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Stereospecific Living Ziegler−Natta Polymerization of 1-Hexene

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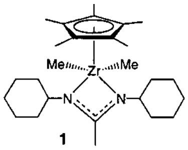
Although major advances have been made during the past decade, the prize of developing highly active homogeneous catalysts that can effect the *living and stereospecific* Ziegler−Natta polymerization of α-olefins remains unclaimed.[1−5] Herein, we make a bid for this challenge by presenting a class of dimethylmonocyclopentadienylzirconium acetamidinates, Cp*ZrMe$_2$[NR^{1}C(Me)NR^2] (Cp* = η^5-pentamethylcyclopentadienyl), that function as catalyst precursors for the living Ziegler−Natta polymerization of α-olefins upon activation by a borate cocatalyst. By manipulating the steric bulk of the two *N*-acetamidinate substituents, R^1 and R^2, and most importantly, by going from C_s to C_1 symmetry as exemplified by compounds **1** and **2**, the stereospecific living polymerization of 1-hexene has been achieved to provide highly isotactic, high molecular weight materials possessing low polydispersities. With all the possibilities for materials engineering that living polymerization processes provide,[6] this new class of Ziegler−Natta catalyst precursor should make available, for the first time, a large number of new stereoregular polyolefins possessing desirable physical properties.



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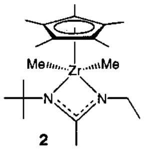

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We have previously shown that insertion of symmetric and unsymmetric carbodiimides, R^{1}N=C=NR^2 (R^1 = R^2 and R^1 ≠ R^2, respectively), into a titanium−methyl bond of (η^5-C$_5$R$_5$)TiMe$_3$ (R = H and Me) cleanly provides dimethylmonocyclopentadienyl titanium acetamidinates that are chiral at the metal center for R^1 ≠ R^2.[7] By employing Cp*ZrMe$_3$[8] as the starting material, this procedure was extended here for the synthesis of several derivatives of Cp*ZrMe$_2$[NR^{1}C(Me)NR^2] represented by compounds **1**, **2**, **3** (R^1 = *t*-Bu, R^2 = cyclohexyl), and **4** (R^1 = *t*-Bu, R^2 = 2,6-diisopropylphenyl).[9] Variable-temperature ^{1}H NMR studies of the racemic complexes **2** and **3**, which possess diastereotopic methyl groups bonded to zirconium, established that much lower barriers to racemization are present in these complexes relative to their titanium analogues.[7a,10] Further, crystallographic analysis of **2** revealed that it is monomeric in the solid state with no unusual bond lengths or coordination geometry being present.[10]

Table 1. Hexene Polymerization Data[9]

entry	catalyst[a]	[Hex] (M)	temp (°C)	time (min)	activity[b]	M_n[c]	M_w/M_n
1	**1**	32	0	30	9	11 032	1.10
2	**2**	32	25[d]	15	110	32 572	1.50
3	**2**	2	0	15	76	43 544	1.23
4	**2**	2	−10	15	64	49 251	1.03
5	**2**	2	−10	30	nd	69 544	1.10

[a] Prepared from equimolar (25 μmol) amounts of the zirconium complex and [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] in chlorobenzene; total reaction volume,10 mL. [b] g$_{\text{poly}}$·mmol$_{\text{cat}}^{-1}$·h^{-1}. [c] Determined by GPC analysis at 35 °C using polystyrene standards and THF as the eluant. [d] Exotherm observed for polymerization initiated at this temperature.

Prior studies with compounds closely related to **1**−**4** have provided only disappointing results with respect to the Ziegler−Natta polymerization of either ethene or propene.[7a,11] As Table 1 shows, however, upon activation with the borate, [PhNMe$_2$H][B(C$_6$F$_5$)$_4$],[12] compound **1** surprisingly proved to be capable of functioning as a competent catalyst precursor for the polymerization of 1-hexene at 0 °C in chlorobenzene. Importantly, the narrow polydispersity (monomodal, M_w/M_n = 1.10), and the lack of olefinic resonances in both the ^{1}H and ^{13}C NMR spectra of the poly(1-hexene) formed,[2d] strongly suggested a living character for this polymerization process that is devoid of termination via β-hydride elimination. Unfortunately, the ^{13}C NMR spectrum of this material also clearly pointed to a lack of stereocontrol of polymer microstructure with this particular system (Figure 1a).[13]

Given the promising results with **1**, and the known ability to produce highly isotactic polypropylene from chiral C_1 symmetric *ansa*-bridged metallocenes,[14] it was of interest to determine if the racemic compounds, **2**−**4**, could serve in a similar capacity. In this regard, while compounds **3** and **4** exhibited dramatically reduced activity, with only oligomers being produced under

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[1] For recent reviews regarding the development of homogeneous Ziegler−Natta polymerization catalysts, including the stereospecific polymerization of propene, see: (a) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170. (b) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 428−447.

[2] For recent stereospecific Ziegler−Natta polymerizations of α-olefins other than propene see: (a) Asanuma, T.; Nishimori, Y.; Ito, M.; Uchikawa, N.; Shiomura, T. *Polym. Bull.* **1991**, *25*, 567−570. (b) Coughlin, E. B.; Bercaw, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 7606−7607. (c) Kesti, M. R.; Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 9679−9680. (d) Babu, G. N.; Newmark, R. A.; Chien, J. C. W. *Macromolecules* **1994**, *27*, 3383−3388. (e) van der Linden, A.; Schaverien, C. J.; Meijboom, N.; Ganter, C.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008−3021. (f) Yamaguchi, Y.; Suzuki, N.; Fries, A.; Mise, T.; Koshino, H.; Ikegami, Y.; Ohmori, H.; Matsumoto, A. *J. Polym. Sci. A: Polym. Chem.* **1999**, *37*, 283−292. (g) Stehling, U. M.; Stein, K. M.; Fischer, D.; Waymouth, R. M. *Macromolecules* **1999**, *32*, 14−20.

[3] For the living Ziegler−Natta polymerization of α-olefins, see: (a) Doi, Y.; Suzuki, S.; Soga, K. *Macromolecules* **1986**, *19*, 2896−2900. (b) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008−10009. (c) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830−3831. (d) Killian, C. M.; Tempel, D. J.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664−11665. (e) Hagihara, H.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 3184−3188.

[4] We define a stereospecific polymerization as one that can provide a particular polymer microstructure with >95% selectivity at the pentad level of analysis.

[5] The stereospecific living polymerization of a functionalized α-olefin, i.e., methyl methacrylate, has been achieved using lanthanide-based catalysts that effect polymerization through an enolate mechanism that is distinctly different than the Ziegler−Natta process, see: (a) Yasuda, H.; Yamamoto, H.; Yokota, K.; Miyake, S.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 4908−4910. (b) Giardello, M. A.; Yamamoto, Y.; Brard, L.; Marks, T. J *J. Am. Chem. Soc.* **1995**, *117*, 3276−3277.

[6] (a) Kennedy, J. P. *Makro Chem. Macro Syn.* **1992**, *60*, 1−9. (b) Gibson, V. C. *Adv. Mater.* **1994**, *6*, 37−42. (c) Pugh, C.; Kiste, A. L. *Prog. Polym. Sci.* **1997**, *22*, 601−691.

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[9] Details provided in the Supporting Information.

[10] Full spectroscopic characterizations of **1**−**4**, including crystallographic analyses, will be presented elsewhere.

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[13] For ^{13}C NMR spectral analyses of poly(1-hexene) microstructure, see: (a) Reference 2d. (b) Asakura, T.; Demura, M.; Nishiyama, Y. *Macromolecules* **1991**, *24*, 2334−2340.

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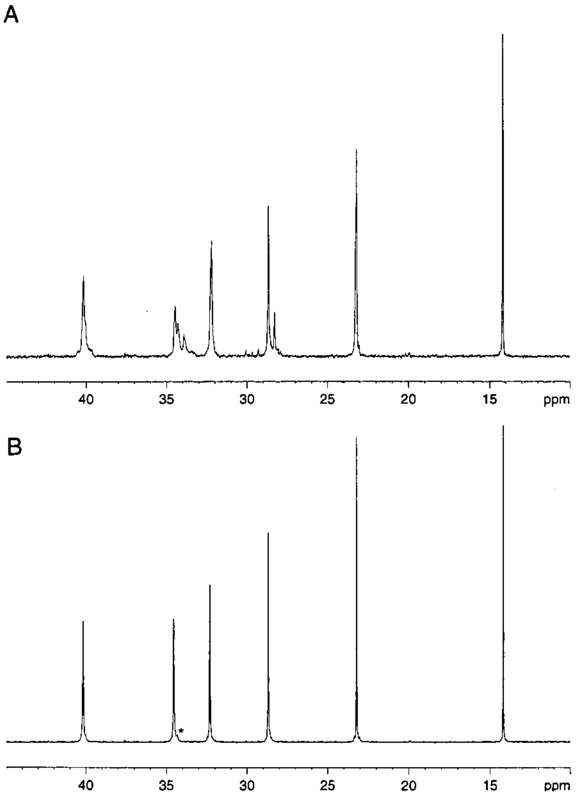

Figure 1. (a) ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) spectrum for poly(1-hexene) produced from **1**/$[B(C_6F_5)_4]$ at 0 °C in chlorobenzene (M_n = 11032; M_w/M_n = 1.10). (b) ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) spectrum (δ 40.19, 34.57, 32.33, 28.69, 23.22, 14.19) for poly(1-hexene) produced from **2**/$[B(C_6F_5)_4]$ at −10 °C in chlorobenzene (M_n = 49251; M_w/M_n = 1.05). The small resonance marked by the asterisk is tentatively assigned to the mmmr pentad [$\Delta\delta$(from mmmm) = −0.21 ppm[13]].

identical conditions as a possible result of too much steric hindrance imposed by these particular acetamidinate substituents, **2** proved to be an exceptional catalyst precursor for the polymerization of 1-hexene with respect to providing both a higher activity and a higher molecular weight for the poly(1-hexene) formed when the process was begun at room temperature (see Table 1, entry 2). Inspection of the ^{13}C NMR spectrum for this material now also revealed it to be highly isotactic (mmmm >95%).[9,13] Indeed, the only indication that these conditions were potentially nonideal for both the stereospecific and living polymerization of 1-hexene was provided by the broader polydispersity index (M_w/M_n) of 1.50 that was obtained for this poly(1-hexene). Fortunately, though, performing the polymerizations with **2** at lower temperatures had the beneficial impact of both increasing the molecular weights and decreasing the polydispersities of the poly(1-hexene)s produced while maintaining relatively high activities (entries 3 and 4). Most significantly, the high molecular weight poly(1-hexene) obtained at −10 °C now had a polydispersity of only 1.03, thereby indicating that this polymerization was most likely living and, as the ^{13}C NMR spectrum shown in Figure 1b reveals, stereospecific for the formation of isotactic material (mmmm >95%).[13] Additional proof for the living character of the polymerization of 1-hexene conducted under these last conditions was provided by a plot of the number-average molecular weight, M_n, of the poly(1-hexene) produced vs the extent of monomer consumed which yielded a linear correlation as shown in Figure 2.[15] Finally, it was shown by one polymerization experiment [initial conditions: 180 equiv of 1-hexene; 50 μmol of **2**/$[B(C_6F_5)_4]$ in chlorobenzene, −10 °C; total reaction volume,10 mL] that the polymer formed (M_n = 20732, M_w/M_n = 1.03) after complete consumption of the monomer (t = 60 min) was still living by the formation of a higher molecular weight polymer (M_n = 35372, M_w/M_n = 1.13) upon introduction of another 180 equiv of 1-hexene and carrying out the polymerization for an additional 40 min.

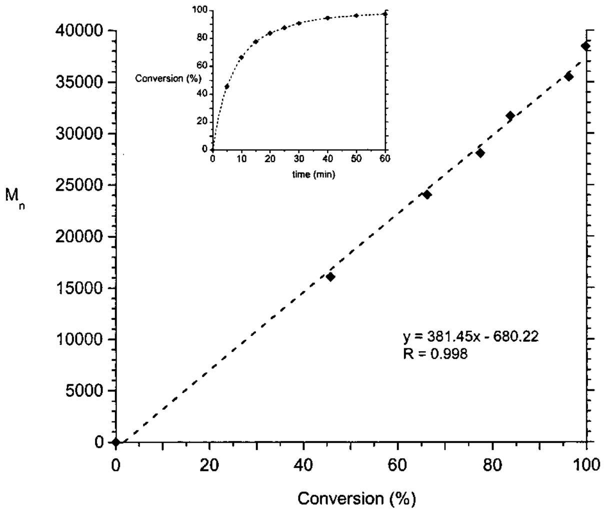

Figure 2. Plot of M_n versus percent conversion of 1-hexene (initial conditions: 1.97 M in 1-hexene; 50 μmol each of **2** and $[PhNMe_2H][B(C_6F_5)_4]$ in chlorobenzene, −10 °C; total reaction volume, 10 mL) (M_w/M_n = 1.03−1.09 for each data point). The dashed line is a linear curve fit of the data. The inset shows a plot of the percent conversion of 1-hexene vs time where the dashed line is a guide for the eye.

Although the ability to produce highly isotactic poly(1-hexene) with **2** may appear somewhat surprising in light of the low barrier to racemization that is present in this compound, it is reasonable to assume that this barrier is higher in the catalytically active cationic complex where propagation must proceed much faster than amidinate ring-flipping.[7] Indeed, we attribute the latter racemization process as being responsible for the small degree of stereoerror observed for the C3 resonance in the ^{13}C NMR spectrum of Figure 1b, marked with the asterisk and tentatively assigned to the mmmr resonance,[13] that potentially gives rise to an isotactic stereoblock microstructure similar to that observed by Ewen[16] for polypropylene. The isospecificity of the **2**/$[B(C_6F_5)_4]$ system further suggests that site-isomerization after olefin insertion must occur much more rapidly than olefin complexation and propagation.[14] Whether a similar rapid site-isomerization process is responsible for the nonstereospecificity of the **1**/$[B(C_6F_5)_4]$ system awaits further investigation.

In conclusion, we present the first catalyst system for the stereospecific living Ziegler−Natta polymerization of an α-olefin. Given the rich variation that is possible with both the cyclopentadienyl and amidinate ligands in $Cp^*ZrMe_2[NR^1C(Me)NR^2]$, together with a facile single-step synthesis for this precatalyst that does not require the separation of stereoisomers, it should be possible to further improve upon these preliminary results.[17]

Supporting Information Available: Details of catalyst and polymer synthesis and characterization (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] **Note Added in Proof**: (a) We have now used **2**/$[B(C_6F_5)_4]$ for the production of *iso*-poly(1-hexene)-*block*-*iso*-poly(vinylcyclohexane) diblock copolymers. (b) In December 1999, it was reported that *rac*-(et)$Ind_2ZrMe_2/B(C_6F_5)_3$ could be used to carry out the isospecific living polymerization of 1-hexene at −78 °C [M_n = 5400; M_w/M_2 = 1.29; activity = 0.05; yield = 0.4% (14 h)], see: Fukui, Y.; Murata, M.; Soga, K. *Macromol. Rapid Commun.* **1999**, *20*, 637−640.