Part III
Homogeneous Hydrogenation by Functional Groups

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14
Homogeneous Hydrogenation of Alkynes and Dienes

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14.1
Stereoselective Homogeneous Hydrogenation of Alkynes to Alkenes

14.1.1
Introduction

The reduction of carbon-carbon double and triple bonds is a very important transformation in synthetic organic chemistry. In this context, the conversion of alkynes into alkenes (i.e., semihydrogenation) is particularly useful, especially the stereoselective addition of one molar equivalent of hydrogen to the triple bond. This allows for the selective preparation of the corresponding (*E*)- or (*Z*)-alkenes depending on the choice of reaction conditions during the reduction. The classical catalytic hydrogenation using a heterogeneous transition-metal catalyst and molecular hydrogen constitutes the most general method for the selective reduction of carbon-carbon triple bonds. However, other pathways involving for instance organoaluminum and organoboron intermediates or hydride-transfer reagents in combination with metal salts have also been successfully applied [1, 2].

The most widely used catalytic procedures for the catalytic hydrogenation of alkynes to afford (*Z*)-alkenes generally employ palladium or nickel as the catalytically active transition metal. The Lindlar catalyst (lead-poisoned Pd on $CaCO_3$) and the P2-Ni catalyst are among the most prominent members of this group [1–3]. These systems show considerable selectivity for a variety of alkynes; however, substrates with triple bonds conjugated to other unsaturated moieties or electron-poor alkynes display low selectivity due to overreduction or other side reactions [1]. The complex nature of the surface of the Lindlar catalyst, containing different domains each of which contributes to the product distribution, makes the outcome of the stereoselective hydrogenation unpredictable. Thus, the yields and selectivity will generally vary, even for identical compounds under identical conditions [2, 4].

A large number of homogeneous transition-metal complexes have been reported as catalysts for the stereoselective hydrogenation of alkynes, although the

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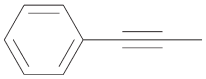
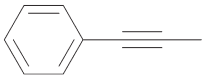
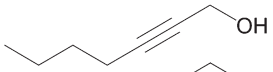
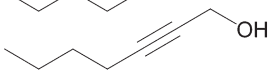
details of this apparently simple reaction remain mostly obscure. Only a few homogeneous catalysts have been investigated in more detail, and some of these show a remarkable selectivity towards a variety of alkynes containing various functional groups. The origin of the stereoselectivity of these catalysts in the semihydrogenation of alkynes can often be ascribed to kinetic factors and sometimes to the lack of interaction of the catalyst with the product alkene, which is consequently not further reduced. The exhaustive reduction of alkynes to alkanes, which can in synthetic terms be useful, is very similar to alkene hydrogenation and will, therefore, not be treated here. This chapter will mainly focus on the homogeneous catalytic semihydrogenation of alkynes using molecular hydrogen. Supported catalysts and cluster-catalyzed hydrogenations will not be treated here. The performance of the catalysts has been the major criterion for selecting the homogeneous catalytic systems discussed in this chapter. Special attention will be given to the mechanistic details of selected systems.

14.1.2 Chromium Catalysts

One of the most selective semihydrogenation catalysts reported concerns a class of chromium tricarbonyl compounds with the generic formula $[Cr(CO)_3(arene)]$ (**1**) [5]. This catalyst is able to hydrogenate a wide variety of polyunsaturated compounds, and has been successfully applied in, for example, the 1,4-hydrogenation of conjugated dienes and *α,β*-unsaturated carbonyl compounds [6]. The outstanding performance of this catalyst in alkyne hydrogenation has been attributed to its complete inactivity towards compounds containing isolated carbon-carbon double bonds (i.e., neither isomerization nor over-reduction is observed). The (*Z*)-alkene is the sole product, which is isolated in very high yields (87–100%; see Table 14.1). Generally, the hydrogenation only proceeds under rather forcing reaction conditions, although, less strongly coordinated arenes (e.g., naphthalene or methyl benzoate) allow for milder conditions while maintaining the high stereoselectivity (see Table 14.1). Details about the reaction mechanism have not been revealed, but the similarity with the $[Cr(CO)_3]$-catalyzed 1,4-hydrogenation of conjugated dienes suggests that $[Cr(CO)_3(S)_3]$ (S = solvent) species is the catalytically active complex.

The applicability of the $[Cr(CO)_3(arene)]$ 1,2-*syn*-hydrogenation has been demonstrated in the syntheses of pheromones where the hydrogenation of the alkyne to the (*Z*)-isomer is a key step in the synthetic scheme [5, 7]. For such compounds, obtaining the correct the stereo- and regio-isomer is essential for its biological activity. In these cases, selectivities up to 100% have been reported. Special attention has been given to conjugated alkyne-diene systems of which the stereo- and regio-chemical outcome can be precisely predicted based on the specific chemistry of the $[Cr(CO)_3(arene)]$ catalyst towards alkynes and conjugated dienes.

Table 14.1 Hydrogenation of alkynes using $[Cr(CO)_3(arene)]$ (**1**) [5].

Entry	Alkyne	Catalyst	Time [h]	H_2 pressure [bar]	(*Z*) alkene [%][c]
1		$[Cr(CO)_3(mbz)]$[a]	23	69	92
2		$[Cr(CO)_3(nap)]$[b]	24	20	92
3		$[Cr(CO)_3(nap)]$[b]	15	69	100
4		$[Cr(CO)_3(mbz)]$[a]	8	69	95
5		$[Cr(CO)_3(nap)]$[b]	8	49	87

a) $[Cr(CO)_3(mbz)]$ = $[Cr(CO)_3$(methyl benzoate)] (**1a**). Reaction conditions: solvent acetone, reaction temp. 120 °C, substrate : catalyst ratio = 5 : 1.

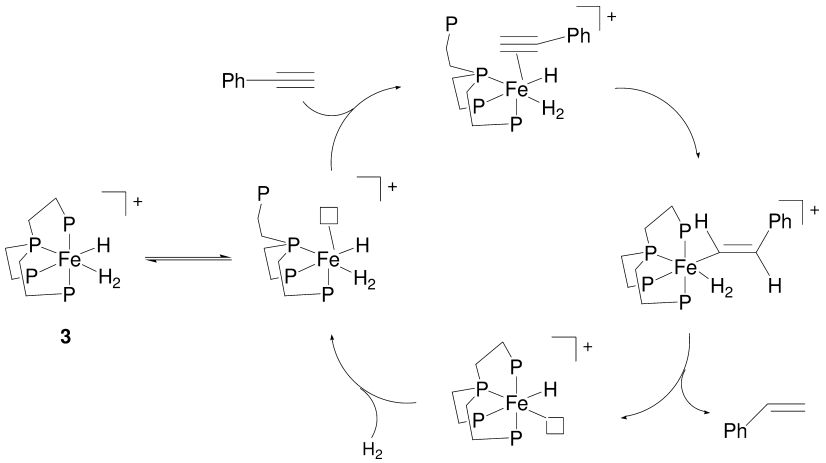
b) $[Cr(CO)_3(nap)]$ = $[Cr(CO)_3$(naphthalene)] (**1b**). Reaction conditions: solvent THF, reaction temp. 45 °C, substrate : catalyst ratio = 5 : 1.

c) Determined by GC analysis relative to internal standard.

14.1.3 Iron Catalysts

Terminal alkynes are selectively hydrogenated to alkenes by the iron(II) catalyst precursors $[(PP_3)FeH(N_2)]BPh_4$ (**2**) and $[(PP_3)FeH(H_2)]BPh_4$ (**3**) ($PP_3 = P(CH_2CH_2PPh_2)_3$) in tetrahydrofuran (THF) under mild conditions (1 bar H_2) [8]. The hydrogenation rates when using complexes **2** and **3** were found to be low at ambient temperature, but increased with increasing reaction temperature. The turnover frequency (TOF) ranges from 8 to 20 mol mol^{-1} h^{-1} at 66 °C for various substrates. Under these conditions, alkynes are converted chemoselectively into alkenes, regardless of the reaction temperature. The only exception is ethynyltrimethylsilane $HC{\equiv}CSiMe_3$, which mainly produces the dimeric product 1,4-bis(trimethylsilyl)butadiene by a reductive coupling reaction [9]. A thorough kinetic study of the hydrogenation of phenyl acetylene employing **2** has provided more insight into the mechanistic details of this reaction.

The mechanism is dominated by the remarkable stability of the Fe(η^2-H_2) bond, which is one of the most stable η^2-H_2 complexes reported in the literature [8, 10]. Remarkably, the free coordination site for the incoming alkyne is provided by the reversible dissociation of one of the phosphine moieties of the PP_3 ligand rather than dissociation of the dihydrogen ligand (see Scheme 14.1). The coordinated alkyne subsequently inserts into the Fe–H bond and the emerging Fe–vinyl bond is



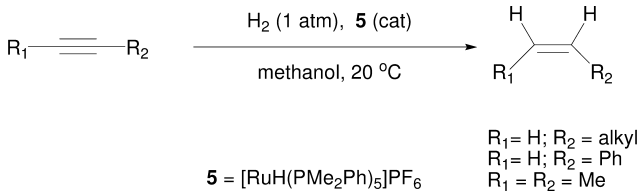
Scheme 14.1 Proposed mechanism for the hydrogenation of phenyl acetylene catalyzed by $[(PP_3)FeH(H_2)]^+BPh_4^-$ (**3**); the anion is BPh_4^- throughout in this scheme.

then cleaved *via* an intramolecular protonolysis (i.e., heterolytic splitting of the dihydrogen molecule occurs). The binding of the alkyne to the metal center appears to be the rate-determining step as it is supported by the zero-order in dihydrogen gas and a first-order in phenyl acetylene. The activation parameters for this reaction are $\Delta H^{\ddagger} = 11 \pm 1$ kJ mol^{-1}, $\Delta S^{\ddagger} = -27 \pm 3$ J K^{-1}, and $\Delta G^{\ddagger} = 19 \pm 4$ kJ mol^{-1}.

The cationic complex $[FeH(\eta^2\text{-}H_2)(PP_3)]^+$ (**3**; $PP_3 = P(CH_2CH_2PPh_2)_3$) displays an identical octahedral structure as the comparable ruthenium complex $[RuH(\eta^2\text{-}H_2)(PP_3)]^+$ (**4**; $PP_3 = P(CH_2CH_2PPh_2)_3$) [11]. Both complexes have been found to be selective catalysts for the hydrogenation of alkynes. Despite their structural similarities, the chemistry of compounds **3** and **4** in the semihydrogenation of alkynes is dominated by the difference in metal–dihydrogen bond strength, which decreases in the order Fe > Ru and has been attributed to a stronger back-donation from iron into the antibonding $\sigma^*(H_2)$ orbital compared to ruthenium [12].

14.1.4
Ruthenium Catalysts

Numerous compounds containing ruthenium are found to be active catalysts for the semihydrogenation of alkynes. Much attention has been devoted to the class of ruthenium carbonyl clusters, and it has been demonstrated that both internal and terminal alkynes can be effectively hydrogenated using such compounds, affording the corresponding alkenes [13]. However, the activities of these catalysts are generally lower than those of the mononuclear complexes and their stereoselectivity is also significantly lower due to extensive isomerization of the (primary) reaction products.

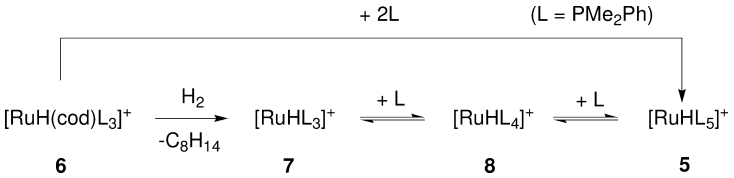


Scheme 14.2 Hydrogenation of terminal and internal alkynes by $[RuH(PMe_2Ph)_5]PF_6$ (**5**) [14].

Mononuclear ruthenium complexes, particularly ruthenium–phosphine complexes, are among the best-characterized catalytic systems. A particular active catalyst for this reaction is based on the sterically crowded complex $[RuH(PMe_2Ph)_5]PF_6$ (**5**) which, in the presence of 25 equiv. PMe_2Ph in methanol, has been shown to be an extremely active catalyst system for the selective hydrogenation of alkynes to alkenes [14] (Scheme 14.2). The rates of hydrogenation were limited by mass transfer processes in this case – that is, by diffusion of hydrogen into the solution. Thus, under these conditions, the TOF reported amounts to 130 mol mol^{-1} h^{-1}. The reaction proceeds affording the corresponding (*Z*)-alkenes without subsequent isomerization or further hydrogenation of the products. In addition, at high phosphine concentrations, the catalyst is completely inactive in the hydrogenation of alkenes to alkanes. In order to prevent catalyst deactivation, a large excess of PMe_2Ph is needed and the reaction temperature should be kept below 20 °C.

A related cationic ruthenium catalyst precursor, $[RuH(cod)(PMe_2Ph)_3]PF_6$ (**6**; cod = cyclooctadiene), was studied in the semihydrogenation of alkynes, and the results demonstrate a distinctly different catalyst behavior and chemoselectivity compared to $[RuH(PMe_2Ph)_5]PF_6$ (**5**) [15]. Under 1 bar H_2, **6** reacts to produce a complex, regarded as $[RuH(PMe_2Ph)_3(solvent)_2]^+$, which is a very active hydrogenation catalyst for alkynes as well as alkenes. The catalyst reveals an unusual order of reactivity – that is, the rate of hydrogenation to *cis*-alkenes increased in the order 1-hexyne < 2-hexyne < 3-hexyne, which has been attributed to the lower tendency of 3-hexyne to form the alleged catalytically inactive ruthenium-bis(alkyne) complexes. The activity of the catalyst for alkene hydrogenation could be significantly suppressed by the addition of 1 equiv. PMe_2Ph, and **6** becomes completely inactive towards alkenes by the addition of 2 equiv. PMe_2Ph. This addition will effectively lead to the more saturated, less-active ruthenium complex ions $[RuH(PMe_2Ph)_4]^+$ (**8**) and $[RuH(PMe_2Ph)_5]^+$ (**5**), respectively.

The two ruthenium complexes $[RuH(PMe_2Ph)_5]PF_6$ (**5**) and $[RuH(cod)PMe_2Ph)_3]PF_6$ (**6**) are considered to be related by Scheme 14.3. Since the cationic catalyst precursors **5** and **6** are both 18-electron species, hydrogenation of cyclooctadiene in **6** and phosphine dissociation from **5** will produce the catalytically active intermediate ions $[RuHL_4]^+$ (**8**) and $[RuHL_3]^+$ (**7**) (L = PMe_2Ph), respectively. It has thus been proposed that **7** is active for the hydrogenation of alkenes as well as alkynes, whereas **8** only hydrogenates alkynes. This scheme



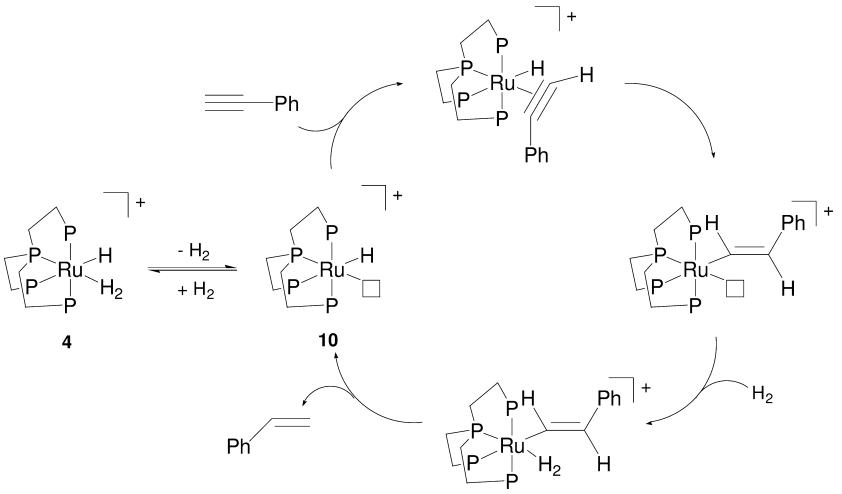
Scheme 14.3 Proposed relationship between different ruthenium–phosphine complexes. The anion has been omitted and is PF_6^+ throughout.

can be further extended to include the ruthenium complex $[Ru(H)(H_2)(PMe_2Ph)_4]^+$ (not shown in Scheme 14.3), which is formed by a reaction of **8** with hydrogen [16]. In the absence of additional phosphine, **8** shows rapid deactivation in the hydrogenation of 1-alkynes and in the isomerization of internal alkenes. However, under similar phosphine-deficient conditions, $[RuH(PMe_2Ph)_5]PF_6$ (**5**) remains active as a hydrogenation catalyst, but it displays a lower rate and a higher selectivity towards (*Z*)-alkenes.

The related cationic complex $[RuH(\eta^2\text{-}H_2)(PP_3)]^+$ (**4**; $PP_3 = P(CH_2CH_2PPh_2)_3$) is a non-classical trihydride complex where the metal is coordinated by the four phosphorus atoms, by a dihydrogen ligand, and a terminal hydride ligand. Although this complex is generally less active than, for instance, $[RuH(PMe_2Ph)_5]^+$ (**5**), it has a better defined chemistry [11]. The kinetic study of the selective hydrogenation of phenyl acetylene employing **4** reveals a first-order dependence on the catalyst concentration and second-order in hydrogen. The order in substrate changes from apparently first-order to zero-order with increasing substrate concentration. This catalytic behavior has been attributed to the formation of $[Ru(\eta^3\text{-}1,4\text{-diphenylbutenynyl})(PP_3)]$ (**9**) complexes by coupling of two substrate molecules. Complex **9** was found to be equally active in the hydrogenation of phenyl acetylene as compared to complex **4** (Scheme 14.4).

The proposed reaction mechanism follows a sequence of reaction steps usually adopted for a monohydride-metal hydrogenation catalyst, although other, more complex ruthenium intermediates contribute to the overall hydrogenation [11, 16]. Here, the η^2-coordinated dihydrogen serves merely as a stabilizing ligand and the formally unsaturated species $[RuH(PP_3)]^+$ (**10**) is the actual, reactive intermediate. Possibly, such a species must be thought of as labile, transient solvento species. Coordination of phenyl acetylene, insertion into the Ru–H bond followed by reaction of dihydrogen will eventually generate styrene and the ruthenium-monohydride species.

A particularly interesting hydrogenation catalyst for the semihydrogenation of alkynes concerns the ruthenium complex $[Cp^*Ru(\eta^4\text{-}CH_3CH{=}CHCH{=}CHCO_2H)][CF_3SO_3]$ (**11**) [17]. This ruthenium complex represents one of the few homogeneous catalysts that allow for the direct *trans*-hydrogenation of internal alkynes, yielding the (*E*)-alkene stereoselectively. Generally, internal alkynes can be transformed selectively into *E*-alkenes using different homogeneous and heterogeneous methods (e.g., dissolving metal reduction). However, under these

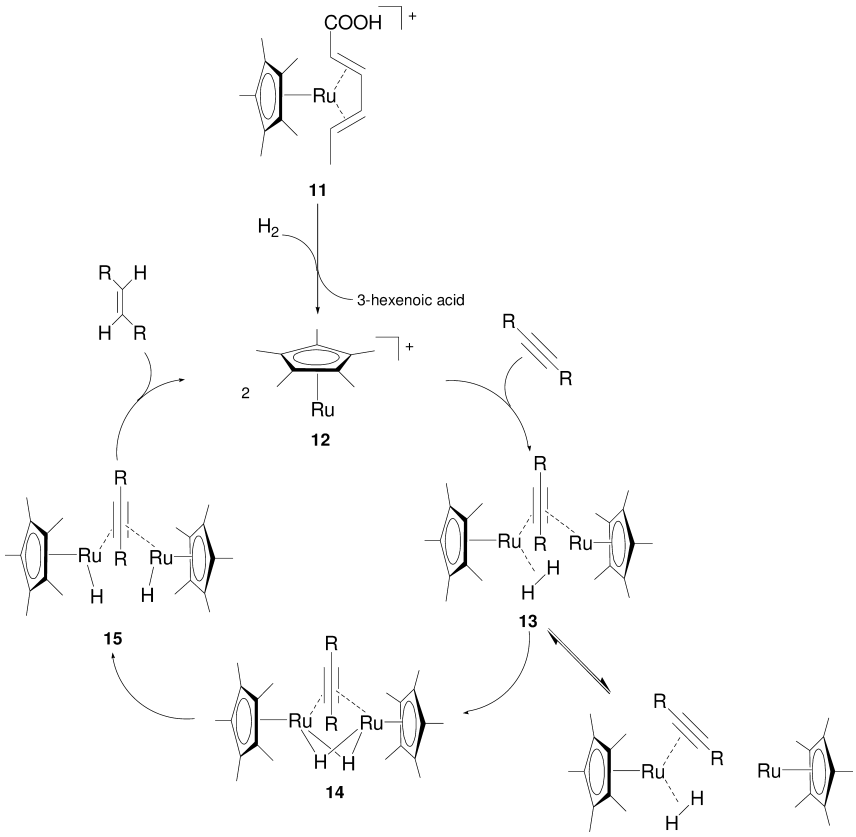


Scheme 14.4 Proposed mechanism for the hydrogenation of phenyl acetylene catalyzed by $[RuH(\eta^2\text{-}H_2)(PP_3)]^+$ (**4**) [11].

reaction conditions other functional groups will be affected and, hence, low chemoselectivities are obtained in these cases.

The $[Cp^*Ru]^+$-catalyzed semihydrogenation of alkynes has been studied in more detail using PHIP-NMR (PHIP = *Para*-Hydrogen Induced Polarization; see Chapter 12). With this method the initially formed hydrogenation products can be identified and characterized, even at very low concentrations and low conversions. Different types of alkynes were probed, and it was found that the reaction is not influenced greatly by the functional groups present in the substrate. However, internal alkynes readily produced polarized signals in the hydrogenation product (i.e., the *E*-isomer), even at low temperature. This finding indicates that the hydrogen is transferred in a *pair-wise* manner and it confirms that the *E*-isomer emerges as the primary reaction product. No polarized signals were detected for terminal alkynes, which has been ascribed to an allegedly inactive vinylidene complex that has been formed *via* a 1,2-hydrogen shift [17].

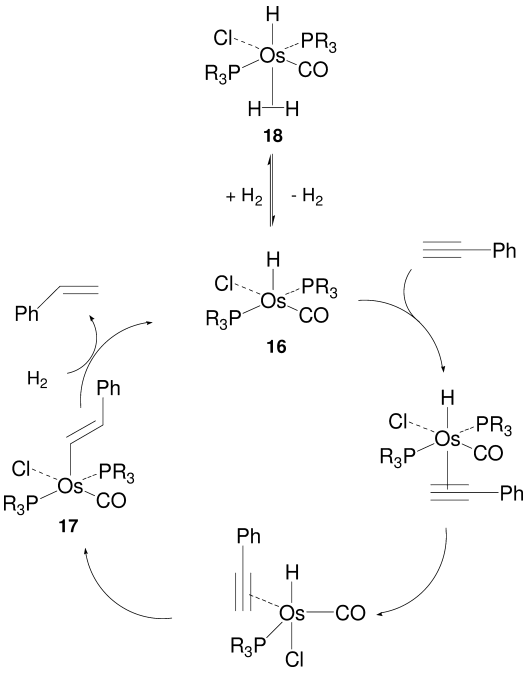
The remarkable stereoselectivity of this catalyst – that is, the *trans*-addition of the two hydrogen atoms – has been explained by the involvement of a dimeric ruthenium complex. In the proposed reaction mechanism (Scheme 14.5) the intermediates are assumed to be alkyne-bridged dinuclear ruthenium complexes (**13**, **14** and **15**). It has been suggested that the hydrogenation should be fast and without total separation of the two *para*hydrogen atoms – that is, without loss of the spin correlation between the two hydrogen atoms. Only under these conditions can *para*-hydrogen polarized signals be observed. The observation of these polarized signals reveals that the hydrogen atoms transferred to the alkyne stem from the same hydrogen molecule and supports the mechanism depicted in Scheme 14.5.



Scheme 14.5 Stereoselective hydrogenation of internal alkynes by complex $[Cp^*Ru(\eta^4\text{-}CH_3CH{=}CHCH{=}CHCOOH)][CF_3SO_3]$ (**11**); the anion is CF_3SO3^- throughout [17].

14.1.5
Osmium Catalysts

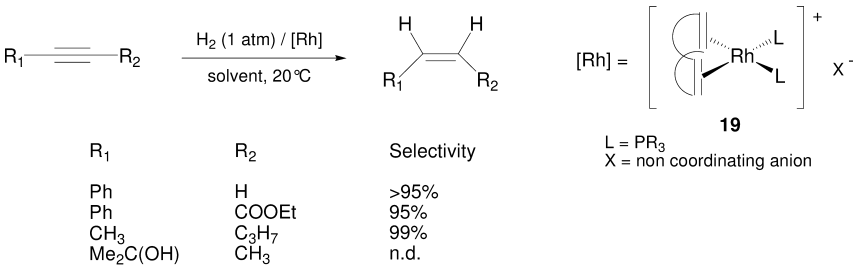
An interesting example of the alkyne hydrogenation by homogeneous transition-metal catalysts is provided by the complexes $[OsH(Cl)(CO)(PR_3)_2]$ (**16**; $PR_3 = PMeBu^t_2$, PPr^i_3), which catalyze the hydrogenation of phenyl acetylene at 1 bar H_2 in 2-propanol solution at 60 °C [18]. These complexes react rapidly with phenyl acetylene to produce the respective stable 16-electron alkenyl-osmium compounds $[Os((E)\text{-}CH{=}CHPh)Cl(CO)(PR_3)_2]$ (**17**) almost quantitatively. Subsequent reaction with dihydrogen produces styrene, ethylbenzene and the dihydrogen complex $[OsH(Cl)(\eta^2\text{-}H_2)(CO)(PR_3)_2]$ (**18**). These reactions constitute a catalytic cycle for the reduction of alkynes affording the corresponding alkenes with selectivities close to 100%.



Scheme 14.6 Proposed mechanism for the hydrogenation of phenyl acetylene catalyzed by $[OsHCl(CO)(PR_3)_2]$ (**16**).

The kinetic investigation of this reaction reveals the reaction is first-order in substrate, catalyst and hydrogen concentration, and thus yields the rate law: $r = k_{cat}[Os][alkyne][H_2]$. The proposed mechanism as given in Scheme 14.6 is based on the rate law and the coordination chemistry observed with these osmium complexes.

In the absence of phenyl acetylene, these Os-complexes catalyze the hydrogenation of styrene to ethyl benzene at rates about ten-fold faster than those observed for the C≡C bond reduction. The authors concluded that the styrene hydrogenation is kinetically favored, so the observed selectivity must originate from a thermodynamic difference. This difference is established by the formation of the very stable vinyl-osmium intermediates, which forms a thermodynamic sink that causes all the osmium present to be tied up in this form; consequently the kinetically unfavorable pathway becomes essentially the only one available in the presence of alkyne. Furthermore, it has been shown that the hydrogenation of phenyl acetylene to styrene by $[OsHCl(CO)(PPr^i_3)_2]$ can also be performed under hydrogen-transfer conditions using 2-propanol as the hydrogen donor [19, 20].



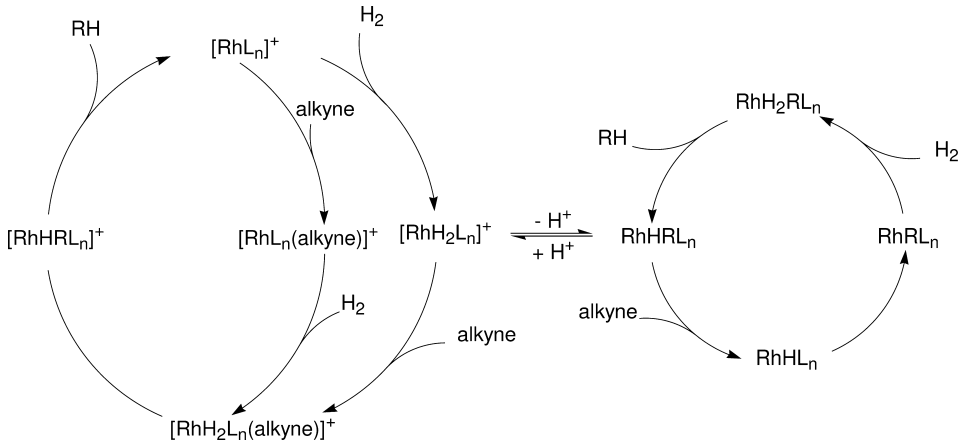
R_1	R_2	Selectivity
Ph	H	>95%
Ph	COOEt	95%
CH_3	C_3H_7	99%
$Me_2C(OH)$	CH_3	n.d.

Scheme 14.7 Hydrogenation of various alkynes using complex $[Rh(nbd)L_n]^+X^-$ (**19**) [21].

14.1.6
Rhodium Catalysts

The Schrock/Osborn cationic Rh-catalyst with the general formula $[Rh(nbd)L_n]^+X^-$ (**19**; wherein nbd is norbornadiene, L is a phosphine ligand and X^- is a – weakly coordinating – anion) is counted among the most successful and most widely applied catalysts for the semihydrogenation of alkynes [21]. The reaction proceeds well in coordinating solvents (such as acetone, ethanol, or 2-methoxyethanol), and under these conditions internal alkynes are reduced efficiently affording the corresponding (*Z*)-alkene in yields as high as 99% (see Scheme 14.7). This catalyst system is a moderately active hydrogenation catalyst with TOF (determined at 50% conversion) ranging between 20 and 80 mol mol^{-1} h^{-1} [21–23]. However, the reduction of terminal alkynes by these systems is less successful since the fairly acidic character of the alkyne destroys the active species (such as $[RhH(L_n)S_y]$) by formation of an alkynyl-rhodium derivative [21].

The mechanism of the semihydrogenation of alkynes in coordinating solvents is assumed to be analogous to the alkene hydrogenation – that is, a catalytic scheme consisting of a mono-hydride route (*via* $RhH(L)_n(solvent)_y$) and a dihydride route (*via* $Rh(H)_2(L)_n(solvent)_y$) (see Scheme 14.8) [21, 24]. The active rhodium(solvento) species are formed by a reaction of **19** with molecular hydrogen. Generally, the cationic rhodium mono-hydride $RhH(L)_n(solvent)_y$ is an extremely active isomerization and hydrogenation catalyst, whereas the rhodium dihydride $[Rh(H)_2(L)_n(solvent)_y]^+$ is a less active hydrogenation catalyst but displays very little isomerization activity [21]. Under catalytic conditions, the mono-hydride and the dihydrido-rhodium(solvento) species are in equilibrium; the amount of each species – and thus the contribution of each route to the product formation – can be shifted by the addition of acid or base. Therefore, performing the semihydrogenation under acidic conditions will generate a highly selective hydrogenation system for the reduction of alkynes to (*Z*)-alkenes. Another method of generating related rhodium species involves protonation of the acetate of a neutral Rh(I) or Rh(II) complex in the presence of a phosphine ligand (such as $[Rh(OAc)(PPh_3)_3]$ or $[Rh_2(OAc)_4/PR_3]$) [20, 25]. Catalytic hydrogenation systems prepared by this method behave in many respects similarly to the systems based on $[Rh(diene)L_2]^+A^-$.



Scheme 14.8 General hydrogenation mechanism catalyzed by cationic $[Rh(nbd)L_n]^+$ species (**19**) [21].

Recovery of the precious Rh-catalyst has been successfully developed by using various strategies. One of the approaches concerns the use of highly fluorous Rh-catalysts for selective hydrogenation of terminal and internal alkynes under fluorous biphasic conditions yielding catalyst retentions of >99.92% (for FC-75/hexanes, 1:3 v/v) [23]. Furthermore, the immobilization of the rhodium catalyst on a solid support has been reported as a feasible approach, which shows only little leaching of the rhodium, while maintaining a high selectivity and activity [26].

In less-coordinating solvents such as dichloromethane or benzene, most of the cationic rhodium catalysts $[Rh(nbd)(PR_3)_n]^+A^-$ (**19**) are less effective as alkyne hydrogenation catalysts [21, 27]. However, in such solvents, a few related cationic and neutral rhodium complexes can efficiently hydrogenate 1-alkynes to the corresponding alkene [27–29]. A kinetic study revealed that a different mechanism operates in dichloromethane, since the rate law for the hydrogenation of phenyl acetylene by $[Rh(nbd)(PPh_3)_2]^+BF_4^-$ is given by: $r = k[\text{catalyst}][\text{alkyne}][pH_2]^2$ [29].

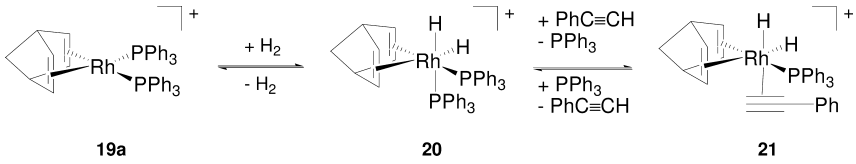
$$[Rh(nbd)(PPh_3)_2]BF_4 + H_2 \rightleftharpoons [RhH_2(nbd)(PPh_3)_2]BF_4 \quad (1)$$

$$[RhH_2(nbd)(PPh_3)_2]BF_4 \rightleftharpoons [RhH_2(nbd)(PPh_3)]BF_4 + PPh_3 \quad (2)$$

$$[RhH_2(nbd)(PPh_3)]BF_4 + PhC{\equiv}CH \rightleftharpoons [RhH(CH=CHPh)(nbd)(PPh_3)]BF_4 \quad (3)$$

$$[RhH(CH{=}CHPh)(nbd)(PPh_3)]BF_4 + H_2 \rightarrow [RhH_2(nbd)(PPh_3)]BF_4 + CH_2{=}CHPh \quad (4)$$

$$[RhH_2(nbd)(PPh_3)]BF_4 + PPh_3 \rightarrow [RhH_2(nbd)(PPh_3)_2]BF_4 \quad (5)$$



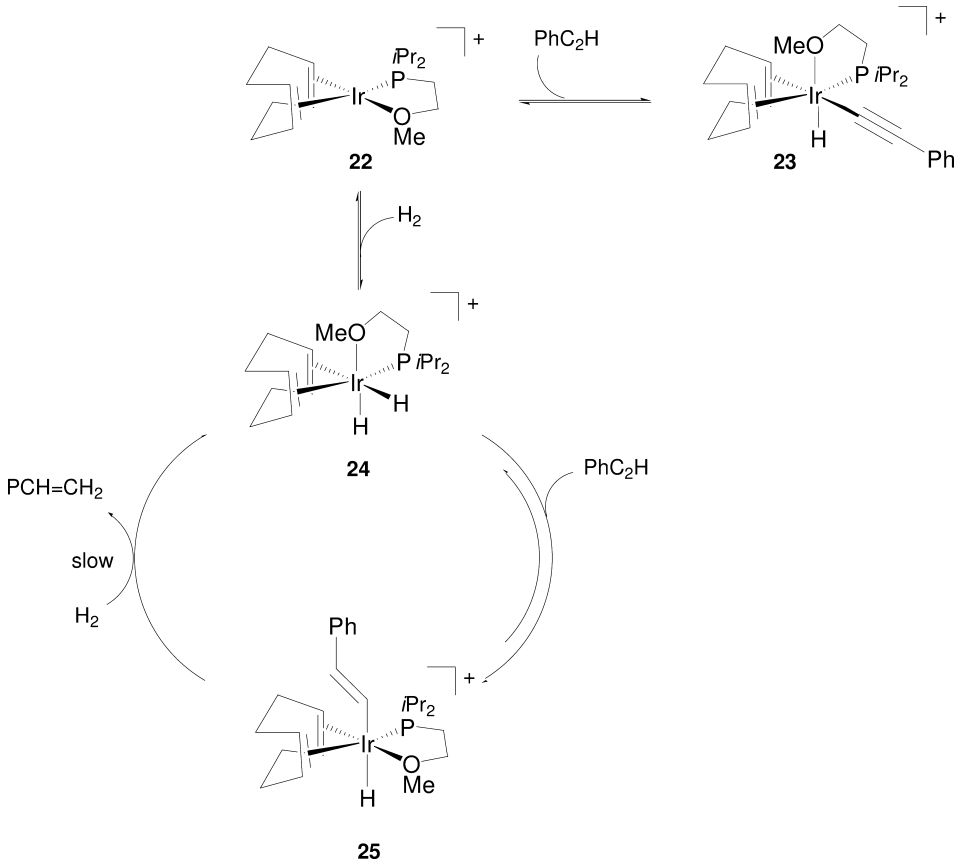
Scheme 14.9 Reaction of $[Rh(nbd)(PPh_3)_2]^+BF_4^-$ (**19**) with H_2 to give *cis*,*cis*-$[RhH_2(nbd)(PPh_3)_2]^+BF_4^-$ (**20**) and the subsequent formation of $[RhH_2(nbd)(PPh_3)(alkyne)]^+BF_4^-$ (**21**).

The proposed mechanism for this case is summarized by Eqs (1) to (5). Note that norbornadiene is *not* hydrogenated under the reaction conditions and remains coordinated to the metal center during the hydrogenation process. This feature has been observed for both rhodium and iridium systems of the general formula $[M(diene)(L)_2]^+X^-$ [28–31]. In the first step of the catalytic sequence, $[Rh(nbd)(PPh_3)_2]^+BF_4^-$ (**19**) reacts with dihydrogen to form the coordinatively saturated intermediate *cis*,*cis*-$[RhH_2(nbd)(PPh_3)_2]^+BF_4^-$ (**20**), which must then dissociate a phosphine ligand in order to create a vacant coordination site for the incoming alkyne, to give the corresponding alkyne complex $[RhH_2(nbd)(PPh_3)(PhC_2H)]^+BF_4^-$ (**21**) (see Scheme 14.9). Most likely, the phosphine *trans* to the hydride would be most labile due to the large *trans*-influence of the hydride ligand. The alkyne would then arrive *cis* to one hydride but *trans* to the other, and migratory insertion will thus lead to the *trans*-hydrido-vinyl species. If the metal center in **21** is stereochemically integer under the hydrogenation conditions, this complex would not facilitate the reductive elimination. Therefore, a subsequent reaction with dihydrogen is required for the formation of the alkene, rationalizing the second-order in hydrogen.

14.1.7 Iridium Catalysts

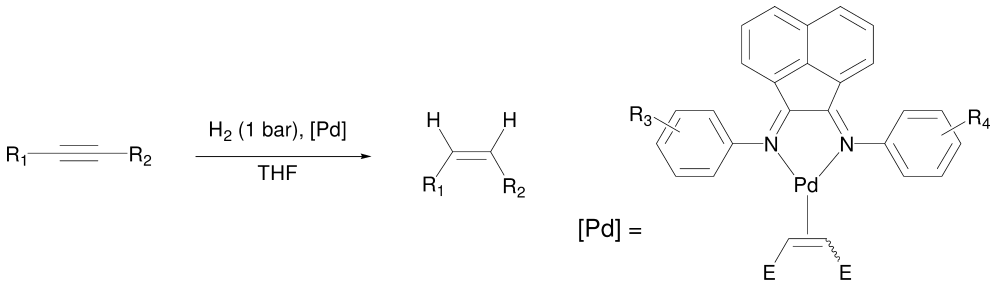
The iridium complex $[Ir(cod)(\eta^2\text{-}^i PrPCH_2CH_2OMe)]^+BF_4^-$ (**22**) in dichloromethane at 25 °C at 1 bar H_2 is a particularly active catalyst for the hydrogenation of phenyl acetylene to styrene [29]. In a typical experiment, an average TOF of 50 mol mol^{-1} h^{-1} was obtained (calculated from a turnover number, TON, of 125) with a selectivity close to 100%. The mechanism of this reaction has been elucidated by a combination of kinetic, chemical and spectroscopic data (Scheme 14.10).

The main species in solution has been identified to be the hydrido-alkynyl complex $[IrH(C_2Ph)(cod)(\eta^2\text{-}^i PrPCH_2CH_2OMe)]^+BF4^-$ (**23**). This is, however, only a sink that results from direct reaction of **22** with the 1-alkyne, draining the active catalyst from the system. The catalysis proceeds *via* the dihydrido-diene intermediate $[IrH_2(cod)(\eta^2\text{-}^i PrPCH_2CH_2OMe)]^+ BF_4^-$ (**24**), which reacts reversibly with the alkyne to yield the hydrido-iridium-styryl complex **25**, followed by a rate-determining reaction of this hydrido-vinyl species with hydrogen to re-



Scheme 14.10 Proposed mechanism for the hydrogenation of phenyl acetylene catalyzed by [Ir(cod)(η^2-^{i}PrPCH$_2$CH$_2$O-Me)]$^+$BF$_4^-$ (**22**); the anion is BF$_4^-$ throughout [29].

generate the dihydrido-diene complex **24** and liberate the alkene. This mechanism is in agreement with the observed rate law $r = k[\mathrm{Ir}][\mathrm{pH_2}]$. As in the case of the hydrogenation of phenyl acetylene by [Rh(nbd)(PPh$_3$)$_2$]$^+$BF$_4^-$ in dichloromethane, the diene is not hydrogenated under these reaction conditions and remains coordinated to the iridium. Furthermore, the origin of the selectivity has been ascribed to kinetic reasons – that is, the alkyne competes more effectively for the position liberated by displacement of the methoxy group of the ether-phosphine ligand than the alkene [29].



26a; $R_3 = R_4 = 4\text{-}OCH_3$
26b; $R_3 = R_4 = 3,5\text{-}(CF_3)_2$

Scheme 14.11 Stereoselective hydrogenation of alkynes to alkenes by [Pd(Ar-bian)(alkene)] (**26**). In compound **26a** the electron-poor alkene is dimethyl fumarate, E=CO_2Me; in **26b** the electron-poor alkene is maleic anhydride, E=C(O)OC(O).

14.1.8 Palladium Catalysts

As mentioned earlier, the Lindlar catalyst has been the most widely used heterogeneous hydrogenation catalyst for the semihydrogenation of alkynes. However, the surface of these catalysts is a rather complex assembly of various domains, each of which contributes to the product distribution in its own way, often resulting in unpredictable overall results. In order to circumvent the presence of different palladium species, much attention has been devoted to the application of homogeneous mononuclear palladium complexes; either in the form of a Pd(II) complex [32, 33] or a Pd(0) compound [34–36]. In most of the reported cases, these mononuclear palladium complexes display a higher chemo- and (sometimes) higher stereoselectivity than the heterogeneous counterparts.

An important advantage of a heterogeneous catalyst over a homogeneous one concerns the ease of catalyst separation from the products. Therefore, much research effort in this field has been directed towards immobilized palladium complexes, where the palladium is coordinated to a ligand attached to a polymer, a clay, or another inorganic support [37–43]. Assuming that a single type of palladium species is formed, these heterogenized palladium catalysts are potentially very important and might compete with the Lindlar catalysts in certain applications. For the sake of completeness, it should be noted that palladium-clusters have been found to be active, with some showing extremely high activities and very good selectivities in the hydrogenation of alkynes to alkenes [44–46]. These Pd-clusters will not be treated here, however.

Elsevier et al. have reported the stereoselective hydrogenation of alkynes by zerovalent palladium catalysts bearing a bidentate nitrogen ligand, which are able homogeneously to hydrogenate a wide variety of alkynes to the corresponding (*Z*)-alkenes (see Scheme 14.11). The semihydrogenation occurs under very

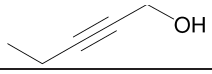
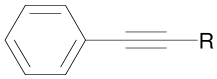
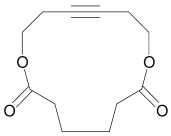
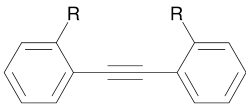
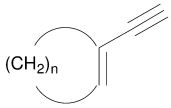
mild conditions (25 °C, 1 bar H_2), and the observed selectivity towards the (*Z*)-alkene for the various alkynes is very high indeed [35]. The precatalysts employed are isolable [Pd(Ar-bian)(alkene)] compounds (**26**), which have previously been used in the homogeneous hydrogenation of electron-poor alkenes [47] and in carbon–element bond-formation reactions [48]. With respect to most other diimine ligands, Ar-bian derivatives are rigid, which imposes the correct geometry for coordination and imparts a high chemical stability. The ease of modifying the electronic as well as the steric properties of these ligands make them ideal to study their complexes in a variety of catalytic reactions.

Using [Pd(*p*-MeO-C_6H_4-bian)(dmfu)] (**26a**; dmfu = dimethyl fumarate), the observed selectivity towards semihydrogenation to the (*Z*)-isomer for the various alkynes is very high (> 99%) at 25 °C and 1 bar H_2 [35]. Typically, TOFs of 100 to 200 mol mol^{-1} h^{-1} have been obtained with this catalyst. The high selectivity, which is in many cases superior to that obtained with Lindlar catalyst, is maintained until full conversion of the alkyne; the selectivity has been determined at > 99.5% conversion. As can be seen from Table 14.2, internal as well as terminal alkynes are reduced to the corresponding (*Z*)-alkenes with great ease and selectivity. Besides the high stereoselectivity, the chemoselectivity is also remarkably high, as was demonstrated by the presence of other reducible functional groups in various substrates, such as carboalkoxy, nitro-groups, or even alkene moieties in conjugated enynes.

The complex [Pd{(*m*,*m*′-$(CF_3)_2C_6H_3$)bian}(ma)] (**26b**; ma = maleic anhydride) displays an unprecedented high reaction rate, while maintaining the high stereo- and chemoselectivity, which is typical for the [Pd(Ar-bian)] systems. In a detailed kinetic study [49] the catalyst behavior was investigated in the hydrogenation of 4-octyne. Under the reaction conditions (7 bar H_2, 21 °C) an average TOF of 16 000 (calculated from TON of 1600) can be reached, though hydrogen diffusion limitations prevent higher rates. The reaction rate is given by the equation: $r = k[\mathrm{Pd}][\mathrm{H_2}][\mathrm{alkyne}]^{0.65}$. Thus, the reaction is first-order in palladium and dihydrogen, confirming that mononuclear species are involved in the catalysis. The broken reaction order for the substrate suggests that an equilibrium between palladium complexes containing the substrate and the reaction product is operative under the reaction conditions. High-level density functional theory (DFT) calculations and *para*hydrogen induced polarization (PHIP) NMR measurements support a mechanism consisting of the following consecutive steps: alkyne coordination, heterolytic dihydrogen activation (hydrogenolysis of one Pd–N bond). Subsequently, hydropalladation of the alkyne, followed by addition of N–H to palladium, reductive coupling of the vinyl and hydride, and finally, substitution of the product alkene by the alkyne substrate (see Scheme 14.12) [49].

At high substrate, or low hydrogen concentration, the semihydrogenation of 4-octyne is inhibited by the formation of catalytically inactive palladacycle species. These species are formed by oxidative coupling of two substrate molecules. In addition, careful kinetic measurements and product analysis has revealed that the activation of the catalyst precursor **26b** during the induction period occurs by hydrogenation of the coordinated maleic anhydride to succinic anhy-

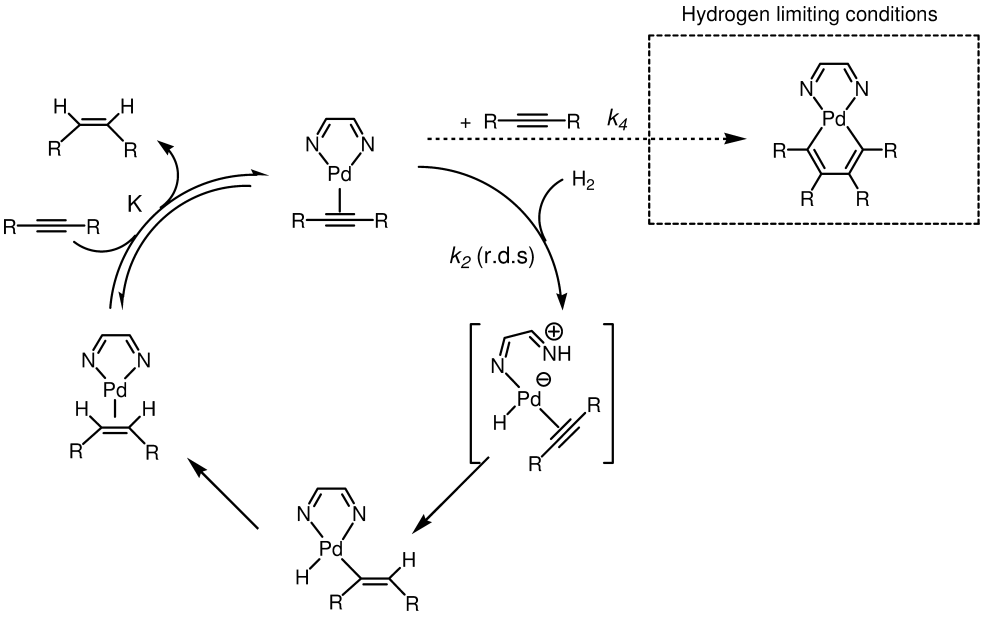
Table 14.2 Product distribution in the hydrogenation of alkynes using [Pd(*p*-MeO-C_6H_4-bian)(dmfu)] (**26a**) [35].[a)]

Entry	Substrate	Product distribution [%][b)]		
		(*Z*)-alkene	(*E*)-alkene	alkane
1	 R = alkyl, CO_2Me	>98	–	–
2		>99	–	–
3	 R = H, Me, *n*-Bu, CO_2H	>99 (R=H)[c)] 91 (R=Me) 92 (R=*n*-Bu) 95 (R=COOMe)	– 2 6 5	– 6 3 –
4		95	5	–
5	 R = H, NO_2	87 (R=H) 97 (R=NO_2)	– 3	13 –
6		n=4, ethenylcyclohexene exclusively[c)] n=6, ethenylcyclooctene exclusively		

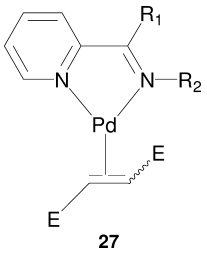
a) Reaction conditions: 80 mM substrate and 0.8 mM using [Pd(*p*-MeO Ar-bian)(dmfu)] (**26a**) in THF at 20 °C and 1 bar H_2.
b) Product distribution determined by GC and ^{1}H-NMR at >99.5% conversion of alkyne.
c) Determined by reaction with D_2.

dride, concurrently producing the catalytically active [Pd(Ar-bian)(alkyne)] complex [49].

It was concluded that the high selectivity observed in the hydrogenation experiments using **26b** is explained by the relatively strong coordination of the alkyne to the palladium center, which only allows for the presence of small amounts of alkene complexes. Only the latter are responsible for the observed minor amounts of (*E*)-alkene, which was shown to be a secondary reaction product formed by a subsequent palladium-catalyzed, hydrogen-assisted isomerization reaction. Since no *n*-octane was detected in the reaction mixture, only a tiny



Scheme 14.12 Mechanism for the selective hydrogenation of alkynes by [Pd{(*m*,*m*′-$(CF_3)_2C_6H_3$)bian}(ma)] (**26b**) [49].



27

Fig. 14.1 Zerovalent [Pd(pyca)(alkene)] (**27**) precatalyst complex.

amount of the intermediate Pd(hydrido)(alkyl) species will reductively eliminate to form the alkane.

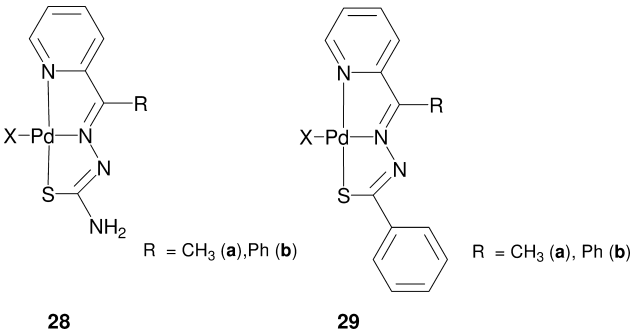
Zerovalent [palladium(alkene)] complexes **27** containing pyca ligands (pyca = pyridine-2-carbaldimine; Fig. 14.1) have been investigated in the stereoselective hydrogenation reaction of 1-phenyl-1-propyne in THF [34]. Most of the obtained inherently high *cis*-selectivities in the semihydrogenation of 1-phenyl-1-propyne are comparable to each other and to the results of the [Pd(Ar-bian)] system. However, the stability of the [Pd(pyca)] systems is generally lower and decomposition occurs in several cases before full consumption of the alkyne has taken place. It was concluded that the nature of the substituents on the imine nitrogen atom seems to be the most important factor determining the stability of the various catalysts precursors under hydrogenation conditions. It appeared

that more donating capacity of the N-substituent results in a more stable catalyst, whereas increased steric bulk reduces its stability.

Members of the Parma group have shown that a large variety of divalent palladium complexes, with the generic formula [Pd(L)X] (X = OAc^- or Cl^-) bearing a hydrazinato-based tridentate ligand L (containing different donor atoms), are able to hydrogenate alkynes to the corresponding alkenes with different degrees of success [32, 50–52]. Considerable mechanistic details have been reported for this reaction employing the catalysts [Pd(thiosemicarbazonato)X] (**28**) and [Pd(thiobenzoylhydrazonato)X] (**29**) (see Fig. 14.2) [32]. The hemilability of these ligands plays an intricate role in the catalysis with such compounds. Under the reaction conditions used (1 bar H_2, 30 °C, substrate : catalyst ratio = 100), the chloro-analogue [Pd(NNS)Cl] (**28a**) exhibits a full conversion in 24 h with 92% selectivity for styrene. The overall reaction rate is low, and TOFs around 4 mol · mol^{-1} h^{-1} have been reported. Although these catalysts are completely unreactive towards styrene present in solution, the ethylbenzene formed during the reaction was proposed to be the result from a second, consecutive hydrogenation step of the primary reaction product – that is, styrene which remains coordinated to the palladium (see Scheme 14.13). The stereoselectivity of the reaction could be tailored by changing the counter ion of the Pd(II) complex.

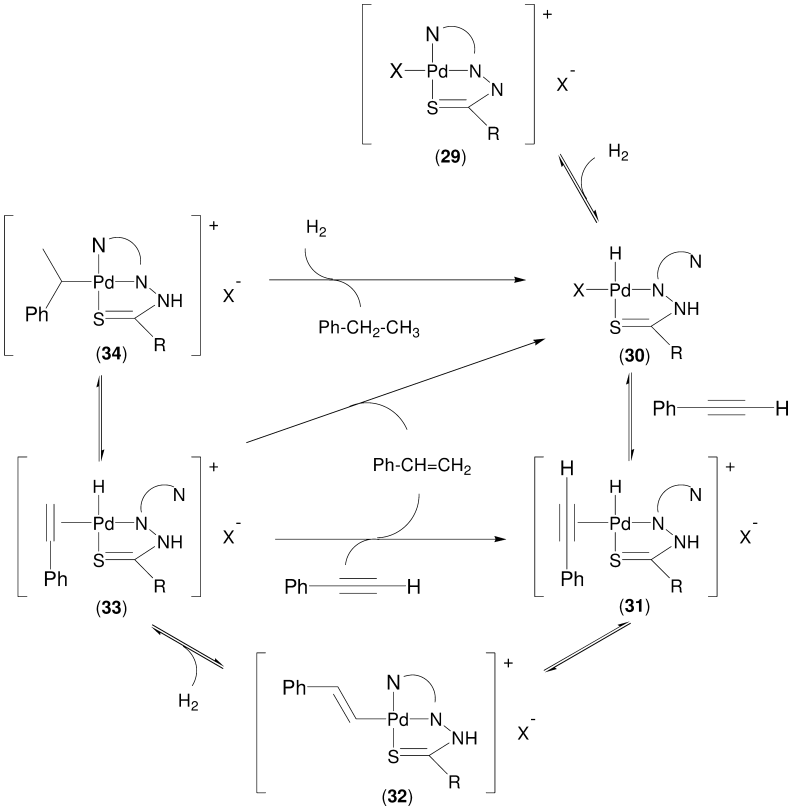
A kinetic investigation was performed using the [Pd(methyl-2-pyridylketone-thiosemicarbazonato)Cl] (**29a**) complex at 50 °C, and this yielded the experimentally obtained rate law; $r = k$[catalyst][alkyne][pH_2] [32]. Based on this rate law and the activity data, a catalytic cycle as depicted in Scheme 14.13 was postulated. The first step of the mechanism is the activation of molecular hydrogen *via* heterolytic hydrogen splitting to generate a palladium hydride species (**30**) and accommodating the proton on one of the basic sites of the ligand (the hydrazone nitrogen). It is assumed that the pyridine moiety acts as a hemilabile ligand, creating the coordination site for the hydride. After hydrogen activation, the incoming alkyne replaces the counterion X^- from the first coordination sphere and generates the [Pd(NNS)(alkyne)] species (**32**). This step appears to be the predominant factor in driving the chemoselectivity of the hydrogenation reaction. It was shown that the weakly bonded acetate anion is easily replaced by both phenyl acetylene and the reaction product styrene, hence displaying low chemoselectivity, while tightly associated anions such as iodide show no hydrogenation activity under the reaction conditions used. The chloride ion appears to take an intermediate position, allowing it to be replaced by phenyl acetylene but not by the reaction product styrene; thus it forms a basis for discriminating between these potential substrates. Subsequently, the hydride is transferred to the coordinated phenyl acetylene forming a [Pd(NNS)(alkenyl)]$^+X^-$ species (**32**) which then reacts with molecular hydrogen, leading to the [Pd(NNS)(H)(styrene)]$^+X^-$ complex (**33**). Either the chloride anion or the phenyl acetylene then displaces the coordinated styrene resulting in complex **30** or **31**, respectively.

In addition, the related divalent palladium complexes [Pd(PNO)X] (**35**) (PNO = *N′*-(2-(diphenylphosphino)benzylidene)acetohydrazonato and related ligands) [50, 51] and [Pd(NNN)X] (**36**) (NNN = *N*-pyridin-2-yl-*N′*-pyridin-2-ylmethy-



28 **29**

Fig. 14.2 Structure of the precursor catalysts [Pd(thiosemicarbazonato)X] (**28**) and [Pd(thiobenzoylhydrazonato)X] (**29**).



Scheme 14.13 Proposed mechanism for the hydrogenation of phenyl acetylene by [Pd(methyl 2-pyridyl ketone thiosemicarbazonato)Cl] (**29a**).

lene hydrazinato) (X=Cl^- or OAc^-) [52] have been reported to be able to hydrogenate alkynes to the corresponding alkenes. For these systems, a heterolytic hydrogen activation similar to catalysts **28** and **29** is suggested. The hemilability of the ligand and the nature of the anion is important feature of the catalytic activity. The rate of phenyl acetylene hydrogenation employing **36** appears similar to the rate reported for **28** and **29**, while **35** displays a distinctively lower reaction rate. Furthermore, no further mechanistic details concerning the chemo- or stereoselectivity of these catalytic systems have been reported.

14.1.9
Conclusions

The stereoselective hydrogenation of alkynes to alkenes can be effected by a wide variety of homogeneous catalysts. The appropriate choice of catalyst and reaction conditions allows the selective formation of either the (*Z*)- or the (*E*)-alkene. Most of the catalysts display a very high chemoselectivity, as they are not reactive towards reducible functional groups such as carbonyl, ester, and double bonds. Many of the details related to catalyst behavior and intricate mechanistic details concerning semihydrogenation of alkynes have often not been unraveled, and will remain a topic of research for the coming years.

14.2
Homogeneous Hydrogenation of Dienes to Monoenes

14.2.1
Introduction

The hydrogenation of polyenes is a research topic that has attracted substantial attention over the past three decades. Especially, the removal of diene constituents from (light) hydrocarbon fractions, polydiene rubbers and fatty acids has been a major focus in the research effort. Although the importance of this reduction is generally recognized, there are only a small number of homogeneous catalysts that have been reported to be active in the diene hydrogenation reaction. Details about the catalytic behavior and mechanism are often very scarce, or these have not been explored at all. Frequently, a distinction is made between the hydrogenation of conjugated and non-conjugated dienes. The latter type is often considered as consisting of two single, isolated double bonds, which are thus fairly easily reduced by most hydrogenation catalysts. Substrates containing conjugated double bonds (either present in the substrate or formed by prior isomerization reactions of non-conjugated double bonds) often pose more difficulty in a hydrogenation reaction. Especially, the formation of stable diene- or allyl complexes often inhibits the reaction and, hence, the selective hydrogenation of conjugated dienes to monoenes forms a particular challenge.

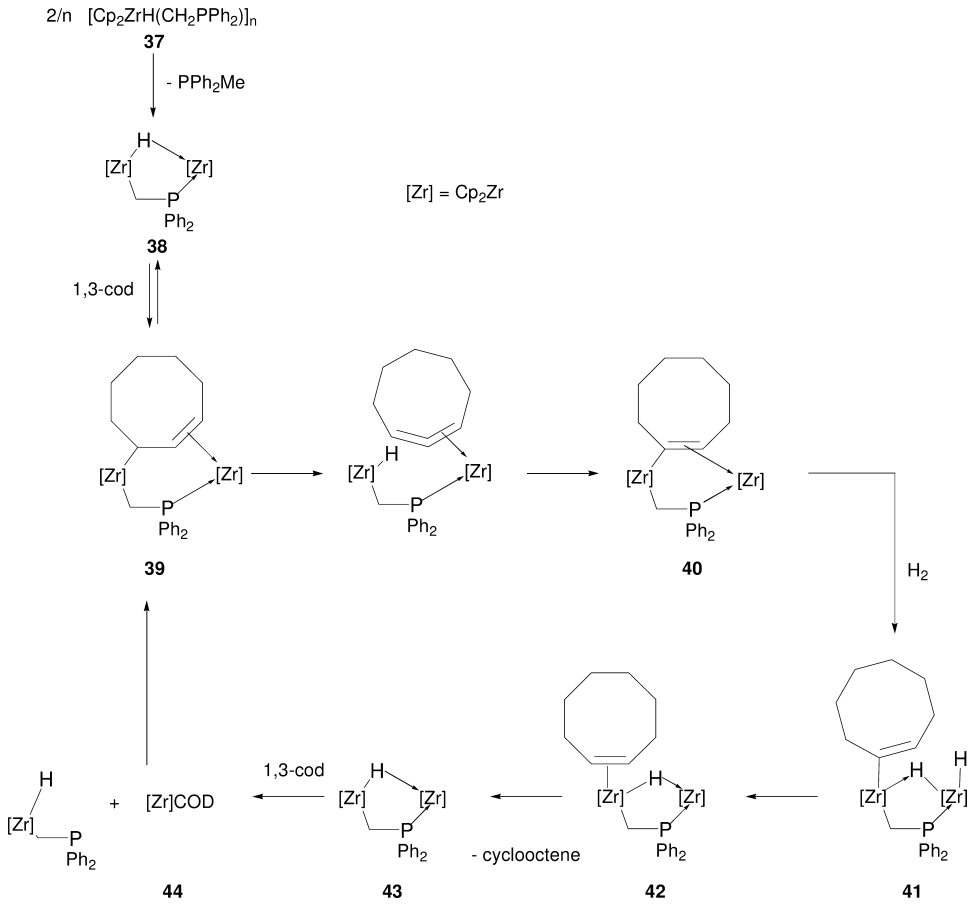
Selectivity in the hydrogenation reaction of dienes to monoenes can be achieved by two types of catalytic system: (i) those which are completely inert with respect to the hydrogenation of the resulting monoenes; and (ii) those for which the selectivity is due to the discrimination based on thermodynamic and/or kinetic factors that suppress the rate of formation of the saturated hydrocarbon. The latter approach is the most common way of achieving selectivity for these hydrogenations.

In this section, an overview will be provided of reported catalysts that can perform the hydrogenation of conjugated dienes to monoenes with a considerable degree of selectivity using molecular hydrogen as a hydrogen source. Most attention will be given to those catalytic systems that show remarkable (high) selectivities, high reaction rates, or which have demonstrated their value in organic synthesis. Furthermore, special attention will be given to the mechanistic details of these homogeneous hydrogenation systems.

14.2.2
Zirconium Catalysts

The oligomeric hydrido-zirconium complexes $[Cp_2Zr(H)(CH_2PPh_2)]_n$ (**37**) constitute selective systems for the hydrogenation of dienes [53]. The reaction is performed at 80 °C at hydrogen pressures between 10 and 40 bar; under these conditions the linear dienes (e.g., 1,3-pentadiene) are hydrogenated consecutively to the corresponding alkanes. The monoene *E*-2-pentene is detected only as intermediate in the reaction mixture. Remarkably, cyclic olefins such as cycloheptatriene, 1,3- and 1,5-cyclooctadiene are selectively hydrogenated to the cycloheptene and cyclooctene, respectively (>98% selectivity). In contrast to linear dienes, cyclic dienes are not fully hydrogenated to the alkane and the hydrogenation stops at the monoene stage.

In order to understand the unusual reactivity of $[Cp_2Zr(H)(CH_2PPh_2)]_n$ towards cyclic dienes, the reaction mechanism was studied using 1,3-cyclooctadiene and butadiene as substrate. It appears that the first step, the activation of the initial zirconium precursor catalyst **37**, is achieved by a sequence of decomposition steps consisting of the reductive elimination of the phosphine PPh_2Me and the simultaneous formation of the zirconocene intermediate $[Cp_2Zr]$. This intermediate will then be trapped, either by the diene, producing $[Cp_2Zr(diene)]$ (**44**) or by **37** to give the homometallic hydride bridged complex $[Cp_2Zr(\mu\text{-}H)(\mu\text{-}CH_2PPh_2)ZrCp_2]$ (**38**) (see Scheme 14.14) [54]. The complexes **44** and **38** are related species. From detailed stoichiometric reactions, using the less sterically demanding butadiene as substrate, it has been shown that the reaction of intermediate **44** with starting material **37** and the reaction of compound **38** with butadiene are viable and produce a common intermediate. This common intermediate has been identified as a dinuclear Zr(IV)–Zr(II) complex in which the butenyl fragment bridges between the two zirconium centers in a $\mu^1\text{-}\eta^1:1,2\text{-}\eta^2$-fashion, structurally similar to compound **39** (Scheme 14.14) [55].



Scheme 14.14 Proposed mechanism for the hydrogenation of 1,3-cyclooctadiene catalyzed by $[Cp_2Zr(H)(CH_2PPh_2)]_n$ (**37**) [53].

Kinetic studies revealed that the order of reaction with respect to the zirconium is a half, reflecting the dissociation of active catalytic species [53]. Since the order in substrate is zero and one in hydrogen, the addition of H_2 is the rate-limiting step in the reaction mechanism. The rate of the reaction, expressed in average TOFs, ranges between 180 and 750 mol mol^{-1} h^{-1}, and the activation energy of the hydrogenation of 1,3-cyclooctadiene was determined to be 29 kJ mol^{-1}. The proposed catalytic cycle, as is depicted in Scheme 14.14, consists of the formation of the initial Zr(IV)–Zr(II) bimetallic complex **39** in which a cyclooctenyl ligand is bridging between the two zirconium centers. Compound **39** then isomerizes to the μ-alkenyl zirconium(IV)/zirconium(II) intermediate **40**, which is considered the key intermediate in the reaction mechanism. Formation of complex **40** is proposed to explain the effective protection of the remaining C=C double bond in the catalytic cycle. This species then reacts with

molecular hydrogen in an oxidative addition manner to form the dinuclear Zr(IV)–Zr(IV) dihydride complex (**41**), having one bridging and one terminal hydride. Reductive elimination of the alkenyl and one of the hydrides yields the dinuclear-monohydride bridged complex (**42**) which then loses the cyclooctene. The unusual selectivity is ascribed to the cooperative effect of two zirconium centers, stabilized and held together by the bridging CH_2PPh_2-ligand, to combine the action of a zirconium(IV) and a zirconium(II) centre, bringing about rapid mono-hydrogenation and at the same time effective protection of the remaining C=C double bond.

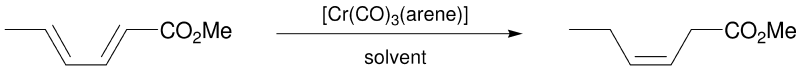
14.2.3 Chromium Catalysts

Group VI metal carbonyls and their derivatives, especially chromium carbonyl compounds, are able to hydrogenate a variety of substrates (e.g., alkynes, enones) with high stereospecificity [6]. The regio- and stereospecific 1,4-hydrogenation of conjugated dienes to (*Z*)-monoenes catalyzed by $[Cr(CO)_3(arene)]$ complexes (**45**) was first reported in 1968 by the groups of Cais et al. [56] and of Frankel et al. [57]. The catalysts $[Cr(CO)_3(benzene)]$, and similar ones containing a benzene derivative that were initially explored, required rigorous reaction conditions (150–160 °C and 50 bar H_2) in order for the stereoselective 1,4-hydrogenation to proceed. However, the activity depends on the substituents attached to the benzene ligand – that is, the presence of more electron-withdrawing substituents and more coordinating solvents allowed milder reaction conditions (Table 14.3).

Spectroscopic studies have revealed that $[Cr(CO)_3(S)_3]$ (S = solvent) is the active species for the hydrogenation, and the formation of these species is promoted either by less strongly coordinated ligands (electron-poor benzene or polyaromatic compounds) or by more strongly coordinating solvents. The use of polyaromatic compounds such as naphthalene, anthracene and phenanthrene as ligands combined with polar coordinating solvents (THF or acetone) has proven to be particular effective for constructing a highly active catalytic system under mild conditions [58]. Whereas several mechanistic schemes have been suggested for the chromium-catalyzed diene hydrogenation, they all share a common feature: the active metal fragment $[Cr(CO)_3]$ is generated *in situ* by thermal or photochemical activation of a coordinatively saturated $[Cr(CO)_3(L)_3]$ complex ($(L)_3$ = arene; L = CH_3CN or CO) [58–60].

At ambient reaction temperatures and hydrogen pressures, kinetic studies employing $[Cr(CO)_3(nap)]$ (nap = naphthalene) (**45a**) as catalyst revealed that two reaction mechanisms operate simultaneously, namely a hydride route and a diene route (Scheme 14.15) [61]. After the initial step, in which $[Cr(CO)_3(nap)]$ reacts with the solvent to generate the active catalyst $[Cr(CO)_3(S)_3]$ (**46**), this solvent complex can then subsequently react either with hydrogen or the conjugated diene. In the hydride route, $[Cr(CO)_3(S)_3]$ undergoes oxidative addition of dihydrogen to give complex **48**, which still has two labile coordination sites nec-

Table 14.3 Hydrogenation of methyl sorbate to 3-hexenoic acid methyl ester with $[Cr(CO)_3(arene)]$ (**45**) catalysts.

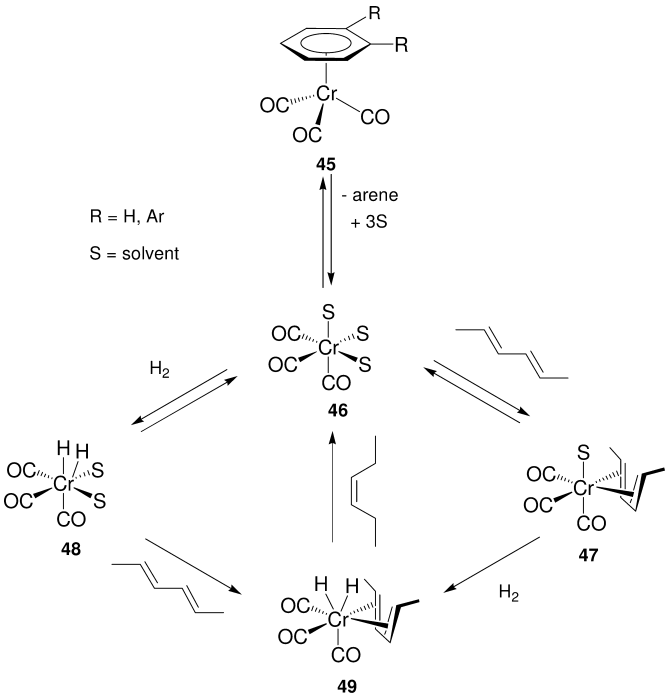


Entry	Catalyst arene (mol.%)	Solvent	Reaction temp. [°C]	H_2 pressure [bar]	Induction period [min]	10^{-5} k_{obs} [s^{-1}]	TOF [mol mol^{-1} h^{-1}][a)]	Selectivity [mol.%]
1	Benzene (5)	Cyclohexane	165	48	285	39.6	14	94.3
2	Benzene (5)	Acetone	165	48	–	246	84	92.2
3	Methyl benzoate (5)	Cyclohexane	120	48	45	56.0	20	99.3
4	Chlorobenzene (5)	Cyclohexane	120	48	15	61.5	21	96.1
5	Phenanthrene (2)	Decalin	120	4	14.3	340	294	–
6	Phenanthrene (3)	THF	40	4	100	53	29	–
7	Phenanthrene (3)	Acetone	40	4	29	361	29	–
8	Naphthalene (2)	Decalin	120	4	1	963	832	–
9	Naphthalene (3)	THF	40	4	8	385	208	–
10	Naphthalene (3)	Acetone	~27	4	4	963	520	–

a) TOF determined at 50% conversion using first-order kinetics.
TOF = 0.5 k_{obs}[substrate]/[catalyst].

essary to accommodate the diene in a η^4-fashion. After coordination of the conjugated diene producing complex **49**, the two hydrides are rapidly transferred, producing a (*Z*)-monoene. The diene route is established by initial coordination of the diene to the solvento complex **46** to produce $[Cr(CO)_3(diene)(S)]$ **47** prior to the hydrogen activation. Although both hydrogenation routes are active under the typical hydrogenation conditions, additional kinetic studies performed at high temperatures and elevated hydrogen pressures employing $[Cr(CO)_3(arene)]$ (arene = substituted benzene derivative) show that, under these conditions, only the hydride route is operative. The oxidative addition of molecular hydrogen is the rate-determining step for this hydrogenation route [62, 63].

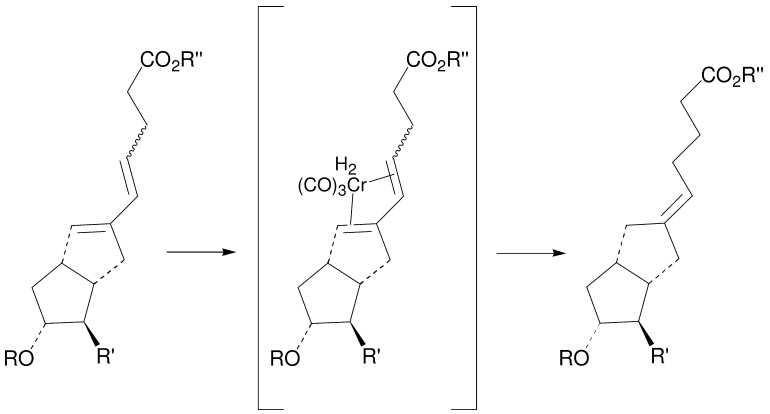
The $[Cr(CO)_3(arene)]$-catalyzed 1,4-hydrogenation of conjugated dienes has become an established route for the stereocontrolled synthesis of alkenes in organic synthesis [6, 7]. The potential of this method has been clearly demonstrated in the synthesis of olfactory compounds (fragrances and insect pheromones), where the 1,4-hydrogenation of dienes was employed in a key step of the synthesis. For such compounds, the stereo- and regio control of the double-bond geometry is extremely important for maintaining its biological activity. Furthermore, the $[Cr(CO)_3(arene)]$-catalyzed hydrogenation displays a remarkably high chemoselectivity, and the outcome of the reaction is not affected by the presence of other functional groups such as non-conjugated carbon-carbon double bonds, esters, ketones, carboxylic acids, epoxides, phosphonate esters, sulfonamides, or even cyano groups [6].



Scheme 14.15 Proposed hydrogenation mechanism for the 1,4-hydrogenation of dienes by $[Cr(CO)_3(arene)]$ (**45**).

An interesting feature of the $[Cr(CO)_3]$-catalyzed 1,4-hydrogenation is the predetermined outcome of the stereocontrolled reaction; the diene must coordinate in a η^4-s-*cis* fashion to the chromium, allowing only one conformationally rigid and predisposed intermediate [6]. The presence of only one accessible catalyst–substrate intermediate structure invokes the 1,4-hydrogenation to proceed with complete regio- and stereocontrol, regardless of the thermodynamic stability of the hydrogenation products. This was demonstrated in the stereocontrolled synthesis of carbacyclin analogues for the production of the exclusively (*E*)-exocyclic isomer (Scheme 14.16). The chromium–diene intermediate, in conjunction with the 1,4-addition, dictates the formation of the exocyclic isomer, and since the chromium catalyst is inactive in the isolated double-bond isomerization reaction, the (*E*)-isomer is obtained solely as the reaction product.

Apart from Cr(0) carbonyl complexes, similar Mo, W and Co complexes also catalyze 1,4-*cis*-hydrogenation of dienes, though the selectivity of these catalysts is relatively low [63].



Scheme 14.16 Stereocontrolled 1,4-hydrogenation of a carbacyclin analogue using $[Cr(CO)_3(arene)]$ (**45**) complexes.

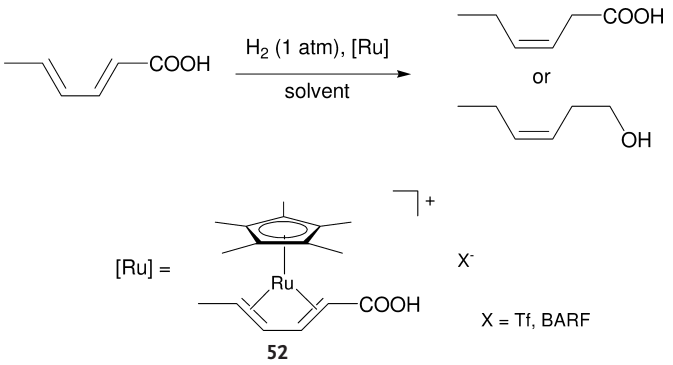
14.2.4
Ruthenium Catalysts

Ruthenium complexes are active hydrogenation catalysts for the reduction of dienes to monoenes. Both zerovalent and divalent ruthenium complexes containing various (alkene, diene and phosphine) ligands have been employed as catalysts that have met with different degrees of success.

Ruthenium(0) complexes containing cyclic polyenes such as Ru(cod)(η^6-triene) (**50**) (cod = 1,5-cyclooctadiene; triene = 1,3,5-cyclooctatriene or 1,3,5-cycloheptatriene) have proven to be selective hydrogenation catalysts for the reduction of cycloheptatriene and cyclooctadiene to the corresponding cyclic monoenes [64, 65]. The [Ru(cod)] fragment is maintained as the catalytic unit throughout the hydrogenation reaction and the η^6-coordinated triene (e.g., cyclooctatriene) is hydrogenated to the monoene during the induction period.

For instance, cycloheptatriene has been selectively hydrogenated at 1 bar H_2 pressure at 20 °C, yielding cycloheptene. The selectivity depended largely on the solvent used, ranging from 100% when *n*-hexane was used, or 99.5% in THF, to very low values when ethanol was employed. The conversion is quantitative in THF and ethanol, but in *n*-hexane it did not exceed 65%; consequently, the authors concluded that THF gives the best combination of selectivity and conversion. In this case, the formation of cycloheptane was observed only after the substrate cycloheptatriene had completely been consumed.

Cyclooctadiene isomers (i.e., 1,5-cod or 1,3-cod) are selectively hydrogenated by [Ru(η^4-cod)(η^6-C_8H_{10})] (**51**) to produce exclusively cyclooctene in THF, under ambient temperature (20 °C) and 1 bar H_2 pressure [64]. Again, cyclooctane is only detected when the diene substrate is completely transformed to the monoene. The rate of hydrogenation is higher in case of the conjugated 1,3-cyclooctadiene substrate, whereas isomerization of the non-conjugated 1,5-cyclooctadiene



Scheme 14.17 Hydrogenation of sorbic acid by [Cp*Ru(η^4-sorbic acid)]$^+X^-$ (**52**). $X^- = CF_3SO_3^-$ or $BARF^-$.

to 1,3-cyclooctadiene has been proposed. This isomerization appeared to be necessary for the catalytic hydrogenation of 1,5-cod.

Cationic ruthenium complexes containing the fragment [Cp*Ru] (**52a**) can stereoselectively hydrogenate sorbic acid or sorbic alcohol to *cis*-3-hexenoic acid or *cis*-3-hexen-1-ol, respectively (Scheme 14.17). The highest rate and stereoselectivity have been obtained with the "naked" [Cp*Ru] – that is, a monocyclopentadiene–ruthenium complex without any additional, inhibiting ligands and [Cp*Ru(η^4-sorbic acid)]$^+X^-$ (**52**) (sorbic acid = (2*E*,4*E*)-MeCH=CHCH=CHCO$_2$H and $X = CF_3SO_3^-$ or $BARF^-$) displays the best results. These ionic ruthenium catalysts have been used successfully in a single phase as well as liquid two-phase systems (such as liquid–liquid, ionic liquid–liquid solvent systems) [66, 67]. The activity of these catalysts depends strongly on the solvent or solvent mixtures used, with the rate of hydrogenation of sorbic acid (in TOF) ranging from 92 to 1057 mol mol^{-1} h^{-1}. The highest rate and selectivity have been reported for the solvent methyl-*tert*-butyl ether (TOF = 1057, *cis*:*trans* ratio 96 : 3). In general, the hydrogenation of sorbic alcohol proceeds with higher activity and almost complete selectivity when using **52** as the catalyst.

Mechanistic studies employing the PHIP phenomenon showed that the homogeneous hydrogenation of sorbic acid (in acetone under 1 bar H_2) proceeds by concerted 1,4-hydrogenation of the diene moiety [68]. Both atoms of the same dihydrogen molecule are transferred to the substrate in a synchronous fashion, yielding *cis*-3-hexenoic acid as the primary reaction product. Furthermore, it was found that the *trans*-isomer is formed by subsequent rearrangement of the *cis*-3-hexenoic acid, and is not the result of direct hydrogenation of sorbic acid.

14.2.5
Cobalt Catalysts

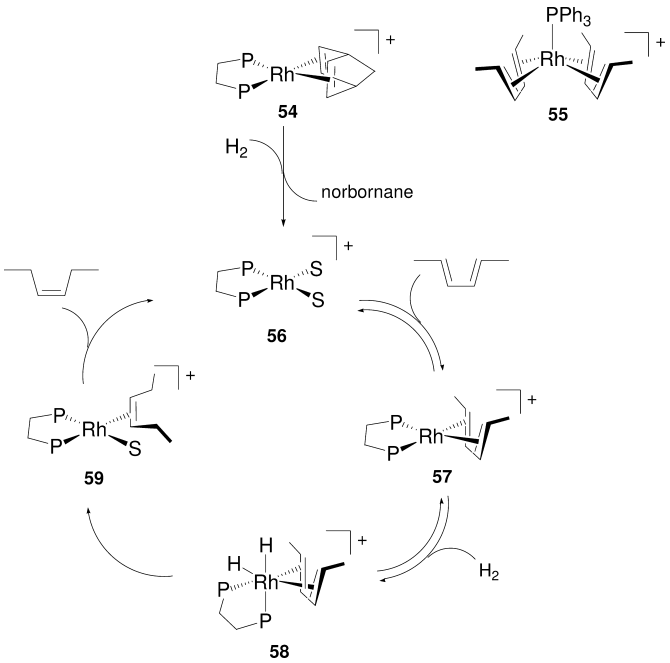
In spite of the number of disadvantages, considerable interest has been given to the hydrogenation of dienes by the water-soluble catalyst $K_3[Co(CN)_5H]$ (**53**) [69, 70]. The catalyst shows a high chemoselectivity towards conjugated carbon-carbon double bonds; that is, isolated carbon-carbon double bonds or carbonyl functional groups will not be affected by the catalyst under the hydrogenation conditions. However, the hydrogenation reaction suffers from short catalyst lifetime, substrate inhibition, low hydrogenation rate (generally TOF ≤ 2) and low regioselectivity of the monoene products [71]. The addition of phase-transfer reagents (e.g., ammonium salts [71], β-cyclodextrin [72]) or surfactants [73, 74] largely overcomes these complications, but the rate of the reaction remains low. In general, the product ratios are dominated by the overall 1,4-addition of hydrogen under the phase-transfer conditions, although in some cases 1,2-addition has been observed [73, 75]. Several modified versions of this catalyst are known where one or more cyanides are replaced by diamines such as ethylenediamine, bipy or phen [75].

14.2.6
Rhodium Catalysts

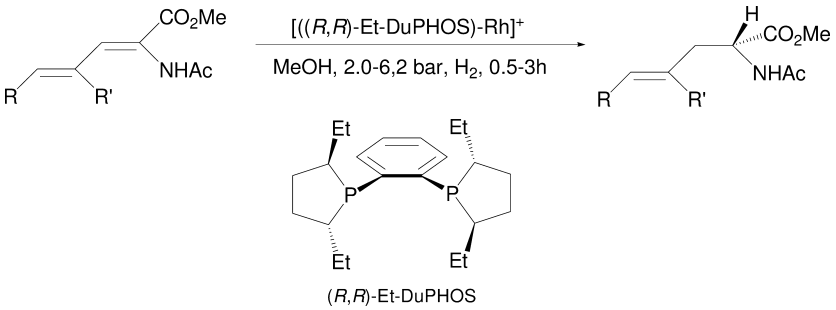
The well-known cationic Osborn catalyst $[Rh(nbd)L_n]^+A^-$ (**54**), which has been an extremely useful catalyst for the reduction of alkenes and alkynes, also facilitates the rapid and selective hydrogenation of dienes in polar solvents, affording the corresponding monoenes [76]. In order to probe this reaction, various substrates such as norbornadiene, substituted butadienes and conjugated and non-conjugated cyclic dienes have been tested. The TOF depends strongly on the reaction conditions (i.e., solvent), the catalyst employed, and on the structure of the substrate. Hence, the rate of hydrogenation typically ranges from 140 to 250 mol mol^{-1} h^{-1}. More sterically encumbered substrates such as 2,5-dimethylhexa-2,4-diene show very low hydrogenation rates (~6 mol mol^{-1} h^{-1}), while 1,3-cyclooctadiene is rapidly hydrogenated to the monoene (330 mol mol^{-1} h^{-1}). The product monoenes, which are formed almost quantitatively (up to 99% yield), result from overall 1,2- and 1,4-addition of H_2 onto the diene moiety [25, 76, 77]. The ratio of the two addition modes depends strongly on the structure of the substrate and on the nature of the ligand, L. For the diene reduction, chelating diphosphines or diarsines are preferred as stabilizing ligands, as catalysts derived from monodentate ligands tend to become easily deactivated due to the formation of an unsaturated $[Rh(diene)_2L]^+$ fragment (**55**).

The proposed hydrogenation mechanism for (conjugated) dienes by the cationic rhodium catalyst $[P_2Rh(nbd)]^+X^-$ (**54**) is depicted in Scheme 14.18. Activation of the precursor catalyst **54** has been studied in considerable detail, and reveals that the hydrogenation of the initially coordinated norbornadiene is fast and complete for most investigated systems (contrary to the often-used $[P_2Rh(cod)]^+X^-$ analogues) [78–80]. In contrast to the reported hydrogenation mechanisms for mono-

enes and alkynes, the hydrogenation of dienes does not depend on the addition of acid and, therefore, it is assumed to proceed by a different catalytic route (Scheme 14.18) [21, 76, 81]. The proposal of an "unsaturated" mechanism, in which the diene coordinates to form $[P_2Rh(diene)]^+$ (**57**), prior to hydrogen activation, can be rationalized by the high coordination constant of the *cis*-s-coordinated (chelating) diene to the rhodium. The hydrogenation mechanism shows a zero order in diene, and it has been suggested that the rate-determining step involves the reaction of H_2 with the cationic $[P_2Rh(diene)]^+$ species (**57**). Detailed *in-situ* NMR studies employing deuterium and *para*-hydrogen-enriched molecular hydrogen has allowed the proposal of the structure of the $[P_2Rh(diene)(H)_2]$ (**58**) intermediate, which was revealed by the cross-relaxation transfer, originating from the enhanced magnetization inflicted by the *para*-hydrogen adducts [78]. In addition, these studies demonstrated that the hydrogenation of norbornadiene and 1,4-cyclooctadiene occurs successively and confirms the mechanism presented in Scheme 14.18 [82]. To date, many details of the hydrogenation of 1,3-dienes have not been resolved, such as the true nature of the $[P_2Rh(R)(H)]$ intermediate between complex **58** and **59** (not shown in Scheme 14.18), possibly being either a [Rh(alkenyl)] or a [Rh(allyl)] species. The first species would lead to 1,2-addition, and the latter one to either 1,2- or 1,4-addition.



Scheme 14.18 Proposed 1,4-hydrogenation mechanism for the hydrogenation of dienes by cationic rhodium complexes $[P_2Rh(diene)]^+A^-$ (**54**).

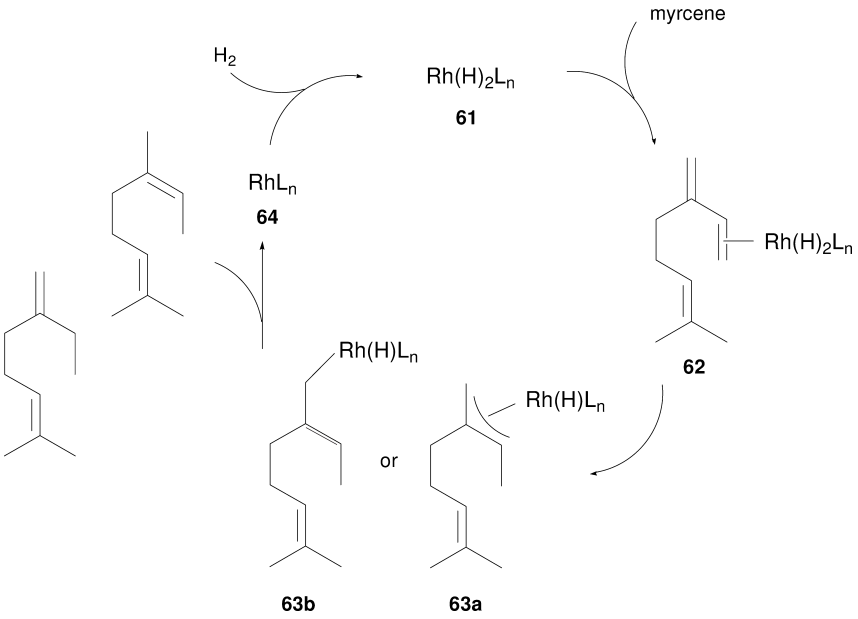


Scheme 14.19 Hydrogenation of conjugated α,γ-dienamide esters by [((*R*,*R*)-Et-DuPHOS)-Rh(cod)]OTf (**54b**) (OTf=triflate) [83].

The characteristics of the hydrogenation of norbornadiene, substituted butadienes and conjugated and cyclic dienes are all very similar. In the case of conjugated dienes, there appears to be hardly any isomerization activity, while in the case of 1,4-dienes an isomerization step to form the corresponding 1,3-diene is assumed prior to hydrogenation. The catalyst behavior changes after the diene has been completely converted to the monoene, whereupon the rhodium catalyst resumes its "normal" monoene hydrogenation behavior.

An interesting example of the use of $[Rh(nbd)L_n]^+A^-$ (**54**) in organic synthesis is provided by the cationic rhodium complex [((*R*,*R*)-Et-DuPHOS)-Rh(cod)]OTf (**54b**), which appears to be particularly effective in the enantiomeric hydrogenation of conjugated α,γ-dienamide esters [83]. Full conversion to the corresponding γ,δ-unsaturated amino acids could be obtained using the Et-DuPHOS-Rh catalyst system, yielding very high regio- and enantioselectivity (>95% and 99% ee, respectively; see Scheme 14.19) with over-reductions as low as <0.5%. The rate of the reaction (expressed as average TOFs, determined at full conversion) for different substrates ranged from 160 to 1000 mol mol^{-1} h^{-1}. Either enantiomer of the γ,δ-unsaturated amino acid could be obtained by the use of (*R*,*R*)- or (*S*,*S*)-Et-DuPHOS. Interestingly, the reaction proceeds by hydrogenation of the enamide C=C double bond, with complete regioselectivity over the distal C=C double bond. Effectively, only 1,2-addition is observed, which can be explained by the chelating effect of the enamide group to the metal center and preventing over-reduction, even after the enamide double bond has been completely converted.

The selective diene hydrogenation of monoterpenes such as myrcene, which contain both isolated monoene and diene moieties, forms a particular challenge [84]. The catalyst $[RhH(CO)(PPh_3)_3]$ (**60**) has been reported to perform remarkably well for such hydrogenation reactions, and the diene moiety was shown to be selectively reduced to the monoene, while the isolated double bond remained unaffected under the reaction conditions used (Scheme 14.20). The rates of reaction expressed as average TOF (determined at ca. 80% conversion) ranged from ca. 640 (in benzene, 20 atm H_2 at 100 °C) to 7600 mol mol^{-1} h^{-1} (in cyclohexane, 20 atm H_2 at 80 °C). The hydrogenation in benzene solution resulted in



Scheme 14.20 Proposed mechanism for the hydrogenation of myrcene by $[RhH(CO)(PPh_3)_3]$ (**60**) and the formation of the major reaction products [84].

the highest chemoselectivity of the reduction of the conjugated diene to the corresponding monoene (98% selectivity). The products arise from overall 1,2- and 1,4-addition onto the diene moiety.

The proposed reaction mechanism differs from the mechanism reported for the cationic rhodium complexes $[Rh(nbd)L_n]^+A^-$ (**54**); that is, in the present case a "dihydride route" is favored by the authors, implying that first molecular hydrogen is activated to yield the rhodium dihydride species $[Rh(H)_2L_n]$ (**61**). This species subsequently reacts with the substrate's conjugated diene fragment. However, formation of the proposed rhodium(dihydride) species from the precursor catalyst $[RhH(CO)(PPh_3)_3]$ **60** has not been disclosed. Based on the product distribution, the authors suggest that the diene initially coordinates in an η^2-fashion (complex **62**), showing preference for the least-substituted double bond (Scheme 14.20). The presence of [Rh(η^4-diene)] complexes has not been ruled out as possible intermediates in the product formation, and could be the bias for the observed chemoselectivity. After transfer of the first hydride to the substrate, either a [Rh(η^3-allyl)] complex (**63 a**) or the [Rh(η^1-allyl)] complex (**63 b**) is formed; the latter species leads to overall 1,2-addition, while [Rh(η^3-allyl)] leads to both 1,2- as well as 1,4-addition. Although the dihydride route is the favored mechanism, a catalytic cycle based on a rhodium-monohydride has not been excluded.

Finally, other rhodium catalysts for the selective diene hydrogenation worth mentioning include $[RhCl(PPh_3)_3]$ (**64**), $[RhCl(nbd)]_2$ (**65**), and the catalytic sys-

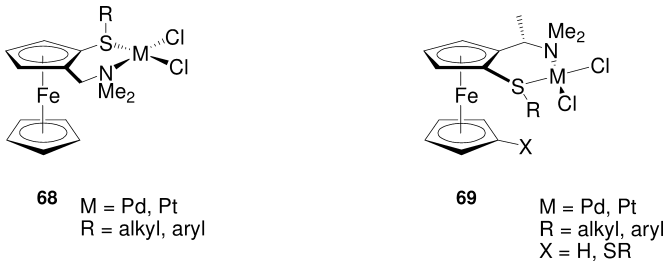


Fig. 14.3 General structures of compounds **68** and **69**.

tems resulting from protonation of $[Rh(CO_2Me)_2(PPh_3)_2]$ (**66**) or $[Rh(CO_2Me)(PPh_3)_3]$ (**67**) precursors [25, 77]. Generally, these complexes show chemoselectivity that is similar to or lower than that of the cationic rhodium complexes $[Rh(nbd)L_n]^+A^-$ (**54**), with comparable reaction rates. The observed selectivity for these systems is attributed principally to the much higher coordinating power of dienes compared with monoenes. Catalysts **64**, **65**, **66** and **67** reduce conjugated dienes by 1,2- as well as 1,4-addition of hydrogen, yielding mixtures of monoenes.

14.2.7
Palladium and Platinum Catalysts

Palladium has been frequently used to reduce conjugated dienes to monoenes. Most of the catalysts based on palladium consist of palladium species – that is, mononuclear complexes and Pd nanoparticles that are heterogenized on a solid support. Both mineral and organic supports have been successfully employed in these systems and, in addition, various hydrogen donors can be used, namely dihydrogen, Group XIII or XIV metal hydrides, and various formate salts. The number of homogeneous palladium complexes able to hydrogenate conjugated dienes to monoenes using molecular hydrogen is very limited. The majority of the accounts reported in the open literature concerning these homogeneous palladium catalysts merely state the observed activity and, hence, the mechanistic details mostly remain obscure.

A large variety of palladium complexes of the general type **68** and **69** (Fig. 14.3), containing ferrocenyl-amine-sulfide or -selenide ligands, are active catalysts for the selective hydrogenation of conjugated dienes to monoenes [85, 86]. The best results (at H_2 pressure of 4–7 bar and room temperature) have been obtained with cyclic substrates. 1,3-Cyclooctadiene is converted into cyclooctene, with the most efficient catalyst reported for this transformation being $[\eta^2\text{-}\{FeCpC_5H_3(CH_2NMe_2)(S(t\text{-}Bu)\}PdCl_2]$, with a TOF of 345 mol mol^{-1} h^{-1} and a selectivity of 97.2% [87]. Higher activities are accompanied by lower selectivities due to a higher degree of over-reduction to cyclooctane. Acyclic dienes yielded less satisfactory results, although these substrates are selectively hydro-

Table 14.4 Selective hydrogenation of 1,3-cyclooctadiene to cyclooctene with various palladium complexes.

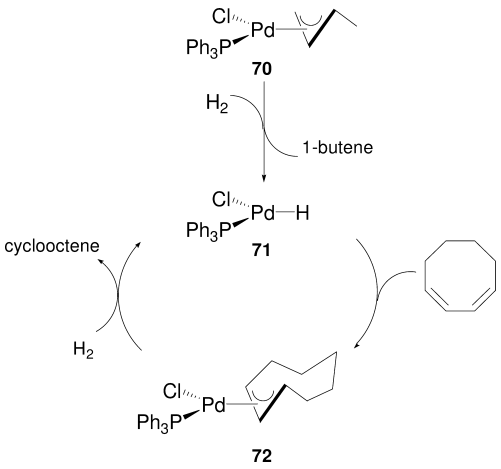
	Catalyst	Induction time [h]	Conversion [%]	TOF [mol mol^{-1} h^{-1}]	Selectivity [%]	Reference
1	[{FeCpC$_5$H$_3$(CH$_2$NMe$_2$)(SMe)}PdCl$_2$] [a)]	49.7	100	14	94.1	87
2	[{FeCpC$_5$H$_3$(CH$_2$NMe$_2$)(SEt)}PdCl$_2$] [a)]	42.3	100	15	98.4	87
3	[{FeCpC$_5$H$_3$(CH$_2$NMe$_2$)(S(*n*-Pr))}PdCl$_2$] [a)]	37.5	100	16	90.9	87
4	[{FeCpC$_5$H$_3$(CH$_2$NMe$_2$)(S(*t*-Bu))}PdCl$_2$] [a)]	0.0	100	345	97.2	87
5	[{FeCpC$_5$H$_3$(CH$_2$NMe$_2$)(S(4-tolyl))}PdCl$_2$] [a)]	0.0	100	691	78.5	87
6	[{FeCpC$_5$H$_3$(CHMeNMe$_2$)(SMe)}PdCl$_2$	42.5	100	17	96.7	85
7	[{FeCpC$_5$H$_3$(CHMeNMe$_2$)(S(4-tolyl))}PdCl$_2$]	0	98.6	465	91.9	85
8	[{FeCpC$_5$H$_3$(CHMeNMe$_2$)(S(4-ClPh)}PdCl$_2$]	0	100	684	96.8	85

a) 9.0 mL acetone, 2.0×10^{-5} mol, 7.45×10^{-3} mol substrate, room temperature, 4 bar H_2.
b) 9.0 mL acetone, 2.0×10^{-5} mol, 7.45×10^{-3} mol substrate, room temperature, 7 bar H_2.

genated by 1,4-addition to give the monoenes. A subsequent isomerization reaction leads to product mixtures and, hence, lower stereoselectivities.

The testing of a wide variety of substituted palladium complexes with ferrocene-based diphosphines has revealed several trends. One of the most apparent trends is that increasing the steric bulk on both the amine and the sulfide substituents increases the rate of the reaction, while the monoene selectivity is retained (Table 14.4). The hydrogenation reaction is strongly dependent on the solvent used, and the best results are obtained in acetone. It has been suggested that the solvent is involved in dissociation of the thioether ligand to create a free coordination site, to accommodate the diene [87]. In line with this observation, it appears that neither the platinum aminothioether complexes nor the palladium or platinum complexes of the homologous amino-selenide ligands are active hydrogenation catalysts. Apparently, the Pt–S, Pt–Se and the Pd–Se bonds are too strong, which prevents the required ligand dissociation needed to form an active catalyst. In addition, some catalysts display an induction period before the active catalyst is formed. No further mechanistic details about these catalytic systems have been reported.

Palladium-allyl complexes in combination with stabilizing ligands (e.g., phosphine, halide, allyl, and dienes) are able to hydrogenate conjugated dienes and non-conjugated dienes to the corresponding monoenes under relatively mild reaction conditions [88]. One of the most effective catalytic systems concerns [Pd(L)(PPh$_3$)Cl] (**70a**, L=allyl; **70b**, L=1-Me-allyl) in *N*,*N*-dimethylformamide. Hydrogenation reactions performed at 55 °C and 1 bar H_2 using **70b** show a moderate rate ($\sim$10 mol mol^{-1} h^{-1} determined at 50% conversion) in the hydrogenation of 1,5- and 1,3-cyclooctadiene. However, these catalysts appear to be completely inactive towards the hydrogenation of monoenes (cyclooctene, cyclohexene and 1-octene), thereby corroborating the proposal that the catalysis is



Scheme 14.21 Selective hydrogenation of 1,3-cyclooctadiene catalyzed by [Pd(1-Me-allyl)PPh_3Cl] (**70**) [88].

performed by the mononuclear palladium species. In case of hydrogenation of non-conjugated dienes, the substrate is isomerized to the corresponding conjugated diene prior to hydrogenation.

The influence of hydrogen pressure, substrate and catalyst concentration has briefly been mentioned. The reaction rate is dependent upon the catalyst concentration and hydrogen pressure, but appears to be independent of substrate concentration. The mechanism is proposed to involve the activation of the parent [Pd(allyl)] species producing an unstable hydrido-Pd(II) species (**71**), ensued by a fast reaction with the diene to restore the [Pd(allyl)] moiety (**72**) (Scheme 14.21). The observation that most of the starting material is isolated after the reaction suggests that only a small portion of the catalyst is active under the reaction conditions. Although a complete selectivity for the monoene is observed (even after full conversion), the presence of catalytically active colloidal palladium has not been completely excluded.

14.2.8 Conclusions

The homogeneous hydrogenation of dienes, especially of conjugated dienes remains a challenge, and only a few catalysts have been reported that show good chemo- and stereoselectivity. Until now, the most widely and best explored catalyst for this reaction is constituted by the group of $[Cr(CO)_3(arene)]$ (**45**) and $[Rh(nbd)L_n]^+A^-$ (**54**) complexes. Clearly, this is a research area that has received relatively little attention in the past, and several of the catalytic systems discussed seem to be promising candidates for future investigations.

Abbreviations

DFT	density functional theory
PHIP	*para*hydrogen induced polarization
THF	tetrahydrofuran
TOF	turnover frequency
TON	turnover number

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