

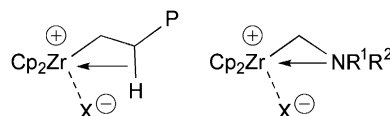
Low-Temperature Kinetic NMR Studies on the Insertion of a Single Olefin Molecule into a Zr–C Bond: Assessing the Counterion–Solvent Interplay**

Luca Rocchigiani, Gianluca Ciancaleoni, Cristiano Zuccaccia,* and Alceo Macchioni*

The insertion of an olefin molecule into a metal–carbon bond is the fundamental step of Ziegler–Natta olefin polymerization that occurs, in homogeneous phase, through the initial association of an olefin molecule with a metal cation of the catalytic ion pair.^[1–5] Not surprisingly, the insertion reaction is strongly affected by the counterion and solvent,^[6–8] the interplay of which determines the type of ion pair. “Sticky” counterions and low polar solvents favor inner sphere ion pairs (ISIPs), where the counterion is located in the first coordination sphere of the catalyst, whereas weakly coordinating counterions and more polar and coordinating solvents lead to outer sphere ion pairs (OSIPs), where the counterion is located in the second coordination sphere.^[9,10]

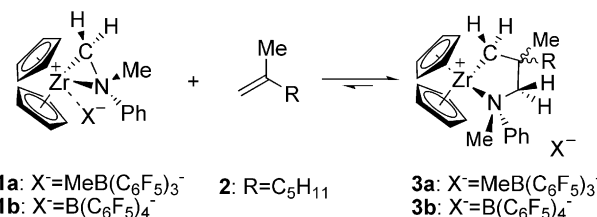
In many studies the kinetic parameters of the olefin insertion into the metal–carbon bond are determined.^[11–15] Nevertheless, to the best of our knowledge, the activation enthalpy ($\Delta H^\ddagger$) and entropy ($\Delta S^\ddagger$) values have never been reported for the same catalytic system featuring the two most frequently used counterions, that is, the “sticky” $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ and the weakly coordinating $\text{B}(\text{C}_6\text{F}_5)_4^-$ anion. This is likely due to the difficulties of synthesizing catalytically relevant ion pairs that are stable in the presence of these counterions, possibly in solvents of different polarity, for which the insertion of an olefin molecule occurs with a rate that can be conveniently followed by standard analytic techniques.^[12,16–19]

During our studies on the effect of the chain length on the self-aggregation tendency of zirconocenium ion pairs,^[20–21] we synthesized zirconaaziridinium^[22,23] ion pairs of the general formula $[(\text{Cp}_2\text{Zr}(\eta^2\text{-CH}_2\text{-NR}^1\text{R}^2))][\text{X}]$ (**1**) which have some remarkable requisites to be used as good models for investigating the insertion of a single olefin molecule into a Zr–C bond. Particularly, these models resemble the β -agostic-stabilized structure that is central to olefin polymerization (Scheme 1)^[3,24–27] with the advantage that the chelation of the nitrogen imparts a larger long-term stability to ion pairs with both $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ and $\text{B}(\text{C}_6\text{F}_5)_4^-$ counterions in solvents with



Scheme 1. Structures of β -agostic and η^2 -aziridinium (P = polymeryl chain; R^1 and R^2 = alkyl or aryl groups).

low to moderately high polarity. Furthermore, because of the presence of a chelating N-arm, ion pair **1** undergoes a single insertion into the Zr–C bond by the selection of a hindered olefin, leading to a stable ion pair **3** featuring a five-membered azametallacycle (Scheme 2).^[28] Finally, counting of the active sites^[12,29,30] is avoided because an insertion of a single olefin molecule occurs for all zirconium centers.



Scheme 2. Olefin insertion into the Zr–C bond.

Taking advantage of these rather unique peculiarities, a low-temperature NMR kinetic study on the single insertion of 2-methyl-1-heptene (**2**)^[31] into the Zr–C bond of **1a** and **1b** (Scheme 2) was performed in $[\text{D}_8]\text{toluene}$ ($\epsilon_r^{297\text{K}} = 2.27$) and a $[\text{D}_8]\text{toluene}/[\text{D}_5]\text{chlorobenzene}$ mixture (1:1 in volume, $\epsilon_r^{297\text{K}} \approx 4.00$). This led to the unprecedented evaluation of how $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values are affected by a change of the counterion and solvent.

Olefin **2** reacted with **1** through a reversible,^[32] 1,2-regioselective single-insertion reaction affording two diastereoisomers because of the presence of the nitrogen and carbon stereogenic centers in **3** (Scheme 2). The regioselectivity of the reaction was established by the observation in the ^{13}C NMR spectrum of CH_2 -resonances at 49.4 and 52.0 ppm, for the *RR/SS* and *RS/SR* isomers of **3**, respectively, which are assigned to two carbon atoms directly bound to zirconium (see the Supporting Information). The discrimination between *RR/SS* and *RS/SR* diastereoisomers was achieved by the observation of selective NOE interactions of NMe protons with the methyl moiety bound to the stereogenic

[*] Dr. L. Rocchigiani, Dr. G. Ciancaleoni, Dr. C. Zuccaccia, Prof. Dr. A. Macchioni
 Dipartimento di Chimica, Università degli studi di Perugia
 Via Elce di sotto, 8, 06123 Perugia (Italy)
 E-mail: alceo@unipg.it

[**] This work was supported by grants from the Ministero dell'Istruzione, dell'Università e della Ricerca through the PRIN 2009 LR88XR program. We thank Prof. Giuseppe Cardaci for helpful discussions.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201105122>.

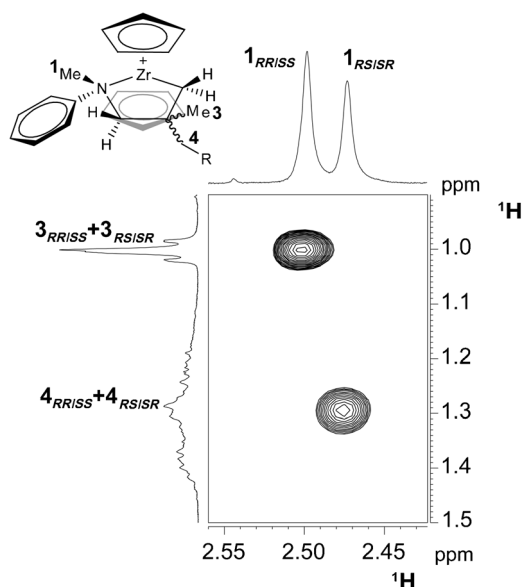


Figure 1. Section of the ^1H NOESY NMR spectrum of **3b** ($[\text{D}_8]\text{toluene}/[\text{D}_5]\text{chlorobenzene}$, $T=297\text{ K}$) showing the selective dipolar interactions allowing to discriminate the RR/SS and RS/SR diastereoisomers.

carbon atom (Me3, Figure 1) and with the first CH_2 moiety of the alkyl chain (H4, Figure 1). A complete NMR characterization is reported in the Supporting Information.

The equilibrium distribution of diastereoisomers is 50:50 at 298 K for both **3a** and **3b** whereas enrichment in the RR/SS diastereoisomers is observed at lower temperature. The abundance ratio of the two diastereoisomers does not change in, at least, 12 h below 240 K and is independent of the excess of olefin.

Kinetic investigations were performed in the presence of a large excess (>15 equiv) of **2** (pseudo first-order) over the 217.3–239.0 K range of temperature by monitoring the disappearance of the Cp resonances of **1a** and **1b** in the ^1H NMR spectrum (Figure 2). Under such conditions the reaction shown in Scheme 2 went to completion. The kinetics

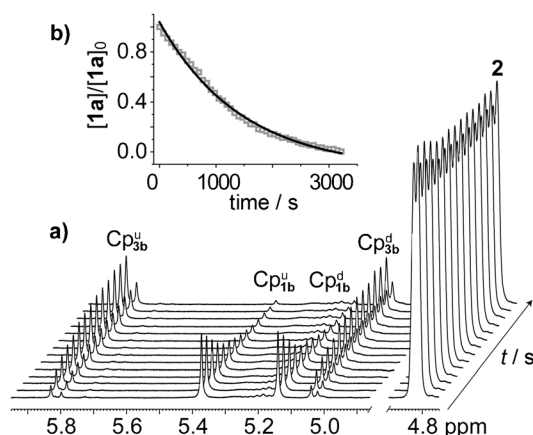


Figure 2. a) Dependence of the ^1H NMR spectrum on the time for the insertion of **2** in **1b** ($[\text{D}_8]\text{toluene}/[\text{D}_5]\text{chlorobenzene}$, 222.5 K); b) mono-exponential decay of the intensity of **1a** in toluene (222.5 K).

of the consumptions of **1a** and **1b** were found to be of first order both for zirconium and the olefin [Eq. (1)].

$$v = -\frac{d[\mathbf{1}]}{dt} = k_2[\mathbf{1}][\mathbf{2}] = k_{\text{obs}}[\mathbf{1}] \quad (1)$$

Values of second-order rate constants at different temperatures (k_2 in $\text{M}^{-1}\text{s}^{-1}$), obtained by dividing pseudo first-order rate constants (k_{obs} in s^{-1}) by the concentration of the olefin, are reported in Table 1.

Table 1: Second-order rate constant k_2 ($\text{M}^{-1}\text{s}^{-1}$)^[a] as a function of temperature T (K) and activation parameters $\Delta G^\ddagger$ (kcal mol^{-1}),^[b] $\Delta H^\ddagger$ (kcal mol^{-1}),^[a] and $\Delta S^\ddagger$ ($\text{cal mol}^{-1}\text{K}^{-1}$)^[a] for the reaction shown in Scheme 2.

Entry	T	$k_2 \cdot 10^3$	$\Delta G^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
1a$\rightleftharpoons$3a $[\text{D}_8]\text{toluene}$					
1	217.3	1.5 ± 0.2	15.4 ± 0.1	8.5 ± 0.5	-32 ± 2
2	222.5	2.1 ± 0.1	15.6 ± 0.1		
3	227.4	3.4 ± 0.2	15.8 ± 0.1		
4	233.5	6.0 ± 0.6	15.9 ± 0.1		
1b$\rightleftharpoons$3b $[\text{D}_8]\text{toluene}$					
5	217.3	52 ± 6	13.9 ± 0.1	4.0 ± 0.5	-45 ± 2
6	222.5	64 ± 2	14.1 ± 0.1		
7	227.4	75 ± 5	14.4 ± 0.1		
8	233.5	108 ± 8	14.6 ± 0.1		
1a$\rightleftharpoons$3a $[\text{D}_8]\text{toluene}/[\text{D}_5]\text{chlorobenzene}$					
9	222.5	0.371 ± 0.002	16.4 ± 0.1	10.9 ± 0.4	-25 ± 3
10	227.4	0.747 ± 0.006	16.4 ± 0.1		
11	233.5	1.28 ± 0.09	16.6 ± 0.1		
12	239.0	2.28 ± 0.05	16.8 ± 0.1		
1b$\rightleftharpoons$3b $[\text{D}_8]\text{toluene}/[\text{D}_5]\text{chlorobenzene}$					
13	222.5	0.363 ± 0.006	16.4 ± 0.1	10 ± 1	-27 ± 6
14	227.4	0.84 ± 0.03	16.4 ± 0.1		
15	233.5	1.3 ± 0.2	16.6 ± 0.2		
16	239.0	2.1 ± 0.2	16.8 ± 0.1		

[a] Confidence intervals presented at the 67% level. [b] Confidence intervals from standard propagation of errors.

In $[\text{D}_8]\text{toluene}$, olefin insertion occurs about 20–30 times faster in **1b** than in **1a** corresponding to a $\Delta\Delta G^\ddagger$ value of about $-1.3/-1.5\text{ kcal mol}^{-1}$ (Table 1, entries 1–8). This result is consistent with the few available literature data.^[33–35] Activation parameters were estimated by the dependence of the k_2 values on the temperature (Table 1, Figure 3a). In the case of **1a**, the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values ($8.5 \pm 0.5\text{ kcal mol}^{-1}$ and $-32 \pm 2\text{ cal mol}^{-1}\text{K}^{-1}$) nicely confirm these values obtained by Landis and co-workers in the classical paper on the polymerization of 1-hexene catalyzed by $[(\text{EBI})\text{ZrMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$ ($\Delta H^\ddagger_{\text{initiation}} = 11.2 \pm 1.5\text{ kcal mol}^{-1}$, $\Delta H^\ddagger_{\text{propagation}} = 6.4 \pm 1.5\text{ kcal mol}^{-1}$, $\Delta S^\ddagger_{\text{initiation}} = -24 \pm 5\text{ cal mol}^{-1}\text{K}^{-1}$, $\Delta S^\ddagger_{\text{propagation}} = -33 \pm 5\text{ cal mol}^{-1}\text{K}^{-1}$).^[12] The $\Delta H^\ddagger$ and $\Delta S^\ddagger$ parameters for **1b** ($4.0 \pm 0.5\text{ kcal mol}^{-1}$ and $-45 \pm 2\text{ cal mol}^{-1}\text{K}^{-1}$) are relevant because they are the first reported values for the insertion of an olefin molecule into a zirconocene ion pair with a $\text{B}(\text{C}_6\text{F}_5)_4^-$ counterion. The value of $\Delta H^\ddagger$ is about 4.5 kcal mol^{-1} lower for **1b** than for **1a**. In line with the associative nature of the reaction, $\Delta S^\ddagger$ is negative but its absolute value is higher in the case of **1b** by about $13\text{ cal mol}^{-1}\text{K}^{-1}$.

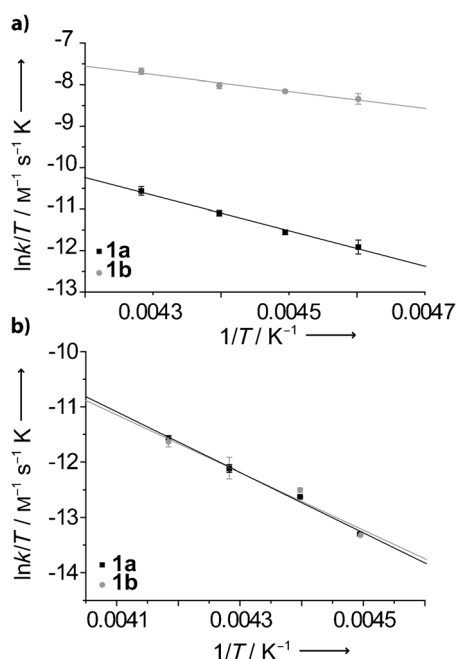


Figure 3. Eyring plots for the insertion of **2** into the Zr–C bond of **1a** and **1b** in $[D_8]$ toluene (a) and a mixture of $[D_8]$ toluene and $[D_5]$ chlorobenzene (b).

A coherent picture emerges: to reach the transition state, a considerable amount of energy is required to remove the “sticky” $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ counterion from the first coordination sphere, but this enthalpic cost is attenuated by an increased mobility of the anion, passing from ISIP to OSIP, that partly compensates the entropic loss related to the association of the olefin. A smaller amount of energy is required to displace the $\text{B}(\text{C}_6\text{F}_5)_4^-$ anion from the first coordination sphere but, because of the fact that the degrees of mobility of $\text{B}(\text{C}_6\text{F}_5)_4^-$ are similar in ISIPs and OSIPs, the recovery of entropy is smaller and approaches the typical value of $\Delta S^\ddagger$ of an associative bimolecular process occurring in low polar solvents (around $-50 \text{ cal mol}^{-1} \text{ K}^{-1}$).^[36–39] Notably, almost the same recovery of entropy ($\Delta S^\ddagger = -44 \pm 5 \text{ cal mol}^{-1} \text{ K}^{-1}$) was observed for the sole olefin polymerization catalyst with the $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ counterion in the second coordination sphere.^[29]

The insertion of **2** in **1a** and **1b** is around 3–5 and 50–100 times slower, respectively, in $[D_8]$ toluene/ $[D_5]$ chlorobenzene than in $[D_8]$ toluene ($\Delta\Delta G^\ddagger = 0.5$ – 1.0 and 2.2 – $2.5 \text{ kcal mol}^{-1}$ for **1a** and **1b**, respectively) and the anion has no effect on the insertion rate (Table 1, entries 9–16). Although it could appear counterintuitive that a reduced insertion rate is observed by increasing the polarity of the reaction medium in a system, the reactivity of which is inhibited by ionic interactions, this is not unprecedented and has already been reported for some metallocene catalysts,^[34] CGC^[40] (Constrained Geometry Catalysts), and non-metallocene^[41] olefin polymerization catalysts. The Eyring analysis^[42] of k_2 values as a function of temperature (Figure 3b) provides a more detailed picture: 1) the counterion does not affect both $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values as clearly shown by the almost coincidence of the two straight lines in Figure 3b and 2) the reduction of rate

constants when the solvent is changed from $[D_8]$ toluene to a $[D_8]$ toluene/ $[D_5]$ chlorobenzene mixture is because of the increase in $\Delta H^\ddagger$ ($\Delta\Delta H^\ddagger = 1.4$ and $6.0 \text{ kcal mol}^{-1}$ for **1a** and **1b**, respectively). The $\Delta S^\ddagger$ values in $[D_8]$ toluene/ $[D_5]$ chlorobenzene are less negative than that of **1b** in $[D_8]$ toluene but not too different in the case of **1a**. Besides the attenuation of the cation–anion interactions, the polar solvent also specifically interacts with the metal center, causing a transformation of **1a** and **1b** ISIPs into the $[\text{Cp}_2\text{Zr}(\eta^2\text{-CH}_2\text{-NMePh})(\text{solvent})][\text{X}]$ OSIPs. This finding was verified in the case of $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ because the ^1H resonance of the B–Me protons shifts from 0.4 to 1.3 ppm, when the solvent is changed from $[D_8]$ toluene to a $[D_8]$ toluene/ $[D_5]$ chlorobenzene mixture and the $\Delta\delta_{\text{mF/pF}}$ changes from 4.3 to 2.8 ppm at 239 K.^[43] The anion does not affect the activation parameters because it is relegated away from the metal center both in the ground and transition states. The olefin must displace the solvent molecule from the first coordination sphere to insert into the Zr–C bond and this costs around 10 kcal mol^{-1} from the enthalpic point of view. For this process, $\Delta S^\ddagger$ is small and negative ($\Delta S^\ddagger = -26 \text{ cal mol}^{-1} \text{ K}^{-1}$) because of the balance between olefin coordination and solvent decooordination. The decooordination of a solvent molecule does not completely compensate the loss of entropy because of the association of an olefin molecule. This is likely due to 1) the higher entropic content of **2**, with respect to chlorobenzene, as a consequence of the presence of the flexible alkyl chain and 2) the more accentuated loss of entropy of **2** that, once coordinated, is rapidly “trapped” into the Zr–C bond. Consistently, the expulsion of a solvent molecule and the coordination and insertion of ethene, a smaller olefin having an intrinsically lower entropic content, in *rac*- $\text{Me}_2\text{Si}-(2\text{-Me-4Ph-1-indenyl})_2\text{ZrCl}_2$, leads to a total recovery of entropy ($\Delta S^\ddagger = 4 \pm 4 \text{ cal mol}^{-1} \text{ K}^{-1}$).^[44]

In conclusion, this study led to the determination of accurate $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values for the insertion of a single olefin molecule into a Zr–C bond, occurring in a system resembling olefin polymerization catalysts. The separation of the enthalpic and entropic contributions provides a clear picture of the counterion/solvent interplay. The displacement of the counterion from the first coordination sphere, as a consequence of olefin association, is enthalpically much more expensive for a “sticky” counterion such as $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ with respect to $\text{B}(\text{C}_6\text{F}_5)_4^-$, in low-polar and non-coordinating solvent. The use of a slightly more polar and coordinating solvent (a toluene/chlorobenzene mixture) causes an increase of the $\Delta H^\ddagger$ value because of the competition of the solvent (specifically, chlorobenzene) with the olefin for the occupancy of a coordination position. The $\Delta S^\ddagger$ value associated with the displacement of the counterion and solvent from the first coordination sphere has been experimentally evaluated. This process partially compensates the loss of entropy associated with the occurrence of a bimolecular association. Interestingly, the compensation is negligible for a weakly interacting counterion, such as $\text{B}(\text{C}_6\text{F}_5)_4^-$, whereas it increases for the “sticky” $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ counterion. A similar recovery is observed for the displacement of a chlorobenzene molecule from the first to the second coordination sphere. We believe that having determined an experimental scale of entropy

recovery [solvent > MeB(C₆F₅)₃[−] > B(C₆F₅)₄[−]] it is important from the basic point of view and may also be of complementary utility to rationalize and, possibly, predict the reactivity of olefin polymerization catalysts.

Received: July 21, 2011

Published online: October 11, 2011

Keywords: counterion effects · ion pairs · kinetics · NMR spectroscopy · olefins

- [1] a) Y. V. Kissin in *Alkene Polymerization Reactions with Transition Metal Catalysts*, Elsevier, Amsterdam, **2008**; b) H. Makio, H. Terao, A. Iwashita, T. Fujita, *Chem. Rev.* **2011**, *111*, 2363–2449.
- [2] R. H. Grubbs, G. W. Coates, *Acc. Chem. Res.* **1996**, *29*, 85–93.
- [3] a) L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, *Chem. Rev.* **2000**, *100*, 1253–1346; b) L. Resconi, J. C. Chadwick, L. Cavallo in *Comprehensive Organometallic Chemistry III, Vol. 4* (Eds.: R. H. Crabtree, D. M. P. Mingos), Elsevier, Oxford, **2007**, chap. 9.
- [4] A. S. Guram, R. F. Jordan in *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson) Elsevier, Oxford, **1995**, chap. 12.
- [5] H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. Waymouth, *Angew. Chem.* **1995**, *107*, 1255–1283; *Angew. Chem. Int. Ed.* **1995**, *34*, 1143–1170.
- [6] a) E. Y. X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 1391–1434; b) M. Bochmann, *Organometallics* **2010**, *29*, 4711–4740.
- [7] M. Bochmann, *J. Organomet. Chem.* **2004**, *689*, 3982–3998.
- [8] C. N. Rowley, T. K. Woo, *Organometallics* **2011**, *30*, 2071–2074.
- [9] A. Macchioni, *Chem. Rev.* **2005**, *105*, 2039–2073.
- [10] D. Zuccaccia, G. Bellachioma, G. Cardaci, G. Ciancaleoni, C. Zuccaccia, E. Clot, A. Macchioni, *Organometallics* **2007**, *26*, 3930–3946.
- [11] K. A. Novstrup, N. E. Travia, G. A. Medvedev, C. Stanciu, J. M. Switzer, K. T. Thomson, N. W. Delgass, M. M. Abu-Omar, J. M. Caruthers, *J. Am. Chem. Soc.* **2010**, *132*, 558–566.
- [12] Z. Liu, E. Somsook, C. B. White, K. A. Rosaaen, C. R. Landis, *J. Am. Chem. Soc.* **2001**, *123*, 11193–11207.
- [13] F. Song, R. D. Cannon, M. Bochmann, *J. Am. Chem. Soc.* **2003**, *125*, 7641–7653.
- [14] M. Dahlmann, G. Erker, K. Bergander, *J. Am. Chem. Soc.* **2000**, *122*, 7986–7998.
- [15] J. Karl, M. Dahlmann, G. Erker, K. Bergander, *J. Am. Chem. Soc.* **1998**, *120*, 5643–5652.
- [16] J. Zhou, S. J. Lancaster, D. A. Walker, S. Beck, M. Thornton-Pett, M. Bochmann, *J. Am. Chem. Soc.* **2001**, *123*, 223–237.
- [17] Y.-X. Chen, M. V. Metz, L. Li, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1998**, *120*, 6287–6305.
- [18] L. Jia, X. Yang, C. L. Stern, T. J. Marks, *Organometallics* **1997**, *16*, 842–857.
- [19] C. R. Landis, M. D. Christianson, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15349–15354.
- [20] L. Rocchigiani, C. Zuccaccia, D. Zuccaccia, A. Macchioni, *Chem. Eur. J.* **2008**, *14*, 6589–6592.
- [21] L. Rocchigiani, G. Bellachioma, G. Ciancaleoni, A. Macchioni, D. Zuccaccia, C. Zuccaccia, *Organometallics* **2011**, *30*, 100–114.
- [22] H. W. Turner, G. G. Hlatky, R. R. Eckman, U.S. Patent 5,198,401, **1993**.
- [23] T. V. Lubben, K. Plossl, J. R. Norton, M. M. Miller, O. P. Anderson, *Organometallics* **1992**, *11*, 122–127.
- [24] R. F. Jordan, P. K. Bradley, N. C. Baezinger, R. E. LaPointe, *J. Am. Chem. Soc.* **1990**, *112*, 1289–1291.
- [25] J. C. W. Lohrenz, T. K. Woo, T. Ziegler, *J. Am. Chem. Soc.* **1995**, *117*, 12793–12800.
- [26] F. Song, S. J. Lancaster, R. D. Cannon, M. Schormann, M. Humphrey, C. Zuccaccia, A. Macchioni, M. Bochmann, *Organometallics* **2005**, *24*, 1315–1328.
- [27] J.-M. Ducéré, L. Cavallo, *Organometallics* **2006**, *25*, 1431–1433.
- [28] Similar reactivity was observed by Jordan on zirconaazidirines derived from pyridine, see: a) S. Rodewald, R. F. Jordan, *J. Am. Chem. Soc.* **1994**, *116*, 4491–4492; b) A. S. Guram, R. F. Jordan, *Organometallics* **1991**, *10*, 3470–3479; c) R. F. Jordan, D. F. Taylor, N. C. Baenziger, *Organometallics* **1990**, *9*, 1546–1557; d) F. Wu, R. F. Jordan, *Organometallics* **2005**, *24*, 2688–2697.
- [29] G. Ciancaleoni, N. Fraldi, P. H. M. Budzelaar, V. Busico, R. Cipullo, A. Macchioni, *J. Am. Chem. Soc.* **2010**, *132*, 13651–13653.
- [30] B. M. Moscato, B. Zhu, C. R. Landis, *J. Am. Chem. Soc.* **2010**, *132*, 14352–14354.
- [31] Olefin **2** was chosen to slow down the reaction rate and render it suitable to be studied with NMR spectroscopy. With 1-hexene, the reaction was too fast to be followed and led to oligomeric poly-1-hexene in the case of **1b**.
- [32] Mixing the reactants in a 1:1 ratio afforded a mixture showing the resonances of **1**, **2**, and **3** in the ¹H NMR spectrum. Addition of five equivalents of **2** to the mixture caused the disappearance of the resonances because of **1**. Removing the excess of olefin by a series of freeze–pump–thaw cycles resulted in the reappearance of resonances of **1** in the ¹H NMR spectrum. This demonstrates the reversibility of the insertion reaction.
- [33] C. R. Landis, Z. Liu, C. B. White, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **2002**, *43*, 301–302.
- [34] M.-C. Chen, J. A. Roberts, T. J. Marks, *J. Am. Chem. Soc.* **2004**, *126*, 4605–4625.
- [35] F. Song, R. D. Cannon, M. Bochmann, *Chem. Commun.* **2004**, 542–543.
- [36] V. M. Vlasov, *Russ. Chem. Rev.* **2006**, *75*, 765–796.
- [37] M. R. Plutino, L. Fenech, S. Stoccoro, S. Rizzato, C. Castellano, A. Albinati, *Inorg. Chem.* **2010**, *49*, 407–411.
- [38] J. H. Groen, J. G. P. Delis, P. W. N. M. van Leuwen, K. Vrieze, *Organometallics* **1997**, *16*, 68–77.
- [39] A. Vigalok, H.-B. Kraatz, L. Konstantinovskiy, D. Milstein, *Chem. Eur. J.* **1997**, *3*, 253–260.
- [40] N. Intaragamjorn, T. Shiono, B. Jongsomjit, P. Praserttham, *Catal. Commun.* **2006**, *7*, 721–723.
- [41] V. Volkis, E. Smolensky, A. Lisovskii, M. S. Eisen, *J. Polym. Sci. Polym. Chem.* **2005**, *43*, 4505–4516.
- [42] G. Lente, F. István, A. J. Poë, *New J. Chem.* **2005**, *29*, 759–760.
- [43] A. D. Horton, J. de With, *Organometallics* **1997**, *16*, 5424–5436, and references therein.
- [44] V. Busico, R. Cipullo, V. Esposito, *Macromol. Rapid Commun.* **1999**, *20*, 116–121.