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Dicyclopentadienyl–titanium and –zirconium complexes as catalysts for hydrogenation of olefins *

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Abstract

The catalytic hydrogenation of 1-hexene, 4-methyl-2-pentene (65% *cis*), cyclohexene, styrene, isoprene, 1,3-cyclooctadiene and 1,5-cyclooctadiene has been studied by using different metallocene-type complexes of stoichiometry $[Cp_2MX_2]$, (M = Ti or Zr), containing equivalent, mixed *ansa* and bridging cyclopentadienyl ligands. The dichloro complexes (X = Cl) were reduced previously with an excess of magnesium, activated by the addition of a small amount of $HgCl_2$, in the presence or absence of $PMePh_2$. Cyclohexane solutions of the dialkyl derivatives (X = Me, CH_2SiMe_3, CH_2PPh_2, CH_2Ph, Ph, p-MeC_6H_4 or PPh_2) were used in reactions generally carried out in dihydrogen at 7 bar pressure and 90°C, with a concentration of catalyst of around 10^{-3} M and an olefin-to-catalyst molar ratio of between 300 and 500. The isolation and structural characterization of the new complexes $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Cl(CH_2PPh_2)]$, $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)(p\text{-}MeC_6H_4)_2]$, $[Ti\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}(CH_2PPh_2)_2]$ and $[Ti(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_4CH_2CH_2PPh_2)Cl_2]$ are also reported.

1. Introduction

Monocyclopentadienyl and dicyclopentadienyl Group 4 transition metal compounds are of increasing interest in relation to many catalytic reactions, in heterogeneous catalysis [1a] and homogeneous olefin polymerization, particularly of propene and other functionalized monomers [1b]. Their use in Ziegler–Natta catalysts for homogeneous olefin hydrogenation has also been studied [2] and recently the role of chiral zirconium metallocenes in enantioselective hydrogenation reactions has been reported [3]. Many organometallic compounds of Group 4 are precursors of active hydrogenation catalysts [2,4]. The active hydride species $[L_nM\text{–}H]$ can be formed by different reactions, *e.g.* by addition of $LiAlH_x(OR)_y$ or AlR_3 [5], MgH_2 or RMgX [6] and NaH, KH or LiR [4b,7] or a reducing agent, such as Na, K [8], sodium–naphthalene or Mg [9] to the metallocene dichlorides, by using dihydride or chlorohydride complexes [10] or by hydrogenolysis of monoalkyl or dialkyl complexes [11]. Although the catalytic activity of this type of complex is very variable, they do not hydrogenate aromatic double bonds [12] and the titanium derivatives are usually more active but less selective than the zirconium compounds [13]. In most reactions other components can be formed together with the final alkane, including oligomerization or polymerization products, and those obtained from isomerization [3,14].

We have reported [15] the isolation of different metallocene-type mononuclear complexes of titanium and zirconium containing mixed cyclopentadienyl or *ansa*-cyclopentadienyl ligands and also dinuclear compounds with bridging cyclopentadienyl systems. We were interested in comparing the catalytic activity of these compounds in the hydrogenation of different types of olefins. Here we report results using the complexes shown in Scheme 1.

2. Results and discussion

2.1. Hydrogenation of 1-hexene

The hydrogenation of 1-hexene was studied by using dichloro-, (chloro)alkyl- and dialkyl-metallocene-type complexes of titanium and zirconium.

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* Dedicated to Professor Michael F. Lappert on the occasion of his 65th birthday.

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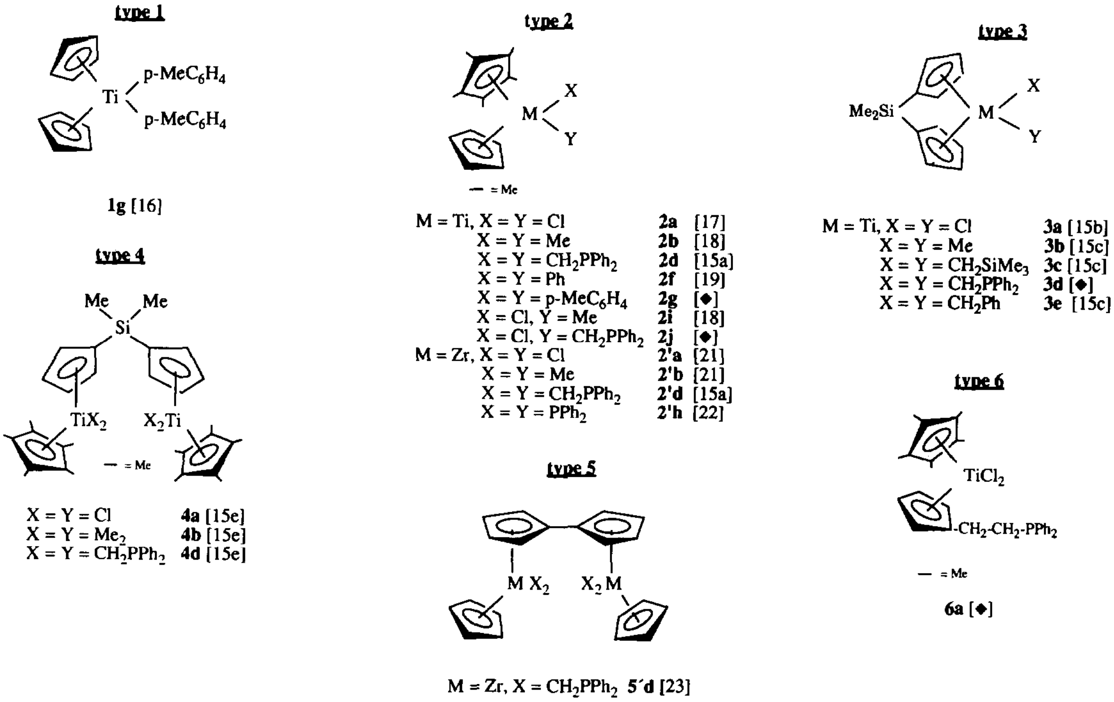


◆These complexes are reported in this paper [20]

Scheme 1.

2.2. Dichlorometallocene-type complexes

The Ti complexes **2a**, **3a** and **6a** and the Zr derivative **2'a** were studied. These dichloro compounds like [Cp_2TiCl_2], are catalysts only when they are previously treated with a reducing agent [9].

As shown in Table 1, no conversion was observed when the catalyst was prepared by the addition of one equivalent of sodium amalgam to tetrahydrofuran (THF) solutions of complexes **2a**, **6a** and **2'a**. The activity increased when two equivalents of sodium amalgam were added to a THF solution of **2'a**, but conversion was still low. The reduction of metallocenes with alkali metals has been reported [24] to induce ring C–H activations, leading to the formation of fulvalene complexes, which are not active for hydrogenation [25] (see below). Such a transformation could explain why the metal(III) species formed by reduction are not active, even in the case of **6a** where the assumed Ti^{III} species might be stabilized by coordination of the phosphorus in the alkyl chain of $C_5H_4CH_2CH_2PPh_2$.

TABLE 1. Hydrogenation of 1-hexene by dichlorometallocene (M = Ti or Zr) complexes in cyclohexane (P_{H_2} = 7 bar: $T = 90°C$; [catalyst] $\approx 10^{-3}$ M; [olefin]/[catalyst] = 300–500)

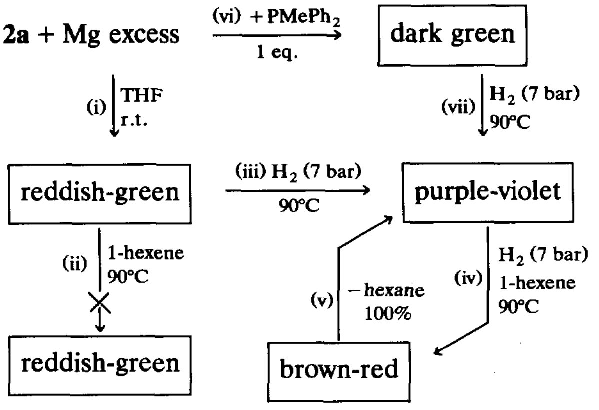
Catalyst	Conversion (%)	Reaction time (min)
2a + Na–Hg [a]	0	–
6a + Na–Hg [a]	0	–
2a + Mg–$HgCl_2$ [b]	100	21
3a + Mg–$HgCl_2$ [b]	100	12
2'a + Na–Hg [a]	0	–
2'a + Mg–$HgCl_2$ [b]	100	55
2'a + 2Na–Hg	31	420

[a] Reaction in THF.

[b] Reductions were carried out by using a ratio of 1/20 excess of Mg activated with a small amount of $HgCl_2$.

However, when the reduction is carried out with an excess of activated magnesium and complexes **2a**, **3a** and **2'a**, 100% conversion to hexane is observed in rather short reaction times, comparable with those observed when using dialkyl derivatives (see below). Moreover, the reduced solutions of all the complexes studied remain unchanged under an inert atmosphere and are still active for hydrogenation after several weeks. This can be explained by assuming that the resulting titanium(III) complex is stabilized by the coordination of $MgCl_2$ to give covalent adducts [26] such as [$Cp_2Ti(\mu\text{-}Cl)_2MgCl$] or ionic species [27] of the type [MgCl][Cp_2TiCl_2]. We were not able to isolate the reduction products, but we still wanted to know the nature of the species present under reaction conditions in the presence of dihydrogen. For this reason, reactions shown in Scheme 2 were carried out.

After reduction with an excess of magnesium (reaction (i)) the THF solution of **2a** is reddish-green. The addition of 1-hexene (reaction (ii)) does not change the



Scheme 2.

colour at room temperature or at 90°C; the gas composition is unaltered as verified by gas chromatography. When the solution is treated with dihydrogen (7 bar) at 90°C (reaction (iii)) in the absence of olefin, a dark purple–violet solution is instantaneously obtained. Analogous behaviour is observed at room temperature after 10 min. After the removal of dihydrogen, the addition of 1-hexene, and finally the introduction of dihydrogen up to 7 bar (reaction (iv)) the solution goes brown–red, with simultaneous absorption of dihydrogen. Quantitative hydrogenation to hexane (reaction (v)) takes place, as proved by gas chromatography, with the solution reverting to the initial purple–violet colour. When the reduction is carried out in the presence of one equivalent of $PMePh_2$ (reaction (vi)), a dark-green product is obtained, which after being treated with dihydrogen at 7 bar (reaction (vii)) yields the purple–violet solution, that reproduces exactly the same catalytic cycle.

Evaporation of the resultant solution, in the presence or absence of phosphine, gives the same purple–grey solid, which was extracted with toluene. The IR spectrum of the solid shows an absorption at 1325 cm^{-1}, probably owing to a bridging hydride system [28], which disappears when the sample is exposed to air. The electron paramagnetic resonance spectrum in THF at room temperature shows one asymmetric doublet ($g = 1.977$; $a(^1H) = 12.5$ G), consistent with the presence of one unpaired electron on titanium, coupled to only one hydrogen atom.

We have carried out several studies at a preparative level, and the results will be shortly reported elsewhere [29]. However, the final product is exactly the same, whether it is prepared in the presence or absence of phosphine, which is not complexed. The addition of $PMePh_2$ after reduction with magnesium does not change the colour of the solution, which shows the same catalytic behaviour as in the absence of phosphine. The active catalyst does not contain phosphine. However, the presence of phosphine is frequently required to obtain a catalytically active species. It seems that coordination of phosphine leads to a selective reduction to give the active species which no longer contains phosphine; this would otherwise convert it into a stable inactive compound.

2.3. Chloro(alkyl)metallocene-type complexes

The two (chloro)alkyl complexes **2i** and **2j** were studied. They are not active catalysts and this is explained by assuming that two coordination positions are required for activity: one for the coordination of the hydride or hydrogen and the other to coordinate the olefin. This is not possible when chloride occupies one of these positions. One Ti–Cl bond also confers additional kinetic stability, preventing the hydrogenolysis of the Ti–alkyl bond. In fact, **2i** is recovered unchanged after attempted reaction, whereas **2j** gives an inseparable mixture of products, probably because of thermal or photochemical decomposition rather than reaction with dihydrogen. Similarly, complex **2d** remains unchanged when treated in dihydrogen at 7 bar pressure for 15 min in the absence of light and olefin, whereas it gives an unidentified paramagnetic compound when heated in sunlight in the absence of dihydrogen. Complex **2j** is also inactive after reduction with sodium amalgam.

2.4. Dialkylmetallocene-type complexes

According to the results shown in Table 2, complexes of type **2** with mixed Cp and Cp* ligands have activities strongly dependent on the alkyl substituents. Complex **2'h** with PPh_2 is hardly active, producing

TABLE 2. Hydrogenation of 1-hexene by dialkylmetallocene (M = Ti or Zr) complexes in cyclohexane ($P_{H_2} = 7$ bar: $T = 90°C$: [catalyst] ≈ 10^{-3} M: [olefin]/[catalyst] = 300–1000)

Catalyst	Conversion (%)	Reaction time (min)
2b	100	90
2d [b]	100	15
2f	6	600
2g	100	10
3b	100	18
3c	100	60
3e	100	200
2'd	100	135
2'h [a]	12	600
2'h + Na–Naphthalene [a]	10	600
5'd	0	–

[a] In THF.

[b] Under the same conditions but, at 60°C, 100% conversion in 45 min.

TABLE 3. Influence of $PMePh_2$ in the hydrogenation of 1-hexene with dialkylmetallocene (M = Ti or Zr) complexes in cyclohexane ($P_{H_2} = 7$ bar: $T = 90°C$: [catalyst] $\approx 10^{-3}$ M: [olefin]/[catalyst] = 300–500)

Catalyst	Conversion (%)	Reaction time (min)
2b	100	90
2b + 1 $PMePh_2$	100	155
2'b	100	50
2'b + 1 $PMePh_2$	0	> 600

conversions lower than 12% in 10 h, but is very dependent on pressure as this leads to a 100% conversion in dihydrogen at 40 bar in the same reaction time [12]. The different activities found for complexes **2f** and **2g** parallel to those reported [16] for the analogous $[Cp_2TiPh_2]$ and $[Cp_2Ti(p\text{-}MeC_6H_4)_2]$ derivatives. It seems that formation of the active hydride is more probable when homolytic or heterolytic dissociation of the M–C bond is favoured by the *p*-Me substituent. A similar behaviour is observed with complexes **2'h** and **2'd** because the dissociation of the M–C bond is more facile than that of the M–P bond, which reportedly has a double-bond character [15a].

In order to establish the influence of the alkyl group we can also compare **2b**, **2d**, **2f** and **2g**. With the exception of **2f** (6% conversion) the remaining three complexes show a 100% conversion but at different rates, the methyl derivative producing the poorest catalyst. This is again a consequence of the different activation periods required to form the active hydride, the methyltitanium complex **2b** requiring a longer activation period, although it is probably more active after activation. A different order is observed for **3b**, **3c** and **3e**, with the *ansa*-dimethylsilylbis(cyclopentadienyl)-ligand.

As for the different cyclopentadienyl ligands, the most active catalysts are all from complexes of type **3**, whereas those of type **5**, containing a bridging fulvalene system, are not active (conversion, 0%) [25]. This is consistent with the reported [15f] capacity of *ansa*-dimethylsilylbis(cyclopentadienyl) to stabilize the lower oxidation states, assumed to be present in the active species.

The influence of the metal can be deduced from **2d** and **2'd**. The time to obtain 100% conversion is shorter for the titanium complex (15 min) than for the zirconium derivative (135 min). As we shall discuss below, both are actually precursors of the catalyst and, although both are equally effective, they require different times of activation to form the active species; in this case the titanium complex requires a shorter activation period.

The presence of $PMePh_2$ is important during the reduction step of the dichloro complexes, but it does not affect the catalytic activity. However, the addition of phosphine changes dramatically the activity of the dialkyl complexes [9]. As shown in Table 3, when $PMePh_2$ is added to the titanium complex **2b**, the hydrogenation of 1-hexene is slower and the 100% conversion requires a longer time. A similar addition to the zirconium derivative **2'b** reduces the activity to

TABLE 4. Activation times, t_0 for hydrogenation of olefins with metallocene (M = Ti or Zr) complexes in cyclohexane ($P_{H_2} = 7$ bar: $T = 90°C$: [catalyst] $\approx 10^{-3}$ M: [olefin]/[catalyst] = 300–500)

Catalyst	t_0 (min)						
	1-Hexene	4-Me-2-pentene	Cyclohexene	Styrene	2-Me-2-butadiene	1,3-Cyclooctadiene	1,5-Cyclooctadiene
1g	3	NR	15	0.5	8	9	1
2a–Mg	0	0	6	0	0	0	0
2b	85	NR	50	25	62	81	265
2d	9	NR	10	0.5	10	9	7
2g	5	NR	7	0	5	6	2
3a–Mg	0	0	0	0	0	0	0
3b	13	28	20	14	30	17	21
3d	9	12	13	2	16	12	6
4a–Mg [a,b]	0	0	25	0	0	0	0
4b	5	70	8	0.5	12	50	69
4d	D	D	D	0.5	D	D	D
2'a–Mg	13	0	NR	7	15	0	0
2'b	30	NR	20	20	60	25	15
2'd	85	NR	NR	105	350	48	NR

NR, no reaction observed, D, decomposition.

[a] Previous reduction in the presence of $PMePh_2$.

[b] 0% conversion when previous reduction in the absence of $PMePh_2$.

zero. This can be explained by assuming that phosphine occupies a vacant coordination site, preventing the coordination of the olefin.

2.5. Hydrogenation of different olefins

Consistent with the previous discussion, we selected the more active complexes **1g**, **2a**, **2b**, **2d**, **2g**, **3a**, **3b**, **3d**, **4a**, **4b**, **4d**, **2′a**, **2′b** and **2′d**, to study their catalytic behaviour in the hydrogenation of different types of mono-olefins and diolefins, as shown in Table 4.

The following parameters were used to define the behaviour of the catalyst: t_0 is the time from when the dihydrogen pressure in the autoclave was set to 7 bar until the absorption of dihydrogen started; t is the total time of the experiment (activation + hydrogenation) until the absorption of dihydrogen stops; conversion (%) is the total amount of olefin hydrogenated; X is the fractional conversion; the average frequency of hydrogenation (AFH) is the average number of moles of olefin being transformed per mole of catalyst (or mole of metal centres for dinuclear complexes) per minute:

$$\mathrm{AFH} = \frac{[\mathrm{olefin}]_0 X}{[\mathrm{cat}]_0 (t - t_0)}$$

2.6. Hydrogenation of mono-olefins

With the exception of complex **2′a**, the reduced dichloro complexes usually do not require any activation time. However, hydrogenation with all the dialkyl derivatives starts after a period of activation, indicating that the active species probably contain the metal in a low oxidation state. Moreover, t_0 depends on the nature of the alkyl substituent and the metal, in the following way: $p\text{-MeC}_6\text{H}_4 < \text{CH}_2\text{PPh}_2 < \text{Me}$ for titanium and $\text{Me} < \text{CH}_2\text{PPh}_2$ for zirconium. However, t_0 is lower for titanium than for zirconium when $\text{R} = \text{CH}_2\text{PPh}_2$ but conversely is lower for zirconium than for titanium when R = Me. This could be the result of simultaneous electronic and steric effects. No correlation could be established between t_0 and the different cyclopentadienyl rings.

Values of the AFH also depend on the metal and the alkyl substituents (Table 5). Generally the AFH is lower for zirconium than for titanium complexes. The influence of the alkyl group follows the order: $\text{Me} < p\text{-MeC}_6\text{H}_4 < \text{CH}_2\text{PPh}_2$ for titanium and $\text{CH}_2\text{-PPh}_2 < \text{Me}$ for zirconium. Hydrogenolysis of the M–C bonds liberates the alkane; when $\text{R} = \text{CH}_2\text{PPh}_2$, this reaction liberates phosphine, which is then coordinated to the metal (particularly to zirconium), hindering or even preventing the coordination of the olefin. There is a

TABLE 5. Average frequency of hydrogenation and percentage conversion of different mono-olefins by metallocene (M = Ti or Zr) complexes (P_{H_2} = 7 bar: T = 90°C: [catalyst] ≈ 10^{-3} M: [olefin]/[catalyst] = 300–500)

Catalyst	1-Hexene		4-Me-2-pentene (65% *cis*)		Cyclohexene		Styrene	
	AFH (min^{-1})	Conversion (%)	AFH (min^{-1})	Conversion (%)	AFH (min^{-1})	Conversion (%)	AFH (min^{-1})	Conversion (%)
1g	79	100	NR	0	83	100	98	100
2a–Mg [a,b]	42	100	*cis* 43		23	100	128	100
			trans 2	100 (2MP)				
2b	80	100	NR	0	83	100	100	100
2d	167	100	NR	0	100	100	160	100
2g	100	100	NR	0	87	100	110	100
3a–Mg [a]	24	100	5	100 (2MP)	25	100	100	100
3b	66	100	56	75 [75, 2MP; 25, 4M2P (65% *cis*)]	51	100	75	100
3d	83	100	65	100 (2MP)	80	100	100	100
4a–Mg [a,b]	80	10	*cis* 10		1	100	5	100
			trans 0	65 (65, 2MP; 35, 4M2P)				
4b	40	100	*cis* 40		40	100	165	100
			trans 17	100 (2MP)				
4d	D	0	D	0	D	0	167	100
2′a–Mg [a,b]	12	100	*cis* < 1		NR	0	16	100
			trans 0	27 [27, 2MP; 73, 4M2P (52% *cis*)]				
2′b	25	100	NR	0	20	100	25	100
2′d	6	100	NR	0	NR	0	3	100

NR, no reaction; D, decomposition; 2MP, 2-methyl-pentane; 4M2P, 4-methyl-2-pentane.

[a] Previous reduction in the presence of PMePh_2.

[b] 0% conversion when previous reduction in the absence of PMePh_2.

good correlation between the AFH and the nature of the cyclopentadienyl ligand, following the order: 2 > 1 > 3 > 4 for the different types of titanium complex. t_0 is always slightly higher for p-MeC$_6$H$_4$ than for C_6H_5 but the latter always reacts more rapidly after activation.

As judged by the t_0 and AFH values, linear (1-hexene) olefins are more reactive than cyclic (cyclohexene) olefins. Even the dichlorotitanium complexes, which generally do not require an activation period, show that $t_0 > 0$ and, with the exception of **2'b**, all the zirconium compounds are inactive.

Complex **4d** is thermally unstable and decomposes before activation in reactions with all the olefins, except with styrene. In this case the olefin is readily hydrogenated, requiring a lower t_0 and giving a higher AFH, owing to the aromatic system. The aromatic system is unaffected by the catalysts.

The behaviour of 4-methyl-2-pentene, a mixture of 65% *cis* and 35% *trans* isomers, deserves particular attention. As an internal olefin, it is the less reactive, and only complexes containing bridging cyclopentadienyl ligands are able to hydrogenate it, whereas those with two Cp ligands or a Cp, Cp* system are inactive. Complexes **2a**, **3a**, **3d** and **4b** reach 100% conversion with slower hydrogenations, both *cis* and *trans* stereomers being hydrogenated. However, **3b** gives only a conversion of 75%, without modification of the *cis*-to-*trans* ratio. Complex **2'a**, which is rather a poor catalyst (reaching a conversion of only 27%) hydrogenates the *cis* stereomer preferentially. The most significant behaviour is that observed for complex **4a**, which is able to reach 65% conversion but hydrogenating selectively only the *cis* component and leaves all the *trans* isomer unchanged. This catalyst has a 100% conversion selectively for the *cis* isomer. The absorption of dihydrogen with time for complexes **2a** and **4b** is similar to that described below for diolefins. The reaction takes place in two steps; the first, with 65% of the total dihydrogen consumption, is the most rapid (the AFH is 43 min^{-1} for **2a** and 40 min^{-1} for **4b**) and corresponds to the hydrogenation of the *cis* stereomer, whereas the second with a consumption of 35% of dihydrogen is slower (the AFH is 2 min^{-1} for **2a** and 17 min^{-1} for **4b**) and corresponds to the hydrogenation of the *trans* isomer. Thus these complexes could be used as selective catalysts for the *cis* isomer under appropriate reaction conditions.

2.7. Hydrogenation of diolefins

The general trends described for mono-olefins are also observed for the three diolefins studied.

As shown in Table 4, $t_0 = 0$ or is very small for most dichloro complexes. The variation observed for dialkyl complexes follows the order p-MeC$_6$H$_4$ < CH$_2$PPh$_2$ < Me for titanium complexes and Me < CH$_2$PPh$_2$ for zirconium complexes.

The values of AFH, as shown in Table 6, are gener-

TABLE 6. Average frequency of hydrogenation and percentage conversion of 1,3- and 1,5-cyclooctadiene with metallocene (M = Ti or Zr) complexes (P_{H_2} = 7 bar; T = 90°C: [catalyst] ≈ 10^{-3} M: [olefin]/[catalyst] = 300–500)

Catalyst	1,3-Cyclooctadiene		1,5-Cyclooctadiene	
	AFH (min^{-1})	Conversion (%)	AFH (min^{-1})	Conversion (%)
1g	(2 ×) 80	100 (COA)	(2 ×) 62	100 (COA)
2a–Mg [a,b]	(2 ×) 15	100 (COA)	(2 ×) 22	100 (COA)
2b	(2 ×) 50	100 (COA)	(2 ×) 33	100 (COA)
2d	(2 ×) 56	100 (COA)	(2 ×) 56	100 (COA)
2g	(2 ×) 100	100 (COA)	(2 ×) 71	100 (COA)
3a–Mg [a]	(2 ×) 10	100 (COA)	(2 ×) 20	100 (COA)
3b	(2 ×) 55	100 (COA)	(2 ×) 35	100 (COA)
3d	(2 ×) 71	100 (COA)	(2 ×) 78	100 (COA)
4a [a]	(2 ×) 9	100 (COA)	(2 ×) 16	100 (COA)
4b	(2 ×) 50	100 (COA)	(2 ×) 50	100 (COA)
4d	D	0	D	0
2'a–Mg [a]	133	(COE)	20	(COE)
	2	100 (COA)	2	100 (COA)
2'b	25	100 (COE)	50	100 (COE)
2'd	20	100 (COE)	NR	0

NR, no reaction; D, decomposition; COA, cyclooctane; COE, cyclooctene.

[a] Previous reduction in the presence of PMePh$_2$.

[b] 0% conversion when previous reduction in the absence of PMePh$_2$.

ally higher for dialkyls than for dichlorides, are higher for titanium than for zirconium and vary with R in the order Me < CH_2PPh_2 < *p*-MeC_6H_4. The AFH values distinguish three types of catalytic system: (a) those that hydrogenate the two double bonds simultaneously, leading to alkane; (b) those able to hydrogenate only one bond, leading to the mono-olefin; (c) those leading to a mixture of the alkane and the mono-olefin, for which two different steps can be distinguished. The AFH values for total hydrogenation of the two double bonds are shown as (2 ×)AFH, to express the number of moles of double bonds hydrogenated per mole of catalyst per minute.

The two cyclic olefins 1,3-cyclooctadiene and 1,5-cyclooctadiene are totally hydrogenated by all the titanium complexes, whereas only **2'a** leaves a part of the mono-olefin and **2'b** hydrogenates selectively only one of the double bonds of both olefins. **2'd** hydrogenates only one bond in 1,3-cyclooctadiene but does not react with 1,5-cyclooctadiene.

The behaviour of complex **2'a** with 1,5-cyclooctadiene is shown in Fig. 1. The hydrogenation of the first double bond (50% total dihydrogen) is faster (AFH, 20 min^{-1}) than that of the second (AFH, 2 min^{-1}). This behaviour is also observed for 1,3-cyclooctadiene, for which the first step is even faster (AFH, 133 min^{-1}) owing to conjugation. The second step has the same value of AFH, as expected for the same olefin.

2-Methyl-butadiene (isoprene) is much more resistant to hydrogenation, although not as much as the linear mono-olefin 4-methyl-2-pentene. As shown in Table 7, most complexes lead to a mixture of 2-methyl-2-butene and 2-methylbutane, which is compatible with a primary 1,4 addition followed by partial hydrogenation of the resulting internal olefin. However, no distinction can be made between the two steps, as noted for the other two cyclic dienes discussed; the pressure of dihydrogen decreases regularly to zero. This means that a simultaneous, probably much slower hydrogenation of the resulting 2-methyl-2-butene takes place but that not all the mono-olefin is hydrogenated. Hence different AFH values cannot be evaluated and the average AFH refers to the total hydrogenation when 100% conversion is obtained. Nevertheless we conclude that all the catalysts produce total hydrogenation to the mono-olefin, but only **1g**, **3b**, **3d** and, unexpectedly, **2'b** are able to produce the second hydrogenation from 2-methyl-2-butene to 2-methylbutane. The reaction with **2'b** is very slow ($t - t_0 = 250$ min) and requires a very long activation time ($t_0 = 60$ min). The least active complexes are **4a**, **4b** and **2a**. It seems that complexes of the type **3** and **4**, containing bridged cyclopentadienyl ligands, are the most active for the second step.

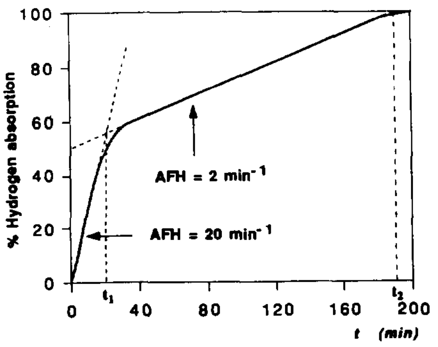


Fig. 1. AFH values for hydrogenation of 1,5-cyclooctadiene (0.4 M) by **2'a**–Mg (10^{-3} M).

TABLE 7. Average frequency of hydrogenation and percentage conversion of 2-methyl butadiene (isoprene) with metallocene (M = Ti or Zr) complexes ($P_{H_2} = 7$ bar: $T = 90°C$: [catalyst] ≈ 10^{-3} M: [olefin]/[catalyst] = 300–500)

Catalyst	AFH (min^{-1})	$(t - t_0)$ (min)	Conversion (%)	Product
1g	(2×)71	7	100	2-Me-butane
2a–Mg [a]		12	62	2-Me-butane
			38	2-Me-2-butene
2b		10	80	2-Me-butane
			20	2-Me-2-butene
2d		5	92	2-Me-butane
			8	2-Me-2-butene
2g		5	87	2-Me-butane
			13	2-Me-2-butene
3a–Mg [a]		18	86	2-Me-butane
			14	2-Me-2-butene
3b	(2×)30	17	100	2-Me-butane
3d	(2×)40	12	100	2-Me-butane
4a–Mg [a]		17	53	2-Me-butane
			47	2-Me-2-butene
4b		12	50	2-Me-butane
			50	2-Me-2-butene
4d		–	D	2-Me-butadiene
2'a–Mg [a]		76	91	2-Me-butane
			8	2-Me-2-butene
2'b	(2×) 2	250	100	2-Me-butane
2'd		550	98	2-Me-butane
			2	2-Me-2-butene

[a] Previous reduction in the presence of $PMePh_2$.

2.8. *Kinetic studies of the hydrogenation of 1-hexene with 2d*

A preliminary study was carried out in order to determine the reaction conditions required for an isothermal process, for which the chemical reaction and not diffusion of dihydrogen into the solution is the controlling step. Several experiments (operating with scrupulous maintenance of anaerobic conditions) al-

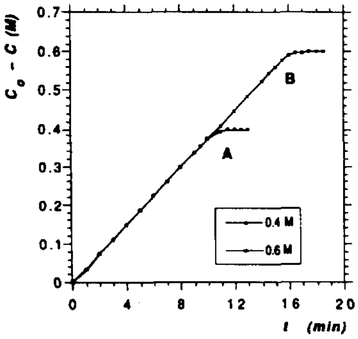


Fig. 2. Hydrogenation of 1-hexene catalysed by **2d** ($P(H_2) = 1$ bar (0.987 atm); $T = 62°C$; [catalyst] $= 5 \cdot 10^{-4}$ M). Olefin concentration as a function of time: curve A, $[1\text{-hexene}]_0 = 0.4$ M; curve B, $[1\text{-hexene}]_0 = 0.6$ M.

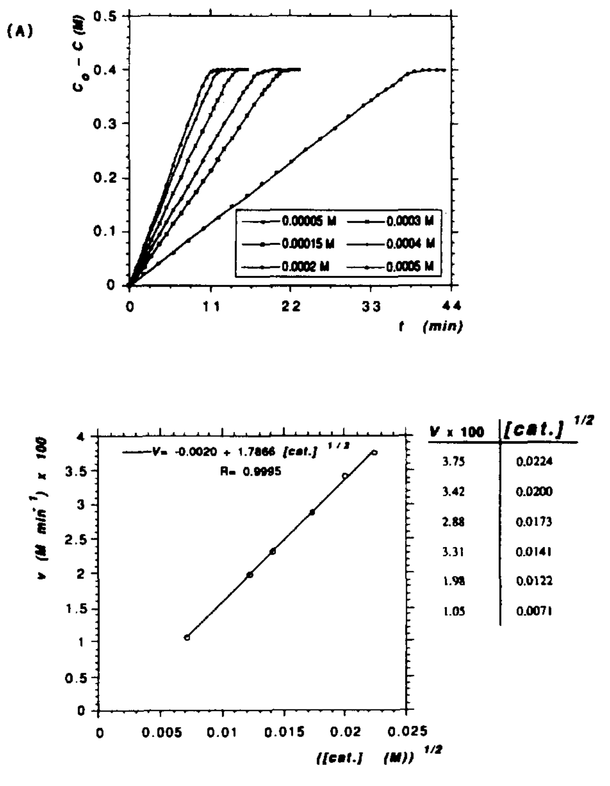
lowed the conditions for which the rate of dihydrogen uptake was not mass transport limited [30] to be determined. No activation time was required when the reaction was carried out in sunlight at dihydrogen pressures lower than 3 bar. For these reasons, the conditions used were as follows: $T = 62°C$; $P_{H_2} = 0.5$–2 bar; stirring speed, 1200 rev min^{-1}; [catalyst] $= 0.5$–5×10^{-4} M; [olefin] less than 0.6 M.

Under these conditions, the linear variation in the concentration of 1-hexene with time (Fig. 2) is exactly the same regardless of the initial amount of olefin used, and therefore the rate of reaction is independent of olefin concentration (zero order). Figure 3(a) shows representative plots of the variation in 1-hexene concentration with time for different catalyst concentrations; least-squares analysis of these data (Fig. 3(b)) leads to an order of reaction of one half in catalyst concentration. The similar plots and least-squares analyses in Fig. 4 for different dihydrogen pressures show a three-halves order of reaction in dihydrogen pressure. The rate constant is $k = 1.74$ atm$^{-3/2}$ min^{-1}. Therefore the rate law reduces to the following equation:

$$v_{1\text{-hexene}} = 1.74[\text{catalyst}]^{1/2} P_{H_2}{}^{3/2} \text{ M min}^{-1}$$

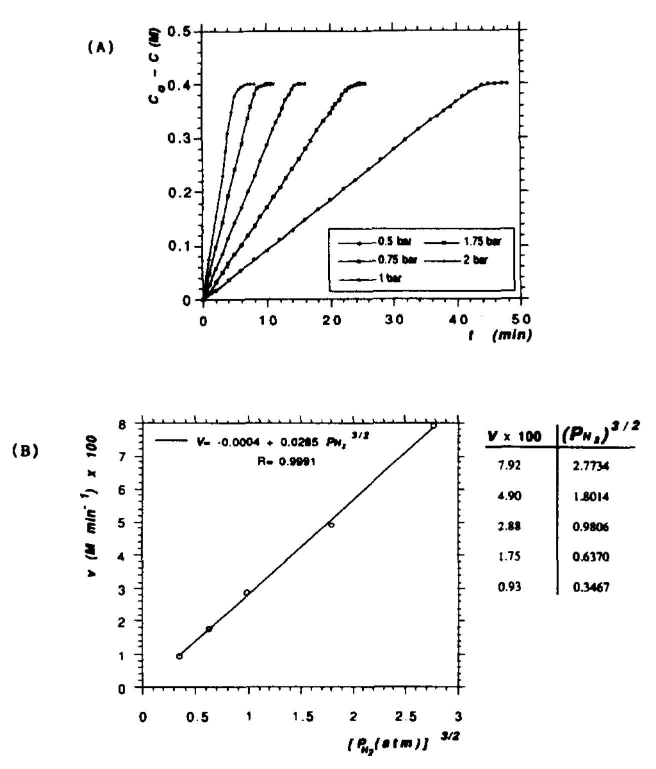
For comparison, we found that $v_{1\text{-hexene}} = 2.88 \times 10^{-2}$ M min^{-1} for [catalyst] $= 3 \times 10^{-4}$ M, $T = 62°C$ and $P_{H_2} = 1$ bar, corresponding to a turn-over frequency $N_t = 5760$ h^{-1}.

Several mechanistic studies on catalytic hydrogenation of olefins by metallocene complexes of the early transition metals have been reported [31]. For lanthanide complexes with dinuclear $M(\mu\text{-H})_2M$ struc-



V x 100	[cat.]$^{1/2}$
3.75	0.0224
3.42	0.0200
2.88	0.0173
3.31	0.0141
1.98	0.0122
1.05	0.0071

Fig. 3. Hydrogenation of 1-hexene catalysed by **2d** ($P(H_2) = 1$ bar (0.987 atm); $T = 62°C$; $[1\text{-hexene}]_0 = 0.4$ M). (A) Olefin concentration as a function of time for different catalyst concentrations. (B) Rate of hydrogenation as a function of catalyst concentration.



V x 100	$(P_{H_2})^{3/2}$
7.92	2.7734
4.90	1.8014
2.88	0.9806
1.75	0.6370
0.93	0.3467

Fig. 4. Hydrogenation of 1-hexene catalysed by **2d** ($T = 62°C$; $[1\text{-hexene}]_0 = 0.4$ M; [catalyst] $= 3 \cdot 10^{-4}$ M). (A) Olefin concentration as a function of time for different hydrogen pressures. (B) Rate of hydrogenation as a function of hydrogen pressure.

tures, one-half orders of reaction in catalyst were observed. The rate law found for hydrogenation of 1-hexene by the titanocene complex **2d** under the conditions described above suggests that the process is not a simple reaction and seems to take place in several steps. The kinetic order in the catalyst reflects the fact that the rate-limiting step involves a reaction in which dissociation of a dimer, perhaps a dinuclear μ-hydride dialkyl complex, takes place with simultaneous hydrogenolysis of both titanium–carbon bonds. Further experiments are necessary to define the catalytic active species better.

3. Experimental details

All operations were carried out under rigorously anhydrous and anaerobic conditions under argon, using Schlenk techniques. Diethyl ether and THF were distilled from sodium–benzophenone. Cyclohexane was distilled from sodium after refluxing for more than 24 h under argon. 1-Hexene (Aldrich) was distilled from KOH. 4-Methyl-2-pentene (Phillips Petroleum Co.) was dried over $CaCl_2$ and was then distilled from CaH_2. Cyclohexene (Aldrich) was passed through an alumina column and then distilled from sodium. Styrene (Repsol Química, 30% solution in cyclohexane) was dried by passing through alumina and molecular sieves columns. Isoprene (Fluka) was distilled from sodium. 1,3-Cyclooctadiene (Aldrich) was distilled from P_2O_5 after refluxing for 24 h under argon. 1,5-Cyclooctadiene (Aldrich) was dried by passing through an alumina column. TlOEt was purchased from Aldrich. Li(*p*-MePh) [32], $LiCH_2PPh_2 \cdot TMEDA$ [33], $C_5H_5CH_2CH_2PPh_2$ [34], $[Ti(\eta^5\text{-}C_5Me_5)Cl_3]$ [35], and titanium and zirconium metallocenes were prepared as described in the literature. IR spectra were recorded (4000–200 cm^{-1}) in solution or as Nujol mulls between polyethylene films on a Perkin–Elmer 583 spectrophotometer. ^1H, $^{13}C\{^1H\}$ and ^{31}P nuclear magnetic resonance (NMR) spectra were measured on a Varian Unix 300 MHz instrument. Chemical shifts are in parts per million (positive chemical shifts to a higher frequency) relative to tetramethylsilane (TMS) and phosphoric acid (H_3PO_4). C and H analyses were carried out on a Perkin–Elmer 240B microanalyser.

3.1. Preparation of $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)(p\text{-}MeC_6H_4)_2]$ *(2g)*

A solution of Li(*p*-MePh) (1.93 g, 19.75 mmol) in toluene was added to a solution of $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Cl_2]$ (3 g, 9.40 mmol) in toluene at −78°C. The reaction mixture was warmed slowly, with stirring, to room temperature. After filtration the solvent was removed under vacuum to give a red oil, which was extracted with hexane. The resulting solution was cooled to −78°C to yield **2g** as a red crystalline solid (yield, 3.20 g (78%)).

Anal. Found: C, 80.91; H, 8.10. $C_{29}H_{34}Ti$ calc.: C, 80.95; H, 7.91%. ^1H NMR (C_6D_6, 25°C, 300 MHz): δ 1.50 (s, 15H, C_5Me_5), 2.24 (s, 6H, CH_3–Ph), 5.76 (s, 5H, C_5H_5), 6.90–6.98 (m, 8H, Ph) ppm. ^{13}C NMR (C_6D_6, 25°C, 75 MHz): δ 13.12 ($C_5\mathit{Me}_5$), 21.12 ($\mathit{C}H_3$–Ph), 116.49 (C_5H_5), 123.82 (C_5Me_5), 127–136 (C_{o-p}, Ph), 192.47 (C_{ipso}, Ph) ppm.

3.2. Preparation of $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Cl(CH_2PPh_2)]$ *(2j)*

To a solution of $[Ti(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Me_5)Cl_2]$ (2.49 g, 7.82 mmol) in toluene (100 ml), was added dropwise a solution of $LiCH_2PPh_2 \cdot TMEDA$ (2.52 g, 7.82 mmol) in THF at −78°C. The reaction mixture was warmed to room temperature and then stirred for 3 h. After filtration and evaporation of the solvent to dryness a red solid was obtained. Recrystallization from toluene–hexane at −30°C gave **2j** as a microcrystalline red product (yield, 2.3 g (60%)).

Anal. Found: C, 70.05; H, 6.82. $C_{28}H_{32}ClPTi$ calc.: C, 69.66; H, 6.63%. ^1H NMR (C_6D_6, 25°C, 300 MHz): δ 1.35 (1H, CH_2–P, ^2J(H–H) = 10.8 Hz, ^2J(H–P) < 1 Hz); 1.65 (s, 15H, C_5Me_5); 2.47 (1H, CH_2–P, ^2J(H–H) = 10.8 Hz, ^2J(H–P) = 5.5 Hz); 5.88 (s, 5H, C_5H_5); 6.95–7.62 (Ph) ppm. ^{13}C NMR (C_6D_6, 25°C, 75 MHz): δ 12.82 (d, $C_5\mathit{Me}_5$, ^4J(C–P) = 2.0 Hz); 59.41 (d, CH_2–P, ^1J(C–P) = 54.9 Hz); 116.59 (d, C_5H_5, ^3J(C–P) = 4.0 Hz); 125.05 (C_5Me_5), 128.5–148 (Ph) ppm.

3.3. Preparation of $[Ti\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}(CH_2PPh_2)_2]$ *(3d)*

To a solution of $[Ti\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}Cl_2]$ (1.36 g, 4.49 mmol) in toluene (100 ml), solid $LiCH_2PPh_2 \cdot TMEDA$ (3.04 g, 9.43 mmol) was added at −78°C. The reaction mixture was warmed slowly with stirring, to room temperature. After filtration, the solution was concentrated to 20 ml and was cooled to −25°C to yield a yellow solid. Recrystallization from toluene–hexane, at −25°C, gave **3d** as a microcrystalline solid (yield, 2.62 g (92%)).

Anal. Found: C, 72.54; H, 6.19. $C_{38}H_{38}P_2SiTi$ calc.: C, 72.19; H, 6.02%. ^1H NMR (C_6D_6, 25°C, 300 MHz): δ −0.01 (s, 6H, $SiMe_2$); 1.88 (d, 4H, CH_2–P, ^2J(P–H) = 3.2 Hz); 5.02 (t, 4H, C_5H_4); 7.02–7.09 (m, 12H, Ph); 7.29 (t, 4H, C_5H_4); 7.43–7.47 (2t, 8H, Ph) ppm. ^{13}C NMR (C_6D_6, 25°C, 75 MHz): δ −5.90 ($SiMe_2$); 59.80 (d, CH_2–P, ^1J(C–P) = 46.0 Hz); 102.58 (C_1, C_5H_4); 117.11 ($C_{3,4}$, C_5H_4); 126–133 ($C_{2,5}$, C_5H_4 + C_{o-p}, Ph); 145.34 (C_{ipso}, Ph) ppm.

3.4. Preparation of [Ti(η^5-C_5Me_5)(η^5-$C_5H_4CH_2CH_2PPh_2$)Cl_2] (6a)

To a solution of $C_5H_5CH_2CH_2PPh_2$ (3.43 g, 12.29 mmol) in diethyl ether (50 ml), TlOEt (0.87 ml, 12.29 mmol) was added by syringe at 0°C. A fine pale-yellow precipitate was immediately formed. The reaction mixture was stirred for 3 h to give a brown powder, which was repeatedly washed with diethyl ether and characterized as [$TlC_5H_4CH_2CH_2PPh_2$] (yield, 0.91 g (15%)). Anal. Found: C, 46.73; H, 3.23. $C_{19}H_{18}PTl$ calc.: C, 47.38; H, 3.74%.

To a suspension of [$TlC_5H_4CH_2CH_2PPh_2$] (0.91 g, 1.89 mmol), in toluene (100 ml), solid [Ti(η^5-C_5Me_5)Cl_3] (0.55 g, 1.89 mmol) was added. The reaction mixture was heated under reflux for 10 h. After cooling to room temperature the mixture was filtered and the resulting solution evaporated to dryness to give a red oil. Recrystallization from toluene–hexane at −78°C yielded **6a** as red crystals (yield, 0.91 g (91%)).

Anal. Found: C, 64.96; H, 5.93. $C_{29}H_{33}Cl_2PTi$ calc.: C, 65.55; H, 6.22%. ^1H NMR (C_6D_6, 25°C, 300 MHz): δ 1.71 (s, 15H, C_5Me_5); 2.42 (t, 2H, $C\mathit{H}_2$–CH_2–P, ^3J(H–H) = 8.2 Hz); 3.06 (dt, 2H, CH_2–$C\mathit{H}_2$–P, ^3J(H–H) = 8.2 Hz, ^2J(H–P) = 6.8 Hz); 5.54 (m, 2H, C_5H_4); 5.94 (m, 2H, C_5H_4); 7.02–7.51 (m, Ph) ppm ^{13}C NMR (C_6D_6, 25°C, 75 MHz): δ 13.22 ($C_5\mathit{Me}_5$); 27.45 (d, $\mathit{C}H_2$–CH_2–P); 28.54 (CH_2–$\mathit{C}H_2$–P); 114.85 ($C_{3,4}$, C_5H_4); 122.12 ($C_{2,5}$, C_5H_4); 133.95 (C_1, C_5H_4); 127–140 (Ph) ppm; C_5Me_5 not assigned. ^{13}C NMR ($CDCl_3$, 25°C, 75 MHz): δ 13.06 ($C_5\mathit{Me}_5$); 26.60 (d, $\mathit{C}H_2$–$\mathit{C}H_2$–P); 28.02 (d, CH_2–$\mathit{C}H_2$–P); 115.13 ($C_{3,4}$, C_5H_4); 121.68 ($C_{2,5}$, C_5H_4); 129.16 (C_5Me_5); 130.52 (C_1, C_5H_4), 128–138 (Ph) ppm.

3.5. Hydrogenation of olefins (General procedure)

The hydrogenation reactions were carried out in a 250 ml glass–metal–Teflon grease-free Büchi glass BEP-280 type I autoclave, fitted with a thermocouple, a high speed agitator, a water jacket connected to a recirculating pump and a constant-temperature bath for thermal regulation, and manifold stainless steel connections to a high vacuum line, dihydrogen and argon. Dihydrogen was passed through a standard gas purification column before entering the constant-volume reservoir; small pressure changes were measured with a differential electronic manometer and pressure data were recorded on a Chino GL two-pen linear system chart with simultaneous recording of temperature. In a typical procedure the dried reaction vessel was repeatedly purged and then filled with the solution containing 0.20 mmol of the metallocene complex (catalyst), 60–100 mmol of the appropriate olefin and solvent up to the 200 ml level marked on the vessel. After evacuation of the argon, the autoclave was heated to the desired temperature with mechanical stirring and dihydrogen was introduced up to 8–9 bar into the reservoir connecting the different measurement units and allowing the system to reach equilibrium (10–15 min). When the dihydrogen valve was carefully opened, a decrease in pressure was registered and the new pressure, temperature and time were reckoned as the starting conditions, until the absorption of hydrogen starts (t_0) to be recorded. The experiment was continued until the pressure became constant (t). The final mixture was analysed by gas chromatography on a Perkin–Elmer Sigma chromatograph to determine the yields and conversions.

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