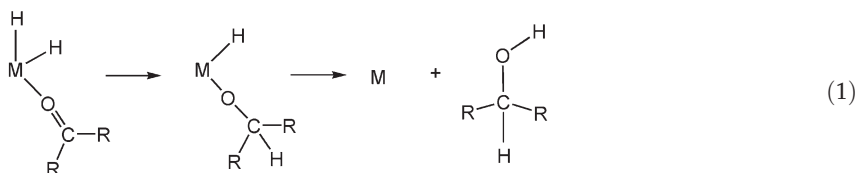


## 7 Ionic Hydrogenations

R. Morris Bullock

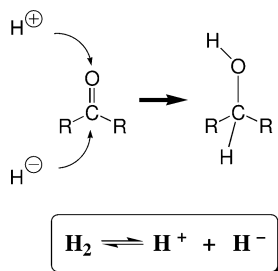
### 7.1 Introduction

One pervasive mechanistic feature of many of the hydrogenations described in other chapters of this handbook concerns the bonding of the unsaturated substrate to a metal center. As illustrated in generalized form in Eq. (1) for the hydrogenation of a ketone, a key step in the traditional mechanism of hydrogenation is migratory insertion of the bound substrate into a metal hydride bond (M–H).



Since this can formally be viewed as an addition of M–H to C=O, the bond order is reduced in this case to a C–O single bond. Reductive elimination generates the hydrogenated product and an unsaturated metal complex that subsequently re-enters the catalytic cycle. Many subtleties of this mechanism have been delineated in studies of hydrogenations of C=C and C=O bonds, and catalysts that follow this mechanism have been very successful.

Most homogeneous catalysts that proceed by traditional insertion mechanisms use precious metals. If the requirement for substrate binding and insertion is removed, then alternative mechanisms would be possible. Such alternative mechanisms could exploit other reactivity patterns accessible to metal hydrides, thus removing the requirement for precious metals. The use of inexpensive metals potentially offers several advantages, if catalysts containing them could be developed with sufficient turnover frequencies (TOFs) and lifetimes. A substantially lower cost of the metal is an obvious advantage, though it is recognized that many factors influence the overall costs of a process, and phosphines or



Scheme 7.1

other ligands can substantially add to the cost of synthesis of an organometallic catalyst precursor. In addition to the initial cost of the metal, other considerations include less stringent requirements for recovery of the catalyst in an industrial process. For processes that might be used in the manufacture of pharmaceutical products, catalysts using abundant metals might be permitted at a higher residual level than other metals, owing to toxicity considerations. The premise of using “Cheap Metals for Noble Tasks” thus has appeal despite these caveats; fundamentally new mechanistic information and novel reactivity patterns have resulted from research directed towards this long-term goal.

Ionic hydrogenations involve addition of  $\text{H}_2$  in the form of  $\text{H}^+$  followed by  $\text{H}^-$ , as shown in Scheme 7.1; the proton and hydride transfers may be either sequential or concerted. A potential advantage of ionic hydrogenations is that the nature of the mechanism would tend to favor hydrogenation of polar bonds such as  $\text{C}=\text{O}$  over less-polar  $\text{C}=\text{C}$  bonds. Kinetic and mechanistic studies have played a key role in the development of ionic hydrogenations. In many cases to be discussed in this chapter, the individual proton-transfer and hydride-transfer steps that comprise the key steps in catalytic cycles can be separately studied in stoichiometric reactions. Mechanistic information can then be used to guide the rational design of new catalysts or the improvement and optimization of initially discovered ionic hydrogenation catalysts.

## 7.2

### Stoichiometric Ionic Hydrogenations

#### 7.2.1

##### Stoichiometric Ionic Hydrogenations using $\text{CF}_3\text{CO}_2\text{H}$ and $\text{HSiEt}_3$

Ionic hydrogenations of  $\text{C}=\text{C}$  and  $\text{C}=\text{O}$  bonds were reported prior to the development of ionic hydrogenations mediated or catalyzed by transition metals. Trifluoroacetic acid ( $\text{CF}_3\text{CO}_2\text{H}$ ) as the proton donor and triethylsilane ( $\text{HSiEt}_3$ ) as the hydride donor are most commonly used, though a variety of other acids and several other hydride donors have also been shown to be effective. A review [1] by Kursanov et al. of the applications of ionic hydrogenations in organic synthe-

sis documents the early progress in this field; a book gives further details [2]. As shown in Eq. (2), proton transfer to the alkene generates a carbenium ion, and hydride transfer from the hydrosilane generates the product.

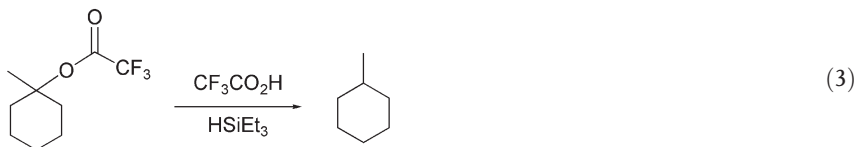


Ionic hydrogenations of C=C bonds generally work well only in cases where a tertiary or aryl-substituted carbenium ion can be formed through protonation of the C=C bond. Alkenes that give a tertiary carbenium ion upon protonation include 1,1-disubstituted, tri-substituted and tetra-substituted alkenes, and each of these are usually hydrogenated by ionic hydrogenation methods in high yields.

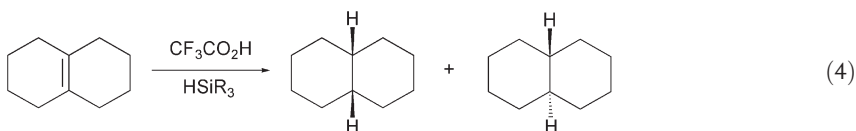
The success of stoichiometric ionic hydrogenations is due to achieving a fine balance that favors the intended reactivity rather than any of several possible alternative reactions. The acid must be strong enough to protonate the unsaturated substrate, yet the reaction of the acid and the hydride should avoid producing H<sub>2</sub> too quickly under the reaction conditions. The commonly used pair of CF<sub>3</sub>CO<sub>2</sub>H and HSiEt<sub>3</sub> meets all these criteria.

The very strong acid, CF<sub>3</sub>SO<sub>3</sub>H (triflic acid, abbreviated as HOTf) can be used in conjunction with HSiEt<sub>3</sub> for the hydrogenation of certain alkenes [3]. These reactions proceed cleanly in 5 minutes at -50 °C. This discovery was surprising, since a review of the use of CF<sub>3</sub>CO<sub>2</sub>H and HSiEt<sub>3</sub> had stated that "... stronger acids cannot be used in conjunction with silanes because they react" [1]. Indeed, rapid evolution of H<sub>2</sub> does occur when HOTf is added to HSiEt<sub>3</sub> in the absence of an alkene. The order of addition is important in the use of HOTf/HSiEt<sub>3</sub> for hydrogenation of C=C bonds, to ensure that acid-induced formation of H<sub>2</sub> is minimized. The addition of HOTf to a solution containing the alkene and the hydrosilane results in rapid and clean hydrogenation, but the reaction is still subject to the limitation of forming a tertiary carbenium ion.

Another potential mechanistic complication is capture of the intermediate carbenium ion by the conjugate base of the acid. When CF<sub>3</sub>CO<sub>2</sub>H is used as the acid, this would lead to trifluoroacetate esters. Kursanov et al. showed that, under the reaction conditions for ionic hydrogenations, trifluoroacetate esters can be converted to the hydrocarbon product (Eq. (3)).

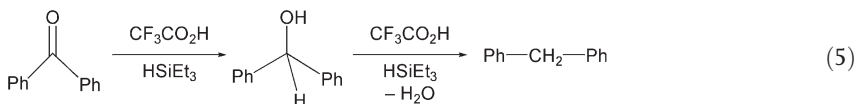


The intermediacy of the trifluoroacetate ester does not undermine the efficacy of the overall hydrogenation reaction, since the ionizing solvent  $\text{CF}_3\text{CO}_2\text{H}$  converts the ester back to the carbenium ion under the reaction conditions, resulting in its ultimate conversion to the hydrogenation product.



Studies of the ionic hydrogenation of  $\Delta^9(10)$ -octalin using  $\text{CF}_3\text{CO}_2\text{H}$  and a variety of hydrosilanes demonstrated that a considerable degree of stereoselectivity can be obtained (Eq. (4)) [4]. Use of  $^n\text{BuSiH}_3$  as the hydride donor led to a 22:78 ratio of *cis*:*trans* decalin. Hydrogenation using the sterically demanding hydrosilane  $t\text{Bu}_3\text{SiH}$ , in contrast, led to predominant formation of the opposite isomer, with 93% of the decahydronaphthalene product being the *cis* isomer. Steric factors of the silane hydride donor appear to dominate the stereoselectivity in this example, though in other examples the effect is much less, suggesting that additional factors can influence the product distribution. Ionic hydrogenation of 4-*tert*-butylmethylenecyclohexane with the same series of hydrosilanes invariably produced a predominance of the *trans* isomer [4].

Ionic hydrogenation of benzophenone using  $\text{CF}_3\text{CO}_2\text{H}$  and  $\text{HSiEt}_3$  proceeds at room temperature and gives high yields of diphenylmethane (Eq. (5)) [1, 5]. This reaction presumably proceeds through the alcohol, as indicated in Eq. (5), but deoxygenation of the alcohol proceeds faster than hydrogenation of the  $\text{C}=\text{O}$  function, so the alcohol is not detected. Similar hydrogenations of the  $\text{C}=\text{O}$  group to  $\text{CH}_2$  were found for aryl alkyl ketones. Dialkyl ketones react with  $\text{CF}_3\text{CO}_2\text{H}$  and  $\text{HSiEt}_3$  to produce trifluoroacetate esters of the secondary alcohols, so conversion to the alcohol requires a subsequent hydrolysis reaction [1].



The hydrogenation of aldehydes by  $\text{CF}_3\text{CO}_2\text{H}/\text{HSiEt}_3$  is often complicated by the formation of ethers. Doyle et al. found that the use of aqueous acids such as  $\text{H}_2\text{SO}_4$ , together with nonreactive solvents ( $\text{CH}_3\text{CN}$ ), allowed some aldehydes and dialkyl ketones to be reduced to alcohols using  $\text{HSiEt}_3$  [6].

## 7.2.2

**Stoichiometric Ionic Hydrogenations using Transition-Metal Hydrides****7.2.2.1 General Aspects**

While stoichiometric ionic hydrogenations using  $\text{CF}_3\text{CO}_2\text{H}$  and  $\text{HSiEt}_3$  have enjoyed significant utility in organic synthetic reactions, they require stoichiometric quantities of both the hydrosilane and an acid. One of the principles of Green Chemistry [7] is that catalytic reactions are preferred over stoichiometric reagents. The development of a catalytic route to ionic hydrogenations would be environmentally attractive. In addition to the requirement of delivering a proton and a hydride to the substrate, catalytic methods additionally require a metal complex that is capable of reacting with  $\text{H}_2$  to regenerate the proton and hydride sources. The following sections will demonstrate how kinetic and mechanistic studies separately documented the proton-transfer and hydride-transfer capabilities of transition-metal hydrides. These studies provided a firm mechanistic basis for the development and understanding of catalytic ionic hydrogenations.

**7.2.2.2 Transition-Metal Hydrides as Proton Donors**

The fact that metal hydrides can be acidic may seem paradoxical in view of the nomenclature that insists that all complexes with a  $\text{M-H}$  bond be referred to as “hydrides” regardless of whether their reactivity is hydridic or not. Not only can some metal hydrides donate a proton, but some can be remarkably acidic. Some cationic dihydrogen complexes are sufficiently acidic to protonate  $\text{Et}_2\text{O}$  [8], and some dicationic ruthenium complexes have an acidity comparable to or exceeding that of  $\text{HOTf}$  [9].

Systematic studies of the thermodynamic and kinetic acidity of metal hydrides in acetonitrile were carried out by Norton et al. [10, 11]. A review of the acidity of metal hydrides presents extensive tabulations of  $\text{p}K_{\text{a}}$  data [12]; only a few of the trends will be mentioned here. Metal hydrides span a wide range of  $\text{p}K_{\text{a}}$  values; considering only metal carbonyl hydrides shown in Table 7.1, the range exceeds 20  $\text{p}K_{\text{a}}$  units. As expected, a substantial decrease in acidity is

**Table 7.1**  $\text{p}K_{\text{a}}$  values of neutral metal carbonyl hydrides in  $\text{CH}_3\text{CN}$ .

Metal hydride	$\text{p}K_{\text{a}}$	Reference
$(\text{CO})_4\text{CoH}$	8.3	11
$\text{Cp}(\text{CO})_3\text{MoH}$	13.9	11
$(\text{CO})_5\text{MnH}$	14.2	12
$(\text{CO})_3(\text{PPh}_3)\text{CoH}$	15.4	11
$\text{Cp}(\text{CO})_3\text{WH}$	16.1	11
$\text{Cp}^*(\text{CO})_3\text{MoH}$	17.1	11
$(\text{CO})_5\text{ReH}$	21.1	11
$\text{Cp}(\text{CO})_2(\text{PMe}_3)\text{WH}$	26.6	11

found when an electron-accepting CO ligand is replaced by an electron-donating phosphine. The cobalt hydride  $[(\text{CO})_4\text{CoH}]$  is quite acidic, being of comparable acidity in  $\text{CH}_3\text{CN}$  to that of  $\text{HCl}$  ( $\text{p}K_{\text{a}}=8.9$  in  $\text{CH}_3\text{CN}$ ); substitution of one CO by  $\text{PPh}_3$  to give  $[(\text{CO})_3(\text{PPh}_3)\text{CoH}]$  reduces the acidity by about seven  $\text{p}K_{\text{a}}$  units. The stronger electron donor,  $\text{PMe}_3$ , has an even larger effect, as exemplified by the acidity of  $[\text{Cp}(\text{CO})_2(\text{PMe}_3)\text{WH}]$  ( $\text{Cp}=\eta^5\text{-C}_5\text{H}_5$ ) being less than that of  $[\text{Cp}(\text{CO})_3\text{WH}]$  by about 10  $\text{p}K_{\text{a}}$  units. Replacement of a Cp by  $\text{Cp}^*$  [ $(\text{Cp}^*=\eta^5\text{-C}_5\text{Me}_5)$ ] also decreases the acidity, by about three  $\text{p}K_{\text{a}}$  units in the case of  $[\text{Cp}(\text{CO})_3\text{MoH}]$  versus  $[\text{Cp}^*(\text{CO})_3\text{MoH}]$ . Third-row metals are less acidic than their first- or second-row analogues, as shown by  $[\text{Cp}(\text{CO})_3\text{MoH}]$  being two  $\text{p}K_{\text{a}}$  units less acidic than  $[\text{Cp}(\text{CO})_3\text{WH}]$ . A larger difference of about seven  $\text{p}K_{\text{a}}$  units was found between first-row  $[(\text{CO})_5\text{MnH}]$  and third-row  $[(\text{CO})_5\text{ReH}]$ .

DuBois and coworkers have studied a wide range of metal hydrides, concentrating on those with two diphosphine ligands [13–19]. Measurements of  $\text{p}K_{\text{a}}$  values for a series of cobalt hydrides (Table 7.2, upper part) showed that the cationic dihydride  $[(\text{H})_2\text{Co}(\text{dppe})_2]^+$  has a  $\text{p}K_{\text{a}}$  of 22.8, while the neutral cobalt hydride  $[\text{HCo}(\text{dppe})_2]$  is far less acidic ( $\text{p}K_{\text{a}}=38.1$ ). Oxidation of this neutral hydride gives the paramagnetic Co(II) hydride,  $[\text{HCo}(\text{dppe})_2]^+$ , which is much more acidic ( $\text{p}K_{\text{a}}=23.6$ ). The dicationic hydride  $[\text{HCo}(\text{dppe})_2(\text{NCCH}_3)]^{2+}$  ( $\text{p}K_{\text{a}}=11.3$ ) is by far the most acidic of this series. This remarkable series of complexes, all containing a  $\text{Co}(\text{dppe})_2$  core, span about 27  $\text{p}K_{\text{a}}$  units as the oxidation states and formal charges are varied. The series of  $[\text{HM}(\text{diphosphine})_2]^+$  complexes in the lower part of Table 7.2 show that altering the electronic properties of substituents on the diphosphine ligand can have a profound effect on acidity. Complexes with two dmpe ligand (with methyl groups on the phosphorus) are six to ten  $\text{p}K_{\text{a}}$  units less acidic than corresponding complexes with a dppe ligand (with phenyl groups on the phosphorus). As was found for the metal carbonyl complexes discussed above, hydrides of the third row metal are

**Table 7.2**  $\text{p}K_{\text{a}}$  values of metal bis(diphosphine) hydrides in  $\text{CH}_3\text{CN}$ .

Metal hydride <sup>a)</sup>	$\text{p}K_{\text{a}}$	Reference
$[(\text{H})_2\text{Co}(\text{dppe})_2]^+$	22.8	16
$[\text{HCo}(\text{dppe})_2]^+$	23.6	16
$\text{HCo}(\text{dppe})_2$	38.1	16
$[\text{HCo}(\text{dppe})_2(\text{NCCH}_3)]^{2+}$	11.3	16
$[\text{HNi}(\text{dppe})_2]^+$	14.2	13
$[\text{HPt}(\text{dppe})_2]^+$	22.0	13
$[\text{HNi}(\text{dmpe})_2]^+$	24.3 <sup>b)</sup>	13
$[\text{HPt}(\text{dmpe})_2]^+$	31.1 <sup>b)</sup>	15

a) dmpe = 1,2-bis(dimethylphosphino)ethane;  
dppe = 1,2-bis(diphenylphosphino)ethane.

b) Value determined in  $\text{PhCN}$ , though these values are usually similar to those found in  $\text{CH}_3\text{CN}$ , typically differing by less than 1  $\text{p}K_{\text{a}}$  unit between the two solvents.

significantly less acidic than those of the first-row metal (Ni versus Pt in the examples shown in Table 7.2).

Morris et al. carried out extensive studies [20] of the acidity of metal hydrides in tetrahydrofuran (THF), including metal hydrides of very low acidity as well as dihydrogen complexes that are reactive with  $\text{CH}_3\text{CN}$ . The dielectric constant of THF is low compared to that of  $\text{CH}_3\text{CN}$ , so ion-pairing issues must be taken into account [21], though these measurements in THF provide useful comparisons to data in  $\text{CH}_3\text{CN}$  and other solvents.

### 7.2.3

#### Transition Metal Hydrides as Hydride Donors

An understanding of the factors that influence the propensity of metal hydrides to function as hydride donors is important in the use of such hydrides in ionic hydrogenations. Thermodynamic hydricities are immensely useful in considering the viability of potential hydride transfer reactions in stoichiometric or catalytic reactions. Since catalysis is a kinetic phenomenon, it is also necessary to understand the factors influencing the kinetics of hydride transfer reactions. Systematic studies that provided quantitative values for the thermodynamic and kinetic hydricity of a wide series of hydrides occurred after studies had been conducted that identified the factors influencing proton-transfer reactions of metal hydrides. A complicating factor in considering tests for hydricity is that removal of  $\text{H}^-$  from  $\text{M-H}$  produces a cationic species  $\text{M}^+$  [22]. When the starting hydride  $\text{M-H}$  is an 18-electron complex, the  $\text{M}^+$  that initially results will be an unsaturated 16-electron species. In most cases these 16-electron metal cations will not be stable but will voraciously seek an additional ligand. Since the overall reaction may involve ligand capture as well as the hydride transfer, comparisons of hydricity may be complicated by the subsequent reactivity of  $\text{M}^+$  following the hydride transfer reaction.

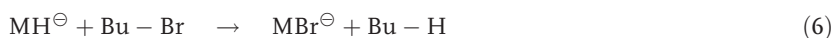
It has long been recognized that the hydricity of a metal hydride can vary according to its position in the Periodic Table. Labinger and Komadina found evidence for this trend from an examination of the reactivity of a series of metallocene hydrides [23]. The Group 4 zirconium dihydride  $[\text{Cp}_2\text{ZrH}_2]_n$  reacts quickly at room temperature with acetone to give  $[\text{Cp}_2\text{Zr}(\text{OCHMe}_2)_2]$ , which releases isopropyl alcohol upon hydrolysis. The Group 5 complex  $[\text{Cp}_2\text{NbH}_3]$  reacts slowly with acetone, but quickly with the more electrophilic ketone  $(\text{CF}_3)(\text{CH}_3)\text{C}=\text{O}$ . The Group 6 dihydride,  $[\text{Cp}_2\text{MoH}_2]$ , did not react with acetone at  $78^\circ\text{C}$ , but did react slowly at  $25^\circ\text{C}$  with  $(\text{CF}_3)(\text{CH}_3)\text{C}=\text{O}$ . The Group 7 hydride  $[\text{Cp}_2\text{ReH}]$  did not react with either acetone or with  $(\text{CF}_3)(\text{CH}_3)\text{C}=\text{O}$ . This study provided evidence that hydricity is higher for metals to the left side of the Periodic Table, though if the ketone coordinates to the metal prior to hydride transfer, these measurements may reflect a combination of factors, rather than measuring only hydricity.

Darensbourg et al. have conducted extensive studies of the nucleophilic reactivity of a series of anionic metal carbonyl hydrides [24], which have been used for the reduction of alkyl halides [25], acyl chlorides [26], and ketones [27]. The

**Table 7.3** Rate constants for reaction of anionic metal hydrides with *n*-BuBr (THF solvent at 26 °C) [25].

Metal hydride	$10^3 \times k_{\text{H}} [\text{M}^{-1} \text{s}^{-1}]$
$[\text{HW}(\text{CO})_4\text{P}(\text{OCH}_3)_3]^-$	50
$[\text{HCr}(\text{CO})_4\text{P}(\text{OCH}_3)_3]^-$	30
$[\text{HW}(\text{CO})_5]^-$	3.3
$[\text{HV}(\text{CO})_3\text{Cp}]^-$	2.2
$[\text{HCr}(\text{CO})_5]^-$	1.8
$[\text{HRu}(\text{CO})_5]^-$	1.0

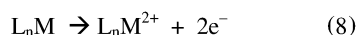
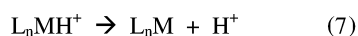
kinetics of bromide displacement from *n*-BuBr by a series of anionic hydrides (Eq. (6)) gave the results shown in Table 7.3.



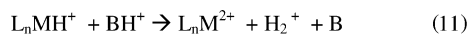
Although the range of rate constants observed is only about a factor of 50, there is a clear trend indicating that the replacement of one CO by a phosphite ligand increases the kinetic hydricity. The third-row tungsten hydrides are faster hydride donors compared to the first-row chromium analogues. Whilst direct displacement of the bromide by hydride is the prevalent mechanism in the reaction of this primary alkyl bromide, a radical chain mechanism involving hydrogen atom transfer from the metal hydride is also operative. This radical chain mechanism ( $S_{\text{H}2}$  pathway) is the predominant pathway in reactions of these same anionic hydrides with sterically encumbered alkyl halides, where the  $S_{\text{N}2}$  hydride displacement pathway is disfavored [28].

DuBois et al. carried out extensive studies on the thermodynamic hydricity of a series of metal hydrides [13, 15–19]. The determination of thermodynamic hydricity generally requires several measurements (coupled with known thermochemical data) to constitute a complete thermochemical cycle. As with other thermodynamic cycles, obtaining reliable values in an appropriate solvent can be a difficult challenge, and this is sometimes coupled with problems in obtaining reversible electrochemical data. Scheme 7.2 illustrates an example in which the hydricity of cationic monohydrides have been determined.

Thus, the thermodynamic hydricity shown in Eq. (10) is determined by evaluating the values for Eqs. (7) to (9). Equation (7) is the  $pK_{\text{a}}$  of the hydride, and

**Scheme 7.2** Thermodynamic cycle for determination of the hydricity of cationic metal hydrides.





**Scheme 7.3** Thermodynamic cycle for determination of the hydricity using heterolytic cleavage of hydrogen.

Eq. (8) requires determination of the two-electron oxidation potential of  $L_nM$  by electrochemical methods. When combined with the two-electron reduction of protons in Eq. (9), the sum provides Eq. (10), the  $\Delta G_{H^-}^{\circ}$  values of which can be compared for a series of metal hydrides. Another way to determine the  $\Delta G_{H^-}^{\circ}$  entails the thermochemical cycle is shown in Scheme 7.3. This method requires measurement of the  $K_{eq}$  of Eq. (11) for a metal complex capable of heterolytic cleavage of  $H_2$ , using a base (B), where the  $pK_a$  of  $BH^+$  must be known in the solvent in which the other measurements are conducted. In several cases, DuBois et al. were able to demonstrate that the two methods gave the same results. The thermodynamic hydricity data ( $\Delta G_{H^-}^{\circ}$  in  $CH_3CN$ ) for a series of metal hydrides are listed in Table 7.4. Transition metal hydrides exhibit a remarkably large range of thermodynamic hydricity, spanning some  $30 \text{ kcal mol}^{-1}$ .

Several trends are revealed by these data. For example, third-row metal hydrides are much more hydridic compared to their first-row analogues, so the trend of higher hydricity for third-row hydrides holds for both kinetic and thermodynamic hydricity. The hydricity of  $[HPt(depe)_2]^+$  exceeds that of  $[HNi(depe)_2]^+$  by  $15 \text{ kcal mol}^{-1}$ , and other Pt hydrides reflect the same trend, by  $11\text{--}14 \text{ kcal mol}^{-1}$  [13]. The second-row hydride  $[HRh(dppb)_2]$  is a very powerful hydride donor, and its hydricity exceeds that of the first-row Co analogue by  $14 \text{ kcal mol}^{-1}$  [17]. Changing the ligands on a metal can also cause a profound change in thermodynamic hydricity. The chelating diphosphine ligand dmpe is much more electron-donating than dppe, with the Pt complex  $[HPt(dmpe)_2]^+$  having a hydricity that exceeds that of  $[HPt(dppe)_2]^+$  by  $10 \text{ kcal mol}^{-1}$  [13, 15]. The same conclusion is reached for comparisons of Ni complexes with different diphosphine ligands. Replacement of one of the electron-withdrawing CO ligands of  $[HW(CO)_5]^-$  with  $PPh_3$  leads to an increase of  $4 \text{ kcal mol}^{-1}$  in the hydricity of  $[HW(CO)_4(PPh_3)]^-$  [18]. DuBois et al. found a dramatic dependence of hydricity on the bite angle of a series of Pd hydrides [19]. A variation of the bite angle of  $33^\circ$  results in tuning of the hydricity over a range of  $27 \text{ kcal mol}^{-1}$ , with smaller bite angles of the diphosphine leading to higher hydricity. Overall, DuBois et al. have concluded that, for isoelectronic complexes, the order of hydricity is second row > third row > first row [17]. The charge on a metal complex can affect its hydricity. For a series of cobalt complexes, the neutral complex  $[HCo(dppe)_2]$  is a stronger hydride donor than the cationic, paramagnetic complex  $[HCo(dppe)_2]^+$  [16]. While this follows the expected trend, it is clear from the data in Table 7.4 that the overall charge is just one factor influencing

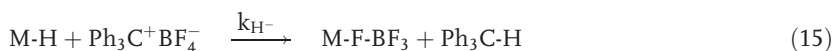
**Table 7.4**  $\Delta G^0$  for hydride transfer from metal hydrides in  $\text{CH}_3\text{CN}$ .

Hydride donor <sup>a)</sup>	$\Delta G^0$ [kcal mol <sup>-1</sup> ] <sup>b)</sup>	Reference
HRh(dppb) <sub>2</sub>	34	17
HW(CO) <sub>4</sub> (PPh <sub>3</sub> ) <sup>-</sup>	36	18
[HPt(dmpe) <sub>2</sub> ] <sup>+</sup>	42	15
HW(CO) <sub>5</sub> <sup>-</sup>	40	18
[HPt(depe) <sub>2</sub> ] <sup>+</sup>	44	15
[HPt(dmpp) <sub>2</sub> ] <sup>+</sup>	51	15
HCo(dppe) <sub>2</sub>	49	16
HCo(dppb) <sub>2</sub>	48	17
[HNi(dmpe) <sub>2</sub> ] <sup>+</sup>	51	13
[HPt(dppe) <sub>2</sub> ] <sup>+</sup>	52	15
HMo(CO) <sub>2</sub> (PMe <sub>3</sub> )Cp	55	91
[HNi(depe) <sub>2</sub> ] <sup>+</sup>	56	13
[HCo(dppe) <sub>2</sub> ] <sup>+</sup>	60	16
[HNi(dmpp) <sub>2</sub> ] <sup>+</sup>	61	13
[HNi(dppe) <sub>2</sub> ] <sup>+</sup>	63	13
[(H) <sub>2</sub> Co(dppe) <sub>2</sub> ] <sup>+</sup>	65	16
[HPd(EtXantphos) <sub>2</sub> ] <sup>+</sup>	70	19
H <sub>2</sub>	76	15
HCPPh <sub>3</sub>	99	92

- a) dmpe and dppe as defined in Table 7.2; dmpp = 1,3-bis(dimethylphosphino)propane; depe = 1,2-bis(diethylphosphino)ethane; dppe = 1,2-bis(diphenylphosphino)ethane; depp = 1,2-bis(diethylphosphino)propane; EtXantphos = 9,9-dimethyl-4,5-bis(diethylphosphino)xanthene.
- b) Estimated uncertainties on  $\Delta G^0$  values are typically  $\pm 2$  kcal mol<sup>-1</sup>.

the hydricity, as many of the cationic hydrides are stronger hydride donors than neutral hydrides. For the series of  $[\text{HM}(\text{diphosphine})_2]^+$  complexes that have been the focus of much of the research by DuBois and colleagues, the high stability of the square-planar products,  $[\text{M}(\text{diphosphine})_2]^{+2}$ , which result from hydride transfer, helps to explain the high hydricity of  $[\text{HM}(\text{diphosphine})_2]^+$ .

The kinetics of hydride transfer from a series of neutral metal carbonyl hydrides have been determined by studying hydride transfer to  $\text{Ph}_3\text{C}^+\text{BF}_4^-$  (Eq. (15)). In  $\text{CH}_2\text{Cl}_2$  solvent, the  $\text{M}^+$  cation resulting from hydride transfer from the metal hydride is captured by the  $\text{BF}_4^-$  anion, forming complexes with weakly bound  $\text{FBF}_3$  ligands. A wide range of  $\text{M}-\text{FBF}_3$  complexes have been studied by Beck and Sünkel [29]. The second-order rate constants for the hydride transfer reaction in Eq. (15) are listed in Table 7.5. The range of rate constants spans a factor of over  $10^6$ , documenting a considerable range of kinetic hydricity.



**Table 7.5** Rate constants for hydride transfer from metal hydrides to  $\text{Ph}_3\text{C}^+ \text{BF}_4^-$  ( $\text{CH}_2\text{Cl}_2$  solvent at 25 °C) [58, 93].

Metal hydride	$k_{\text{H}}$ [ $\text{M}^{-1} \text{s}^{-1}$ ]
HRu(CO) <sub>2</sub> Cp*	$>5 \times 10^6$
<i>trans</i> -HMo(CO) <sub>2</sub> (PMe <sub>3</sub> )Cp	$4.6 \times 10^6$
HFe(CO) <sub>2</sub> Cp*	$1.1 \times 10^6$
<i>trans</i> -HMo(CO) <sub>2</sub> (PPh <sub>3</sub> )Cp	$5.7 \times 10^5$
<i>trans</i> -HMo(CO) <sub>2</sub> (PCy <sub>3</sub> )Cp	$4.3 \times 10^5$
HOs(CO) <sub>2</sub> Cp*	$3.2 \times 10^5$
HW(NO) <sub>2</sub> Cp	$1.9 \times 10^4$
<i>cis</i> -HRe(CO) <sub>4</sub> (PPh <sub>3</sub> )	$1.2 \times 10^4$
HMo(CO) <sub>3</sub> Cp*	$6.5 \times 10^3$
HRe(CO) <sub>5</sub>	$2.0 \times 10^3$
HW(CO) <sub>3</sub> ( $\eta^5$ -indenyl)	$2.0 \times 10^3$
HW(CO) <sub>3</sub> Cp*	$1.9 \times 10^3$
HMo(CO) <sub>3</sub> Cp	$3.8 \times 10^2$
HW(CO) <sub>3</sub> (C <sub>5</sub> H <sub>4</sub> Me)	$2.5 \times 10^2$
<i>cis</i> -HMn(CO) <sub>4</sub> (PPh <sub>3</sub> )	$2.3 \times 10^2$
HSiEt <sub>3</sub>	$1.5 \times 10^2$
HW(CO) <sub>3</sub> Cp	$7.6 \times 10^1$
HCr(CO) <sub>3</sub> Cp*	$5.7 \times 10^1$
HMn(CO) <sub>5</sub>	$5.0 \times 10^1$
W(CO) <sub>3</sub> (C <sub>5</sub> H <sub>4</sub> CO <sub>2</sub> Me)	$7.2 \times 10^{-1}$

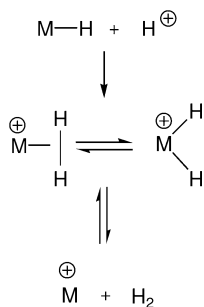
This systematic study reveals how changes in the metal and both steric and electronic changes of the ligand can alter the hydricity. Third-row metal hydrides are substantially more kinetically hydridic than their first-row analogues, with  $[\text{Cp}^*(\text{CO})_3\text{WH}]$  being about 33-fold faster at hydride transfer than  $[\text{Cp}^*(\text{CO})_3\text{CrH}]$ , and a factor of about 40–50 being found for Re versus Mn hydrides. The second-row hydrides of Mo are about three- to five-fold faster than those of the third-row W hydrides. Changes in ligands cause an even more dramatic change in the kinetic hydricity. When a Cp ligand in  $[\text{CpM}(\text{CO})_3\text{H}]$  is replaced by Cp\*, the kinetic hydricity increases by a factor of 25 for M=W and a factor of 17 for M=Mo. Compared to Cp, the Cp\* ligand is much larger, so steric effects would predict a lower reactivity of the Cp\* compared to the Cp complex. Since Cp\* is a much better electron donor than Cp, the higher rate constant for the Cp\* complex makes it clear that electronic effects dominate over steric effects in these reactions. Even a single methyl group has a small, but measurable, effect on the hydricity, as indicated by the larger rate constant for  $[(\text{C}_5\text{H}_4\text{Me})(\text{CO})_3\text{WH}]$  compared to  $[\text{Cp}(\text{CO})_3\text{WH}]$ . An even more prominent effect upon substitution of a single substituent on the Cp ligand was found for the compound containing an electron-withdrawing group on the Cp ligand, with the hydricity of  $[\text{Cp}(\text{CO})_3\text{WH}]$  exceeding that of  $[(\text{C}_5\text{H}_4\text{CO}_2\text{Me})(\text{CO})_3\text{WH}]$  by about a factor of 100. Replacement of one CO by a phosphine ligand has an even larger effect in enhancing the kinetic hydricity of metal hydrides. The

PMe<sub>3</sub>-substituted Mo hydride *trans*-[Cp(CO)<sub>2</sub>(PMe<sub>3</sub>)MoH] is about 10<sup>4</sup> times as hydridic as [Cp(CO)<sub>3</sub>MoH]. Some evidence for steric effects is apparent from the kinetic hydricity of *trans*-[Cp(CO)<sub>2</sub>(PCy<sub>3</sub>)MoH]. The PCy<sub>3</sub> is similar to PMe<sub>3</sub> electronically, but it is much more sterically demanding. The hydricity of *trans*-[Cp(CO)<sub>2</sub>(PCy<sub>3</sub>)MoH] is about 10 times less than that of *trans*-[Cp(CO)<sub>2</sub>(PMe<sub>3</sub>)MoH], presumably due to steric effects. Yet even with this large ligand, the hydricity of *trans*-[Cp(CO)<sub>2</sub>(PCy<sub>3</sub>)MoH] exceeds that of Cp(CO)<sub>3</sub>MoH by about three orders of magnitude, again providing strong evidence of the predominance of electronic over steric effects in these kinetic hydricity studies.

#### 7.2.4

#### Stoichiometric Ionic Hydrogenation of Alkenes with Metal Hydrides as the Hydride Donor

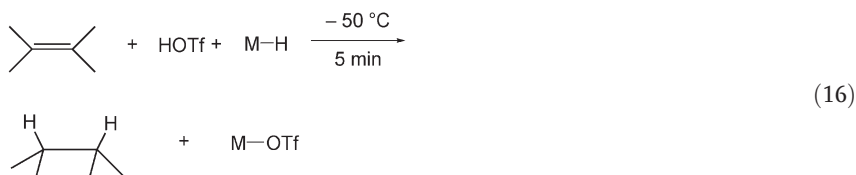
As discussed earlier, Kursanov et al. showed that some alkenes can be hydrogenated using acids in conjunction with HSiEt<sub>3</sub> as the hydride donor. Compared with silanes, transition-metal hydrides as hydride donors offer substantial advantages, if their hydride donor capability can be coupled into a catalytic cycle that regenerates the M–H bond through reaction with H<sub>2</sub>. Additionally, the versatile reactivity patterns of metal hydrides reveal another benefit. Whilst silanes generally react with acids to immediately evolve H<sub>2</sub>, many transition-metal hydrides can be protonated (Scheme 7.4) to give dihydrogen complexes [30] or dihydrides. Protonation at the M–H to produce a dihydrogen complex is often kinetically preferred [31] over direct protonation at the metal to generate a dihydride; in many cases, the dihydrogen and dihydride forms are in equilibrium with each other. For the purposes of hydrogenation, it may not make much difference which form is predominant, as long as the complex is sufficiently acidic to transfer a proton to the substrate that is to be hydrogenated. Thus, the possibility of protonation of a metal hydride provides an alternate mechanistic pathway for stoichiometric ionic hydrogenations. Proton transfer from an external acid may occur to the substrate directly, or may involve protonation of a metal hydride, with subsequent delivery of the proton to the substrate. Deprotonation of a cationic dihydride or dihydrogen complex will generate a neutral metal hy-



Scheme 7.4

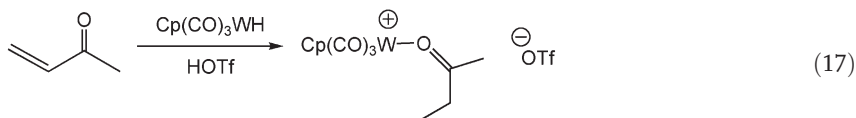
dride, which can then serve as a hydride donor. Failures can occur if irreversible loss of  $H_2$  from the metal occurs more quickly than proton transfer to the unsaturated substrate.

Ionic hydrogenation of certain C=C double bonds is readily accomplished through reaction with HOTf and transition-metal hydrides (Eq. (16)). These reactions proceed in high yield (>90%) in less than 5 minutes at 22 °C, and were shown in some cases to occur at temperatures as low as -50 °C. The limitations on the olefin substrate are the same as those encountered in the stoichiometric ionic hydrogenations using  $HSiEt_3$  as the hydride donor – the alkene starting material must be able to be protonated to give a tertiary carbenium ion, which essentially limits the starting materials to 1,1-disubstituted, tri-substituted, and tetra-substituted alkenes. Styrene, stilbene and related phenyl-substituted C=C bonds were hydrogenated by this method also, but the yields were lower (46–57%).



Metal hydrides that were shown to be suitable hydride donors for this reaction included  $[Cp(CO)_3WH]$ ,  $[Cp^*(CO)_3WH]$ ,  $[Cp(CO)_3MoH]$ ,  $[(CO)_5MnH]$ ,  $[(CO)_5ReH]$  and  $[Cp^*(CO)_2OsH]$ . As discussed above, a metal hydride may fail if it loses hydrogen too quickly after protonation (see Scheme 7.4). The failure of  $[Cp^*(CO)_2FeH]$ ,  $[Cp^*(CO)_3MoH]$ , and  $[Cp(PPh_3)(CO)_2MoH]$  in the ionic hydrogenation of olefins is attributed to thermal decomposition occurring instead of proton transfer following protonation of these hydrides. Insufficient acidity of the protonated form (a cationic dihydride or dihydrogen complex) was found as the reason for failure of  $[Cp(PMe_3)(CO)_2WH]$  and  $[Cp(PMe_3)(CO)RuH]$ . These stoichiometric studies revealed the required characteristics of metal hydrides for them to be suitable for ionic hydrogenations. They must be able to function as hydride donors in the presence of acids. Protonation of the metal hydride is not required, but if it is protonated, it must be able to transfer the proton to the unsaturated substrate, and this requires both sufficient kinetic acidity and thermal stability to overcome alternate pathways that could thwart the desired reactivity.

Stoichiometric ionic hydrogenation of the C=C bond of  $\alpha,\beta$ -unsaturated ketones by HOTf and  $[Cp(CO)_3WH]$  results in the formation of  $\eta^1$ -ketone complexes of tungsten [32]. As exemplified in Eq. (17), hydrogenation of methyl vinyl ketone gives a 2-butanone complex of tungsten. The bound ketone is displaced by the triflate counterion, giving the free ketone. Similar reactions were reported for hydrogenation of the C=C bond of  $\alpha,\beta$ -unsaturated aldehydes.

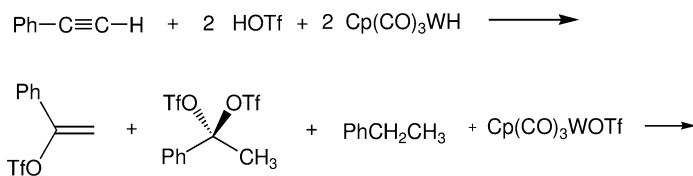


## 7.2.5

**Stoichiometric Ionic Hydrogenation of Alkynes**

Ionic hydrogenations of  $\text{C}\equiv\text{C}$  bonds of alkynes has only been studied in a few cases. Kursanov et al. reported that low yields were obtained upon attempted hydrogenation of aryl alkynes using  $\text{CF}_3\text{CO}_2\text{H}$  and  $\text{HSiEt}_3$  [2]. In contrast, ionic hydrogenation of phenylacetylene by  $\text{HOTf}$  and  $[\text{Cp}(\text{CO})_3\text{WH}]$  produced ethylbenzene as the product of double ionic hydrogenation of the  $\text{C}\equiv\text{C}$  bond [33]. In addition to the ethylbenzene that was promptly formed, the vinyl triflate and the geminal ditriflate shown in Scheme 7.5 were also observed; these organic triflates are formed by the addition of one or two equivalents of  $\text{HOTf}$  to the  $\text{C}\equiv\text{C}$  bond.

In the presence of  $\text{HOTf}$  and  $[\text{Cp}(\text{CO})_3\text{WH}]$ , these organic intermediates were slowly consumed, with more ethylbenzene being produced, the yield of which reached 92% after 28 h. Reaction of  $\text{PhC}\equiv\text{CCH}_3$  with  $\text{HOTf}$  and  $[\text{Cp}(\text{CO})_3\text{WH}]$  also led to the observation of vinyl triflates as intermediates. In addition to these organic intermediates, both *cis*- and *trans*-isomers of the  $\beta$ -methylstyrene complex  $[\text{Cp}(\text{CO})_3\text{W}(\eta^2\text{-PhHC}=\text{CHCH}_3)]^+\text{OTf}^-$  were observed, with this tungsten alkene complex reaching a maximum yield of 40% during the reaction. Ultimately, this complex as well as the vinyl triflates were converted to propylbenzene, which was observed in 91% yield. Ionic hydrogenation of  $\text{BuC}\equiv\text{CH}$  by  $\text{HOTf}$  and  $[\text{Cp}(\text{CO})_3\text{WH}]$  led to vinyl triflate intermediates, but conversion to *n*-hexane was slow, requiring several days in the presence of excess  $\text{HOTf}$ . Since ionic hydrogenation of alkynes is so much slower than that of ionic hydrogenation of alkenes, the requirements of a suitable hydride donor are much more stringent. The ability of  $[\text{Cp}(\text{CO})_3\text{WH}]$  to function as a hydride donor in the presence of acid is a key characteristic of this metal hydride that distinguishes it from  $\text{HSiEt}_3$ . Reaction of this tungsten hydride with  $\text{HOTf}$  leads to partial formation of the cationic dihydride  $[\text{Cp}(\text{CO})_3\text{W}(\text{H})_2]^+\text{OTf}^-$  [34], but formation of  $\text{H}_2$



**Scheme 7.5**  $\text{PhCH}_2\text{CH}_3$  (92%)

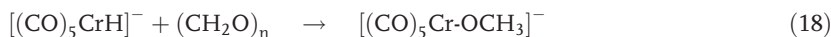
from this dihydride is very slow, occurring over a time scale of weeks at room temperature.

### 7.2.6

#### Stoichiometric Ionic Hydrogenation of Ketones and Aldehydes using Metal Hydrides as Hydride Donors and Added Acids as the Proton Donor

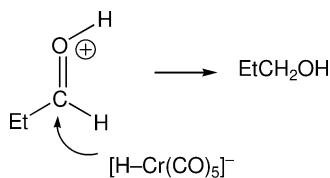
Several systems have been reported involving stoichiometric hydrogenation of ketones or aldehydes by metal hydrides in the presence of acids. An ionic hydrogenation mechanism accounts for most of these hydrogenations, though in some examples alternative mechanisms involving the insertion of a ketone into a M–H bond are also plausible.

An early example came from the report in 1985 by Darensbourg et al. on the reactions of  $[\text{HCr}(\text{CO})_5]^-$  and  $[\text{HCr}(\text{CO})_4\text{P}(\text{OMe})_3]^-$  with aldehydes and ketones, in the presence and absence of acids [27]. Paraformaldehyde reacts readily with  $\text{PPN}^+[\text{HCr}(\text{CO})_5]^-$   $\{\text{PPN}^+ = \text{N}(\text{PPh}_3)_2^+\}$  giving the alkoxide complex  $[(\text{CO})_5\text{CrOCH}_3]^-$  through insertion of formaldehyde into the Cr–H bond (Eq. (18)). The addition of HOAc produced methanol (Eq. (19)).



In contrast, only a sluggish reaction between propionaldehyde and  $[\text{HCr}(\text{CO})_5]^-$  was observed over several days, though addition of HOAc led to a 98% yield of *n*-propanol within 1 h. This striking change in reactivity between the two aldehydes suggests that propionaldehyde is hydrogenated to propanol not by an insertion mechanism, but rather through an ionic hydrogenation which protonation of the aldehyde activates it toward hydride transfer (Scheme 7.6). The phosphite-substituted anionic hydride  $[\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3]^-$  was more reactive with propionaldehyde in the absence of acids, providing evidence for a tungsten alkoxide complex that subsequently reacted with HOAc to produce a high yield of propanol. In the absence of acids, cyclohexanone showed little reactivity with any of the anionic hydrides  $[\text{HM}(\text{CO})_4\text{L}]^-$  (M = Cr or W, L = CO or P(OMe)<sub>3</sub>).

As was found for aldehydes, however, the addition of HOAc led to the alcohol product. For less-reactive ketones, lower yields were found in some cases, and loss of some of the metal hydride occurs through formation of H<sub>2</sub> from reaction



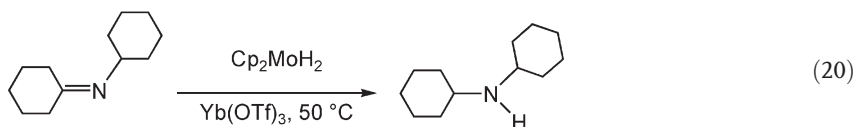
Scheme 7.6

of HOAc with  $[\text{HCr}(\text{CO})_5]^-$ . In some cases, the weaker acid phenol could be used instead of HOAc.

In contrast to the lack of reactivity of ketones with  $\text{PPN}^+[\text{HCr}(\text{CO})_5]^-$ , Brunet et al. reported different reactivity with  $\text{K}^+$  rather than  $\text{PPN}^+$  as the counterion. They found that  $\text{K}^+[\text{HCr}(\text{CO})_5]^-$  reacts with cyclohexanone in the absence of acid [35]. Hydrolysis with acid led to a 50% yield of cyclohexanol. These results suggest assistance from the  $\text{K}^+$  cation; ion-pairing in metal anions has been studied in detail by Darensbourg [36].

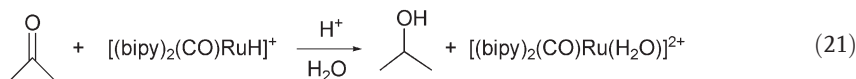
Gibson and El-Omrani found that aldehydes were hydrogenated in refluxing THF by the bimetallic Mo hydride  $[(\mu\text{-H})\text{Mo}_2(\text{CO})_{10}]^-$  in the presence of HOAc [37]. These reactions most likely proceed through generation of the mononuclear hydride  $[\text{HMo}(\text{CO})_5]^-$ , in analogy to the results discussed above for the Cr and W analogues.

Ito et al. found that hydrogenation of acetaldehyde, acetone, or cyclohexanone occurs at room temperature using  $[\text{Cp}_2\text{MoH}_2]$  and HOAc [38]. An ionic hydrogenation pathway was favored, in which protonation of the ketone or aldehyde was followed by hydride transfer from the metal, though a mechanism involving insertion of the  $\text{C}=\text{O}$  into the  $\text{Mo}\text{-H}$  bond was also considered possible. Both of the  $\text{Mo}\text{-H}$  bonds are active for this reaction. For example, in stoichiometric reactions using HOAc as the acid, the first hydride transfer occurs from  $[\text{Cp}_2\text{MoH}_2]$ , which produces  $[\text{Cp}_2\text{MoH}(\text{OAc})]$ , and this complex functions as a hydride donor for the second equivalent. The reactivity of  $\text{Cp}_2\text{MoH}_2$  is greater than that of  $[\text{Cp}_2\text{MoH}(\text{OAc})]$ , so that the first step is faster than the second. Using  $[\text{Cp}_2\text{MoH}(\text{OTs})]$  ( $\text{Ts} = p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2$ ) as the hydride donor, a very high diastereoselectivity was found for hydrogenation of the  $\text{C}=\text{O}$  bond of 4-*tert*-butylcyclohexanone, which gave only the *cis* isomer of 4-*tert*-butylcyclohexanol. Hydrogenation of the  $\text{C}=\text{N}$  bond of imines is also accomplished using  $[\text{Cp}_2\text{MoH}_2]$  and HOAc; good yields of imines were obtained from reactions carried out at room temperature from 18 to 92 h. While most of these hydrogenations used protic acids, hydrogenation of *N*-cyclohexylidenecyclohexylamine was carried out using  $[\text{Cp}_2\text{MoH}_2]$  and the Lewis acid  $[\text{Yb}(\text{OTf})_3]$ , giving a 90% yield of the amine in 24 h at  $50^\circ\text{C}$  (Eq. (20)).



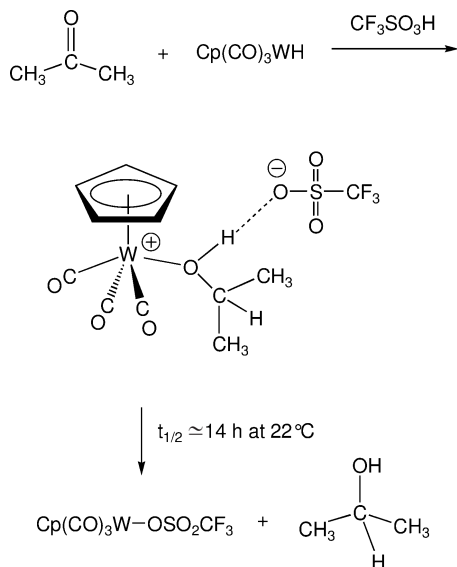
Hydride transfer from  $[(\text{bipy})_2(\text{CO})\text{RuH}]^+$  occurs in the hydrogenation of acetone when the reaction is carried out in buffered aqueous solutions (Eq. (21)) [39]. The kinetics of the reaction showed that it was a first-order in  $[(\text{bipy})_2(\text{CO})\text{RuH}]^+$  and also first-order in acetone. The reaction proceeds faster at lower pH. The proposed mechanism involved general acid catalysis, with a fast pre-equilibrium protonation of the ketone followed by hydride transfer from  $[(\text{bipy})_2(\text{CO})\text{RuH}]^+$ .



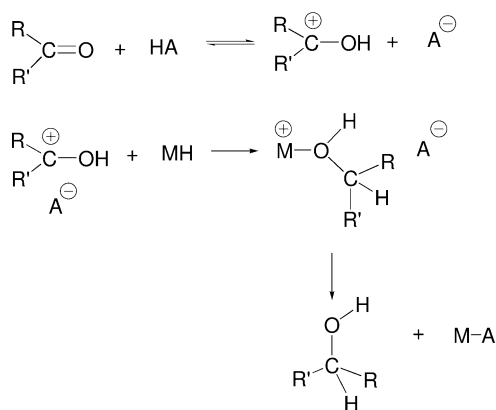


Harman and Taube found that the diamagnetic dihydrogen complex  $[(\text{NH}_3)_5\text{Os}(\eta^2\text{-H}_2)]^{+2}$  does not react with acetone [40]. Oxidation gives the  $\text{Os}^{\text{III}}$  complex  $[(\text{NH}_3)_5\text{Os}(\eta^2\text{-H}_2)]^{+3}$ , which hydrogenates acetone to isopropyl alcohol. The reaction is slow, taking place over two days at room temperature. These results suggest that proton transfer to the ketone occurs from the acidic dihydrogen complex  $[(\text{NH}_3)_5\text{Os}(\eta^2\text{-H}_2)]^{+3}$ , and that hydride transfer from  $[(\text{NH}_3)_5\text{OsH}]^{+2}$  to the protonated acetone generates the alcohol.

Extensive studies on stoichiometric hydrogenations of ketones have been carried out using HOTf as an acid, and metal carbonyl hydrides such as  $[\text{Cp}(\text{CO})_3\text{WH}]$  as the hydride donor [41, 42]. The addition of HOTf to a solution containing acetone and the tungsten hydride  $[\text{Cp}(\text{CO})_3\text{WH}]$  at  $22^\circ\text{C}$  results in hydrogenation of the  $\text{C}=\text{O}$  bond to the alcohol, with the kinetically stabilized product having an alcohol ligand bound to the metal (Scheme 7.7) [41, 42]. Most previously reported alcohol complexes had been prepared by adding an alcohol ligand to a metal complex with a weakly bound ligand, but in this case the alcohol ligand is formed in the reaction, without leaving the metal. The OH of the alcohol ligand is strongly hydrogen bonded to the triflate counterion, as shown by the short  $\text{O}\cdots\text{O}$  distance of  $2.63(1)$  Å found in the crystal structure of  $[\text{Cp}(\text{CO})_3\text{W}(\text{HO}^i\text{Pr})]^+\text{OTf}^-$ . Evidence that the hydrogen bonding is maintained in solution comes from the appearance of the OH of the bound alcohol ligand at  $\delta 7.34$  (d,  $J=7.4$  Hz) in the  $^1\text{H}$ -NMR spectrum, a chemical shift substantially downfield of



Scheme 7.7

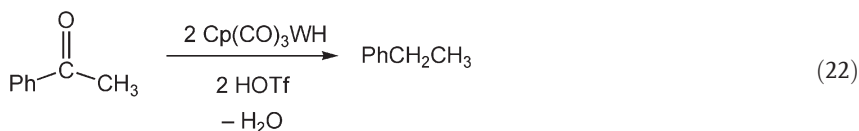


Scheme 7.8

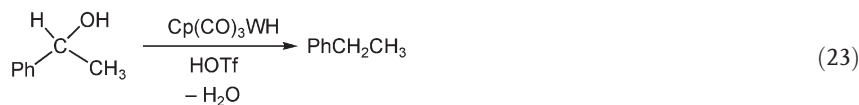
that found for free alcohols. The bound alcohol is displaced by the triflate counterion, producing free alcohol and  $[\text{Cp}(\text{CO})_3\text{WOTf}]$ . Other substrates that are readily hydrogenated by HOTf and  $[\text{Cp}(\text{CO})_3\text{WH}]$  include propionaldehyde, cyclohexanone, 2-adamantanone; in all of these cases fully characterized  $\text{W}(\text{alcohol})$  complexes were isolated.

The kinetics of the ionic hydrogenation of isobutyraldehyde were studied using  $[\text{CpMo}(\text{CO})_3\text{H}]$  as the hydride and  $\text{CF}_3\text{CO}_2\text{H}$  as the acid [41]. The apparent rate decreases as the reaction proceeds, since the acid is consumed. However, when the acidity is held constant by a buffered solution in the presence of excess metal hydride, the reaction is first-order in acid. The reaction is also first-order in metal hydride concentration. A mechanism consistent with these kinetics results is shown in Scheme 7.8. Pre-equilibrium protonation of the aldehyde is followed by rate-determining hydride transfer.

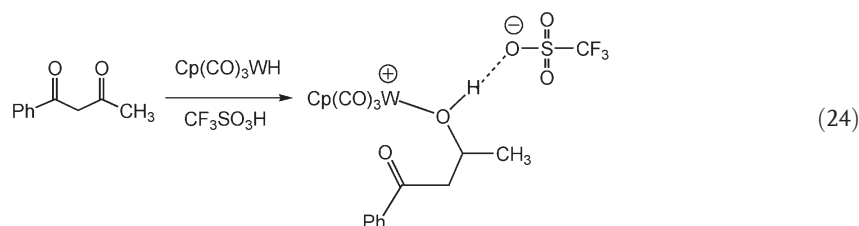
Ionic hydrogenation of acetophenone by HOTf (1 equiv.) and  $[\text{Cp}(\text{CO})_3\text{WH}]$  (1 equiv.) consumes only half of the ketone, and generates ethylbenzene (Eq. (22)) and  $[\text{Cp}(\text{CO})_3\text{WOTf}]$  [42].



No intermediate tungsten complexes were observed in this reaction. The alcohol, *sec*-phenethylalcohol, is consumed at a rate which is much faster than that of its formation. It was shown separately to be converted to ethylbenzene (Eq. (23)) by HOTf and  $[\text{Cp}(\text{CO})_3\text{WH}]$ . This reaction presumably proceeds through loss of water from the protonated alcohol, followed by hydride transfer from  $[\text{Cp}(\text{CO})_3\text{WH}]$  to give ethylbenzene.



A competition between stoichiometric hydrogenation of acetone and acetophenone resulted in hydrogenation of the acetone [42]. Competitions of this type could be influenced by both the basicity of the ketone, as well as by the kinetics of hydride transfer to the protonated ketone. An intramolecular competition between an aliphatic and aromatic ketone resulted in preferential hydrogenation of the aliphatic ketone, with the product shown in Eq. (24) being isolated and fully characterized by spectroscopy and crystallography. Selective ionic hydrogenation of an aldehyde over a ketone was also found with HOTf and  $[\text{Cp}(\text{CO})_3\text{WH}]$ .



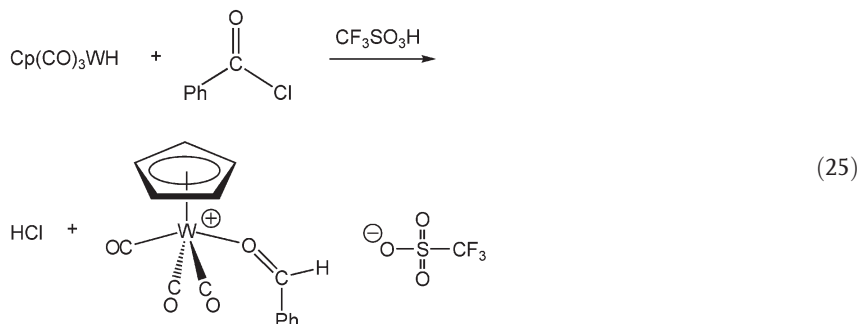
Bakmutov et al. reported the ionic hydrogenation of acetone or benzaldehyde by  $[\text{ReH}_2(\text{CO})(\text{NO})(\text{PR}_3)_2]$ , ( $\text{R} = i\text{Pr}, \text{CH}_3, \text{O}i\text{Pr}$ ) and  $\text{CF}_3\text{CO}_2\text{H}$  [43]. The resultant alcohol complexes were characterized by low-temperature NMR, and the OH protons had downfield chemical shifts. For example, the OH of the bound isopropyl alcohol in  $[\text{ReH}(\text{CO})(\text{NO})(\text{PMe}_3)_2(\text{HO}^i\text{Pr})]^+\text{CF}_3\text{CO}_2^-$  appears as a doublet at  $\delta$  8.17. The alcohol is subsequently released through displacement by the counterion, giving  $[\text{ReH}(\text{CO})(\text{NO})(\text{PR}_3)_2(\text{O}_2\text{CCF}_3)]$ . A significant kinetic preference was found for hydrogenation of benzaldehyde over acetone. Protonation of the dihydride  $[\text{ReH}_2(\text{CO})(\text{NO})(\text{PR}_3)_2]$  produces the cationic dihydrogen complexes  $[\text{ReH}(\text{H}_2)(\text{CO})(\text{NO})(\text{PR}_3)_2]^+$ , so protonation of the aldehyde or ketone can occur from these observable species, prior to hydride transfer to generate the alcohol. Whilst these hydrogenations produced alcohol complexes at low temperature, carrying out the reactions at room temperature gave mostly  $\text{H}_2$  elimination, and only 10–15% yields of the alcohol as the hydrogenation product.

### 7.2.7

#### Stoichiometric Ionic Hydrogenation of Acyl Chlorides to Aldehydes with HOTf/Metal Hydrides

Conversion of acyl chlorides to aldehydes occurs upon reaction with HOTf and  $[\text{Cp}(\text{CO})_3\text{WH}]$  [32]. The reaction of HOTf with benzoyl chloride and  $[\text{Cp}(\text{CO})_3\text{WH}]$  led to the isolation of  $[\text{Cp}(\text{CO})_3\text{W}(\text{PhCHO})]^+\text{OTf}^-$  (Eq. (25)), in which the aldehyde is bound to the metal [32]. The spectroscopic properties and

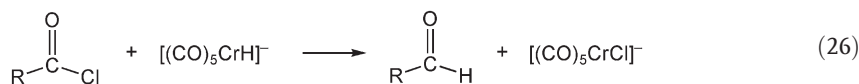
crystal structure of this aldehyde complex revealed that it was bound through the oxygen, as an  $\eta^1$ -aldehyde. As was found in the case of the alcohol complexes, the aldehyde complex is kinetically stabilized. The triflate counterion displaces the bound aldehyde in a first-order process ( $k=3.6\times 10^{-4}\text{ s}^{-1}$ ,  $t_{1/2}\approx 33\text{ min}$  at  $25^\circ\text{C}$ ), releasing the free aldehyde and generating  $[\text{Cp}(\text{CO})_3\text{WOTf}]$ .



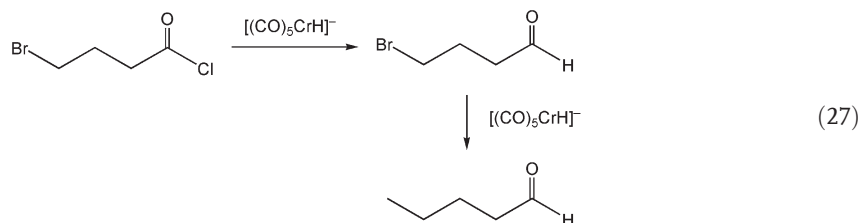
An analogous reaction occurs when  $\text{CH}_3(\text{C}=\text{O})\text{Cl}$  is reacted with HOTf and  $[\text{Cp}(\text{CO})_3\text{WH}]$ , with the acetaldehyde complex  $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_3\text{CHO})]^+\text{OTf}^-$  being isolated [32]. Reaction with  $>1$  equiv. each of HOTf and  $\text{Cp}(\text{CO})_3\text{WH}$  led to subsequent hydrogenation of the  $\text{CH}_3\text{CHO}$  to ethanol, which was initially present as a bound ethanol ligand. It is possible that the mechanism of formation of the aldehyde complex involves protonation of the acyl chloride and hydride transfer from the metal, leading to a bound chlorohydrin complex,  $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_3\text{C}(\text{Cl})(\text{H})\text{OH})]^+\text{OTf}^-$ , which could expel HCl to produce  $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_3\text{CHO})]^+\text{OTf}^-$ . Since acyl chlorides are known to react with HOTf to produce acyl triflates, an alternative mechanism is formation of  $\text{CH}_3\text{C}(\text{=O})\text{OTf}$  followed by reaction with  $[\text{Cp}(\text{CO})_3\text{WH}]$ . The acyl triflate  $\text{CH}_3\text{C}(\text{=O})\text{OTf}$  was prepared and shown to react with  $[\text{Cp}(\text{CO})_3\text{WH}]$  to give  $[\text{Cp}(\text{CO})_3\text{W}(\text{CH}_3\text{CHO})]^+\text{OTf}^-$ , documenting the viability of this mechanistic pathway. It has not been established which of the two pathways is operative for these reactions.

Several anionic metal carbonyl hydrides stoichiometrically convert acyl chlorides to aldehydes. The anionic vanadium complex  $[\text{Cp}(\text{CO})_3\text{VH}]^-$  reacts quickly with acyl chlorides, converting them to aldehydes [44]. Although no further reduction of the aldehyde to alcohol was observed, the aldehydes reacted further under the reaction conditions in some cases, so a general procedure for isolation of the aldehydes was not developed.

Darensbourg et al. found that  $\text{HCr}(\text{CO})_5^-$  converts acyl chlorides to aldehydes rapidly at  $25^\circ\text{C}$  (Eq. (26)) [26]. Yields  $>90\%$  were detected by gas chromatography (GC) for preparation of  $\text{CH}_3\text{CHO}$ ,  $n\text{-BuCHO}$ ,  $\text{PhCHO}$ , and  $\text{PhCH}_2\text{CHO}$ . Since  $\text{CH}_3\text{OD}$  converts  $\text{HCr}(\text{CO})_5^-$  to  $\text{DCr}(\text{CO})_5^-$ , the reaction of  $[\text{HCr}(\text{CO})_5]^-$  with  $\text{PhCOCl}$  in the presence of  $\text{CH}_3\text{OD}$  provided a convenient synthesis of the deuterated aldehyde,  $\text{PhCDO}$ .



As noted earlier,  $[\text{HCr}(\text{CO})_5]^-$  also converts alkyl halides to alkanes, but the reactivity of the acyl chloride is much higher, such that it was possible to selectively convert the acyl chloride to an aldehyde in one step, without interference from the alkyl bromide functionality. A second equivalent of  $[\text{HCr}(\text{CO})_5]^-$  further reduced the alkyl bromide (Eq. (27)).



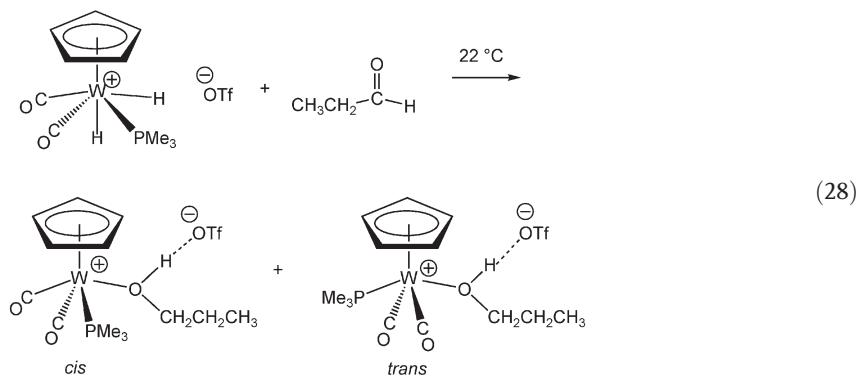
### 7.2.8

#### Stoichiometric Ionic Hydrogenation of Ketones with Metal Dihydrides

Many examples of stoichiometric ionic hydrogenation discussed above involved hydride transfer from metal hydrides, following proton transfer from an *external* acid source. Achieving a catalytic system still requires the hydride transfer step, but will additionally require a source of protons from a metal complex. In many cases the proton source will be an acidic M–H bond, so examples of stoichiometric hydrogenation involving a metal-based proton and hydride source are an important step in documenting the viability of catalytic ionic hydrogenation methodology.

The cationic tantalum dihydride  $\text{Cp}_2(\text{CO})\text{Ta}(\text{H})_2]^+$  reacts at room temperature with acetone to generate the alcohol complex  $[\text{Cp}_2(\text{CO})\text{Ta}(\text{HO}^i\text{Pr})]^+$ , which was isolated and characterized [45]. The mechanism appears to involve protonation of the ketone by the dihydride, followed by hydride transfer from the neutral hydride. The OH of the coordinated alcohol in the cationic tantalum alcohol complex can be deprotonated to produce the tantalum alkoxide complex  $[\text{Cp}_2(\text{CO})\text{Ta}(\text{O}^i\text{Pr})]$ . Attempts to make the reaction catalytic by carrying out the reaction under  $\text{H}_2$  at  $60^\circ\text{C}$  were unsuccessful. The strong bond between oxygen and an early transition metal such as Ta appears to preclude catalytic reactivity in this example.

The cationic tungsten dihydride  $[\text{Cp}(\text{CO})_2(\text{PMe}_3)\text{W}(\text{H})_2]^+$  hydrogenates the C=O bond of propionaldehyde within minutes at  $22^\circ\text{C}$ , leading to the formation of *cis* and *trans* isomers of  $[\text{Cp}(\text{CO})_3\text{W}(\text{HO}^n\text{Pr})]^+\text{OTf}^-$  (Eq. (28)) [42]. The *cis* isomer of the alcohol complex released the free alcohol faster than the *trans* isomer. A similar stoichiometric ionic hydrogenation of acetone was also observed using  $[\text{Cp}(\text{CO})_2(\text{PMe}_3)\text{W}(\text{H})_2]^+$ .



### 7.3

#### Catalytic Ionic Hydrogenation

##### 7.3.1

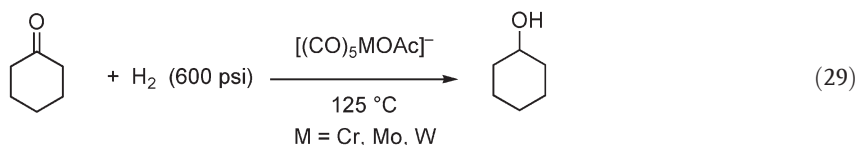
##### Catalytic Ionic Hydrogenation of C=C Bonds

A series of cationic cobalt and rhodium complexes with a tetradentate chelating phosphine ligand have been reported [46]. These complexes were initially formulated as dihydrogen complexes,  $[(PP_3)Co(H)_2]^+$   $\{PP_3 = P(CH_2CH_2PPh_2)_3\}$ , but subsequent NMR studies conducted by Heinekey et al. showed that they were dihydride complexes  $[(PP_3)Co(H)_2]^+$  [47]. Bianchini et al. found that, under an argon atmosphere,  $[(PP_3)Co(H)_2]^+$  hydrogenates the C=C bond of dimethyl maleate in 3 h at room temperature [46]. When the reaction is conducted under  $H_2$ , catalytic hydrogenation of the C=C bond is observed, with a TOF of  $1.5\ h^{-1}$ . This reaction was suggested to proceed by an ionic mechanism, in which the cationic dihydride transfers a proton to the electron-deficient alkene, followed by hydride transfer from the neutral cobalt hydride complex. The acidity of Bianchini's  $[(PP_3)Co(H)_2]^+$  would be expected to be roughly similar to that of  $[(dppe)_2Co(H)_2]^+$ , for which a  $pK_a$  of 22.8 was determined in  $CH_3CN$  (see Table 7.2). The low acidity of the dihydride raises questions about the likelihood of a proton-transfer mechanism for the initial step.

##### 7.3.2

##### Catalytic Ionic Hydrogenation of Ketones by Anionic Cr, Mo, and W Complexes

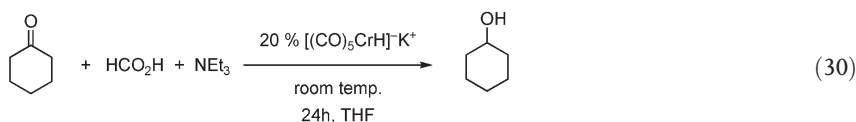
Extensive studies on the hydride transfer reactivity of metal carbonyl anions such as  $[HCr(CO)_5]^-$  presaged the development of anionic catalysts using Cr, Mo, and W. Darensbourg and coworkers found that 5 mol.%  $[(CO)_5M(OAc)]^-$  ( $M = Cr, Mo, W$ ) catalyzed the hydrogenation of cyclohexanone to cyclohexanol at  $125\ ^\circ C$  in THF using 36 bar  $H_2$  (Eq. (29)) [48]. Under these conditions, TON determined after 24 h were 10 for W, 3.5 for Mo, and 18 for Cr.



The organometallic products included recovered  $[(\text{CO})_5\text{M}(\text{OAc})]^-$ , along with  $\text{M}(\text{CO})_6$  and the bimetallic bridging hydride complex  $[(\mu\text{-H})\text{M}_2(\text{CO})_{10}]^-$ . It was proposed that, under the reaction conditions,  $[(\text{CO})_5\text{MH}]^-$  and HOAc were produced, and that insertion of the ketone into the M–H bond gave a metal alkoxide that reacted with HOAc to produce the alcohol.

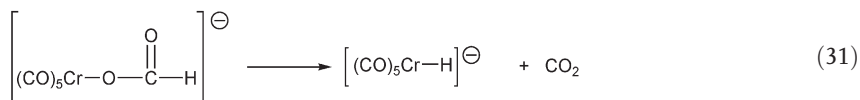
Catalytic hydrogenations of cyclohexanone and benzaldehyde were also reported by Darensbourg et al. using 5%  $[(\mu\text{-H})\text{M}_2(\text{CO})_{10}]^-$  (M=Cr, Mo, W) at 125 °C for 24 h; between four and 18 turnovers were observed under these conditions [48]. Related observations were made by Markó, who found that ketones (acetophenone, cyclohexanone, acetone, isobutyl methyl ketone) and aldehydes (benzaldehyde, butyraldehyde) could be catalytically hydrogenated at 160 °C under 100 bar of CO + H<sub>2</sub> [49]. Their experiments used 5 mol.%  $[\text{Cr}(\text{CO})_6]$  as the catalyst precursor, together with NaOCH<sub>3</sub> in methanol solution; under these conditions  $[(\text{CO})_5\text{CrH}]^-$  and  $[(\mu\text{-H})\text{Cr}_2(\text{CO})_{10}]^-$  are formed. Similar hydrogenations were carried out starting with  $[\text{W}(\text{CO})_6]$  and with  $[\text{Mo}(\text{CO})_6]$ . For the molybdenum example, milder conditions were used, with 91% hydrogenation of acetophenone being found after 3 h at 70 °C starting with 5 mol.%  $\text{Mo}(\text{CO})_6$  in methanol with added NaOCH<sub>3</sub>. Fuchikami et al. found that  $[(\mu\text{-H})\text{Cr}_2(\text{CO})_{10}]^-$  is much more active as a catalyst in dimethoxyethane (DME) than in THF [50]. Hydrogenation (50 bar H<sub>2</sub>) of benzaldehyde at 100 °C using 1 mol.%  $[(\mu\text{-H})\text{Cr}_2(\text{CO})_{10}]^- \text{PPN}^+$  produced 100 turnovers of benzyl alcohol after 13 h in DME, whereas using THF for 24 h at 125 °C gave only 14 turnovers.

Brunet et al. developed a transfer hydrogenation catalyst based on chromium, using 20%  $\text{K}^+[(\text{CO})_5\text{CrH}]^-$  as the catalyst precursor in THF solution, together with 5 equiv. each of HCO<sub>2</sub>H and NEt<sub>3</sub> (Eq. (30)) [35, 51].



In reactions carried out for 24 h at room temperature, a 95% yield of cyclohexanol from cyclohexanone was obtained. Other ketones and aldehydes were also hydrogenated under identical conditions, but with slower rates (38% conversion for hydrogenation of 2-hexanone, 25% conversion of acetophenone, 45% for 3-methyl-2-butanone). Insertion of the C=O bond of the ketone or aldehyde into the Cr–H bond was proposed as the first step, producing a chromium alkoxide complex that reacts with acid to generate the alcohol product. The anionic chromium hydride  $[(\text{CO})_5\text{CrH}]^-$  is regenerated from the formate complex by

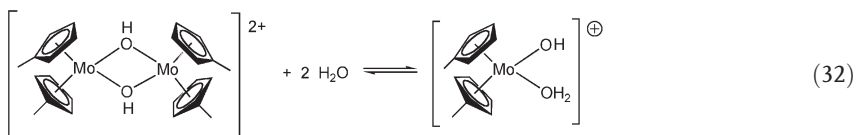
decarboxylation (Eq. (31)). The role of the triethylamine is to moderate the strength of the formic acid, since formic acid alone is too strong of an acid, converting  $[(\text{CO})_5\text{CrH}]^-$  into  $[(\mu\text{-H})\text{Cr}_2(\text{CO})_{10}]^-$ .



### 7.3.3

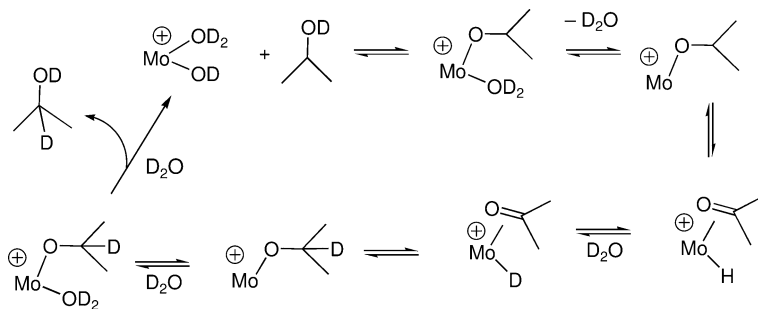
#### Catalytic Ionic Hydrogenation of Ketones by Molybdenocene Complexes

Hydride transfer reactions from  $[\text{Cp}_2\text{MoH}_2]$  were discussed above in studies by Ito et al. [38], where this molybdenum dihydride was used in conjunction with acids for stoichiometric ionic hydrogenations of ketones. Tyler and coworkers have extensively developed the chemistry of related molybdenocene complexes in aqueous solution [52–54]. The dimeric bis-hydroxide bridged dication dissolves in water to produce the monomeric complex shown in Eq. (32) [53]. In  $\text{D}_2\text{O}$  solution at  $80^\circ\text{C}$ , this bimetallic complex catalyzes the H/D exchange of the  $\alpha$ -protons of alcohols such as benzyl alcohol and ethanol [52, 54].



The proposed mechanism for this H/D exchange is shown in Scheme 7.9. The formation of the alkoxide complex likely proceeds by displacement of the water ligand by the alcohol, forming an unobserved alcohol complex that transfers  $\text{D}^+$  to the OD ligand, producing an  $\text{OD}_2$  ligand.

The key step involves C–H bond activation, and produces a molybdenum complex with hydride and ketone ligands from the alkoxide ligand. Subsequent



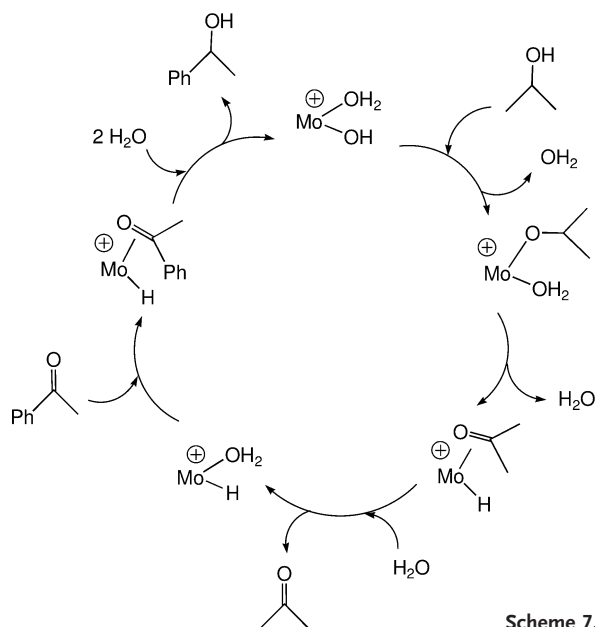
Scheme 7.9



H/D exchange leads to deuterium incorporation into the  $\alpha$ -position of the alcohol.

Heating the bimetallic complex in  $D_2O$  solution also results in deuteration of the  $CH_3$  sites on the cyclopentadienyl ring, through a mechanism involving oxidative addition of a C–H bond of the  $CH_3$  group, followed by deuterium incorporation into the methyl group [54]. Heating of a mixture of the molybdenum complex with isopropyl alcohol and 2-butanone led to hydrogenation of the ketone, producing 2-butanol, and dehydrogenation of the isopropyl alcohol, generating acetone [52, 54]. Kuo et al. carried out further studies on these hydrogenations [55, 56]. Acetone is hydrogenated to isopropyl alcohol by  $[Cp_2MoH(OTf)]$  in water. The rates are faster in acidic solution than when the solution is buffered at pH 7, consistent with a general acid-catalyzed pathway in which the ketone is protonated prior to hydride transfer from the molybdenum hydride [55]. An alternative mechanism would involve insertion of the ketone into a Mo–H bond to give a metal alkoxide, which could then generate the alcohol by hydrolysis with water. The transfer hydrogenation of acetophenone by isopropyl alcohol in water is catalyzed by  $[Cp_2Mo(\mu-OH)_2MoCp_2]^{2+}(OTf^-)_2$  [56]. At 75 °C, the TOF is about  $0.1\text{ h}^{-1}$ . Scheme 7.10 shows the proposed mechanism for this transfer hydrogenation; several of these steps have precedent in Tyler's H/D exchange reactions shown in Scheme 7.9 [52].

The catalytic ketone hydrogenation reaction is accelerated by addition of KOH. In the presence of 25 equiv. KOH, 1 mol.% of the molybdenum complex completely hydrogenated acetophenone overnight in refluxing 2-propanol



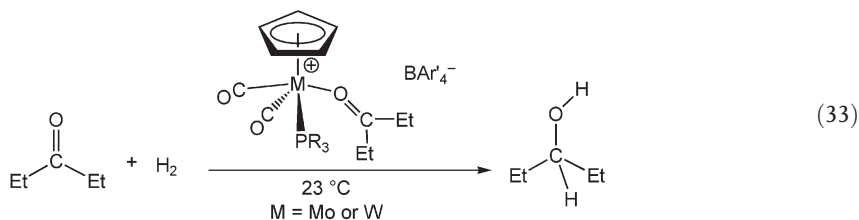
(82 °C). The exact role of the base is not clear, but it may accelerate the formation of the molybdenum alkoxide complex from a bound alcohol ligand.

### 7.3.4

#### Catalytic Ionic Hydrogenation of Ketones by Cationic Mo and W Complexes

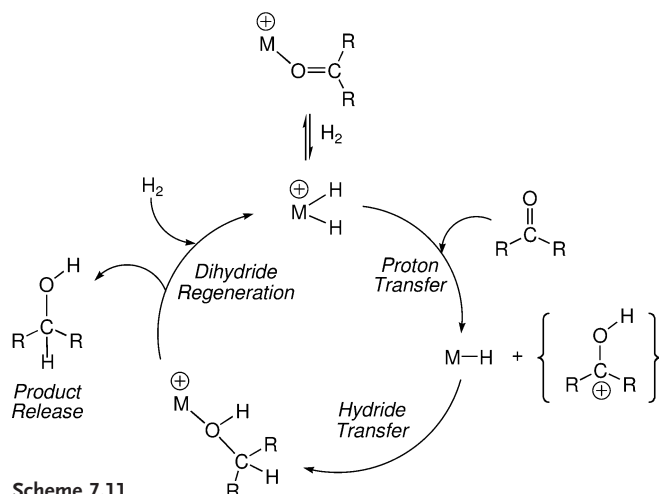
##### 7.3.4.1 In Solution

Molybdenum and tungsten carbonyl hydride complexes were shown (Eqs. (16), (17), (22), (23), (24); see Schemes 7.5 and 7.7) to function as hydride donors in the presence of acids. Tungsten dihydrides are capable of carrying out stoichiometric ionic hydrogenation of aldehydes and ketones (Eq. (28)). These stoichiometric reactions provided evidence that the proton and hydride transfer steps necessary for a catalytic cycle were viable, but closing of the cycle requires that the metal hydride bonds be regenerated from reaction with H<sub>2</sub>.

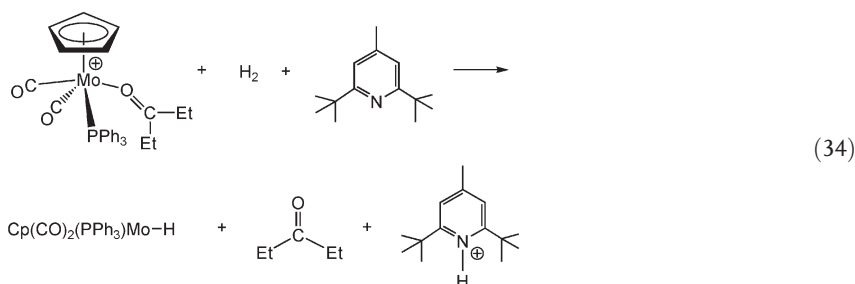


Tungsten and molybdenum ketone complexes,  $[\text{Cp}(\text{CO})_2(\text{PR}_3)\text{M}(\text{O}=\text{C}(\text{Et})_2)]^+ \text{BAr}'_4^-$  [ $\text{Ar}' = 3,5\text{-bis}(\text{trifluoromethyl})\text{phenyl}$ ], could be isolated for  $\text{PR}_3 = \text{PMe}_3$  and  $\text{PPh}_3$  but were prepared *in situ* for the  $\text{PCy}_3$  ( $\text{Cy} = \text{cyclohexyl}$ ) complexes [57]. A series of experiments were carried out in  $\text{CD}_2\text{Cl}_2$  solvent at 23 °C under 4 bar H<sub>2</sub>, with about 10 equiv.  $\text{Et}_2\text{C}=\text{O}$  (Eq. (33)). Formation of the alcohol ( $\text{Et}_2\text{CH-OH}$ ) was accompanied at later times by small amounts of the ether,  $(\text{Et}_2\text{CH})_2\text{O}$ , which arises from condensation of the alcohol. Under these reaction conditions, since the ketone substrate was not present in large excess, it was possible to monitor simultaneously the progress of the hydrogenation, as well as to detect the organometallic species present under catalytic hydrogenation conditions. As the reaction proceeds, the concentration of the ketone complex decreases, with concomitant formation of the alcohol complex. For example, in the case of the W complexes with a  $\text{PPh}_3$  ligand, NMR evidence indicated the formation of  $\text{trans-}[\text{CpW}(\text{CO})_2(\text{PPh}_3)(\text{Et}_2\text{CHOH})]^+$ , with the concentration of this alcohol complex exceeding that of the ketone complex at later reaction times. As discussed earlier, alcohol complexes were previously found to be the kinetic product of stoichiometric ionic hydrogenation of ketones, so the observation under catalytic conditions indicates that the stoichiometric reactivity provides a good model in this case for the catalytic reactivity, even with some changes in ligands and counterions between the stoichiometric and catalytic reactions.

The proposed mechanism shown in Scheme 7.11 is supported by stoichiometric proton- and hydride-transfer reactions of metal hydrides that were dis-



cussed earlier. The key step to closure of the cycle, regeneration of the M–H bonds by  $H_2$ , is accomplished by reaction of the ketone complex with  $H_2$ . Tungsten dihydride complexes were sufficiently stable to be isolated and fully characterized [34], but molybdenum analogues were not directly observed. Evidence for the intermediacy of molybdenum dihydrides (or dihydrogen complexes) comes from heterolytic cleavage of  $H_2$  by a molybdenum ketone complex in the presence of a hindered amine base (Eq. (34)). When  $H_2$  is added to  $[CpW(CO)_2(PPh_3)(Et_2C=O)]^+$  (with no added ketone), the dihydride  $[CpW(CO)_2(PPh_3)(H)_2]^+$  is formed, providing further support for the operation of this step under catalytic conditions.



Conversion of  $[CpW(CO)_2(PPh_3)(Et_2C=O)]^+$  to *trans*- $[CpW(CO)_2(PPh_3)(Et_2CH_2OH)]^+$  was observed when  $Et_2C=O$  was hydrogenated under high pressure (65 bar) of  $H_2$  for 17 h at 22 °C. Hydride transfer from  $[CpW(CO)_2(PPh_3)H]$  to  $Ph_3C^+BAR_4^-$ , followed by addition of the alcohol  $Et_2CHOH$ , led to the isolation of the *cis* isomer of  $[CpW(CO)_2(PPh_3)(Et_2CHOH)]^+$ . The studies of kinetic hydricity of metal hydrides had shown that hydride transfer from *trans*- $[Cp(CO)_2(PCy_3)MoH]$  to  $Ph_3C^+BF_4^-$  occurs much faster than hydride transfer

from the *cis* isomer of the hydride, *cis*-[Cp(CO)<sub>2</sub>(PCy<sub>3</sub>)MoH] [58]. Since the *trans* isomer of the alcohol complex is observed under catalytic conditions, the alcohol binds to the metal at the site from which hydride transfer took place. The studies of stoichiometric ionic hydrogenation of ketones had previously provided evidence that some amount of W–O bond formation is taking place in the transition state, before W–H bond cleavage is complete [41, 42].

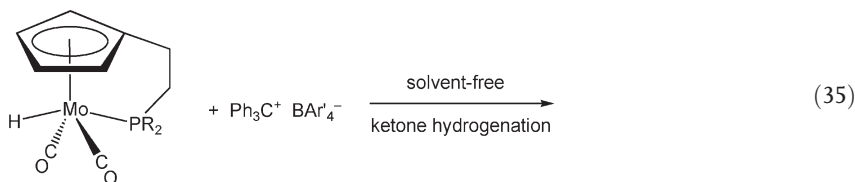
Comparison of the rates of hydrogenation in these systematic studies of ionic hydrogenation of ketones by [Cp(CO)<sub>2</sub>(PR<sub>3</sub>)M(O=CEt<sub>2</sub>)]<sup>+</sup> indicated the trends in metal and phosphine ligand [57]. For comparisons involving the same PR<sub>3</sub> ligand, the Mo complexes are invariably faster catalysts compared to the W analogue. The initial rate of hydrogenation is about eight-fold faster for Mo than for W for the PPh<sub>3</sub> complexes, and the difference is roughly two orders of magnitude for the PCy<sub>3</sub> complexes. For the Mo catalysts, the rate varies substantially with different phosphine ligands, in the order PCy<sub>3</sub> > PPh<sub>3</sub> > PMe<sub>3</sub>. The approximate initial rate was about two turnovers per hour for the Mo–PCy<sub>3</sub> complex. For the W complexes, the same order was found, though the range of relative rates was smaller for W than for Mo. The phosphines PCy<sub>3</sub> and PMe<sub>3</sub> are similar electronically, so the much higher rate of catalysis found with the PCy<sub>3</sub> complexes makes it clear that steric effects predominate over electronic effects.

For the PPh<sub>3</sub> and PMe<sub>3</sub> complexes, the ketone or alcohol complexes were observed spectroscopically during the hydrogenation reaction, and those species are the resting states. Formation of the dihydride complexes under catalytic conditions is proposed to involve dissociation of the ketone or alcohol followed by addition of H<sub>2</sub>. The higher rate of catalysis with the PCy<sub>3</sub> complexes suggests that the steric bulk of this ligand promotes ketone dissociation more than in the case of the PPh<sub>3</sub> or PMe<sub>3</sub> complexes. In contrast to the PPh<sub>3</sub> and PMe<sub>3</sub> complexes, the predominant tungsten complex observed during hydrogenation with the PCy<sub>3</sub> complex was [Cp(CO)<sub>2</sub>(PCy<sub>3</sub>)W(H)<sub>2</sub>]<sup>+</sup>. In this case, proton transfer from the metal to the ketone is slow and has become the turnover-limiting step of the catalytic cycle. Ketone binding to the metal is destabilized by steric factors for the PCy<sub>3</sub> complex, compared to analogues with PMe<sub>3</sub>. In addition, the steric effects of the bulky PCy<sub>3</sub> ligand likely disfavor proton transfer from the metal to the free ketone. Norton et al. reported a pK<sub>a</sub> of 5.6 in CH<sub>3</sub>CN for [CpW(CO)<sub>2</sub>(PMe<sub>3</sub>)(H)<sub>2</sub>]<sup>+</sup> [31]. The pK<sub>a</sub> of protonated acetone in CH<sub>3</sub>CN is about –0.1 [59, 60]. Presuming that there is not a large change in relative pK<sub>a</sub> values in CH<sub>3</sub>CN (in which the pK<sub>a</sub> measurements were made) and CD<sub>2</sub>Cl<sub>2</sub> (in which the hydrogenations were carried out), the thermodynamics of proton transfer from the dihydride to the ketone are uphill in all of these cases. The tungsten dihydride [CpW(CO)<sub>2</sub>(PMe<sub>3</sub>)(H)<sub>2</sub>]<sup>+</sup> (for which pK<sub>a</sub> data are available) is the one that leads to the slowest hydrogenation, so it is likely that this represents the least thermodynamically favorable example for proton transfer. Based on the trends in acidity identified above, [CpW(CO)<sub>2</sub>(PPh<sub>3</sub>)(H)<sub>2</sub>]<sup>+</sup> is expected to be more acidic than [CpW(CO)<sub>2</sub>(PMe<sub>3</sub>)(H)<sub>2</sub>]<sup>+</sup>; similarly, Mo hydrides are more acidic than W hydrides. Rate constants for hydride transfer to protonated ketones have not been as extensively studied as those for hydride transfer to Ph<sub>3</sub>C<sup>+</sup> (see Table 7.5), but

hydride transfer from  $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{MoH}$  to protonated acetone occurs in  $\text{CH}_3\text{CN}$  with a reported rate constant of  $1.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  at  $25^\circ\text{C}$  [60]. Proton transfer from the dihydride to the ketone is thermodynamically uphill, but this does not prevent catalytic ionic hydrogenations with these W and Mo complexes from proceeding smoothly, since rapid hydride transfer from the neutral hydride follows the proton transfer.

Evidence for a major mode of catalyst deactivation in this system came from the observation of phosphonium cations ( $\text{HPR}_3^+$ ) in the reaction mixture, which could form through the protonation of free  $\text{PR}_3$  by the acidic dihydride complex. It is not known which species decomposes to release free  $\text{PR}_3$ , but the decomposition pathway is exacerbated by the subsequent reactivity in which protonation of phosphine removes a proton from the metal dihydride, effectively removing a second metal species from the cycle.

Knowledge of the pathway for catalyst deactivation suggested that catalysts with longer lifetimes might result if phosphine dissociation could be suppressed. A series of Mo complexes was prepared that had a two-carbon chain chelating the cyclopentadienyl ligand to the phosphine [61]. Hydride abstraction from  $[\text{HMo}(\text{CO})_2\{\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{PR}_2\}]$  ( $\text{R} = \text{Cy}, t\text{Bu}, \text{and Ph}$ ) using  $\text{Ph}_3\text{C}^+\text{BAR}_4^-$  in the presence of  $\text{Et}_2\text{C}=\text{O}$  led to ketone hydrogenation catalysts (Eq. (35)) that exhibited several advantages over the unbridged complexes.



Comparisons of catalysis of these  $\text{C}_2$ -tethered P,C chelate complexes with the non-chelate analogues in  $\text{CD}_2\text{Cl}_2$  solvent showed that the former were somewhat slower catalysts than the latter, but the compelling advantage of the chelate complexes is that they had much longer lifetimes.

#### 7.3.4.2 Solvent-free

Environmental concerns have caused an intense emphasis on the development of chemical reactions that reduce waste. Solvents are used on a huge scale, with more than 15 billion kilograms of organic solvents being produced each year [62]. One of the Principles of Green Chemistry [7] indicates that the use of a solvent should be avoided whenever possible, and it has been found that the hydrides  $[\text{HMo}(\text{CO})_2\{\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{PR}_2\}]$  can be used as catalyst precursors for the solvent-free [62,63] hydrogenation of  $\text{Et}_2\text{C}=\text{O}$ . Hydrogenations can be carried out at higher temperatures, since the  $\text{C}_2\text{-PR}_2$  complexes have significantly improved stability compared to the unbridged complexes. Another attractive feature of these bridged catalysts is that they can be used at low catalyst loading,

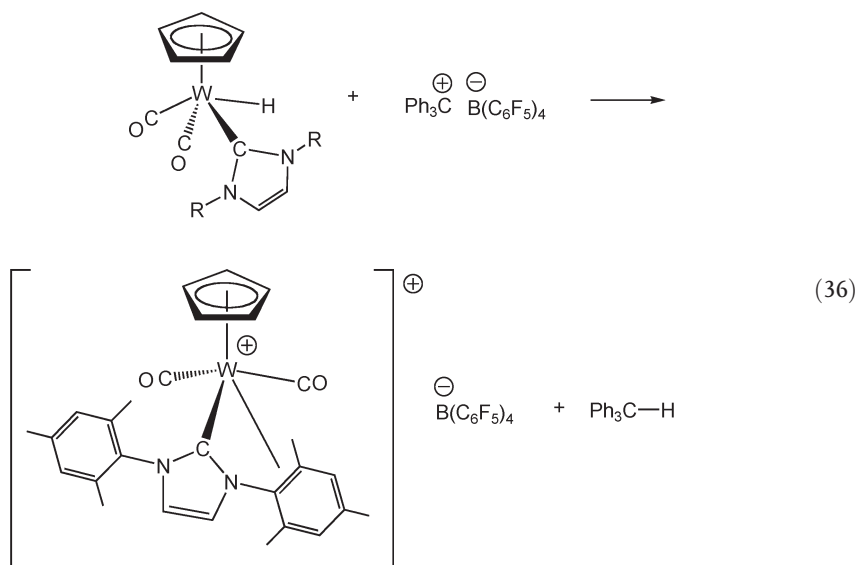
less than 1 mol.% typically, and as low as 0.09 mol.% in one example. Solvent-free hydrogenation of  $\text{Et}_2\text{C}=\text{O}$  using  $[\text{HMo}(\text{CO})_2\{\eta^5:\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{PCy}_2\}]$  (0.35 mol.%) as the catalyst precursor (activated by hydride removal using  $\text{Ph}_3\text{C}^+\text{BAr}'_4^-$ ) was carried out under 4 bar  $\text{H}_2$  at  $50^\circ\text{C}$  for 10 days, and 132 turnovers were observed (Eq. (35)). Only 62 turnovers were found when the analogous  $\text{C}_2\text{-PPh}_2$  complex was employed under identical conditions, indicating that the performance of the catalyst with  $\text{R}=\text{Cy}$  was superior to that found with  $\text{R}=\text{Ph}$ , the same trend that was found for the unbridged complexes. Although the steric bulk of the  $\text{Cy}$  group on the phosphines was recognized as an advantage, the use of the  $\text{C}_2\text{-PtBu}_2$  complex (82 turnovers under identical conditions) was superior to that of the  $\text{C}_2\text{-PPh}_2$  complex but not as high as the  $\text{C}_2\text{-PCy}_2$  complex. Higher pressure of  $\text{H}_2$  led to faster rates of catalysis – complete hydrogenation of  $\text{Et}_2\text{C}=\text{O}$  was accomplished using  $[\text{HMo}(\text{CO})_2\{\eta^5:\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{PCy}_2\}]$  (0.35 mol.%) as the catalyst precursor at  $50^\circ\text{C}$  under 55 bar  $\text{H}_2$  for 8 days.

Most of the studies of these Mo catalysts were carried out with  $\text{BAr}'_4^-$  as the counterion; catalysis is also observed using  $\text{BF}_4^-$  or  $\text{PF}_6^-$  as the counterion, albeit with lower turnover numbers [61]. Triflate is an attractive counterion; it offers advantages of lower cost compared to  $\text{BAr}'_4^-$ , but may be slightly different mechanistically since it coordinates to the metal. Protonation of  $[\text{HMo}(\text{CO})_2\{\eta^5:\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{PCy}_2\}]$  with HOTf leads to the formation of the triflate complex  $[\text{Mo}(\text{CO})_2\{\eta^5:\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{PR}_2\}\text{OTf}]$ , presumably through an unobserved dihydride or dihydrogen complex. Solvent-free hydrogenation (4 bar  $\text{H}_2$ ) of  $\text{Et}_2\text{C}=\text{O}$  using 0.35 mol.%  $[\text{Mo}(\text{CO})_2\{\eta^5:\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{PCy}_2\}\text{OTf}]$  ( $50^\circ\text{C}$ , 10 days) gave 120 turnovers, only slightly less than the 132 turnovers found under identical conditions using the  $\text{BAr}'_4^-$  counterion. Even lower catalyst loading was successfully carried out with  $[\text{Mo}(\text{CO})_2\{\eta^5:\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{PCy}_2\}\text{OTf}]$ : 0.09 mol.% catalyst loading at  $75^\circ\text{C}$  for 10 days provided 462 turnovers in the hydrogenation of  $\text{Et}_2\text{C}=\text{O}$  under solvent-free conditions.

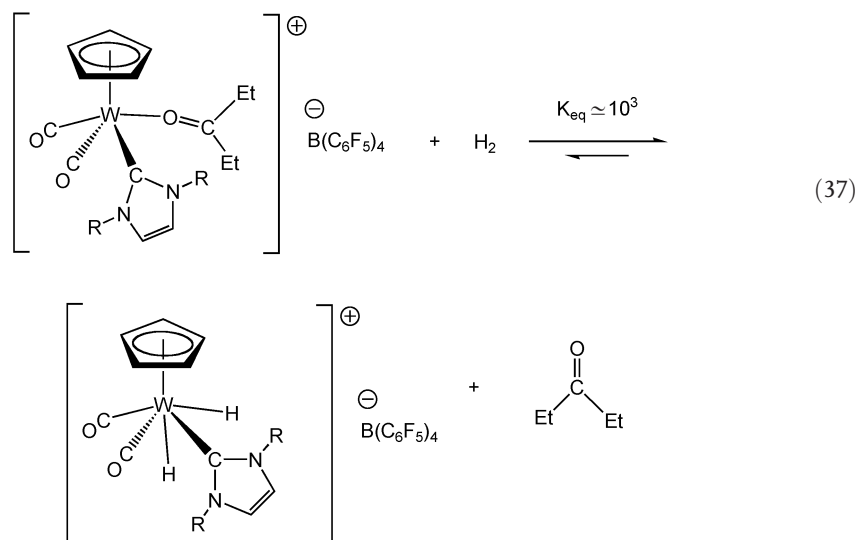
These Mo catalysts with a  $\text{C}_2$ -tether connecting the phosphine and cyclopentadienyl ligand provide an example of the use of mechanistic principles in the rational design of improved catalysts, in this case based on information about a decomposition pathway for the prior generation of catalysts. The new catalysts offer improved lifetimes, higher thermal stability, and low catalyst loading. The successful use of a triflate counterion and solvent-free conditions for the hydrogenation are additional features that move these catalysts closer to practical utility.

#### 7.3.4.3 N-Heterocyclic Carbene Complexes

N-heterocyclic carbenes have recently been used as alternatives to phosphines in many catalytic reactions, owing in part to a decreased propensity to dissociate from the metal [64]. Hydride abstraction from the tungsten hydride  $[\text{Cp}(\text{CO})_2(\text{IMes})\text{WH}]$  (IMes = the carbene ligand 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene) using  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  leads to the formation of an unusual complex in which one  $\text{C}=\text{C}$  of a mesityl ring has a weak bonding interaction with the tungsten (Eq. (36)) [65].



This complex can be used as a catalyst precursor for hydrogenation of ketones, though only two turnovers occurred in one day for solvent-free hydrogenation of  $\text{Et}_2\text{C}=\text{O}$  at  $23^\circ\text{C}$  using 0.34 mol.% catalyst at 4 bar  $\text{H}_2$ . At the same catalyst loading, 61 turnovers occurred in 7 days at higher temperature ( $50^\circ\text{C}$ ) and higher  $\text{H}_2$  pressure (54 bar), though some decomposition of the catalyst is also observed. These catalysts are thought to operate by a mechanism analogous to that shown above (see Scheme 7.11) for the related phosphine complexes.

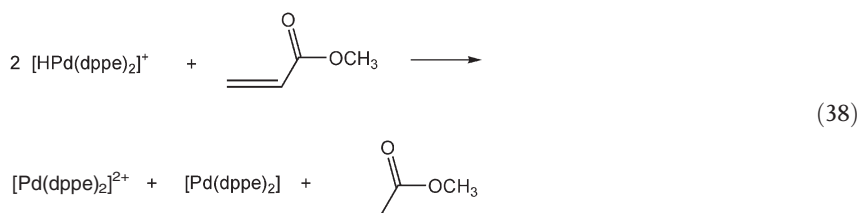


Displacement of the bound ketone by  $H_2$  was directly observed by NMR (Eq. (37)), and an approximate equilibrium constant was determined. The cationic tungsten complex can also be used for catalytic hydrosilylation of ketones. In the case of catalytic hydrosilylation of aliphatic substrates using  $HSiEt_3$ , the catalyst precipitates at the end of the reaction, facilitating recycle and reuse [66].

### 7.3.5

#### Use of a Pd Hydride in Hydrogenation of C=C Bonds

DuBois et al. reported extensive studies on the thermodynamics of acidic and hydridic reactivity of a large series of complexes  $[HM(diphosphine)_2]^+$ . Aresta et al. found that protonation of the Pd complex  $[Pd(dppe)_2]$  leads to the cationic hydride  $[HPd(dppe)_2]^+$  [67]. The Pd–H bond can be cleaved as either a proton or as a hydride. Solutions of  $[HPd(dppe)_2]^+$  decompose to give  $H_2$ ,  $[Pd(dppe)_2]$  and  $[Pd(dppe)_2]^{2+}$ . Reaction of  $[HPd(dppe)_2]^+$  with methyl acrylate at  $20^\circ C$  resulted in hydrogenation of the C=C bond, producing methyl propionate (Eq. (38)). In contrast to the previously discussed examples of ionic hydrogenation, two equivalents of the same palladium hydride complex are thought to furnish both the proton and the hydride in this case. Computations suggested that hydride transfer occurs first, producing a carbanionic intermediate that is then protonated by a second equivalent of the metal hydride. Catalytic hydrogenation of the C=C bond of cyclohexene-2-one was observed when  $[HPd(dppe)_2]^+BF_4^-$  was used as the catalyst precursor under  $H_2$  (4 MPa). A maximum TOF of about  $16 h^{-1}$  was found at  $50^\circ C$ . At higher temperatures ( $67^\circ C$ ), higher TOF values were found, but decomposition of the Pd complex was observed, producing decomposition products (Pd black) that are also catalytically active.

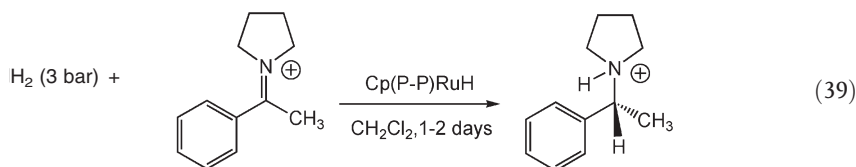


### 7.3.6

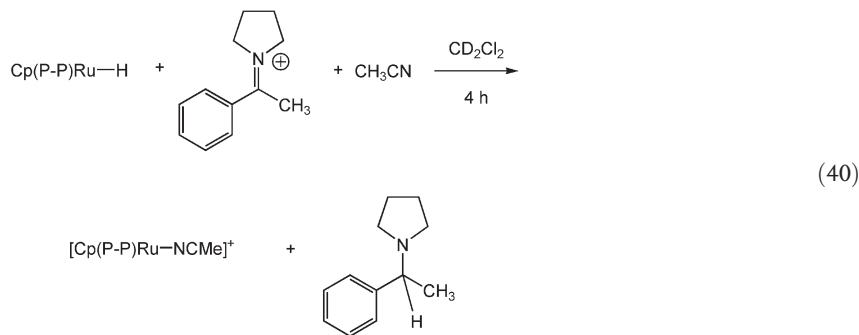
#### Catalytic Hydrogenation of Iminium Cations by Ru Complexes

Norton and coworkers found that catalytic enantioselective hydrogenation of the C=N bond of iminium cations can be accomplished using a series of Ru complexes with chiral diphosphine ligands such as Chiraphos and Norphos [68]. Even tetra-alkyl-substituted iminium cations can be hydrogenated by this method. These reactions were carried out with 2 mol.% Ru catalyst and 3.4–3.8 bar  $H_2$  at room temperature in  $CH_2Cl_2$  solvent (Eq. (39)).

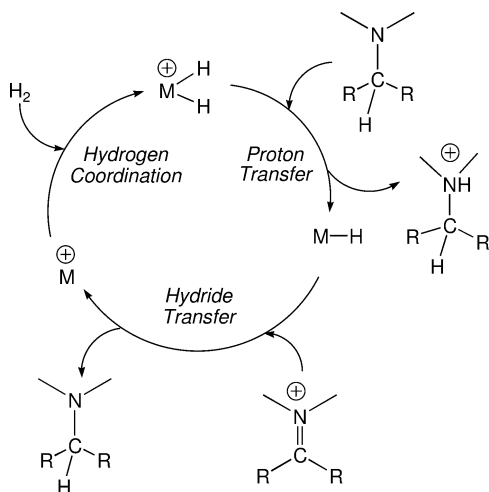




The enantiomeric excess (ee) obtained under catalytic conditions was similar to that found when the hydride transfer was carried out in a stoichiometric reaction (Eq. (40)); these stoichiometric reactions were carried out in the presence of excess  $\text{CH}_3\text{CN}$ , which captures the 16-electron cationic Ru complex following hydride transfer.



No change in the rate or ee of the catalytic reaction was observed when the pressure of  $\text{H}_2$  was varied, indicating that  $\text{H}_2$  does not play a role in the turnover-limiting step or in the determination of enantioselectivity. When the catalytic reaction was monitored by NMR under  $\text{H}_2$  (5 bar), the neutral hydride was observed. All of these observations support the proposed mechanism shown in Scheme 7.12. This



Scheme 7.12

mechanism is similar to the mechanism for ionic hydrogenation of ketones (Scheme 7.11), except that in the hydrogenation of iminium cations the hydride transfer occurs first, whereas proton transfer from cationic dihydrides to the ketone occurs first in Scheme 7.11. Hydride transfer to the iminium cation is the turnover-limiting and enantioselectivity-determining step of the mechanism.

The kinetics of hydride transfer (Eq. (40)) were determined for a series of chelating diphosphines. The rate constant of hydride transfer was found to be highly dependent on the bite angle of the diphosphine, increasing as the bite angle decreases [69]. The rate constant for [Cp(dppm)RuH] (dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>; bite angle 72°) was about 200 times higher than that for [Cp(dppp)RuH] (dppp = Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>; bite angle 92°). The rate constant for the Ru complex of the diphosphine with a C<sub>2</sub> bridge, [Cp(dppe)RuH] (dppe = Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>; bite angle 85°) was intermediate between the two. The increased *kinetic* hydricity resulting from a decreased bite angle parallels the observations of DuBois and colleagues, who found the same trend for *thermodynamic* hydricity [19].

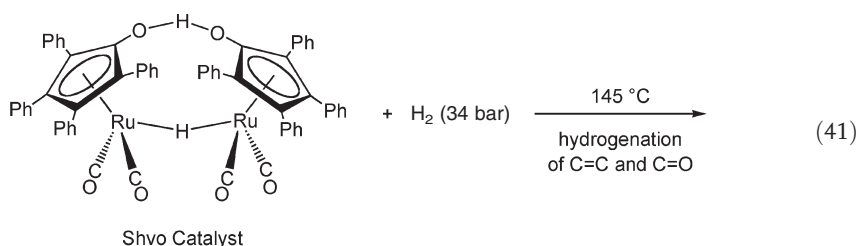
## 7.4

### Ruthenium Complexes Having an OH Proton Donor and a RuH as Hydride Donor

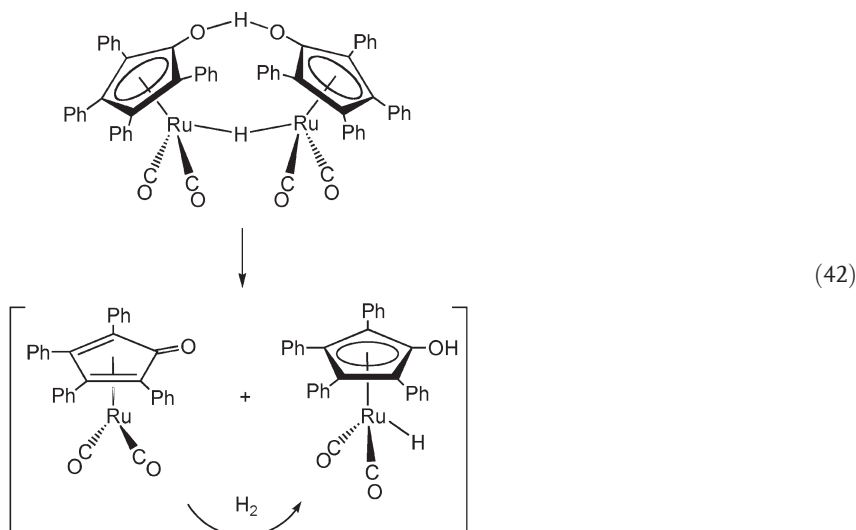
#### 7.4.1

##### The Shvo System

Shvo and coworkers prepared a bimetallic complex in which the two metals are joined by a bridging hydride as well as by an O–H–O hydrogen bond joining the two substituted Cp ligands [70]. Shvo used this versatile catalyst precursor for hydrogenation of C=C and C=O bonds at 145 °C under 34 bar H<sub>2</sub> (Eq. (41)) [71].

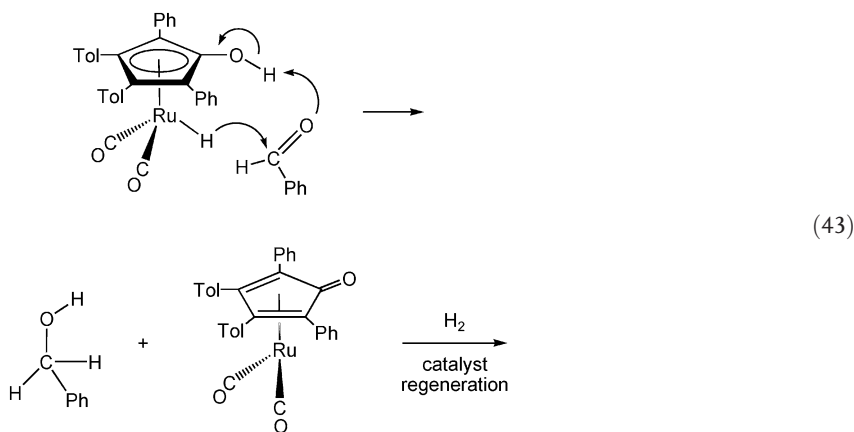


Under these conditions, the bimetallic complex is cleaved into an 18-electron complex that performs the hydrogenations, and an unsaturated 16-electron complex. Addition of H<sub>2</sub> to the 16-electron complex produces the 18-electron complex that has an acidic OH and a hydridic RuH (Eq. (42)).



Solvent-free hydrogenations of 1-octene, 2-pentene, cyclohexene, and styrene were carried out with catalyst loadings as low as 0.05 mol.% of the dimer, in some cases with TOF values as high as  $6000 \text{ h}^{-1}$  [71]. Total turnover numbers of almost 2000 were obtained in most of these cases. Solvent-free hydrogenation of ketones such as  $\text{Et}_2\text{C}=\text{O}$ , cyclohexanone, and diisopropyl ketone were also reported at the same temperature and  $\text{H}_2$  pressure, but with somewhat lower TOFs for the hydrogenation of  $\text{C}=\text{O}$  compared to  $\text{C}=\text{C}$  hydrogenations.

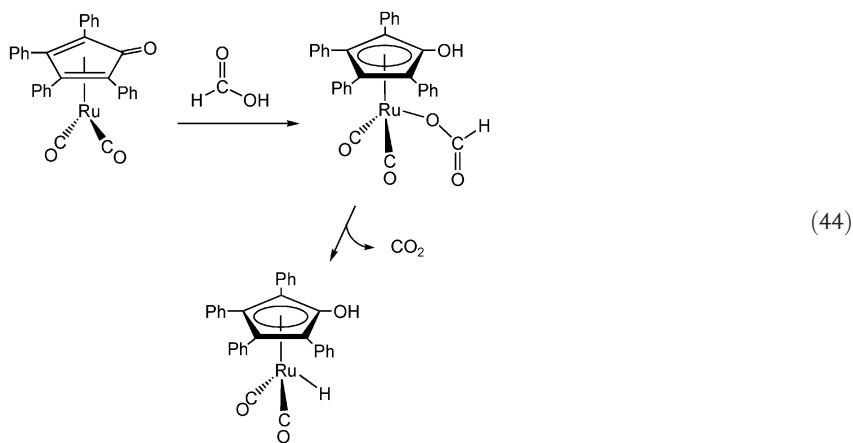
Kinetic and mechanistic studies by Casey et al. provided further insight into the mechanistic details of the hydrogenation of ketones and aldehydes, using a more soluble analogue of Shvo's catalyst (with *p*-tolyl groups instead of two of the Ph groups) [72]. The kinetics of hydrogenation of benzaldehyde by the Ru complex shown in Eq. (43) were first order in aldehyde and first order in the Ru complex; the



second-order rate constant at  $-10^{\circ}\text{C}$  was determined to be  $k = (3.0 \pm 0.2) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ . The activation enthalpy was  $\Delta H^{\ddagger} = 12.0 \pm 1.5 \text{ kcal mol}^{-1}$ , and the very negative entropy of activation ( $\Delta S^{\ddagger} = -28 \pm 5 \text{ cal K}^{-1} \text{ mol}^{-1}$ ) further supports a highly ordered transition state.

Isotope effects have been very useful in understanding the detailed mechanisms of many organometallic reactions [73], and have been used extensively in studies of Shvo complexes. Separate kinetic isotope effects were measured for hydrogenation of PhCHO at  $0^{\circ}\text{C}$  (Eq. (43)); deuteration at the RuH(D) and OH(D) positions gave values of  $k_{\text{RuH}}/k_{\text{RuD}} = 1.5 \pm 0.2$  and  $k_{\text{OH}}/k_{\text{OD}} = 2.2 \pm 0.1$ . Deuteration of both the RuH and OH sites gave a combined kinetic isotope effect of  $k_{\text{RuHOH}}/k_{\text{RuDOD}} = 3.6 \pm 0.3$ . The proposed mechanism involves concerted proton transfer from the OH site and hydride transfer from the Ru hydride, and is supported by the product of the two individual isotope effects ( $1.5 \times 2.2 = 3.3$ ) being within experimental uncertainty of the combined isotope effect of 3.6. Since the actual hydrogenation step (Eq. (43)) occurs at low temperatures, the elevated temperature required for the catalytic reaction starting with the bimetallic complex as the catalyst precursor (see Eq. (41)) is necessary to generate the active mononuclear species. A  $\text{p}K_{\text{a}}$  of 17.5 was determined in  $\text{CH}_3\text{CN}$  for the OH of  $[[2,5\text{-Ph}_2\text{-3,4-Tol}_2(\eta^5\text{-C}_4\text{COH})]\text{Ru}(\text{CO})_2\text{H}]$ , so this OH is significantly more acidic than either phenol ( $\text{p}K_{\text{a}} = 26.6$  in  $\text{CH}_3\text{CN}$ ) or benzoic acid ( $\text{p}K_{\text{a}} = 20.7$  in  $\text{CH}_3\text{CN}$ ). As shown in Table 7.5,  $[\text{Cp}^*\text{Ru}(\text{CO})_2\text{H}]$  has high kinetic hydricity, so this remarkable combination of acidity of an OH site and hydricity of the RuH combine to make the concerted proton- and hydride-transfer mechanism feasible in this type of complex.

A variety of ketones were hydrogenated using Shvo's catalyst at  $100^{\circ}\text{C}$  using excess formic acid rather than  $\text{H}_2$  as the source of hydrogen [74]. Excellent yields ( $>90\%$ ) of alcohols were generally obtained in 6 h or less, with total turn-overs in the range of 6000–8000. The unsaturated 16-electron Ru complex that results after hydrogen is delivered to the substrate is proposed to react with for-



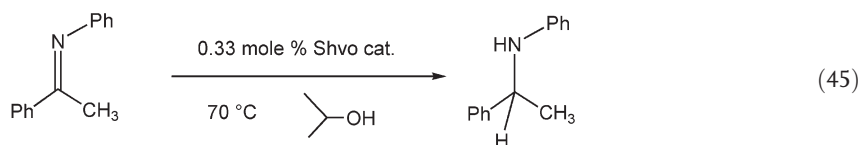
mic acid to produce a formate complex that expels CO<sub>2</sub>, regenerating the metal hydride (Eq. (44)). Subsequent studies by Casey et al. showed that the formate complex is formed upon reaction of excess formic acid (HCO<sub>2</sub>H) with Shvo's catalyst at low temperature [75]. This formate complex loses CO<sub>2</sub> above 0 °C, but the formate complex does not hydrogenate benzaldehyde directly.

Casey has suggested that the hydrogenation of alkenes by Shvo's catalyst may proceed by a mechanism involving loss of CO from the Ru–hydride complex, and coordination of the alkene. Insertion of the alkene into the Ru–H bond would give a ruthenium alkyl complex that can be cleaved by H<sub>2</sub> to produce the alkane [75]. If this is correct, it adds further to the remarkable chemistry of this series of Shvo complexes, if the same complex hydrogenates ketones by an ionic mechanism but hydrogenates alkenes by a conventional insertion pathway.

#### 7.4.2

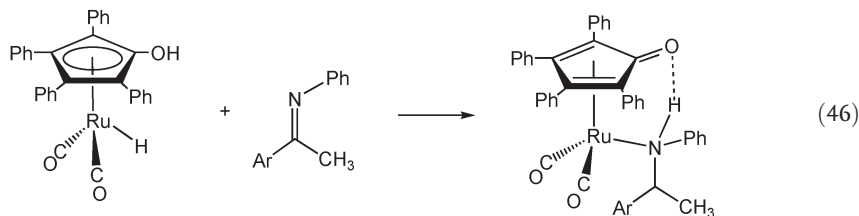
##### Hydrogenation of Imines by Shvo Complexes

Samec and Bäckvall found that the dinuclear Shvo complex catalyzes the transfer hydrogenation of imines using benzene as solvent and isopropanol as the hydrogen source (Eq. (45)) [76]. These catalytic hydrogenations were typically carried out at 70 °C, and gave >90% yields of the amine in 4 h or less.

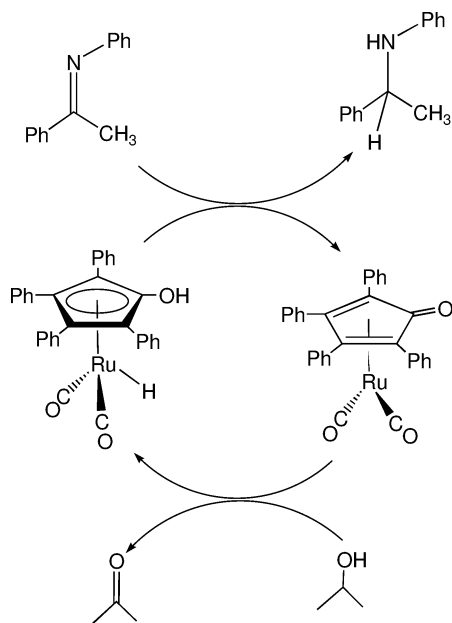


Ketimines were hydrogenated faster than aldimines, and electron-donating groups accelerated the rate of hydrogenation. The OH and RuH bonds are regenerated by hydrogen transfer to the unsaturated 16-electron Ru complex from isopropanol, generating acetone (Scheme 7.13).

Kinetic studies were carried out by Bäckvall and coworkers at –54 °C on the hydrogenation of a ketimine, which produces a ruthenium complex with a bound amine (Eq. (46)) [77].



The crystal structure of an isopropylamine complex of Ru of this type has been reported [78]. Surprisingly, a negligible kinetic isotope effect ( $k_{\text{RuHOH}}/k_{\text{RuDOD}} = 1.05 \pm 0.14$ ) was found when D labels on both the OH and RuH sites were used,

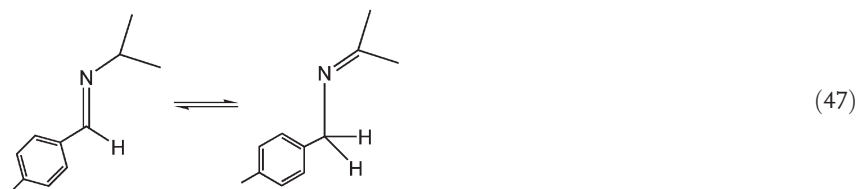


Scheme 7.13

indicating that the rate-determining step does not involve hydrogen transfer. The reaction is first order in amine and also first order in ruthenium. Bäckvall proposed a mechanism involving a ring slip ( $\eta^5 \rightarrow \eta^3$ ) followed by coordination of the imine. Proton transfer from the OH concerted with hydride transfer from the RuH to an  $\eta^2$ -coordinated imine would give the coordinated amine, then rearrangement of the substituted cyclopentadiene ligand to  $\eta^4$  was proposed to generate the observed product. An alternative mechanism consistent with the data was proposed by Casey and Johnson [79].

Casey and Johnson also reported kinetics and isotope effects for the hydrogenation of imines [79]. Hydrogenation of an electron-deficient imine, *N*-benzildene-pentafluoroaniline, gave the free amine as the organic product. Deuteration of the RuH site gave  $k_{\text{RuH}}/k_{\text{RuD}} = 1.99 \pm 0.13$  at 11 °C, and deuteration of the acidic OH site gave a kinetic isotope effect of  $k_{\text{OH}}/k_{\text{OD}} = 1.57 \pm 0.07$ . The experimentally determined combined isotope effect ( $k_{\text{RuHOH}}/k_{\text{RuDOD}} = 3.32 \pm 0.17$ ) is within experimental uncertainty of the product of the two individual isotope effects ( $1.99 \times 1.57 = 3.12$ ). These observations are similar to those for hydrogenation of the C=O bond discussed above, and the data are consistent with the proposed concerted proton and hydride transfer for this imine hydrogenation.

Examination of a series of imines of differing electronic properties showed that a change in the rate-determining step of this stoichiometric C=N hydrogenation occurs as the imine becomes more electron-rich. Hydrogenation of *N*-isopropyl-(4-methyl)benzylidene amine led to an amine complex of ruthenium. In addition, the C=N hydrogenation was accompanied by isomerization of the imine to a ketimine (Eq. (47)).



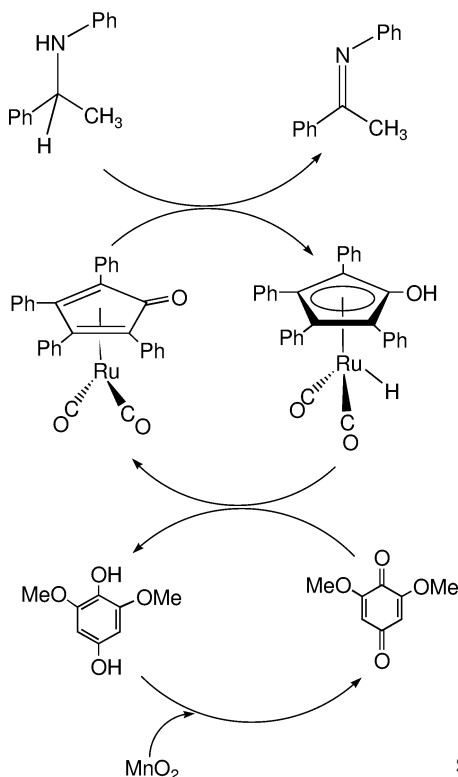
When the hydrogenation was carried out with RuD labels, scrambling of D into the starting material and product was observed, indicating reversible hydrogen transfer. Hydrogenation of *N*-benzylidene-*tert*-butylamine was studied; this substrate has no  $\beta$ -hydrogens, so its reactions are not complicated by isomerization or exchange reactivity. Hydrogenation of this imine produces an amine complex (cf. Eq. (46)), and the kinetics at  $-48^\circ\text{C}$  were first order in imine and first order in Ru. In contrast to the normal kinetic isotope effects discussed above for the hydrogenation of aldehydes or other imines, inverse isotope effects were observed for the hydrogenation of this electron-rich *tert*-butyl imine. Deuteration of the RuH site resulted in  $k_{\text{RuH}}/k_{\text{RuD}}=0.64\pm 0.05$ , and this is thought to be due to an inverse equilibrium isotope effect that favors deuterium on the carbon in the reversible transfer between ruthenium and carbon. Deuteration of the acidic OH site gave a kinetic isotope effect of  $k_{\text{OH}}/k_{\text{OD}}=0.90\pm 0.07$ . The rate-determining step of the reaction is proposed to be coordination of the nitrogen of the amine to the ruthenium. Since the proton and hydride transfers occur prior to the amine coordination, the mechanistic information does not distinguish between concerted or stepwise proton and hydride transfer in this ionic mechanism.

### 7.4.3

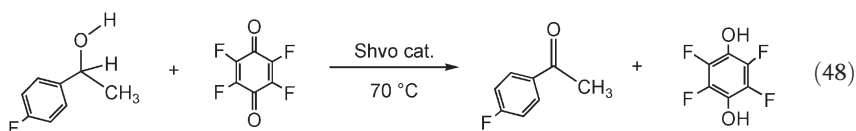
#### Dehydrogenation of Imines and Alcohols by Shvo Complexes

Remarkably, the same Shvo complex can be used for the catalytic transfer *dehydrogenation* of aromatic amines to give imines (Scheme 7.14) [80]. This reaction produces high yields when carried out for 2–6 h in refluxing toluene with 2 mol.% catalyst. A quinone is used as the hydrogen acceptor, giving the corresponding hydroquinone.

The reaction can be made catalytic in 2,6-dimethoxy-1,4-benzoquinone (20 mol.%) by the addition of 1.5 equiv.  $\text{MnO}_2$  to regenerate the quinone from the hydroquinone. Dehydrogenation is the slow step in this reaction; separate experiments had documented that conversion of the benzoquinone to the hydroquinone has a TOF of  $> 4000 \text{ h}^{-1}$  [81]. Kinetic isotope effects showed that the rate-limiting step was cleavage of the C–H bond, and that the transfer of the two hydrogens is not concerted [82]. The proposed mechanism involved slow  $\beta$ -elimination from a coordinated amine followed by proton transfer to the oxygen of the cyclopentadienone ligand.



Johnson and Bäckvall reported that the bimetallic Shvo catalyst can also catalyze the transfer dehydrogenation of alcohols (Eq. (48)) [83].



Using tetrafluorobenzoquinone as the hydrogen acceptor, the kinetics at 70 °C showed that the reaction was first order in alcohol, zero order in the quinone, and half-order in the Ru<sub>2</sub> catalyst. The half-order in bimetallic catalyst is expected in cases where a bimetallic species must dissociate into a monomeric active species. Proton and hydride transfer outside of the coordination sphere of the ruthenium is a possible mechanism, and this is essentially the reverse of the reaction shown in Eq. (42). An alternative mechanism favored by Bäckvall and colleagues [81, 83] and by Menashe and Shvo [84] involves the formation of an alcohol complex which undergoes proton transfer from the alcohol's OH to the oxygen of the ligand, together with β-hydride elimination to form the RuH

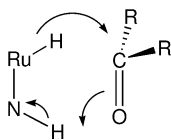


bond. Kinetic isotope effects found with deuteration of the OH and CD sites of the alcohol were  $k_{\text{CHOH}}/k_{\text{CHOD}}=1.87 \pm 0.17$  and  $k_{\text{CHOH}}/k_{\text{CDOH}}=2.57 \pm 0.26$ . This provides evidence for a concerted ionic mechanism, since the experimentally observed isotope effect with both sites labeled ( $k_{\text{CHOH}}/k_{\text{CDOD}}=4.61 \pm 0.37$ ) is within experimental uncertainty of the product of the individual isotope effects ( $1.87 \times 2.57 = 4.80$ ). The ability of the Shvo and other ruthenium catalysts to reversibly dehydrogenate alcohols has been used by Bäckvall and coworkers to accomplish the dynamic kinetic resolution of secondary alcohols, where the metal catalyst is used in conjunction with enzymes [85].

#### 7.4.4

#### Catalytic Hydrogenations with Metal–Ligand Bifunctional Catalysis

The concerted delivery of protons from OH and hydride from RuH found in these Shvo systems is related to the proposed mechanism of hydrogenation of ketones (Scheme 7.15) by a series of ruthenium systems that operate by metal–ligand bifunctional catalysis [86]. A series of Ru complexes reported by Noyori, Ohkuma and coworkers exhibit extraordinary reactivity in the enantioselective hydrogenation of ketones. These systems are described in detail in Chapters 20 and 31, and mechanistic issues of these hydrogenations by ruthenium complexes have been reviewed [87].

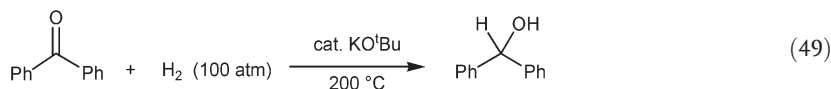


Scheme 7.15

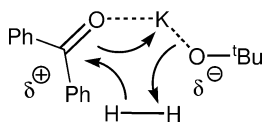
### 7.5

#### Catalytic Hydrogenation of Ketones by Strong Bases

As documented throughout this handbook, the diversity of reaction patterns of transition-metal complexes leads to a remarkably rich chemistry, with a tremendous mechanistic diversity in the details of how  $\text{H}_2$  is added to unsaturated substrates. Over forty years ago, Walling and Bollyky reported a catalytic hydrogenation of benzophenone that required no transition metal at all! They found that the  $\text{C}=\text{O}$  bond of benzophenone can be catalytically hydrogenated using  $\text{KO}^t\text{Bu}$  as a base [88], but harsh conditions ( $200^\circ\text{C}$ , 100 bar  $\text{H}_2$ ) were used (Eq. (49)). Berkessel et al. recently examined details of this reaction and provided evidence that it was first order in ketone, first order in hydrogen, and first order in base [89].



This ketone hydrogenation is limited to non-enolizable ketones; hydrogenation rates are similar for benzophenone and  $\text{Ph}(\text{C}=\text{O})t\text{Bu}$ , slower for  $(t\text{Bu})_2\text{C}=\text{O}$ , and still slower for 2,2,5,5-tetramethylcyclopentanone. The relative initial rates as the alkali metal was changed were the same for  $\text{K}^+$  and  $\text{Rb}^+$  (relative initial rate=100), slightly faster for  $\text{Cs}^+$  (relative initial rate=105), slower for  $\text{Na}^+$  (relative initial rate=50), and much slower for  $\text{Li}^+$  (relative initial rate=7). The proposed six-membered cyclic transition state is shown in Scheme 7.16. Recent molecular orbital calculations on a simplified model of this system (hydrogenation of formaldehyde by  $\text{NaOCH}_3$ ) suggest that the slow rates are due in large part to high entropic barriers to properly assemble and orient the highly ordered transition state required [90].



Scheme 7.16

## 7.6

### Conclusion

Ionic hydrogenations are far less developed than hydrogenations that proceed by traditional insertion mechanisms. Despite this later historical development, recent developments have shown that ionic hydrogenations have become more widely recognized, and the prevalence of this area is expected to continue to expand. The development of ionic hydrogenations has benefited immensely from mechanistic experiments on model organometallic complexes. Fundamental studies of the acidity and hydricity of metal hydrides have – and will continue – to play an important role in helping the rational design of ionic hydrogenation catalysts. Both thermodynamic and kinetic studies of acidity and hydricity of metal hydrides are helpful in assessing the specific combinations of ligands and metals that may be suitable for consideration as catalysts. Despite being less extensively developed than other hydrogenation methods, there is burgeoning interest in ionic hydrogenations, and there are numerous promising avenues for future research into this area.

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## Abbreviations

DME	dimethoxyethane
HOTf	triflic acid
THF	tetrahydrofuran
TOF	turn over frequency
TON	turn over number

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