphonic acid hydrate or trifluoromethylsulphonic acid have been used. The initial product is evidently the (solvated) cation $[Ru(PPh_3)_3]^{2+}$, but in presence of alkene a bis species such as $[Ru(PPh_3)_2(alkene)]^{2+}$ is formed. On standing, or on treatment with H_2 or CO in absence of alkene, the orange–red tris species are converted to catalytically inactive yellow species, this reaction being faster in presence of water. From aged solutions the salt $[(Ph_3P)_2Ru(OH)_2RuPPh_3)_2](BF_4)_2$ has been isolated.

Ruthenium complexes possessing triphenylphosphine, diethyl sulfide, carbon monoxide, methanol, pyridine (Py), 1,2-bis(diphenylphosphino)ethane (diphos), chloride, and hydride ligands have been examined as homogeneous catalysts,[96] gradually increasing the temperature of their solutions with CDT 1,5,9,cyclododecatriene under 200 psig of hydrogen. For several complexes, the hydrogenation activity was vastly improved when $NaBF_4$ was employed as a cocatalyst. All complexes surveyed were active hydrogenation catalysts under appropriate conditions, and those' affording the most selective catalysts are arranged at the top under each solvent in Table IX. Two distinct types of behavior were observed regarding the selectivities of the catalysts. The catalysts derived from the formally zerovalent complexes $(Ph_3P)_2(CO)_3Ru$ and $[(CO)_4Ru]_3$ were more active, while the higher-valent ruthenium complexes gave more selective catalysts in N,N-dimethylformamide (DMF) solutions. Most of the complexes gave catalysts which decomposed under the reaction conditions.

B. $[Ru(\pi\text{-}C_6H_6)Cl_2]_n$

This catalyst[97] is very similar to $Ru(PPh_3)_3Cl_2$ behavior. The active catalyst is presumed to be the monohydride H–$Ru(C_6H_6)Cl$ since catalysis is speeded up by addition of small amounts of base (e.g. pyrroldyne or NEt_3); also, n.m.r. experiments have shown high field and phenyl region peaks in relative intensity 1:6 attributed to $HRu(C_6H_6)(DMSO)Cl$. The complex catalyzes slow hydrogenation of olefins in strongly coordinating solvents (as CH_3CN, DMSO), but very rapid reduction of terminal olefins (with some isomerization) at 30° C, 20 Kg/cm² H_2 in benzene. Unlike the tris-phosphine analogue, which fails to catalyze the reduction of internal olefins, the benzene complex slowly hydrogenates 2-pentene. This reaction is attributed to the less steric hindrance of the benzene ring than the three very phosphine ligands.

C. $Rhpy_2(amide)(BH_4)Cl_2$

This versatile series has been investigated by McQuillin and coworkers.[98–103] The most commonly used system is generated by the reaction of $Rhpy_3Cl_3$ with $NaBH_4$ and H_2 in DMF to form the species $Rhpy_2(DMF)(BH_4)Cl_2$. Inhibition by added pyridine sug-

TABLE IX.[96] Hydrogenation of 1,5,9-cyclododecatriene (CDT) Catalyzed by Ruthenium Complexes.[a]

Ru Complex	Temp, °C	Reaction Time, h	Dec[b]	Yield, %			
				CDA[e]	CDE	CDD	CDT
		In Benzene Solution					
$(Ph_3P)_2(CO)_3Ru$	158	1.2	p	2.7	94.6	2.3	0.4
$[(CO)_4Ru]_3$	158	1.2	p	11.2	85.0	2.9	0.9
$(Ph_3P)_3RuCl_2$	85	4.0		42.3	29.6	15.6	12.4
		In *N*,*N'*-Dimethylformamide Solution					
$(Et_2S)_3RuCl_3$	135	3.5	p	2.8	92.6	3.2	1.4
$(Ph_3P)_2(CO)_2RuCl_2$	140	4.0		13.3	84.7	1.8	0.3
$(Ph_3P)_2(CH_3OH)RuCl_3$	140	4.5	p	14.3	80.4	4.2	1.1
$(Ph_3P)_3(CO)RuH_2$	140	5.0	c	5.3	74.8	13.2	6.7
$(Ph_3P)_2(CO)_3Ru$	140	4.0	c	1.3	51.0	27.4	20.3
$[(CO)_2RuCl_2]_n$	145	3.3	c	0.2	22.8	38.4	38.6
$(Py)_4RuCl_2$	145	3.0	c	2.3	36.0	30.2	31.5
$(Py)_4RuCl_2$–$NaBH_4$[c]	110	1.8	p	36.0	59.8	2.4	1.7
$(Py)_2(CO)_2RuCl_2$–$NaBH_4$[d]	125	2.2	p	21.8	47.2	15.5	15.5
$(Diphos)_2RuCl_3$–$NaBH_4$[d]	105	2.1	c	8.6	29.0	22.5	39.9
$(Ph_3P)_3RuCl_2$	125	5.0		31.4	51.1	8.4	9.1

[a] Solutions were composed of 0.10 g of complex, 2.0 g (1.2 mmol) of CDT, and 20 ml of solvent. [b] p denotes partial catalyst decomposition during reaction and c denotes complete catalyst decomposition. [c] 0.10 g of $NaBH_4$. [d] 0.050 g of $NaBH_4$. [e] CDA = cyclododecane; CDE = cyclododecene; CDD = cyclododecadiene.

gests that the active form has lost pyridine. Replacement of DMF by optically active amides causes asymmetric hydrogenation of certain substrates; thus the amide must be retained in the catalyst.

Hydrogen transfer is rate-limiting in the reduction of cycloolefins. The following order of rate of hydrogenation has been determined: norbornene > cyclohexene > cycloheptene > cyclopentene > cyclooctene. This order infers that the transition state is mostly alkane-like and that the activation energy is controlled by the energetics of the $sp^2 \rightarrow sp^3$ substrate transformation.

The catalyst (amide = DMF) has several rather unusual features. First, unexpected stero-specificity in hydrogenation of 3-oxo-$\Delta^{4,5}$-steroids is observed, with a large dependence on the two substituents at the 12-position. Next, reduction of several functional groups not commonly reduced by homogeneous systems is catalyzed by the complex as shown in Table X.

Finally, seemingly opposite stereoreductions occuring in hydrogenation of alkynes. For RC≡CR, *cis*-addition of H_2 is observed for R = CO_2Me, CH_2OH, but *trans*-addition in the reduction with R–Ph results in formation of *trans*-stilbene (not due to isomerization of *cis*-stilbene). Reduction of diphenylacetylene with D_2 has shown that two atoms of deuterium are incorporated into the substrate but one of these is at the *ortho* position on the phenyl ring (rationalized by a 1,3-hydride shift analogous to that postulated in heterogeneous hydrogenation for reduction of the double bond *alpha* to the ring).

TABLE X. Functional Groups Reductions Catalyzed by $Rhpy_2(DMF)(BH_4)Cl_2$.

(1) $PhN{=}NPh \rightarrow PhNH\text{–}NHPh \rightarrow 2\ PhNH_2$
(2) $PhNO_2 \rightarrow PhNH_2$
(3) $PhCH{=}NPh \rightarrow PhCH_2\text{–}NHPh$
(4) Pyridine→Piperidine[a]
(5) Quinoline→1,2,3,4-Tetrahydroquinoline

[a] Rate increases after uptake of first equivalent of H_2.

Catalysis of asymmetric hydrogenation occurs with optically active amides as solvents. Table XI illustrates the effectiveness of the catalyst.

TABLE XI.[102] Asymmetric Hydrogenation Using $py_2RhCl_3 + NaBH_4$ in Optically Active Amides.

Amide	Substrate	Product	Optical Yield
(–)PhMeHCNHCHO	$Ph(Me)C{=}CH(CO_2Me)$	R-(–)	47%
(+)PhMeHCNHCHO		S-(+)	54%

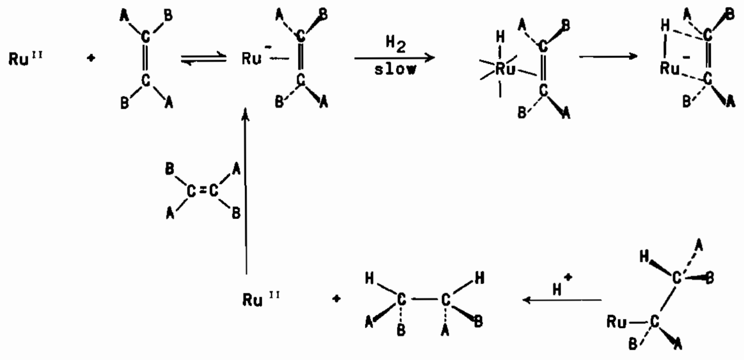


Diagram 7

The relactively high optical yields can be attributed to minimization of steric interaction in the alkyl intermediate by a precise arrangement of the groups on the active carbon sites located on ligands *cis* to each other.

D. Ruthenium(II) Complexes in Aqueous HCl

Ru^{II} in 3*M* HCl catalyzes hydrogenation of maleic[104] and fumaric[105] acids but not of ethylene, propilene or norbornadiene at 80° C, 1 atm H_2 (even though a stable complex is formed with ethylene.[106] A kinetic study has determined that at excess olefin, rate = $k[H_2][Ru^{II}](\text{olefin})$ with little if any dependence on $[H^+]$ Table XII lists activation parameters for the reaction.

A set of experiments interchanging ^1H and $^2H(D)$ in H_2, HCl or H_2O has given the following results: (i) $D_2 + HCl$, $H_2O \rightarrow$ no HD or H_2 in gas, addition of H_2 to substrate; (ii) D_2 or $H_2 + DCl$, $D_2O \rightarrow d_2$-product, no exchange of substrate hydrogen with solvent; (iii) $D_2 + DCl$, $D_2O \rightarrow$ only *cis* addition of D_2 (infrared).

TABLE XII.[104,105] Activation Parameters for Reduction of Olefins by Ru(II) Complexes in Aqueous HCl(80° C, 1 atm H_2).

Substrate	$k(M^{-1}sec^{-1})$	ΔH^*(kcal/mol)	ΔS^*(eu)
Maleic acid	2.3 ± 0.1	14	−17
Fumaric acid	3.6 ± 0.6	17	− 8

These results have been accounted for in the mechanism set forth in Diagram 7.

A similar complex[107], $Ru(bipy)Cl_4$, reduces maleic acid at 80° C, 1 atm H_2, in aqueous HCl. In this case, hydrogen activation by heterolytic splitting is thought to occur before, not after, complexation of the substrate in the catalytic path, for rate studies have noted an induction period followed by a linear rate of H_2 uptake. Hui and James[107] have postulated the mechanism shown below in Diagram 8:

E. $HCoL_n$ (n = 3,4)

Precursors $CoH(N_2)(PPh_3)_3$[108,109] or $CoH_3(PPh_3)_3$[110–112] form the active catalyst $HCo(PPh_3)_3$ by dissociation of N_2 and H_2 respectively. The catalyst readily hydrogenates ethylene, and cyclohexene in benzene at 25° C, 1 atm H_2 (the rate increase with temperature and pressure). The hydride also reduces n-heptaldehyde[111] to a mixture (2:1) of n-heptanol and n-hexane and reduces 1,5,9-cyclododecatriene[112] under harder conditions (80° C, 50 atm H_2, 2h) to a mixture of alkane (16%), monoene (41%), and diene (27%).

With $HCo(diphos)_2$,[113] more drastic conditions are needed for reduction of olefins (150° C, 100 atm H_2 for 1-hexene).

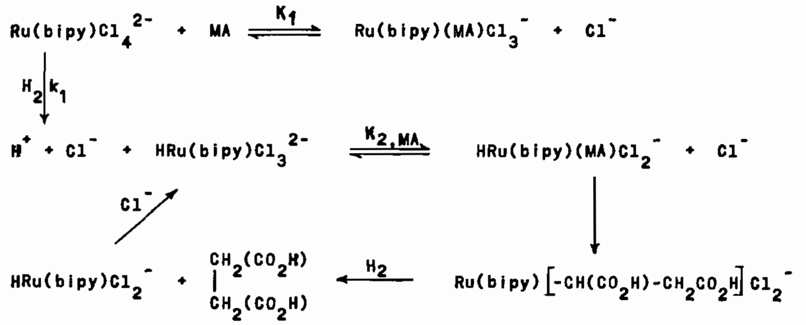


Diagram 8

For L = PEt_3[114] the complex appears to be active only in ethanol and is formed by heterolytic fission of H_2 by $Co[P(OEt)_3]_4Cl$; $Co_2[P(OEt)_3]_8$ fails to form the active catalyst even at 150° C and 120 atm H_2.[115]Hydrogenations of alkynes and activated olefins are catalyzed under mild conditions. The mechanism proposed involves coordination of alkyne to Co–H, insertion to form the vinyl complex, and hydrogenolysis to give product olefin and regenerate Co–H.

F. Hydridotetracarbonylcobalt

Cobalt hydridocarbonyl was first discovered as a hydrogenation catalyst in side reaction of the oxo process.[2–4] In many cases, hydroformylation of olefin is followed by reduction of the product aldehyde to alcohol.[116–122] Other cases show competition between hydrogenation and hydroformylation. Formation of significant quantities of 2-formylbutane from butadiene[123] (proposed hydroformylation of 2-butene formed by 1,4-hydrogenation), and a 10% yield of octane in the Oxo reaction of diisobutylene.[124] Marko has pointed out that hydrogenation is thermodynamically favored over hydroformylation,[125] so the reaction product must be kinetically determined. He has also shown that product distribution depends on the olefin structure; hydrogenation predominates for $R_2C{=}CH_2$ and hydroformylation for $RCH{=}CH_2$ and $RCH{=}CHR$ (see Table XIII).

This distribution may be understood by examining the properties of the alkyl intermediate formed on insertion of the olefin into the Co–H bond. Diagram 7 shows why $RCH{=}CH_2$ and $RCH{=}CHR$ are both so prone to hydroformylation.

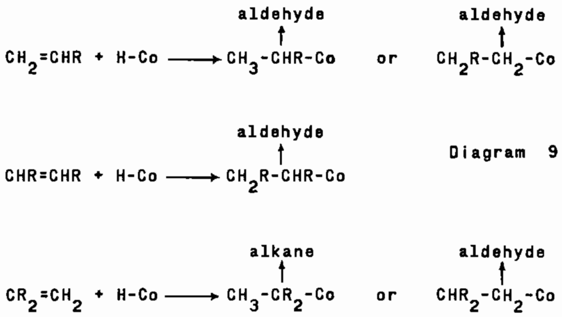


Diagram 9

TABLE XIII.[125] Product of Reaction with CO/H_2 (2:1) at 200° C, 300 atm H_2 in the $HCo(CO)_4$ Hydrogenation Catalysis.

Olefin	% Hydrogenation
Propene	0.2
Cyclohexene	2.9
Isobutylene	53.3
Diisobutylene	63.1

From Diagram 7 only $R_2C{=}CH_2$ can form a tertiary alkyl (form which migration onto CO is very badly sterically hindered) which will then kinetically favor hydrogenolysis over migration to Co and onto aldehyde.

A special case where no hydroformylation occurs is the hydrogenation of α,β-unsaturated aldehydes, ketones and esters.[126] The aldehydes undergo a two-step reduction.[127] With lower temperature and pressure (125° C, 200 atm synthesis gas), the reaction can be stopped at the saturated aldehyde stage; but 185° C and 300 atm synthesis gas result in saturated alcohol.[128,129]

Several other specialized cases of uncommon hydrogenations have been carried out with $HCo(CO)_4$. Ketones can be reduced under strong conditions; acetone is converted to isopropanol with 300 atm sunthesis gas at 185° C.[127] Polynuclear aromatic are reduced to some extent; with 200 atm synthesis gas anthracene is easily reduced to 9,10-dihydroanthracene at 135° C, but 200° C is required to convert naphthalene to tetralin.[130] Thiophene[131] is reduced at 185° C, 200 atm, but requires a longer time than for reduction of aldehyde as shown in the two step sequence SC_4H_3–$CHO \rightarrow SC_4H_3$–$CH_2OH \rightarrow SC_4H_7CH_2OH$.

Polyene fatty acid esters[132] are reduced by conjugation of two double bonds and then hydrogenation;[133] monoenes are not reduced until all non-conjugable dienes are converted. Several heteroatomic unsaturated groups are also reduced by the carbonyl hydride system: $PhNO_2$ (to $PhNH_2$),[134,135,136] $PhN{=}CHPh$ (to $PhNHCH_2Ph_2$),[134] $PhN{=}NPh$ (to $PhNH_2$),[134] $R_2C{=}S$ (to R_2CH–SH)[134] but not $RC{\equiv}N$.[134]

The hydrogenation of 9,10-dimethylanthracene can be achieved with cobalt hydrocarbonyl at room conditions, the product consists of a mixture of *cis*- and *trans*-9,10-dimethylanthracenes.[137]

The rhodium catalyst system $HRh(CO)_4$ is analogous[138] to $HCo(CO)_4$ in that it is also an oxo catalyst, requires a mixture of CO and H_2 for stability (usually 1:1 used), and is formed from metal–metal bonded carbonyl. (Heil and Markó[138] postulate $Rh_2(CO)_6 + H_2 \rightleftharpoons 2HRh(CO)_4$). The catalyst is useful only for reduction of aldehyde to alcohol, for hydrogenation is greatly favored over hydrogenation of olefins. $HRh(CO)_4$ catalyzes the reduction of nitro groups by synthesis gas (1:1 H_2:CO) but unlike $HCo(CO)_4$, only at temperatures greater than 150° C; thus the rhodium system can be used for oxo reactions of nitroolefins at lower temperatures (–60° C).

Work in the Russian literature[139] has reported research on the analogous iridium carbonyl systems $HIr(CO)_4$ with H_2 and olefins.

G. Substituted Cobalt Carbonyl Hydrides

Substitution of more electron donating ligands for CO in the cobalt hydrido carbonyl system stabilizes the hydride so that CO is no longer required for stability along with H_2 in hydrogenation reactions. The complex $HCo(CO)_3(PBu_3)$[140,141] catalyzes selective reduction of 1,5,9-cyclododecatetraene to monoene by conjugation and preferential reduction of double bonds (at 150° C and 30 atm H_2); with PBu_3:CO significantly higher than 1, selectivity is lost and more saturated product is obtained. The catalyst HCo(CO) $(PBu_3)_3$[142] has been utilized for selective reduction of alkynes by manipulation of temperature as demonstrated in Table XIV.

TABLE XIV.[142] Relative Amount of C_8 Hydrocarbons: 1-octyne (40.9 mmol), 11.2 mmol $HCo(CO)(PBu_3)_3$ in Heptane (120 ml), 20 atm H_2.

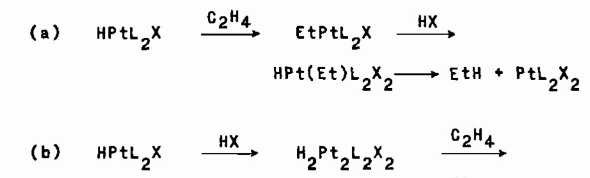
Temp. (° C)	Alkane	Alkene	Alkyne
50	2.63	36.6	1
98	39	1	

$HCo(CO)(PPh_3)_3$[112] is an active catalyst at 150° C and 50 atm H_2 for the reduction of olefins; much more drastic conditions than are needed for HCo $(PPh_3)_3$ because a phosphine must be dissociated. Excess dialkyl sulfide in $Co_2(CO)_8 + H_2$ system most likely reacts to form $HCo(CO)_3(SR_2)$ which is a much less active catalyst for hydroformylation or reduction of the oxo aldehyde to alcohol.[143]

H. *trans-HPt(PEt3)2Cl*

This platinum hydride catalyzes[144] reduction of 1-hexene, cycloexene, and 2-methyl-2-butene, but not acrylonitrile; no isomerization of 1-hexene is observed under hydrogenation conditions. The hydrogenation is only stoichiometric and requires strong acid (HCl or $HClO_4$) for hydrolysis of the Pt–alkyl bond; rate studies indicate a linear dependence of the rate on $[Cl^-]$ with a non-zero intercept corresponding to the rate with $HClO_4$. Two mechanism are possible (see Diagram 10); but the complex $H_2Pt(PEt_3)_2Cl_2$ has been shown not to reduce olefins, so path (a) must be operative:

Diagram 10



I. *IrLnH3 (n = 2,3)*

The activity of this series of catalysts depends primarily on the number n of ligands L. With n = 3, only terminal olefins are reduced with $L = PPh_3$.[145,146] For n = 2 and $L = PPh_3$ or PEt_2Ph, both terminal and internal olefins are hydrogenated under mild conditions (PEt_2Ph system somewhat more active) as are phenylacetylene (stepwise) and 1,5-cicloocta-diene.[145,146] At 100° C, 100 atm H_2 in benzene ketones are reduced to alcohols, PEt_2Ph once again giving a more reactive catalyst; arsines and stilbens are also effective ligands.[145] The mechanism has been elucidated by Giustiniani *et al.*[147] $Ir(PPh_3)_2H_3$ fails to reduce ethylene or 1-hexene at 20° C, 1 atm H_2. However, upon standing under N_2, the colorless solution of the trihydride forms a green solution of Ir $(PPh_3)_2H$ by dissociation of H_2. In the absence of H_2, the monohydride reacts rapidly with 1-hexene to form what is postulated as the alkyl. Thus the following mechanism has been proposed. (Diagram 11).

J. *HRh(CO)(PPh3)3*

The characteristics of this catalyst have been reviwed recently by Wilkinson.[148] The structure has been shown to be a slightly distorted trigonal bipiramid with a Rh–H bond distance of 1.72±o,15 Å.[149] This catalyst is highly active and selective for reduction of terminal olefins; at 25° C, ≦ 1 atm H_2, cycloexene, *cis*-4-methyl-2-pentene and 1,3-pentadiene are not reduced.[150] The selectivity is attributed to the bulk of the phosphines.[151] The catalyst does not interact with be following groups: –CHO, –OH, –CN, –O–, –Cl, $-CO_2H$.

A minor difficulty[152] is disactivation of the catalyst by dimer formation, which is reversed by H_2 pressure: $[Rh(CO)PPh_3)_2]_2 + H_2 \rightleftharpoons 2HRh(CO)(PPh_3)_2$.

Table XV lists rates of reduction for various substrates.

Wilkinson's group has done extensive work on rate studies of hydrogenation to determine the mechanism.[151] The rate low is given by $-d\,[\text{substrate}]/dt = k_1K_1\,[\text{substrate}][\text{catalyst}]/(1+K_1[\text{substrate}])$; the rate-determining step is olefin diplacement of solvent in the coordination sphere. The kinetics fails to distinguish between (i) oxidative addition of H_2 and then coordination of olefin, and (ii) coordination of olefin, its insertion into the Rh–H bond, and then oxidative addition of H_2. The former has been rejected on the basis of the non-activity of the known $Rh(CO)(PPh_3)_2$ H_3 species. No inhibition of the rate of reduction of

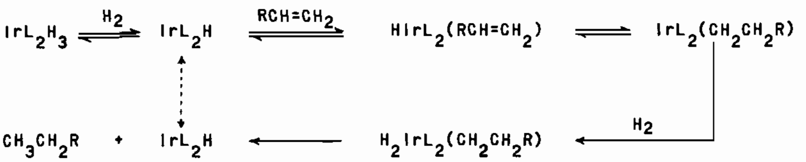


Diagram 11

TABLE XV. Olefin Reduction by Means of $HRh(CO)(PPh_3)_3$.

Substrate	Rate[a]
Allyl alcohol	20.3
1-hexene	16.7
1,5-hexadiene	15.2
1-decene	14.8
Allyl benzene	11.1
4-vinylcyclohexene	7.43
Allyl cyanide	5.57
Styrene	1.39

[a] H_2 uptake in ml min^{-1} at 50 cm H_2; catalyst 1.25 m*M* in C_6H_6, 25° C; [substrate] = 0.6 *M*.

1-olefin is caused by 2-olefin. At low catalyst concentrations (< 4m*M*), stereoselectivity for terminal olefins is lost, most likely due to formation of a much less hindered complex created by dissociation of second phosphine. The previous observation are accounted for in the following mechanism:

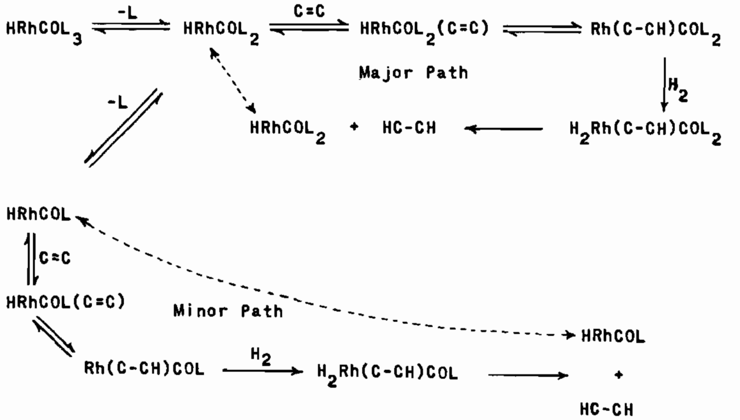


Diagram 12

Several studies have been done on isomerization of olefins by $HRh(CO)(PPh_3)_3$. At 1 atm H_2 and 27° C, the rate of reduction is identical to that of isomerization.[153] On the absence of H_2, 1-pentane is isomerized preferentially to *cis*-2-pentane, but this isomer is quickly converted to the *trans* form.[153,155] Internal olefins are isomerized slowly than terminal ones. With $DRh(CO)(PPh_3)_3$, the half-times of H–D exchange with olefins are 20 sec and 60 min respectively for terminal and internal olefins.

Like its rhodium analogue, $HIr(CO)(PPh_3)_2$ reacts only slowly[154] with ethylene and hydrogen to give ethane. It also reduces acetylene to form a mixture of ethylene and ethane.

K. $HIrCl_2L_3$

With L = DMSO, this Ir–H system catalyzes reduction of dyphenylacetylene[156] and carbon–carbon double bonds of α,β-insaturated ketones.[157] Acid is required for hydrolysis of the Ir–C bond of the respective intermediate vinyl and alkyl complexes. Hydrogenated solvents (as i-PrOH) serve as a source of hydrogen for the regeneration of Ir–H. Reduction of the acetylene results in approximately a 30: 1 ratio of *cis* to *trans* stilbenes. In both cases the respective vinyl and alkyl intermediates have been isolated, and the structure[158] of the intermediate of $HIrCl_2(DMSO)_3 + PhCOCH=CHPh$ has been shown to contain the alkyl as a five membered ring with Ir–C and Ir–O linkages. With $L = P(OMe)_3$ ketones can be reduced by hydrogen transfer from isopropanol. Substituted cyclohexanones[159,160] are reduced primarily to axial product (> 95%) even though equatorial is sterically favored; DMSO is also effective for this reduction but with much less axial specificity. This catalytic reaction (> 200 moles substrate reduced for mole Ir) forms acetone as a coproduct. Similar systems (Ir^{III} or Ir^{IV} halides + $P(OMe)_3$ + isopropanol) which appear to form $HIrCl_2[P(OMe)_3]_3$ *in situ* (induction period is required) are useful for selective reduction of steroids.

Brown and Kirk[161] have observed reduction of the 3-oxo function leaving 6-, 7-, 11-, 12-, 17- and 20-oxo groups untouched, while Orr *et al.*,[162] have noted selective conversion of steroidal 2-, 3- and 17-keto groups to alcohols with some degree of stereospecificity.

The system $IrHX_2L_3$[163] ($L = PPh_3$, $AsPh_3$, $SbPh_3$) has been reported to reduce alkenes. Terminal olefins are reduced more rapidly than di- and trisubstituted. $HOs(CO)(PPh_3)_3Cl$ has been reported to reduce acetylene to a mixture of ethylene and ethane.[154]

L. Assorted Rh^{III} Complexes

"$RhCl_3$" in ethanol is reported to hydrogenate 1-hexene after an induction period, as does 1,2,6-$Rhpy_3Cl_3$.[164] Under oxo conditions, the pyridine complex reduces the product aldehyde to alcohol if $H_2:CO > 1$ atm $\geqq$ 100° C. If $H_2:CO \gg 1$, some n-hexene is found.[165]

With the system RhL_3Cl_3 where L is a phosphine or arsine, results similar to those with pyridine are observed.[165] With L = PPh_3, oxo conditions yield the same products; and in the absence of CO, this complex in $EtOH/C_6H_6$ at 110° C, 50 atm H_2, reduces aldehydes to alcohols and converts 1-hexene to hexane. $Rh(AsMe_2Ph)_3Cl_3$ also reduces 1-hexene under these conditions. Using L = phenyl-α-naphtyl-p-biphenylphosphine, internal and highly substituted α,β-unsaturated carbonyl compounds have their carbon–carbon double bonds efficiently reduced in $C_6H_6/EtOH$ at 50° C, 80 psi H_2.[166]

Two similar RhL_3Cl_3 complexes with L = SEt_2 or DMSO have been reported to reduce dimethylsulfoxide (DMSO) to the sulphide.[167] The complex with SEt_2 is twice as fast at that with DMSO. A side reaction – formation of an unactive Rh^I compound may be circumvented by using a mixture of hydrogen and oxygen gas oxygen oxidizes the metal back to the Rh^{III} state). Diagram 13 illustrates two possible mechanisms proposed for reduction of the sulphoxide. The latter alternative is intriguing in that it involves heterolytic splitting of H_2 with retention of both hydride (by metal) and proton (by a ligand).

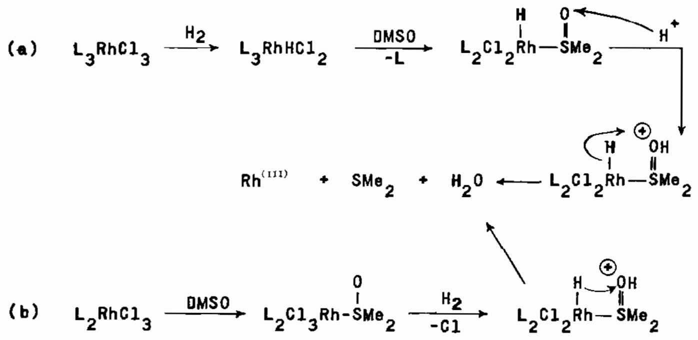


Diagram 13

M. Third Triad Group VIII Metal–SnX_2 Systems

One system of this type is $H_2PtCl_6 + SnCl_2$ in methanol. The system reacts to form Pt^{II} in the reaction[168]

$$H_2PtCl_6 + 6SnCl_2 + 3\,Cl^- \rightarrow SnCl_6^{2-} + 2H^+ + Pt(SnCl_3)_5^{3-}$$

This five-coordinate complex activates H_2 by heterolytic fission to form the anion $HPt(SnCl_3)_4$, a salt of which has been isolated.[169] The system products rapid hydrogenation (at 1 atm H_2) of ethylene to ethane and of acetylene to a mixture of ethylene and ethane; higher olefins are less easily reduced because they coordinate less readily. Slow hydrogenation cause they coordinate less readily. Slow hydrogenation but rapid isomerization of 1-pentene has also been reported.[170] Bond and Hellier[171] have proposed that the active catalyst is obtained in the system by the reaction

$$PtCl_n(SnCl_3)_{4-n} \xrightarrow{H_2} HPtCl_n(SnCl_3)_{3-n}$$

with $0 \leqq n \leqq 2$. Added halide (especially Br^-) promotes the reduction with the order of reducibility terminal > disubstituted > trisubstituted olefins.[172]

With HBr as promoter[173] hydrogenation is greatily favored over isomerization with rapid and sterospecific reduction of 4-t-butylmethylenecyclohexene (95%) *trans*. Use of other polar solvents (*e.g.* aliphatic, acids, ketones, ethers, nitrobenzene) increases the efficiency of this catalyst systems.[174]

Another system of the SnX_2 combination type utilizes $ML_2X_2 + SnX_2$ with L = phosphine, arsine, stilbine, sulfide, or selenide. The catalycally active species appear to involve a series of complex hydrides, one of which has been isolated, $HPt(PEt_3)(SnCl_3)$.[169]

Bailar's group[175–183] has carried out a series of investigations with systems of this type and has found them to be fairly selective catalysts for reduction of polyenes and isomerization of isolated double bonds. Their findings are summarized briefly below:

(a) for $PtL_2X_2 + SnX_2$ X = Br is more effective than X = Cl; with X = Cl, activity decreases as $P(OPh)_3 > AsPh_3 > PPh_3 > SbPh_3 \sim PBu_3$ (reduction of linoleate) with SPh_2 and $SePh_2$ also effective; (b) for $PdL_2X_2 + SnX_2$, L = PPh_3, $AsPh_3$, SPh_2 and $SePh_2$ are effective; (c) $Ni(PPh_3)_2I_2$ is the only nickel system effective; (d) $GeCl_2$ also works as cocatalyst (not as good as $SnCl_2$).

The mechanism is postulated to involve the following aspects: (a) *cis–trans* isomerization of isolated double bonds; (b) the main path by migration of isolated double bonds to give conjugation, then reduction to monoene; (c) a minor pathway of reduction of isolated double bonds; (d) migration of double bonds occurring with *cis–trans* isomerization; (e) hydrogen for reduction supplied by H_2 or protic solvent.

Catalysts of the system $ML_2X_2 + SnCl_2$ also reduce monoenes and acetylenes. $HPt(PPh_3)_2(SnCl_3)$ has been reported to reduce 2,5-dimethyl-hex-3-yn-2,5-diol.[91] Removal of the double bonds from the terminal position reduces hydrogenation and increases isomerization.

TABLE XVI. Olefin Reduction by the $PtL_2Cl_2 + SnCl_2$ System.[a]

Olefin	% Reduction	% Isomerization
C_2H_4	100	0
$1\text{-}C_3H_6$	34	0
$1\text{-}C_4H_8$	11	77
$1\text{-}C_5H_{10}$	12	77
$1\text{-}C_6H_{12}$	12	70

[a] $Pt(PPh_3)_2Cl_2 + SnCl_2$ in 3:2 C_6H_6:MeOH; 1 hr reaction time at 90° C, 34 atm H_2.

Reduction of ethylene by $PtL_2Cl_2 + SnCl_2$ with L = PR_3 or AsR_3 with D_2/MeOH or H_2/MeOD yields C_2H_5D,[184] supporting the theory of heterolytic splitting of H_2 for activation in this system. A study of Abley and McQuillin[185] of the hydrogenation by $ML_2X_2 + SnCl_2$ of 1-octene in 1:1 C_6H_6:MeOH at 20° C and 1 atm H_2 has yielded the following data: (a) activity of X = CN $<$I $<$ Br $<$ Cl; (b) isomerization with X = Cl, Br, but none with X = I, CN; (c) Pd $>$ Pt in activity.

The Rh^I catalyst $[Rh(SnCl_3)_2Cl]_2^{4-}$ has been shown to reduce aldehydes to alcohols at 110° C and 50 atm H_2 methanol; it hydrogenates 1-hexene under much milder conditions.[165]

Solutions of $PtCl_2$ in molten $[R_4N][SnCl_3]$, like the discrete complex $[R_4N]_3[Pt(SnCl_3)_5]$, are efficient catalysts for the hydrogenation of olefins. For example, ethylene is cleanly reduced to ethane in the presence of an equimolecular amount of hydrogen.[186]

The rate of ethylene hydrogenation is quite sensitive to changes in the medium. In matched experiments with 1.3 mmol each of ethylene and of hydrogen and 0.1 mmol of catalyst at 100° C, the following extents of reaction were attained in 5 hr: $PtCl_2$–Et_4NGeCl_3, 20; $PtCl_2$–Et_4NSnCl_3, 50; *cis*-$(Et_3As)_2PtCl_2$–Et_4NSnCl_3, 27; *cis*-$(Ph_3P)_2PtCl_2$–Et_4NSnCl_3, 20; *cis*-$(Et_3P)_2PtCl_2$–Et_4NSnCl_3, 17%. The rates attained with the phosphine and arsine complexes are significantly lower than that for the $PtCl_2$ solution even though these complexes, used in conjunction with $SnCl_2$, are known to be olefin hydrogenation catalyst.[174] Hydrogenation of ethylene in molten tetra-*n*-butylammonium trichlorostannate is slightly slower than in the tetraethylammonium salt, but the lower melting point (59–60° C) permits operation at lower temperatures. Hydrogenation activity was observed even at 50° C in a solution of $PtCl_2$ in a eutectic mixture of the two trichlorostannate salts.

Vinyl chloride is cleanly hydrogenated to ethane at 120° C and 3 atm pressure in a $PtCl_2$ solution in molten $[(C_2H_5)_4N][SnCl_3]$.

Platinum chloride solutions in molten $[(C_2H_5)_4N][SnCl_3]$, like trichlorostannate complexes in more conventional media,[175,174,183] selectively hydrogenate dienes and trienes to monoolefins. A substantial advantage of the molten salt medium, however, is that the product may be separated by decantation or simple distillation. This simplicity of isolation is especially useful in the reduction of high-boiling polyenes such as the linoleate esters in soybean oil.[174,175] Methyl linoleate is hydrogenated at 150° C and 100 atm pressure in the presence of a 1% solution of $PtCl_2$ in $[(C_2H_5)_4N][SnCl_3]$ to give a mixture of esters containing 63% methyl oleate.

As shown in Table XVII the hydrogenation of 1,5,9-cyclododecatriene *(cis,trans,trans)* can be directed to give primarily cyclododecene under similar conditions.

N. $ML_2(CO)_3X_2 + SnCl_2$ *(M = Mo, W)*[187]

Reaction of $ML_2(CO)_3X_2$ (L = $AsPh_3$ or PPh_3 and X = Cl) with $SnCl_2$ gives the complex $ML_2(CO)_2Cl_2(SnCl_3)$; heterolytic splitting of H_2 by this species can give the probable active catalyst, $HML_2(CO)_2(SnCl_3)$. This system has been reported to selectively reduce polyenes to monoenes. Drastic conditions (150° C, 500 psig H_2) are needed, probably to force dissociation of a ligand to allow both double bonds to coordinate. 1,4-addition of H_2 is observed for reduction of 2,4-hexadiene to only 2- and 3-hexene (prob-

TABLE XVII.[186] Hydrogenation of 1,5,9-Cyclododecatriene by Fused Salt Solutions of $PtCl_2$.[a]

Medium	Temp. (° C)	Pressure (atm)	Time (h)	Products (%)			
				Triene	Diene	Monoene[b]	$C_{12}H_{24}$
Et_4NSnCl_2	100	100	6	85	2	12	Trace
	140	100	8	2	18	80	Trace
	160	100	8	2	10	87	Trace
	140	500	6	5	18	73	4
	140	30	6	7	23	65	5
$Ph_3MePSnBr_3$	150	100	6	0		64	18

[a] In each experiment 5.0 ml of *cis,trans,trans*-1,5,9-cyclododecatriene and *ca.* 50 g of a 1% $PtCl_2$ solution were allowed to react under the conditions indicated in an 80-ml Hastelloy shaker tube. [b] The cyclododecene appeared to contain roughly equal amounts of the *cis* and *trans* isomers.

ably via a π-allyl intermediate which can give either 1,4- or 1,2-addition). Terminal olefins are not reduced but are isomerized. Internal olefins are neither hydrogenated nor isomerized.

O. Miscelaneous Monohydrides

The system $[PtCl_2(C_2H_4)]_2$ has been one of the first homogeneous hydrogenation catalysts to be investigated.[5] In the reduction of ethylene to remain completely homogeneous the system requires low temperature (0° C) and fairly high ethylene:hydrogen ratios; lower temperatures (–20° C) need smaller ethylene:hydrogen ratios. From this data, the active catalyst is thought to be $HPt(C_2H_4)_2Cl$ which is generated by heterolytic splitting of H_2 by $Pt(C_4H_4)_2$ Cl_2.

The complex, Rh(1,5–COD)(PPh_3)Ph has been observed to catalyze the reduction of olefins, dienes, diphenyacethylene under mild conditions.[188] The active catalyst is formed by hydrogenolysis on the Rh–Ph bond to give benzene and Rh(1,5–COD)PPh_3)H.

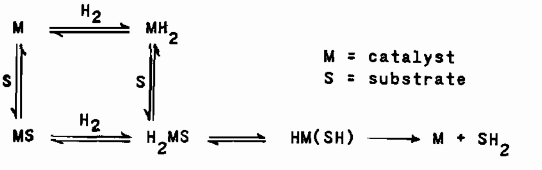
The series of catalysts L_nRhH (n = 3,4) with L = PR_3, PAr_3, 1/2 diphos has been reported to hydrogenate various olefins at 20–130° C and 20–100 atm H_2.[113] The monohydride is believed to be the active catalyst even though under H_2 pressure the monohydride adds hydrogen reversibly to form RhL_3H_3.

The system $PdCl_2 + OAc^-$ has only been briefly investigated for the reduction of ethyl crotonate.[189] Maxted and Ismail have postulated a strange (and unlikely) mechanism involving Pd^I. A more probable mechanism involves formation of a Pd–crotonate complex with heterolytic splitting of H_2 by this species to form the active monohydride catalyst.

4. Known Dihydrides

Quite a number of hydrogenation catalysts which function by a dihydride pathway (activation of H_2 by oxidative addition the metal complex) have been discovered in the last few years. The mechanism is thought to involve two possible routes, both of which may be simultaneously operative; both routes require free coordination sites for addition of H_2 and complexation of substrate.[36]

Diagram 14



One route termed the "*hydride path*" involves oxidative addition of H_2 followed by coordination of substrate to form a dihydride intermediate with complexed substrate. The alternate route, called the "*unsaturated path*", consists of coordination of substrate before oxidative addition of H_2 to form the same dihydride–substrate intermediate. In most systems, the hydride path is thought to predominate because coordination of substrate (generally on olefin or acetylene) removes a sufficient amount of electrondensity from the metal by strong π-back-bonding such that H_2 cannot oxidatively add to the complex to a significant extens, if at all.

Dihydride catalysts are generally more stereospecific and less prone to isomerization of substrate and exchange of hydrogen than monohydride catalysts. Because the two hydride transfers of a dihydride system are adjacent in the mechanism, with the second transfer often more rapid than the first, less time is available in the metal alkyl stage for "bad things" to happen. On the other hand, the monohydride system has an oxidative addition of H_2 between the first and the second hydride transfers, usually giving the alkyl sufficient time to the olefin–hydride intermediate in the process of which hydrogen exchange and isomerization may occur.

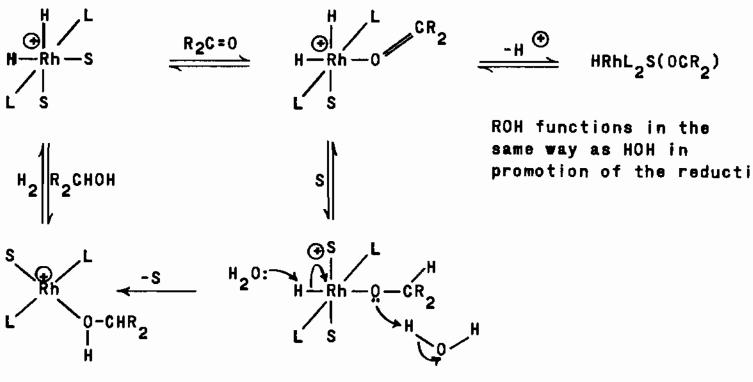
A. $ML_2(S)_2^+$ *(M = Rh, Ir)*

This new system has been studied by Osborn's group.[190–193] The active catalyst is generated by treatment of $[M(diene)Cl_2]_2$ with four equivalent of phosphine L in a polar solvent to give $[M(diene)L_2]^+$, which on treatment with H_2 yelds $H_2ML_2(S)_2$ where S can be THF, EtOH, methylethylketone, *etc.* The structure is proposed as a *cis*-dihydride with *trans*-phosphine. A special effect is observed with $[Rh(diene)(PPh_3)_2]BPh_4$. Treatment of this intermediate with H_2 results only in formation of $Rh(PPh_3)_2(BPh_4)$, with an aromatic ring of the anion π-bonded to the metal whose hydrogenation abilities are totally impaired.

Rapid rates of reduction of olefins and alkynes have been noted for M = Rh and L = PPh_3, with the following order of substrate reducibilities: 1-hexyne > 2-hexyne > 1-hexene > cyclohexene > *cis*-2-hexene > *trans*-2-hexene ≫ 1-methylcyclohexene. α,β-unsaturated ketones and aldehydes can be hydrogenated without affecting the carbonyl group. Similar rates are found for reductions by the iridium analogue. Inhibition is observed for PPh_3 and strong donor solvents as CH_3CN.

Homogeneous catalytic reduction of ketones (25° C, 1 atm H_2) has been reported for $RhL_2(S)H_2^+$ with L = $PMePh_2$, PMe_2Ph, PMe_3 but not PPh_3 and S = THF and acetone; aldehydes are also reduced, but with rapid deactivation of catalyst. The reduction has been shown not to proceed *via* keto–enol tautomerism. Dry ketone is reduced only very slowly but the rate increases as the alcohol reduction product accumulates. The best rates occur at 1% H_2O, for a hydroxylic compound greatly aids the reduction as shown in Diagram 15.

The validity of this mechanism is reinforced by the fact that use of D_2 in 1% aqueous acetone gives only $CH_3CD(OH)–CH_3$.



ROH functions in the same way as HOH in promotion of the reduction

Diagram 15

One further interest is the ability[194] of the rhodium complex $[Rh(diene)L_2]^+$ to reduce internal alkynes specifically (>95%) to the corresponding *cis*-alkene in high yield (>98%). Although the corresponding Ir^I complexes are less effective hydrogenation catalysts, $[Ir(COD)_2]^+$ (COD = cyclooctene) is very effective for rapid deduction of 1,5-cyclooctadiene solely to cyclooctene. However, the attempted catalytic hydrogenation of norbornadiene with $[Rh(NBD)_2]^+$ in acetone led to the uptake of only 0.4–0.5 mol of hydrogen per norbornadiene double bond to yield *ca.* 80% of a species $C_{14}H_{18}$.

B. $Rh(SEt_2)_3Cl$[195,196]

This catalyst has been obtained by reduction (quite rapid) of the Rh^{III} complex $Rh(SEt_2)_3$ with H_2 (heterolytic splitting of H_2 to form $Rh(SEt_2)_3HCl_2$) followed by reductive elimination of olefin (H_2 reduces the Rh^I species to metal). At 1 atm H_2 and 80° C, the catalyst reduces the double bond of some unsaturated carboxylic acids with the following sequence of rates: cinnamic > fumaric > maleic. The mechanism is postulated to follow the "unsaturated" path with addition of substrate, oxidative addition of H_2 (rate-determining step), and hydride transfer onto saturated product. This mechanism fits the experimental rate law: $-d[\text{substrate}]/dt = k_2[H_2][Rh^I(S)]$ where S = substrate.

Inhibition by SEt_2 is demonstrated by the experimental rate constants for reduction of maleic acid by the two species $Rh(SEt_2)_2Cl$ and $Rh(SEt_2)_3Cl$: $k(L_2)/k(L_3) = 2.85/0.33 = 8.6$.

C. Nitrosyls, $M(NO)L_3$

The complexes used are of the type $M(NO)L_2$ with M = Rh, Ir and L = PPh_3, $PMePh_2$, $P(F\text{-}C_6H_4)_3$, $As(PPh_3)$, P(*o*-tolyl)$_3$, P(*p*-anisyl)$_3$. These complexes are the first d^{10} systems reported to hydrogenate olefins and alkynes.[197–201] Most of the work has been done with $Rh(NO)(PPh_3)_3$, a complex in which the metal has a formal oxidation state −1.[199,200]

Catalytic activity for $RhNOL_3$ shows the following dependence on L: P(*p*-anisyl)$_3$ > (*p*-CH_3-C_6H_4)$_3$P > $P(C_6H_5)_3$ > (*p*-FC_6H_4)$_3$P > $P(CH_3)(C_6H_5)_2$. Substrates are reduced by $Rh(NO)(P(C_6H_5)_3)_3$ in the order alk-1-yne > alk-2-yne > alk-1-ene > exo-methylene > cycloalkene > *cis*-alk-2-ene > *trans*-alk-2-ene > tri-substituted olefin > tetra-substituted olefin. Ethylene, propylene, and allene are easily reduced at 1 atm H_2 and 25° C. Non-conjugated non-chelating dienes are reduced at the same rate as monoalkenes. Conjugated dienes and strongly bonding chelating dienes are generally reduced at significantly lower rates or not at all (probably due to blocking of a coordination site needed for oxidative addition of H_2). Isoprene, 1,3-butadiene, and 2,4-hexadiene are only slowly reduced, forming all possible monoene isomers. 1,5-cyclooctadiene cannot be reduced even at 30° C and 8 atm H_2; it also inhibits the hydrogenation of cyclohexene. For 1,3-cyclooctadiene and norbornadiene, however, hydrogenation proceeds at rates nearly those of terminal olefins; the dienes are not isomerized and are reduced faster than the monoenes produced in the first stage of hydrogenation.

The stereochemistry of $Rh(NO)(P(C_6H_5)_3)_3$-catalyzed hydrogenation of olefins has been elucidated by utilizing Wilkinson's adaptation of the work of Childs and Bloch.[198] With an average 25 psig D_2 in dichloromethane, the deuteration of dimethyl maleate was taken to completion. Since the relative rates of *(A)* reduction of maleate to succinate, *(B)* isomerization of maleate to fumarate, and *(C)* reduction of fumarate to succinate were determined in previous experiments with the nitrosyls catalyst as (A):(B):(C) ≈ 150:1:8, calculations showed that products resulting from a path through fumarate would be insignificant within the accuracy of the infrared measurements. The product succinate was purified by preparative glc; mass spectroscopy showed it to be completely dideuterated. Infrared studies in CS_2 showed the product to be ~90% *meso*-d_2-dimethylsuccinate (formed by *cis*-addition of D_2 to maleate). Thus, it appears that reduction of olefin occurs in two steps (hydride transfers) and that the second step usually occurs before the Rh–C bond can rotate; otherwise the *trans*-addition D,L product would be formed to a greater extent.

Two other experiments have also substantiated the stereospecificity of the nitrosyl hydrogenation catalysis. Reduction of cyclohexene with D_2 yields only d_2-cyclohexene. Hydrogenation of 2-hexyne produces ≧99% *cis*-2-hexene (glc analysis) which would be formed by *cis*-addition of H_2 to the alkyne.

The rhodium nitrosyl in the absence of H_2 and O_2 was shown not to catalyze the isomerization of terminal olefins. On slight exposure to air, however, a solution in CH_2Cl_2 slowly converted an excess of 1-hexene into its internal isomers, with phosphine oxide detected by infrared. Presumably oxidation of a phosphine gives the complex a free site with which to coordinate olefin for isomerization *via* a π-allyl–hydride intermediate.

The analogous $Ir(NO)(PPh_3)_3$ fails to reduce 1-hexane at 30° C, 5 atm H_2 in $CHCl_2$ or C_6H_6.[200]

A moderate rate for hydrogenation of 1-hexene (with some isomerization) and cyclohexene has been observed at 25° C and 1 atm H_2 in the presence of a 1:1 mixture of $Co(NO)P_3$ ($L = Ph_3P$ and Ph_2MeP) and $NaBH_4$.[200] The mechanism for hydrogenation proposed in Diagram 16 follows the "hydride path" with an extra effect from the nitrosyl group in one of two alternative schemes.

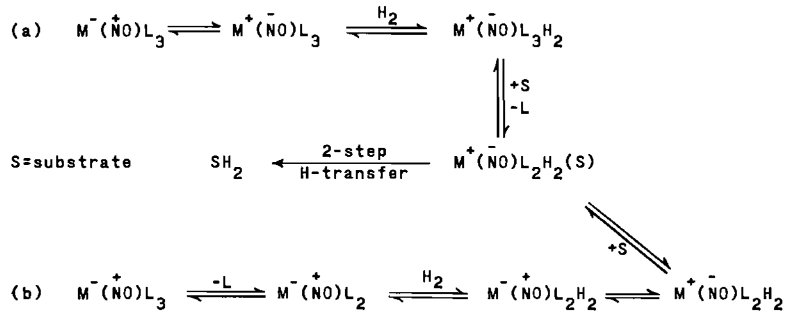


Diagram 16

The equilibrium constant for the reaction with H_2 (with or without substrate present) must be quite small, for no changes in vibrational or electronic spectra are observed at 1 atm H_2. The difference between activates of the rhodium and iridium complexes may be attributed to a much lower ability of the iridium nitrosyl to dissociate a phosphine or to undergo the nitrosyl bending (linear NO^+ to bent NO^-) to give the required free coordination site. Preliminary kinetic studies seem to support the S_N2 dissociative mechanism (b) of Diagram 16.[201]

D. Fe(CO)₅ and Fe(CO)₃(diene)

$Fe(CO)_5$ was used first by Japanese workers to hydrogenate unsaturated fatty acid esters.[202] More recent work in selective reduction of these esters has shown that the substituted iron carbonyl complex with diene fatty acid ester (dfae), $Fe(CO)_3$(dfae), is actually a more active catalyst than $Fe(CO)_5$.[203,204] Work by Frankel and coworkers has more thoroughly explored the system.[205–208] The reduction requires strong conditions, 7 atm H_2 and 180° C. The mechanism can be descrived as follows: *(i)* both the "hydride" and "unsaturated" paths may be active; *(ii)* $Fe(CO)_3$(dfae) reduces polyenes more rapidly than $Fe(CO)_5$; *(iii)* conjugated double bonds are preferentially hydrogenated; monoene is reduced only when the supply of conjugated diene has been exhausted; *(iv)* conjugation of non-conjugated polyenes is achieved by the catalyst through a π-allyl–hydride mechanism.

E. M(arene)(CO)₃ (M = Cr, Mo, W)

This family of catalysts has been investigated by Frankel *et al.*[209–214] The first system tried is M = Cr with arene = $PhCO_2Me$, cycloheptatriene, *etc.*, which selectively reduces dienes to monoenes at 150° C, 700 psig H_2. Convincing evidence has been produced for 1,4-addition of $H_2 \cdot Cr(CO)_3(PhCO_2Me)$ converts methyl sorbate to methyl hex-3-enoate in ≧99% yield; n.m.r. analysis of the product from deuteration of sorbate shows only 1,4-addition of D_2.

Conjugated dienes are rapidly reduced to monoenes; 1,4-dienes are easily conjugated by the catalyst and then reduced; but 1,5- and 1,6-dienes are conjugated very slowly so they are very slowly hydrogenated to monoene. Reduction of both 1,3- and 1,4-hexadienes with D_2 yields only 2,5-d_2-cyclohexene. Reduction of linoleate (a 9,12,15-triene) proceeds by *(a)* conjugation of two double bonds, *(b)* 1,4-addition of H_2 to conjugated diene, *(c)* conversion to conjugated diene, *(d)* 1,4-hydrogenation to monoene. Monoenes are not reduced to any significant extent.

The $Cr(CO)_3$(arene) system works for a wide variety of arenes, with selectivity dependent very little on ring substituents. Activity is increased by electron-withdrawing groups on the ring by decreasing π-back bonding which consequently increases dissociation of arene to form a coordinatively unsaturated species.

Similar results are found for the molybdenum and tungsten analogues. The selectivity for diene reduction is the same as for chromium but the stereospecificity of the hydrogenation is different indeed; with sorbate, the molybdenum system gives 4-ene while the tungsten forms 2-ene.

A similar system[215] which must involve the same type of catalysis is demonstrated in the reaction of Diagram 17:

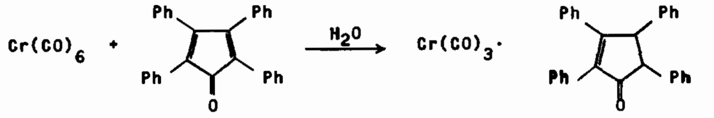


Diagram 17

The hexacarbonyl apparently forms a dihydride carbonyl species from reaction with H_2O and reduces the diene–ene to ene–one, which coordinates to Cr through a phenyl ring; no experiment was run with D_2O, so apparent lack of 1,4-addition of H_2 may result from isomerization after 1,4-addition or from a different stereospecificity due to the stability of an α,β-unsaturated ketone. The mechanism proposed by Frankel *et al.* involves the "hydride" path: *(a)* dissociation of arene to give an unsaturated d^6 species $M(CO)_3$, *(b)* reaction with H_2 to form the dihydride $M(CO)_3H_2$, *(c)* coordination of conjugated diene to form a metal diene dihydride, $M(CO)_3(diene)H_2$, *(d)* 1,4-reduction of diene and elimination of monoene. To account for 1,4-hydrogenation, simultaneous transfer of two hydrides from metal to the terminal portions of a *cisoid* metal–diene center is suggested. Since the idea of simultaneous transfer of two hydrides from metal to substrate is currently in disfavour, an alternate pathway involving allyl–hydride complexes is presented in Diagram 18:

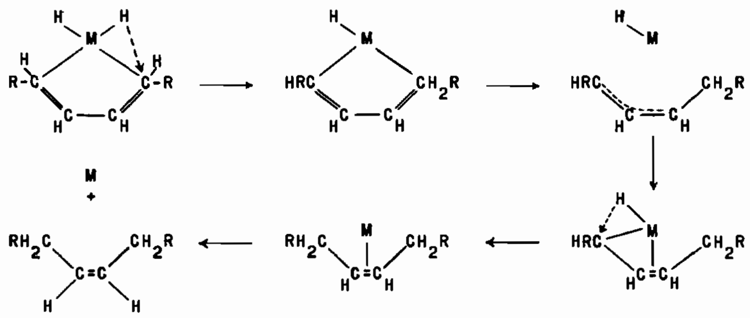


Diagram 18

F. Trans-IrL$_2$(CO)X System

The first investigators[216–218] of this catalyst studied the complex $Ir(PPh_3)(CO)Cl$. This complex forms a stable adduct with H_2 and catalyzes the reduction of acetylene and olefins. At 60° C and 1 atm H_2, C_2H_4 is reduced to C_2H_6, C_3H_6 to C_3H_8 and C_2H_2 to a mixture of C_2H_4 and C_2H_6. H_2–D_2 exchange is also promoted during reduction of ethylene.

TABLE XVIII. Rate of Reaction *(k)* of $IrL_2(CO)Cl$ with H_2.

Ligand	ν(C–O)	*k*	K[a]
$P(C_6H_{11})_3$	1932	0.1	.03
$P(i\text{-}C_3H_7)_3$	1935	0.8	.03
$P(n\text{-}C_4H_9)_3$	1940	36	1.3
$P(CH_2Ph)_3$	1956	64	2.3
P(*p*-tolyl)$_3$	1963	89	3.2
PPh_3	1967	59	2.1
$P(OPh)_3$	2001	7.2	.26

[a] Rate of H_2 uptake (K) with $IrL_2(CO)Cl$ and dimethyl maleate in ml min^{-1} mmol^{-1}.

A more thorough investigation of the energetics of the system has been made by Strohmeier *et al.*[219–225] The rate constants for the reaction

$$IrL_2(CO)X + H_2 \rightarrow IrL_2(CO)XH_2$$

have been found to vary as k(I) > k(Br) > k(Cl). Table XVIII shows the effect of different ligands on the rate as expressed for k. Equilibrium constants for dissociation of H_2 from the dihydride species have been shown to follow the sequences X = Cl > Br > I and L = P $(C_6H_{11})_3 > PPh_3 > P(OPh)_3$. Experiments with activated olefins have yielded dissociation constants for the complex $IrL_2(CO)X$(olefin) and shown that *(i)* binding of olefin decreases with increasing basicity of L, *(ii)* binding decreases with decreasing electronegativity of X, and *(iii)* binding decreases with decreasing π-acceptor strength of olefins. Tendency of $IrL_2(CO)X$ to complex with solvent (S) follows the orders L = $P(C_6H_{11})_3 \ll P(OPh)_3 < PPh_3$ (X = Cl < Br < I), and S = $PhCH_3 < C_6H_6 < CHCl_3 < CS_2$. The effect of hydrogenation rates (for maleic acid, L =

PPh_3, in DMA or DMSO, 1 atm H_2, 65–80° C) has been shown by James and Memon[226] to follow the ratio Cl : Br : I = 1 : 2.5 : 4. The effect of L on hydrogenation[223] (measured as H_2 uptake rate R) is demonstrated in Table XVIII; a maximum rate appears at L = P(*p*-tolyl)$_3$ with both more and less basic phosphines giving lower activities.

From the large volume of data gathered in their many experiments. Strohmeier and coworkers have deduced the mechanism of hydrogenation of dimethyl maleate in toluene at 80° C. The rate law follows neither k[IrL_2(CO)X] nor k[M] where M = dimethyl maleate. A kinetic study with added L has shown that the "unsaturated" pathway, not the "hydride", is utilized. The rate-determining step is addition of H_2 to a complex IrL(CO)MX where M has replaced one L. Diagram 19 illustrates the proposed mechanism:

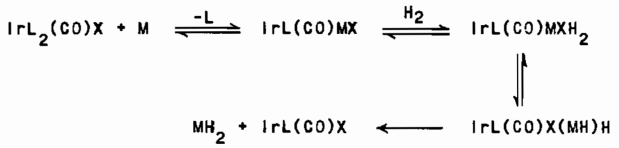


Diagram 19

Formation of IrL(CO)MX from IrL_2(CO) is suggested to proceed *via* an S_N2 associative process, although the S_N1 dissociative path cannot be ruled out.

Hydrogen and hydridocarbonyltris(triphenylphosphine)iridium(I) have been found to establish the equilibrium[227]

$$IrH(CO)(PPh_3)_3 + H_2 \rightleftarrows IrH_3(CO)(PPh_3)$$

This system in dimethylformamide at 50° C has been found to hydrogenate catalytically ethylene to ethane.[228] The active catalytic species is the trishydrido complex. Kinetic studies show that the reaction of ethylene with $IrH_3(CO)(PPh_3)_2$ controls the rate of ethylene activation while the inhibitory effect of hydrogen and triphenylphosphine is thought to originate in subsequent competition between reactions of the ethylene intermediate giving ethane and those with hydrogen and phosphine reforming ethylene.

G. *Trans-RhL$_2$(CO)X System*

Vaska has observed that $Rh(PPh_3)_2(CO)Cl$ is a less active hydrogenation catalyst than its iridium analogue.[217] The Rh–PPh_3 system has been reported to add H_2 reversibly at 70° C.[229] Hydrogenation of olefins and dienes is extremely dependent on temperature; at 70° C, no reduction of cyclooctene, and at 80° C, slow reduction. The following relative activities of hydrogenation have been reported:[229,230] (a) for X = Cl, L = PPh_3 > $P(C_6H_{11})_3$ > $P(OPh)_3$; (b) for L = PPh_3, X = Cl > Br > I; (c) PPh_3–I > $AsPh_3$–Cl > $P(C_6H_{11})_3$ > $P(OPh)_3$–Cl.

Little correlation is observed between activity and ν(C–O) of the RhL_2(CO)X system for various L and X.[231] With L = PPh_3, X = Cl reportedly gives the lowest degree of isomerization and the fastest hydrogenation.[232]

Strohmeier and Rehder–Stirnweiss[229] have concluded that RhL_2(CO)X catalyzes hydrogenation by a mechanism different from that of the analogous iridium complex. A kinetic study[229] has shown that the former system requires an induction period. This induction period can be eliminated by heating the catalyst at 90° C under N_2 with a toluene solution of the olefin for 5 hr, but the slopes of the rate *vs* temperature plots are different for the "treated" and "regular" systems.

A very similar system recently discovered is $Rh(PPh_3)_2(CO)(C_2F_4H)$, formed by insertion of C_2F_4 into the active oxo catalyst hydride.[233] This catalyst is moderately active for hydrogenation of alk-1-enes at 25° C, 1 atm H_2. Activity is attributed to dissociation in solution, which is supported by molecular weight measurements.

To gain further information about the RhL_2(CO)X system, Hartwell and Clark[234] have designed the series $RhCl(CO)[Ph_2P(CH_2)_nCH{=}CH_2]_2$. For n = 2, at 25° C and 1 atm H_2, no reaction occurs in benzene (non conducting solution), but in methanol or ethanol (1 : 1 electrolyte) the complex is fairly rapidly converted to $RhCl(CO)(Ph_2PBu)_2$. In methanol solution uncoordinated olefin protons are detected by n.m.r.; a very labile coordination of ligand olefin is postulated. Experiments using D_2 for reduction have shown that conversion of each double bond incorporates an average of 2.5 deuterium atoms (1.6 in terminal, 0.9 in C-2); thus the reaction evidently involves a two-step hydride transfer with the first easily reversed before the second occurs. With n = 0, 1, 3, the rate of hydrogenation is considerably slower but still utilizes a two step hydride transfer.

H. *ML$_n$X (M = Rh, Ir; n = 2,3)*

(i) *RhL$_n$X*

The first literature reports on the catalytic activity of $Rh(PPh_3)_3Cl$ are those from Wilkinson's[235,236] group in which the reaction of the Rh(I) complex with H_2 has been reported to give the stable adduct $Rh(PPh_3)_2H_2Cl$; reaction of this dihydride (or RhL_3Cl under H_2) with 1-hexene gives hexane, while acetylene forms a mixture of ethylene and 1-hexyne yields a mixture of 1-hexene and hexane (alkene reduced more rapidly than alkyne).

Independent work has been done by both Dewhirst[237] and Coffey[238] on more general RhL_3X systems, but the reports have been delayed in the patent process.

Most of the work on general catalytic properties and mechanistic behavior of $Rh(PPh_3)_3X$ has been recorded in two master papers[239,240] by Wilkinson and coworkers. The first of these articles reports various observations (including a kinetic study on the reduction of olefin) listed below which allow the authors to postulate a definite mechanism: (a) molecular weight studies (osmometry in an inert atmosphere) have shown complete dissociation of phosphine (L) to form the species $RhL_2(S)Cl$ where S = solvent; (b) the reaction with H_2 is reversible as $RhL_3Cl + H_2 \rightleftarrows RhL_2Cl(S) + L$; (c) osmometry of $Rh(PPh_3)_3Cl$ under H_2 shows complete dissociation of one ligand in the dihydride form; (d) n.m.r. shows two high-field peaks of equal area for RhL_2H_2Cl in pyridine, suggesting six coordinate species with *cis*-hydrides; (e) formation of chloride-bridged dimer with elimination of phosphine is observed in benzene; the dimer adds H_2 at both metal atoms but fails to hydrogenate olefins; (f) a kinetic study has shown that rate = $k'[H_2][\text{olefin}][\text{catalyst}]/(1 + K_1[H_2] + K_2[\text{olefin}])$; ($K_1$ for reaction with H_2; K_2 for complexation of olefin by RhL_3X to give $RhL_2[\text{olefin}]X$); this rate law does not eliminate either the unsaturated or hydride pathway; the maximum catalytic activity results for larger k′ and smaller K_2; (g) addition of ketone, alcohol, or THF increases the rate of reduction: a polar intermediate or transition state is indicated.

From these data the authors have concluded that only the "hydride path" is operative (polstulating that the coordinated olefin or alkyne withdraws too much electron density from the central metal to permit formation of the dihydride by oxidative addition of H_2) and have proposed the mechanism below:

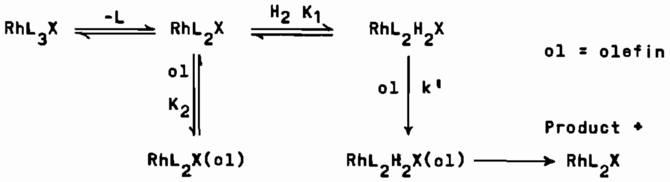


Diagram 20

Several pieces of evidence have led Wilkinson and coworkers to put forth the idea of concerted simultaneous transfer of both hydrides from metal to substrate. *Cis* addition of D_2 is observed by infrared study of deuterated products from maleic and fumaric acids. 2-hexyne is reduced to 2-hexene of isomer ratio *cis/trans* > 20. No allyl intermediate is detected at −50° C for $RhL_2H_2Cl + C_2H_4$ in the n.m.r. No H–D exchange occurs for $D_2 + Rh(PPh_3)_3Cl$. Reduction of an olefin with H_2–D_2 mixtures forms primarily d_0 and d_2 alkenes.

In the second of these two master papers,[240] H_2 uptakes rates and activation parameters have been measured for a large number of substrates with $Rh(PPh_3)_3Cl$ as catalyst. At 1 atm H_2 and ambient temperature, terminal olefins are reduced so rapidly that a 1 m*M* solution in benzene will actually boil. Olefins and acetylenes are reduced with little or no isomerization. Terminal olefins are faster than internal, *cis* faster than *trans,* and alkenes faster than alkynes. Conjugated dienes are not hydrogenated at ≦ 1 atm but are at 60 atm H_2. Chelating dienes (non conjugated) reduced slowly at 1 atm except at higher temperatures. Ethylene (itself not hydrogenated unless catalyst pretreated with H_2) inhibits reduction of cyclohexene. Even tetraphenylethylene is slowly hydrogenated at higher pressures and temperatures.

Three other major Wilkinson group papers[242–244] have investigated ligand effects on catalytic activity. Using RhL_3Cl, a series of reductions of substrates with different L has been carried out (see Table XIX); the nature of the ligand L influences the rate of reduction markedly but has little effect on the relative rates at which different substrates are hydrogenated. Ligands slightly more basic than PPh_3 are the most effective; more basic ligands should favor addition of H_2 and coordination of olefin, but if L becomes too basic the dihydride complex reassociates the third phosphine. With $L = PPh_3$ the complex RhL_3Cl shows a molecular weight in benzene appropriate for one ligand completely dissociated both under N_2 and H_2; but with $L = PEtPh_2$, the molecular weights found are 415 and 780 respectively under N_2 and H_2 (corresponding to $RhL_2Cl + L$ and RhL_2H_2Cl).

Using $[Rh(C_8H_{14})_2L_2]$, addition of 2n mols L per mol of dimer to give RhL_nCl forms catalysts of highest activity with n = 2. As Table XX shows, alkyl phosphines are not good for activity at L/Rh = 3 (saturated dihydride) and too much basicity may lower the effectiveness of the complex even at L/Rh = 2. Wilkinson has attributed this unexpected trend to far stronger Rh–H bonds in more basic phosphine catalysts which result in a rate-controlling step not for coordination of olefin but for transfer of hydride to coordinated olefin.

Further work done by other groups on ligand effects has supported the previously noted data. Hormer *et al.*[245] have found that a maximum rate occurs at L/Rh = 2.2 (utilizing a new synthetic method: $RhCl_3 \cdot 3H_2O + nL + \text{base} + H_2$) and that for RhL_3Cl alyphatic group and aromatic rings substituted with electron acceptors on P decrease the rate relative to

TABLE XIX. Ligand Effect on the Olefin Reduction for RhL_3Cl System.[a]

L	1-hexene	Cyclohexene	*cis*-4-methyl-2-pentene	*trans*-4-methyl-2-pentene
$P(p\text{-}C_6H_4OMe)_3$	99.5	68.00	34.7	8.23
$P(p\text{-}C_6H_4Me)_3$	85.3	58.8	29.0	6.85
PPh_3	38.9	28.1	14.1	3.12
$PEtPh_2$	17.5			
$P(p\text{-}C_6H_4F)_3$	5.78	3.93	1.75	0.35
$P(p\text{-}C_6H_4Cl)_3$	1.58	1.20	0.44	0.10
$P(CH_2Ph)_3$	1.39			
$P(o\text{-}C_6H_4Me)_3$	0.11			
$P(2,3\text{-}C_6H_3Me_2)_3$	0.12			
$P(2,4,6\text{-}C_6H_2Me_3)_3$	0.09			
$P(OPh)_3$	0.02			
$AsPh_3$	4.63			
$SbPh_3$	2.59			

[a] H_2 uptake by RhL_3Cl in ml min^{-1}; 50 cm H_2, 25° C, 1.25 m*M* catalyst, 0.6 *M* olefin in C_6H_6.

TABLE XX. H_2 uptake in ml min^{-1} with Cyclohexene for RhL_nCl.

L	L/Rh = 3	L/Rh = 2
PEt_3	0	0.5
PEt_2Ph	0	1.7
$PEtPh_2$	1.8	18.5
PPh_3	12.4	$\geqq 17.9$
$P(p\text{-}C_6H_4OMe)_3$	19	60

PPh_3 while donor substituted aromatic rings on P increase the rate. Thus it appears that ligands slightly more basic than PPh_3 give the maximum rate of hydrogenation and that either an increase or decrease in basicity lessens catalytic activity. The data of Stern and coworkers[246,247] with aminophosphines have formed the following sequence for activity of RhL_3: $PPh(NR_2)_2 > PPh_2(NR_2) > PPh_3 > P(NR_2)_3 \geqq PR_2Ph > PR_3$ and $PR_2(NR_2) > PR_2Ph$ where NR_2 = piperidyl and R = cyclohexyl.

The work by Horner *et al.*[245] has also supported Wilkinson's group's results for steric effects of substrates on reductions rate.

Various pieces of research have reinforced the concept of stereospecific addition of H_2 to olefins. Birch and Walker[248] have reported that D_2 adds only *cis* across the 5,6-double bond of 22-dihydroergosteryl acetate. Morandi and Jensen[249] have found that deuteration of C_{10}–C_{20} monoenes incorporates only two deuteriums per olefin and these go only to the original unsaturated sites.

Birch and Walker[250] have also shown that deuteration of cyclohexene and methyl oleate yields only the d_2-products and that deuteration of methyl linoleate gives only d_4-product. Smith and Shuford[251] have found that deuteration of styrene produces only d_2-product in benzene and methylene chloride but in $CHCl_3$ and $CDCl_3$ the same isotopic distribution of products in found with less d_2 and more d_0; this strange solvent effect may be due to a 1,3-hydride shift as postulated for the reduction of PhC≡CPh with D_2 catalyzed by $Rhpy_2(DMF)(BH_4)Cl_2$.[101]

Although Wilkinson's general mechanistic scheme is still considered essentially correct, many of its minor points have run many contradictory new evidence.

The first point of dissention is the extent of dissociation of the complex RhL_3Cl. Eaton and Suart[252] have shown with ^{31}P n.m.r. that dissocation to RhL_2Cl + L at concentrations of the order of 10^{-3} *M* is $\leqq$ 5%. Brown and Green[253,254] have presented ^{31}P and ^{103}Rh n.m.r. evidence for non-dissociation of $Rh(PPh_3)_3X$ (no temperature stated): but as the temperature is raised above room temperature the four lines at high field (P *trans* to P) and six lines at low field (P *trans* to X) collapse into a single line; the tendency to coalesce follows $X = Cl < Br < I$ indicating that RhL_3I dissociates more readily than RhL_3Cl. A kinetic study of reaction of cycloalkene by Hussey and Takeuchi[255] requires incomplete dissociation for the rate law to fit the data. Schriver and coworkers[256] have shown that no reaction is noted when $Rh(PPh_3)_3Cl$ is treated with BF_3; since free PPh_3 reacts very rapidly with BF_3 to form the stable adduct $Ph_3P\text{–}BF_3$ the degree of dissociation cannot be very large. Wilkinson himself has come to doubt molecular weights measured by osmometry, as strange results are found with a fairly wide range of organometallic complexes.[257]

Dissociation of $P(C_6H_5)_3$ from $RhCl[P(C_6H_5)_3]_3$ with $K_1 = 1.4 \times 10^{-4}$ *M* has recently been suggested on the basis of spectrophotometric experiments on dilute benzene solutions.[258] Jesson *et al.*[259] have repeated these experiments and found that RhCl $[P(p\text{-tolyl})_3]_3$ behaves similarly. While it is clear that phosphine dissociation occurs in dilute solutions, they prefer to ascribe effects of added L and deviations from Beer's law to the following equation based on studies on the soluble dimer

$$2RhClL_3 \rightleftarrows [RhClL_2]_2 + 2L$$

with $L = P(p\text{-tolyl})_3$ where $K \sim 4 \times 10^{-4}$ *M* in benzene at 25° C. The dimer obeys Beer's law and has a ^{31}P spectrum consisting of a non-first-order doublet of triplets. In any event the spectrum is inconsistent with a monomeric species $RhClL_2$. In the presence of 0.01 *M* or higher added L, solutions of $RhClL_3$ complexes do obey Beer's law, showing that equilibrium is forced to the left under these conditions. There is no evidence for $RhClL_4$ formation even in 0.5 *M* L.

Their studies show that $RhCl[P(C_6H_5)_3]_3$ and $RhH_2Cl[P(C_6H_5)_3]_3$ are the major species present in solutions of tris(triphenylphosphine)rhodium chloride and hydrogen.

The proposed pathway is represented in Diagram 21:

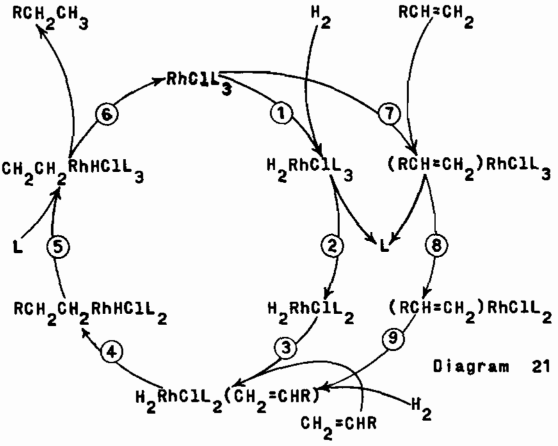


Diagram 21

The mechanism in Diagram 21 is somewhat different from the one originally proposed, which included phosphine ligand dissociation as the first step in the reaction and simultaneous addition of both hydrogens to the double bond. Dissociation to $H_2RhCl(PPh_3)_2$ is slight, but does provide a mechanism for ligand exchange. Wilkinson's isolation of $(C_2H_4)RhClL_2$ and observation that the ethylene complex is not readily hydrogenated[239] suggest that step (9) is very slow, so that the bulk of the reaction goes via the loop which contains steps (1)–(6). The inhibition of hydrogenation on addition of triphenylphosphine to the system can be understood in terms of its suppression of ligand dissociation in step (2). This mechanism is in harmony with the basic postulate that, in general, only 16 and 18-electron complexes are present in homogeneous reactions catalyzed by group VIII transition metal complexes, other species being energetically unfavourable.[260] A similar sequence of reactions obeying this rule can be written both for the "hydride" and "unsaturated" route to hydrogenation.[239,261]

The second point of disagreement is simultaneous transfer of two hydrides from metal to substrate. Biellmann and Jung[262] have shown that although most methylene groups in cyclic compounds are smoothly reduced, only isomerization of damsin to isodamsin is noted (no isomerization without H_2); with D_2 58% of the isodamsin product is d_1; thus an alkyl–Rh–H intermediate must be involved wich cannot transfer the second hydride. Reduction of α-cyclopropylolefins[263] yields a product wich can only come from the rearrangement of another alkyl–rhodium–hydride. Deuteration of 1,4-dimethylcyclohexene[264] produces HD in the gas phase and d_1–d_4 alkane. The reduction of cyclohexene with a mixture of H_2 and T_2 causes H–T exchange.[265] Reduction of *cis*-2-pentene with Rh $(PPh_3)_3X$ at 1 atm H_2 in 1:1 benzene–ethanol is accompained by a significant amount of isomerization ($X = Cl > Br > I$).[266] Stopping a $Rh(PPh_3)_3Cl$-catalyzed deuteration of cyclooctane at 50% completion has shown that the unreduced olefin contains an average of 0.4 deuteriums per molecule, with d_0–d_4 species present.[267] This large collection of data requires a revision of the mechanism such that a two-step hydride transfer process from rhodium to substrate occurs. Stepwise rather than simultaneous addition of hydrogens during olefin hydrogenation is indicated by deuteration[268] and olefin isomerization studies[261]; in many cases, however, the second transfer may be so rapid that for all practical effects it may be considered concerted and simultaneous.

The third point of controversy involves the possibility of an operative unsaturated path for activation of H_2. Candlin and Oldham[261] have assembled impressive display of evidence, much of which contracts a great deal of data from the Wilkinson group papers (such as catalytic reduction of ethylene by $Rh(PPh_3)$ Cl and $Rh(PPh_3)_2(C_2H_4)Cl$). The weakness of the Candlin–Oldham data, as pointed out by Wilkinson,[257] lies in their use of impure substrates (no mention of purification techniques is given in the article); peroxide impurities would invalidate all data.

Several groups have investigated the effect of oxidizing agents on catalytic hydrogenation by Rh $(PPh_3)_3$ Cl. Van Bekkum *et al.*[269] have found that oxygen or hydrogen peroxide in amounts equivalent to catalyst concentration increase the rate of catalysis. Infrared studied have shown that free phosphine oxide is present in solution. The H_2 uptake rate for cyclohexene with one equivalent of oxidant is approximately that for the system with $PPh_3/Rh = 2$ obtained by treating $[Rh(C_8H_{14})_2Cl]_2$ with PPh_3. Table XXI shows how the rate varies with oxidizing agent to catalyst ratio.

TABLE XXI.[269] Rate Variation with Oxidizing Agent to Catalyst Ratio for RhL_3Cl System.

H_2O_2/Rh	0	0.2	0.4	0.6	0.8	1.0	1.2	1.4
Initial rate H_2 uptake[a]	7.4	10.1	11.2	12.2	12.5	12.9	12.7	10.8

[a] H_2 uptake in ml min^{-1}, 50 cm H_2, 25° C.

Augustine and Van Peppen[268,272] have carried out extensive research on the species actually present in oxidant-treated solutions of $Rh(PPh_3)_3Cl$. They have found that ethanol blocks dissociation of the complex and that no isomerization occurs in benzene with $O_2/Rh = 1$ unless ethanol is present; thus they have concluded that isomerization is due to undissociated catalyst. In benzene they have observed formation of $Rh(PPh_3)_2(O_2)Cl$, but the presence of hydroxylic solvents (methanol, ethanol) results in what is formulated as an oxide-bridged dimer, with each rhodium bonded to O_2. In the preference of hydrogen, these oxide dimers are converted to a slow, isomerization-prone catalyst species; but if two equivalents of PPh_3 are added, H_2 produces a complex which rapidly reduces 1-heptene with no isomerization.

$Rh(PPh_3)_3Cl$ is probably the organometallic homogeneous hydrogenation catalyst most widely used by organic chemists. Wilkinson's group[239] has reported that at 25° C, 1 atm H_2, the catalyst does not effect the following functional groups: $\supset C=O$, –OH, –CN, –NO, –N=N–, Cl, –O–, CO_2H. Harman *et al.*[273] have reported that $Rh(PPh_3)_3Cl$ at 60° C, 60–80 psig H_2, reduces only the carbon–carbon double bond of α,β-unsaturated acids, esters, aldehydes, ketones, nitriles, and nitro compounds. Utilization of asymmetric phosphines in the catalyst systems RhL_3Cl[274,275] and RhL_2Cl[276] has produced optical yields on hydrogenation of up to 15%; much lower enantiomeric efficiency of reduction (1%) results when the asymmetric center is on a carbon chain rather than at the phosphorous with the major exception for $Rh(PPh_2R)_3Cl$ (R = neomenthyl). In this case a degree of chirality is obtained even greater than that of ligands with asymmetry at P, with special enantiomeric efficiency in reduction of α,β-unsaturated carboxylates. $Rh(PPh_3)_3Cl$ has been shown to be active even with a 2.5 molar excess of C_6H_5SH for reduction of 1-octene and dehydrolinalol (with only slight inhibition).[277] Several groups[250,278–282] have utilized the difference in rates for di- and trisubstituted polyenes for selective reduction. Using high H_2 pressure and catalyst concentration with low substrate concentration, Jardine and Wilkinson[283] have shown that $Rh(PPh_3)_3Cl$ preferentially hydrogenates the double bond of α,β-unsaturated aldehydes rather than extract CO from the aldehyde; the bromide and iodide complexes, however, are more prone to the CO extraction side-reaction. Reduction of 4-t-buthylmethylenecyclohexene with a series of complexes $Rh(PAr_3)_3Cl$ (where PAr_3 is a ring substituted analogue of PPh_3) has resulted in a *cis/trans* product ratio of 70:30 with non isomerization except with *ortho* substituted phosphines.[173] $Rh(PPh_3)_3Cl$ has been used to reduce only the carbon–carbon double bond between the two *para* keto groups of naphthoquinone and juglone; quinone itself is converted in two stages to hydroquinone, while quinones of high oxidation potential destroy the catalyst.[284] The chloride catalyst is also selective for reduction of disubstituted double bonds in 1,4-dihydroaromatics, leaving only the tetra-substituted internal double bond (little or no rearrangement to aromatic species as heterogeneous catalysts cause).[285] $Rh(PPh_3)_3Cl$ has also been reported to reduce conjugated 1,4-dienes in refluxing benzene or chloroform.[286] In i-propanol with added $P(OMe)_3$ the 3-keto group of 5-β-androstane-3,17-dione is reduced to the alcohol with 50:1 axial:equatorial specificity.[162]

(ii) IrL_nCl

The complex IrL_3Cl[287,288] where $L = PPh_3$, $AsPh_3$ and $SbPh_3$ reacts readily with H_2 to form the stable dihydride IrL_3H_2Cl; but this complex does not hydrogenate olefins because the dihydride remains completely associated and no substrate can enter the coordination sphere.

The very recently discovered system IrL_2Cl,[289] obtained from treatment of the dimer $[Ir(C_8H_{14})_2Cl]_2$ with the appropriate amount of ligand ($L = PPh_3$, $AsPh_3$) is, however, a most active catalyst. The formulation of catalyst composition as IrL_2Cl is inferred from a maximum rate at $L/Ir = 2$. This double unsaturated Ir^I complex (whose coordinatively unsaturated Ir^{III} dihydride can now complex the substrate easily) is a most effective catalyst for the reduction of 1-hexene, ten times more reactive than the corresponding Rh^I system. The initial rate drops off sharply because of rapid isomerization of the hex-1-ene to a mixture of 2-hexenes, which are reduced at a rate only 1/180th as fast as 1-hexene. Isomerization is probably due to very strong Ir–H bonds (relative to Rh–H) which allow the intermediate alkyl–hydride to drop back to olefin–dihydride before the second hydride transfer occurs.

I. Miscellanous Dihydrides

The d^8 complex $Ru(PPh_3)_2(CO)_3$ adds H_2 only photochemically[290] to give the unstable $Ru(PPh_3)_2(CO)_2H_2$. This dihydride reacts with cyclohexene (with or without light) to form cyclohexane.

The iridium–acetate system $IrH_2(PPh_3)_3(OAc)$ reduces[293] aldehydes and "activated" olefins catalytically at 50° C, 1 atm H_2. The catalyst is formed by treatment of the trihydride $Ir(PPh_3)_3H_3$ with acetic acid, HOAC. Reduction fails to occur with just $Ir(PPh_3)_3H_3 + H_2$ in neat aldehyde (showing that the trihydride is not a catalytically active species); addition of acetic acid, however, causes a rapid reaction forming the alcohol. In toluene, octenes are not hydrogenated, but acrylic acid and methyl acrylate are converted to propionic acid and methyl proprionate respectively (at a rate about one third that of aldehyde reduction).

The catalyst system $[Ti(\pi\text{-}C_5H_5)]_n$ can be obtained from $Ti(\pi\text{-}C_5H_5)_2$,[290] $(\pi\text{-}C_5H_5)_2Ti(CO)_2$[291] or $(\pi\text{-}C_5H_5)TiMe_2$.[292] It has been reported to reduce olefins, and to reduce alkynes to a mixture of olefins and alkenes (50–60° C, 50 atm H_2 in benzene or heptane). For $RC{\equiv}CH$, reduction goes as R = Ph > t-Bu > n-alkyl; for $R'C{\equiv}CR'$ reduction decreases as R' = Ph > n-alkyl–. With $PhC{\equiv}CH$, one equivalent on H_2 gives 30% $PhCH_2CH_3$ and 40% $PhCH{=}CH_2$ but with $HC{\equiv}C\text{–}C_3H_7$, one equivalent of H_2 forms only the olefin product.

Reduction of Rh^{III} salts in the presence of amino acids with phenyl groups (*e.g.* tyrosine or α-phenylalanine) yields Rh^I half sandwich complexes with the aromatic ring of the amino acid acting as a π-acceptor ligand.[294,295] These complexes are reported to hydrogenate various unsaturated compounds including aromatics (reducibility goes has anthracene > benzene > naphthalene) under mild conditions. With an asymmetric center in the amino acid (*e.g.* L-tyrosine), the ketone function of acetoacetic ester is reduced with a significant degree of asymmetry to ethyl-β-hydroxybutyrate.

A catalyst system, Rh^I–maleic acid complex is generated in dimethylacetammide (DMA) by treatment of $[Rh(C_8H_{14})Cl]_2$ with LiCl and maleic acid or by reduction of $RhCl_3 \cdot 3H_2O$ by H_2 in the presence of maleic acids (MA).[296–298] The labile system probably involves $[Rh(MA)_2Cl_2]^-$, $[Rh(MA)Cl_3]^{2-}$ and $[Rh(MA)(DMA)Cl_2]^-$ species. This catalyst reduces maleic acid to succinic acid at 50–85° C, 1 atm H_2, at a rate given by $k_2[Rh][H_2]$. The hydrogenation is inhibited by addition of excess maleic acid which is postulated to produce an inactive complex $[Rh(MA)_2Cl_2]^-$. Rhodium metal precipitates when all substrate has been consumed.

During their studies on activation of small molecules Chan and James[331] found that benzene or N,N'-dimethylacetamide(DMA) solutions of iridium(I) cyclooctene complex $[(C_8H_{14})IrCl_2]$ (10^{-4} to 10^{-3} *M*) react with H_2 rapidly at ambient conditions to produce iridium metal. This is a powerful heterogeneous catalyst. Benzene and monoolefins are readily hydrogenated to the saturated products. After completion of the hydrogenations, metal was always formed, indicating that olefin coordinates and stabilizes Ir(I) against hydrogen reduction to the metal. Kinetic studies have shown that the rates were first order in H_2 up to 1 atm and were first order in catalyst.

The nature of the Ir species in DMA is not yet established.

Van der Est and coworkers published a report[300] on the activity of benzene solutions of the cyclooctene iridium(I) complex (in presence of 0–3 mols of triphenylphosphine per Ir) for the hydrogenation of hexenes.

The stable catalyst $Rh(C_2H_4)_2Cl_2$ is formed[296] by the action of ethylene on $RhCl_3 \cdot 3H_2O$ in DMA at 80° C. At 40° C and 1 atm H_2 the catalyst reacts with hydrogen and ethylene to produce ethane.

The system $[M(L\text{–}L')]^+X^-$ (M = Rh, Ir) has been studied; with M = Ir, the series $Ir[R_nZ(CH_2)_rZR_n]_2{}^+Cl^-$ ($1 \leqq r \leqq 4$ and Z = P, As, S) has been studied. The iridium complexes react with H_2 to form stable dihydrides (*e.g.* $[Ir(diphos)_2H_2]^+$). At 150–175° C, 1200 psig H_2, the iridium systems are hydrogenation catalysts with the following substrate and catalyst activates; alkynes > alkenes and $IrBr(Ph_2PCH_2CH_2SPh)_2 < IrCl(diphos)_2 < IrBr(CO)(diphos)_2$. The complex $Rh(diphos)_2$, less basic than the analogous iridium complex, does not form a stable adduct with H_2 but at 115° C, 1 atm H_2, it does reduce 1-octene while Ir(diphos)Cl fails.[38,301]

5. Miscellaneous Hydrogenation Catalysts

The class of catalyst system represents a “grab bag” collection of complexes which are known to hydrogenate unsaturated compounds but whose methods of hydrogen activation have not been established in the literature.

A. Ziegler-type Catalysts

Ziegler catalysts have been used primarily for polymerization of certain olefins and dienes. Many of these polymerization catalysts (the systems consist of transition metal salts – halides, carboxylates, acetylacetates – plus reducing agents, with or without ligands present) have also been reported to reduce olefinic and acetylenic compounds. Depending on the individual system, either the monohydride or dihydride pathway of hydrogenation may be utilized.

The publication most often cited as the first major paper on hydrogenation catalyzed by Ziegler-type catalysts is that by Sloan, Mathck and Breslow.[302] Using 30–50° C and 3.7 atm H_2 with reducing agent ALR_3 (*e.g.*, $AlEt_3$) or AlR_3H^-, a range of olefins (cyclohexene > 1-octene > *trans*-2-pentene > 2-methyl-2-butene > *trans*-stilebene > tetramethylethylene) has been hydrogenated by the following series of compounds: $Ti(O\text{-}iPr)_4$; $Ti(\pi\text{-}C_5H_5)_2Cl_2$; $Zr(\pi\text{-}C_5H_5)_2Cl_2$; $VO(O\text{-}nBu)_3$; $Cr(acac)_3$; $Co(PPh_3)_2Cl_2$; $MeO_2(acac)_2$; $Mn(acac)_3$; $Ni(PBu_3)_2Cl_2$; $Mn(acac)_2$; $Fe(acac)_3$; $Pd(PBu_3)_2Cl$ and $Ru(acac)_3$. The series of acetylacetonates found to be the most efficient follows the sequence $Co^{III} > Fe^{III} > Cr^{III}$. The mechanism of catalyst formation postulated by the authors involves a zero or low valent complex (formed by reaction with the aluminium reductant) adding H_2 to follow the dihydride mechanism; evidence to this type of catalyst has been found for the $Cr(acac)_3$–$AlEt_3$ system in which the active catalyst is suggested to be a Cr^0 species.[303]

Another publication of significance is that bv Kroll[304] who has reported that with $AliBu_3$ catalytic activity follows the sequence $Co(acac)_2 > Ni(acac)_2 > Fe(acac)_3$. Best rates are found for the ratios Al/Co = 6, Al/Ni = 6 and Al/Fe = 9; stabilization of the catalyst by AlR_3 is postulated, except at large excess. No isomerization of olefins is observed unless H_2 is present: substrates are hydrogenated in the order: cyclohexene < 1-hexene < phenylacetylene.

The chemical literature contains a long series of papers[304–309] dealing with catalyst systems similar to those explored by Kroll and by Sloan, Mathachk and Breslow. Several cobalt, nickel and iron Ziegler systems have been tried for reduction of polyenes.[310–312] These catalyst show little tendency to carry the reduction past the monoene stage.

Many investigations have been conducted into the catalytic properties of Ziegler systems containing π-cyclopentadienyl ligands. Stern and coworkers[313] have found that various $Ti(\pi\text{-}C_5H_5)_2X_2$ (where X = Cl, OPh, SPh) with aluminium hydrides reduce olefins in the order terminal > cyclic > di-substituted > tri-substituted, while tetrasubstituted alkenes are not hydrogenated. Taima and Kunioka[314] have studied a range of metal–cyclopentadienyls (using BuLi or PhMgBr as reductant) for hydrogenation of conjugated dienes and have concluded that the π-cyclopentadienyl ligand greatly inhibits rates of catalysis.

A most interesting system is that noted by Lapporte and Schuett.[315,316] The catalyst is obtained by treating a metal salt MY_2 with AlR_3 in heptane, benzene, *etc.*; the effectiveness follows the orders Y = 2-ethylhexanoate > $PhCO_2$ > acac > OAc > Cl and M = Ni > Co > Fe > Cr > Cu (22° C, 4 atm H_2). The systems reduce alkynes and conjugated polienes very exothermically and hydrogenate aromatic rings (*e.g.,* benzene, xylenes, phenol, pyridine, and naphthalene, one ring much faster) faster than known heterogeneous catalysts. The nickel system works best for Al/Ni = 3–4. Ketones are reduced to alcohols, and olefins are hydrogenated with relative facility (terminal > methylenes > cyclic > disubstituted). The nickel and cobalt catalysts are specially good for reduction of polystyrene rings. Slow isomerization, even without H_2 present, is seen during reduction of alkenes. The active catalyst itself, in the nickel case (with $AlEt_3$), is diamagnetic and involves Ni–H and Ni–C_2H_4 intermediates (n.m.r.). The catalyst may be a Ni(O) species (possibly the same that trimerizes butadiene which Wilke[317] terms "bare" nickel atoms with very labile ligands). Other researchers[318,319] have observed very similar facts with this type of Ziegler catalyst.

Unsaturated organic polymers are an industrial-type class of substrates which are hydrogenated with difficulty even by heterogeneous catalysts. Certain Ziegler systems of Ni, Co, Fe and Cr have been reported to reduce a variety[320] of polymers under relatively mild conditions, such as polybutadiene[321,322] and butadiene–styrene copolymer.[323]

B. Assorted Other Catalysts

(i) $M(NO)(PPh_3)_2X_2$ (M = Co,Rh,Ir; X = Cl,I, maleic anhydride)

Using the above nitrosyl in C_6H_6 or THF, a moderate rate for hydrogenation of 1-hexene (also isomerization) and cyclohexene has been obtained at 25° C and 5 atm H_2, with M = Co, Rh, Ir. When NEt_3 is added, a white precipitate forms ($HNEt_3^+I^-$) and the rate increases somewhat.[198,200]

The cobalt nitrosyls $Co(NO)P_2X_2$ (P = Ph_3P, Ph_2MeP, and X = Cl, I) in presence of H_2 were shown not to catalyse hydrogenation or isomerization of terminal olefins. Reduction of these cobalt complexes by a stoichiometric amount of $NaBH_4$ produces a rapid hydrogenation and isomerization of 1-hexene, and hydrogenation of cyclohexene with an appreciable rate.[200] The catalyst active form may involve $M(NO)(PPh_3)_3HX$ (monohydride), $M(NO)(PPh_3)_2H_2$ (dihydride), or a combination of two paths.

Reaction of the maleic anhydride complexes $M(NO)(P(C_6H_5)_3)_2$(maleic anhydride) (M = Rh, Ir), prepared by simple ligand exchange as reported by Cenini *et al.*,[324] with H_2 (4 atm) for five hours in dichloromethane at 25° C followed by addition of 1-decene with stirring at 4 atm H_2 produced only very slow reduction of 1-decene (much slower than that catalyzed by the saturated rhodium nitrosyl); the iridium maleic anhydride complex was found to be approximately five times as active as its rhodium analogue.[198]

Use of the unsaturated species L_2MNO theoretically obtained by reduction of the dihalonitrosyl *in situ* (with various reducing agents $LiAlH_4$, Zn, $NaBH_4$, Mg, Redal) failed to produce highly active homogeneous systems for reduction of terminal olefins. 1-decene was rapidly reduced under 1 atm H_2 over a slurry of reduced dihalonitrosyl $RhCl_2(NO)L_2$ (L = $P(C_6H_5)_3$, $P(CH_3)(C_6H_5)_2$, or $P(n\text{-}C_4H_9)_3$) and sodium amalgam, but catalytic activity was reduced to levels comparable to that of $RhNO(P(C_6H_5)_3)_3$ when the supernatant solution was filtered under an inert atmosphere to remove any rhodium metal formed in the amalgam reduction. The similarly reduced iridium solution after filtration was a moderately active catalyst for reduction of terminal olefins[198] at 25° C, in marked contrast with the saturated nitrosyl $IrNO(P(C_6H_5)_3)_3$ which is inactive under these conditions. Use of the H_2 plus base reducing system for rhodium dichloronitrosyls formed a solution only moderately active for catalytic hydrogenation: a nitrosyl species was demonstrated to be present by solution infrared of reduced $RhCl_2(NO)(P(CH_3)(C_6H_5)_2)_2$ showing ν(N–O) at 1605 cm^{-1}.

(ii) $Cu_2(OAc)_2$ *in quinoline*[1,325,326]

In quinoline (Q), cuprous acetate catalyzes the reduction of quinone to hydroquinone. The complex is thought to form the dimer $(CuQ)_2H_2$ (in the rate-determining step) which then reduces the quinone. Quinone inhibits the reaction by complexation with the catalyst; 2,3-5,6-tetrachloroquinone forms such a strong complex that no reduction is observed.

(iii) M–M bridged carboxylates

The first system[327] of this type has been obtained by treating the bridged carbocylates with an acid HX ($X = FSO_3$, F, BF_4, CF_3SO_3) and PPh_3 in MeOH, forming cationic M–M dimers with coproducts free carboxylic acid and uncoordinated anion X^-. The resulting complexes catalyse rapid reduction of organic substrates (conjugated dienes–alkynes > alk-1-enes > *cis*-internal olefins > cycloalkenes), as well as oxo and carbonylation reactions. Catalyst activity follows the order $Ru(O_2CMe)_4Cl > Rh_2(O_2CMe)_4 > Mo_2(O_2CMe)_4$; the ruthenium system requires $AgClO_4$ to remove Cl.

A second system[328] has been formed by dissolution of bridged carboxylate in a polar solvent, S, forming the species $S_2M_2(O_2CMe)_4$ where S = DMA, THF, EtOH, *etc.* and M = Rh, Ru. Solvent is coordinated on the terminal positions of the dimer and is very labile. This solvent activated system is not as effective as the protonated; but it is not destroyed by O_2 (reduced to H_2O), does not require added phosphine, and allows starting materials to be recovered intact. $Rh_2(O_2CMe)_4$ reduces ethylene and terminal and cyclic olefins ($\leqq$ 1 atm H_2, 25–80° C); it reduces diethylmaleate but not the fumarate. The same complex with M = Ru hydrogenates the substrates listed for M = Rh and also *trans*-alkenes and dienes. The active catalyst is non-ionic, and no evidence for paramagnetism has been found; non change in the electronic spectrum results on addition of H_2, olefin, or both together. A kinetic study for the rhodium system (1 atm H_2, 50° C, DMA) with 1-decene has shown the rate law to be first order in dimer and H_2, with substrate between zero and first-order. Hui and Rampel[328] have suggested that reduction proceeds only at one rhodium atom, for the induced hydridic character of hydrogens on coordination of a single rhodium of the dimer results in deactivation of the other rhodium (due to a shift of electron density back to the first rhodium). A mechanism fitted to the kinetic study has been proposed in Diagram 22:

Diagram 22

$$Rh_2(O_2CMe)_4 + H_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H_2Rh_2(O_2CMe)_4 \xrightarrow[\text{olefin}]{k_3} \text{alkane} + Rh_2(O_2CMe)_4$$

(iv) $[Ni_2(CN)_6]^{4-} + H^+CN^-$

This system may function analogously to $Co(CN)_5{}^{3-}$ a radical path. A patent report[329] has noted the conversion of acetylene to ethylene at 0–60° C. A more recent publication[330] has shown that $Ni_2(CN)_6{}^{4-}$ alone stoichiometrically reduces maleic acid with hydrogen extracted from the solvent water; in D_2O, the product is 2,3-d_2-succinic acid. For reduction of crotonic acid, the rate increases as pH decreased and $[CN^-]$ rises. Addition of $NaBH_4$ to $Ni(CN)_4{}^{2-}$ results in a catalytic cycle.

(v) Ruthenium carbonyls

Reduction of nitrobenzene to aniline[331] has been reported to be catalyzed by several ruthenium carbonyls as $Ru(CO)_5$, $Ru_3(CO)_{12}$, and after an induction period $Ru(acac)_3$. High pressures of synthesis gas (100 atm H_2) have been used at 140–160° C; CO is oxidized to CO_2 in the process. For $CO:H_2 > 1$, a side reaction begins to produce N,N′-diphenylurea; at $CO:H_2$, a 66% of aniline is obtained with no urea, but at 3.1 $CO:H_2$, the yields of aniline and urea are 57% and 21% respectively. To account for the side reaction, a mechanism has been proposed which involves a binuclear bis-nitrene intermediate; at lower $CO:H_2$ ratios, this intermediate undergoes hydrogenolysis to give aniline, while for larger $CO:H_2$ ratios carbonyl insertion may precede hydrogenolysis to form the urea.

(vi) Ru^I *in amides*

An early article[332] has reported that ruthenium(II) in DMA or DMF reduces simple olefins (*e.g.* ethylene and cyclohexene). A more recent paper by Hui and James[333] has reported data that suggest the so called "Ru^{II}" is actually converted to a ruthenium(I) species which is the active catalyst. Treatement of "$RuCl_3 \cdot 3H_2O$" in DMA at 25° C, 1 atm with H_2 rapidly forms pure ruthenium(III) which is then slowly reduced to blue ruthenium(II). If the temperature is then raised to 60° C, the blue solution turns brown, Ru^I form for which no Ru–H is detected in the n.m.r.; both reductions are first-order in Ru and H_2. This ruthenium(I) solution at 80° C, 1 atm H_2, catalyzes hydrogenation of maleic acid. The reaction has a rate law showing the following dependence:

$[H_2]^1$, $[\text{substrate}]^{0-1}$ and $[Ru]^{1/2}$. The authors have suggested the mechanism presented below:

Diagram 23

$$Ru^{I}_{2} \xrightleftharpoons{K} 2Ru^{I} + H_2 \xrightleftharpoons[k_1]{k_1} Ru^{I}H_2 \xrightarrow[\text{substrate}]{k_2} \text{product} + Ru^{I}$$

(vii) Miscellaneous

A lot of other systems are found to catalyze homogeneous hydrogenation of organic compounds.

$Zr(CH_2Ph)_4$,[334] reacts with H_2 (1 atm, 50° C) to produce toluene and a complex that reduces aromatic rings (1 atm, 50° C) and terminal olefins (some isomerization) even at 0° C, 1 atm H_2. The analogous titanium complex is inactive because the Ti–C bond is too strong to be hydrogenolyzed (Ti–C less polar than Zr–C because of titanium lower electronegativity).

Aqueous solutions of $NiSO_4$ have been reported[335] to reduce cyclohexanone, benzene, and 2-pentene.

$Ru_3(CO)_{10}(NO)_2$, a cluster with bridging nitrosyls has been observed to catalyze a small amount of hydrogenation of 1-hexene (in benzene, 5 atm H_2) with extensive isomerization.[336]

In DMF various metal salts (Rh, Ru, Ir, Mo) stabilized by chloroquinone or mesitylene catalyze[337] rapid reduction of olefins at 25° C, 1 atm H_2.

The CoF_2–NaF system has been reported[338] to hydrogenate ethylene and butadiene in aqueous solution.

Nickelocene has been reported[339] to react with H_2 at 50° C in THF (400 psig) to form $Ni(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_7)$; an induction period is required. With D_2, the product is $Ni(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_5D_2)$, which mass spectroscopic data shows to contain *cis*-deuteriums. A report in the patent literature[340] has noted that polyethylene (from CrO_3/SiO_2 + ethylene) is converted on treatment with H_2 and $Ni(\pi\text{-}C_5H_5)_2$ from terminal unsaturation only to a lower degree of unsaturation, with some internal olefinic bonds formed.

A series of metal acetylacetonates has been reported[341] to hydrogenate unsaturated (polyene) fatty acid esters in methanol at 100–180° C, 100–1000 psig H_2. The effectiveness of the catalysts ranks as $Ni(acac)_2 > Co(acac)_3 > Ci(acac)_2 > Fe(acac)_3$. The catalysts are stereoselective towards greater degrees of unsaturation: k(linolenate)/k(linoleate) = 3.4 and k(linoleate)/k(oleate) = 20. The mechanism postulated involves a metal hydride which slowly conjugates double bonds and then rapidly reduces the conjugated system to a lone, isolated double bond.

Tulupov and coworkers[342–349] have reported hydrogenation of cyclohexene in ethanol at 20° C, 1 atm H_2 for a large series of metal stearates: cobalt(II), nickel(II), manganese(II), chromium(III), iron(III), copper(II) and zinc(II).

A system comprising $Ni(acac)_2$–$PhP(i\text{-}OPr)_2$–$NaBH_4$ has been reported to catalyze reactions between 1,3-dienes and active hydrogen compounds[252,253,254]. Nickel salts have been used to catalyze reactions of active hydrogen compounds and butadiene.[355]

C. Homogeneous Supported Catalysts

For many years, it has been customary to classify catalysts as "homogeneous" or "heterogeneous". The former commonly operate through the formation of "intermediate compounds", and the latter by adsorption of the reactants on the catalyst surface. The line between the two is a fine one, for the distinction between adsorption and compound formation is not all clear, and seems to be becoming less and less clear as we learn more about adsorption. In recent years, several writers[356,357,358] have stressed the point that there is a good deal of overlap between homogeneous and heterogeneous catalysis. Experimental evidence supporting this point of view is accumulating, and while we are not prepared to say that there is no distinction, we can say with certainty that many homogeneous catalysts can be converted into heterogeneous ones, retaining the advantages of great activity and selectivity inherent in homogeneity, and, at the same time, assuming the ready recovery which is the great advantage of heterogeneity.

The catalytic properties of most compounds, however, are dependent upon the properties of ions and their immediate surroundings. Soluble catalysts of this type can be heterogenized if they can be attached to a stable base without disturbing the catalytic center. For example, benzenesulfonic acid, which is insoluble, is a heterogeneous acid catalyst. Reactions carried out with these two types follow the same kinetics. Similarly, Manassen has shown that polybenzenequinones catalyze oxidative dehydrogenation heterogeneously in the same manner that benzenequinone does homogeneously. He has shown similar effects in hydroformylations, hydrogenations, and oxidations, and has concluded that, in general, in the field of organic catalysis, the solid state properties of the catalyst have little influence.

Biochemists have known for many years that enzymes, which are the catalysts for many biological reactions, are bound to cell walls and other membranes.[359]

Haag and Whitehurst, at Mobil Oil Company, have been pioneers in the field of heterogenizing homogeneous catalysts for industrial use[360]. They have prepared salts of $[Pd(NH_3)_4]^{2+}$ with both simple and polymeric counter ions. In another piece of work,[361] these authors caused sodiumdiphenylphosphide to react with a chloromethylated polystyrene (cross-linked with divinyl benzene):

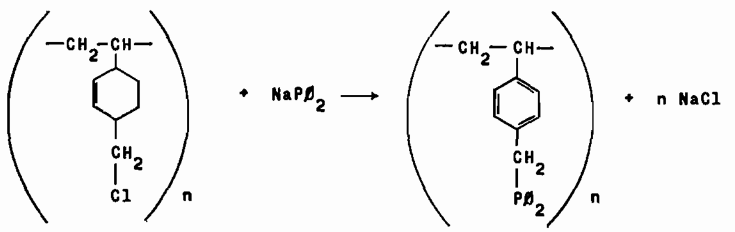


Diagram 24

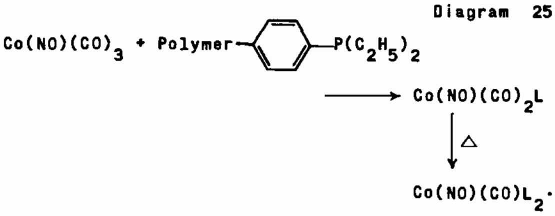
The resultant polymer was caused to coordinate with rhodium chloride to give an active catalyst for hydrogenation. Bruner and Bailar[362] followed this lead in preparing similar complexes containing palladium(II) chloride and platinum(II) chloride, which they used in the selective hydrogenation of soybean methyl ester. As in previous work with the homogeneous catalysts, $[Pd(PPh_3)_2Cl_2]$ and $[Pt(PPh_3)_2Cl_2]$, they found the palladium complex to be more active than the one containing platinum.[363] The latter required activation by tin(II) chloride. Reaction of the polymeric phosphine with the metal salts is slow and incomplete.

The heterogeneous palladium complex is not as thermally stable as its platinum analog.[364] With the palladium complex at reaction temperatures above 90° C, less hydrogenation was observed and black speacks (supposedly metallic palladium) were found in the recovered polymer. The platinum complex, even with added tin chloride, was not active below 150° C. Analysis of the recovered polymer showed a change in composition, but, after the addition of more tin(II) chloride, the catalyst was still active.

Grubbs and Kroll[365] made a further advance in this technology, when they prepared a similar catalyst containing rhodium(I) and showed that the rate of hydrogenation of olefins with this catalyst depends to a large extent upon the size and shape of the olefin molecule. Increasing the ring size of cyclic olefins reduced the rate at which they were hydrogenated, as did changing from acyclic to cyclic olefins. As the authors suggest, this indicated that most of the hydrogenation took place inside the polystyrene bed. They found that their catalyst gained activity up to a maximum as it was used repeatedly.

Collman and his coworkers[366] have made another advance by treating the polystyrene–phosphine polymer with metallic complexes such as $IrCl(CO)(P(C_6H_5)_3)_2$. The $P(C_6H_5)_3$ groups were eliminated to give MCl $(CO)L_2$ (L = the resin). Similarly, two PPh_3 groups and one ethylene group were eliminated from RhCl $(PPh_3)_2C_2H_4$ to give $RhClL_3$. They found that the polymer chain was flexible enough to form chelate rings. They also reported some cases in which the phosphine groups were not eliminated. Thus, the polymeric phosphine reacts with $[Rh(COD)Cl]_2$ to give a 1:1 complex by splitting the chloro bridge. They also observed the reactions

Diagram 25



All of these complexes show the same catalytic reactions as their monomeric analogs, but have somewhat longer lives.

Finally, Collman's group has prepared polynuclear complexes from the multinuclear $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$. These, like the others, were active catalysts for hydrogenation of arenes.[366]

New classes of homogeneous supported catalysts have been recently reported by Allum *et al.*,[367] reacting rhodium(I) complexes with amberlite resins, silica and silica–PPh_2.

The catalyst prepared from amberlite HAD-2 and $[RhCl(COD)]_2$ catalyses the hydrogenation of 1-hexene and cyclohexene at 55° C in benzene. The catalyst prepared from silica and $RhCl(CO)(PPh_2PCH_2CH_2Si(OEt)_3)_2$; (140° C, benzene) catalyzes the same hydrogenations.[367]

TABLE XXII. Rates of Reduction with Polymer Attached Titanocene.

Olefin (~ 0.5 M in hexane)	Rate of reduction, ml of H_2/min (1 atm of H_2)
40 mg of Catalyst (in 10 ml of hexane)	
1,3-Cyclooctadiene	1.81
1,5-Cyclooctadiene	1.54
Styrene	2.05
3-Hexyne	1.26 (hexane)
1-Hexene	1.80
1-Hexyne	Polymer
Cholestenone	0
Vinyl acetate	0
420 mg of Catalyst	
Diphenylacetylene	3.62 (eq)
Cyclohexene	8
1-Methylcyclohexene	0.92
1,2-Dimethylcyclohexene	0

Grubbs *et al.*,[368] have found that treatment of chlorobis(cyclo-octadiene)rhodium(I) dimer with a 3-equiv excess of polystyryl–diphenylphosphine (prepared from 20% divinylbenzene–styrene macroreticular copolymer) produces a good hydrogenation catalyst when reacted with (π-C_5H_5)$TiCl_2$. The results are summarized in Table XXII.

The polymer obtained from the reaction of easily accessible macroreticular chloromethylated styrene–divinylbenzene (20% crosslinking) and benzene solution of lithiodiphenylphosphine reacts with $RhCl_3 \cdot 3H_2O$ affording a substance which catalyzes the hydrogenation of 1-heptene to heptane (with some isomerization).[369]

6. Future Trends in Hydrogenation Homogeneous Catalystic

There obviously remain many organometallic systems yet to be explored which will catalyze hydrogenation of unsaturated organic compounds. As the excitement among chemists concerning the general novelty of homogeneous hydrogenation dies down (as it now appears to be doing from the relative paucity of paper concerning the subject in the current literature), research in this area will be directed more to finding new catalysts systems which are "*super*stereoselective" and "*super*stereospecific", for particular uses in organic syntheses, especially for industrial applications; a type of organometallic compound which has been little investigated is that of various metal clusters which may provide a new mechanism for hydrogenation. More work will also be aimed at theoretically developing parameters by which complexes may be examined to determine their catalytic abilities. Thus homogeneous hydrogenation should remain a quite significant topic in chemistry for many years to come.

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