3
Ruthenium and Osmium

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3.1
Introduction

There is much current excitement and activity in the field of homogeneous hydrogenation using ruthenium catalysts. This is reflected in the recent, explosive increase in the number of research publications in this area, now rivaling those for rhodium catalysts (Fig. 3.1). Meanwhile, the price of rhodium metal has risen dramatically, becoming about ten times that of ruthenium, on a molar basis. The number of reports on the use of osmium catalysts has remained low, partly because of the higher price of osmium compounds – about ten times that of ruthenium – and partly because the activity of osmium catalysts is often lower.

During the early years of catalyst development (1960–1980), rhodium chemistry dominated the scene, led by the investigations, for example, of Wilkinson, Kagan, Osborn, and Knowles [1]. The more complex catalytic chemistry of ruthenium was slower to develop, starting with studies by Halpern [2] and Wilkinson [3] during the 1960s. This continued with an exploration of the types of ruthenium complexes that were active hydrogenation catalysts in the 1970s, as reviewed by James [4, 5]. During the 1980s the search for new chemistry for synthesis gas (CO, H_2) and coal utilization to combat petroleum shortages (the "energy crisis") shifted attention to Ru and Os complexes, and promising activity was found for the hydrogenation of difficult substrates such as arenes, simple ketones, nitriles, and esters. For both economic and scientific reasons, attention then shifted to enantioselective hydrogenations using ruthenium complexes. Japanese scientists were on the crest of this new wave, with Noyori leading the way. Noyori was awarded the Nobel prize for this work in 2001 and his lecture has subsequently been published [6, 7].

The current research areas with ruthenium chemistry include the effective asymmetric hydrogenation of other substrates such as imines and epoxides, the synthesis of more chemoselective and enantioselective catalysts, CO_2 hydrogenation and utilization, new methods for recovering and recycling homogeneous catalysts, new solvent systems, catalysis in two or three phases, and the replace-

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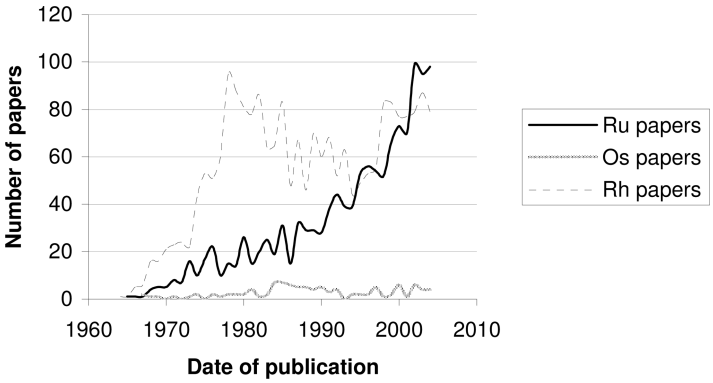


Fig. 3.1 Graphical illustration of numbers of reports per year versus date of publication. Data were obtained by searching the Chemical Abstracts Database using the term "hydrogenation catalyzed by ruthenium complexes" or osmium complexes or rhodium complexes. These are not comprehensive searches but are still representative of the activity in the field.

ment of phosphine ligands with other donors such as stable carbene and nitrogen donors.

3.2 Ruthenium

3.2.1 The First Catalysts for Alkene Hydrogenation: Mechanistic Considerations

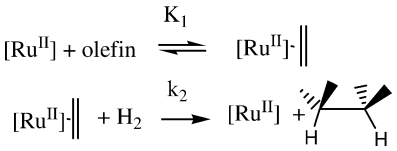
In 1961, Halpern's group reported that the water-soluble, activated alkenes, fumaric, acrylic and maleic acid, could be catalytically hydrogenated in a solution containing chlororuthenium(II) species at 70 to 90 °C and 1 bar H_2 [2]. Interest in such chloro complexes grew out of reports about their electron-transfer behavior, a topic of interest at the time due to the extensive studies of Taube and others. Details of the hydrogenation of maleic acid are provided in Table 3.1. The kinetics of this system were thoroughly investigated by H_2 uptake measurements and spectroscopy, and the rate law was consistent with a mechanism where the alkene first binds to the metal in a pre-equilibrium followed by the turnover-limiting reaction of the alkene complex with dihydrogen where hydrogen is added *cis* on the double bond, as in Scheme 3.1.

Chatt and Hayter reported the first ruthenium and osmium hydride complexes of the type $MHCl(PR_2CH_2CH_2PR_2)_2$ in 1959, but these are not catalysts [9, 10]. Subsequently, in 1965, Wilkinson and coworkers found that the reaction of $RuCl_2(PPh_3)_3$ with hydrogen and a base gave the hydride complex $RuHCl(PPh_3)_3$, a very active hydrogenation catalyst [3]. A modern interpretation

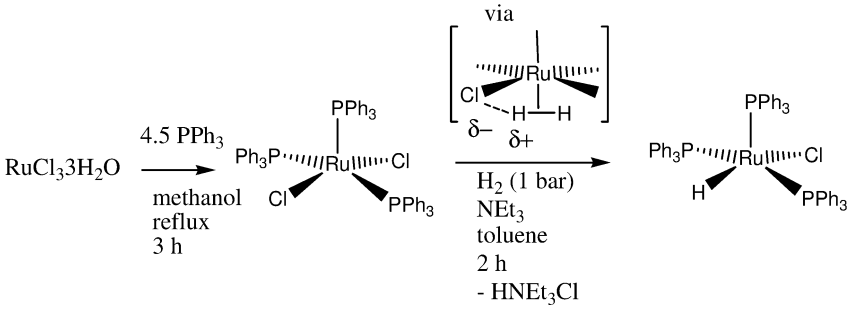
Table 3.1 Representative conditions for the hydrogenation of alkenes.

	Precatalyst (Ru)	Substrate (S)	S:C	Solvent	p(H_2) [bar]	Product	Conversion [%]	Temp [°C]	TON	TOF [h^{-1}]	Reference
1	$[RuCl_6]^{4-}$ by reduction of $[RuCl_6]^{2-}$ with $TiCl_3$	Maleic acid (*cis*-HOOCCH=CHCOOH) (0.061 M)	100	3 M HCl	1	Succinic acid	100	80	100	3	8
2	$RuHCl(PPh_3)_2$	1-Octene (1.1 M)	1400	Toluene	0.66	Heptane		25	1400	$<1\times10^{4}$ a)	12
3	$RuCl_2(PPh_3)_2$	Maleic acid	100	Dimethyl-acetamide	1	Succinic acid	100	35	100	10 b)	4
4	Ru(1,5-COD)(1,3,5-COT)	1,3,5-Cycloheptatriene	46	THF	1	Cycloheptene	90	37	46	7	39
5	$Os(\eta^2\text{-}H_2)HCl(CO)(P^iPr_3)_2$	Styrene	100	*i*PrOH	1	Ethylbenzene	100	60	100	1200	123

a) With other conditions constant as listed, the TOF varies with the alkene concentration as $TOF = 2.1\times10^4$ [octene]/(1.3+[octene]).
b) TOF varies depending on the concentration of several species; the rate law and kinetic parameters have been reported [4].



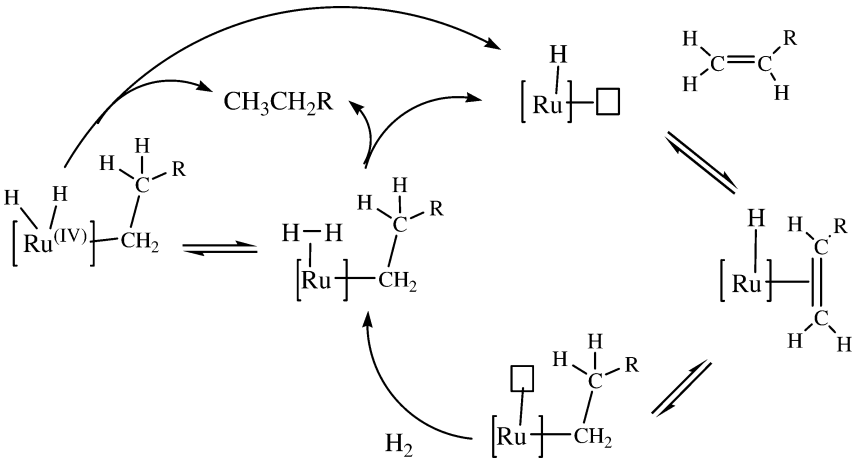
Scheme 3.1



Scheme 3.2 Preparation of the alkene hydrogen catalyst $RuHCl(PPh_3)_3$.

of the formation of the hydride is that it proceeds via an acidic η^2-dihydrogen complex [11] (Scheme 3.2). This monohydride complex is an extremely active and selective catalyst for the hydrogenation of 1-alkenes in benzene at 25 °C [3, 12]. The turnover frequency (TOF) for 1-octene hydrogenation is about 10^4 h^{-1} for the mild conditions listed in Table 3.1, entry 1 (e.g., 0.66 bar H_2, 25 °C), and this changes with the alkene concentration, as listed. Disubstituted alkenes are hydrogenated about 1000-fold more slowly. The catalyst is only soluble to the extent of 10^{-4} M in toluene. It is about 20 times more active than the well-known alkene hydrogenation catalyst $RhCl(PPh_3)_3$ under similar conditions [12].

It has been a challenge to determine the mechanism of catalysis of this very oxygen-sensitive system (the current view is summarized in Scheme 3.3). $RuHCl(PPh_3)_3$ is an unusual case of a coordinatively unsaturated (5-coordinate) d^6 complex. The three bulky triphenylphosphine ligands prevent the coordination of other large ligands. In the catalytic reaction, this complex reacts with the alkene substrate to form an unstable alkyl intermediate by hydride addition to the double bond. In the turnover-limiting step, dihydrogen coordinates and becomes acidic. Proton transfer to the alkyl carbon releases the hydrogenated product with retention of configuration at carbon, and regenerates the starting hydride. The hydrogenolysis of a ruthenium–carbon bond via protonation by an acidic dihydrogen ligand *cis* to the alkyl has become a well-accepted mechanism [11, 13, 14], and would provide the observed *cis* stereochemistry of the addition of dihydrogen to the double bond. The formation of an alkyl intermediate is supported by the observation that the related complex $RuH(OC(O)CF_3)(PPh_3)_3$ reacts with ethylene in the absence of H_2 to give, reversibly, an ethyl complex $Ru(Et)(OC(O)CF_3)(PPh_3)_3$. Such a β-addition/elimination of hydride explains why such monohydride complexes are alkene isomerization catalysts. This po-



Scheme 3.3 Mechanism for the hydrogenation of 1-alkenes catalyzed by $RuHCl(PPh_3)_3$. [Ru] represents the $RuCl(PPh_3)_n$ fragment. The box represents an empty coordination site on ruthenium(II).

tentially undesirable side reaction may have been a reason why rhodium catalysts were favored over Ru(II) catalysts during the early days of these studies. Most rhodium catalysts proceed through a dihydride intermediate that hydrogenates, but does not isomerize, alkenes.

Quantitative rate measurements under a variety of conditions support such a mechanism [4, 15]. A complete kinetic analysis is available for the hydrogenation of acrylic acid derivatives using the precatalysts $RuCl_2(PPh_3)_3$ in the solvent dimethylacetamide, although the system is much less active in this more polar and coordinating solvent (e.g., entry 3, Table 3.1).

The triphenylphosphine complexes of the type $RuCl_2(PPh_3)_3$, $RuHX(PPh_3)_3$, X=Cl, O_2CR, etc., $RuH_2(PPh_3)_4$, $RuH(CO)X(PPh_3)_3$, $RuCl_2(CO)_2(PPh_3)_2$ all proved to be catalysts for a variety of reductions, although the carbonyl complexes tended to require higher temperatures [5]. For example, the last complex is a catalyst for the selective hydrogenation of 1,5,9-cyclododecatriene to cyclododecene in dimethylformamide (DMF) at 140 °C and 10 bar H_2 in the presence of PPh_3 [16]. The complex $RuCl_2(PPh_3)_3$ proved active in the hydrogenation of the C=C bond in *α,β*-unsaturated ketones by hydrogen transfer from formic acid or benzylalcohol [17]. Later, it was demonstrated that the addition of base greatly accelerates such transfer reactions by promoting the formation of hydride species, as reviewed elsewhere [18, 19]. Thus, $RuCl_2(PPh_3)_3$ in the presence of a base catalyzes the transfer of hydrogen to ketones or imines from *i*PrOH or formic acid [18]. Transfer hydrogenation reactions will be discussed further in Chapters 20 and 32.

3.2.2
Synthesis of Ruthenium Precatalysts and Catalysts

The modification of these precursor compounds with other ligands, including a vast array of chiral phosphorus-donors, has resulted in an ever-expanding list of useful ruthenium hydrogenation catalysts, as described in the following sections. Figure 3.2 illustrates how the PPh_3 ligands of $RuCl_2(PPh_3)_3$ are readily displaced by a wide range of ligands to produce new catalysts. The reaction with diphosphines with medium bite angles (dppb, diop, binap) (Fig. 3.3) produces complexes $RuCl_2$(diphosphine)(PPh_3) that are used as catalysts for the hydrogenation of 1,3-diketones [20], the hydrogenation of benzonitrile [21], and the hydrogenation of imines [22]. The dppb complex can be converted to the binuclear dihydrogen complex $(\eta^2\text{-}H_2)$(dppb)Ru$(\mu\text{-}Cl)_3$Ru(dppb)Cl, which is a precatalyst for the hydrogenation of styrene and aldimines [23, 24]. The reactions with P-N ligands (chiral phosphinooxazolines [25] or phosphine-imines [26]) produce $RuCl_2(PPh_3)$(P-N) precatalysts for the enantioselective transfer hydrogenation of ketones. The reaction with diamines such as ethylene diamine produces $RuCl_2(PPh_3)_2$(diamine) complexes for the efficient H_2-hydrogenation of simple ketones [27] (see below). The reaction with 2 equiv. of chiral β-aminophosphine ligands produces $RuCl_2(P\text{-}NH_2)_2$, very active enantioselective hydrogenation cat-

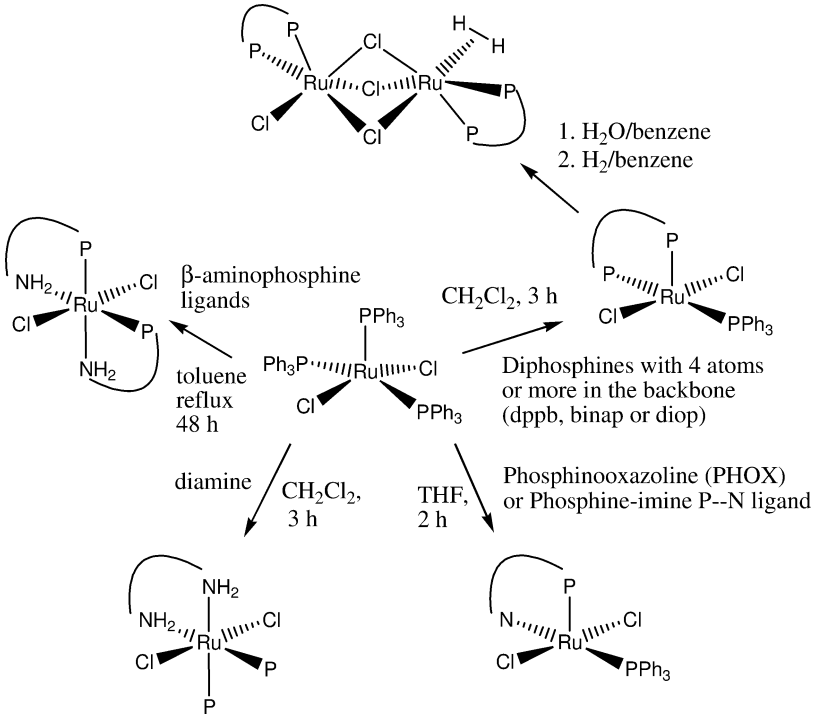


Fig. 3.2 Synthetic routes to ruthenium precatalysts starting from $RuCl_2(PPh_3)_3$.

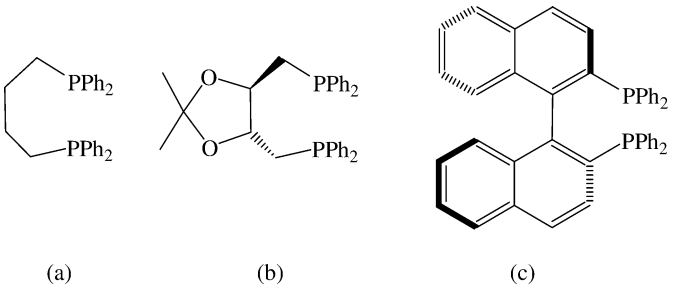


Fig. 3.3 The structures of diphosphines with four atoms in the backbone: (a) dppb; (b) (–)-(*R*,*R*)-diop; (c) (*R*)-binap.

alysts for ketones and imines [28, 29]. Finally, the reaction with water-soluble sulfonated tri-arylphosphines (not shown in Fig. 3.2) produces water-soluble complexes such as $[RuCl_2(P(C_6H_4\text{-}m\text{-}SO_3Na)_3)_2]_2$ that catalyze the H_2-hydrogenation of aldehydes in water [30] and $[RuCl_2(PPh_2(C_6H_4\text{-}m\text{-}SO_3Na))_2]_2$ which, in the presence of excess phosphine, selectively hydrogenates the C=C bond of α,β-unsaturated aldehydes at pH 3 but switches to selectively hydrogenating the aldehyde C=O at pH 9 [31].

The PPh_3 ligands in $RuHCl(PPh_3)_3$ can be displaced in a similar fashion to produce a range of analogous precatalysts such as $RuHCl(diamine)(PPh_3)_2$ and *trans*-RuHCl(diamine)(diphosphine). When the former diamine compound is activated with alkoxide base under H_2, it is an active catalyst for ketone and imine hydrogenation [32, 33], while the latter is a precatalyst for the asymmetric hydrogenation of imines and ketones under mild conditions [34, 35].

The compounds $[RuCl_2(C_6H_6)]_2$ [36] (Fig. 3.4 a), $Ru(\eta^3\text{-methylallyl})_2(COD)$ [37] (Fig. 3.4 b), COD = η^4-1,5-cyclooctadiene and $[RuCl_2(COD)]_n$ [38, 39] are also very useful starting materials that are commercially available. The complex $RuCl_2(dmso)_4$ [40] in Figure 3.4 c has relatively labile ligands. The starting material Ru(COD)(COT) [38] (Fig. 3.4 d) is a source of Ru^0 complexes and the dihydrogen complex $RuH_2(H_2)_2(PCy_3)_2$ (see Fig. 3.6). The complex Ru(COD)(COT) is also a useful catalyst for the hydrogenation of trienes to monoenes (see Table 3.1, entry 4) [39].

The structure of $[RuCl_2(COD)]_n$ is not well defined, but it is a very useful starting material to catalysts (Fig. 3.5). Its reaction with binap (see Fig. 3.3) and NEt_3 can lead to the chloride-bridged dimer $[NEt_2H_2][Ru_2Cl_5(binap)_2]$, or with sodium acetate to the excellent catalyst precursor $Ru(binap)(OAc)_2$ (see below). The former complex [41] was originally thought to be $Ru_2Cl_4(binap)_2(NEt_3)$ [42]; however, the ethyl group in NEt_3 appears to undergo an interesting fragmentation reaction. It is an excellent precatalyst for the enantioselective hydrogenation of dehydroamino acids [24, 41–43]. The reaction of the $Ru(\eta^3\text{-methylallyl})_2(COD)$ complex with enantiopure diphosphines, and then with HBr, yields catalyst solutions thought to contain a solvated form of $RuBr_2$(diphosphine) that are useful for the asymmetric hydrogenation of functionalized alkenes and ketones in-

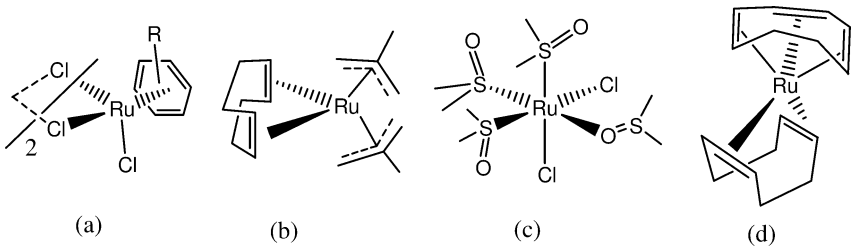


Fig. 3.4 Useful starting ruthenium complexes.

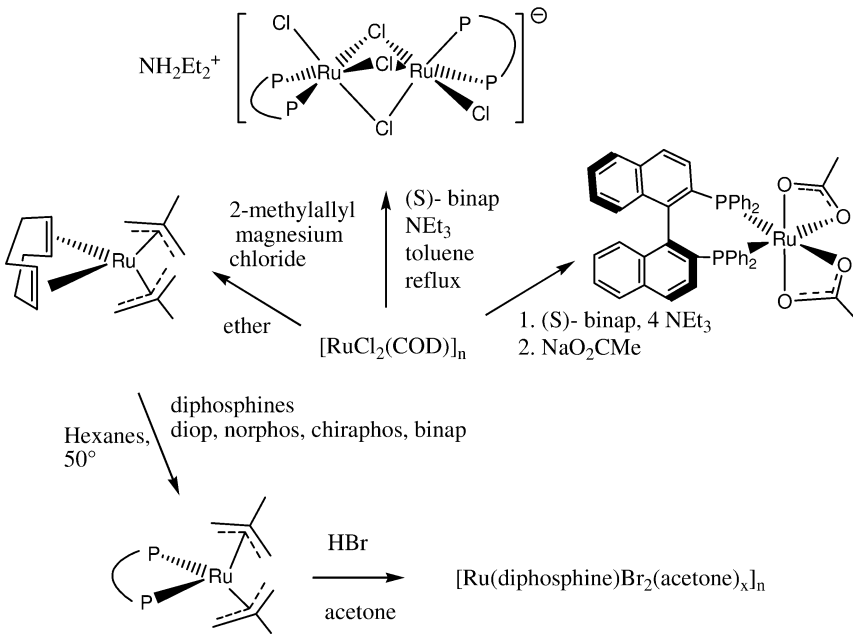


Fig. 3.5 Reactions starting with $[RuCl_2(1,5\text{-cyclooctadiene})]_n$.

cluding unsaturated acids, β-ketoesters, and allylic alcohols [44, 45]. The π-allyl complex can also be reacted with chiral diphosphines and HBF_4/BF_3 to generate a very active hydrogenation catalyst for tetrasubstituted alkenes that are precursors to fragrances [46].

3.2.3
Dihydrogen Complexes and Non-Classical Hydrogen Bonding in Catalysis

Schemes 3.2 and 3.3 show intermediates containing dihydrogen ligands with the H–H bond intact. It has only been appreciated since the discovery of the first dihydrogen complexes by Kubas and coworkers in 1984 [14] that such complexes are key intermediates in catalytic cycles [11, 13, 14].

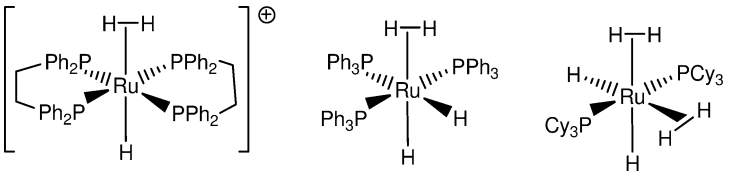


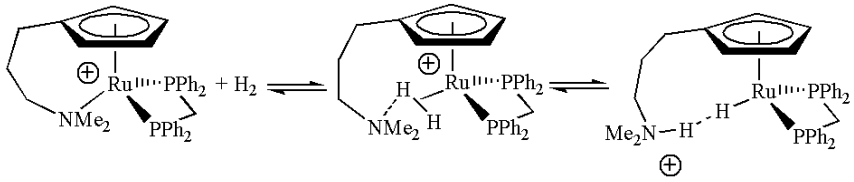
Fig. 3.6 The dihydrogen complexes $[Ru^{II}(\eta^2\text{-}H_2)H(dppe)_2]^+$, $Ru^{II}(\eta^2\text{-}H_2)(H)_2(PPh_3)_3$ and $Ru^{II}(\eta^2\text{-}H_2)_2(H)_2(PCy_3)_2$.

Before 1984, the oxidative addition of H_2 to square-planar Ru^{II} to produce octahedral Ru^{IV} ($H_2 + [Ru^{II}] \rightarrow [Ru^{IV}](H)_2$) was thought to be the turnover-limiting step in this cycle (c.f., the left equilibrium of Scheme 3.3) by analogy to rhodium systems. The discovery that the complexes $[RuH_3(diphosphine)_2]^+$ [47] and $RuH_4(PPh_3)_3$ [48] are not seven-coordinate Ru^{IV} structures but instead are octahedral, Ru^{II} complexes $[Ru(\eta^2\text{-}H_2)H(diphosphine)_2]^+$ and $Ru(\eta^2\text{-}H_2)(H)_2(PPh_3)_3$ (Fig. 3.6) supports the inner pathway of Scheme 3.3. The dihydrogen ligands in these complexes have H–H distances of 0.94 Å [49] and about 1.1 Å, respectively, longer than that of free H_2 at 0.74 Å. Even $RuH_6(PCy_3)_2$ [50, 51] retains an octahedral, Ru^{II} configuration.

Dihydrogen complexes display a wide range of acidity or, in other words, a propensity to undergo heterolytic splitting. The neutral dihydrogen complexes of Figure 3.6 have approximate pK_a^{THF} values of about 36–40 [52] (similar to cyclohexanol in THF), while the cationic complex has a value of about 14 [53]. Dicationic complexes in CH_2Cl_2 containing a π-acid ligand become very acidic; for example, *trans*-$[Ru(\eta^2\text{-}H_2)(CO)(PPh_2CH_2CH_2CH_2PPh_2)_2]^{2+}$ has a $pK^{CH_2Cl_2}$ value of –7 relative to $HPCy_3^+/PCy_3$ defined as 9 [54]. Such values are determined by measuring an equilibrium constant, usually by use of nuclear magnetic resonance (NMR), for a reaction of the dihydrogen complex with a base, the conjugate acid of which has a known pK_a value [52]. For example, the dihydrogen complex $[Ru(\eta^2\text{-}H_2)(\eta^2\text{-}C_5H_5)(dppm)]^+$, dppm = $PPh_2CH_2PPh_2$, has an approximate pK_a^{THF} of about 7.3 as determined from the equilibrium constant of Eq. (1) [52].

$$[Ru(\eta^2\text{-}H_2)(C_5H_5)(PPh_2CH_2PPh_2)]^+ + PBu_3 \rightleftharpoons RuH(C_5H_5)(PPh_2CH_2PPh_2) + HPBu_3^+ \quad (1)$$

The easy heterolytic splitting of dihydrogen in such cationic cyclopentadienyl complexes can be exploited in the hydrogenation of CO_2. Lau and coworkers found that heating solutions of $[(\eta^5,\eta^1\text{-}C_5H_4(CH_2)_3NMe_2)Ru(dppm)]BF_4$, under H_2/CO_2 (40 bar/40 bar) at 80 °C for 16 h gave formic acid in low yields (TON = 8) [55]. These authors proposed that dihydrogen undergoes heterolytic splitting into a hydride and a proton on the amine as shown in Scheme 3.4, and that the hydride and proton then react with the CO_2 to produce formic acid. This ligand-assisted splitting of dihydrogen is also observed in the enantioselective hydrogenation of tiglic acid and in the Noyori ketone hydrogenation catalysts (see below). A feature of such a reaction is that when the dihydrogen is deprotonated by the base in a



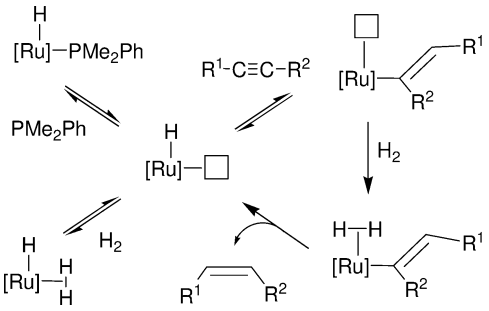
Scheme 3.4 The heterolytic splitting of dihydrogen at Ru(II) to give a hydridic-protonic bond, as proposed by Chu et al. [55] in the mechanism of the homogeneous hydrogenation of carbon dioxide.

low-dielectric solvent such as toluene or THF, the protonated base can donate a non-classical hydrogen bond (also referred to as a dihydrogen bond [56]) to the hydride, as shown in Scheme 3.4. This type of MH···HN or MH···HO hydrogen bond was discovered by Crabtree's group [58] and Morris' group [59] in 1994, and can have an energy of several kcal mol^{-1} and have an H···H distance of 1.8–2.3 Å. These are now known to be important features of mechanisms of reactions involving transition metal hydrides.

A related chiral complex $[Ru(\eta^2\text{-}H_2)(\eta^5\text{-}C_5H_5)(chiraphos)]^+$ has been used for the enantioselective outer-sphere hydrogenation of iminum salts [60].

The cationic complexes $[RuH(\eta^2\text{-}H_2)(PP_3)]BPh_4$, $PP_3 = P(CH_2CH_2PPh_2)_3$ [61] and $[RuH(L)(PMe_2Ph)_4]PF_6$, $L = PMe_2Ph$ [62] or $\eta^2\text{-}H_2$ [63], are catalysts for the selective hydrogenation of alkynes to alkenes, even in the presence of added alkenes. The PMe_2Ph compounds are sources of $[RuH(PMe_2Ph)_4]^+$ that hydrogenates terminal and internal alkynes in the presence of excess PMe_2Ph, probably as shown in Scheme 3.5. The alkyne coordinates to ruthenium and is attacked by the hydride to give an intermediate vinyl species. This is hydrogenolyzed, probably via proton transfer from an acidic η^2-dihydrogen ligand situated cis to the vinyl. However, the alternative oxidative addition of dihydrogen and reductive elimination of the hydrogenolyzed product has not been ruled out. 1-Hexyne is hydrogenated to 1-hexene with an initial TOF of 4 h^{-1} at 1 bar H_2, 30 °C. Steric effects of the phosphine ligands in $[RuHL_5]^+$ are very important. The rate is smaller, the smaller the cone angle of the phosphine used ($PMe_2Ph > PMe_3 > P(OMe)_3$) [64].

The $[RuH(\eta^2\text{-}H_2)(PP_3)]BPh_4$ complex is also thought to operate by the mechanism of Scheme 3.5, and the hydrogenolysis step is shown to be turnover-limiting [61]. A representative TOF for 94% conversion of phenylacetylene to styrene is 376 h^{-1} at 40 °C, 5 bar H_2 with a turnover number (TON) of 940 [61]. At higher pressures the TOF is reduced, probably because the dissociation of H_2 from the starting dihydrogen complex is quickly reversed. Terminal alkynes can undergo a side reaction where they couple to form other complexes that are inactive or less active as hydrogenation catalysts. This coupling is prevented in the case of the PMe_2Ph systems by adding excess PMe_2Ph. The complex $[Ru(COD)(H)(PMe_2Ph)_3]PF_6$ is, under H_2 gas, a source of $[RuH(PMe_2Ph)_3(solvent)_2]^+$; this species is a very active hydrogenation catalyst for alkynes and alkenes, although



Scheme 3.5 Hydrogenation of alkynes to alkenes catalyzed by $[RuH(\eta^2\text{-}H_2)(P(CH_2CH_2PPh_2)_3)]BPh_4$ ([Ru] = $[Ru(P(CH_2CH_2PPh_2)_3)]^+$) or $[RuH(PMe_2Ph)_5]PF_6$ or $[RuH(\eta^2\text{-}H_2)(PMe_2Ph)_4]PF_6$ ([Ru] = $[Ru(PMe_2Ph)_4]^+$). The square represents a vacant site on ruthenium.

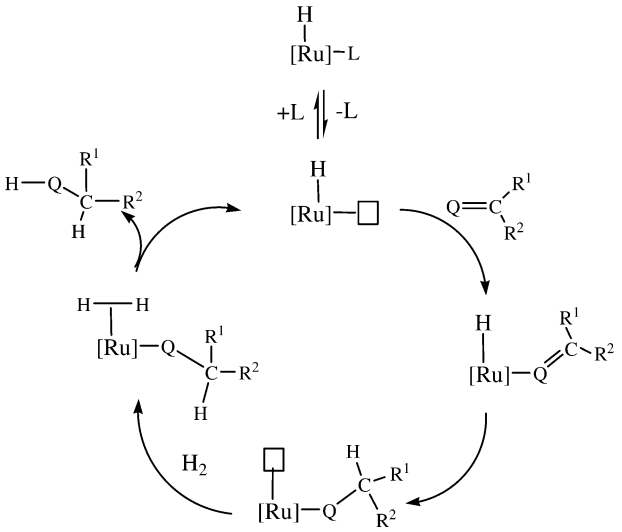
the system deactivates rapidly for terminal alkynes [64]. The rate of hydrogenation to cis alkenes increased as 1-hexyne < 2-hexyne < 3-hexyne.

3.2.4
Toward the Reduction of Simple Ketones, Nitriles, Esters and Aromatics with Monodentate Phosphine Systems

At the end of the 1970s, chemists were focusing on applying ruthenium catalysts to enantioselective hydrogenation reactions (see below), and to the hydrogenation of more difficult substrates such as simple ketones, nitriles and esters and reactions related to coal and synthesis gas (H_2/CO) chemistry. Important to the utilization of coal (and lignin [65]) is the hydrogenation of arenes and polycyclic aromatics. The very oxygen- and water-sensitive anionic hydride complexes $K[RuH_2((C_6H_4)PPh_2)(PPh_3)_2]$ and $K_2[Ru_2H_4(PPh_2)(PPh_3)_3]$ were reported by Pez and coworkers to catalyze a variety of difficult hydrogenations, including simple ketones to alcohols (e.g., acetone to *i*PrOH in toluene, 80 °C, 6 bar, TON 380, TOF 24 h^{-1}), esters activated with CF_3 groups to the alcohols (90 °C, 6 bar, toluene), nitriles to amines with selectivities up to 90% for the primary amine (acetonitrile to ethylamine in toluene, 90 °C, 6 bar, TON 150, TOF 8 h^{-1}) [66], and anthracenes to 1,2,3,4-tetrahydroanthracenes. The rate of ketone hydrogenation tripled when 18-crown-6 was added to complex the potassium.

Linn and Halpern later found that the active catalyst in the ketone and anthracene hydrogenation reactions of Pez was likely to be $Ru(\eta^2\text{-}H_2)(H)_2(PPh_3)_3$ (Fig. 3.6) [67]. For example, cyclohexanone is converted to cyclohexanol under mild conditions in toluene (see Table 3.3). The TOF depends on the substrate concentration, and the rate law for the catalytic reaction was determined to be given by Eq. (2), with $k = 1.3 \times 10^{-3}$ M^{-1} s^{-1} at 20 °C.

$$\text{Rate} = k[RuH_4(PPh_3)_3][\text{ketone}] \qquad (2)$$

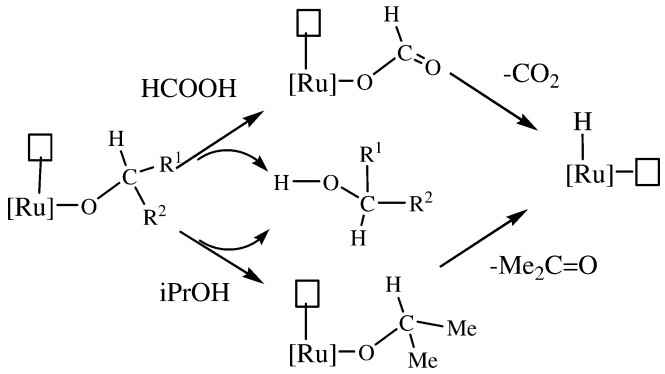


Scheme 3.6 Conventional mechanism for the H_2-hydrogenation of aldehydes, ketones (Q=O) and imines (Q=NR). Ruthenium remains as Ru^{II} throughout the cycle. The square represents a vacant site on ruthenium.

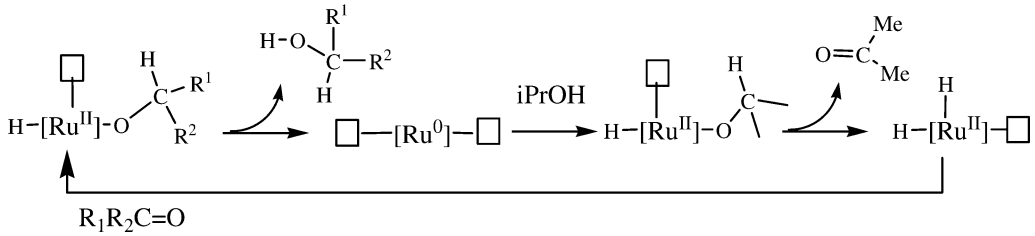
Linn and Halpern proposed a mechanism where the lack of a dihydrogen concentration dependence in the rate law of Eq. (2) was rationalized by the canceling effects of a pre-equilibrium H_2 dissociation and then rate-determining re-addition step. In this mechanism, H_2 dissociates from $RuH_4(PPh_3)_3$ when the ketone coordinates, an alkoxide intermediate $RuH(OR)(PPh_3)_3$ forms, and then H_2 re-coordinates to this intermediate in the rate-determining step. This is followed by the rapid elimination of alcohol and reaction with H_2 to reform $RuH_4(PPh_3)_3$. These steps are commonly proposed for inner-sphere hydrogenation mechanisms (HI) of carbonyl compounds (Scheme 3.6, [Ru]=$RuH(PPh_3)_3$, Q=O, L=H_2) [19]. Note the striking similarities between Schemes 3.3 and 3.6.

Directly related to the cycle shown in Scheme 3.6 is the mechanism of transfer-hydrogenation of ketones and imines catalyzed by, for example, $RuCl_2(PPh_3)_3$/base or $RuH_2(PPh_3)_4$ solutions in *i*PrOH. Here, instead of the H_2 in Scheme 3.6, the *i*PrOH solvent, formic acid or formate is the source of H^+/H^- for regeneration of the starting hydride catalyst, as shown in Scheme 3.7. In the case of dihydride catalysts, Scheme 3.8 has been proposed [18]. Note that the former mechanism involves β-hydride elimination from formate or alkoxide that maintains a Ru^{II} oxidation state, while the later mechanism involves reductive elimination of an alkoxide and hydride with a resulting reduction of the metal to Ru^0.

More recently, dihydrogen complexes have been patented for nitrile hydrogenation. For example, the complex $Ru(\eta^2\text{-}H_2)_2(H)_2(PCy_3)_2$ (Fig. 3.6) catalyzes the hydrogenation of adiponitrile to hexamethylenediamine (HMD) in toluene at 90 °C, 70 bar H_2 with TON 52, TOF 5 h^{-1} [68]. At intermediate conversions, the



Scheme 3.7 Generation of the active hydride catalyst by hydrogen transfer from formic acid or *iso*-propanol via β-hydride elimination from formate or alkoxide intermediates. The square represents a vacant site on ruthenium.



Scheme 3.8 Generation of the active dihydride catalyst by transfer hydrogenation by reductive elimination of the product to give a ruthenium(0) intermediate ([Ru]=$Ru(PPh_3)_3$).

system displays an interesting, non-statistical reduction of the two CN groups, giving a higher ratio of aminocapronitrile to HMD than expected.

Several ruthenium systems catalyze the hydrogenation of aromatic rings, and this topic is detailed in Chapter 16. An early example reported by Bennett and coworkers was that of $RuHCl(\eta^6\text{-}C_6Me_6)(PPh_3)$, which catalyzed the hydrogenation of benzene to cyclohexane at 25 °C, 1 bar H_2 [69]. Since ruthenium colloids are very active for this reaction under certain conditions, there is evidence that at least some of the reported catalysts are heterogeneous [70].

The hydrogenation of esters remains a challenge. Some recent progress has been reported by Teunissen and Elsevier [71, 72] where a mixture of $Ru(acac)_3$ and $MeC(CH_2PPh_2)_3$ was used to hydrogenate aromatic and aliphatic esters to the alcohols in MeOH at 100–120 °C with 85 bar H_2.

The use of $Ru(acac)_3$ under very high temperature (268 °C) and pressure (1300 bar of H_2/CO) in THF provides a catalyst for the hydrogenation of carbon monoxide to methanol and methyl formate [73]. The active species is derived from $Ru(CO)_5$.

3.2.5 Enantiomeric Hydrogenation of Alkenes with Bidentate Ligand Systems

More than one-half of the reports in Figure 3.1 are associated with asymmetric hydrogenation and its application in organic synthesis. The first studies from the groups of James and Bianchi in the 1970s involved Kagan's readily prepared chiral, chelating ligand (–)-diop (see Fig. 3.3), in ruthenium complexes such as $Ru_2Cl_4(diop)_3$ [74], *trans*-$RuHCl(diop)_2$ [5], and $Ru_4H_4(CO)_8(diop)_2$ [75]. The chloro complexes were moderately active and selective for the hydrogenation of acrylic acid derivatives (Table 3.2). A kinetic study revealed that the active catalyst contained only one diop ligand per ruthenium [76].

Complexes containing one binap ligand per ruthenium (Fig. 3.5) turned out to be remarkably effective for a wide range of chemical processes of industrial importance. During the 1980s, such complexes were shown to be very effective, not only for the asymmetric hydrogenation of dehydroamino acids [42] – which previously was rhodium's domain – but also of allylic alcohols [77], unsaturated acids [78], cyclic enamides [79], and functionalized ketones [80, 81] – domains where rhodium complexes were not as effective. Table 3.2 (entries 3–5) lists impressive TOF values and excellent ee-values for the products of such reactions. The catalysts were rapidly put to use in industry to prepare, for example, the perfume additive citronellol from geraniol (Table 3.2, entry 5) and alkaloids from cyclic enamides. These developments have been reviewed by Noyori and Takaya [82, 83].

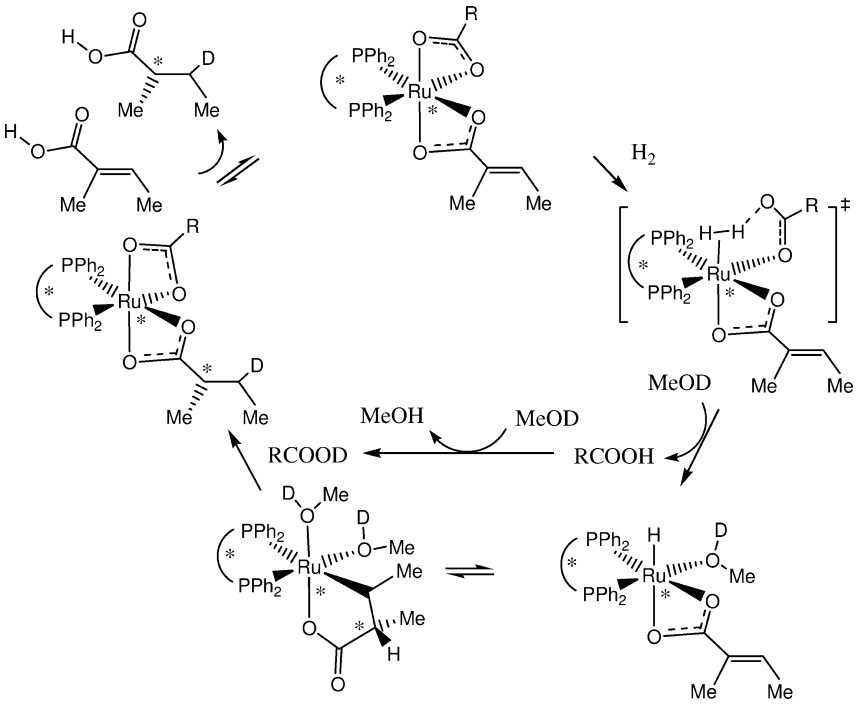
Ashby and Halpern deduced the mechanism of the hydrogenation of tiglic acid catalyzed by $Ru(binap)(OAc)_2$ in MeOD [84]. This is shown in Scheme 3.9, with some modification to accommodate more recent knowledge of the heterolytic splitting of dihydrogen assisted by a ligand [57]. In the turnover-limiting addition of dihydrogen, this molecule splits into a hydride on the metal and a proton on the carboxylate ligand. The enantioselectivity of the process is directed by the binap ligand ((*S*)-binap in this case) that sets the chirality at the metal (Δ in this case) and the carbon on the C=C double bond to which the hydride adds. The difference from the classical alkene hydrogenation mechanism of Scheme 3.3 is that the alkyl intermediate is protonated by the carboxylic acid and not by a dihydrogen ligand. The evidence for this is the selective formation of (*S*)-3-deutero-2-methylbutanoic acid when MeOD is used as the solvent.

By contrast, a recent, detailed mechanism of the enantiomeric hydrogenation of α-(acylamino)acrylic esters catalyzed by $Ru((S)\text{-binap})(OAc)_2$ follows that of Scheme 3.3, where both H atoms from the dihydrogen add to the C=C double bond [85]. The high enantioselectivity of the process is produced, in part, by the chelation of the alkene substrate via the C=C double bond and by a carbonyl oxygen of the substrate [86].

Table 3.2 Representative conditions for the enantiomeric hydrogenation of alkenes.

	Precatalyst (Ru)	Substrate (S)	S:C	Solvent	p(H_2) [bar]	Product	Conversion [%]	ee [%]	Time [h]	Temp. [°C]	TON	TOF [h^{-1}]	Reference
1	Ru_2Cl_4((–)-diop)$_3$	Atropic acid H_2C=CPh(COOH) (0.2 M)	50	Dimethyl-acetamide	1	(*R*)-2-phenyl-propionic acid	100	40		60	50	8	127
2	Ru_2Cl_4((–)-diop)$_3$	2-Acetamidoacrylic acid	50	Dimethyl-acetamide	1	(*S*)-acetylalanine	100	59		60	50	1	127
3	"Ru_2Cl_4((*S*)-binap)$_2$-NEt_3" (now thought to be NEt_2H_2-[Ru_2Cl_5((*S*)-binap)$_2$])	PhHC=C(COOH) (NHCOPh)	80	EtOH/THF (NEt_3 added)	2	(*R*)-phenylalanine derivative	100	>90	<24	35	80	>3	42
4	Λ-Ru((*R*)-binap)-$(O_2CMe)_2$	Tiglic acid MeHC=C-MeCOOH (0.05 M)	500	MeOH	1	(*R*)-EtCMeH-(COOH)	100	93 (*R*)	0.3	21	500	<4000 [a]	128
5	Δ-Ru((*S*)-binap)$(O_2CCF_3)_2$	Geraniol (5.8 M)	20000	MeOH	30	(*R*)-citronellol	100	92 (*R*)	13	20	20000	1500	77
6	[RuH((*R*)-binap)-$(NCMe)_{3-n}(sol.)_n]^+$	(*Z*)-methyl-*R*-acetamidocinnamate (0.13 M)	50	Acetone	4	(*R*)-$PhCH_2$CH-(COOMe) (NHCOMe)	100	92 (*R*)	96	30	980	54	129

a) TOF varies with alkene concentration as TOF = 8×10^4 [alkene] h^{-1}.

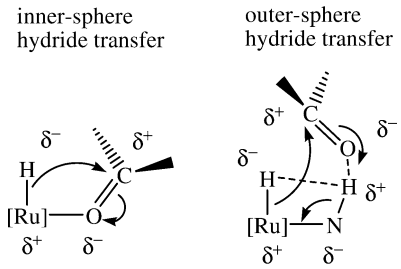


Scheme 3.9 A possible mechanism of the hydrogenation of tiglic acid catalyzed by Ru((*S*)-binap)$(OAc)_2$ (as adapted from [84]). The stereochemistry of the metal center and coordination geometries are speculative at this stage.

3.2.6
Enantiomeric Hydrogenation of Carbonyl Compounds

Complexes of the type RuX_2(diphosphine), where X is a halogen or carboxylic acid (see Fig. 3.5), are precatalysts for the hydrogenation of ketones that have a functional group such as an ester carbonyl or amino group in the vicinity of the C=O bond so that the two groups can chelate to the metal [45, 80, 81]. The mechanism is thought to involve a monohydride route (as shown in Scheme 3.6), with a step that involves an inner-sphere transfer of hydride to the carbonyl of the ketone (Scheme 3.10). Similarly, the cationic catalyst $[RuH((R)\text{-binap})(NCMe)_{3-n}(sol.)_n]^+$, sol. = solvent, is very active for the hydrogenation of ketoesters (Table 3.3) and in this case, the intermediate alkoxide complex, where the hydride has added to the carbonyl group, has been completely characterized [87].

In a series of breakthroughs during the 1990s, Noyori's group discovered that simple prochiral ketones that do not contain such functional groups are hydrogenated to pure, optically active alcohols by use of extremely active ruthenium complexes containing primary or secondary amine groups [88, 89]. These cata-



Scheme 3.10 Inner-sphere versus outer-sphere hydride transfer to the ketone.

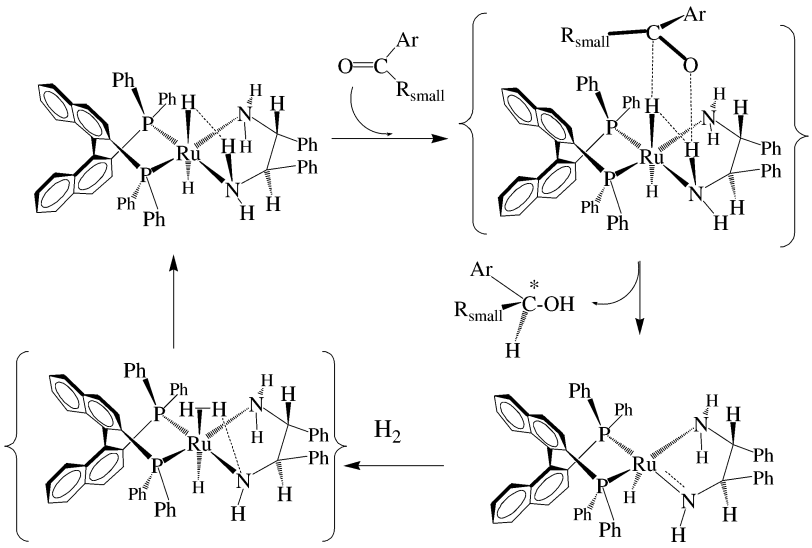
lysts follow a fundamentally different, newly discovered mechanism, involving the outer-sphere transfer of the hydride to the carbonyl assisted by an N–H group (Scheme 3.10). Noyori has called this "metal–ligand bifunctional catalysis", where both the ruthenium and the amine are involved in the hydrogenation of the ketone and also in the dihydrogen activation (see below). First, they reported that the presence of a diamine with at least one N–H group in Ru^{II} precatalysts of the type $RuCl_2$(diamine)$(PR_3)_2$ and $RuCl_2$(diamine)(diphosphine) spectacularly increased the activity of ruthenium complexes toward the hydrogenation of simple ketones [90]. The chirality of the diamine, such as (*R,R*)-$NH_2CHPhCHPhNH_2$ ((*R,R*)-dpen), and the diphosphine, such as (*R*)-binap, must be properly matched to obtained high ee-values in the hydrogenation of a wide range of ketones [89]. The precatalysts are activated by reaction with dihydrogen and base to give the active catalyst solution. The example in Table 3.3 for the hydrogenation of acetophenone catalyzed by the $Ru(Cl)_2$((*S*)-tolbinap) ((*S,S*)-dpen)/KO^tBu system shows an astounding TOF of $2\times10^5\ h^{-1}$ at 30 °C, 45 bar H_2 (TOF increases as the hydrogen pressure increases). This illustrates the orders of magnitude effect of the N–H group compared to the first two entries of Table 3.3 that probably involve inner-sphere hydride transfer. Clapham et al. [19] have reviewed the mechanisms of ruthenium hydrides in catalytic hydrogenation proposed in the literature up to 2004, and have systematized them according to the inner-sphere and outer-sphere classification.

Recent mechanistic studies conducted by the present author and colleagues [32, 33, 91, 92] and Noyori and colleagues [93] suggest that a *trans*-dihydride complex and an amineamido complex are the active catalysts in the main cycle (Scheme 3.11). The dihydride forms a six-member RuH···C-O···HN ring with the aryl ketone in the transition state, while simultaneous outer-sphere hydride and proton transfer gives the alcohol and an amineamido complex with a distorted trigonal bipyramidal geometry about ruthenium. Addition of dihydrogen to the ruthenium-amido bond via an unstable dihydrogen complex regenerates the *trans*-dihydride. The amido ligand assists in the heterolytic splitting of the dihydrogen. There is evidence that the alcohol solvent also assists in this splitting process. The lack of coordination sites *cis* to the hydride means that C=C bonds cannot be hydrogenated by an inner-sphere mechanism, and so these catalysts are selective for the hydrogenation of polar bonds (C=O) or (C=N) [34] over C=C bonds.

Table 3.3 Representative conditions for the hydrogenation of carbonyl compounds including enantiomeric reactions.

	Precatalyst (Ru)	Substrate (*S*)	S:C	Solvent	p(H_2) [bar]	Conversion [%]	ee [%]	Time [h]	Temp. [°C]	TOF [h^{-1}]	Reference
1	$Ru(H)_2(H_2)(PPh_3)_3$	Cyclohexanone	36	Toluene	0.6	3		1	20	1	67
2	$[RuH((R)\text{-binap})(NCMe)_{3-n}(sol.)_n]^+$	$MeOOCCMe_2C(=O)COOMe$	200	MeOH	50	100	59 (*R*)	50	50	4	87
3	$Ru(Cl)_2((S)\text{-tolbinap})((S,S)\text{-dpen})/KO^tBu$	PhMeC=O	2,400,000[a]	*i*PrOH	45	100	80 (*R*)	48	30	2×10^5	89
4	$RuH_2((R)\text{-binap})(NH_2CMe_2CMe_2NH_2)$	PhMeC=O	400	Benzene	8	100	62–68 (*R*)	2	20	200	91
5	$OsH(NHCMe_2CMe_2NH_2)(PPh_3)_2$	PhMeC=O	346	Benzene	5	100		0.3	20	1400	125

a) Substrate: base = 100: 1.

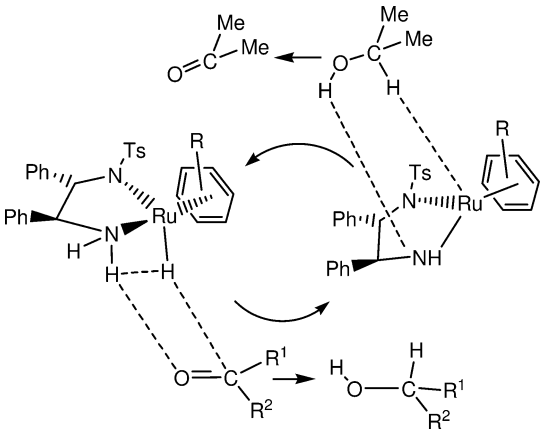


Scheme 3.11 Partial mechanistic scheme for the hydrogenation of aryl ketones to give the (*S*)-alcohol catalyzed by $RuCl_2$((*R*)-binap)((*R*,*R*)-dpen)/KO^tBu/H_2 as based on the observed mechanism for RuH_2((*R*)-binap)($NH_2CMe_2CMe_2NH_2$).

Noyori and coworkers reported well-defined ruthenium(II) catalyst systems of the type RuH(η^6-arene)($NH_2CHPhCHPhNTs$) for the asymmetric transfer hydrogenation of ketones and imines [94]. These also act via an outer-sphere hydride transfer mechanism shown in Scheme 3.12. The hydride transfer from ruthenium and proton transfer from the amino group to the C=O bond of a ketone or C=N bond of an imine produces the alcohol or amine product, respectively. The amido complex that is produced is unreactive to H_2 (except at high pressures), but readily reacts with *i*PrOH or formate to regenerate the hydride catalyst.

An interesting catalytic ruthenium system, Ru(η^5-C_5Ar_4OH)$(CO)_2H$ based on substituted cyclopentadienyl ligands was discovered by Shvo and coworkers [95–98]. This operates in a similar fashion to the Noyori system of Scheme 3.12, but transfers hydride from the ruthenium and proton from the hydroxyl group on the ring in an outer-sphere hydrogenation mechanism. The source of hydrogen can be H_2 or formic acid. Casey and coworkers have recently shown, on the basis of kinetic isotope effects, that the transfer of H^+ and H^- equivalents to the ketone for the Shvo system and the Noyori system (Scheme 3.12) is a concerted process [99, 100].

Palmer and Wills in 1999 reviewed other ruthenium catalysts for the asymmetric transfer hydrogenation of ketones and imines [101]. Gladiali and Mestroni reviewed the use of such catalysts in organic synthesis up to 1998 [102]. Review articles that include the use of ruthenium asymmetric hydrogenation catalysts cover the literature from 1981 to 1994 [103, 104], the major contributions



Scheme 3.12 Enantioselective hydrogenation of a ketone by transfer from *iso*-propanol catalyzed by the hydride complex RuH(η^6-arene)($NH_2CHPhCHPhNTs$) and the amido complex Ru(η^6-arene)(NHCHPhCHPhNTs) [94].

by the group of Genêt until 2003 [45], and the field from an industrial perspective to 2003 [105] (see also Chapter 25). The field of asymmetric imine hydrogenation, that includes ruthenium catalysts, has been reviewed both in 1997 [106] and 2001 [107]. The specific use of the following ligand systems in ruthenium H_2-hydrogenation catalysts has been summarized: aminophosphine-phosphinite ligands in 1998 [108], P-chirogenic diphosphine ligands in 2003 [109], chiral ferrocenyl phosphines [110], and a range of new chiral ligand systems in 2003 [111]. Much current research effort is directed at immobilizing these valuable chiral catalysts [112] or keeping them in the aqueous phase [113] so that they can be recovered and recycled. Aqueous-phase and biphasic catalysis involving ruthenium complexes is an active area that was reviewed in 2002 [31, 114].

3.3 Osmium

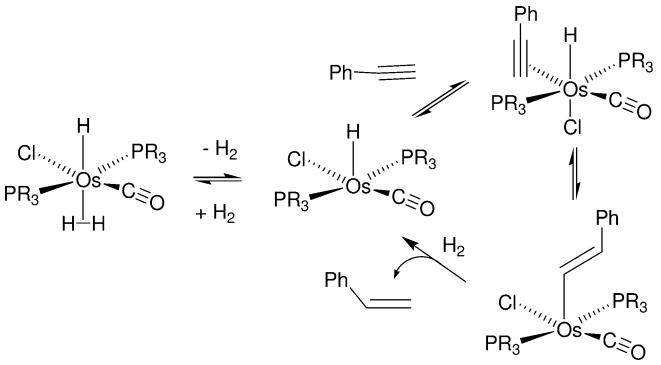
Complexes of Os^{II} have similar properties to those of Ru^{II}, and can often be prepared in analogous fashions. However, fewer exploratory investigations have been conducted into the starting materials for osmium chemistry than for ruthenium chemistry. In a review of the few osmium hydrogenation catalysts known up to 1995, Sanchez-Delgado et al. [115] point out that the stronger bonding of this 5d metal results in catalysts with higher thermal and oxidative stability than its 4d counterpart, ruthenium, and this – along with other interesting properties – may counter the high cost of using osmium. These authors have since discussed the mechanism of related ruthenium and osmium systems to 2000 [116]. Esteruelas and Oro have described the catalysts based on dihydro-

gen complexes of osmium [13], and specifically on the derivatives of the five-coordinate compound $OsHCl(CO)(P^iPr_3)_2$ [117].

The investigation of osmium hydrogenation catalysts began with a brief report by Vaska in 1965 that the six-coordinate trisphosphine complex $OsHCl(CO)(PPh_3)_3$ could catalyze the hydrogenation of acetylene to ethylene and ethane [118]. Activity during the 1970s and early 1980s focused mainly on the potential of osmium carbonyl clusters as catalysts for the hydrogenation of CO [119]. An interest here is whether a molecule that is made up of a well-defined multimetallic cluster could act like a metal surface found in a Fisher-Tropsch catalyst. The activity of such clusters is relatively low, even for the catalytic hydrogenation of alkenes, as reported, for example, for $Os_3(H)_2(CO)_{10}$ by Keister and Shapely in 1976 [120]. At 50 °C and 3 bar H_2, the hydrogenation of 1-hexene to *n*-hexane proceeded at a TOF of 1 h^{-1} for a TON of 31, but at the same time the isomerization of some of the hexene to internal alkenes proceeded at a TOF of 2 h^{-1} with a TON of 69. The observation of triosmium intermediates in the reaction indicated that the triangular cluster remains intact throughout the cycle. The catalyst $OsHBr(CO)(PPh_3)_3$ is somewhat less active, isomerizing hexene in the same way, but eventually hydrogenating the intermediates to hexane with a TON of about 60 and a TOF of 5 h^{-1} at 100 °C, 1 bar H_2. Under similar conditions, cyclohexene was hydrogenated to cyclohexane at a TOF of 0.5 h^{-1}, while the C=C bond of cyclohex-2-en-1-one was reduced with a TOF of 24 h^{-1} with a TON of 80. Osmium and ruthenium complexes of the type $MHX(CO)(PR_3)_3$, X = halogen, carboxylate, showed similar, low activity of about TOF 0.5 to 3 h^{-1} for the hydrogenation of propionaldehyde in toluene at 150 °C, 30 bar H_2. Acetone was hydrogenated at a slow rate at 150 °C, 65 bar H_2 [121] until the catalyst decomposed to metal, at which point the rate increased and also the solvent, toluene, was hydrogenated [122]. Several other substrates were investigated as described elsewhere [115].

The five-coordinate bisphosphine complexes $MHCl(CO)(PR_3)_2$, M = Ru, Os, $PR_3 = PMe^tBu_2$, P^iPr_3, PCy_3 and their air-stable precatalysts forms such as $OsHCl(CO)(\eta^2\text{-}O_2)(PR_3)_2$ or $RuHCl(CO)(styrene)(PR_3)_2$ are active alkene hydrogenation catalysts and ketone transfer hydrogenation catalysts in the presence of $NaBH_4$. The dihydrogen complex $OsHCl(CO)(\eta^2\text{-}H_2)(P^iPr_3)_2$, presumably a source of $OsHCl(CO)(P^iPr_3)_2$ by loss of H_2, catalyzes the H_2-hydrogenation of styrene in *i*PrOH at 60 °C, 1 bar H_2 with a TON of 100 and a TOF of 1200 h^{-1} [123]. Phenyl acetylene is hydrogenated slowly by $OsHCl(CO)(\eta^2\text{-}H_2)(P^iPr_3)_2$, first completely to styrene, because a stable styryl intermediate $OsCl(CO)(CH{=}CHPh)(P^iPr_3)_2$ ties up all of the osmium and prevents reactions with styrene (Scheme 3.13). This styryl complex is hydrogenolyzed in the turnover-limiting step. The styrene that is produced cannot be hydrogenated until this compound is consumed, after which the hydrogenation to ethylbenzene is rapid [117]. The catalyst precursor $OsHCl(CO)(\eta^2\text{-}O_2)(PCy_3)_2$ is effective, and more active than $RhCl(PPh_3)_3$, for the selective hydrogenation of the disubstituted C=C bonds instead of the C≡N triple bonds of nitrile-butadiene rubbers at 5–40 bar H_2, 130 °C in monochlorobenzene [124].

The mildest conditions for the osmium-catalyzed hydrogenation of a simple ketone (in this case acetophenone) were reported recently by Clapham and Mor-



Scheme 3.13 Proposed mechanism for the hydrogenation of phenyl acetylene catalyzed by $OsHCl(CO)(P^iPr_3)_2$ [115].

ris [125] by use of the catalyst $OsH(NHCMe_2CMe_2NH_2)(PPh_3)_2$ in benzene with a maximum TOF of 1400 h^{-1} and TON of 346 at 20 °C, 5 bar H_2. This reaction is thought to proceed through a mechanism analogous to the one shown in Scheme 3.11. Here, the osmium complex appears to be as active as the ruthenium analogue.

Bianchini and coworkers [126] found a difference in the chemoselectivity between the metals Fe, Ru, and Os in the complexes $[M(H_2)H(P(CH_2CH_2PPh_2)_3)]BPh_4$ in the hydrogenation of benzylideneacetone by transfer from *iso*-propanol. The Fe and Ru catalysts reduced the C=O bond to give the allyl alcohol, with Ru more active than iron (TOF 79 h^{-1} at 60 °C for Ru versus 13 h^{-1} at 80 °C for Fe), while the Os catalyst first reduced the C=O bond but then catalyzed isomerization of the allyl alcohol to give the saturated ketone (TOF 55 h^{-1} at 80 °C). The difference in reactivity was attributed to the weak binding of the alkene of the allyl alcohol to Fe and Ru relative to Os in these complexes. A variety of selectivities was noted for other unsaturated ketones, whereas unsaturated aldehydes were not hydrogenated.

In future, it will be interesting to identify a catalytic hydrogenation process that justifies the use of osmium over ruthenium, though one possibility might be a high temperature application such as that required in the hydrogenation of unsaturated rubbers.

Acknowledgment

The author wishes to thank NSERC Canada for the provision of a discovery grant.

Abbreviations

DMF	dimethylformamide
ee	enantiomeric excess
HMD	hexamethylenediamine
SCR	substrate catalyst ratio
TOF	turnover frequency
TON	turnover number

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