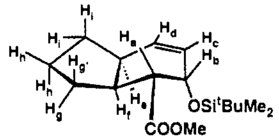
oxybicyclo[4.3.0]non-4-ene (25). A solution of the triene **24** (13 mg, 0.042 mmol) in toluene (1 mL) was stirred at 170 °C for 4 days in Pyrex sealed tube. After the solution was cooled to 23 °C, the solvent was removed. The residue was purified by silica gel flash chromatography (ether–hexane, 1:80) to give the adduct **25** (10.3 mg, 79%) as a colorless oil: ^{1}H NMR (270 MHz, CDCl$_3$) δ 0.00 (s, 3 H), 0.02 (s, 3 H), 0.83 (s, 9 H), 1.06–1.25 (m, 1 H, H$_i$), 1.30 (dddd, $J_{g'g}$ = 14.0, $J_{g'f}$ = 4.0, $J_{g'h}$ = 6.9, $J_{g'h}$ = 6.9 Hz, 1 H, H$_{g'}$), 1.42–1.73 (m, 2 H, H$_h$), 1.82–1.92 (m, 1 H, H$_i$), 2.08 (dddd, $J_{gg'}$ = 14.0, J_{gf} = 8.1, J_{gh} = 8.1, J_{gh} = 4.8 Hz, 1 H, H$_g$), 2.37 (dd, J_{af} = 11.5, J_{ab} = 3.7 Hz, 1 H, H$_a$), 2.42–2.54 (m, 1 H, H$_e$), 2.67 (dddd, J_{fa} = 11.5, J_{fg} = 8.1, J_{fe} = 8.1, $J_{fg'}$ = 4.0 Hz, 1 H, H$_f$), 3.67 (s, 3 H), 4.38 (dd, J_{bc} = 5.1, J_{ba} = 3.7 Hz, 1 H, H$_b$), 5.73 (ddd, J_{cd} = 9.9, J_{cb} = 5.1, J_{ce} = 1.8 Hz, 1 H, H$_c$), 5.88 (dd, J_{dc} = 9.9, J_{de} = 4.0 Hz, 1 H, H$_d$); NOE H$_a$→H$_i$ (3%), H$_a$→H$_b$ (7%), H$_a$→H$_g$ (3%), H$_f$→H$_e$ (2%), H$_f$→H$_g$ (4%); IR (neat) 1750, 1730, 1650 cm^{-1}; MS *m/z* 310 (M$^+$), 309, 295, 279, 253 (M$^+$ – ^{t}Bu, base beak), 89; HR-MS (M$^+$ – H) calcd for C$_{17}$H$_{29}$O$_3$Si 309.1886, found 309.1904. The most stable conformer suggested by Allinger's MM$_2$ (85) calculations is as follows.



Enantioselective Hydrogenation of Olefins with Homogeneous Ziegler–Natta Catalysts[†]

R. Waymouth*[,1] **and P. Pino***[,2]

Contribution from the Institute fur Polymere, Swiss Federal Institute of Technology, 8092 Zurich, Switzerland, and the Department of Chemistry, Stanford University, Stanford, California 94305.

Received November 10, 1989

Abstract: Styrene, 2-methyl-1-pentene, 2-phenyl-1-butene, and *cis*- and *trans*-2-hexene have been hydrogenated in the presence of catalysts derived from [Al(CH$_3$)-O]$_n$ and (–)-[ethylenebis(4,5,6,7-tetrahydro-1(*R*)-indenyl)]zirconium derivatives. α-Olefins are readily polymerized with this catalytic system; in the presence of hydrogen, hydrogenated monomers can be obtained depending on the hydrogen pressure. Terminal olefins substituted in the 2- or 3-positions and internal olefins are not polymerized but undergo hydrogenation. Styrene is hydrogenated at 12 turnovers/min at 20 atm of H$_2$ at 25 °C with this catalytic system. The catalytic deuteriation of styrene with [(–)-(EBTHI)ZrX, X = (*R*)-1,1′-bi-2-naphtholate] **2** yields (–)-(*R*)-1,2-dideuterioethylbenzene in 93% yield with an optical purity of 65%, indicating that the (Re) enantioface of styrene is deuterated preferentially. This is the opposite enantioface selectivity as observed in propylene oligomerization with the same catalytic system. In the presence of **2**, 2-phenyl-1-butene is hydrogenated to give (–)-(*R*)-2-phenylbutane in 95% yield with an optical purity of 36%. These results are discussed on the basis of a simple stereochemical model for the transition state of the olefin insertion step.

Although olefin hydrogenation in the presence of homogeneous Ziegler–Natta catalysts has been known since the early sixties,[3] up to now no reports have appeared on the use of these catalysts in enantioselective hydrogenation reactions,[4] primarily due to the lack of chiral transition metal species, which show the appropriate stereoselectivity and catalytic activity. A key breakthrough was the development by Brintzinger and co-workers of chiral group 4 metallocenes,[5,6] which were shown to be important components of homogeneous stereospecific polymerization catalysts.[7,8,9]

We became interested in olefin hydrogenation with these catalyst systems during our investigations on the asymmetric hydrooligomerization of propylene in the presence of the chiral homogeneous Ziegler–Natta system ethylenebis(tetrahydro-1-indenyl)zirconocene/aluminoxane.[9] In view of both large substrate selectivity and remarkably high stereospecificities of these catalysts in polymerization reactions of α-olefins, we investigated the activity of these systems for enantioselective hydrogenation reactions.

In this paper, we report our investigations on the chemoselectivity of these catalysts in the hydrogenation of olefins and the enantioselectivity in the hydrogenation of 1,1-disubstituted olefins and in the deuteriation of α-olefins. Besides the potential synthetic significance, these studies have provided key information on the origin of stereocontrol in hydrogenation and polymerization reactions with these catalyst systems.

Results

Dependence on Catalyst Precursor. We had previously observed that catalysts derived from zirconocene dichloride precursors exhibit a different response to hydrogen than catalysts derived from zirconocene dimethyl precursors.[9b] Therefore, we investigated the hydrogenation activity of these catalysts as a function of the

Table I. Hydrogenation of Styrene as a Function of the Zirconium Catalyst Precursor

catalyst precursor^a	[cat], ×10^3 M	Al/Zr	[olefin], M	gas	P_0, atm	yield, %
1	1.5	112	1.39	H$_2$	20	93
2	1.5	172	1.47	D$_2$	17.5	89
3	1.5	119	1.38	H$_2$	20	0

^{a} [Ethylenebis(tetrahydro-1-indenyl)dimethylzirconium (**1**); (–)-[ethylenebis(tetrahydro-1(*R*)-indenyl)]zirconium (*R*)-binaphtholate (**2**), [α]$^{25}_{436}$ 1761 (*c* = 1.1 mg/mL in CHCl$_3$); [ethylenebis(tetrahydro-1-indenyl)]zirconium dichloride (**3**).

[†] This paper is dedicated to the memory of Professor Piero Pino.

[1] Department of Chemistry, Stanford University. Author to whom correspondence should be addressed.

[2] Deceased July 9, 1989.

[3] Sloan, M. F.; Matlack, A. S.; Breslow, D. S. *J. Am. Chem. Soc.* **1963**, *85*, 4012.

[4] For previous studies on enantioselective hydrogenation reactions in the presence of chiral group 4 metallocenes see—Ti: (a) Halterman, R. L.; Vollhardt, K. P. C.; Welker, M. E.; Blaser, D.; Boese, R. *J. Am. Chem. Soc.* **1987**, *109*, 8105. (b) Halterman, R. L.; Vollhardt, K. P. C. *Organometallics* **1988**, *7*, 883. (c) Halterman, R. L.; Vollhardt, K. P. C. *Tetrahedron Lett.* **1986**, *27*, 1461. (d) Paquette, L. A.; McKinney, J. A.; McLaughlin, M. L.; Rheingold, A. L. *Tetrahedron Lett.* **1986**, *27*, 5599. (e) Cesarotti, E.; Ugo, R.; Vitiello, R. *J. Mol. Catal.* **1981**, *12*, 63. Zr: (f) Couturier, S.; Gautheron, B. *J. Organomet. Chem.* **1978**, *157*, C61. Couturier, S.; Tainturier, G.; Gautheron, B. *Ibid.* **1980**, *195*, 291.

[5] Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *232*, 233.

[6] Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 63.

0002-7863/90/1512-4911$02.50/0

Table II. Hydrogenation of Olefins with Homogeneous Ziegler–Natta Systems at 25 °C in Benzene or Toluene

olefin	cat[a]	[cat], $\times 10^3$	Al/Zr	[olefin], M	gas	P_0, atm	conversion	yield,[b] %	TOF[c]
1-decene	1	2.1	56	0.85	H_2	1	100	9	
1-decene	1	0.8	180	0.85	H_2	10	95	28	
1-pentene[d]	1	0.1	390	1.95	D_2	9	100	10	
styrene	1	1.5	112	1.39	H_2	20	94	93	11.5
2-methyl-1-pentene	1	1.5	101	1.30	H_2	20	100	97	
2-phenyl-1-butene	2	1.3	287	0.63	H_2	20	100	95	
cis-2-hexene				0.37			96		
	1	2.2	252		H_2	1		50[e]	
trans-2-hexene				0.37			4		
trans-stilbene	1	1.7	112	0.73	H_2	20	0	0	

[a] 1 = [ethylenebis(tetrahydroindenyl)]dimethylzirconium; 2 = (−)-[ethylenebis(tetrahydro-1(*R*)-indenyl)]zirconium (*R*)-binaphtholate. [b] Yield of hydrogenated monomer. [c] In mol olefin/mol catalyst/min. [d] Reference 10. [e] Calculated from total initial moles of hexenes.

zirconium catalyst precursor. For these studies, the hydrogenation of styrene (vide infra) was used as a test reaction. In Table I we compare the activity of catalysts prepared from [ethylenebis(tetrahydro-1-indenyl)]dimethylzirconium (**1**), (−)-[ethylenebis(tetrahydro-1(*R*)-indenyl)]zirconium (*R*)-binaphtholate (**2**) ($[\alpha]^{25}{}_{436}$ −1761 (c = 1.1 mg/mL in $CHCl_3$)), and [ethylenebis(tetrahydro-1-indenyl)]zirconium dichloride (**3**) and methyl aluminoxane. From the table it can be seen that the dimethyl and the binaphtholate derivatives (**1** and **2**, respectively) yield active catalysts for the hydrogenation of styrene, while the dichloride derivative **3** does not. The competence of the catalyst mixture prepared from the dichloride **3** was tested by introducing ethylene into the reactor after 2 h (no decrease in hydrogen pressure was observed in this time). The polymerization of ethylene was taken as evidence that the catalyst was not adventitiously poisoned or inactive. Thus, under these conditions, the catalyst derived from the dichloride precursor is *inactive* for styrene hydrogenation.

Chemoselectivity, Substrate Selectivity. The goal of these studies was to determine the factors that govern the selectivity of this catalyst system for hydrogenation versus polymerization and to establish the substrate selectivity of various olefins with different substituents and geometries.

Presented in Table II are results on the hydrogenation chemoselectivity and catalytic activity for various olefins. As seen in the table, 1-decene and 1-pentene[10] are competitively hydrogenated and polymerized. As might be expected, the selectivity for hydrogenation of 1-decene increases as the hydrogen pressure is increased. In contrast, terminal olefins substituted in the 2-position, styrene and internal olefins do not polymerize under these conditions but are selectively hydrogenated. Styrene, 2-methyl-1-pentene, and 2-phenyl-1-butene are hydrogenated in yields of 93–97%. NMR and GC–mass spectroscopy of the dideuterioethylbenzene obtained in the deuteration of styrene gave no evidence for mono- or trideuteriated species.

The hydrogenation of internal olefins depends on the substituents as well as the geometry. A competition experiment between *cis*- and *trans*-2-hexenes at 1 atm of hydrogen with **1** as the catalyst precursor revealed that *cis*-2-hexene is consumed much faster than the *trans*-2-hexene; after 1 h under these conditions, 96% of the cis olefin was consumed and only 4% of the trans (Table II). *trans*-Stilbene was not hydrogenated with **1** as the catalyst precursor after 2 h at 20 atm H_2; however, ethylene polymerized rapidly when introduced into the reactor after 2 h.

Table III. Enantioselective Deuteration and Hydrogenation of Olefins at 25 °C with (−)-[Ethylenebis(tetrahydro-1(*R*)-indenyl)]zirconium (*R*)-Binaphtholate (**2**)

olefin	cat	gas	P_0, atm	yield, %	ee, %	abs config
1-pentene[a]	2	D_2	9	10	23	(+)-(*R*)
styrene	2	D_2	17.5	61	65	(−)-(*R*)
2-phenyl-1-butene	2	H_2	17.5	95	36	(−)-(*R*)

[a] Data from ref 10.

Enantioselective Hydrogenation and Deuteration of Olefins. Resolution of the racemic ansa-metallocene derivatives can be carried out by preparing the binaphtholate derivatives.[5] As we had observed that the binaphtholate complexes afforded active hydrogenation catalysts, our studies were carried out with **2** as the catalyst precursor.[11] This compound was greater than 97% pure by NMR and showed a specific optical rotation of $[\alpha]_{436}$ −1761 (c = 1.1 mg/mL in $CHCl_3$). The results of these investigations are summarized in Table III. Included in this table are results from the deuteration of 1-pentene; a full report on the deuteriation and deuteriooligomerization of 1-pentene has been published elsewhere.[10] The sign of the optical rotation of the products indicates that the Re face of 1-pentene and styrene are prevailing deuteriated to give products with (*R*) absolute configuration. Similarly, the hydrogenation of 2-phenyl-1-butene occurs prevailingly on the Si enantioface (the descriptor changes because of the higher CIP priority for the ethyl group) to give (*R*)-2-phenylbutane. The optical purities of the products were determined from the magnitude of the specific optical rotations and range from 23% in the deuteriation of 1-pentene to 65% in the deuteriation of styrene.

Discussion

Dependence on Catalyst Precursor. The homogeneous polymerization system used in these experiments consists of an early transition metal metallocene in the presence of a 100–1000-fold excess of polymeric methyl aluminoxanes in an aromatic solvent.[12] Little is known concerning the interactions between the ill-defined aluminoxanes and early transition metal complexes. Although the nature of the catalytically active species in unknown, model studies by Jordan,[13] Turner,[14] and Eisch[15] implicate the formation of an ion pair of the type $[Cp_2M\text{-}R]^+[X(Al(CH_3)\text{-}O)_n]^-$. According to this model, the nature of the X group initially bound to the metallocene precursor should have little effect on the activity of the catalysts.

---

(7) (a) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. (b) Ewen, J. A.; Haspeslagh, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* **1987**, *109*, 6544. (c) Ewen, J. A.; Jones, R. L.; Razavi, A. *J. Am. Chem. Soc.* **1988**, *110*, 6255.

(8) Kaminsky, W.; Kulper, K.; Brintzinger, H. H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507.

(9) (a) Pino, P.; Cioni, P.; Wei, J. *J. Am. Chem. Soc.* **1987**, *109*, 6189. (b) Pino, P.; Cioni, P.; Galimberti, M.; Wei, J.; Piccolrovazzi, N. In *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Kaminsky, W., Sinn, H., Eds.; Springer-Verlag: New York, 1980; p 269.

(10) Pino, P.; Galimberti, M. *J. Organomet. Chem.* **1989**, *370*, 1.

(11) Studies on the deuteration and deuteriooligomerization of 1-pentene in the presence of both the optically active dimethyl and binaphtholate ethylenebis(tetrahydroindenyl)zirconocene precursors yielded the same enantioface selectivity with similar optical yields,[10] indicating that the binaphtholate ligand has little effect on the stereochemistry of these reactions.

(12) Kaminsky, W.; Luker, H. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 224 and references therein.

(13) (a) Jordan, R. F. *J. Chem. Educ.* **1988**, *65*, 285. (b) Jordan, R. F.; LaPointe, R. E.; Bagjur, C. S.; Echols, S. F.; Willett, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 4111. (c) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410.

(14) (a) Turner, H. W. U.S. Patent 4,752,597, 1988. (b) Hlatky, G. C.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728.

(15) Eisch, J. J.; Pitrowski, A. M.; Brownstein, S. K.; Gabe, E. G.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219.

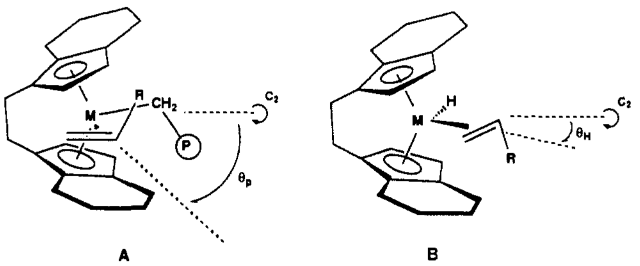


Figure 1. Simplified stereochemical model for the olefin insertion step for polymerization (A) and hydrogenation (B).

In contrast to the above prediction, the results from this study suggest that the activity of the catalytic systems derived from [ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium derivatives ((EBTHI)ZrX_2) for hydrogenation *depends* on the nature of X. In the presence of aluminoxane, both the dimethyl (**1**) and the binaphtholate (**2**) precursors are active for the hydrogenation of styrene; the dichloride precursor (**3**) is inactive. This result clearly demonstrates that different catalysts are produced depending on the nature of the X group of the metallocene precursor.[16,17] The origin of this difference is not clear. It may be that in the putative ion pair derived from the dichloride precursors, a bridging chloride between the aluminoxane and the zirconium center moderates the activity of the catalyst.

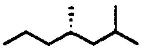
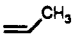
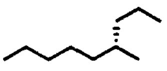
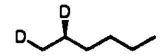
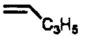
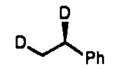
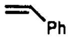
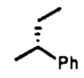
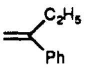
Chemoselectivity, Substrate Selectivity. The use of hydrogen to control the molecular weight of polymers produced with Ziegler–Natta catalysts was intensively investigated by the Natta group.[18] The addition of hydrogen dramatically lowers the average molecular weight of the polymers produced; under certain conditions, low molecular weight oligomers and hydrogenated monomers can be obtained.

For homogeneous Ziegler–Natta catalysts described, the chemoselectivity for hydrogenation depends on the structure and substitution pattern of the olefin as well as the hydrogen pressure. Linear α-olefins are competitively polymerized and hydrogenated; the selectivity for hydrogenation increases as the hydrogen pressure is increased. Qualitatively, the selectivity for hydrogenation also increases as the chain length of the α-olefin is increased (compare 1-decene and 1-pentene in Table II).

In our previous studies, we had observed that styrene and olefins substituted in the 3-position were not polymerized with these homogeneous polymerization catalyst systems.[19] On the basis of other indications in our laboratories, we had anticipated that these olefins might be hydrogenated. In fact, as shown in Table II, styrene and olefins substituted in the 2-position, such as 2-methyl-1-pentene and 2-phenyl-1-butene, do not polymerize but are readily hydrogenated with these catalyst systems. Internal olefins are also hydrogenated, and for isomeric 2-hexenes the cis olefin is hydrogenated more rapidly than the trans.

Enantioselective Hydrogenation and Deuteration of Olefins. One of the most remarkable results of these studies is the observation that *the enantioface which is prevailingly hydrogenated for 1-pentene,*[10] *styrene, and 2-phenyl-1-butene with these catalysts is the opposite of that which is prevailingly polymerized for 1-pentene*[10] *and propene*[9] (Table IV). The presence of the growing chain must be responsible for the opposite topicity of the two reactions.[20] One possibility is that the coordination site for hydrogenation is different than the coordination site for polymerization (Figure 1).[21] For polymerization, the position of the polymer chain is likely to be close to the C_2 axis where the Cp wedge is at its widest, forcing the olefin to approach at a large angle to the C_2 axis (Figure 1A; for clarity, the (*S*,*S*) catalyst is shown). For hydrogenation, because of the smaller size of the hydride, the olefin is free to approach the metal center at smaller angles to the C_2 symmetry axis, which would lead to a reversal in the coordinated enantioface as shown in Figure 1B. This model assumes that olefin coordination is the enantioselective step;[22] other factors may well be important. A complete understanding of this remarkable change in enantioface selectivity must await further study.

Table IV. Enantioface Selectivity for Polymerization and Hydrogenation with (−)-[Ethylenebis(tetrahydro-1(*R*)-indenyl)]zirconium R_2 Derivatives (R = Me, (*R*)-Binaphtholate)

olefin	reaction[a]	prevailing product	preferred enantioface
propene	polym		 CH3
1-pentene	polym		 C3H5
1-pentene	deuter	 D D	 C3H5
styrene	deuter	 D D Ph	 Ph
2-phenyl-1-butene	hydrog	 Ph	 C2H5 Ph

[a] Polymerization = polym; deuteration = deut; hydrogenation = hydrog.

Summary. We have demonstrated that the homogeneous Ziegler–Natta polymerization catalysts derived from group 4 metallocenes and aluminoxane are active olefin hydrogenation catalysts and show remarkable substrate selectivity. α-Olefins are polymerized rapidly; more highly substituted olefins are not polymerized but are hydrogenated. The stereoselectivity for hydrogenation is lower than that of polymerization.[9,10] Not only is the stereoselectivity lower for hydrogenation, but hydrogenation and polymerization occur on *different* enantiofaces with these chiral metallocene catalysts. This is a remarkable result for such a sterically constrained system and underscores the role of the growing polymer chain in stereospecific polymerization reactions.

Experimental Section

All manipulations involving air-sensitive compounds were carried out under nitrogen with standard Schlenk techniques. All solvents were distilled under nitrogen prior to use: toluene and benzene from NaK benzophenone, CH_2Cl_2 from P_2O_5, and ether and pentane from $LiAlH_4$. 1-Decene and 2-methyl-1-pentene (Fluka) were distilled from sodium under nitrogen. Styrene (Fluka) was distilled from CaH_2 under reduced pressure. *cis*- and *trans*-2-hexene (Fluka) were used as received. 2-Phenyl-1-butene was prepared from propiophenone by the method of Cannizzo and Grubbs.[23] [Ethylenebis(tetrahydro-1-indenyl)]dimethylzirconocene (**1**),[24] [ethylenebis(tetrahydro-1(*R*)-indenyl)]zirconocene (*R*)-binaphtholate (**2**)[5] ($[\alpha]_{436}$ −1731 (*c* = 1.1 mg/mL)), [ethylenebis(tetrahydro-1-indenyl)]zirconocene dichloride (**3**),[6] and methylaluminoxane[25] were prepared as described in the literature. All

---

[16] Studies on ethylene polymerization with $Cp_2ZrR_2/(Al(CH_3)\text{-}O\text{-})_n$ revealed different productivities depending on the nature of the R group. Giannetti, E.; Nicoletti, G. M.; Mazzocchi, R. *J. Polym. Sci. Polym. Chem.* **1985**, *23*, 2117.

[17] These results are in contrast to solution XPS studies which suggest that similar catalysts are produced from either metallocene dichlorides or metallocene dialkyls in the presence of aluminoxane. Gassman, P. G.; Callstrom, M. R. *J. Am. Chem. Soc.* **1987**, *109*, 7875.

[18] Natta, G.; Mazzanti, G.; Longi, P.; Bernandini, F. *Chim. Ind.* (*Milan*) **1959**, *41*, 519.

[19] Pino, P.; Rotzinger, B.; von Achenbach, E. In *Catalytic Polymerization of Olefins*; Keii, T., Soga, K., Eds.; Kodanska: Tokyo, 1986; p 461.

[20] For theoretical studies on the origin of stereoselectivity with these catalysts, see: Cavallo, L.; Guerra, G.; Oliva, L.; Vacatello, M.; Corradini, P. *Polym. Commun.* **1989**, *30*, 16 and references therein.

[21] In this model, it is assumed that (1) the catalyst precursor maintains its configuration (*R*,*R*) in the active catalytic complex, (2) the active catalyst is an ion pair[13-15] of the type $[L_2Zr]^+[X(Al(CH_3)\text{-}O)_n]^-$, and (3) the binaphtholate has little influence on the enantioface selectivity.[11]

[22] This may not be a valid assumption, especially in light of studies on enantioselective hydrogenations with rhodium catalysts. (a) Halpern, J.; Landis, C. R. *J. Am. Chem. Soc.* **1987**, *109*, 1746. (b) Brown, J. M.; Chaloner, P. A. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983, Chapter 4.

[23] Cannizzo, J. F.; Grubbs, R. H. *J. Org. Chem.* **1985**, *50*, 2386.

[24] Waymouth, R. M.; Bangerter, F.; Pino, P. *Inorg. Chem.* **1988**, *27*, 758.

Table V. Optical Rotation of 1,2-Dideuterioethylbenzene (c = 0.685 g/mL in Benzene) Obtained with **2** ($[\alpha]^{25}_{436}$ −1236)

α^{20}	λ (nm)	$[\alpha]^{20}$
−0.213	583	−0.311
−0.223	578	−0.325
−0.258	546	−0.377
−0.485	436	−0.708
−0.863	365	−1.256

compounds were greater than 95% pure by NMR analysis versus an internal standard.

Hydrogenation at Atmospheric Pressure with 1: General Procedure. A round-bottomed flask fitted with a gas diffusion tube and an oil bubbler was charged with **1**, evacuated, and placed under an atmosphere of H_2. A solution of aluminoxane, 5 mL of olefin, 1 mL of octane internal standard, and 25 mL of toluene were added, with rapid stirring, to the reaction flask under H_2. Polymerization and hydrogen uptake commenced within 5 min. The extent of reaction was monitored by removing aliquots of the reaction solution, filtering through a plug of alumina, and analyzing by GC (3 mm × 2 m stainless steel column, 25% SF 96, T = 70 °C). The yield of hydrogenated olefin was determined by comparison with standard solutions of authentic samples. For the reaction of 1-decene, poly- and oligodecenes (1.7 g) were isolated as a viscous, cloudy oil but were not further characterized.

Hydrogenation at Elevated Pressure: General Procedure. These reactions were carried out in an 80-mL stainless steel autoclave fitted with a pressure gauge, a gas inlet valve, and a valve connected to a hose adapter. Samples of the zirconium catalyst precursor were sealed under nitrogen in 5-mL glass ampules and placed in the autoclave along with a small steel nut. The autoclave was evacuated and a solution of the olefin, aluminoxane, and solvent was introduced by suction through a section of tygon tubing. The autoclave was then pressurized with H_2 or D_2 and shaken gently to equilibrate the gases. The reaction was initiated by shaking the autoclave vigorously to break the ampule. The autoclave was agitated at room temperature with a mechanical rocker. The extent of reaction was determined by monitoring the decrease in hydrogen pressure with time. Upon cessation of hydrogen uptake, the contents of the autoclave were poured into a round-bottomed flask and the yields and conversions determined by GC. For measurements of optical rotation, the crude reaction mixture was vacuum transferred and the optical rotation measured in solution, typically at several different concentrations.

A blank reaction was carried out with 1-decene and aluminoxane in toluene. No hydrogenation or polymerization was observed after 4 h at room temperature.

Attempted Hydrogenation of Styrene with 3. Styrene (4.473 g, 42.9 mmol), aluminoxane (326 mg, 5.62 mmol), and benzene (26 mL) were introduced into the autoclave containing 20.1 mg (0.0471 mmol) of **3**. The autoclave was pressurized to 20 atm of H_2, the ampule broken, and the autoclave placed in a mechanical rocker. After 2 h, there was no decrease in H_2 pressure; the autoclave was vented until 5 atm of H_2 remained and 20 atm of ethylene was introduced. Polymerization of ethylene commenced immediately. The autoclave was vented and the reaction solution was filtered to remove the solid polyethylene and analyzed by GC (3 mm × 2 m stainless steel column, 20% SF96, T = 70 °C). GC analysis indicated that there was almost quantitative recovery of styrene; there was no evidence for ethylbenzene. GC analysis at higher temperature (120 °C) revealed several peaks at low concentrations that were presumably oligomers of ethylene.

Enantioselective Deuteration of Styrene with 2. Styrene (10 mL, 87.3 mmol), aluminoxane (526 mg, 9.067 mmol), and benzene (20 mL) were introduced into the autoclave containing 32.7 mg (0.051 mmol) of **2** ($[\alpha]^{25}_{436}$ −1761 (c = 1.1 mg/mL)). The autoclave was pressurized to 17.5 atm of D_2. After 1 h, the pressure had decreased to 2 atm; the autoclave was repressurized to 17 atm and after an additional 28 h the pressure had decreased to 9 atm. The autoclave was vented and the crude reaction mixture vacuum transferred to give a solution of (−)-(*R*)-1,2-dideuterioethylbenzene in benzene (61% yield), with a specific optical rotation of $[\alpha]^{25}_{D}$ −0.520 (c = 0.192 g/mL). Concentration and yield of 1,2-dideuterioethylbenzene were determined by GC (50 m fused silica capillary column, T = 100 °C). A similar experiment, carried out with a zirconium catalyst precursor of lower optical purity ($[\alpha]^{25}_{436}$ −1234) yielded (−)-(*S*)-1,2-dideuterioethylbenzene (89% yield) with a specific optical rotation, after rectification, of $[\alpha]^{20}_{D}$ −0.311 (c = 0.685 g/mL in benzene, see Table V). The literature value[26] for (+)-(*S*)-1,2-dideuterioethylbenzene is $[\alpha]^{20}_{D}$ +0.800. NMR (^1H, ^{13}C, DEPT) and GC–mass spectra of this sample gave no evidence of mono- or trideuterated ethylbenzenes.

Enantioselective Hydrogenation of 2-Phenyl-1-butene with 2. 2-Phenyl-1-butene (2 mL, 14 mmol), styrene (0.5 mL, 4.35 mmol, internal standard), aluminoxane (511 mg, 8.81 mmol), and benzene (20 mL) were introduced into the autoclave containing 19.6 mg (0.031 mmol) of **2**. The autoclave was pressurized to 20 atm of H_2 and after 3 h 5 atm of H_2 had been consumed. The autoclave was vented and rinsed with pentane, and the crude reaction solution was filtered through a 5 cm × 3 cm column to silica gel. This solution was rectified to give (−)-(*R*)-2-phenyl-1-butane in 74% yield as a solution containing 12% ethylbenzene and 12% benzene with a specific optical rotation of $[\alpha]_D$ −10.1 (c = 0.71 g/mL); lit.[27] value for (+)-(*S*)-2-phenyl-1-butane: $[\alpha]_D$ +28.4.

Acknowledgment. This work was supported by the "Schweizerischer Nationalfonds zur Forderung der Wissenshaftlichen Forschung". The authors thank W. Businger for assistance in the high-pressure laboratory, F. Bangerter for obtaining the NMR spectra, and M. Galimberti and P. Prada for preparing the aluminoxane.

---

[25] Kaminsky, W.; Hauser, H. German Offen., DE 3 240 383, 1982.

[26] Eisenbaumer, R. L.; Mosher, H. S. *J. Org. Chem.* **1979**, *44*, 600.

[27] Lardicci, L.; Menicagli, R.; Salvadori, P. *Gazz. Chim. Ital.* **1968**, *98*, 738.