6

Hydrogenation with Early Transition Metal, Lanthanide and Actinide Complexes

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6.1

Introduction

Homogeneous hydrogenation catalysts have been mainly based on late transition-metal complexes since the discovery of Wilkinson's catalyst, $[(Ph_3P)_3RhCl]$ [1]. Nonetheless, some of the first homogeneous catalysts to emerge were based on early transition metals. In fact, soon after the discovery of metallocene complexes [2, 3], which were rapidly exploited as the soluble equivalent of Ziegler-Natta olefin polymerization catalysts [4], these systems were introduced as homogeneous hydrogenation catalysts [5–11]. Other Ziegler-Natta-type olefin polymerization catalysts, $[L_nMX_n/M'R]$ {M=Ti, Zr, V, Cr, Mo, Mn, Fe, Co, Ni, Pd, Ru; X=Cl, OR; M′=Al or Li, R=H, Et, Bu or *i*Bu} were also investigated, and the results obtained showed that all metals could indeed activate H_2 and hydrogenate olefins. This pioneering chemistry most likely formed the basis for the discovery of most homogeneous catalyzed processes known to date, and has led to the development of well-defined systems and to the success of molecular organometallic chemistry and homogeneous catalysis [12, 13].

In hydrogenation, early transition-metal catalysts are mainly based on metallocene complexes, and particularly the Group IV metallocenes. Nonetheless, Group III, lanthanide and even actinide complexes as well as later metals (Groups V–VII) have also been used. The active species can be stabilized by other bulky ligands such as those derived from 2,6-disubstituted phenols (aryloxy) or silica (siloxy) (*vide infra*). Moreover, the catalytic activity of these systems is not limited to the hydrogenation of alkenes, but can be used for the hydrogenation of aromatics, alkynes and imines. These systems have also been developed very successfully into their enantioselective versions.

This chapter will provide an overview of the development and use of early transition-metal complexes in hydrogenation, and in consequence has been divided into several sections. Section 6.2 will focus on the mechanistic differences in the hydrogenation reaction between early and late transition metals. The following three sections will describe the various systems based on Group IV (Sec-

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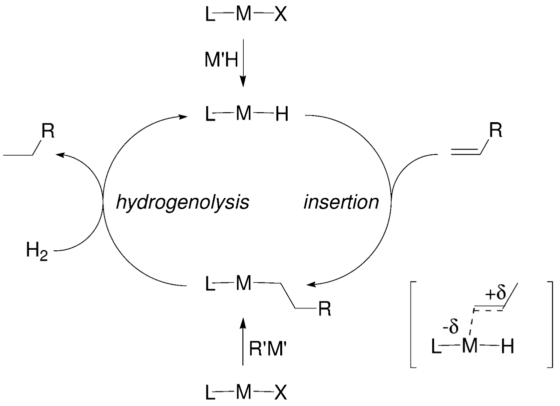
tion 6.3), earlier (Section 6.4: Group III, lanthanides and actinides) and later metals (Section 6.5: Groups V–VII). In each section, the hydrogenation of alkenes, dienes, alkynes, aromatics and imines will be described, and the development of enantioselective hydrogenation catalysts will be discussed. Section 6.6 will be devoted to their heterogeneous equivalents. Finally, Section 6.7 will provide a brief conclusion of the current state of the art in this area, its scope, and its limitations.

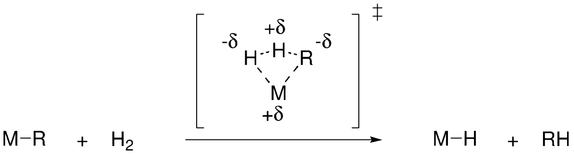
6.2
Mechanistic Considerations

For late transition metals, one of the key elementary steps is the oxidative addition of H_2 (see Chapter 1) [12, 13], and therefore the process requires transition-metal complexes which can readily undergo oxido-reduction processes (low oxidation state, d^n configuration). In contrast, most early transition-metal hydrogenation catalysts are based on d^0 metal complexes, having ligands, which often excludes the possibility to change the oxidation of the metal center. Therefore, the activation of H_2 and formation of the alkane must proceed through elementary steps other than oxidative addition and reductive elimination. Additionally, because these metal complexes have a d^0 configuration, they cannot generate stable π-alkene complexes. Three types of catalyst precursors can be used: L_nM-R, L_nM-H, or L_nM-X, the latter being used in combination with an alkylated agent or a metal hydride to generate the L_nM-R or the L_nM-H catalytically active species (Scheme 6.1).

Starting from L_nM-H, the first step is insertion of the alkene in the M–H bond to generate the corresponding alkyl complex [12]. Note that successive insertion and β-H transfer steps allow the starting alkene to be isomerized, and it can be



Scheme 6.1 Elementary steps for the hydrogenation of olefins with d^0 transition-metal complexes.



Scheme 6.2 σ-Bond metathesis transition state.

observed when hydrogenation is carried out under H_2-limiting conditions (low pressure, diffusion control experiments, poor stirring, etc.). The insertion step is probably preceded by a polarization of the alkene by the metal complex. While such types of intermediates have not been observed on d^0 L_nM-H complexes, they have been found on the corresponding d^0 L_nM-X complexes (X = Cl, OR, CH_2R) [14–28]. The following step is the direct hydrogenolysis of the metal–carbon bond by H_2 through a four-centered σ-bond metathesis transition state [29–34] which does not require a change of oxidation state, thereby regenerating the M–H species. While this step corresponds to an exchange of four atoms between two molecules, the geometry of this transition state does not have a kite-shape geometry, but rather a triangular shape, where three atoms are almost co-linear. Overall, it corresponds to a transfer of a proton between the H_2 molecule coordinated to the metal center and an alkyl ligand (Scheme 6.2). The reverse step, which is usually slightly endothermic for early transition metals, corresponds to a C–H activation on a metal–hydride. Successive C–H bond activation and hydrogenolysis will be responsible for H-scrambling, which can be possible under H_2-deprived conditions and can be observed by using D_2 in place of H_2.

Finally, the hydrogenation of other substrates such as imines involve similar elementary steps.

6.3
Group IV Metal Hydrogenation Catalysts

6.3.1
Hydrogenation of Alkenes

In Group IV metal complexes, metallocene complexes are the main catalyst precursors for hydrogenation. Two major catalytic systems have been used: 1) Cp_2MR_2 (R = H, Alkyl, Aryl); and 2) Cp_2MX_2 in combination with alkylating agent or an hydride (Table 6.1). The catalytic tests are typically run with 50 equiv. of substrate per metal, but in some cases turnover numbers (TONs) exceeding 1000 can be achieved [35].

The hydrogenation is usually limited to nonpolar alkenes (terminal and internal cyclic and acyclic alkenes), even though Ti systems have been used to hydrogenate alkenes containing ether and ester functionalities such as vinyl ethers or methyl oleate [42, 45, 59, 62].

Table 6.1 Catalytic systems based on Group IV dicyclopentadienyl complexes.

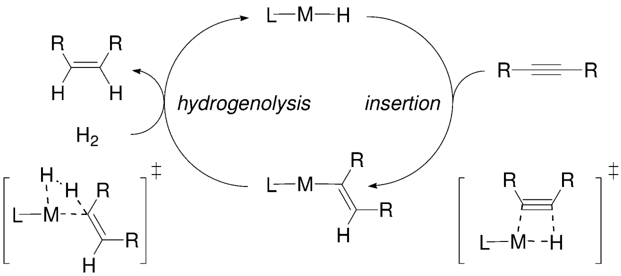
Ti Catalytic systems	Reference(s)	Zr and Hf catalytic systems	Reference(s)
$Ti(OiPr)_4/R_3Al$	5	$Cp_2ZrCl_2/BuLi$ (Cp_2Zr-olefin)	36, 37
$Ti(OiPr)_4/RLi$	5	Cp_2ZrCl_2/R_3Al	5
$Cp_2TiCl_2/BuLi$	6	$(RC_5H_4)_2ZrH_2$ R = H, Me, *i*Pr, Bn	7, 38, 39
$AnsaCp_2TiCl_2/EtLi$	40	$(RC_5H_4)_2HfH_2$ R = Me, *i*Pr, Bn	38, 39
$Cp_2TiCl_2/PhMgBr$	6	$[Cp^*(carboranyl)HfH]_2$	25
$Cp_2TiCl_2/RMgBr$	6, 41, 42		
Cp_2TiCl_2/R_2Mg	43		
$Cp_2Ti(CO)_2$	44		
Cp_2TiCl_2/Mg	45, 46		
$Cp_2Ti(CO)(Ph_2C_2)$	10, 11		
$CpCp'Ti(PMe_3)(Ph_2C_2)$ $Cp' = Cp^*$, MeC_5H_4	47		
$Cp_2Ti(Ph_2C_2)$	48, 49		
$Cp_2Ti(AlH_4)_2$	50–52		
Cp_2TiCl_2/NaH	35, 53–57		
Cp_2TiPh_2	9, 58		
$Cp_2TiR_2 + h\nu$ R = Me, CH_2Ph, Ph	59		
$Cp_2TiMe_2/RSiH_3$	60, 61		

In the Cp_2Ti system, Brintzinger et al. have shown that the angle between the two cyclopentadienyl ligands is important. For example, the activity in the hydrogenation of cyclohexene varies as follows: $[(CH_2)_2(C_5H_4)_2TiCl_2]$ (turnover frequency (TOF) = 266 000 mol H_2 cons. mol^{-1} h^{-1}) > $[(CH_2)_3(C_5H_4)_2TiCl_2]$ (TOF = 223 000 mol H_2 cons. mol^{-1} h^{-1}) > $[(CH_2)(C_5H_4)_2TiCl_2]$ (TOF = 118 000 mol H_2 cons. mol^{-1} h^{-1}) > $[(C_5H_5)_2TiCl_2]$ (TOF = 90 000 mol H_2 cons. mol^{-1} h^{-1}) [40].

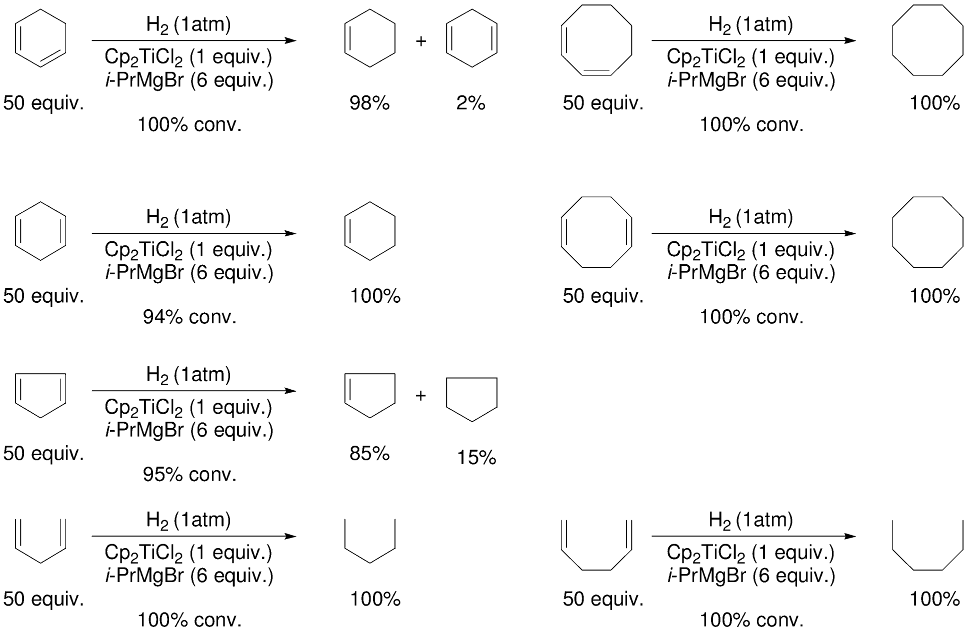
This field is still active today: numerous recent patents [46, 63–89] and several reports [90–92] have detailed the efficiency of such types of systems for the hydrogenation of unsaturated polymers resulting from the polymerization of dienes (butadiene, isoprene, 1,3-cyclohexadiene) or the co-polymerization of dienes and styrenes (block co-polymers of butadiene and styrene: SB, SBS, SBSB polymers).

6.3.2
Hydrogenation of Alkynes and Dienes

Alkynes are hydrogenated to *cis* olefins with the same catalytic systems, and subsequently undergo hydrogenation to yield the corresponding alkanes [7, 42, 45, 47, 49, 59, 93]. For example, Jordan et al. reported the selective hydrogenation of 3-hexyne into *cis* 3-hexene with a TOF of 25 h^{-1} [25], and *cis* 3-hexene is



Scheme 6.3



Scheme 6.4

subsequently hydrogenated at 12 h^{-1} (Scheme 6.3). Typically, the hydrogenation of alkynes is slower than that of alkenes (hydrogenolysis is probably rate determining in this case), but because alkynes react more rapidly with the metal hydride intermediate than alkenes do, they can be hydrogenated selectively, especially at low conversions (*vide infra* for a thorough study of reaction rates with lanthanide and actinide complexes).

Similarly, in some cases, dienes can be selectively hydrogenated into the corresponding alkenes, but they usually provide the corresponding alkane or a mixture of alkanes and alkenes [6, 45, 49, 59]. For example, the hydrogenation of 50 equiv. of 1,3- or 1,4-cyclohexadiene in the presence of [Cp_2TiCl_2]-*i*PrMgBr

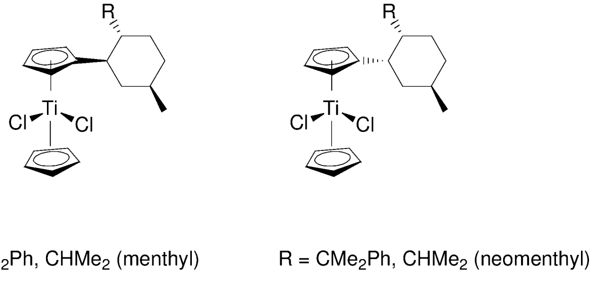
(1 : 6 ratio) gives selectively cyclohexene (> 98%; Scheme 6.4) [42]. On the other hand, using the same experimental procedure, cyclopentadiene is converted (95% conv.) into a mixture of cyclopentene (85%) and cyclopentane (15%), and 1,3- or 1,5-cyclooctadienes give only cyclooctane. Additionally, linear nonconjugated dienes such as 1,4-pentadiene and 1,5-hexadiene are directly converted into the corresponding alkanes.

6.3.3
Enantioselective Hydrogenation of Olefins

Kagan et al. were the first to report the corresponding enantioselective catalytic hydrogenation using chiral metallocene derivatives [94, 95]. By using menthyl- and neomenthyl-substituted cyclopentadienyl titanium derivatives in the presence of activators (Scheme 6.5) [96], these authors observed low ee-values (7–14.9%) for the catalytic hydrogenation of 2-phenyl-1-butene into 2-phenylbutane. In contrast, no enantiomeric excess was obtained with the corresponding zirconocene derivatives.

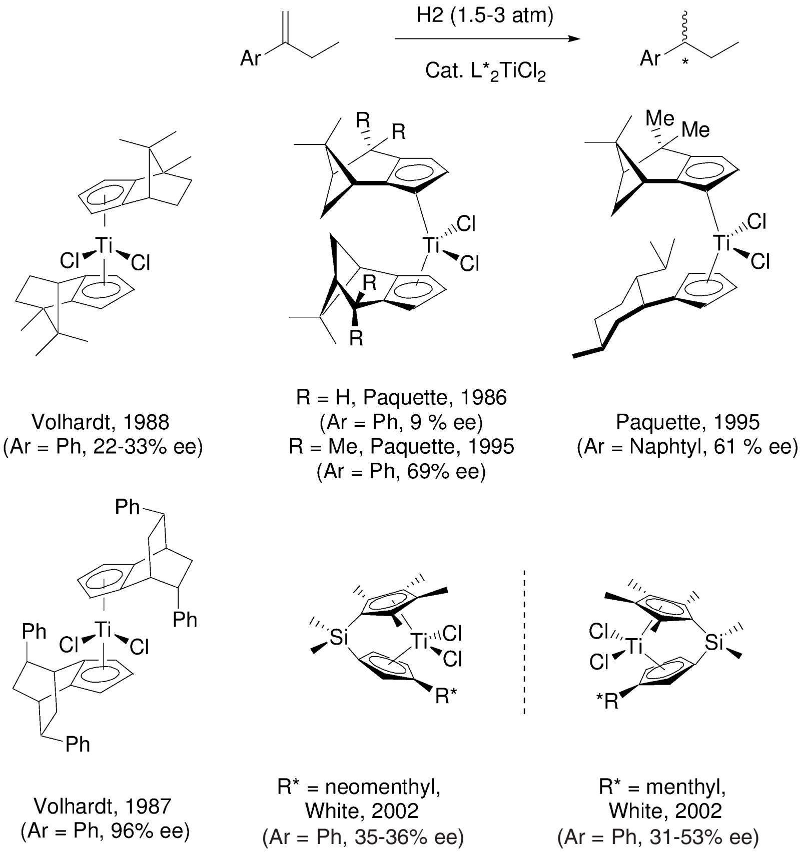
The use of other simple chiral cyclopentadienyl systems proved to be unsuccessful [39]. The design of better catalysts was directed first at preparing bulkier chiral cyclopentadienyl ligands. The chirality was introduced by preparing substituted cyclopentadienes derived from pinene and camphor (Scheme 6.6), but the ee-values were still low (< 35%) [97, 98]. The ee-values have been improved to 61–69% by introducing more steric bulk in the system (Scheme 6.6; R = H versus Me) [99]. The first high ee-values were obtained using a C_2 symmetric cyclopentadienyl ligand, for which both enantiomers are accessible in an enantiomerically pure form [100]. This system hydrogenates 2-phenyl-1-butene at –78 °C with enantiomeric excess up to 96%, albeit with a low TON (e.g., 10). It should be noted that *ansa* titanocene derivatives prepared by White et al. give low ee-values compared to the Group III and lanthanide derivatives developed by Marks et al. (*vide infra*, Section 6.4.1) [101].

The best results were obtained with the Brintzinger indenyl zirconene and titanocene derivatives [(EBTHI)MX_2], developed earlier for the stereocontrolled po-



R = CMe_2Ph, $CHMe_2$ (menthyl) R = CMe_2Ph, $CHMe_2$ (neomenthyl)

Scheme 6.5 First enantioselective hydrogenation by a Group IV metallocene catalysts.



Volhardt, 1988
(Ar = Ph, 22-33% ee)

R = H, Paquette, 1986
(Ar = Ph, 9 % ee)
R = Me, Paquette, 1995
(Ar = Ph, 69% ee)

Paquette, 1995
(Ar = Naphtyl, 61 % ee)

Volhardt, 1987
(Ar = Ph, 96% ee)

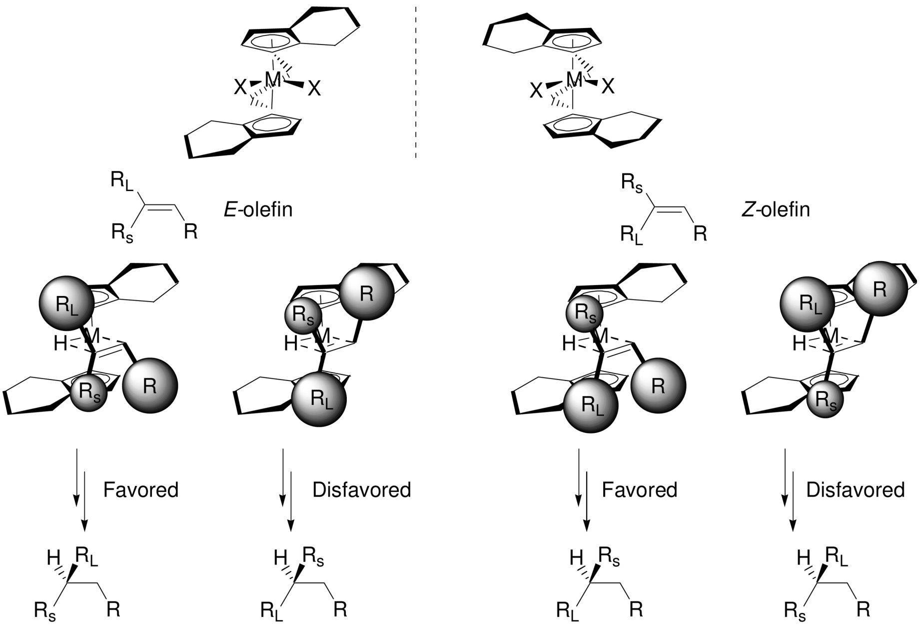
R* = neomenthyl,
White, 2002
(Ar = Ph, 35-36% ee)

R* = menthyl,
White, 2002
(Ar = Ph, 31-53% ee)

Scheme 6.6

lymerization of propene (Scheme 6.7) [102, 103]. When 2-phenyl-1-butene is used as the standard test substrates, low ee% are still obtained, despite high activity [104, 105]. However, tri-substituted [106] and tetra-substituted [107] alkenes are hydrogenated with very high enantioselectivities. In the case of tri-substituted alkenes [106], the catalytic system is generated by the treatment of [(EBTHI)TiX$_2$] (5 mol.%) (X$_2$=binolate) with BuLi in the presence of 2.5 equiv. PhSiH$_3$, which is used to stabilize the catalytic system. The active species is probably [(EBTHI) Ti^{III}H]. Acyclic and cyclic tri-substituted alkenes are hydrogenated in typically 70–90% yields, with enantiomeric excesses ranging from 83% to >99% (Table 6.2). The favored enantiomer is formed through the pathway in which the substituent R points as far away as possible from the indenyl ligand (Scheme 6.7).

When the hydrogenation of (*E*)-1,2-diphenylpropene is performed under D$_2$, 1,2-diphenylpropane is selectively deuterated in positions 1 and 2, which shows that no isomerization of the alken takes place under these conditions. Noteworthy, the reaction rate is highly dependent on the substrate, and typically



Scheme 6.7

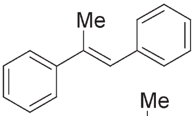
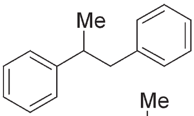
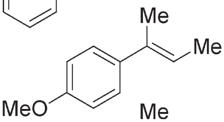
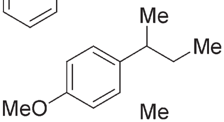
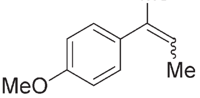
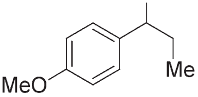
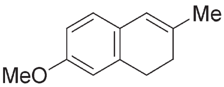
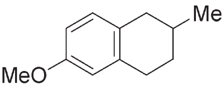
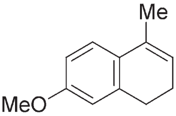
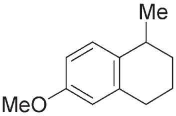
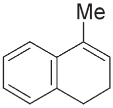
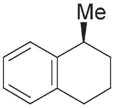
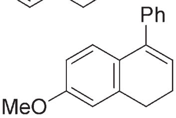
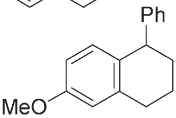
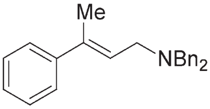
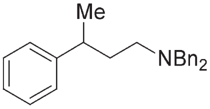
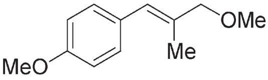
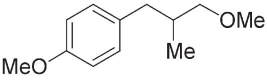
Z-alkenes are reduced much more slowly than are E-isomers. For instance, the (E)-(1,2)-diphenylpropene is reduced in 9 h at 65 °C under 5.3 bar, while the Z-isomer reaches only 3% conversion after 48 h at 70 °C under 133 bar of H_2. These data are fully consistent with the model proposed to predict the stereochemical outcome of the reaction (see Scheme 6.7), which shows that, for the Z-isomers, the R_L substituent points towards the indenyl ligands in the favored pathway, thus decreasing the reaction rate.

For tetra-substituted alkenes [107], it was necessary to rely on the more reactive cationic Zr equivalent generated from [(EBTHI)ZrMe$_2$] and either methylaluminoxane or $[PhMe_2NH]^+[Co(C_2B_9H_{11})_2]^-$ developed earlier by Waymouth et al. [104]. Using H_2 pressure ranging between 5 and 133 bar, it was possible to obtain the hydrogenated products with 80–98% ee in most cases (Table 6.3).

6.3.4
Enantioselective Hydrogenation of Imines and Enanimes

One of the best enantioselective olefin hydrogenation catalysts, (EBTHI)TiH, was originally developed for the enantioselective hydrogenation of imines [108, 109]. The catalytic system is generated by the treatment of [(EBTHI)TiX$_2$] (5 mol%, X = binolate) with BuLi in the presence of 2.5 equiv. $PhSiH_3$, and the hydrogenation is typically performed with 5 mol% of catalyst at 65 °C under 133 bar H_2. High pressure is usually required to obtain high ee-values with this

Table 6.2 Enantioselective hydrogenation of tri-substituted alkenes catalyzed by [(*S,S,S*)-(EBTHI)TiX_2].[a)]

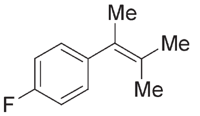
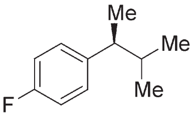
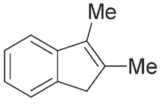
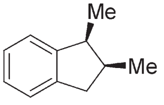
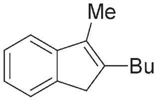
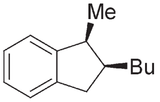
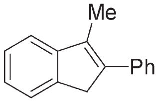
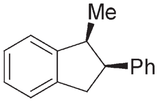
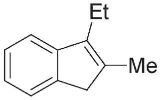
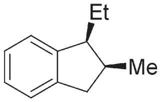
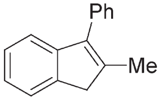
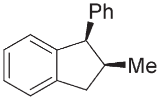
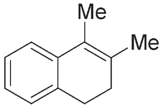
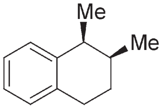
Substrate	Product[b)]	Time [h]	Yield [%]	ee [%]
		48	91	99
		48	79	95
		146	80	31
		44	77	92
		132	70	93
		184	70	83
		169	87	83
		43	75	95
		48	80–86	93–94

a) Reaction conditions: 65 °C, 133 bar H_2 in THF with 5 mol% [(*S,S,S*)-(EBTHI)TiX_2].

b) No absolute configuration given when unknown.

system. Acyclic benzyl protected imines, used as mixture of diastereomers, are converted to their corresponding amines in good yields (66–93%) and moderate enantioselectivities (58–85% ee). Better results are obtained for cyclic imines, which are hydrogenated in 97–99% ee (Tables 6.4 and 6.5). The absolute configuration of the amine can be predicted using the following model and rules

Table 6.3 Enantioselective hydrogenation of tetra-substituted alkenes catalyzed by [(*S*,*S*)-(EBTHI)$ZrMe_2$]/[$PhMe_2NH^+B(C_6F_5)_4^-$].[a]

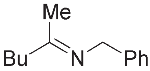
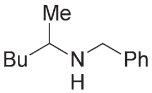
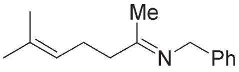
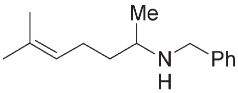
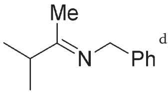
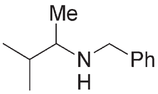
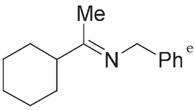
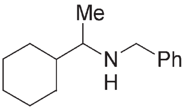
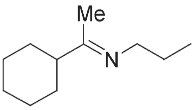
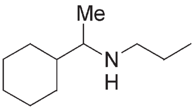
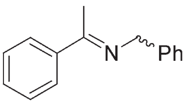
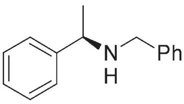
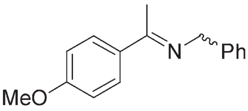
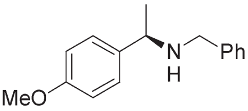
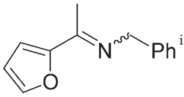
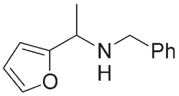
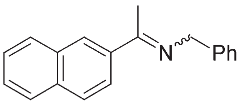
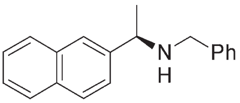
Substrate	Product	P_{H2} [bar] (% cat)	Yield [%]	ee [%] (*cis*:*trans*)
		5.3 (8) 110 (8)	79 77	84 96
		5.3 (5) 110 (8)	76 87	86 (95:5) 93 (>99:1)
		5.3 (8)	96	92 (99:1)
		5.3 (5) 67 (8)	34 89	97 98 (>99:1)
		5.3 (5) 110 (8)	57 95	5 (9:1) 52 (95:5)
		5.3 (5) 133 (8)	44 94	29 (>99:1) 78 (>99:1)
		133 (5)	91	92 (>99:1)

[a] Reaction conditions: 25 °C, 5.3–133 bar H_2 with 5–8 mol% [(*S*,*S*,*S*)-(EBTHI)$ZrMe_2$].

(Scheme 6.8): the substituent (R) on the nitrogen should point as far away as possible from the indenyl ligand. This model predicts that hydrogenation of *syn*- and *anti*-imines give rise to enantiomers of opposite stereochemistry as observed experimentally. The model also predicts that if one takes into consideration the influence of R_S and R_L substituents, the energy difference of the two possible pathways should be lower for the *syn* imines, giving rise to lower enantioselectivities.

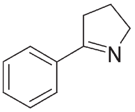
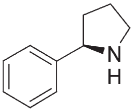
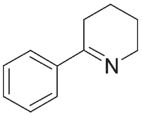
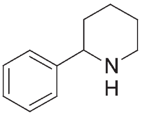
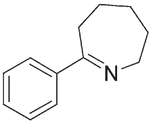
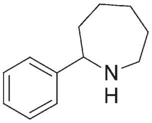
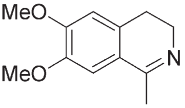
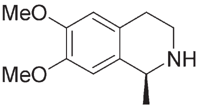
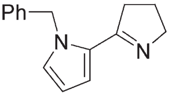
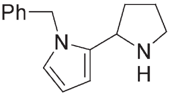
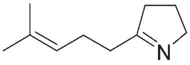
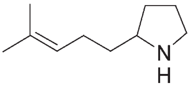
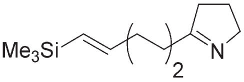
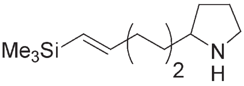
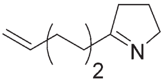
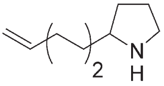
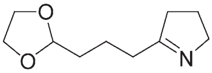
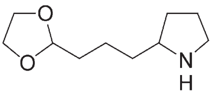
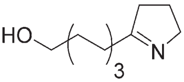
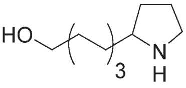
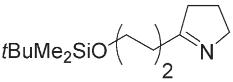
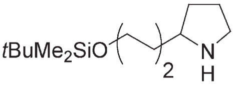
As illustrated in the hydrogenation of cyclic imines, the system is compatible with a wide range of functional groups, such as olefins, protected or unpro-

Table 6.4 Enantioselective hydrogenation of imines catalyzed by [(*R*,*R*,*R*)-(EBTHI)TiX_2] [108, 109].[a]

Substrate	Product[k]	Yield [%][a]	ee [%]
 b)		68	56
 c)		64	62
 d)		66	75
 e)		93	76
 f)		70	79
 g)		93	85
 h)		86	86
 i)		70	83
 j)		82	70

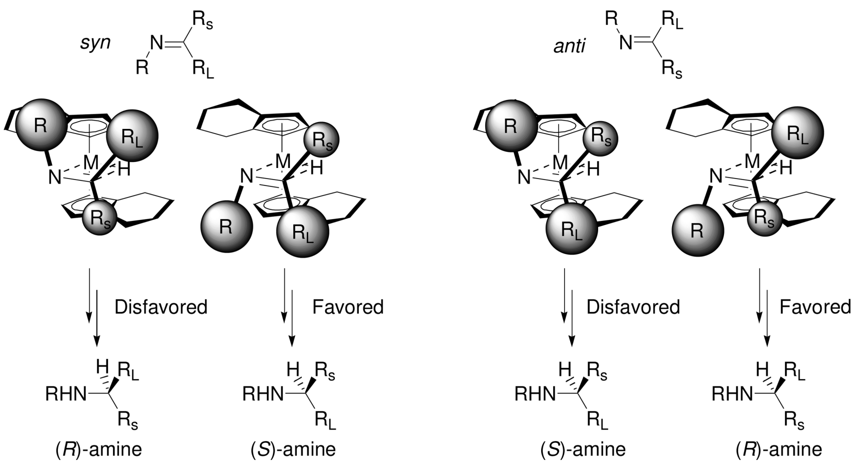
a) Reaction conditions: 65 °C, 133 bar H_2 in THF with 5 mol.% [(*R*,*R*,*R*)-(EBTHI)TiX_2].
b) *anti/syn* = 3.3.
c) *anti/syn* = 3.
d) *anti/syn* = 13.
e) *anti/syn* = 9.
f) *anti/syn* = 17.
g) *anti/syn* = 17.
h) *anti/syn* = 17.
i) *anti/syn* = 10.
j) *anti/syn* = 3.3.
k) No absolute configuration given when unknown.

Table 6.5 Enantioselective hydrogenation of cyclic imines catalyzed by [(*R*,*R*,*R*)-(EBTHI)TiX_2].

Substrate	Product[b]	Conditions [P/T/t][a]	Yield [%]	ee [%]
		5.3/65/42	83	99
		33/65/24	70	97
		5.3/65/30	74	97
		5.3/65/50	79–82	98
		5.3/65/6	72	99
		5.3/50/23	79	99
		5.3/50/27	73	99
		5.3/45/23	72	99
		5.3/65/16	82	99
		5.3/65/8	84	99
		5.3/65/10	72	99

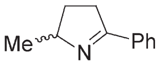
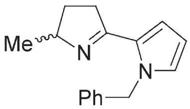
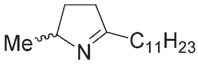
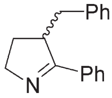
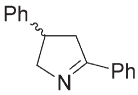
a) P=pressure (bar); T=temperature (°C); t=time (h).

b) No absolute configuration given when unknown.



Scheme 6.8

Table 6.6 Kinetic resolution of di-substituted 1-pyrrolines catalyzed by [(*R,R,R*)-(EBTHI)TiX_2] [111].[a]

Substrate	Yield [% recovered S]	ee [%]	Yield [% product]	ee [%]
	37	99	34	99
	42	96	44	98
	43	98	41	98
	41	>95	41	>95
	–	75	42	>95
	33	49	44	99

a) 5 mol% cat., THF, 65–75 °C, 5.3 bar H_2, reaction run to 50% completion.

Table 6.7 Enantioselective hydrogenation of enamines catalyzed by [(*R*,*R*,*R*)-(EBTHI)TiX_2] [112].[a)]

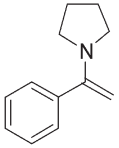
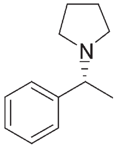
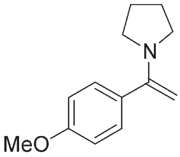
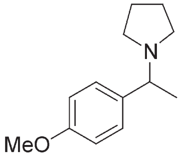
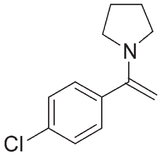
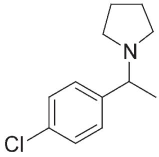
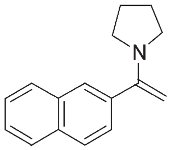
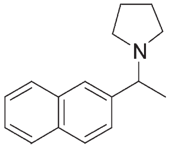
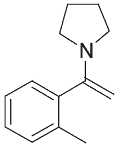
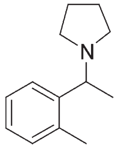
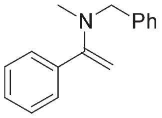
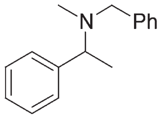
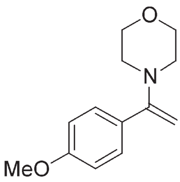
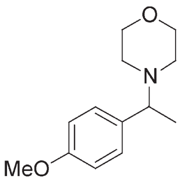
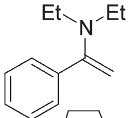
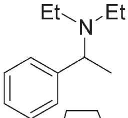
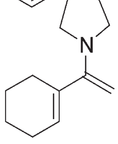
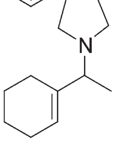
Substrate	**Product**[b)]	**Pressure [bar]**	**Yield [%]**[a)]	**ee [%]**
		1	75	92
		1	72	92
		1	89	89
		1	77	96
		5.3	87	98
		5.3	83	96
		5.3	88	91

Table 6.7 (contributed)

Substrate	Product	Pressure [bar]	Yield [%][a]	ee [%]
		5.3	72	99
		5.3	72	95

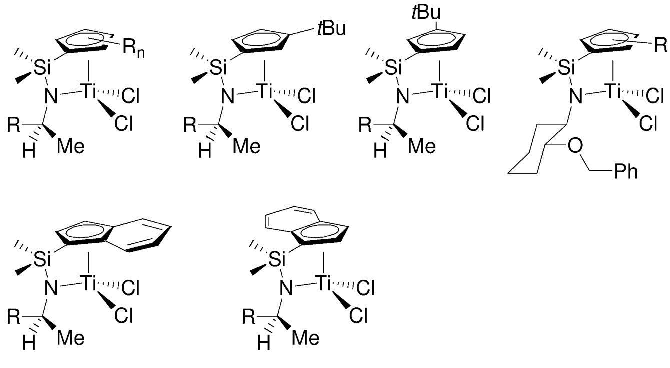
a) Using 5 mol% of catalyst.
b) No absolute configuration given when unknown.

tected alcohols, acetals and aromatic groups [109, 110]. The same model can be used to predict the absolute stereochemistry of the amine product – that is, formation of the *S*-amine from the (*R*,*R*,*R*)-catalyst (Scheme 6.8).

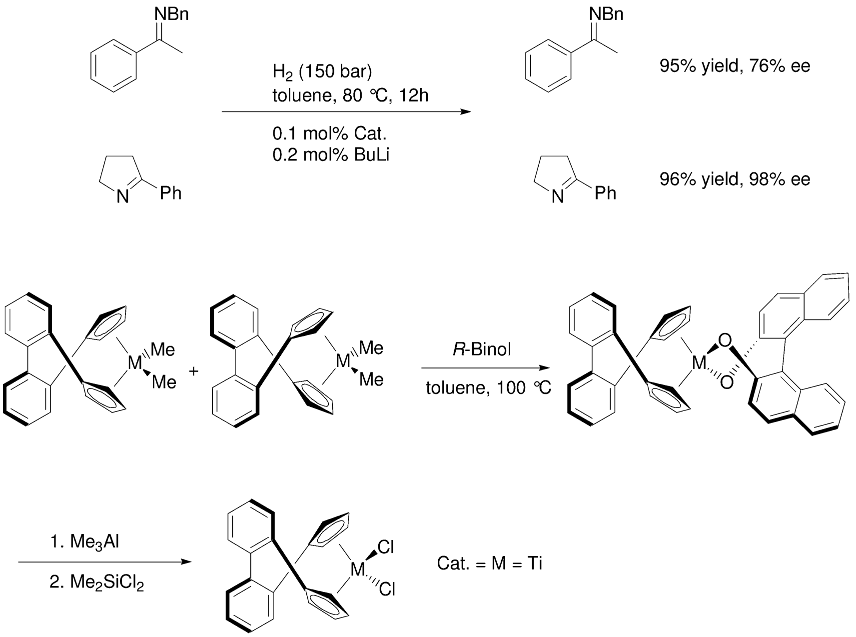
This catalytic system can be used for the kinetic resolution of di-substituted 1-pyrrolines, for which high ee-values are achieved for both the amine and the recovered materials, especially when they are substituted in positions 2 and 5 (Table 6.6) [111]. Moreover, it should be noted that acyclic enamines are converted with high ee-values into their corresponding amines (89–98% ee; Table 6.7), which is in sharp contrast to what is obtained for acyclic imines (*vide supra*) [112].

Hydrogenation is not limited to the use of (EBTHI)MX_2-type catalysts. In polymerization, linked amido-cyclopentadienyl ligands have emerged as very important systems, and the corresponding chiral derivatives have been prepared (Scheme 6.9) [113–116]. Nonetheless, whilst high TON can be achieved (500–1000), the ee-values are quite low (< 25%).

Finally, Brintzinger et al. have reported a different type of *ansa*-metallocene, which can be readily prepared enantiomerically pure, and which catalyzes the



Scheme 6.9



Scheme 6.10

hydrogenation of imines very efficiently (TON of 1000) with enantiomeric excesses comparable to those reported with (EBTHI)MX_2 [117, 118]. The synthesis of the enantiomerically pure catalyst is noteworthy because it relies on the preparation of a racemate. After reaction of this racemate with pure (*R*)-binol, two diastereomers are formed, but after heating at 100 °C a single diastereomer is obtained. This single diastereomer is converted into the enantiomerically pure dichloro complex by treatment of the binolate complex with Me_3Al and then Me_3SiCl (Scheme 6.10).

6.4
Hydrogenation Catalysts Based on Group III, Lanthanide, and Actinide Complexes

6.4.1
Hydrogenation of Alkenes with Group III Metal and Lanthanide Complexes

The hydrogenation of unfunctionalized alkenes is readily performed by Group III and lanthanide cyclopentadienyl hydride derivatives, one key feature being the high TOFs of these systems (up to 120 000 h^{-1} for hydrogenations catalyzed by Lu, Tables 6.8 and 6.9) [119, 120]. The reaction rate depends heavily on the metal and the ligands. It is inversely proportional to the metal radius (Lu > Sm > Nd > La), and it is faster for the Cp_2^*M derivatives than for the *ansa* di-

Table 6.8 Rate constants for the catalytic hydrogenation of alkenes catalyzed by Group III and lanthanide complexes.[a]

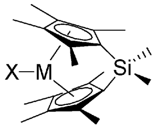
	$[Cp^*_2LaH]_2$	$[Cp^*_2NdH]_2$	$[Cp^*_2SmH]_2$	$[Cp^*_2LuH]_2$
1-Hexene	6.2	21.6	23.8	34.5
(*E*) 2-Hexene	1.7	7.1	7.9	9.0
(*E*) 3-Hexene	7.3	33.4	51	240
(*Z*) 2-Hexene	–	6.6[b]	–	13.4[c]
(*Z*) 3-Hexene	–	2.2[b]	3.8[b]	8.1[c]
Cyclohexene	0.015[b]	0.014[b]	0.005[b]	0.023[c]

a) Based on $r = k[M][H_2]$ unless otherwise specified, in units of $atm^{-1}\ s^{-1}$ (multiply by 224 to convert to $M^{-1}\ s^{-1}$).
b) $r = k[M]^{1/2}[alkene]$, in units of $M^{-1/2}\ s^{-1}$.
c) $r = k[M][alkene]$, in units of $M^{-1}\ s^{-1}$.

Table 6.9 Hydrogenation of alkenes catalyzed by Group III and lanthanide complexes.

	$[Me_2SiCp''_2NdH]_n$	$[Me_2SiCp''_2SmH]_n$	$[Me_2SiCp''_2LuH]_n$
1-Hexene	21.6[a]	23.8[a]	34.5[a]
Cyclohexene	0.014[b]	0.005[b]	0.023[b]

a) Based on $r = k[M][H_2]$ unless otherwise specified, in units of $atm^{-1}\ s^{-1}$ (multiply by 224 to convert to $M^{-1}\ s^{-1}$).
b) $r = k[M]^{1/2}[alkene]$, in units of $M^{-1/2}\ s^{-1}$.

$Me_2SiCp''_2M\text{-}X =$ 

cyclopentadienyl derivatives, $Me_2SiCp''_2MR$ (Tables 6.8 and 6.9). Kinetic studies show that the rate-determining step depends on the alkene. In terms of elementary steps, these hydrides are dimers, and need to dissociate (Eq. (1)) prior to insertion of the alkenes (Eq. (2)). Hydrogenolysis subsequently liberates the alkane and re-forms the hydride (Eq. (3)).

$$(LMH)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2\ LMH \tag{1}$$

$$LM\text{-}H + alkene \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} LM\text{-}R \tag{2}$$

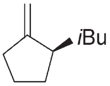
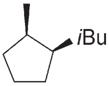
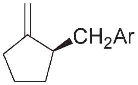
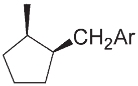
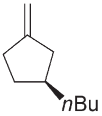
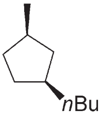
$$LM\text{-}R + H_2 \xrightarrow{k_3} LM\text{-}H + RH \tag{3}$$

For 1-hexene, the rate can be expressed as: $r = k[L_nM][H_2]$, which is consistent with hydrogenolysis being rate-determining (Eq. (3)). In contrast, for bulkier alkenes the rate law is as follows: $k[L_nM]^{1/2}[olefin]$, which is consistent with insertion being rate-determining (Eq. (2); cyclohexene and internal *cis* acyclic alkenes). In the case of Lu, the dimer readily dissociates, and therefore the rate law is independent of the mechanism and the substrate, as observed experimentally $\{k[L_nM][\text{alkene}]\}$. Moreover, independently of the catalyst, hydrogenation of 1-hexene under D_2 generates 1,2-d_2-hexane, along with small amount of d_1-2-hexene, suggesting that β-H elimination can be competitive (the reverse step of insertion, Eq. (2)). In the case of cyclohexene however, Lu-based catalysts generate large quantities of various polydeuterated cyclohexane, suggesting that successive β-H elimination–insertion processes occur. Finally, when operating under deprived D_2 conditions, the amount of polydeuterated compounds increases, suggesting that the β-H elimination process becomes competitive with hydrogenolysis.

It should be noted that, in the case of $[(R)(Me)SiCp''_2YR]$, the TOF of the hydrogenation of 1-hexene decreases dramatically, from 11 100 h^{-1} (R = Me) to 200 h^{-1} when an ether functional group is bound on the *ansa* bridge ($R = (CH_2)_5OMe$), which shows the sensitivity of Group III metal complexes towards polar functionalities [121].

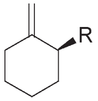
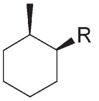
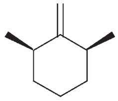
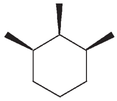
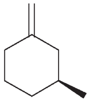
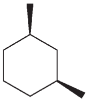
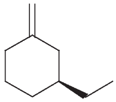
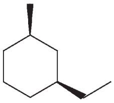
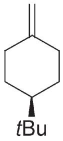
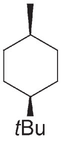
These types of catalysts, $[Cp^*_2LnCH(SiMe_3)_2]$, are also used to hydrogenate substituted methylenecyclopentenes and cyclohexenes in good to very good diastereoselectivities, especially when the substituent is in the α-position to the alkene (Tables 6.10 and 6.11). However, the presence of functional groups such as amine or ether is detrimental to catalysis.

Table 6.10 Hydrogenation of substituted methylenecyclopentene catalyzed by $Cp^*_2LnCH(SiMe_3)_2$ [122].

Substrate	Catalyst	SCR (temp., °C)	Product	Yield [%] (dr, %)
	Ln = Sm	10 (25)		84 (>99/1)
 Ar=2-Cl-C_6H_4	Ln = Sm	10 (25)	 Ar=2-Cl-C_6H_4	32 (>99/1)
	Ln = Sm	33 (0)		32 (60/40)

dr = diastereomeric ratio; SCR = substrate : catalyst ratio.

Table 6.11 Hydrogenation of mono-substituted methylenecyclohexene catalyzed by Cp$^*_2$LnCH(SiMe$_3$)$_2$ [122].

Substrate	Catalyst	SCR (temp., °C)	Product	Yield [%] (dr, %)
				
R = Me	Ln = Sm	33 (–20)	R = Me	77 (93/7)
R = *i*Bu	Ln = Sm	33 (–20)	R = *i*Bu	90 (95/5)
R = *t*Bu	Ln = Sm	20 (25)	R = *t*Bu	95 (>99/1)
R = CH$_2$Ph	Ln = Sm	33 (–20)	R = CH$_2$Ph	95 (93/7)
R = (CH$_2$)$_3$NMe$_2$	Ln = Sm	33 (50)	(CH$_2$)$_3$NMe$_2$	76 (91/9)
R = OMe	Ln = Sm	20 (70)	R = OMe	0 (–)
	Ln = Sm	20 (70)		0 (–)
	Ln = Yb	33 (–20)		73 (61/39)
	Ln = Yb	33 (–20)		79 (73/27)
	Ln = Yb	33 (–20)		73 (77/23)

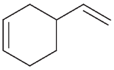
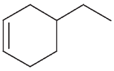
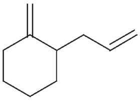
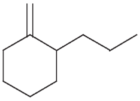
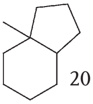
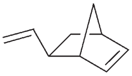
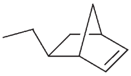
dr = diastereomeric ratio; SCR = substrate : catalyst ratio.

6.4.2

Hydrogenation of Dienes and Alkynes with Group III and Lanthanide Complexes

It is possible to selectively hydrogenate dienes into monoolefins when there is a large difference in reactivity between the two olefins. For example, vinylcyclohexene and 4-vinylnorbornene undergo a selective hydrogenation of the acyclic olefins in the presence of catalytic amount of [Cp$^*_2$YMe] (Table 6.12). Note that α-allylmethylenecyclohexene gives a mixture of α-propylmethylenecyclohexene and the reductive cyclization product, which shows that the intramolecular insertion of a second alkene can be competitive with hydrogenolysis (Table 6.12).

Table 6.12 Hydrogenation of dienes catalyzed by Cp^*_2YMe [123].

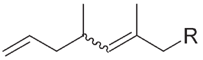
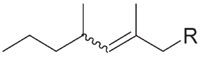
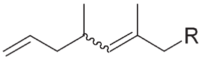
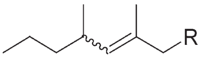
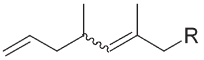
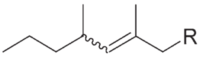
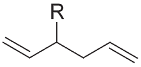
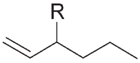
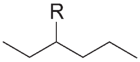
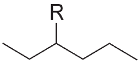
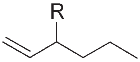
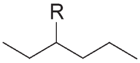
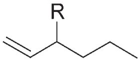
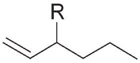
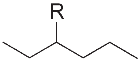
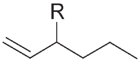
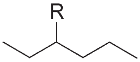
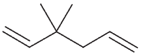
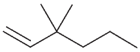
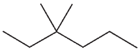
Substrate	SCR (time, h)	Product	Yield [%]	Byproduct [%]
	100 (2)		70	–
	25 (1)		67	 20
	100 (1)		72	–

SCR = substrate : catalyst ratio.

Similarly, when a diene is constituted of both terminal and tri-substituted olefins, the terminal olefin is selectively hydrogenated. Note that ether substituted systems could be hydrogenated in these cases. Moreover, for 3-substituted 1,5-hexadienes, the less-hindered olefins can be selectively hydrogenated into the corresponding 2-substituted 1-hexene, especially when the substituent in position 2 is large (Table 6.13). However, when no substituent is present on the alkyl chain, 1,5-dienes undergo reductive cyclization in the presence of *ansa* Cp derivatives of Y and Lu to give the corresponding cyclic alkanes in quantitative yields (Table 6.14) [124]. Note that no conversion is observed when an ether group is present in the starting material.

An original report by Evans reports the catalytic hydrogenation of 3-hexyne and diphenylacetylene into the corresponding alkanes by generating *in situ* [Cp^*_2SmH] from [Cp^*_2Sm] [120, 125]. Later, Evans showed that *cis*-3-hexene was formed selectively at the beginning of the reaction [126]. In a comprehensive study, Marks et al. have shown that the reaction rate of hydrogenation of alkynes, namely 3-hexyne, is slower (Table 6.15) than that of olefins (*vide supra*) [120, 125]. The rate law is as follows: $r = k[L_nMH][H_2]$, and it is fully consistent with hydrogenolysis being rate-determining. Since the rate of hydrogenation is faster for *cis* alkenes in the absence of alkynes, it shows that alkynes react faster with the hydride than alkenes.

Table 6.13 Hydrogenation of acyclic dienes catalyzed by Cp^*_2YMe [123].

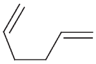
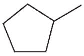
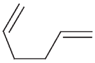
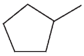
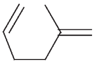
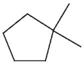
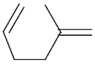
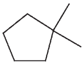
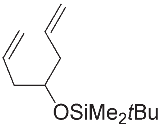
Substrate	SCR (time, h)	Product	Yield [%]	Byproduct [%]
 R = $OSiMe_2tBu$	50 (1)	 R = $OSiMe_2tBu$	98	–
 R = OMe	50 (2)	 R = OMe	74	–
 R = OCH_2Ph	50 (2)	 R = OCH_2Ph	99	–
 R = $OSiMe_2tBu$	33 (1)		85	10 
R = $OSiMe_2tBu$	25 (1.5)		99	–
R = Ph	33 (1)		64	23 
R = Ph	25 (1.5)		92	–
*i*Pr	33 (1.1)		70	16 
R = $OCPh_3$	33 (1)		96	1 
	33 (1)		42	20 

SCR = substrate : catalyst ratio.

6.4.3
Hydrogenation of Imines with Group III and Lanthanide Complexes

The hydrogenation of imines is typically carried out with 1 mol% of the lanthanocene catalyst under an H_2 pressure of 13 bar at 90 °C [127]. The best catalysts are based on Sm having Cp* ligands, the *ansa* systems being unreactive. The rate and the total conversion are improved by the addition of $PhSiH_3$, probably because it stabilizes the system (Table 6.16), and both are very sensitive to the

Table 6.14 Reductive cyclization of dienes catalyzed by $Me_2SiCp^*CpLnCH(SiMe_3)_2$ [124].

Substrate	Ln	SCR (P_{H_2}, atm)	Product	Yield [%]
	Y	200 (1)		100
	Lu	200 (1)		100
	Y	200 (1)		100
	Lu	200 (1)		100
	Y Lu	200 (1) 200 (1)	– –	0 0

SCR = substrate : catalyst ratio.

Table 6.15 Rate constants for the catalytic hydrogenation of olefins catalyzed by Group III and lanthanide complexes. [a)]

	$[Cp^*_2LaH]_2$	$[Cp^*_2NdH]_2$	$[Cp^*_2SmH]_2$	$[Cp^*_2LuH]_2$
3-Hexyne	0.2	0.46	0.82	2.3

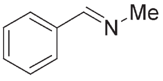
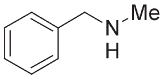
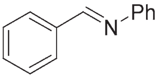
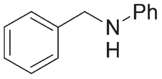
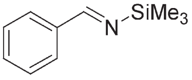
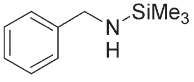
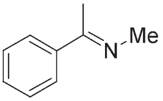
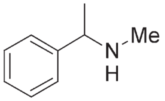
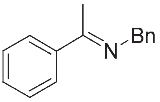
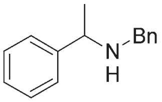
a) Based on $r = k[M][H_2]$, in units of $bar^{-1}\,s^{-1}$ (multiply by 224 to convert to $M^{-1}\,s^{-1}$).

substituents on the imine. Acyclic imines are fully converted into the corresponding amines under these conditions, while the cyclic ones do not react. Additionally, di-substituted imines at the carbon atom are less reactive than their mono-substituted counterparts. Finally, substitution at the nitrogen atom is also important, with their reactivity varying as follows: =N-Alkyl > =N-Aryl > =N-SiR_3.

6.4.4
Hydrogenation of Alkenes with Actinide Complexes

Biscyclopentadienyl actinide complexes catalyze the hydrogenation of alkenes. In the hydrogenation of 1-hexene, $[Cp^*_2UH_2]$ is more efficient (higher TOF) than the corresponding Th complex, and up to 812 TON can be achieved with the U complex (Table 6.17) [128]. Using cationic Th complexes improves the rate by an order of magnitude [129], but the strongest positive effect is obtained when Cp* ligands are replaced by a Si-tethered *ansa* dicyclopentadienyl ligand,

Table 6.16 Hydrogenation of imines catalyzed by Group III and lanthanide complexes.

Substrate	**Product**	**Catalyst**	**Conditions [R/P/T/t]**[a]	**Conv. [%]**[a]	**Rate [h^{-1}]**
		Cp$^*_2$SmR	100/13/90/92	83	1.0
		Cp$^*_2$SmR	100/13/50/122	57	0.5
		Cp$^*_2$SmR	100/14/25/51	4	0.04
		Cp$^*_2$SmR + PhSiH$_3$	100/13/90/44	98	2.2
		Cp$^*_2$LaR	100/10/25/50	11	0.05
		Cp$^*_2$LuR	100/13/25/90	51	0.60
		Cp$^*_2$SmR	100/13/90/120	16	0.10
		Cp$^*_2$SmR + PhSiH$_3$	100/13/90/120	10	–
		Cp$^*_2$SmR	100/13/90/58	21	0.40
		Cp$^*_2$SmR	100/13/90/144	26	0.20
		Cp$^*_2$SmR + PhSiH$_3$	100/13/90/134	98	0.70

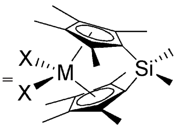
a) SCR = substrate : catalyst ratio; P = pressure (bar); T = temperature (°C); t = time (h).

Table 6.17 Hydrogenation of alkenes catalyzed by actinide complexes.

Catalyst	**Substrate**	**SCR (P_{H_2})**[a]	**TOF [h^{-1}]**
[Cp$^*_2$ThH$_2$]	1-hexene	14 (1)	0.5
[Cp$^*_2$UH$_2$]	1-hexene	14 (1)	70
[Cp$^*_2$ThMe$^+$B(C$_6$F$_5$)$_4^-$]	1-hexene	330 (1)	5.2
[Cp$^*_2$ThMe$_2$]/ {*t*BuCH[B(C$_6$F$_5$)$_2$]$_2$HNBu$_3$}	1-hexene	330 (1)	6
[Me$_2$SiCp$''_2$ThH$_2$]	1-hexene	– (1)	610
[Cp$^*_2$ThH$_2$]	*E* 2-hexene	14 (1)	0.086
[Me$_2$SiCp$''_2$ThH$_2$]	*E* 2-hexene	– (1)	2.45

a) SCR = substrate : catalyst ratio; P_{H_2} = H$_2$ pressure (bar).

Me$_2$SiCp$''_2$MX$_2$ =

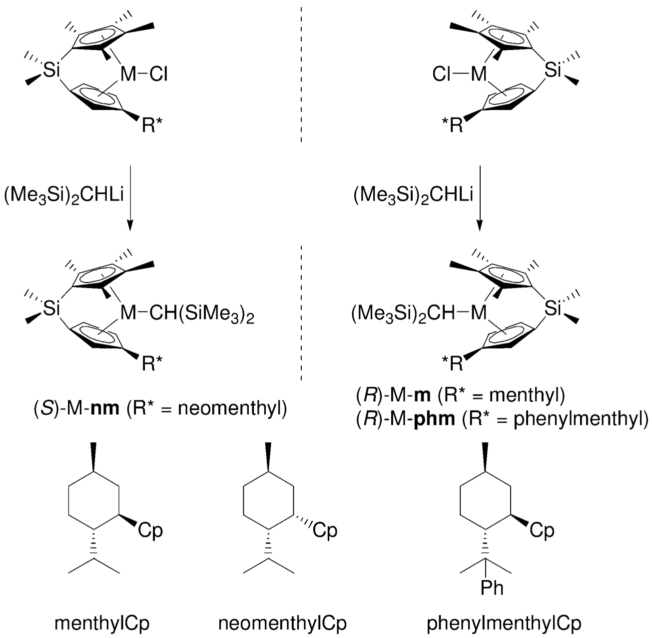


for which TOFs up to 610 h^{-1} are obtained [130]. For all these systems, the rate of hydrogenation decreases sharply (10- to 100-fold) in going from 1-hexene to *trans*-2-hexene, showing that the insertion step is highly sensitive to the substitution on the olefin [128, 130].

6.4.5
Enantiomeric Hydrogenation of Alkenes

Enantiomeric hydrogenation of alkenes can be performed with chiral lanthanide complexes. The design of an enantiomerically pure catalyst has been based on the introduction of the chirality (*R**) through the preparation of menthyl- or neomenthyl-substituted cyclopentadienyl derivatives [$R^*CpSiMe_2(C_5Me_4)$] (Scheme 6.11) [131]. Formation of the *ansa* dichloro lanthanide complexes generates two diastereomers, usually with a high level of diastereoselection, and these can be separated by simple crystallization. Access to two enantiomorphous families as pure diastereomers is possible by using the menthyl and neomenthyl derivatives, respectively [121, 124, 132]. The catalyst precursor is then formed by a simple alkylation step, which takes place with retention of configuration.

In the Sm series, the two diastereomers of one enantiomorphous family give rise to very different ee-values (Table 6.18). For example, the hydrogenation of



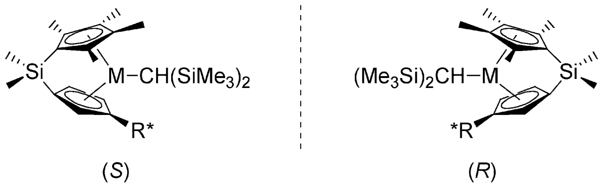
Scheme 6.11 Enantioselective hydrogenation Group III and lanthanide metallocene catalysts.

Table 6.18 Enantioselective hydrogenation of alkenes catalyzed by Group III and lanthanide complexes.

Catalyst[a)]	Substrate	SCR (P_{H2})[b)]	Temp. [°C]	ee [%]
(*R*)-[$\mathrm{Me_2SiCp'Cp^{nm}SmH}$]$_2$	2-phenyl-1-butene	100–500 (1)	25	71 (–)
(*S*)-[$\mathrm{Me_2SiCp'Cp^{nm}SmH}$]$_2$	2-phenyl-1-butene	100–500 (1)	25	19 (+)
(*R*)-[$\mathrm{Me_2SiCp'Cp^{nm}SmH}$]$_2$	Styrene[c)]	100 (1)	25	43 (–)
(*R*)-[$\mathrm{Me_2SiCp'Cp^{nm}SmR}$]	2-phenyl-1-butene	100–1000 (1)	25	71 (–)
(*S*)-[$\mathrm{Me_2SiCp'Cp^{nm}SmR}$]	2-phenyl-1-butene	100–1000 (1)	25	19 (+)
(*R*)-[$\mathrm{Me_2SiCp'Cp^{m}SmR}$]	2-phenyl-1-butene	100–1000 (1)	25	8 (–)
(*S*)-[$\mathrm{Me_2SiCp'Cp^{m}SmR}$]	2-phenyl-1-butene	100–1000 (1)	25	19 (–)
(*R*)-[$\mathrm{Me_2SiCp'Cp^{m}SmR}$]	2-phenyl-1-butene	100–1000 (1)	25	43 (–)
(*S*)-[$\mathrm{Me_2SiCp'Cp^{m}YR}$]	2-phenyl-1-butene	100–1000 (1)	25	3 (–)
(*S*)-[$\mathrm{Me_2SiCp'Cp^{m}YR}$]	2-phenyl-1-butene	100–1000 (1)	25	3 (–)

a) nm = neomenthyl, M-**nm**; m = menthyl, M-**m**.

$\mathrm{Me_2SiCp'Cp^{x}M\text{-}R}$ =



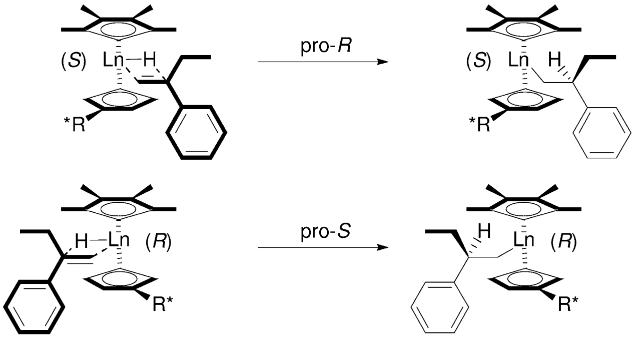
M-**m** (R* = menthyl)
M-**phm** (R* = phenylmenthyl)
M-**nm** (R* = neomenthyl)

b) SCR = substrate : catalyst ratio; $P_{H2} = H_2$ pressure (bar).

c) Using D_2 instead of H_2.

2-phenyl-1-butene at 25 °C gives (*R*)-(–)-2-phenylbutane in 70% ee with the (*R*)-Sm-**nm**, while it is (*S*)-(+)-2-phenylbutane in 19% ee with the (*S*)-Sm-**nm**. When using the other enantiomorphous family, opposite enantioselection is usually observed: the (*S*)-Sm-**m** gives the (*R*)-(–)-2-phenylbutane in 8% ee under the same conditions. Moreover, when a 70/30 mixture of the (*S*) and (*R*)-Sm-**m** is used, 64% ee in (*S*)-(+)-2-phenylbutane is observed. Reducing the temperature of the reaction to –78 °C increases the level of enantioselection to 96% e.e. Finally, using D_2 instead of H_2 provides exclusively the corresponding deuterated product, arising from a *cis*-addition. The best model to explain the observed stereochemistry corresponds to a frontal approach of the alkene towards the metal center (Scheme 6.12).

Kinetic studies show that insertion (the enantioselection step) is very rapid, and that the rate-determining step is the hydrogenolysis of the M–C bond. Nonetheless, under H_2-starving conditions, there is evidence that *β*-H elimination can be competitive with hydrogenolysis. *β*-H elimination of the alkyl intermediate gives back the starting alkene and, through an equilibration process, it



Scheme 6.12

induces an erosion of the enantioselectivity [132]. Noteworthy is the finding that, when Sm is replaced by Group III or other lanthanide metals, the following trend for ee-values is observed: La > Nd > Sm > Y > Lu, which parallels the decrease in ionic radius on going from La to Lu [132]. Other *ansa* dicyclopentadienyl systems have been designed, but this was only applicable to Y and Lu. Whilst the catalysts could be prepared as stable enantiomers, they show only low ee-values in the hydrogenation of styrene derivatives [124].

6.5
Hydrogenation Catalysts Based on Groups V–VII Transition-Metal Complexes

6.5.1
Hydrogenation of Alkenes and Dienes with Groups V–VII Transition-Metal Complexes

As shown by Breslow et al. during the mid-1960s, most transition-metal alkoxide or acetylacetonate complexes catalyze the hydrogenation of alkenes in the presence of an activator (Table 6.19) [5]. Other precursors have been used such as $[CpCr(CO)_3]_2$, but it is more difficult to understand how the active species are formed [133].

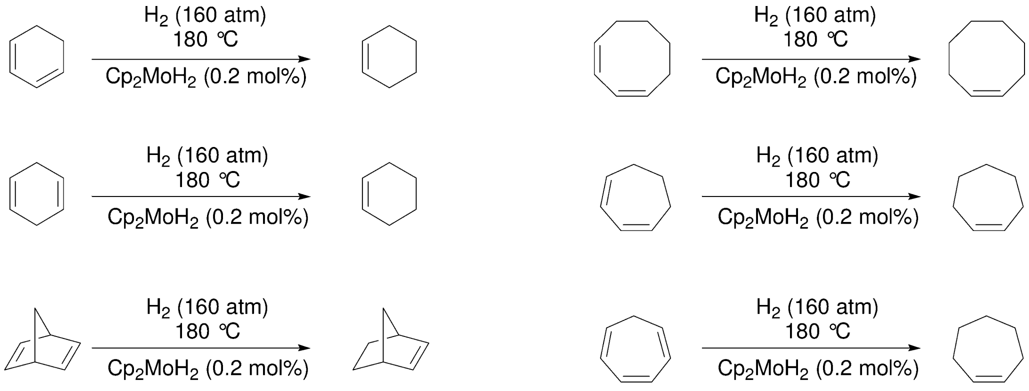
Moreover, systems based on Group V and VI transition metals can be used to selectively hydrogenate dienes into mono-enes. For example, Cp_2VCl_2 in combination with 2 equiv. BuLi or PhMgBr selectively hydrogenate butadiene into butenes, while the system based on $[Cp_2TiCl_2]/R'M$ gives butane [6]. Similarly, the V system hydrogenates isopropene selectively into 2-methyl-2-butene (92–93% selectivity), along with the other branched pentene isomers as well as traces of 2-methylbutane. Similarly, a catalytic amount of $[Cp_2MoH_2]$ (0.2 mol%) converts dienes and trienes selectively into the corresponding mono-enes in 50–90% yields at 180 °C (Scheme 6.13) [134, 135]. It has been reported that methyl acrylate, methyl crotonate, crotonaldehyde, and mesityl oxide can be hydrogenated under the same

Table 6.19 Hydrogenation catalysts based on Group V–VII transition-metal complexes activated with Al*i*Bu$_3$.

M complex	Activator [a]	Temp. [°C]	Olefin (SCR) [b]	Conv. [%] (time, h)
[VO(O*i*Pr)$_3$]	*i*Bu$_3$Al (3.9)	40	Cyclohexene (52)	100 (<20)
[VO(O*i*Pr)$_3$]	*i*Bu$_3$Al (3.9)	40	1-Octene (52)	100 (<20)
[Cr(acac)$_3$]	*i*Bu$_3$Al (6.0)	30	Cyclohexene (105)	100 (2)
[Cr(acac)$_3$]	*i*Bu$_3$Al (6.0)	30	1-Octene (105)	55 (1.2)
[MoO$_2$(acac)$_2$]	*i*Bu$_3$Al (7.1)	30	Cyclohexene (63)	100 (<16)
[MoO$_2$(acac)$_2$]	*i*Bu$_3$Al (7.1)	30	1-Octene (67)	100 (<21)
[Mn(acac)$_2$]	*i*Bu$_3$Al (6.0)	30	Cyclohexene (63)	100 (<16)

a) Values in parentheses correspond to the number of equivalents of activator per transition-metal complex.

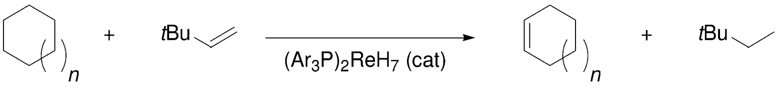
b) SCR = substrate : catalyst ratio.



Scheme 6.13

reaction conditions, but no yields were reported. In sharp contrast, [Cp$_2$Cr, Cp$_2$WH$_2$] and [Cp$_2$ReH] are completely inactive under the same reaction conditions.

Finally, whilst rhenium hydride complexes have not been reported to hydrogenate alkenes, there are several reports of the dehydrogenation of alkanes in the presence of *t*BuCH=CH$_2$ as an hydrogen acceptor (Scheme 6.14) [136–142]. For example, cycloalkanes are transformed catalytically into the corresponding cyclic alkene, which shows that, in principle, a Re-based catalyst could be designed.



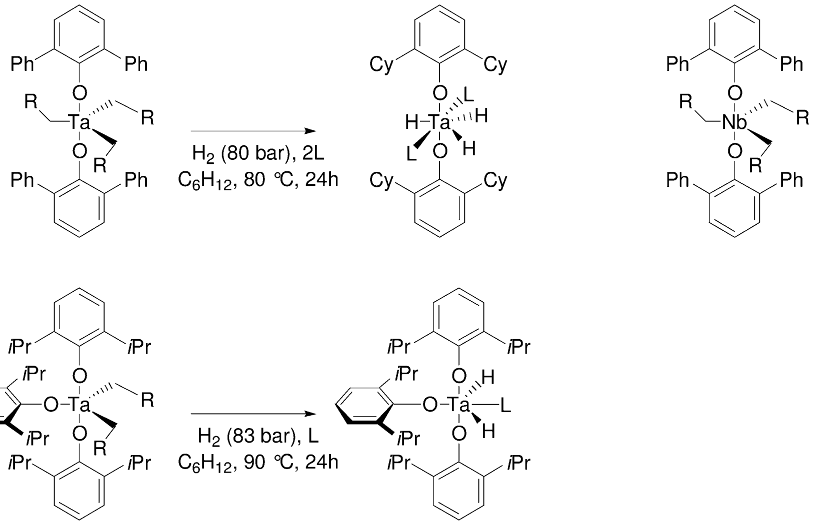
Scheme 6.14

6.5.2
Hydrogenation of Aromatics with Well-Defined Nb and Ta Aryloxide Complexes

Treatment under H_2 of $[(2,6\text{-diPhC}_6H_3O)_2Ta(CH_2R)_3]$ ($R{=}CH_2Ar$) in the presence of different arylphosphine ligands generated well-defined monomeric Ta hydride complexes, $[(2,6\text{-diCyC}_6H_3O)_2Ta(H_3)(PCy_3)_2$ (Scheme 6.15) [143, 144]. During this treatment, the four phenyl substituents of the aryloxide ligands are hydrogenated into cyclohexyl units, which demonstrates the catalytic potential of these systems for the hydrogenation of aromatics.

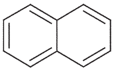
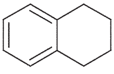
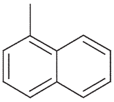
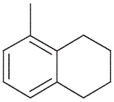
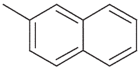
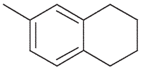
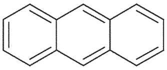
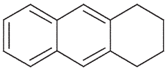
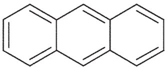
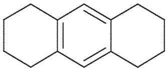
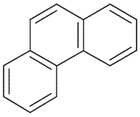
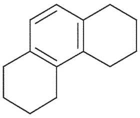
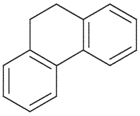
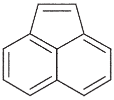
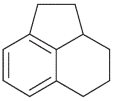
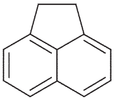
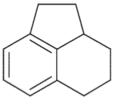
In fact, this Ta complex catalyzes the hydrogenation of naphthalene into tetraline, and that of anthracene into 1,2,3,4-decahydroanthracene [145]. The corresponding dihydride, $[(2,6\text{-di-}i\text{PrC}_6H_3O)_3Ta(H_2)(PMe_2Ph)_2]$, prepared by treatment under H_2 of $[(2,6\text{-di-}i\text{PrC}_6H_3O)_3Ta(CH_2Ar)_2]$ in the presence of PMe_2Ph, is an efficient hydrogenation catalyst of aromatics such as naphthalene [146].

Similarly, $[(2,6\text{-diPhC}_6H_3O)_2NbR_3]$ ($R{=}CH_2Ph\text{-}4\text{-}Me$) is an hydrogenation catalyst precursor for aromatics. It catalyzes the hydrogenation of naphthalenes into the corresponding tetraline, giving selectively the product of hydrogenation of the nonsubstituted ring (Table 6.20). It is noteworthy that anthracene is converted exclusively into 1,2,3,4,5,6,7,8-octahydroanthracene, with no trace of 9,10-dihydroanthracene, whilst phenanthrene yields 9,10-dihydroanthracene (78%) along



Scheme 6.15

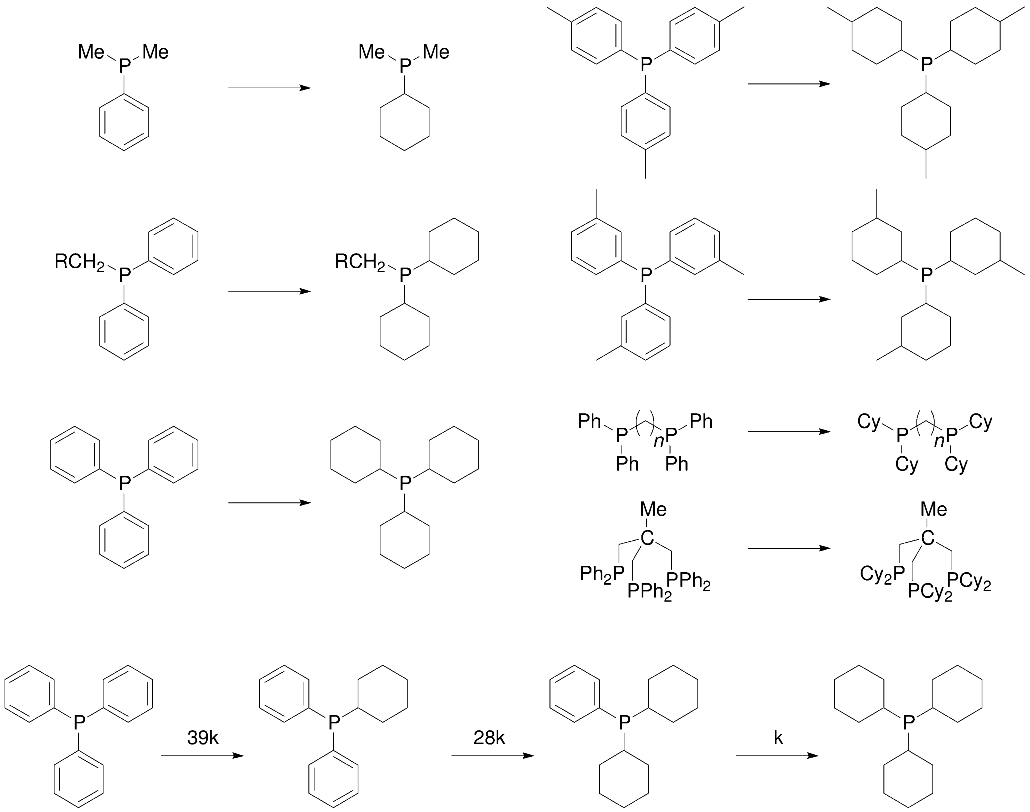
Table 6.20 Hydrogenation of aromatics catalyzed by [(2,6-diPh$C_6H_3O)_2NbR_3$] and [(2,6-diCy$C_6H_3O)_2Ta(H)_3(PCy_3)_2$] [145].

Substrate	Catalyst	SCR (P) [a)]	Product	Yield [%]	Byproduct [%]
	Nb Ta	20 (80) 20 (80)		>95 >95	– –
	Nb	20 (80)		>95	–
	Nb	20 (80)		>95	–
	Nb	20 (80)		>95	–
	Ta	20 (80)		>95	–
	Nb	20 (80)		78	22 
	Nb	20 (80)		>95	–
	Nb	20 (80)		>95	–

a) SCR = substrate : catalyst ratio; P = pressure (bar).

with 1,2,3,4,5,6,7,8-octahydroanthracene (22%) [143–156]. Both, acenaphthylene and anthracene are transformed into 1,2,2a,3,4,5-hexahydronaphthalene. For both catalyst precursors, the hydrogenation of perdeuterated naphthalene gives exclusively the tetraline product with six hydrogens *cis*, all on one face.

Moreover, the Nb complex hydrogenates catalytically aryl- and benzyl-substituted phosphine under similar conditions (Scheme 6.16) [149]. Kinetic studies show that the hydrogenation of triphenylphosphine into the monocyclohexyl, dicyclohexyl, and tricyclohexylphosphine are successive reactions, and the rate of hydrogenation of the arylphosphine decreases as the number of cyclohexyl substituents increases [153].

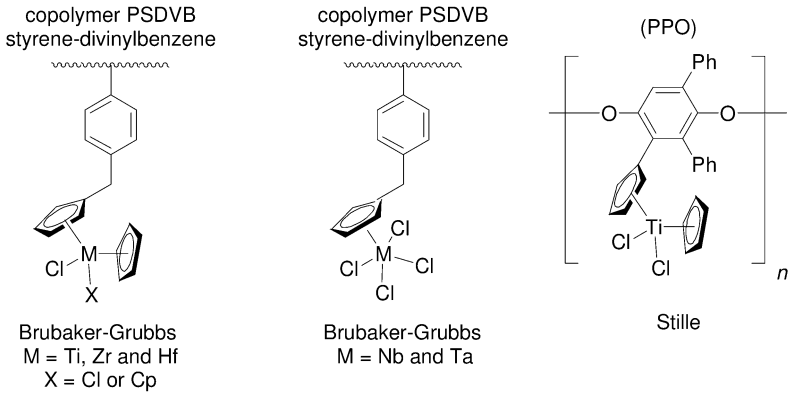


Scheme 6.16 Relative rates indicated above arrows.

6.6
Supported Early Transition-Metal Complexes as Heterogeneous Hydrogenation Catalysts

6.6.1
Supported Homogeneous Catalysts

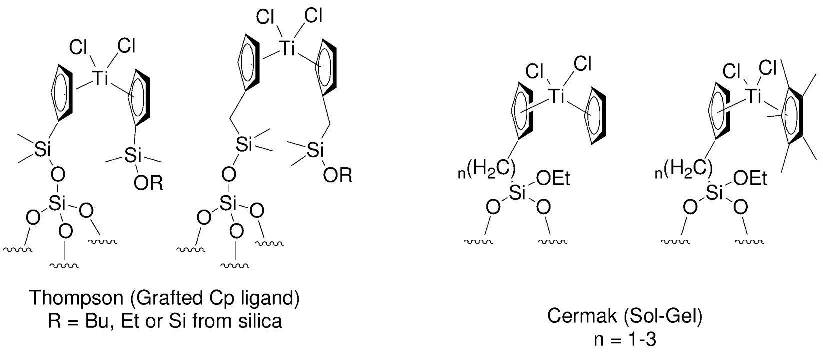
Several strategies have been adopted to prepare the heterogeneous equivalents of the metallocene hydrogenation catalysts. One approach centers on the preparation of cyclopentadienyl-containing polymers based on either co-polymers of styrene and divinylbenzene (PSDVB) [157–164] or poly(phenylene oxide) (PPO) (Scheme 6.17) [165]. For the PSDVB system, the rate of hydrogenation of the supported systems is much greater than the molecular complex. For example, the TOF for the hydrogenation of cyclohexene for the polymer-supported Ti complex and [Cp_2TiCl_2] activated by BuLi are 1900 and 18 h^{-1}, respectively [160]. Note that critical factors are low metal loadings and small particle sizes (grind-



Scheme 6.17

ing of the polymer-supported catalysts prior to activation with BuLi is necessary for good activities). This system hydrogenates 1-hexene, styrene, 1,3- and 1,5-cyclooctadienes with comparable TOF, while tri-, tetra-substituted and functionalized alkenes do not undergo hydrogenation [158]. Several other metals have been used, but Ti is by far the most active [159, 163, 164]. Similarly, PPO-supported Ti complexes are more active (e.g., 10- to 70-fold) than their molecular equivalents [165].

Another approach has consisted of preparing a cyclopentadiene having an alkoxy silane substituent, which is grafted onto a silica support and then transformed into the corresponding metal cyclopentadiene complex (Scheme 6.18) [166]. After activation with BuLi or PrMgBr, their performances in the hydrogenation of 1-octene are about three- to five-fold better than the corresponding homogeneous catalysts (0.24–0.4 versus 0.08 h^{-1}, [$CpTiCl_3$]). Finally, a cyclopentadiene-containing silica has been prepared by sol-gel condensation of trisalkoxysilyl-substituted cyclopentadiene and then used to anchor the Ti center [167]. This system catalyzes the hydrogenation of 1-octene in the presence of BuLi,



Scheme 6.18

with activities comparable to those of the homogeneous systems (2 mol% Ti): [$CpTiCl_3$] (5640 h^{-1}) > [($\equiv$SiO-$(CH_2)_nC_5H_4$)Cp*$TiCl_2$] (1730 h^{-1}) > [Cp*$TiCl_3$] (1300 h^{-1}) > [($\equiv$SiO-$(CH_2)_nC_5H_4$)Cp$TiCl_2$] (865 h^{-1}).

6.6.2
Heterogeneous Catalysts Prepared via Surface Organometallic Chemistry

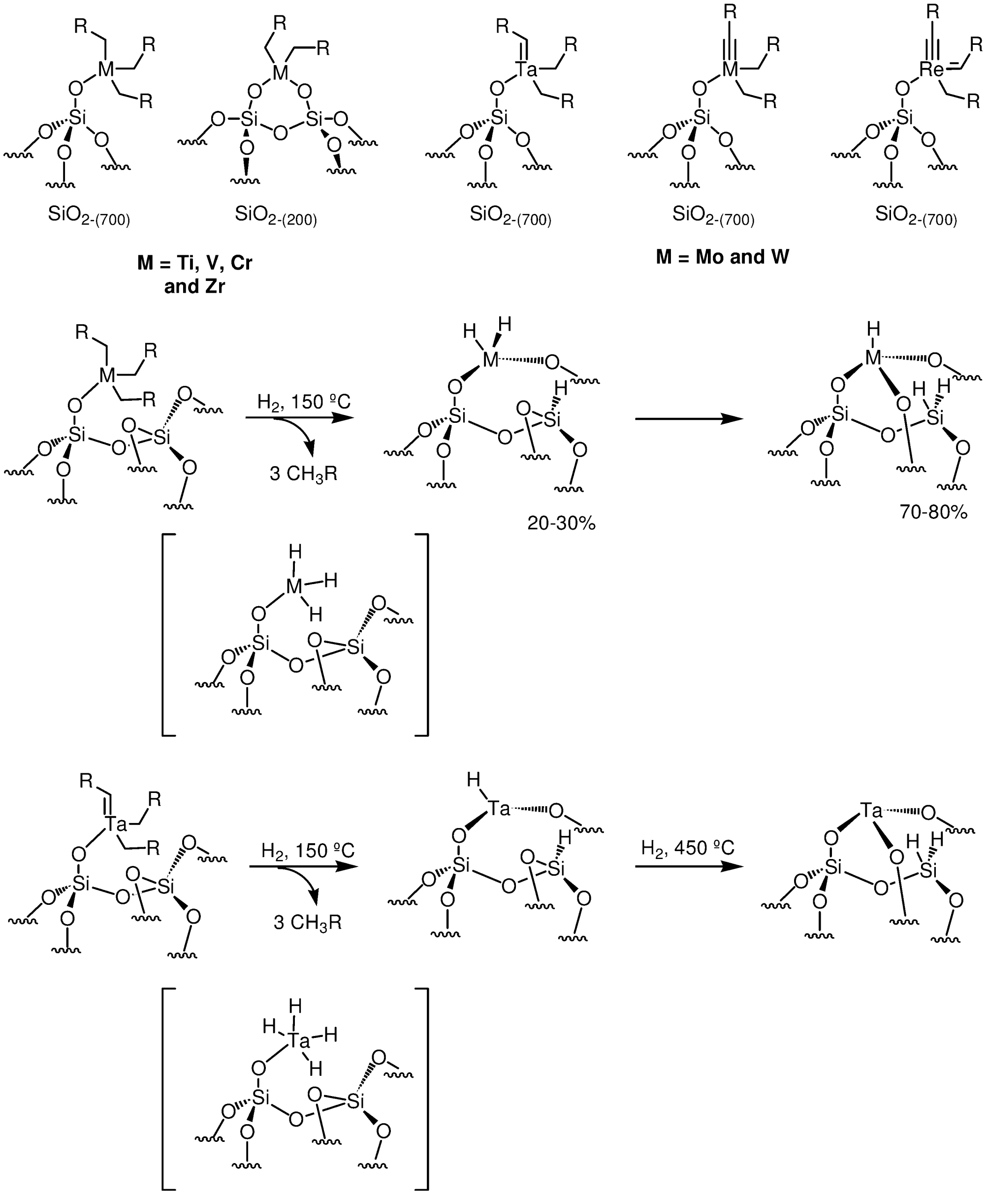
In contrast to supported homogeneous catalysis, surface organometallic chemistry (SOMC) uses an inorganic oxide (E_xO_y) as a solid ligand, on which the metal is directly attached by at least a bond with a surface atom, usually an oxygen, through a M–OE bond.

During the late 1960s, polymer chemists were interested in developing well-defined equivalents of the Ziegler-Natta catalysts [168, 169], and prepared supported Group IV complexes by reacting organometallic complexes with oxide supports. Yermakov et al. showed that, under treatment under H_2, these systems evolved into the corresponding hydrides. All of these systems are efficient polymerization catalysts [169–172]. Moreover, the Ti- and Zr- hydrides have turned out to be efficient hydrogenation catalysts of alkenes and aromatics (TOF = 3600 to 360 000 h^{-1} for the hydrogenation of cyclohexene or benzene) [173–176]. The structure of these systems has required a detailed understanding of the surface chemistry. In short, as a general rule, the structure of the surface organometallic complex depends on the temperature of pretreatment of silica [177]. When silica is treated at a low temperature under vacuum (e.g., 200 °C), the reaction with an organometallic complex yields a bis(siloxy) surface complex. On the other hand, when silica is treated at a high temperature under vacuum (e.g., 700 °C), a mono(siloxy) surface complex is formed (Scheme 6.19). Under H_2, Group IV and V surface complexes generate well-defined surface metal hydrides (Ti [178], Zr [179, 180], Hf [181], and Ta [182]).

The hydrogenation catalysts can be prepared *in situ*, starting from the surface alkyl complex. In terms of catalytic performances, these catalysts are highly effective (Table 6.21) [150]. The best hydrogenation systems are based on silica supported dinuclear complexes, for which the structures of the active sites have not been investigated. Hydrogenation of toluene and xylenes can be achieved under similar conditions.

Similarly, the cyclopentadienyl Zr derivatives supported on alumina are highly active olefin hydrogenation catalysts [183, 184]. The initial rates of propene hydrogenation depending on the cyclopentadienyl derivatives and the level of dehydroxylation of alumina are as follows: [Cp*$ZrMe_3$]/$Al_2O_{3\text{-}(1000)}$ (3960 h^{-1}) > [Cp*$ZrMe_3$]/$Al_2O_{3\text{-}(500)}$ (1080 h^{-1}) ≈ [Cp_2ZrMe_2]/$Al_2O_{3\text{-}(1000)}$ (1080 h^{-1}) > [Cp*Cp$ZrMe_2$]/$Al_2O_{3\text{-}(1000)}$ (720 h^{-1}) > [Cp_2ZrMe_2]/$Al_2O_{3\text{-}(500)}$ (360 h^{-1}) > [Cp*Cp$ZrMe_2$]/$Al_2O_{3\text{-}(500)}$ (216 h^{-1}) [185]. Typically, highly dehydroxylated alumina ($Al_2O_{3\text{-}(1000)}$) is a better support, and it has been associated with the formation of cationic surface species.

Several other supports have been used in order to generate more-electrophilic Zr systems, including sulfated zirconia [186], sulfated alumina [187], or other sulfated oxide supports [188], though the surface species are quite complex for these systems. The catalytic activities in the hydrogenation of benzene are as follows: $[Cp^{*}Zr(CH_3)_3]/ZrO_{2\text{-sulfated}}$ (970 h^{-1}) > $[Cp^{*}Zr(CH_3)_3]/Al_2O_{3\text{-sulfated}}$ (360 h^{-1}) > $[Cp^{*}Zr(CH_3)_3]/SnO_{2\text{-sulfated}}$ (10 h^{-1}) > $[Cp^{*}Zr(CH_3)_3]/SnO_{2\text{-sulfated}}$ (5 h^{-1}) > $[Cp^{*}Zr(CH_3)_3]/TiO_{2\text{-sulfated}}$ (< 3 h^{-1}), and they are correlated with the surface Brönsted acidity [188].



Scheme 6.19

Table 6.21 Hydrogenation of benzene and naphthalene catalyzed by silica-supported Group IV–VI transition-metal complexes.

Catalytic system	**Substrate**	**Time [min]**	**Conversion [%]**	**Selectivity [%]**
$Ti(CH_2SiMe_3)_4/SiO_2$	Benzene a)	360	39	100
	Naphthalene b)	150	100	55:45 d)
$Zr(CH_2Ph)_4/SiO_2$	Benzene a)	240	100	100
	Naphthalene b)	30	100	25:75 d)
$Hf(CH_2Ph)_4/SiO_2$	Benzene a)	600	100	100
	Naphthalene b)	60	100	19:81 d)
$Ta(CH_2Ar)_5/SiO_2$	Benzene a)	24 h	100	100
Ar = 4-Me-C_6H_4	Naphthalene b)	160	100	20:80 d)
$[Nb(CSiMe_3)(CH_2SiMe_3)_2]_2/SiO_2$	Benzene a)	300	100	100
	Naphthalene b)	20	100	15:85 d)
	Benzene c)	25	100	100
	Toluene c)	33	100	100
	o-Xylene c)	30	100	57:43 d)
	m-Xylene c)	20	100	78:22 d)
	p-Xylene c)	25	100	57:43 d)
$[Ta(CSiMe_3)(CH_2SiMe_3)_2]_2/SiO_2$	Benzene a)	720	100	100
	Naphthalene b)	70	100	20:80 d)
	Benzene c)	55	100	100
	Toluene c)	64	100	100
	o-Xylene c)	75	100	91:9 d)
	m-Xylene c)	70	100	92:8 d)
	p-Xylene c)	65	100	82:18 d)
$[Mo_2(CH_2SiMe_3)_6]/SiO_2$	Benzene a)	720	100	100
	Naphthalene b)	70	100	20:80 d)

a) 0.056 mmol M loaded on 5 g silica treated at 200 °C under vacuum, 17.5 g C_6H_6 (4000 equiv.), 80–100 bar H_2 at 120 °C.

b) 0.056 mmol M loaded on 5 g silica treated at 200 °C under vacuum, 2.0 g naphthalene (280 equiv.), 25 mL hexane, 100 bar H_2 at 120 °C.

c) 0.056 mmol M loaded on 5 g silica treated at 200 °C under vacuum, 26 mmol substrate (280 equiv.), 80–100 bar H_2 at 120 °C.

d) *cis/trans* ratio.

Soon after the discovery that dimeric actinide hydride complexes were active hydrogenation catalysts, Marks et al. investigated the formation of monomeric actinide active species by supporting them on an oxide support [184, 189]. The supported complexes on alumina are much more active than the corresponding molecular complexes. For comparison, the rate of hydrogenation of propene at 25 °C can be ranked as follows: $[Cp^*_2U(CH_3)_2]/Al_2O_{3\text{-}(1000)}$ ($1080\ h^{-1}$) > $[Cp^*_2Th(CH_3)_2]/Al_2O_{3\text{-}(1000)}$ ($580\ h^{-1}$) > $[Cp^*_2U(CH_3)_2]$ ($68\ h^{-1}$) > $[Cp^*_2Th(CH_3)_2]$ ($0.54\ h^{-1}$). Using partially dehydroxylated silica or an alumina dehydroxylated at a lower temperature as supports produces poorer catalysts [190]. Other supports have been used, but highly dehydroxylated alumina remains the best available to date. For example, the TOFs for the hydrogenation of propene at 25 °C are: $[Cp^*_2Th(CH_3)_2]/Al_2O_{3\text{-}(1000)}$ ($580\ h^{-1}$) > $[Cp^*_2Th(CH_3)_2]/SiO_2\text{-}Al_2O_3$ ($160\text{–}230\ h^{-1}$) > $[Cp^*_2Th(CH_3)_2]/MgCl_2$ ($25\text{–}43\ h^{-1}$) > $[Cp^*_2Th(CH_3)_2]/SiO_2\text{-}MgO$ ($0\ h^{-1}$) [191]. Note also that the TOF depends on the alkenes as measured by the hydrogenation at –45 °C: *cis*-butene ($3960\ h^{-1}$) > *trans*-2-butene ($2900\ h^{-1}$) ≫ propene ($470\ h^{-1}$) ≫ isobutene ($13\ h^{-1}$). Finally, some of these systems are highly active aromatic hydrogenation catalysts. At 90 °C and 13 bar, the TOF of hydrogenation is as follows: $[Th(allyl)_4]/Al_2O_{3\text{-}(1000)}$ ($1970\ h^{-1}$) ≫ $[Th(CH_2Ar)_4]/Al_2O_{3\text{-}(1000)}$ ($825\ h^{-1}$) > $[Cp^*Th(CH_2Ar)_3]$ ($765\ h^{-1}$) [192, 193]. Noteworthy, the TOF for the hydrogenation of benzene with $[Th(allyl)_4]/Al_2O_{3\text{-}(1000)}$ is comparable to Rh or Pt heterogeneous catalysts. The hydrogenation TOF is also function of the aromatic compounds: benzene (6850 k) > toluene (4100 k) > xylene (1450 k) ≫ naphthalene (1 k). Using D_2 in place of H_2 shows that hydrogenation corresponds to a random 1,2-*cis* addition of H_2.

6.7
Conclusions

Early transition-metal complexes have been some of the first well-defined catalyst precursors used in the homogeneous hydrogenation of alkenes. Of the various systems developed, the biscyclopentadienyl Group IV metal complexes are probably the most effective, especially those based on Ti. The most recent development in this field has shown that enantiomerically pure *ansa* zirconene and titanocene derivatives are highly effective enantioselective hydrogenation catalysts for alkenes, imines, and enamines (up to 99% ee in all cases), whilst in some cases TON of up to 1000 have been achieved.

Moreover, Group III, lanthanide and actinide biscyclopentadienyl complexes are efficient hydrogenation catalysts exhibiting a very rapid rate of hydrogenation. These catalysts are, nonetheless, somewhat more sensitive to the presence of functional groups, even though they can be used to hydrogenate imines. Enantiomerically pure chiral catalysts have also been developed for the enantiomeric hydrogenation of olefins in good enantiomeric excess (up to 71% ee).

Hydrogenation with Group V–VII transition metals has not yet been investigated in detail, despite the early discoveries of Breslow et al. Nonetheless, the findings of Rothwell et al. are noteworthy as Group V aryloxy systems can hydrogenate aromatics, including triphenylphosphine.

Finally, some of these systems have been supported on polymers or oxides, and these are typically more active than their homogeneous equivalents.

In general, the rate of alkene hydrogenation is typically ordered as follows: terminal > di-substituted > tri-substituted ≫ tetra-substituted. In fact, this allows terminal or di-substituted olefins to be hydrogenated selectively in the presence of tri- or tetra-substituted ones. Additionally, the rate of hydrogenation of alkynes is much slower than that of alkenes, although the *cis*-alkene intermediate can be observed and in some cases formed selectively, before its hydrogenation into the corresponding alkanes.

Whilst hydrogenation catalysts based on early transition metals are as active and selective as those based on late transition metals, they are usually not as compatible with functional groups, and this represents the major difficulty for their use in organic synthesis. Nonetheless, titanocene derivatives have been used in industry to hydrogenate unsaturated polymers.

Undoubtedly, further studies in this area are required, and it is most likely that, based on such investigations, new systems based on Group III–VII metals will emerge during the coming years.

Acknowledgments

These studies are dedicated to I.P. Rothwell for his pioneering contributions towards the development of early transition-metal hydrogenation catalysts. The author thanks the CNRS for financial support.

Abbreviations

ee	enantiomeric excess
PPO	poly(phenylene oxide)
PSDVB	co-polymers of styrene and divinylbenzene
SOMC	surface organometallic chemistry
TOF	turnover frequency
TON	turnover number

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