Catalyst Design

DOI: 10.1002/anie.200701703

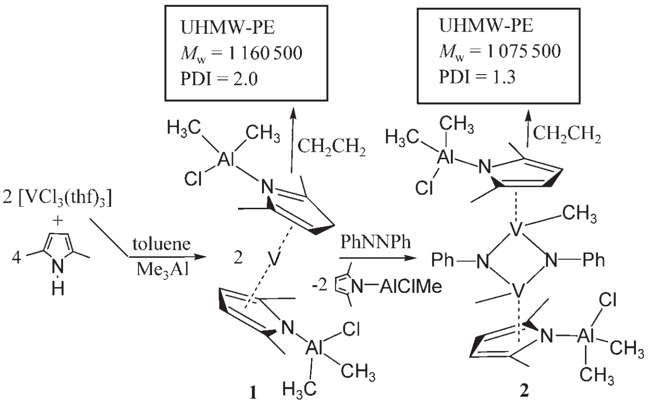
Single-Site, Single-Component Catalysts for Very High Molecular Weight Polyethylene: A Robust "Ready-To-Go" Vanadium π-Bonded Complex Without a Preformed V−C Bond**

Amir Jabri, Ilia Korobkov, Sandro Gambarotta, and Robbert Duchateau**

Among the plethora of metals capable of performing ethylene polymerization, oligomerization, and copolymerization, vanadium has traditionally played a relatively minor role.[1,2] Nonetheless, the perfectly random copolymerization performed by some vanadium catalysts makes these derivatives commercially irreplaceable for EPDM production (EPDM = ethylene propylene diene monomer).[3] In addition, di- and trivalent vanadium complexes have in some instances shown very high potential as precursors to highly active catalytic systems.[1b,4]

Given that the CpV moiety (Cp = C_5H_5) has been shown to be capable of forming stable ethylene complexes,[5] we argued that perhaps a low-valent vanadium complex of a hemilabile π-bonded ligand system (analogous to Cp) could push the reactivity beyond the realm of olefin coordination and possibly provide a self-activating catalyst. Indeed, ligand hemilability has proven beneficial for catalytic C−C bond forming reactions.[6] Thus, this work was initially aimed at exploring the use of the pyrrolyl anion as a possible hemilabile Cp analogue. Previous reports have clearly pointed out the tendency of the pyrrolide anion to form σ- instead of π-bonded vanadium complexes.[7] However, we reasoned that once a strong Lewis acid, such as AlX_3 (X = halogen, alkyl), would lock the N atom through σ-bonding, a π-bonding mode with the transition metal could occur. The resulting π-bonded pyrrolide complex would have the benefit that its π-bonding interaction and thus its hemilability could be tuned via the appropriate choice of the strength of the Lewis acid coordinated to the pyrrolide N atom.

Given the above rationale, we have treated trivalent vanadium with 2,5-Me_2pyrrole in the presence of six equivalents of $AlMe_3$ and obtained the divalent complex $[(\eta^5\text{-}\{2,5\text{-}Me_2C_4H_2N(AlClMe_2)\})_2V]$ (**1**; Scheme 1; UHMW-PE = ultrahigh molecular weight polyethylene, M_w = weight-average molecular weight, PDI = polydispersity index). The connectivity of this paramagnetic complex ($\mu_{eff} = 3.79\mu_B$) was elucidated by X-ray diffraction. The crystal structure (Figure 1) shows a vanadocene-type arrangement with the



Scheme 1.

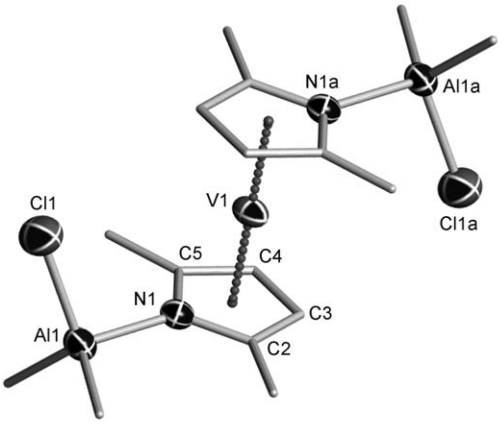


Figure 1. Crystal structure of **1** with thermal ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: V1–N1 2.234(3), V1–C2 2.261(3), V1–C3 2.290(3), V1–C4 2.315(4), V1–C5 2.275(3), C2–C3 1.387(5), C3–C4 1.416(6), C4–C5 1.389(5).

---

[*] A. Jabri, I. Korobkov, Prof. Dr. S. Gambarotta
Department of Chemistry
University of Ottawa
10 Marie Curie, Ottawa ON K1N 6N5 (Canada)
Fax: (+1) 613-562-5170
E-mail: sgambaro@uottawa.ca
Prof. Dr. R. Duchateau
Department of Chemistry
Eindhoven University of Technology
P.O. Box 513, 5600 MB (The Netherlands)
Fax: (+31) 40-247-4918
E-mail: r.duchateau@tue.nl

[**] This work was supported by the Natural Science and Engineering Council of Canada (NSERC) and by the Eindhoven University of Technology. Mr. A. P. Jekel (University Groningen) is gratefully aknowledged for the GPC measurements.

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

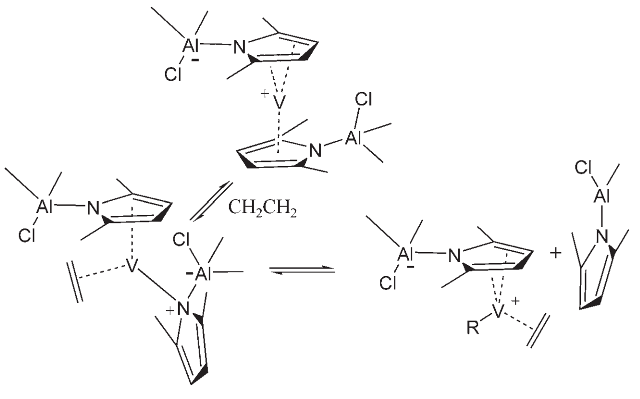
two parallel rings symmetrically π-bonded to the vanadium atom. As expected, each pyrrolyl nitrogen atom coordinates to one coplanar Me_2AlCl residue. The ring C−C bond lengths show only a very minor extent of double-bond localization, thus suggesting a six-electron π-bonding interaction (Cp-like) to the vanadium center. The complex is thermally robust and does not decompose upon heating in toluene solution at 100 °C for 12 h. During the formation of **1**, $AlMe_3$ has both anionized pyrrole and reduced vanadium to the divalent state. Given the poor stability of trivalent organovanadium, this reduction is hardly surprising. In spite of the divalent state and the thermal robustness, complex **1** is single-component, single-site catalyst. It is highly unusual in this category of catalysts since it does not have a preformed V−R bond. Exposure of a toluene solution to ethylene under pressure and at moderately high temperature started the polymerization reaction, which produced PE with very high molecular weight, high linearity, and with polydispersity characteristic of a single-site catalyst (Table 1). The best catalytic activity was $0.18\,kg\,(g\,V)^{-1}\,h^{-1}\,bar^{-1}$. Moderate heating (75 °C) is necessary to start the polymerization reaction, thus indicating that a molecular reorganization of **1** must occur in order to fulfill the polymerization prerequisites. Lower pressure also seems to have a detrimental effect on the activity. Instead, polymerization reactions carried out in the presence of methylalumoxane (MAO) as activator show both a decrease in catalytic activity and formation of broadly dispersed polymers with lower molecular weight. Entries 1 and 3–6 of Table 1 show a melting point in the first heating curve above 141 °C, which is characteristic for linear UHMW-PE. The melting points in the second heating curve are as expected for linear polyethylene.

Table 1: Polymerization of ethylene.

Entry	MAO (equiv)	T [°C]	Yield [g]	T_m^{1st} [°C]	T_m^{2nd} [°C]	M_w	PDI
1[a,c,d]	0	100	5.1	144.9	135.6	1 135 500	2.1
2[a,c,d]	1000	100	1.9	132.8	130.8	79 660	8.4
3[a,c,d]	0	75	12.5	141.2	137.1	1 160 500	2.0
4[a,c,d]	0	50	6.0	143.0	134.9	1 689 500	1.6
5[a,c,d]	0	25	0.4	144.0	136.7	1 546 000	3.3
6[a,c,e]	0	75	0.5	146.1	137.4	1 494 000	2.2
7[b,c,d]	0	75	7.6	146.1	137.4	1 075 500	1.3

[a] Complex **1**. [b] Complex **2**. [c] 30 μmol. [d] 35 bar. [e] 17 bar.

Homogeneous single-component ethylene polymerization catalysts capable of starting polymerization without further activation by alkyl aluminum are known but are generally limited to cationic alkyl complexes containing borate anions[8] as well as neutral lanthanide[9] and late-transition-metal complexes.[8] In all these species, either a cationic center or a highly Lewis acidic element, an M−C bond, or both are pre-existing. The only exception is provided by $[Cp^*{}_2Sm(thf)_2]$, $(Cp^* = C_5Me_5)$ which is also s a single-site, single-component ethylene polymerization catalyst.[10] Similar to samarocene, complex **1** does not contain a metal–alkyl bond and yet acts as an efficient single-component catalyst to produce UHMW-PE. Since **1** appears to be thermally robust and coordinatively saturated, intriguing questions arise about the polymerization mechanism. We propose that the presence of ethylene triggers a reorganization (possibly through an equilibrium) involving either dissociation or slippage of one ring with or without switching of the coordination mode from π to σ (Scheme 2). A complete ring dissociation must necessarily imply formation of $2,5\text{-}Me_2C_4H_2N(AlClR)$ and transfer of one alkyl group from Al to V, thus affording the coordinatively unsaturated organovanadium species $[\eta^5\text{-}\{2,5\text{-}Me_2C_4H_2N(AlClR_2)\}VR]$. Incidentally, the coordination of the pyrrolide ring may be formally described in terms of a zwitterionic structure, which would imply that the vanadium atom is acquiring some extent of formal positive charge.



Scheme 2.

In search for clues, we have embarked on a study of the reactivity of **1** with a variety of trapping agents including CO, phosphines, deactivated alkenes, and mild oxidizing agents. To this end, the reaction with azobenzene proved to be successful.

When a solution of **1** was treated with half an equivalent of azobenzene, a sudden color change took place and crystals of a new complex $[\{\eta^5\text{-}\{2,5\text{-}Me_2C_4H_2N(AlClR_2)\}VMe(NPh)\}_2]$ (**2**) were isolated after workup. The complex is a symmetry-generated dimer (Figure 2) formed by two identical $\{\eta^5\text{-}(2,5\text{-}Me_2C_4H_2N\{AlClMe_2\})VMe\}$ residues linked by a bridging

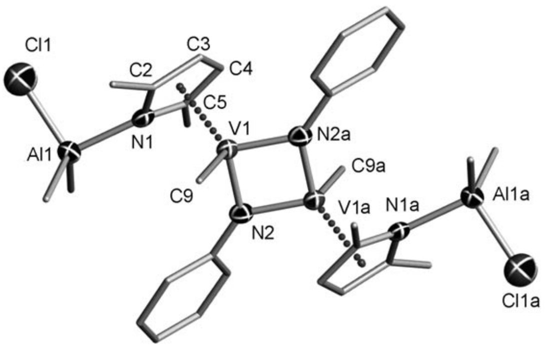


Figure 2. Crystal structure of **2** with thermal ellipsoids set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: V1–N1 2.359(5); V1–C2 2.324(6), V1–C3 2.297(7), V1–C4 2.315(4), V1–C5 2.389(6), V1–C9 2.083(7), C2–C3 1.397(10), C3–C4 1.401(10), C4–C5 1.381(9), V1–N2 1.861(5), V1⋯V1a 2.511(2).

PhN imido group. The short V–V contact is in the range of what might be normally regarded as a V–V single bond. Nonetheless, the complex displays a small residual paramagnetism that indicates the presence of antiferromagnetic coupling. The magnetism, together with the very poor solubility in any solvent with which the complex does not react, prevented us from obtaining meaningful data from NMR spectroscopy.

Formation of **2** is easily rationalized in terms of overall dissociation of a 2,5-$Me_2C_4H_2N(AlClMe_2)$ unit and formation of a {η^5-(2,5-$Me_2C_4H_2N\{AlClMe_2\}$)VMe} residue. A four-electron oxidative attack at the azobenzene molecule by two of these intermediates results in N–N double-bond cleavage and formation of the imido group. The presence of the V–Me bond in **2** demonstrates that alkyl migration from Al to V is indeed possible by dissociation of one of the two rings during an oxidative addition reaction.

Accordingly, complex **2** also is a single-component catalyst that starts polymerization with no need for further activation. In the present case, either the same ring slippage or dissociation as mentioned above could take place, or simple dimer–monomer dissociation equilibrium may generate the required empty coordination site for ethylene bonding. The catalytic activity is somewhat lower than for **1** under the best polymerization conditions, but the polymer properties appears to be similar, with improved polydispersity (entry 7, Table 1). Complexes **1** and **2** will obviously form different intermediates during the polymerization. Whether the active species derived from **1** remains in the divalent oxidation state or, for example, undergoes oxidative addition as was observed for the pentamethyl samarocene[10] is not yet clear.

In conclusion, we have reported herein the synthesis and characterization of a single-site, single-component ethylene polymerization catalyst (**1**) that does not contain a preformed organyl–transition-metal functionality. This ligand system provides a robust π complex in the dormant state, but its latent Lewis acidity and its ability to undergo intramolecular alkyl shift to form a transition-metal–carbon bond provides an unprecedented self-activating catalyst system. This system has some stimulating but not yet fully elucidated implications as far as the polymerization mechanism is concerned, which will be the target of further studies. Furthermore, the fact that even complex **2** (perhaps more predictably) is also a single-component catalyst adds generality to these findings and encourages further exploration in the domain of other metals that are well-established for their performance as polymerization catalysts.

Experimental Section

1: A purple suspension of [$VCl_3(thf)_3$] (373 mg, 1 mmol) in toluene (7 mL) was combined with a freshly prepared solution of $AlMe_3$ (432 mg, 6 mmol) and 2,5-dimethylpyrrole (190 mg, 2 mmol) in toluene (7 mL). The color of the mixture immediately changed to black-green. The solution was stirred for a period of 10 minutes, centrifuged to eliminate a small amount of insoluble residue, and layered with an equal portion of hexanes to yield black-green plates of **1a** (250 mg, 0.63 mmol, 63%). $\mu_{eff} = 3.83\mu_B$. Elemental analysis (%) calcd for $C_{16}H_{28}Al_2Cl_2N_2V$: C 45.01, H 6.53, N 6.51; found: C 45.30, H 6.65, N 6.60.

2: Method A. A greenish-black solution of **1** (398 mg, 1 mmol) in chlorobenzene (15 mL) was treated with azobenzene (91 mg, 0.5 mmol). The color immediately changed to dark red. Crystals of **2** (270 mg, 88%) separated upon slow diffusion of hexane into the chlorobenzene solution.

Method B. A solution of $AlMe_3$ (432 mg, 6 mmol) and 2,5-dimethylpyrrole (190 mg, 2 mmol) in chlorobenzene (7 mL) was added to a purple solution of [$VCl_3(thf)_3$] (367 mg, 1 mmol) and azobenzene (91 mg, 0.5 mmol) in chlorobenzene (7 mL). The addition was accompanied by an immediate color change to dark red. The solution was stirred for a period of 10 minutes, centrifuged, and layered with an equal portion of hexanes to yield dark red crystals of **2** (225 mg, 73%). $\mu_{eff} = 1.4\mu_B$ per vanadium center. Elemental analysis (%) calcd for $C_{30}H_{44}Al_2Cl_2N_4V_2$: C 52.38, H 6.38, N 8.07; found: C 52.41, H 6.45, N 8.15.

Polymerization results: Samples were tested in a 200-mL high-pressure Büchi reactor containing a heating/cooling jacket. A preweighed portion of catalyst was dissolved in toluene (100 mL) under N_2 prior to loading the reaction vessel. Solutions were heated using a thermostatic bath and charged with ethylene, maintaining the pressure throughout the run. Polymerizations were quenched by addition of MeOH and HCl. The resulting polymer was isolated by filtration, sonicated with a solution of HCl, rinsed, and thoroughly dried prior to measuring the mass. Gel permeation chromatography (GPC) analysis of the polyethylene was referenced to polystyrene standards ($M_w = 65500$, PDI = 1.02).

Crystal data for **1**: $C_{16}H_{28}Al_2Cl_2N_2V$, $M_r = 424.20$, monoclinic, space group $P2_1/n$, $T = 203(2)$ K, $a = 8.227(2)$, $b = 18.349(5)$ $c = 8.263(2)$ Å, $\beta = 119.116(4)°$, $V = 1089.7(5)$ Å^3, $Z = 2$, $\mu(Mo_{K\alpha}) = 0.781$ mm^{-1}; 7694 reflections were collected, of which 1804 were unique ($R_{int} = 0.0329$), GOF = 1.0151, final $R_1[I>2\sigma(I)] = 0.0486$, $wR_2 = 0.1341$.

Crystal data for **2**: $C_{30}H_{44}Al_2Cl_2N_4V_2$, $M_r = 687.43$, triclinic, space group $P\bar{1}$, $T = 203(2)$ K, $a = 9.031(2)$, $b = 9.889(2)$ $c = 10.313(3)$ Å, $\alpha = 66.972(3)$, $\beta = 88.399(4)$, $\gamma = 89.769(4)°$, $V = 847.3(4)$ Å^3, $Z = 1$, $\mu(Mo_{K\alpha}) = 0.787$ mm^{-1}; 5604 reflections were collected, of which 1847 were unique ($R_{int} = 0.0463$), GOF = 1.060, final $R_1[I>2\sigma(I)] = 0.0632$, $wR_2 = 0.1615$.

CCDC-644253 (**1**) and 644254 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: April 17, 2007
Published online: July 12, 2007

Keywords: homogeneous catalysis · polymerization · single-component catalyst · vanadium

---

[1] For recent reviews: a) V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283; b) S. Gambarotta, *Coord. Chem. Rev.* **2003**, *237*, 229; c) H. Hagen, J. Boersma, G. van Koten, *Chem. Soc. Rev.* **2002**, *31*, 357; d) K. Nomura, *New Dev. Catal. Res.* **2005**, 199.

[2] a) P. T. Witte, A. Meetsma, B. Hessen, *J. Am. Chem. Soc.* **1997**, *119*, 10561; b) V. J. Murphy, H. Turner, *Organometallics* **1997**, *16*, 2495; c) S. Scheuer, J. Fisher, J. Kress, *Organometallics* **1995**, *14*, 2627; d) A. Zambelli, A. Proto, P. Longo, *Ziegler Natta Catalysis* (Eds.: G. Fink, R. Mulhaupt, H. H. Brintzinger), Springer, Berlin, **1995**; e) W. K. Kim, M. J. Fevola, L. M. Liable-Sands, A. L. Rheingold, K. H. Theopold, *Organometallics* **1998**, *17*, 4541; f) K. J. Feher, J. F. Walzer, R. L. Blanski, *J. Am. Chem. Soc.* **1991**, *113*, 3618; g) K. Czaja, M. Bialek, *Macromol. Rapid Commun.* **1998**, *19*, 163; h) M. Bühl, *Angew. Chem.* **1998**, *110*, 153; *Angew. Chem. Int. Ed.* **1998**, *37*, 142; i) M. C. W. Chan, J. M.

Cole, V. C. Gibson, J. A. K. Howard, *Chem. Commun.* **1997**, 2345, and references therein; j) V. C. Gibson, C. Redshaw, M. R. J. Elsegood, *J. Chem. Soc. Dalton Trans.* **2001**, 767; k) R. A. Henderson, D. L. Hughes, Z. Janas, R. L. Richards, P. Sobota, S. Szafert, *J. Organomet. Chem.* **1998**, *554*, 195; l) R. Choukroun, P. Moumboko, S. Chevalier, M. Etienne, B. Donnadieu, *Angew. Chem. Int. Ed.* **1998**, *110*, 3363; *Angew. Chem. Int. Ed.* **1998**, *37*, 3169; m) C. Lorber, B. Donnadieu, R. Choukroun, *Organometallics* **2000**, *19*, 1963; n) H. Hagen, C. Bezemer, J. Boersma, H. Kooijman, M. Lutz, A. L. Spek, G. van Koten, *Inorg. Chem.* **2000**, *39*, 3970.

[3] See, for example: a) Y. Doi, S. Suzuki, K. Soga, *Macromolecules* **1986**, *19*, 2896; b) T. Ouzumi, K. Soga, *Makromol. Chem.* **1992**, *193*, 823; c) A. Gumboldt, J. Helberg, G. Schleitzer, *Makromol. Chem.* **1967**, *101*, 229; d) E. Adisson, *J. Polym. Sci. Part A* **1994**, *32*, 1033; e) S. C. Davis, W. von Hellens, H. Zahalka, *Polymer Material Encyclopedia*, *Vol. 3* (Ed.: J. C. Salamone), CRC Press, Boca Raton, FL, **1996**.

[4] a) P. D. Smith, J. L. Martin, J. C. Huffman, R. L. Bansemer, K. G. Caulton, *Inorg. Chem.* **1985**, *24*, 2997; b) H. Hagen, J. Boersma, G. van Koten, *Chem. Soc. Rev.* **2002**, *31*, 357.

[5] a) B. Hessen, A. Meetsma, J. Teuben, *J. Am. Chem. Soc.* **1988**, *110*, 4860; b) P. T. Witte, A. Meetsma, B. Hessen, P. H. M. Budzelaar, *J. Am. Chem. Soc.* **1997**, *119*, 10561.

[6] a) P. J. W. Deckers, B. Hessen, J. H. Teuben, *Angew. Chem.* **2001**, *113*, 2584; *Angew. Chem. Int. Ed.* **2001**, *40*, 2516; b) P. J. W. Deckers, B. Hessen, J. H. Teuben, *Organometallics* **2002**, *21*, 5122.

[7] For example, see: a) J. Edema, S. Gambarotta, A. Meetsma, A. L. Spek, N. Veldman, *Inorg. Chem.* **1991**, *30*, 2062; b) J. Edema, S. Gambarotta, A. Meetsma, F. Van Bolhuis, A. L. Spek, W. J. J. Smeets, *Inorg. Chem.* **1990**, *29*, 2147.

[8] For example, see: a) G. W. Coates, P. D. Hustad, S. Reinartz, *Angew. Chem.* **2002**, *114*, 2340; *Angew. Chem. Int. Ed.* **2002**, *41*, 2236, and references therein; b) C. Qihui, Y. Jing, H. Jiling, *Organometallics* **2007**, *26*, 617; c) J. W. Strauch, G. Erker, G. Kehr, R. Frohlich, *Angew. Chem.* **2002**, *114*, 2662; *Angew. Chem. Int. Ed.* **2002**, *41*, 2543; d) M. J. Brookhart, J. M. DeSimone, B. E. Grant, M. J. Tanner, *Macromolecules* **1995**, *28*, 5378; e) T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R. H. Grubbs, D. A. Bansleben, *Science* **2000**, *287*, 460; f) I. Göttker-Schnetmann, P. Wehrmann, C. Röhr, S. Mecking, *Organometallics* **2007**, *26*, 2348; g) L. K. Johnson, C. M. Killian, M. Brookhart, *J. Am. Chem. Soc.* **1995**, *117*, 6414; h) W. Keim, F. H. Kowaldt, R. Goddard, C. Kruger, *Angew. Chem.* **1978**, *90*, 493; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 466; i) K. A. Ostoja Starzewski, J. Witte, *Angew. Chem.* **1985**, *97*, 610; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 599; j) U. Klabunde, S. D. Ittel, *J. Mol. Catal.* **1987**, *41*, 123; k) P. Kuhn, D. Semeril, C. Jeunesse, D. Matt, M. Neuburger, A. Mota, *Chem. Eur. J.* **2006**, *12*, 5210; l) F. A. Hicks, M. Brookhart, *Organometallics* **2001**, *20*, 3217; m) W. Liu, J. M. Malinoski, M. Brookhart, *Organometallics* **2002**, *21*, 2836; n) O. Daugulis, M. Brookhart, P. S. White, *Organometallics* **2003**, *22*, 4699; o) S. J. Diamanti, P. Ghosh, F. Shimizu, G. C. Bazan, *Macromolecules* **2003**, *36*, 9731; p) J. C. Jenkins, M. Brookhart, *Organometallics* **2003**, *22*, 250; q) F. A. Hicks, J. C. Jenkins, M. Brookhart, *Organometallics* **2003**, *22*, 3533; r) J. C. Jenkins, M. Brookhart, *J. Am. Chem. Soc.* **2004**, *126*, 5827; s) I. Gottker-Schnetmann, B. Korthals, S. Mecking, *J. Am. Chem. Soc.* **2006**, *128*, 7708.

[9] For example, see: a) G. Desurmont, Y. Li, H. Yasuda, T. Maruo, N. Kanehisa, Y. Kai, *Organometallics* **2000**, *19*, 1811; b) P. J. Shapiro, E. E. Bunel, W. P. Schafer, J. E. Bercaw, *Organometallics* **1990**, *9*, 867.

[10] a) W. J. Evans, K. J. Forrestal, J. W. Ziller, *Angew. Chem.* **1997**, *109*, 798; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 774; Erratum: W. J. Evans, K. J. Forrestal, J. W. Ziller, *Angew. Chem.* **1997**, *109*, 1371; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1437; b) W. J. Evans, D. M. De Coster, J. Greaves, *Macromolecules* **1995**, *28*, 7929; c) W. J. Evans, I. Bloom, W. E. Hunter, J. L. Atwood, *J. Am. Chem. Soc.* **1981**, *103*, 6507.