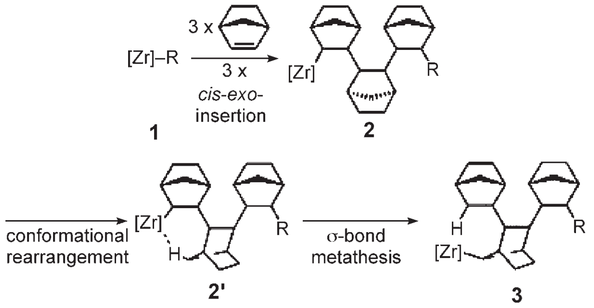
DOI: 10.1002/anie.200604264

Polymer Structures

Helical Microstructure of Polynorbornene

Christos Karafilidis, Klaus Angermund, Barbara Gabor, Anna Rufińska, Richard J. Mynott, Georg Breitenbruch, Walter Thiel, and Gerhard Fink**

Some time ago[1] we reported a metallocene-catalyzed hydro-oligomerization of norbornene (NB) in which a C7 linkage is formed as a result of σ-bond metathesis. Based on the crystal structure of the pentamer, we were able to show that two of the norbornene molecules are joined by 2-exo-7′-*syn* linkages and we proposed a mechanism in which a change of conformation of the chain brings the *syn* hydrogen atom on C7 of the second last inserted monomer into the vicinity of the Zr atom of the metallocene unit so that a σ-bond metathesis takes place (Scheme 1: **1**→**2**→**2′**→**3**).

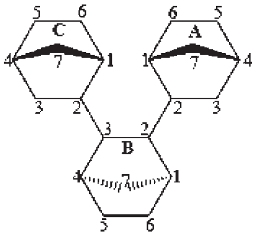


Scheme 1. σ-Bond metathesis during the norborene polymerization. R = H or D, CH_3, polymer, [Zr] = *rac*-[*i*Pr(Ind)$_2$Zr]$^+$; Ind = indenyl.

The crucial question remained unanswered—whether this σ-bond step is repeated regularly in the growing chain and in this way determines the as yet unknown structure of the polynorbornene and its properties. Herein we show through norbornene oligomerizations in a deuterium atmosphere and structural analysis of the higher oligomers that this is indeed the case.

The oligomerization reactions were carried out in a 250-mL Büchi autoclave under a 0.5–1.25 bar hydrogen or deuterium atmosphere.[2] The oligomers were preparatively fractionated according to their hydrodynamic volumes (≥ 100 mg; gel permeation chromatography (GPC)) and the samples obtained were analyzed by NMR spectroscopy.

First let us consider the hydrotrimer (Scheme 2): If **2** (Scheme 1 with R = D) were present at the moment of chain termination in a deuterium atmosphere, then C3a and C3c would both be deuterated, the rings A and C would be enantiotopic, and the product would have a mirror plane. Figure 1 shows the $^{13}C\{^1H\}$ NMR spectra of the *meso,meso*-coupled NB hydrotrimers prepared in a hydrogen atmosphere and a deuterium atmosphere.



Scheme 2. Structure and numbering scheme: the norbornene frameworks are named according their insertion sequence (A,B,C, ...), the C atoms are additionally labeled a,b,c, ... according to the ring name.

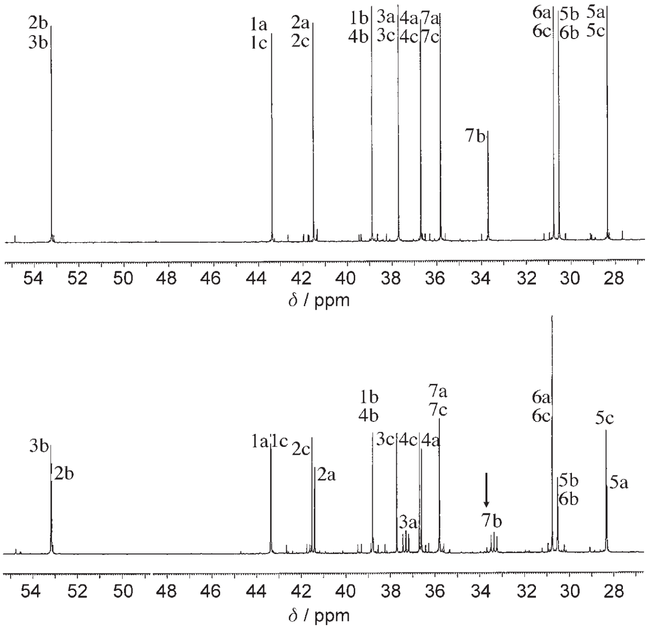


Figure 1. $^{13}C\{^1H\}$-NMR-Spectra of the *meso,meso*-linked norbornene hydrotrimer generated with hydrogen (above) and deuterium (below).

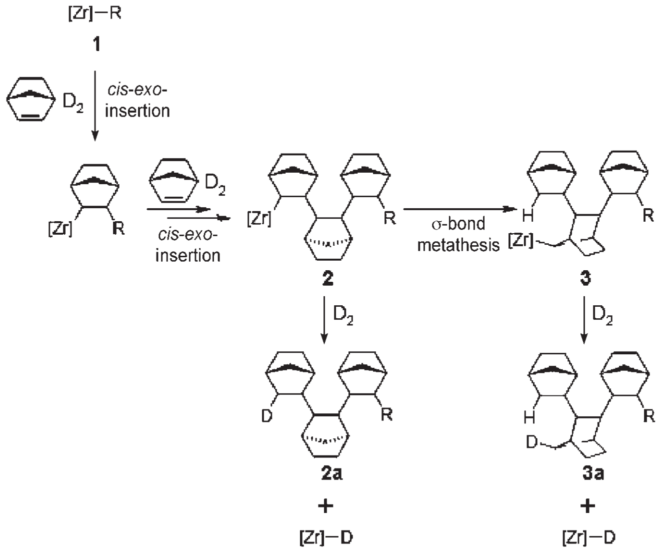
As can be clearly seen, the resonance at δ = 33.68 ppm of the bridging carbon atom C7b of the second monomer to be inserted (Figure 1; upper spectrum) has almost disappeared in the deuterated compound (Figure 1; lower spectrum), while a new signal with the characteristic 1:1:1 triplet of a carbon

---

[*] Dr. C. Karafilidis, Dr. K. Angermund, B. Gabor, Dr. A. Rufińska, Dr. R. J. Mynott, G. Breitenbruch, Prof. W. Thiel, Prof. G. Fink
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr (Germany)
Fax: (+49) 208-306-2980
E-mail: fink@mpi-muelheim.mpg.de

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

atom bound to deuterium is observed at $\delta = 33.36$ ppm, showing unambiguously that one of the hydrogen atoms on C7b has been formally replaced almost entirely ($\geq 96\,\%$) by deuterium. This observation shows that when the chain-propagation reaction was stopped, the metal catalyst was almost exclusively bound to the bridging atom C7b (**3** in Scheme 3), a situation that can only result from a σ-bond metathesis reaction (**2**→**3** in Scheme 3) between C3c and C7b. This interpretation is supported by the further finding that only *one* of the C3 atoms (i.e., C3a) is deuterated. The resulting deuterated compound therefore has C_1 symmetry. As a result of the deuterium isotope shifts, the signals of C2a and C4a, the carbon atoms closest to the substituted C3a atom, differ significantly from those of C2c and C4c, respectively. Similarly, the signals C1a/C1c and also C5a/C5c and C3b/C2b are resolved. Accordingly, the trimer is the asymmetrical compound **3a** in Scheme 3 with R = D.

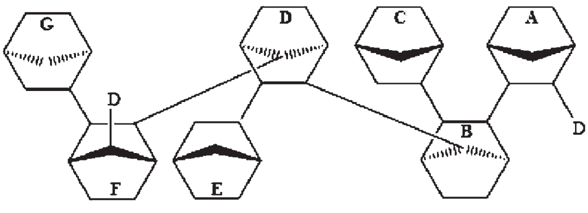


Scheme 3. Reaction scheme demonstrating the σ-bond metathesis during the norbornene-oligomerization. R = H or D, CH_3, [Zr] = *rac*-$[i\text{Pr(Ind)}_2\text{Zr}]^+$.

Since the trimer is found almost exclusively as **3a**, the σ-bond metathesis reaction must play a central role in the oligomerization of norbornene with the catalyst system *rac*-$[i\text{Pr(Ind)}_2\text{Zr}]\text{Cl}_2$/MAO (MAO = methylaluminoxane). Consistent with this scenario, the tetra- and pentamers also have 2-*exo*,7′-*syn* linkages and are formed in large excess.

Since the tetramer and all higher oligomers are chiral, rings A and C in these molecules are diastereotopic. Therefore, the NMR signals of these rings differ from each other much more strongly than in the trimer. The structures of the deuterated oligomers we report herein are confirmed by analysis of their NMR spectra in detail, taking into account the $^1J(^{13}C,^2D)$ splittings, broadening of signals through unresolved $^2J(^{13}C,^2D)$ and $^3J(^{13}C,^2D)$ couplings and deuterium isotope shifts.[3]

The heptamer, which was studied in detail, has two 2-*exo*,7′-*syn* linkages (Scheme 4). The heptamer prepared in a deuterium atmosphere has a deuterium atom on the carbon atom C3a in *exo* position and on C7f in *syn* position (Scheme 4). Information about the preferred conformation can be obtained from the 2D-NOESY NMR spectrum.[3] This information correlates with molecular modeling calculations on models of polynorbornene (see below). In the course of the formation of the heptamer a total of three σ-bond metathesis reactions occur before the chain growth is halted by deuterium, and it is clear that to form the octamer the next monomer unit will be inserted into the zirconium–C7f bond. The fact that the σ-bond metathesis occurs three times is a clear indication that this is a repeated step in the polymerization of NB with the catalyst system *rac*-$[i\text{Pr(Ind)}_2\text{Zr}]\text{Cl}_2$/MAO. In other words, the repeated element is formed by two *cis-exo* insertions and a subsequent σ-metathesis step.



Scheme 4. 2-*exo*,2′-*exo*- and 2-*exo*,7′-*syn*-linked norbornene D_2-heptamer, generated with the catalyst system *rac*-$[i\text{Pr(Ind)}_2\text{Zr}]\text{Cl}_2$/MAO.

A further observation of note is related to the cycle of repeated metathesis steps. In general, it would be expected that the distribution curve for the oligomers would have a more or less smooth bell shape, but the curves in Figure 2 have maxima for the trimers, pentamers, and heptamers and minima for the tetramers, hexamers, and octamers. When the H_2 or D_2 pressure decreases the distribution is as expected extended further toward higher oligomers.

As shown above, the hydrotrimerization in D_2 atmosphere yields the metathesis product **3a** in Scheme 3 almost quanti-

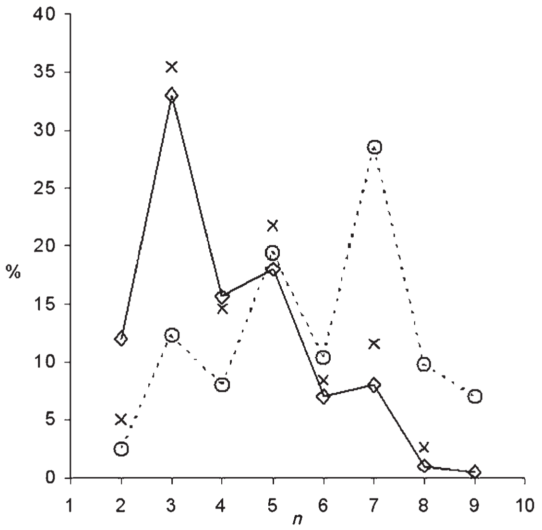


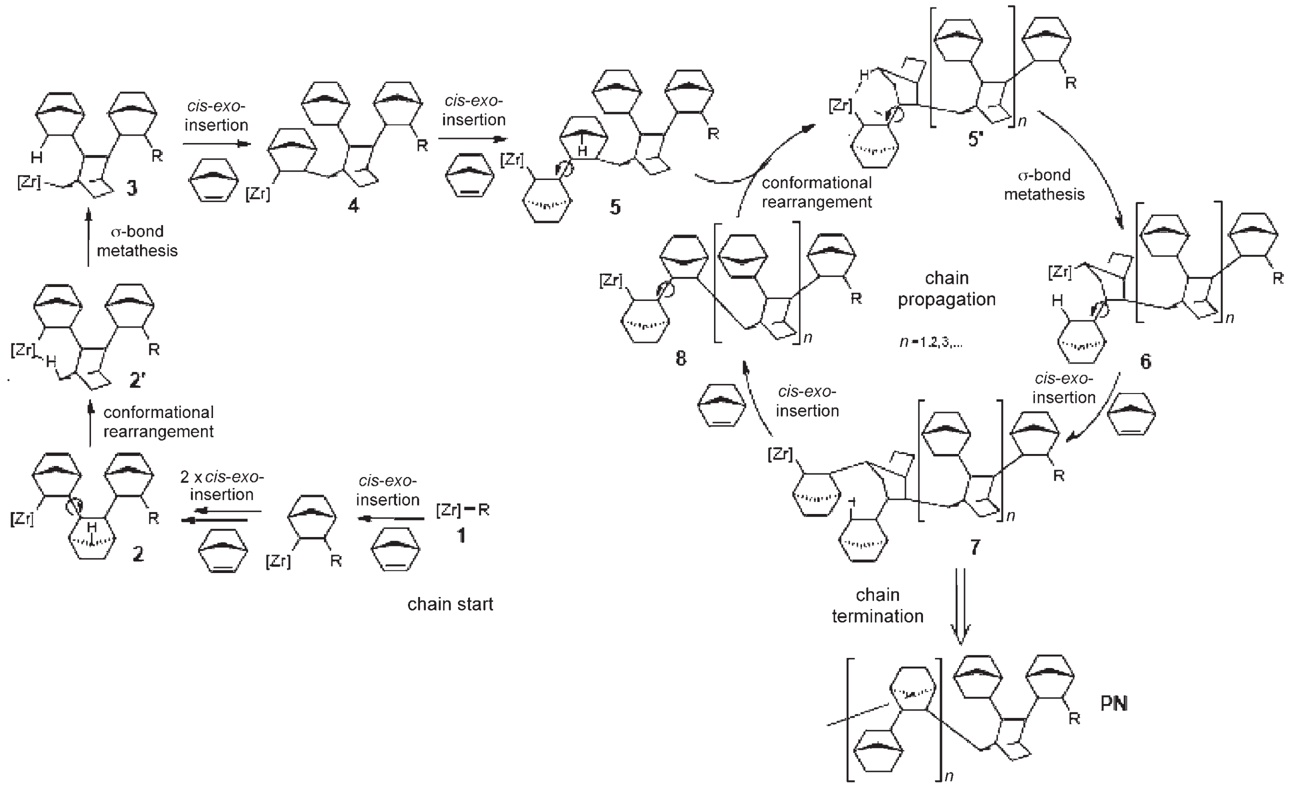
Figure 2. Norbornene oligomer distributions (area integrals in gel chromatogram) generated in the presence of different H_2 or D_2 pressures with the catalyst system *rac*-$[i\text{Pr(Ind)}_2\text{Zr}]\text{Cl}_2$/MAO: ◇ 1.25 bar H_2, × 1.0 bar D_2, ○ 0.5 bar H_2.

tatively. The ^{13}C NMR spectroscopy analyses show that the same applies for the pentamer and heptamer—deuterium is always found on C7 of the penultimately inserted monomer unit. This situation means that in these oligomers the σ-bond metathesis has taken place and because they are found in higher concentrations (i.e., local maxima in Figure 2), the next stage, that is, the subsequent 2,3-*exo*-insertion, is more difficult. The even-numbered oligomers that are present after this insertion are able to accommodate the second *cis*-2,3-*exo*-insertion more easily since they are present in smaller quantities (local minima in Figure 2). The reason that the insertion of norbornene into the Zr−C7 bond is more difficult (slower) after the σ-bond metathesis step must be related to the microstructure of the polynorbornene chain and in particular to its compact helical structure (see below).

Naturally, we would have liked to study higher oligomers than the heptamer. Unfortunately, the limits of preparative separation using the currently available GPC column materials have been reached. However, even though we do not have the octamer, it is clear that the eighth insertion step would again occur *syn* on C7 of the last-but-one inserted norbornene because C7f is deuterated.

Scheme 5 summarizes the entire mechanism of the catalytic homopolymerization of norbornene based on all the information that we have available. The species at the beginning of the chain is, for example, a zirconium hydride. As revealed by the dimer and trimer, the first three monomer insertions take place by *cis*-2,3-*exo* coupling steps and result in the linear trimer **2**. This trimer now preferentially takes up a conformation in which the *syn* hydrogen atom on C7 of the penultimate monomer inserted interacts with the zirconium atom in **2′**. This step is followed by a σ-bond metathesis reaction, with the result that the Zr atom is now located in the *syn* position on C7 of the penultimate inserted monomer unit. In this way the 2-*exo*,2′-*exo*-coupled mononorbornyl branch in **3** is formed. Two further *cis*-2,3-*exo*-insertions lead stepwise to the observed tetramer **4** and pentamer **5**. The latter then undergoes a conformational change (**5′**) and σ-bond metathesis to form **6**. Exactly two further *cis*-2,3-*exo* insertions lead to **7** and **8**, which again after a conformation change (**5′**) can undergo a further σ-bond metathesis to **6**. This completes another cycle of the chain-growth sequence in which exactly two *cis*-2,3-*exo* insertions are followed by a σ-bond metathesis step. This shows that a strictly repeated sequence of polymerization steps based on two different reaction steps is taking place. The mechanism is fully supported by the analysis of all the oligomers up to and including the heptamer and by the deuterium experiments. If the polymerization were to be continued, the resulting polynorbornene (PN) would contain a repeated unit with 2-*exo*,7′-*syn*-coupling in the main chain and 2-*exo*,2′-*exo*-coupled mononorbornyl branches. The beginning of the chain is made up of a *meso*,*meso*-linked trimer with a 7-syn linkage on the central (second inserted) monomer unit.

The product obtained with the *rac*-[*i*Pr(Ind)$_2$Zr]Cl$_2$/MAO system is extremely insoluble, so that it was not possible to obtain NMR spectra of the polymer in solution. Thus it was naturally challenging to see whether the experimental solid-



Scheme 5. Mechanism for the norbornene-homopolymerization with combined vinylic insertion and σ-bond metathesis with only *meso*-linkages to generate the polynorbornene structure; R = H or D, CH$_3$; [Zr] = *rac*-[*i*Pr(Ind)$_2$Zr]$^+$.

state NMR spectrum of the polynorbornene, which has strikingly narrow and resolved signals and differs very distinctly from the spectra of other polynorbornenes, is consistent with the detailed structural information obtained for the oligomers in solution.

The postulated structure of the polynorbornene contains a repeating unit of 14 different carbon atoms. For the further interpretation we consider the chemical shifts of rings D and E of the heptamer in solution, since we assume that the connectivities and possibly also the conformation of this fragment are similar to those of the corresponding groups in the polymer (see Figure 1 and 2 of the Supporting Information).

Taking the chemical shifts of the solution ^{13}C NMR spectrum and applying typical line widths gives a predicted spectrum that looks rather similar to the experimental solid-state spectrum.[3] We therefore carried out a deconvolution analysis of the ^{13}C-cross-polarization (CP)/magic-angle-spinning (MAS)-spectrum and showed that the solid-state NMR spectrum is reproduced well by fourteen signals of approximately equal intensities (Figure 3). The line widths of the eight signals assigned to the methylene atoms are, in line with general experience, significantly broader than those of the methylene C atoms. The difference between the chemical shifts of rings D and F of the heptamer in solution and the corresponding signals in the deconvolution analysis is greatest for C1 and C3 (ca. $\delta = 3.4$ and 2.2 ppm, respectively), while for atoms C11–C17 the differences amount to only around $\delta = 0.5$ ppm.

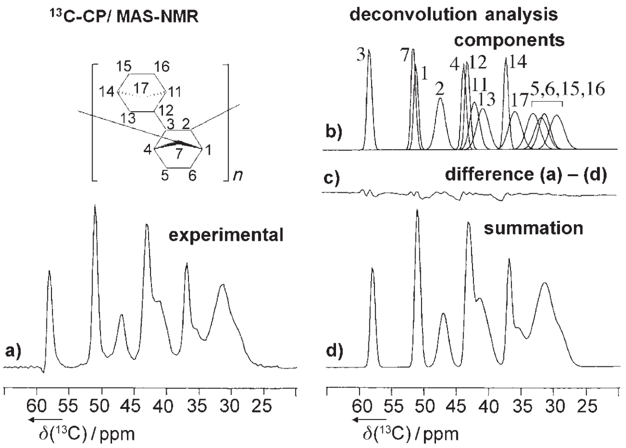


Figure 3. ^{13}C-CP/MAS-spectra of polynorbornene: a) measured spectrum (75.5 MHz), Lorentz–Gauss transformed; b) deconvolution analysis. The line widths of the Gauss lines at half height are 150–170 Hz for the methylene carbon signals and 60–70 Hz for the methine carbon signals; c) difference between the experimental spectrum (a) and the sum of the components (d).

Although the similarity between the experimental ^{13}C solid-state NMR spectrum and the deconvolution analysis with the ^{13}C NMR data of the central region of the heptamer in solution should not be overstated, the agreement provides support for the correctness of the proposed polymer structure.

The very detailed NMR spectroscopic results provide a basis for a model of the microstructure of this polynorbornene. Starting with the crystal structure of the pentamer,[1] a model for the heptamer was developed using the usual force field techniques.[4] The model is compatible with all the NMR coupling constants and NOE data. Copies of this heptamer were then linked together to form a polymer chain. After the geometry had been optimized the structure shown in Figure 4 was obtained. This structure shows a helix made up of 22 monomer units (dark gray polynorbornylene units in Figure 4) to each of which—quasi as a side chain—a further monomer unit is bound (light gray norbornyl units). The pitch of the helix and the number of units per turn could not be determined exactly because of the large number of local minima. In principle, an enantiomeric helix with the opposite sense of rotation is also possible. The space-filling representation (Figure 4, bottom) provides a visual impression of the compactness of the structure. Figure 5 shows a view along the axis of the helix, at the tip of which the umbrella-like metallocene catalyst is located.

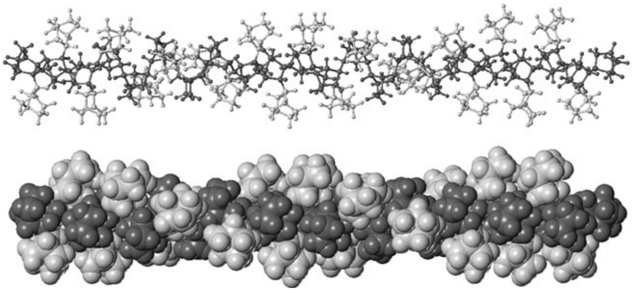


Figure 4. A model of polynorbornene viewed perpendicular to its helical axis. On each monomer of the helical polymer chain (dark norbornylene units) another norbornyl-unit (light mononorbornyl branches) is bound. Top: ball and stick model; bottom: space-filling model.

In view of the compact helical structure of the polynorbornene chain it is not surprising that molecular dynamic calculations[5] indicate that there is no significant reduction in the end-to-end distance of the chain at 400 K over 100 ps

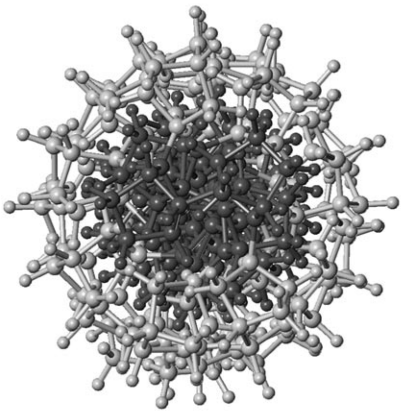


Figure 5. View along the helical axis.

(Figure 3 of the Supporting Information). In other words, the rigid helical structure of the polynornornene resulting from the interactions with the side chains restricts the changes in the conformation that are required for a polymer to melt and which strongly influence its solubility.

Recently Porri et al. reported the oligomerization of norbornene by the "classical" catalyst system $TiCl_4/AlEt_2Cl$. In addition to other oligomers a crystalline heptamer was obtained with a stereoregular 2,3-*exo*-disyndiotactic structure.[6] While no evidence for a σ-bond metathesis was found with this catalyst system, it must be acknowledged that such reactions occur much less frequently with titanium catalysts than with zirconium catalysts.[7]

Received: October 18, 2006
Revised: January 17, 2007

Keywords: bond metathesis · helical structures · metallocenes · molecule dynamic simulation · polynorbornene

---

[1] C. Karafilidis, H. Hermann, A. Rufińska, B. Gabor, R. J. Mynott, G. Breitenbruch, C. Weidenthaler, J. Rust, W. Joppek, M. S. Brookhart, W. Thiel, G. Fink, *Angew. Chem.* **2004**, *116*, 2498–2500; *Angew. Chem. Int. Ed.* **2004**, *43*, 2444–2446.

[2] Deuterium: 99% D.

[3] Details of the NMR spectroscopic studies are to be published separately. The structures were determined unambiguously by means of various 2D-NMR techniques including 2D-INEPT-INADEQUATE.

[4] Program SYBYL 6.9.1, Tripos Inc., St. Louis, USA.

[5] Program SYBYL, Tripos-forcefield, $T = 400$ K, equilibration phase 10 ps, simulation phase 90 ps, time step 1 fs.

[6] L. Porri, V. N. Scalera, M. Bagatti, A. Famulari, S. V. Meille, *Macromol. Rapid Commun.* **2006**, *27*, 1937–1941.

[7] T. K. Woo, P. M. Margl, T. Ziegler, P. E. Blöchl, *Organometallics* **1997**, *16*, 3454.