New NMR Spectroscopic Probe of the Absolute Stereoselectivity for Metal-Hydride and Metal-Alkyl Additions to the Carbon−Carbon Double Bond. Demonstration with a Single-Component, Isospecific Ziegler−Natta α-Olefin Polymerization Catalyst

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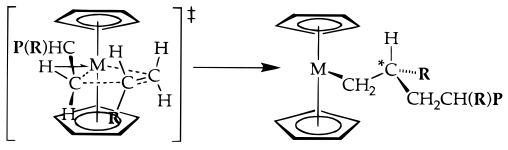
Abstract: Optically active (98% ee) (*R*)-1,1,3,4,4,5,5,5-octadeutero-1-pentene (**1**) was prepared and used to evaluate the stereoselectivity of Y-H and Y-*n*-pentyl additions for the optically pure C_2-symmetric (*R*,*S*)-(BnBp)Y-R/(*S*,*R*)-(BnBp)Y-R and racemic (±)-(BnBp)Y-R isospecific polypropylene catalysts (BnBp = {($OC_{10}H_6C_{10}H_6O$)Si(C_5H_2-2-$SiMe_3$-4-CMe_3)$_2$}). Deuteration and deuterodimerization of **1** mediated by (*R*,*S*)-, (*S*,*R*)-, and (±)-(BnBp)Y-D provide alkanes whose ^{1}H NMR spectra indicate the sense and magnitude of olefin facial selectivity for insertions into metal−hydride and metal−*n*-pentyl bonds. It is shown that useful information concerning the stereochemistry of olefin insertion can be deduced from the ^{2}H NMR spectra of 1-pentene deuterodimers without the requirement of a stereochemically labeled pentene or a resolved catalyst.

Introduction

Ziegler−Natta polymerizations of α-olefins represent some of the most enantioselective processes devised by man. Enantiofacial discriminations in isotactic propylene polymerizations exceeding 99.8% are possible with modified C_2-symmetric *ansa*-zirconocene catalysts.[1] Although syndiospecific systems generally exhibit lower selectivities, *alternating* enantiofacial discrimination exceeding 99% has been achieved for C_s-symmetric metallocene catalyst systems.[2,3] Delineation of the steric and electronic factors responsible for such remarkably selective reactions for prochiral substrates as simple as α-olefins not only would aid in the design of new types of selective polymerization catalysts but also could point the way to new types of asymmetric catalytic reactions of unsaturated substrates.

Since it is clear that α-olefin polymerizations generally operate under kinetic control, it is the chain-propagating (C−C bond forming) step that determines tacticity. There appears to be a growing consensus concerning the structure of the transition state for C−C bond formation with these metallocene catalyst systems; that for the parent (achiral) [(η^5-C_5H_5)$_2$M] system is shown below (P = polymer chain; R = CH_3, alkyl):



The general features common to all metallocene catalysts are (1) a 14-electron, hence doubly coordinatively unsaturated metallocene alkyl (*i.e.,* M = $[Zr^{IV}]^+$, $[Hf^{IV}]^+$, Sc^{III}, Y^{III}, or trivalent lanthanide) to allow for (2) α agostic assistance[4] in C−C bond formation and (3) "1,2" insertion to generate a primary alkyl product with an asymmetric β carbon center. For isospecific polymerizations of propylene with chiral metallocene catalysts, it has been shown that stereoregularity is controlled by the metallocene chirality and not by the asymmetry of the last inserted unit.[4d] While these features are fairly well established, the important stereodirecting interactions that operate in the transition state for a highly stereospecific polymerization system have not yet been fully elucidated.

Of the two most common stereospecific catalyst systems, isospecific and syndiospecific, we have undertaken an investigation of the seemingly simpler isospecific systems in order to evaluate the various interactions that result in enantiofacial discriminations for α-olefin insertion. Defining the diastereomeric transition state structure for a chiral metallocene catalyst system is a formidable challenge. One must both specify the absolute configuration for the metallocene catalyst and establish the enantiofacial preference for olefin insertion. Pino and coworkers reported the first studies of the absolute enantioselectivity with which α-olefins insert into the metal−hydride and metal−alkyl bonds for metallocene Ziegler−Natta polymerization catalysts.[5] Under hydrogen optically pure zirconium complexes of the ethylene *bis*(4,5,6,7-tetrahydroindenyl) (EBTHI) ligand, activated by methylaluminoxane (MAO), convert α-olefins to low molecular weight hydro-oligomers, including hydrogenated monomers. Polarimetric measurements showed that olefin insertions into [(*R*)-(EBTHI)Zr−H]$^+$ and [(*R*)-(EBTHI)Zr−*n*-pentyl]$^+$ bonds proceed from opposite enantiotopic faces of pentene. For example, under D_2 the (*R*)-

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(1) Spaleck, W.; Antberg, M.; Aulbach, M.; Bachman, B.; Dolle, V.; Haftka, S.; Küber, F.; Rohrmann, J.; Winter, A. In *Ziegler Catalysis-Recent Scientific Innovations and Technological Improvements*; Fink, F., Mülhaupt, R., Brintzinger, H. H., Eds.; Springer Verlag: Berlin, Heidelberg, 1995; p 83.

(2) (a) Ewen, J. A. Reference 1, p 99 and references therein. (b) Razavi, A. Reference 1, p 111 and references therein.

(3) Herzog, T. A.; Zubris, D. L.; Bercaw, J. E. *J. Am. Chem. Soc.*, in press.

(4) (a) Piers, W. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 9406. (b) Krauledat, H.; Brintzinger, H. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *102*, 1412. (c) Leclerc, M. K.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1995**, *117*, 1651. (d) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (e) Grubbs, R. H.; Coates, G. W. *Acc. Chem. Res.* **1996**, *29*, 85.

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

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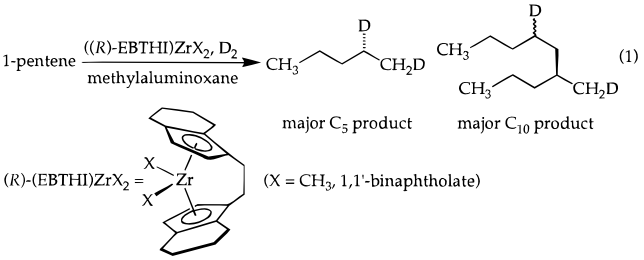
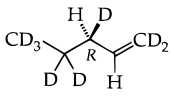
(EBTHI)ZrX_2/MAO catalyst system ($X_2 = (CH_3)_2$ or 1,1′-di-2-naphtholate) gives predominantly (*R*)-1,2-dideuteropentane from 1-pentene, indicating selective Zr-D addition to the *Si* face of the olefin (eq 1). Deuterated 4-methylnonanes of predominant *S* absolute configuration at C-4 were isolated from the same reaction mixtures, indicating attack on the *Re* face of the olefin by a zirconium 1-pentyl complex (eq 1). The precision of these



experiments is limited by (1) persistent H/D exchange leading to C_5H_{12}, $CH_3CH_2CH_2CH_2CH_2D$, and $CH_3CH_2CH_2CHDCH_3$, as well as $CH_3CH_2CH_2CHDCH_2D$, and (2) the very small rotations for the isotopomeric mixtures 0.18° ($X_2 = (CH_3)_2$) and 0.32° (X_2 = 1,1′-di-2-naphtholate), corresponding to ee's of 23% and 35%. Moreover, the hydrodimerization products, 4-methylnonane-d_{0-4}, produced a rotation of only 0.013°, leading the authors to interpret their findings of opposite enantiofacial preference with considerable caution.

Subsequent studies on resolved EBTHI zirconium catalysts also demonstrated *Si*-selective insertions into (*R*)-(EBTHI)Zr−hydrogen bonds and *Re*-selective insertions into (*R*)-(EBTHI)-Zr−alkyl bonds for other olefins.[6] Moreover, Krauledat and Brintzinger interpreted their findings of excess *threo*-6-deuterio-5-methylundecane (*threo*:*erythro* = 2.30 ± 0.03) for the (±)-(EBTHI)$ZrCl_2$/MAO-catalyzed hydrodimerization of (*E*)-1-deutero-1-hexene as resulting from opposite enantioselectivities for insertions into [(EBTHI)Zr−H]$^+$ and [(EBTHI)Zr−*n*-hexyl]$^+$ bonds.[4b]

In view of the very small optical rotations exhibited by such chiral alkane products, we have designed and prepared isotopically chiral olefin **1** as a new probe of the stereoselectivity of

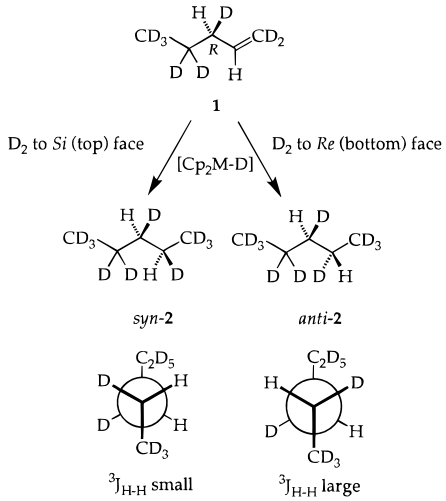


1

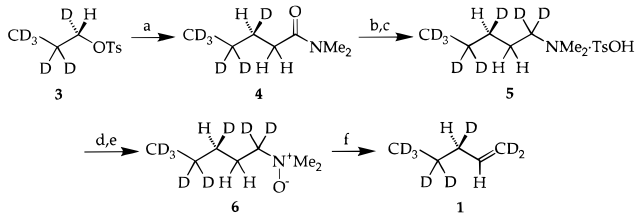
olefin insertion that does not rely on the measurement of optical rotations. Deuteration of **1** gives diastereomeric products that can be distinguished and quantitated using {^{2}H} ^{1}H NMR spectroscopy. Because the absolute configuration of **1** is known, the olefin face utilized for insertion into metal−deuterium bonds can be determined by establishing (via the relative magnitudes of $^3J_{H-H}$) the preferred pentane (**2**) diastereomer (Scheme 1).

Moreover, pentene **1** may be used to probe the enantiofacial preferences for additions of groups other than D_2 (such as M-alkyl) to the carbon−carbon double bond, if the products give rise to sufficiently different ^{1}H chemical shifts or ^{1}H−^{1}H coupling constants.

Scheme 1

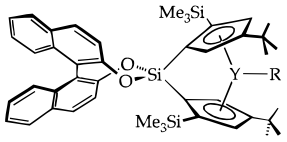


Scheme 2. Preparation of Olefin **1**[a]



[a] (a) CH_2=C(NMe_2)(OLi), THF, CH_3CONMe_2, 55%; (b) $LiAlD_4$, Et_2O; (c) TsOH, Et_2O, 91% from **4**; (d) NaOH; (e) mCPBA, 66% from **5**; (f) 90−135 °C, 83% from **6**.

Described below are some investigations of the deuteration and deuterodimerization of **1** which establish the absolute enantioselectivity of 1-pentene insertions into yttrium−hydrogen and yttrium−*n*-pentyl bonds for some optically pure yttrocene Ziegler−Natta polymerization catalysts developed in our laboratories, *e.g.*[7]



Results and Discussion

Preparation of Isotopically Chiral Pentene. Chiral pentene **1** of 99% optical purity (*vide infra*) was prepared as shown in Scheme 2.

(*S*)-1,2,2,3,3,3-Hexadeutero-1-propanol, conveniently prepared from $CD_3CD_2CD_2OH$ by Simon's enzymatic isotope exchange method,[8] was converted *via* tosylate **3** to *N*,*N*-dimethylvaleramide **4** with inversion. Reduction with $LiAlD_4$ and oxidation[9] to amine oxide **6**, followed by Cope elimination, provided **1** without detectable amounts of 2-pentene isomers. The isolation of ammonium tosylate **5** and amine oxide **6** as recrystallized solids and the solvent free conditions of the Cope

(6) (a) Waymouth, R.; Pino, P. *J. Am. Chem. Soc.* **1990**, *112*, 4911. (b) Pino, P.; Cioni, P.; Wei, J. *J. Am. Chem. Soc.* **1987**, *109*, 6189. (c) 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: Berlin, 1988; p 269. (d) Kaminsky, W.; Bark, A.; Spiehl, R.; Möller-Lindenhof, N; Niedoba, S. *Ibid.* p 291. (e) Kaminsky, W.; Steiger, R. *Polyhedron* **1988**, *7*, 2375. (f) Kaminsky, W.; Ahlers, N.; Möller-Lindenhof, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1216. (g) Pino, P.; Galimberti, M.; Prada, P.; Consiglio, G. *Makromol. Chem.* **1990**, *191*, 1677.

(7) Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. I.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 1045. Note: (*R*,*S*)-BnBp yttrium complexes are those derived from (*R*)-(+)-binaphthol and having *S* metallocene stereochemistry. (*S*,*R*)-BnBp complexes are derived from (*S*)-(−)-binaphthol and have *R* metallocene stereochemistry. (±)-BnBp yttrium complexes, derived from racemic binaphthol, contain exclusively the diastereomers indicated for the resolved complexes.

(8) Günther, H.; Biller, F.; Kellner, M.; Simon, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 146.

(9) Craig, J. C.; Purushothaman, K. K. *J. Org. Chem.* **1970**, *35*, 1721.

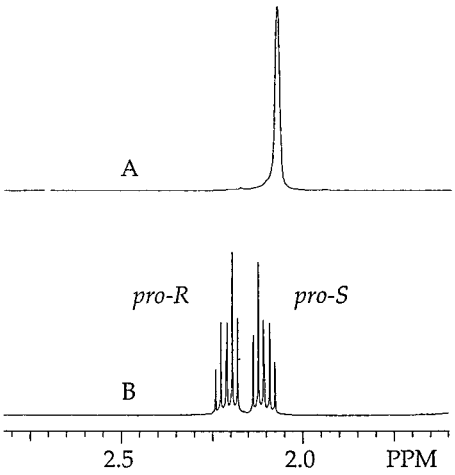
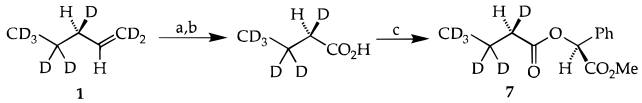


Figure 1. ^{1}H NMR spectra (butyryl α proton region) of esters **7** (A) and **8** (B).

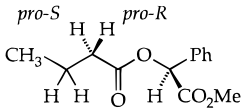
Scheme 3. Degradation and Chiral Derivatization of **1**[a]



[a] (a) $KMnO_4$, $NaIO_4$, K_2CO_3, *t*-C_4H_9OH, H_2O, C_6D_6; (b) $NaHSO_4$, H_2O, 91%; (c) (*S*)-(+)-methyl mandelate, DCC, DMAP, CH_2Cl_2, $CDCl_3$, 65%.

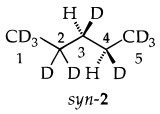
elimination allow the isolation of **1** in high chemical purity (>99% by GC).

Degradation of **1** was carried out to determine its optical purity and to verify its absolute configuration. Oxidative cleavage followed by ester formation with (*S*)-(+)-methyl mandelate provides ester **7** (Scheme 3). Parker has shown that the *pro-S* proton α to the butyryl carboxyl group resonates upfield in the ester **8** derived from (*S*)-(+)-methyl mandelate and unlabeled butyric acid.[10] These portions of the ^{1}H NMR spectra of esters **7** and **8** are shown in Figure 1. The



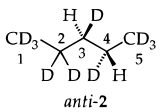
predominance of the upfield ^{1}H butyryl α signal[11] for **7** verifies the absolute stereochemistry of **1** as *R*, consistent with the stereochemistry of the starting hexadeutero-1-propanol and the expected inversion in the formation of **5**. No isotopic exchange was detectable when the oxidative degradation of unlabeled 1-pentene was performed in deuterated media. Thus, the observed integrated intensity ratio is a reasonable estimate of the enantiomer ratio (*ca.* 99:1) for olefin **1**.

Hydrogenation of 1. The hydrogenation of **1** in benzene-d_6 using D_2 was carried out using as catalyst precursors (BnBp)-YCH($SiMe_3$)$_2$ derived from *R*, *S*, and racemic binaphthol. The {^{2}H} ^{1}H NMR spectra of the products are shown in Figure 2. ^{1}H NMR chemical shifts in benzene-d_6 of the two epimeric pentanes are assigned as shown below:



syn-**2**

C-3H: δ 1.15 (d, 1H, $^3J_{HH}$ = 5.6 Hz)
C-4H: δ 1.21 (d, 1H, $^3J_{HH}$ = 5.6 Hz)



anti-**2**

C-3H: δ 1.14 (d, 1H, $^3J_{HH}$ = 9.1 Hz).
C-4H: δ 1.21 (d, 1H, $^3J_{HH}$ = 9.1 Hz).

It is clearly evident that *syn*- and *anti*-**2** are formed with only

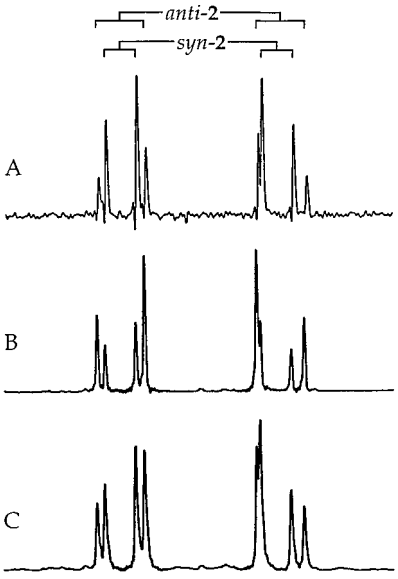
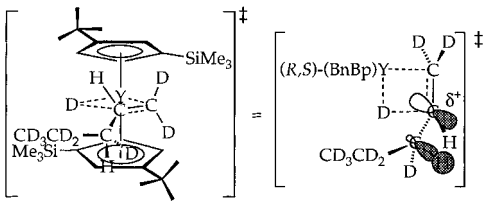


Figure 2. {^{2}H} ^{1}H NMR spectra of pentane diastereomers **2** obtained using (A) (*R*,*S*)-BnBpYCH($SiMe_3$)$_2$, (B) (*S*,*R*)-BnBpYCH($SiMe_3$)$_2$, and (C) (±)-BnBpYCH($SiMe_3$)$_2$ as catalysts precursors.

modest preference by the catalysts derived from (*R*)- and (*S*)-binaphthol, respectively, indicating that the active species (*R*,*S*)-(BnBp)Y-D and(*S*,*R*)-(BnBp)Y-D preferentially utilize the *Si* and *Re* faces of the olefin, respectively, in the hydrogenation.

A small isotope effect favoring the formation of *syn*-**2** observed in the addition of D_2 is readily apparent from the (1.17 ± 0.07):1 mixture of *syn*:*anti* products obtained from racemic (±)-(BnBp)Y-D. We attribute this deviation from 1:1 to a small hyperconjugative kinetic deuterium isotope effect arising from preferential alignment of the allylic C−H (rather than C−D) σ-bonding orbital of **1** parallel to the p orbital at C-2 in the transition structures for olefin insertion.



Previous substituent effects for the rate of the microscopic reverse, β-H elimination, for permethylscandocene phenylethyl complexes revealed a linear free energy correlation with $\rho = -1.9 \pm 0.1$, indicative of substantial positive charge development at the β carbon in the transition state for insertion/β-H elimination.[12] Thus, such a β hyperconjugative isotope effect was not unexpected.

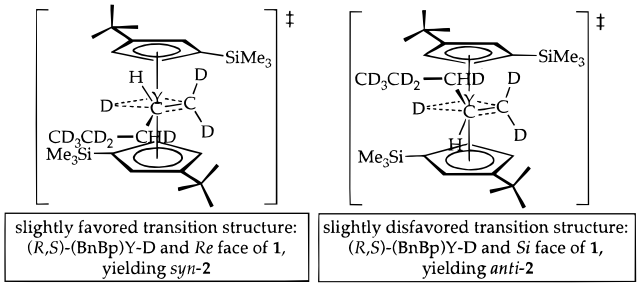
Accordingly, the nonreciprocity of the *syn*:*anti*-**2** ratio for (*R*,*S*)-(BnBp)YD, (2.33 ± 0.21):1, and (*S*,*R*)-(BnBp)YD, 1:(1.78 ± 0.10), may be understood in terms of a dominant steric preference ((2.06 ± 0.23):1 favoring the major isomer for each of the enantiomers of the catalyst, Scheme 4), which is either reinforced or somewhat offset by this smaller hyperconjugative deuterium kinetic isotope effect ((1.15 ± 0.06):1 favoring the *syn* isomer for both enantiomers of the catalyst).

(10) Parker, D. *J. Chem. Soc., Chem. Commun.* **1983**, 83.

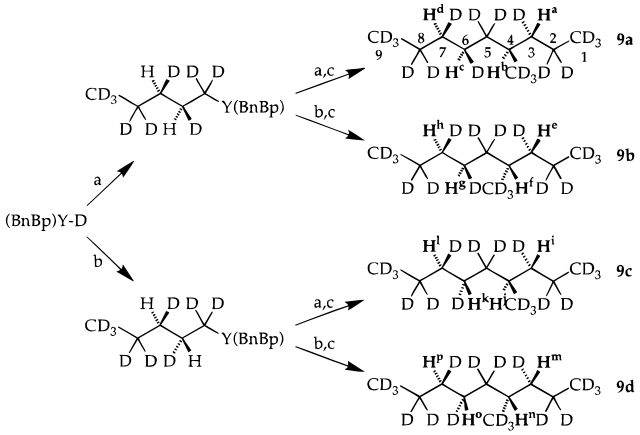
(11) The signal for the *pro-R* protons measured <0.5% of the integrated intensity for the *pro-S* proton signal. Additional signals measuring <0.5% of the intensity for the *pro-S* proton signal are tentatively assigned to molecules with two ^{1}H butyryl α hydrogens.

(12) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566.

Scheme 4



Scheme 5. Deuterodimerization of **1**[a]



[a] (a) **1**, *Si* insertion; (b) **1**, *Re* insertion; (c) D_2.

Deuterodimerization of 1. Stirring neat olefin **1** containing $(BnBp)YCH(SiMe_3)_2$ as catalyst precursor under D_2 (1 atm) produces a mixture of deutero-oligomers from which deuterodimers **9a**−**d** are isolable by preparative gas chromatography (Scheme 5).

Reasoning that the most sensitive indicators of the stereochemistry for insertion of the second equivalent of **1** into the $Y-CD_2CHDCHDCD_2CD_3$ bond of the intermediate to **9** would be the protons at C-3 ($\mathbf{H^a}$ and $\mathbf{H^i}$ *syn* to the CD_3 substituent at C-4; $\mathbf{H^e}$ and $\mathbf{H^m}$ *anti* to the CD_3 substituent at C-4), specifically deuterated 4-methylnonanes were prepared to aid in assigning those chemical shifts. Thus, the chemical shifts of the protons at C-3 and C-4 of deuterodimers **9** were determined by comparison to the ^2H NMR spectra of specifically deuterated 4-methylnonane **10** (Figure 3A), prepared in racemic form by *syn* deuterium addition to olefin **11** (Scheme 6) and **12** (Figure 3B), obtained as a *ca.* 1:1 mixture with **10** by *syn* deuterium addition to an isomeric mixture of olefins **11** and **13** (Scheme 6).

The doublet at 1.20 ppm in the ^1H NMR spectrum of the deuterodimers (principally **9b**,**d**) formed using (*R*,*S*)-(BnBp)-Y-$CH(SiMe_3)_2$ as a catalyst precursor (Figure 3D) indicates that the corresponding C-3 protons, $\mathbf{H^e}$ and $\mathbf{H^m}$, bear *anti* relationships to the CD_3 groups at C-4; a similar ^2H chemical shift is observed for the methylene ^2H resonance, $\boldsymbol{D^b}$, of alkane **10** (δ 1.25, Figure 3A).[13] Since the (*R*,*S*)-(BnBp)Y-D catalyst selectively yields **9b**,**d**, this enantiomer of the catalyst selectively utilizes the *Re* face of the olefin for insertion into the $Y-CD_2CHDCHDCD_2CD_3$ bond. The other ^1H NMR chemical shifts for **9a**−**d**, while tentative, were assigned by correlating the data given in Figure 3C,D with those of Figure 3A,B. Thus, protons labeled $\mathbf{H^f}$ and $\mathbf{H^n}$ (δ 1.32, Scheme 5) are assigned to the so-labeled peaks in the spectrum (Figure 3D) on the basis of the close similarity of their chemical shifts to that for the

(13) Isotopic chemical shifts account for the small differences observed. For example, $\mathbf{H^e}$ and $\mathbf{H^m}$ are attached to carbon atoms adjacent to CD_2 groups, whereas $\mathbf{D^b}$ is attached to carbon atoms adjacent to CH_2 groups.

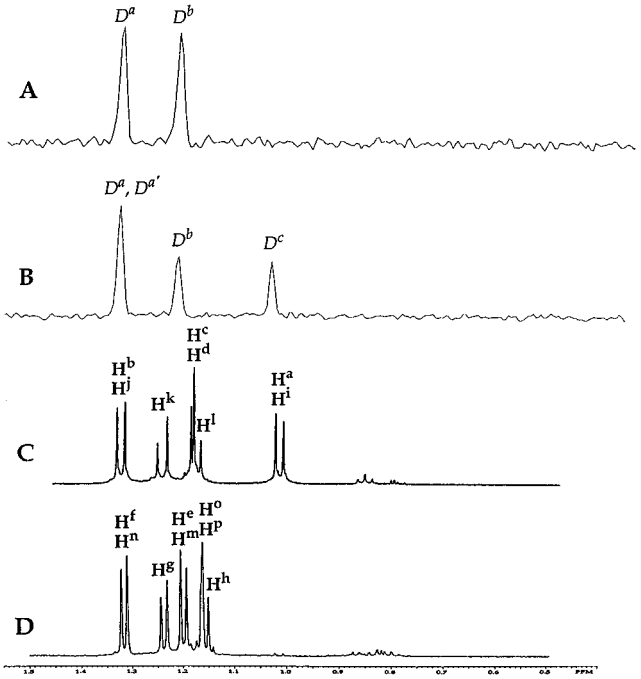
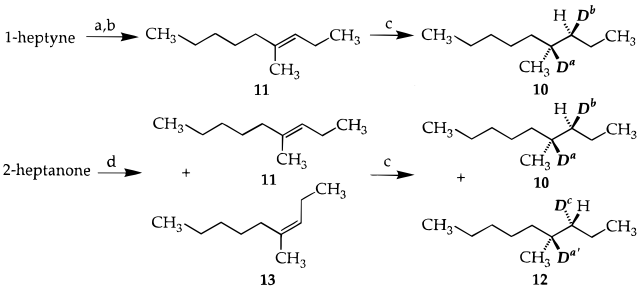


Figure 3. (A) ^2H NMR spectrum of 4-methylnonane-d_2 **10**, (B) ^2H NMR spectrum of a *ca.* 1:1 mixture of 4-methylnonane-d_2 **10** and 4-methylnonane-d_2 **12**, (C) $\{^2H\}$ ^1H NMR spectrum of deuterodimers of **1** (principally **9a**,**c**) obtained using (*S*,*R*)-$BnBpYCH(SiMe_3)_2$ as a precatalyst, and (D) $\{^2H\}$ ^1H NMR spectrum of deuterodimers of **1** (principally **9b**,**9d**) obtained using (*R*,*S*)-$BnBpYCH(SiMe_3)_2$ as a precatalyst. Labels correspond to those shown in Schemes 5 and 6.

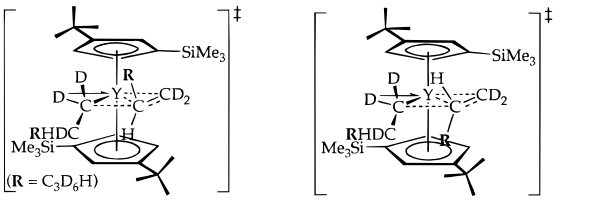
Scheme 6. Preparation of Specifically Deuterated 3-Methylnonanes[a,b]



[a] (a) 1. $AlMe_3$, Cp_2ZrCl_2; 2. I_2; (b) Et_2Zn, $(Ph_3P)_4Pd$, THF; (c) $KO_2CN{=}NCO_2K$, CH_3CO_2D; CH_3OD; (d) $Ph_3P{=}CHCH_2CH_3$, THF. [b] Prepared in racemic forms.

methine ^2H atom ($\boldsymbol{D^a}$) in alkane **10** (δ 1.36). The equal coupling constants ($^3J_{HH}$ = 5.6 Hz) and intensities of the $\mathbf{H^e}$,$\mathbf{H^f}$ and $\mathbf{H^m}$,$\mathbf{H^n}$ sets of peaks verify that we are dealing with the protons on the C-3/C-4 portion of the molecule. The remaining resonances in the ^1H NMR spectrum in Figure 3D derive from the protons attached to C-6 and C-7 and are assigned as follows: insertion of **1** into the Y−D bond of the (*R*,*S*)-(BnBp)Y-D catalyst was found to be selective ((2.33 ± 0.21):1) for the *Si* face of the olefin (*vide supra*), so that the major diastereomer in the mixture should be **9b** (rather than **9d**). The assignments shown for the protons at C-6 (Scheme 5, Figure 3D) are consistent with the relative integration of the signal labeled $\mathbf{H^g}$ to that of the group of peaks labeled $\mathbf{H^h}$ and $\mathbf{H^o}$, $\mathbf{H^p}$. Moreover, $\mathbf{H^h}$ and $\mathbf{H^p}$ should be nearly isochronous because they bear the same stereochemical relationships to the CD_3 groups at C-4 in both isomers. Also note that the intensity and splitting ($^3J_{HH}$ = 5.8 Hz) of the doublet labeled $\mathbf{H^h}$ are the same as those for $\mathbf{H^g}$, consistent with $\mathbf{H^g}$ and $\mathbf{H^h}$ being coupling partners. Evidently, $\mathbf{H^o}$ and $\mathbf{H^p}$ share a coupling constant larger than their difference in chemical shifts, giving rise to an AB quartet (*vide infra*).

Scheme 7

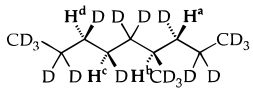


strongly favored transition structure: (*R*,*S*)-(BnBp)Y-*n*-pentyl and *Re* face of **1**

strongly disfavored transition structure: (*R*,*S*)-(BnBp)Y-*n*-pentyl and *Si* face of **1**

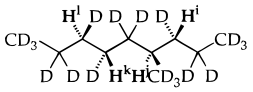
As noted above, deuterodimerization of **1** using (*R*,*S*)-(BnBp)-YCH(SiMe$_3$)$_2$ as a precatalyst results in the formation of hydrodimers **9b**,**d** with high (>95%) stereoselectivity at C-4, indicative of use of the *Re* face of **1** for the second insertion step. The complementary utilization of the *Si* face of the olefin is observed for insertion into the yttrium−carbon bond of the (*S*,*R*)-(BnBp)Y-CD$_2$CHDCHDCD$_2$CD$_3$ intermediate (Figure 3C). The relative intensities of the {^{2}H} ^{1}H NMR resonances for the deuterodimers (principally **9a**,**c**, with [**9c**] ≈ 2[**9a**]) reinforce the tentative assignments made above. Significantly, the doublet at 1.01 ppm ($^3J_{HH}$ = 7.9 Hz) in the ^{1}H NMR spectrum of deuterodimers **9a**,**c** formed when (*S*,*R*)-(BnBp)YCH(SiMe$_3$)$_2$ was used as a precatalyst further confirms that these protons (**H^a** and **H^i**) bear a *syn* relationships to the CD$_3$ groups at C-4; their chemical shift closely approximates that observed for the methylene ^{2}H resonance (***D^c***) of **12** (δ 1.07, Figure 3B).

The ^{1}H NMR chemical shift assignments for the four possible deuterodimers of **1** (**9a**−**d**) are as summarized below:



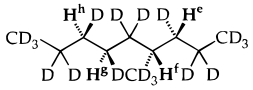
9a

H^a: δ 1.01 (d, 1H, $^3J_{HH}$ = 7.9 Hz)
H^b: δ 1.32 (d, 1H, $^3J_{HH}$ = 7.8 Hz)
H^c,**H^d**: δ 1.18 (2H, $^3J_{HH}$ ≈ Δδ)



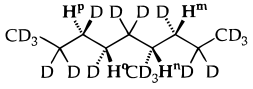
9c

H^i: δ 1.01 (d, 1H, $^3J_{HH}$ = 7.9 Hz)
H^j: δ 1.32 (d, 1H, $^3J_{HH}$ = 7.8 Hz)
H^k: δ 1.24 (d, 1H, $^3J_{HH}$ = 9.5 Hz)
H^l: δ 1.18 (d, 1H, $^3J_{HH}$ = 9.5 Hz)



9b

H^e: δ 1.20 (d, 1H, $^3J_{HH}$ = 5.6 Hz)
H^f: δ 1.32 (d, 1H, $^3J_{HH}$ = 5.6 Hz)
H^g: δ 1.24 (d, 1H, $^3J_{HH}$ = 5.8 Hz)
H^h: δ 1.16 (d, 1H, $^3J_{HH}$ = 5.8 Hz)



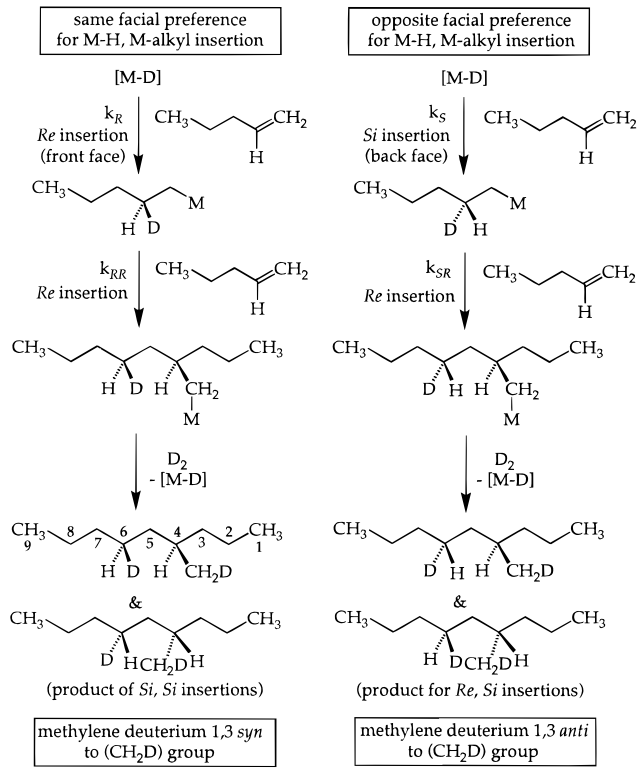
9d

H^m: δ 1.20 (d, 1H, $^3J_{HH}$ = 5.6 Hz)
H^n: δ 1.32 (d, 1H, $^3J_{HH}$ = 5.6 Hz)
H^o,**H^p**: δ 1.17 (2H, $^3J_{HH}$ = ≈ Δδ)

Thus, the favored and disfavored diasteromeric transition structures for insertion of **1** into the Y−*n*-pentyl bond are shown in Scheme 7 (only one of the two enantiomeric transition structures is shown for each).

Deuterodimerization of 1-Pentene. As has been established from the preceding studies, the [(BnBp)Y] system utilizes opposite faces for insertion into Y−H and Y−*n*-pentyl bonds, albeit the former preference is only slight. These findings are in accord with the tentative conclusions from Pino's group for α-olefin insertions into Zr−H and Zr−alkyl bonds of the [(*R*)-(EBTHI)Zr] system.[5,6] Further considerations of the stereochemical consequences for same *vs* opposite enantiofacial preferences for 1-pentene insertions suggest a simple, quantitative test that involves only ^{2}H NMR analysis. Deuterodimerization of (unlabeled) 1-pentene produces four possible isomeric dideuterated 4-methylnonanes (Scheme 8). Two isomers wherein the deuterium atom at C-6 is 1,3-*syn* to the deuteromethyl group at C-4 result from olefin insertion into the metal−deuterium and metal−carbon bonds with the same enantiofacial selectivity. In the isomers resulting from insertions with opposite facial

Scheme 8



selectivity, the C-6 deuterium atom and C-4 deuteromethyl group have a 1,3-*anti* relationship (Scheme 8). Of course, since each of the diastereomers bears the characteristic 1,3-*syn* or 1,3-*anti* relationships, there is no need to use a resolved chiral catalyst to establish whether the same or opposite enantiofaces of the α-olefin are used for M-H and M-alkyl additions; the mixture obtained by using the racemic chiral metallocene catalyst may be used in the analysis.

The results described in the preceding sections have provided the sense and selectivity for (BnBp)Y-H and (BnBp)Y-*n*-pentyl additions to 1-pentene. We have therefore examined the deuterodimerization of (unlabeled) 1-pentene for the [(BnBp)Y] system in order to establish the chemical shifts of the diagnostic 1,3-*syn* or 1,3-*anti* deuterons. The ^{2}H NMR spectrum of a mixture of isomers generated using racemic (BnBp)Y-CH(SiMe$_3$)$_2$ as a precatalyst is shown in Figure 4. In each isomer, the deuteromethyl group contributes a resonance at 0.86 ppm. The methylene deuteron at 1.27 ppm, corresponding to the major product, is assigned to the 1,3-*anti* diastereomers, since opposite facial selectivities for hydride vs *n*-pentyl insertions have been demonstrated using isotopically chiral olefin **1**. The minor deuterium methylene resonance at 1.33 ppm is assigned to the 1,3-*syn* isomers, resulting from hydride and alkyl insertions occurring with selectivity for the same olefin enantioface. In the present case, olefin insertion into metal−carbon bonds occurs with ≥95% selectivity, so the ratio of diastereomers should nearly equal the selectivity for insertion into the metal−hydrogen bond. Indeed, the product ratio ($[I_{anti}]^{\delta 1.27}/[I_{syn}]^{\delta 1.33}$ = 64:36, ee = 28%) is in good agreement with the major-to-minor product ratios observed in the hydrogenation of olefin **1** (67:33, ee = 34%, after correcting for the hyperconjugative deuterium isotope effect).

For the general situation, the ratio of *syn*:*anti* products in the product mixture can be related to the stereoselectivity of the hydride and alkyl insertion steps by eq 2, if certain reasonable

$$\frac{[I_{syn}]}{[I_{anti}]} = \frac{k_R k_{RR} + k_S k_{SS}}{k_R k_{RS} + k_S k_{SR}} \approx \frac{k_R k_{RR} + k_S k_{SS}}{k_R k_{SS} + k_S k_{RR}} \qquad (2)$$

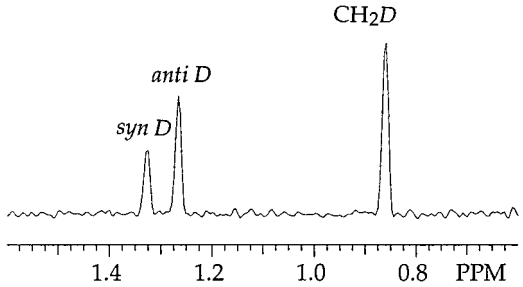


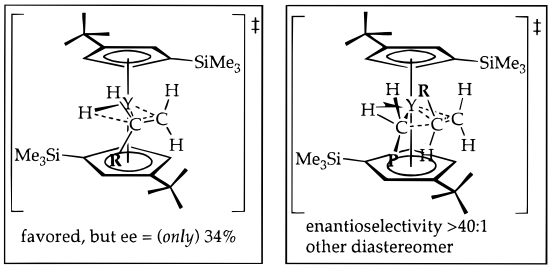
Figure 4. ^{2}H NMR spectrum of deuterodimers of 1-pentene obtained using (±)-BnBpYCH(SiMe$_3$)$_2$ as the catalyst precursor.

assumptions[14] are made regarding the relative rates of olefin insertion and hydrogenolysis of metal−alkyl bonds. Here k_R and k_S are the rate constants for insertion into the metal−hydrogen bond of a given metal complex utilizing the *Re* and *Si* faces of 1-pentene, respectively. The rate constants with double subscripts are for insertions of 1-pentene into metal−pentyl bonds; for example, k_{SR} is the rate constant for insertion into a metal−pentyl bond utilizing the *Re* face of 1-pentene following insertion into a metal−hydrogen bond utilizing the *Si* face of 1-pentene. Other doubly subscripted rate constants are named similarly.

It can be seen that (1) the *syn* and *anti* products will be favored when the same or the opposite enantiotopic faces, respectively, are selectively utilized for insertions into metal−hydrogen and metal−pentyl bonds and (2) if either insertion occurs with no selectivity, the *syn* and *anti* products will be formed in equal amounts. Hence, observation of unequal amounts of *syn* and *anti* products is indicative of enantiofacial selectivity, but the test described here does not specify individually the degree of selectivity for 1-pentene addition to M-H or M-*n*-pentyl.

Conclusion

Isotopically chiral 1-pentene **1** provides a convenient, new spectroscopic probe of the absolute stereochemistry for additions to α-olefin double bonds. The diastereomeric transition structures for 1-pentene insertions into Y−H and Y−*n*-pentyl bonds for (BnBp) yttrium complexes have been established, *e.g.*



We have a working model to explain the different stereochemical outcomes of the insertions into metal−hydride and −alkyl bonds.[15] According to this model, the steric interactions between the [BnBp] ligand and the incoming olefin are minimal in the transition structures for olefin insertion. Thus, addition of **1** to (*R*,*S*)-(BnBp)Y-H occurs with only 34% enantiomeric excess. The favored transition structure for addition of **1** to (*R*,*S*)-(BnBp)Y-*n*-pentyl involves an α-agostic interaction preferentially with one of the two α methylene hydrogens, the one that orients the C$_\alpha$−C$_\beta$ bond of the pentyl group away from the bulky *tert*-butyl group at the front of the metallocene wedge. In forming the carbon−carbon bond, the alkyl group extending from the α carbon (a butyl group for Y-pentyl or the remainder of the polymer chain (**P**) in a Ziegler−Natta polymerization) provides the discriminating steric surface, and the olefin adds with the enantioface that places its substituent in a *trans* fashion to this group in order to minimize steric interactions. Thus, the chirality of the C_2-symmetric metallocene is indirectly transmitted through the orientation of the C$_\alpha$−C$_\beta$ bond to the olefin monomer. This model of "chain segment control" is also in accord with conclusions that have been reached by others.[4cd,16−18]

Although we would very much like to establish the enantiofacial preference for Y-CH$_3$ addition to **1** (predicted to be the same as that for Y-*n*-pentyl addition, but of low selectivity as for Y-H addition), (BnBp)Y-CH$_3$ has proven exceedingly difficult to prepare.[19] Using ^{13}C NMR analysis of chain ends, Zambelli has reported very low enantioselectivities for additions of α-olefins into the titanium−methyl bond of (ethylenebisindenyl)Ti−^{13}CH$_3$, yet high selectivities for insertion with (ethylenebisindenyl)Ti−^{13}CH$_2$CH$_3$,[20] in accord with this model.

Finally, we have demonstrated that simple ^{2}H NMR analysis of the deuterodimers from 1-pentene may be used to establish (1) whether the same or opposite enantiofaces are used in the insertion into metal−hydride and metal−*n*-pentyl bonds or (2) whether one of the two insertions occurs with no selectivity.

Experimental Section

General Considerations. All air- and moisture-sensitive compounds were manipulated using standard vacuum line, Schlenk, or cannula techniques, or in a drybox under a nitrogen atmosphere. Argon and nitrogen gases were purified and dried by passage over columns of MnO on vermiculite and activated molecular sieves.[21] Solvents for air- and moisture-sensitive reactions were stored under vacuum over sodium benzophenone ketyl and freshly distilled immediately prior to use. Buffers for enzymatic reactions were prepared using water purified on a Barnstead NANOpure system, filtered through a 0.2 μm nylon membrane filter, and refrigerated until used. The preparations of racemic and optically pure (*R*,*S*)- and (*S*,*R*)-(BnBp)YCH(SiMe$_3$)$_2$ were carried out as described previously.[7] *n*-Propanol-d_8 (99.0% D) was

(14) Certain assumptions are made in invoking eq 2, that (1) The rate of *Re* insertion of 1-pentene is independent of whether M-H addition occurred from either the *Re* or *Si* face, *i.e.* $k_{RR} = k_{SR}$ and $k_{SS} = k_{RS}$ and (2) the rate of hydrogenation of the metal carbon bond for the 2-pentyl−pentyl intermediate is independent of the absolute configuration at the β carbon. For a C_2-symmetric catalyst such as (BnBp)Y-R, these assumptions appear reasonable.

(15) Burger, B. J.; Cotter, W. D.; Coughlin, E. B.; Chacon. S. T.; Hajela, S.; Herzog, T. A.; Köhn, R. D.; Mitchell, J. P.; Piers, W. E.; Shapiro, P. J.; Bercaw, J. E. Reference 1, p 317.

(16) (a) Corradini, P.; Guerra, G.; Vacatello, M.; Villani, V. *Gazz. Chim. Ital.* **1988**, *118*, 173. (b) Corradini, P.; Busico, V.; Cavallo, L. Guerra, G.; Vacatello, M.; Venditto, V. *J. Mol. Catal.* **1992**, *74*. 433. (c) Corradini, P.; Guerra, G.; Cavallo, L.; Moscardi, G.; Vacatello, M. In reference 1, p 237.

(17) Leclerc, M. K.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1996**, *118*, 9024.

(18) Recently it has been established that stereoselectivities are limited by epimerization at the β carbon atom of the bound alkyl group (believed to initiate by β hydrogen elimination), as much as by enantiofacial preference, especially at low monomer concentrations; see, for example: (a) Busico, V.; Cipullo, R. *J. Am. Chem. Soc.* **1994**, *116*, 9329. (b) Leclerc, M. K.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1995**, *117*, 1651. For the (BnBp)Y−alkyl systems described here, crossover initiated by fast and reversible β hydrogen elimination would lead, for example, to CD$_3$CD$_2$-CHDCD$_2$CD$_3$ and CD$_3$CD$_2$CHDCH$_2$CD$_3$. The {^{2}H} ^{1}H NMR spectra (Figure 2) show no evidence for these crossover products. Likewise, no other ^{1}H NMR signals attributable to methylnonane products with protons at the 5 carbon are in evidence (Figure 3). Thus, chain epimerization does not appear to compete significantly with deuteration and deuterodimerization of **1** by (BnBp)Y-D.

(19) Attempted methylation of the chloride, using methyllithium or methyl Grignard reagents, consistently results in formation of what appears (^{1}H NMR) to be the dimethylyttrate anion: Loeber, C.; Gilchrist, J. H.; Bercaw, J. E. Unpublished results.

(20) (a) Longo, P.; Grassi, A.; Pellecchia, C.; Zambelli. A. *Macromolecules* **1987**, *20*, 1015. (b) Zambelli, A.; Pellecchia, C.; Oliva, L. *Makromol. Chem. Macromol. Symp.* **1991**, *48/49*, 297.

(21) Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; ACS Symposium Series No. 357; Wayda, A. L., Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 4.

purchased from Isotec. Chiral gas chromatograms were obtained using a J&W Scientific 30 m × 0.25 mm i.d. CDX-B column. (*S*)-(+)-Methyl mandelate (Aldrich) was recrystallized six times from hexane to 99.4% ee as determined by GLC with correction for the *R* enantiomer's response.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 500 spectrometer at 500.13 and 125.77 MHz, respectively. A Bruker AMX 500 spectrometer operating at ^{1}H and ^{2}H frequencies of 500.13 and 76.77 MHz, respectively, was used to record ^{2}H decoupled ^{1}H NMR spectra. The WALTZ-16 pulse sequence was used for ^{2}H decoupling on the broad-band coil of a 5 mm ^{109}Ag−^{31}P probe. Unless otherwise noted, ^{1}H and ^{13}C NMR chemical shifts are relative to TMS using the ^{1}H (residual) or ^{13}C chemical shift of the solvent as a secondary standard. Deuterium-labeled compounds **1**−**7** had chromatographic behaviors and ^{1}H NMR spectra (including the chemical shifts of residual protons at otherwise deuterated positions) comparable to those of unlabeled compounds.

(*S*)-1,2,2,3,3,3-Hexadeutero-1-propanol. According to Mosher's[22] modification of Simon's method,[8] to 400 mL of a buffer containing 4.25 g of Na_2HPO_4, 1.38 g of $NaH_2PO_4{\cdot}H_2O$, and 0.117 g of H_4EDTA (pH = 7.26) were added 244.3 mg of albumin (Sigma A4378), 74.1 mg of NAD (Sigma N 7004), 74.0 mg of NADH disodium salt (Sigma N 8129), 120.3 mg of yeast alcohol dehydrogenase (Sigma A7011), 50 units of porcine heart diaphorase (Sigma D 3752), and 9.77 g of *n*-propanol-d_8 (144 mmol) with gentle shaking to dissolve each added reagent. The mixture was allowed to stand at 34 ± 0.1 °C in the dark for 50 h. The propanol was azeotropically distilled from the reaction mixture (bp = 86−99 °C at ambient pressure). ^{13}C NMR spectroscopy using inverse-gated ^{1}H decoupling indicated a 9:1 ratio of *C*HDOH to *C*D$_2$OH resonances (no resonance for *C*H$_2$OH was detectable). The distillate was added to a freshly prepared buffer solution of enzymes as above and allowed to stand at 34 ± 0.1 °C in the dark for another 50 h. Distillation provided (*S*)-1,2,2,3,3,3-hexadeutero-1-propanol as an aqueous solution, total mass = 35.5 g: ^{1}H NMR (D$_2$O, chemical shifts relative to HDO at 4.80 ppm) δ 3.48 (br, 1 H, C*H*DOH); ^{13}C NMR (H$_2$O, shifts relative to $CHCl_3$ capillary at 77.2 ppm) δ 63.27 (t, J_{C-D} = 21.6 Hz, C-1), 23.98 (quintet, J_{C-D} = 19.2, Hz C-2), 8.74 (septet, J_{C-D} = 19.2 Hz, C-3). An anhydrous solution of (*S*)-1,2,2,3,3,3-hexadeutero-1-propanol in CH_2Cl_2 was prepared by adding 8.0 g of Na_2SO_4 to the aqueous azeotrope of (*S*)-1,2,2,3,3,3-hexadeutero-1-propanol, extracting with CH_2Cl_2 (10 × 10 mL), and drying the organic layers over Na_2SO_4 and then activated Linde 4 A molecular sieves. This solution was used directly in the preparation of (*S*)-1,2,2,3,3,3-hexadeutero-1-propyl *p*-toluenesulfonate.

(*S*)-1,2,2,3,3,3-Hexadeutero-1-propyl *p*-Toluenesulfonate. To a 100 mL solution of (*S*)-1,2,2,3,3,3-hexadeutero-1-propanol in dry CH_2Cl_2 (assumed to contain 138 mmol of (*S*)-1,2,2,3,3,3-hexadeutero-1-propanol, the theoretical yield of the previous step, less an aliquot withdrawn for characterization purposes) was added 50 mL of dry pyridine, and with stirring at 0−5 °C, a solution of 27.6 g (145 mmol) of TsCl in 40 mL of CH_2Cl_2 was added. Gas chromatography indicated complete consumption of (*S*)-1,2,2,3,3,3-hexadeutero-1-propanol after 16 h at 0 °C. The mixture was shaken with ice cold aqueous 2.5 M HCl (600 mL, then 3 × 150 mL), ice water (150 mL), and ice cold saturated $NaHCO_3$ (150 mL). The organic layer was dried over K_2CO_3 and concentrated *in vacuo* to an oil containing principally (*S*)-1,2,2,3,3,3-hexadeutero-1-propyl *p*-toluenesulfonate and TsCl. The crude product was dissolved in 200 mL of pentane and loaded on an 11 in. bed of silica gel in a 55 mm diameter column. TsCl was washed off the column using pentane, and (*S*)-1,2,2,3,3,3-hexadeutero-1-propyl *p*-toluenesulfonate was eluted with 60% Et$_2$O/pentane. Concentration *in vacuo* gave 24.82 g of a colorless oil (82% from 1-propanol-d_8): ^{1}H NMR (C$_6$D$_6$) δ 7.74 (d, 2H, J = 8.3 Hz), 6.75 (d, 2H, J = 8.2 Hz), 3.69 (br s, 1H), 1.87 (s, 3H); ^{13}C NMR (C$_6$D$_6$) δ 144.14, 134.66, 129.78, 128.06, 71.31 (t, J_{C-D} = 22.8 Hz), 21.43 (quintet, J_{C-D} = 20.0 Hz), 21.10, 8.74 (septet, J_{C-D} = 19.1 Hz); IR (neat) 2954, 2927, 2227, 1598, 1363, 1190, 1177, 1098, 947, 913, 816, 663, 554 cm^{-1}.

***N*,*N*-Dimethyl-(*S*)-3,4,4,5,5,5-hexadeuterovaleramide.** To a stirred solution of 25.0 mL (18.0 g, 178 mmol) of diisopropylamine in 100 mL of THF at −78 °C was added 102 mL (162 mmol) of 1.59 M *n*-BuLi in hexanes. The solution was warmed to 0 °C, and 30.1 mL (28.2 g, 324 mmol) of *N*,*N*-dimethylacetamide was added with stirring. The volume was reduced *in vacuo* to ca. 60 mL, and 23.78 g (108 mmol) of (*S*)-1,2,2,3,3,3-hexadeutero-1-propyl *p*-toluenesulfonate was added with stirring over 10 min. After 5 h at room temperature, the reaction mixture was cooled to 0 °C, and 50 mL of an ice cold solution of 1 M H_2SO_4 saturated with Na_2SO_4 was added, followed by 200 mL of water. The mixture was extracted with CH_2Cl_2 (4 × 60 mL), the organic layers were back-extracted with water (2 × 100 mL), the aqueous layers were extracted with CH_2Cl_2 (2 × 60 mL), and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo* to an oil. The crude product was dissolved in 150 mL of Et$_2$O and eluted with Et$_2$O through a 150 g bed of basic alumina (to remove most of the excess *N*,*N*-dimethylacetamide). The eluate was concentrated *in vacuo* to an oil containing principally *N*,*N*-dimethyl-*S*-3,4,4,5,5,5-hexadeuterovaleramide and dialkylation product. Flash chromatography (90% EtOAc/hexane, 6 in. × 55 mm column, 2−2.5 g portions of crude product) gave 8.07 g (55%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.95 (s, 3H, *N*CH$_3$), 2.88 (s, 3H, *N*CH$_3$), 2.44 (d, 2H, J = 7.7 Hz, CH$_2$), 1.52 (t, 1H, J = 7.6 Hz, CHD); ^{13}C NMR (neat) δ 171.84, 36.77, 34.68, 32.67, 26.93 (t, J_{C-D} = 19.5 Hz) 21.60 (quintet, J_{C-D} = 19.1 Hz) 12.85 (septet, J_{C-D} = 19.0 Hz); IR (neat) 2929, 2215, 2112, 1651, 1644, 1496, 1397, 1265, 1146, 1057 cm^{-1}.

***N*,*N*-Dimethyl-(*S*)-1,1,3,4,4,5,5,5-octadeuteropentylammonium *p*-Toluenesulfonate.** To a stirred suspension of 1.64 g (39.1 mmol) of $LiAlD_4$ in 45 mL of Et$_2$O at 0 °C was added *N*,*N*-dimethyl-(*S*)-3,4,4,5,5,5-hexadeuterovaleramide (4.73 g, 35.0 mmol) over 20 min (exothermic). IR spectroscopy indicated that the reaction was complete immediately. The reaction mixture was cautiously quenched with 60 mL of 10% aqueous NaOH, and the aqueous layer was extracted with Et$_2$O (2 × 40 mL). The combined ether layers were dried over K_2CO_3 and added to 38.3 mmol of *p*-TsOH (dried by dissolving in 500 mL of 20% benzene/ether and concentrating *in vacuo*) in 400 mL of dry Et$_2$O under a nitrogen atmosphere. After cooling to 0 °C, crude *N*,*N*-dimethyl-(*S*)-1,1,3,4,4,5,5,5-octadeuteropentylammonium *p*-toluenesulfonate (9.49 g) was collected by filtration under nitrogen, then recrystallized by dissolving in 72 mL of CH_2Cl_2 and adding 400 mL of dry ether. Small lustrous plates of *N*,*N*-dimethyl-(*S*)-1,1,3,4,4,5,5,5-octadeuteropentylammonium *p*-toluenesulfonate were collected by filtration and washed with 200 mL of cold ether. Vacuum desiccation gave 9.37 g (91%): mp = 107.5−108.5 °C; ^{1}H NMR ($CDCl_3$) δ 10.16 (br s, 1H, N-H), 7.66 (d, 2H, J = 8.2 Hz), 7.09 (d, 2H, J = 8.1 Hz), 2.72 (d, 6H, J = 5.0 Hz), 2.27 (s, 3H), 1.54 (d, 2H, J = 7.8 Hz) 1.10 (t, 1H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 142.50, 139.81, 128.63, 125.66, 57.14 (quintet, J_{C-D} = 21.5 Hz), 42.78, 27.53 (t, J_{C-D} = 19.1 Hz), 23.62, 21.07, 20.76 (quintet, J_{C-D} = 19.3 Hz), 12.37 (septet, J_{C-D} = 19.1 Hz); IR (free base, CCl_4 solution) 2971, 2939, 2815, 2766, 2215, 2035, 1464, 1451, 1167, 1044, 991 cm^{-1}.

***N*,*N*-Dimethyl-(*S*)-1,1,3,4,4,5,5,5-octadeuteropentylamine *N*-Oxide.** The amine was oxidized according to the procedure of Craig and Purushotham.[23] A mixture of 20 mL of 10% aqueous NaOH and 1.96 g (6.63 mmol) of *N*,*N*-dimethyl-(*S*)-1,1,3,4,4,5,5,5-octadeuteropentylammonium *p*-toluenesulfonate was extracted with 3 × 12 mL of $CHCl_3$, and the organic layers were dried over K_2CO_3 and cooled to 0 °C. A solution of mCPBA (1.26 g, 7.30 mmol) in 15 mL of $CHCl_3$ was added. After 2 min at 0 °C the product was loaded onto a column of 60 g of basic alumina, the column was washed with 200 mL of $CHCl_3$, and the product was eluted with 25% MeOH/$CHCl_3$. The eluate was concentrated *in vacuo* to an oil which was converted to a crystalline solid by two cycles of adding 4 mL of toluene and *in vacuo* solvent removal. Recrystallization from dry THF under an argon atmosphere gave 0.61 g (66%) of *N*,*N*-dimethyl-(*S*)-1,1,3,4,4,5,5,5-octadeuteropentylamine *N*-oxide as a white solid: dec > 90 °C; ^{1}H NMR (C$_6$D$_6$) δ 2.61 (s, 6H), 1.71 (br d, 2H, J = 7.8 Hz), 0.98 (br t, 1H, J = 7.6 Hz); ^{13}C NMR (C$_6$D$_6$) δ 70.46 (quintet, J_{C-D} = 20.8 Hz), 58.94 (s), 28.66 (t, J_{C-D} = 19.4 Hz), 23.14 (s), 21.67 (quintet, J_{C-D} = 19.4 Hz), 12.96 (septet, J_{C-D} = 19.0 Hz); IR (CCl_4 solution) 2944, 2281, 2216, 2120, 2097, 1730, 1468, 1445, 908, 498 cm^{-1}.

(*R*)-1,1,3,4,4,5,5,5-Octadeutero-1-pentene (1). In a 10 mL flask connected by a liquid nitrogen cooled trap containing 5 mL of 5% aqueous HCl to a vacuum/Ar manifold, *N*,*N*-dimethyl-(*S*)-1,1,3,4,4,5,5,5-octadeuteropentylamine *N*-oxide (593 mg, 4.26 mmol) was slowly heated at a pressure of 20 mmHg. Reaction was evident at 90 °C and

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complete at 135 °C. The trap containing the product was sealed, thawed, and shaken. The product was vacuum transferred onto 2.1 g of $MgSO_4$ in a 25 mL glass bomb with a Teflon needle valve. After 10 min of vigorous shaking, the product was vacuum transferred onto a small piece of sodium in a 2 mL bomb with a Teflon needle valve. After standing for 12 h, the product was transferred to a second, tared, 2 mL bomb containing a small droplet of Na/K alloy. Yield = 276 mg (83%): ^{1}H NMR (benzene-d_6) δ 5.72 (m, 1H), 1.87 (m, 1H); ^{13}C NMR (benzene-d_6) δ 138.66 (s), 114.03 (quintet, J_{C-D} = 23.7 Hz), 35.41 (t, J_{C-D} = 19.2 Hz), 21.26 (quintet, J_{C-D} = 19.3 Hz), 12.50 (septet, J_{C-D} = 19.2 Hz); IR (CCl_4 solution) 2997, 2885, 2217, 2119, 2072, 1598, 1454, 1301, 1288, 1057, 953, 918 cm^{-1}.

(*R*)-2,3,3,4,4,4-Hexadeuterobutyric Acid. To a mixture of $KMnO_4$ (109 mg 0.688 mmol), $NaIO_4$ (1.763 g, 8.24 mmol), K_2CO_3 (318 mg, 2.30 mmol), 5 mL of water, and 4 mL of *tert*-butyl alcohol at −196 °C were vacuum transferred **1** (53.6 mg, 0.686 mmol) and 0.8 mL of benzene-d_6. The mixture was thawed and stirred at room temperature for 12 h, and the excess oxidant was destroyed with 3.5 g of Na_2SO_3 (105% of the theoretical amount). The mixture was basified with solid K_2CO_3, filtered to remove $MnCO_3$, acidified with concentrated H_2SO_4, and added to a suspension of $AgSO_4$ (1.55 g, 9.94 mmol Ag) in 75 mL of water. After being stirred for 15 min, the mixture was basified with solid K_2CO_3, filtered to remove AgI and $AgCO_3$, and concentrated *in vacuo* to dryness. To the residue at 0 °C was added 10.4 g of $NaHSO_4$ and 5 g of ice. The slurry was extracted with four 8−12 mL portions of CH_2Cl_2. The extracts were dried over Na_2SO_4, the solvent was removed *in vacuo* (0 °C, 60 Torr), and the residue was dissolved in Et_2O, dried over Na_2SO_4, and concentrated *in vacuo*. Vacuum distillation gave 59.0 mg of (*R*)-2,3,3,4,4,4-hexadeuterobutyric acid as a colorless liquid (91%): ^{1}H NMR ($CDCl_3$) δ 11.19 (br s, 1H, CO_2H), 2.27 (br, 1H, C-2 H), residual ^{1}H signals: δ 1.60 (br d, J = 6.8 Hz, C-3 H), 0.89 (br, C-4 H). Butyric acid obtained commercially or prepared from unlabeled 1-pentene by an analogous procedure had a comparable ^{1}H NMR spectrum.

Methyl *O*-(2,3,3,4,4,4-Hexadeutero-(*R*)-butyryl)-(*S*)-mandelate. According to Parker's procedure,[10] solutions of DMAP (2 mg, 0.016 mmol), (*S*)-(+)-methyl mandelate (109.4 mg, 0.658 mmol), and DCC (136 mg, 0.659 mmol) each in 1 mL of CH_2Cl_2 were added to a stirred solution of (*R*)-2,3,3,4,4,4-hexadeuterobutyric acid (59.0 mg, 0.627 mmol) in 0.8 mL of $CDCl_3$ at −10 °C. After 3 h at −10 to −20 °C, workup and flash chromatography (10% EtOAc/hexane on silica gel)[24] provided methyl *O*-(2,3,3,4,4,4-hexadeutero-(*R*)-butyryl)-(*S*)-mandelate as a colorless oil (98.2 mg, 65%): ^{1}H NMR (C_6D_6) δ 7.44 (m, 2H), 7.01−7.10 (m, 3H), 6.07 (s, 1H), 3.18 (s, 3H), 2.08 (br, 1H, major isomer butyryl C-2 H); residual ^{1}H signals: δ 1.50 (br d, J = 6.8 Hz, butyryl C-3 H), 0.72 (br, butyryl C-4 H); IR (thin film) 2954, 2222, 1758, 1744, 1217, 1187, 1172, 1051 cm^{-1}. Unlabeled methyl *O*-butyrylmandelate had comparable ^{1}H NMR and IR spectra.

(*E*)-4-Methyl-3-nonene. To a suspension of $Pd(PPh_3)_4$ (76 mg, 0.066 mmol) in 1.0 mL of THF was added 411 mg (1.73 mmol) of (*E*)-2-methyl-1-iodo-1-heptene[25] in 1 mL of THF. To the resulting solution was added 1.25 mL (1.25 mmol) of 1.0 M diethylzinc in hexanes over 2 min. When gas chromatography indicated complete reaction (15 min), 4 mL of pentane and 4 mL of 0.2 M aqueous HCl were added with stirring. The organic layer was shaken with water (2 × 2 mL) and dried over K_2CO_3. The yellow solution was passed through a 1 in. bed of silica gel, the solvents were distilled at atmospheric pressure from the resulting colorless solution, and the product was purified by bulb-to-bulb distillation (60 °C at 45 mmHg), yield = 145 mg (60%) of a >20:1 (^{1}H NMR, GC) mixture of *E* and *Z* isomers: ^{1}H NMR ($CDCl_3$) δ 5.09 (m, 1H, C-3 H), 1.97 (quintet, 2H, J = 7.4 Hz, C-2 H), 1.93 (m, 2H, C-5 H, 1.56 (br, 3H, C-4 CH_3), 1.36 (m, 2H, C-6 H), 1.28 (m, 2H, C-8 H), 1.22 (m, 2H, C-7 H), 0.92 (t, 3H, J = 7.5 Hz, C-1 H), 0.87 (t, 3H, J = 7.2 Hz, C-9 H); ^{13}C NMR ($CDCl_3$) δ 134.71, 126.17, 39.64, 31.57, 27.71, 22.59, 21.15, 15.72, 14.37, 14.03.

Mixture of (*E*)- and (*Z*)-4-Methyl-3-nonene. To a suspension of 2.36 g (6.12 mmol) of *n*-propyltriphenylphosphonium bromide in THF (6 mL) was added a solution of 1.11 g of potassium hexamethyldisilazide (5.56 mmol) in THF (6 mL). The mixture was brought to reflux and 570 mg (4.95 mmol), of 2-heptanone was added. Gas chromatography indicated complete reaction after 4 h of reflux. The reaction mixture was diluted with 12 mL of pentane and extracted with 25 mL of cold 1 M HCl. The aqueous layer was extracted with 12 mL of pentane, and the combined organic layers were washed with 10 mL of cold 1 M HCl and 5 × 10 mL of water. The organics were dried over K_2CO_3 and concentrated *in vacuo*. Two bulb-to-bulb distillations (50−55 °C at 40 mmHg) gave 473 mg (68%) of a colorless oil; gas chromatography indicates a 98.5% pure mixture of *Z* and *E* olefin isomers in a 1.10:1 ratio: ^{1}H NMR ($CDCl_3$) δ 5.10 (m, 1H, C-3 H), 2.03−1.91 (m, 4H), 1.66 (br, 3H, C-4 CH_3), 1.41−1.19 (m, 6H), 0.92 (t, 3H, J = 7.5 Hz), 0.88 (t, 3H, J = 7.1 Hz), in addition to signals for the *E* isomer; ^{13}C NMR ($CDCl_3$) δ 134.97, 126.95, 31.84, 31.68, 27.79, 23.33, 22.63, 21.04, 14.62, 14.01, in addition to signals for the *E* isomer.

***anti*-3,4-Dideutero-4-methylnonane.** According to the method of Berson and co-workers,[26] to a 3.0 mL CH_3OD solution of olefin **11** (29.5 mg, 0.210 mmol) was added 2.50 g (12.9 mmol) of potassium azodicarbonate. The suspension was stirred at 50 °C, and CH_3CO_2D (1.58 g, 25.9 mmol) was added over 45 min. Gas chromatography indicated ca. 15% conversion of the olefin to the dideuteroalkane. The mixture was diluted with 10 mL of water and extracted with 10 mL of pentane. The organic layer was shaken with 2 × 10 mL of water and dried over K_2CO_3. The pentane was removed by distillation at atmospheric pressure, and the colorless residue containing **10** and olefin **11** was taken up in dry acetone for ^{2}H NMR analysis. A small portion of $(CD_3)_2CO$ was added as a chemical shift standard.

Mixture of *anti*- and *syn*-3,4-Dideutero-4-methylnonane (10 and 12). These were preared by a procedure analogous to that for **10**, starting with a mixture of olefins **11** and **13**. The diimide reduction proceeded to 14% completion.

(*S*,*R*)-(BnBp)YCH(SiMe$_3$)$_2$-Mediated Hydrogenation of 1. To a rapidly stirred solution of 23 mg (0.29 mmol) of **1** and 11 mg (0.012 mmol) of (*S*,*R*)-(BnBp)YCH(TMS)$_2$ in 0.9 mL of C_6D_6 at 20 °C in a 250 mL round-bottom flask was admitted 1 atm of D_2 gas. Gas chromatography typically indicates complete reaction in <10 s. The volatiles were vacuum transferred to a 5 mm NMR sample tube for analysis. (*R*,*S*)-(BnBp)YCH(SiMe$_3$)$_2$-mediated hydrogenation of **1** and (±)-(BnBp)YCH(SiMe$_3$)$_2$-mediated hydrogenation of **1** were carried out similarly.

(*S*,*R*)-(BnBp)YCH(SiMe$_3$)$_2$-Mediated Hydrodimerization of 1. To a stirred 0 °C solution of (*S*,*R*)-(BnBp)YCH(TMS)$_2$ (8.0 mg, 0.0085 mmol) in olefin **1** (4.25 mmol) was admitted D_2 at 1 atm. After 3 h stirring at 0 °C, the mixture was diluted with 2 mL of pentane and filtered through a 1 in. bed of silica gel. The pentane was removed by distillation at atmospheric pressure, and the hydrodimers were isolated by preparative gas chromatography. (*R*,*S*)-(BnBp)YCH(SiMe$_3$)$_2$-mediated hydrodimerization of **1** and (±)-(BnBp)YCH(SiMe$_3$)$_2$-mediated deuterodimerization of 1-pentene were carried out using an analogous procedure.

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