

Zirconium complexes incorporating diaryldiamidoferrocene ligands: generation of cationic derivatives and polymerization activity towards ethylene and 1-hexene

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Dedicated to Professor R.R. Schrock

Abstract

Palladium-catalyzed coupling of ArX (ArX = MesBr, 2,6-dichloriodobenzene and 9-bromonaphthalene) with 1,1'-diaminoferrocene afforded a series of substituted diamide ligands Fc(NHAr)₂ (**1**). A Zr-dibenzyl complex **2** of the mesityl-substituted ligand was synthesized using ZrBn₄, and its ability to act as precatalyst for olefin polymerization was investigated. Abstraction of one benzyl group using B(C₆F₅)₃ resulted in the zwitterionic species [LZrBn][BnB(C₆F₅)₃] (**3**), which reacted slowly (approximately 30 min) with ethylene to afford the monoinsertion product [LZrCH₂CH₂CH₂Ph][BnB(C₆F₅)₃]. Further insertions of ethylene were slower and led, after 2 h, to the di- and tri-insertion products. Use of [Ph₃C][B(C₆F₅)₄] as an activator resulted in a competent 1-hexene polymerization catalyst affording high molecular weight poly-1-hexene with a PDI of 1.3–1.4.

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1. Introduction

Diamide donor ligands are among the most actively investigated non-Cp ligand systems for catalytic olefin polymerization with Group 4 metals [1–10]. Our own recent efforts have been focused on developing ferrocene-based diamide ligands. The ferrocene backbone provides for a relatively rigid coordination environment, with a well-defined directionality of the nitrogen donor vectors. The system, however, is not completely inflexible, allowing for partial relief of cyclic strain through the opening of the Cp–Cp dihedral angle by as much as 12°. In addition, further stabilization is possible by distortions [11] that serve to bring the electron-rich ferrocene group in close proximity to electron-deficient cationic metal centers [12–14].

We recently reported the synthesis of the silylated diaminoferrocene Fc(NHSiMe₃)₂, from which, a series of Ti and Zr complexes were prepared [15]. We also communicated the results of our study of the activation of Fc(NSiMe₃)₂TiMe₂ with B(C₆F₅)₃ and [Ph₃C][B(C₆F₅)₄] (TB) which highlighted the unusually short interaction between the iron and the electron-deficient Ti center in the μ -Cl dimer [Fc(NSiMe₃)₂TiCl][B(C₆F₅)₄] [16]. When Fc(NSiMe₃)₂TiMe₂ is activated with TB, the resulting cation reacts with 1-hexene, however only short-chain oligomers are produced whose olefinic end groups are suggestive of a β -H elimination termination pathway.

With the goal of producing more competent 1-hexene polymerization catalysts, we prepared a series of aryl-substituted Fc ligands. Aryl-substituted diamines are well known to act as supporting ligands for active olefin-polymerization catalysts [2,4,5,17]. In this paper we report the synthesis of aryl-substituted ligands through a Pd-mediated C–N bond formation. In addition, a Zr dibenzyl complex was prepared and its ability to

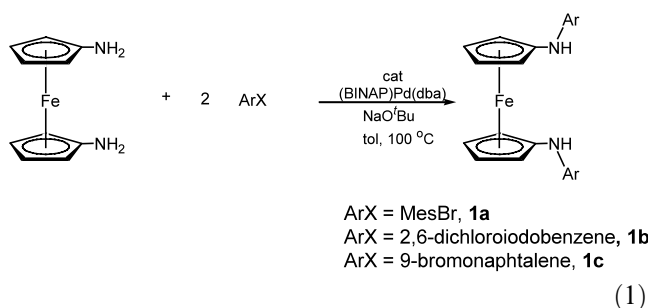
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function as an olefin polymerization catalyst was studied.

2. Results and discussion

The functionalized diamine **1a** was synthesized through Pd⁰-mediated cross-coupling of 1,1'-diaminoferrocene with mesityl bromide (Eq. (1)) following a procedure developed by Buchwald and coworkers [18]. This procedure has already been applied by Schrock et al. to the synthesis of mesityl-substituted diamido-amino donor ligands [2].



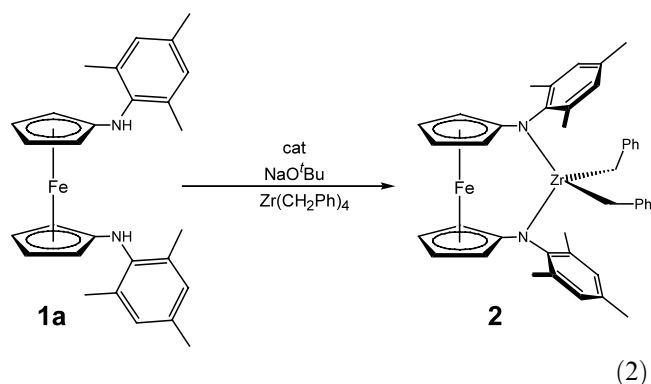
The reaction was complete after 8 h of heating at 100 °C and the pure product was obtained following recrystallization from Et₂O. The ¹H NMR spectrum of **1a** is typical of 1,1'-disubstituted ferrocenes, containing two pseudo-triplets for the ferrocene backbone in addition to the typical resonances associated with the NH and the mesityl groups. Related phenyl-substituted aminoferrocenes have been reported by others [19,20].

Encouraged by the ease of the C–N bond formation in the case of MesBr, we decided to probe the effectiveness of the catalyst with other aryl halide reagents. Schrock et al. reported that 2,6-dichlorobromobenzene is an effective arylating agent under similar conditions [3]. In our system, the corresponding product **1b** was obtained using 2,6-dichloriodobenzene, although 2 weeks of heating to 100 °C were required to drive the reaction to completion. Similarly, the use of 9-bromonaphthalene upon heating the reaction mixture to 100 °C for 40 h led to the formation of the diamine **1c** in 80%

yield. Sterically more demanding 2,6-diisopropyl-bromobenzene and 2,4,6-tris-*t*-bu-bromobenzene failed to couple to any noticeable extent under these conditions. Furthermore, attempts to couple 1,1'-dibromoferrocene with aniline proved unsuccessful.

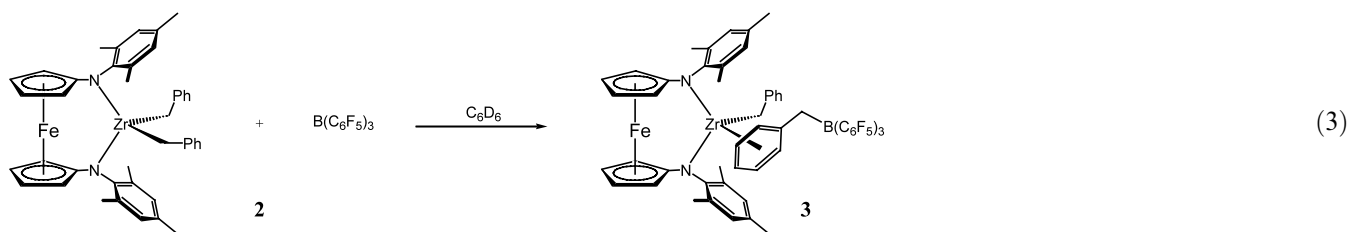
The ¹H NMR spectra of both **1b** and **1c** exhibited the ferrocene pattern consisting of two pseudo-triplets. Compounds derived from **1a** will be discussed in this report, while **1b** and **1c** will be the subject of a future publication.

The Zr-dibenzyl complex **2** was obtained by reacting **1a** with Zr(CH₂Ph)₄ in toluene (Eq. (2)). The resulting complex was isolated from a toluene/pentane mixture as a red crystalline air- and moisture-sensitive solid in moderate yields. The ¹H NMR spectrum of the product is consistent with C_{2v} symmetry and, as in the free ligand, contains two ferrocenyl pseudo-triplets.



Interestingly, while crude, unrecrystallized **1a** reacted readily with Zr(CH₂Ph)₄, the pure crystalline diamine appeared to react sluggishly, if at all. The culprit in this unusual behavior was traced to the presence of a small amount of NaO^{*t*}Bu that was present in the crude ligand from the cross-coupling step. Apparently then, a trace of base is necessary in order to catalyze the protonolysis reaction [21].

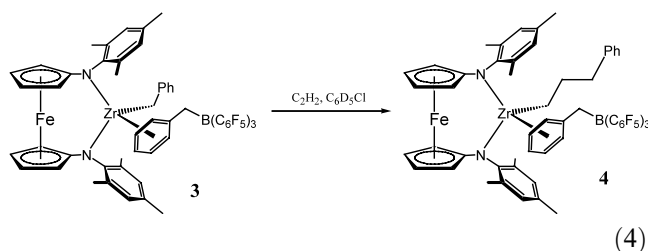
In typical fashion, the strong Lewis acid B(C₆F₅)₃ reacted cleanly with **2** via benzyl abstraction to form the zwitterionic π-complex **3** (Eq. (3)). The compound is soluble in benzene, suggesting a close ion-pairing in solution.



A single sharp resonance at -12.5 ppm was observed in the ^{11}B NMR spectrum, confirming the presence of a tetrahedral borate environment. The symmetry of the resulting species is reduced from C_{2v} to C_s as evidenced by the presence of four ferrocenyl resonances (4.09, 3.93, 3.65 and 3.43 ppm) in the ^1H NMR spectrum. This splitting pattern is typical of the ferrocenyl ABCD spin system, indicating that each Cp-bound proton resides in a unique chemical environment (note that the two Cp rings are still related by a mirror plane). Two new benzyl resonances—a sharp singlet at 3.20 ppm and a broad doublet 2.96 ppm—were assigned to the Zr-bound and the boron-bound methylene groups, respectively. Restricted rotation of the mesityl groups around the N–C bond is evidenced by the presence of three mesityl methyl and two aromatic mesityl CH resonances. The aromatic benzyl borate resonances are shifted upfield (6.35 *ortho*, 6.24 *meta* and 5.79 *para*) in the typical manner observed for π -bound arene ligands. Coordination of a benzylborate anion to cationic Ti and Zr centers is well documented and leads to the stabilization of an otherwise extremely electron-deficient metal center [22–25].

Although stable in C_6D_6 for several days, the cation **3** decomposed upon attempted isolation. The ^1H NMR spectrum of the solid isolated from C_6H_6 /pentane shows two doublets (at 0.35 and 2.95 ppm) resulting from a pair of diastereotopic methylene hydrogens ($J_{\text{HH}} = 12.3$ Hz). Attempts to characterize the material further have been unsuccessful, nevertheless, the pattern is consistent with C–H bond activation of one of the mesityl methyl groups to form a Zr-metallacycle, and we note that related reactions have been observed previously [3,26].

Solutions of **3** did not react with 1-hexene even upon heating to 60°C for several hours, as judged by ^1H NMR spectroscopy. In the case of ethylene, however, **3** reacted slowly at room temperature as shown in Eq. (4). Thus, injection of approximately 4 equiv. of ethylene into an NMR tube containing a solution of **3** in $\text{C}_6\text{D}_5\text{Cl}$ led after 30 min to the consumption of 1 equiv. of ethylene and a complete conversion of **3** to the mono-insertion product **4**.



The methylene hydrogens of the newly formed γ -phenylpropyl ligand appeared as multiplets at 2.72, 2.61 and 1.64 ppm. Four new ferrocene multiplets were also present, as well as a new set of mesityl resonances. Further insertion of ethylene was slow, but after 2 h,

new sets of resonances appeared corresponding to di- and tri-insertion products.

The reaction mixture was hydrolyzed with 1 M HCl and the resulting solution was analyzed by GC–MS. In addition to propylbenzene ($m/z = 120$, 66%), the mixture contained pentyl- and heptylbenzenes ($m/z = 148$ (20%) and 176 (4%), respectively).

The use of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**TB**), rather than $\text{B}(\text{C}_6\text{F}_5)_3$, as a co-catalyst often leads to an increased activity of the resulting catalytic species. Indeed, while the $2/\text{B}(\text{C}_6\text{F}_5)_3$ combination did not yield a viable 1-hexene polymerization catalyst, addition of 1-hexene to a mixture of **2** and TB in chlorobenzene led to an exothermic reaction which, after quenching with acid, afforded poly-1-hexene.

Up to 400 equiv. of 1-hexene were consumed, yielding poly-1-hexene with molecular weights of up to 20 000 with relatively low polydispersities ($\text{PDI} = 1.3\text{--}1.4$). Addition of more than approximately 400 equiv. of 1-hexene does not lead to higher molecular nor higher production of the polymer. This finding, along with the fact that no olefinic resonances were observed in the ^1H NMR, leads us to believe that the catalyst deactivation occurs through the CH activation of a mesityl methyl group, a situation encountered by the Schrock group with a related mesityl-functionalized amido system [3]. Indeed, combining **2** and TB in $\text{C}_6\text{D}_5\text{Cl}$ at -30°C led, upon warming to 0°C , to a mixture of two highly asymmetric products, both of which appear to contain an activated methyl group as part of a metallacycle with zirconium. In both compounds the methylene hydrogen atoms ($\text{mes-CH}_2\text{-Zr}$) are diastereotopic and are found at significantly different shifts (2.70 and 0.03 ppm). The scope and mechanism of these, and related, reactions is presently under active investigation.

3. Experimental

3.1. General considerations

Standard Schlenk-line and glove box techniques were used unless otherwise indicated. Pentane, $\text{C}_6\text{H}_5\text{CH}_3$, C_6H_6 and Et_2O were purified by passage through a column of activated alumina and degassed with Ar prior to use. PhCl was distilled from CaH_2 . $\text{Fc}(\text{NH}_2)_2$ [27], ZrBn_4 [28], $\text{B}(\text{C}_6\text{F}_5)_3$ [29] and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ [30] were prepared according to published procedures. The Pd catalyst (*rac*-BINAP)Pd(dba) was prepared and used according to a procedure established by Buchwald and coworkers [18]. MesBr was distilled from CaH_2 . GC–MS measurements were done using an Agilent 6890 Series GC system equipped with an Agilent 5973N Mass Detection System. C_6D_6 was vacuum-transferred from Na/benzophenone. $\text{C}_6\text{D}_5\text{Cl}$ was vacuum transferred from CaH_2 . All ^1H , and $^{13}\text{C}\{^1\text{H}\}$ and ^{11}B NMR spectra

were recorded on a Bruker DRX 500 MHz spectrometer. ^1H NMR chemical shifts in C_6D_6 are given relative to $\text{C}_6\text{D}_5\text{H}$ (7.16 ppm). Due to the presence of a large number of peaks in the aromatic region, the ^1H NMR shifts in $\text{C}_6\text{D}_5\text{Cl}$ are given relative to an internal standard $\text{Ph}_3\text{CCH}_2\text{Ph}$ (3.85 ppm for CH_2), which was either generated during a reaction or added to the reaction mixture. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are relative to C_6D_6 (128.3 ppm). ^{11}B NMR spectra are referenced to an external $\text{BF}_3\text{--Et}_2\text{O}$ in C_6D_6 standard (0.0 ppm). Elemental analyses were determined at the Microanalytical Laboratory of the College of Chemistry, University of California, Berkeley.

3.2. Synthesis of complexes

3.2.1. $\text{Fc}(\text{NHMe})_2$ (**1a**)

A 100 ml flask was charged with $\text{Fc}(\text{NH}_2)_2$ (2.00 g, 9.26 mmol), NaO^tBu (2.60 g, 27 mmol), and (BI-NAP) $\text{Pd}(\text{dba})$ (96 mg, 100 μmol , 0.5 mol%). Toluene (30 ml) and MesBr (3.05 ml, 20.0 mmol) were added and the mixture was heated to 100 $^\circ\text{C}$ for 10 h. The reaction mixture was allowed to cool and the volatiles were removed under vacuum. Extraction with CH_2Cl_2 , filtration and removal of the solvent resulted in 3.65 g of red crystalline product (87%). Analytically pure compound was obtained by recrystallization of the product from Et_2O (2.70 g, 64%). ^1H NMR (C_6D_6): δ 6.78 (s, 4H, *MesH*), 4.05 (s, 2H, *NH*), 3.80 (t' , 4H, Fc), 3.78 (t' , 4H, Fc), 2.17 (s, 6H, Me), 2.12 (s, 12H, Me) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 140.1 (Ar), 132.7 (Ar), 131.3 (Ar), 130.2 (Ar), 108.5 (*ipso*-Fc), 65.0 (Fc), 60.7 (Fc), 21.2 (*p*-Me), 19.0 (*o*-Me) ppm. *Anal.* Calc. for $\text{C}_{28}\text{H}_{32}\text{FeN}_2$: C, 74.33; H, 7.13; N, 6.19. Found: C, 74.31; H, 7.27; N, 6.08%.

3.2.2. $\text{Fc}[\text{NH}(2,6\text{-Cl}_2\text{C}_6\text{H}_3)]_2$ (**1b**)

A 50 ml flask was charged with $\text{Fc}(\text{NH}_2)_2$ (300 mg, 1.39 mmol), NaO^tBu (355 mg, 3.70 mmol), (BI-NAP) $\text{Pd}(\text{dba})$ (14 mg, 14 μmol , 0.5 mol%) and 2,6-dichloriodobenzene (791 mg, 2.90 mmol). Toluene (15 ml) was added and the mixture was heated to 100 $^\circ\text{C}$ for 14 days. The volatile fraction was removed and the product was extracted with CH_2Cl_2 . Removal of the solvent afforded 420 mg of **1b** as a red powder (60%). ^1H NMR (C_6D_6): δ 6.92 (d, 4H), 6.27 (t, 2H), 5.28 (s, 2H, *NH*), 4.01 (t' , 4H, Fc), 3.82 (t' , 4H, Fc) ppm.

3.2.3. $\text{Fc}[\text{NH}(9\text{-Nap})]_2$ (**1c**)

A 50 ml flask was charged with $\text{Fc}(\text{NH}_2)_2$ (400 mg, 1.85 mmol), NaO^tBu (444 mg, 4.63 mmol), (BI-NAP) $\text{Pd}(\text{dba})$ (20 mg, 20 μmol , 0.5 mol%) and 9-bromonaphthalene (780 mg, 3.80 mmol). Toluene (15 ml) was added and the mixture was heated to 100 $^\circ\text{C}$ for 40 h. After cooling to room temperature the solution was filtered and cooled to -40 $^\circ\text{C}$ affording yellow

crystals of **1c** (530 mg, 62%). ^1H NMR (C_6D_6): δ 7.67 (d, 2H), 7.38–7.17 (m, 10H), 6.98 (m, 2H), 5.40 (s, 2H, *NH*), 4.19 (t' , 4H, Fc), 3.94 (t' , 4H, Fc) ppm.

3.2.4. $[\text{Fc}(\text{NMe})_2]\text{ZrBn}_2$ (**2**)

Diamine **1a** (2.42 g, 5.35 mmol), ZrBn_4 (2.73 g, 6.00 mmol) and NaO^tBu (20 mg) were combined in a flask and 40 ml of $\text{C}_6\text{H}_5\text{CH}_3$ was added. The resulting mixture was stirred for 12 h, at which point the solvent was removed and the solid was extracted with $\text{C}_6\text{H}_5\text{CH}_3$ (2×30 ml). The solution was concentrated to 10 ml and C_5H_{12} was added to induce crystallization. The mixture was then cooled to -40 $^\circ\text{C}$ for 12 h and the resulting red crystalline product was isolated by filtration. Yield: 1.95 g, 51%. ^1H NMR (C_6D_6): δ 7.06 (t, 4H), 6.85 (m, 6H), 6.70 (d, 4H), 4.06 (t' , 4H, Fc), 3.85 (t' , 4H, Fc), 2.38 (s, 12H, *o*-Me), 2.32 (s, 4H, ZrCH_2), 2.18 (s, 6H, *p*-Me) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 149.2 (Ar), 145.9 (Ar), 134.8 (Ar), 134.5 (Ar), 130.2 (Ar), 130.0 (Ar), 127.6 (Ar), 123.1 (Ar), 93.5 (*ipso*-Fc), 69.8 (Fc), 69.6 (Fc), 69.5 (Zr-CH_2), 21.2 (*p*-Me), 20.5 (*o*-Me) ppm. *Anal.* Calc. for $\text{C}_{42}\text{H}_{44}\text{FeN}_2\text{Zr}$: C, 69.69; H, 6.13; N, 3.87. Found: C, 69.38; H, 6.48; N, 3.63%.

3.2.5. Observation of

$\{[\text{Fc}(\text{NMe})_2]\text{ZrBn}\}\{\text{BnB}(\text{C}_6\text{F}_5)_3\}$ (**3**)

A solution of **2** (17 mg, 23 μmol) in 0.3 ml of C_6D_6 was added to a solution of $\text{B}(\text{C}_6\text{F}_5)_3$ (12 mg, 23 μmol) in 0.3 ml of C_6D_6 . A dark red solution was formed immediately. ^1H NMR (C_6D_6): δ 7.379 (m, 2H, *m*-Ph), 7.193 (d, 2H, *o*-Ph), 7.092 (t, 1H, *p*-Ph), 6.859 (s, 2H, *m*-Mes), 6.798 (s, 2H, *m*-Mes), 6.358 (d, 2H, *o*-Ph), 6.261 (m, 2H, *m*-Ph), 5.797 (t, 1H, *p*-Ph), 4.086 (m, 2H, Fc), 3.926 (m, 2H, Fc), 3.653 (m, 2H, Fc), 3.433 (m, 2H, Fc), 3.197 (s, 2H, Zr-CH_2), 2.963 (br d, 2H, B-CH_2), 2.227 (s, 6H, Me), 2.213 (s, 6H, Me), 1.950 (s, 6H, Me) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 152.1 (Ar), 149.7 (Ar), 136.2 (Ar), 134.5 (Ar), 133.5 (Ar), 130.8 (Ar), 129.8 (Ar), 129.7 (Ar), 129.3 (Ar), 129.1 (Ar), 128.6 (Ar), 128.5 (Ar), 126.3 (Ar), 125.6 (Ar), 123.9 (Ar), 91.5 (*ipso*-Fc), 75.3 (Fc), 74.7 (Fc), 68.5 (Fc), 67.6 (Fc), 63.1 (Zr-CH_2), 36 (B-CH_2) (chemical shift inferred from a $^{13}\text{C-}^1\text{H}$ HMQC experiment), 20.5 (Me), 19.9 (Me) ppm. ^{11}B NMR (C_6D_6): δ -12.5 ppm.

3.2.6. Observation of

$\{[\text{Fc}(\text{NMe})_2]\text{ZrCH}_2\text{CH}_2\text{CH}_2\text{Ph}\}\{\text{BnB}(\text{C}_6\text{F}_5)_3\}$ (**4**)

Ethylene gas (2.0 ml) was injected through a septum, via syringe, into an NMR tube containing a solution of **2** (17 mg, 23 μmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (12 mg, 23 μmol) in 0.6 ml of $\text{C}_6\text{D}_5\text{Cl}$. Progress of the reaction was monitored by ^1H NMR spectroscopy. After 30 min, 1 equiv. of ethylene was found to be consumed and conversion of **3** to **4** was complete. ^1H NMR ($\text{C}_6\text{D}_5\text{Cl}$): δ 7.2–6.8 (m, 7H, Ar), 6.35 (t, 2H, Ar), 4.37 (m, 2H, Fc), 4.04 (m, 2H, Fc), 3.88 (m, 2H, Fc), 3.56 (m, 2H, Fc), 2.72 (m, 2H,

CH_2), 2.61 (m, 2H, CH_2), 2.28 (s, 3H, Me), 2.18 (s, 3H, Me), 2.10 (s, 3H, Me), 1.64 (m, 2H, CH_2) ppm.

3.3. Polymerization of 1-hexene

In a typical procedure, a solution of **2** (34 mg, 47 μmol) and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (42 mg, 45 μmol) was prepared in PhCl (7.0 ml). After stirring the mixture for 5 min, 1-hexene was added via syringe. After stirring for an additional 30 min, the mixture was quenched with 2 ml of 1 M HCl. The volatile components were removed under vacuum and the residue was extracted with THF; after filtration, the solvent was again removed to yield poly-1-hexene as a very viscous gum. The resulting polymer was characterized using GPC calibrated using polystyrene standards.

4. Supplementary material

The material is available from the authors on request.

Acknowledgements

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