Catalysis Letters Vol. 101, Nos. 3–4, June 2005 (© 2005)
DOI: 10.1007/s10562-005-4900-8

Bis(imino)pyridyl Co(II) and Fe(II) catalysts immobilized on SBA-15 mesoporous material: new highly active supported catalysts for the polymerization of ethylene

Il Kim*, Byeong Heui Han, Jae Sung Kim, and Chang-Sik Ha

Department of Polymer Science and Engineering, Pusan National University, Jangjeon-dong, Geumjeong-gu, Busan, 609-735, Korea

Received 11 January 2004; accepted 02 April 2005

A series of bis(imino)pyridyl Co(II) and Fe(II) complexes containing allyloxy group on the pyridine ring were prepared. These metal complexes were heterogenized covalently immobilizing on modified SBA-15 mesoporous material in the presence of Karstedt catalyst. This immobilization technique was demonstrated to be an ideal one since the resulting supported catalysts resembled closely their homogeneous counterparts, mirroring the feature of active sites.

KEY WORDS: catalysis; organometallic catalysts; polyethylene; supports; transition metal chemistry.

1. Introduction

A new series of iron and cobalt complexes with bis(imino)pyridyl ligands were reported by Gibson [1], Bennett from Dupont [2] and Brookhart [3,4], which showed exceptionally high activity for the ethylene polymerization. Bulky bis(imino)pyridyl ligands have drawn considerable interest because they offer the potential advantages of modulating steric and electronic properties by varying the amine or aniline used in the ligand synthesis. Brookhart group reported that by reducing the steric bulk of these bis(imino)pyridyl ligands the resultant iron catalysts oligomerized ethylene to linear α-olefins with remarkably high activity and selectivity while maintaining desirable oligomer distributions [5].

Homogeneous catalysis is gaining considerable interest due to its high activity and selectivity under mild reaction conditions for a wide variety of reactions. However, their practical applications have been limited by the difficulties in achieving industrially practical catalyst-product separation. Therefore, heterogenization of the homogeneous catalyst has become an attractive goal in materials and catalytic research in recent years. Zeolites, owing to their varied intrinsic properties, have been extensively used in fine chemistry for more than two decades. But the limitation of pore sizes of these microporous materials illustrates the demands for new materials with larger pore sizes. The discovery of a new family of mesoporous materials has given an enormous stimulus to research in heterogeneous catalysis [6]. This is due to their outstanding advantages, such as extremely high surface areas, combined with large and defined pore sizes. The presence of a large number of silanol (Si–OH) groups on the inner surface provides the opportunity to support or anchor various functional groups by different post-synthetic modification methods, such as silylation, esterification, and chemical depositions [7,8].

Herein we report a versatile heterogenization technique to covalently immobilize bis(imino)pyridyl Co(II) and Fe(II) complexes on the modified SBA-15 mesoporous material, which exhibit high activity in ethylene polymerization after activation with methylaluminoxane (MAO).

2. Experimental

2.1. Chemicals

All metal complexes were manipulated by standard schlenk techniques. Polymerization grade of ethylene (SK Co., Korea) was purified by passing it through columns of Fisher RIDOX catalyst and molecular sieve 5 Å/13×. Organic solvents were distilled from Na/benzophenone and stored over molecular sieves (4 Å). Used all reagents were purchased from Aldrich Chemical Co. and used without purification. The MAO was purchased from Akzo Chemical as 8.4 wt% total Al solution in toluene.

2.2. Polymerization and characterization

Ethylene polymerizations were performed in 250 mL Parr® reactor equipped with a mechanical stirrer and a thermometer at 5.0 atm of ethylene pressure. ^{1}H-NMR, ^{13}C-NMR spectra were recorded on a Varian Gemimi

* To whom correspondence should be addressed.
E-mail: ilkim@pnu.edu

1011-372X/05/0600–0249/0

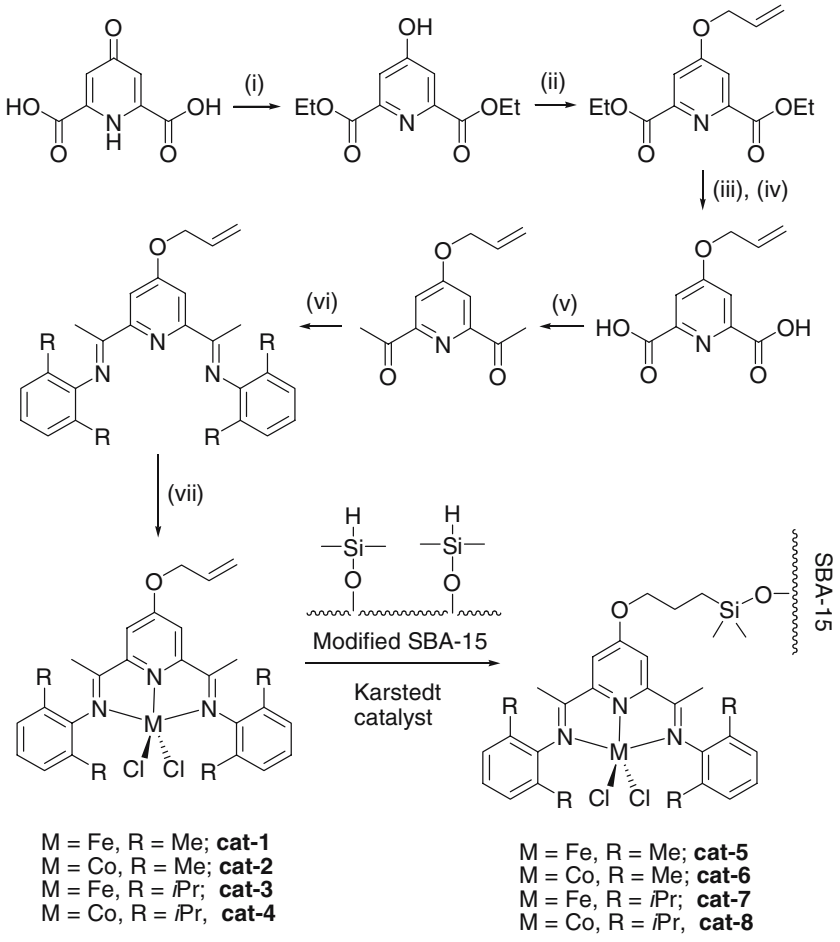
2000 & HP5P (300 MHz). Low resolution and high resolution FAB Mass spectra were determined by using JMS-700 Mstation from Jeol Lt. Analytical thin layer chromatography (TLC) was conducted using Merck 0.25 mm silica gel 60F precoated aluminum plates with fluorescent indicator UV_{254}. Elementary analysis was carried out using Vario EL. Thermal analysis of PE was carried out by using DSC (Perkin-Elmer DSC, model: Pyris 1) at 10 °C min^{-1} heating rate under nitrogen atmosphere. The GPC curves were obtained at 135 °C using a Water 150-C in 1,2-dichlorobenzene, equipped with polystyrene gel columns. BET specific surface areas and the porosities were calculated typically from the nitrogen adsorption experiments measured at 77 K.

2.3. Synthesis of ligands and metal complexes

The synthetic route of new supported 2,6-bis(imino)pyridyl ligand is shown in scheme 1.

N-((*E*)-1-{4-(Allyloxy)-6-[(1*E*)-*N*-(2,6-dimethylphenyl)ethanimidoyl]-2-pyridinyl}ethyli-dene)-2,6-dimethylaniline (**1**) ligand: To a stirred solution of 2.44 g (11.1 mmol) of 4-(allyloxy)-2,6-diacetylpyridine, which was prepared starting from chelidamic acid (scheme 1), in 30 mL of dried ethanol was added 2.74 mL (22.26 mmol) of 2,6-dimethylaniline. After the addition of a few drops of glacial acetic acid, the solution was refluxed overnight. Upon cooling to room temperature, the product crystallized from ethanol. After filtration the yellow solid was washed with cold ethanol and dried in a vacuum oven at 50 °C overnight to give 2.45 g (51%) of **6**as a white powder. ^{1}H-NMR (300 MHz, $CDCl_3$) δ2.07 (s, 12H), 2.25 (s, 6H), 4.78 (d, 2H, J = 3.8 Hz), 5.38 (d, 1H, J = 6.9 Hz), 5.54 (d, 1H, J = 11.5 Hz), 6.02–6.21 (m, 1H), 7.00 (t, 2H, J = 6.6 Hz), 7.15 (d, 4H, J = 7.4 Hz), 8.15 (s, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ17.58, 17.85, 69.1, 110.3, 118.5, 123.0, 127.8, 128.1, 131.2, 142.2, 154.4, 166.4. Anal. Calcd for $C_{28}H_{31}N_3O$: C, 79.02; H, 7.34; N, 9.87. Found: C, 79.09; H, 7.40; N, 9.82.

N-((*E*)-1-{4-(Allyloxy)-6-[(1*E*)-*N*-(2,6-dimethylphenyl) ethanimidoyl]-2-pyridinyl}ethyli-dene)-2,6-diisopropylaniline (**2**) ligand: The **2** ligand was prepared according to the similar procedures employed for the preparation of **1** ligand to get a yellow solid as a 58% yield. ^{1}H-NMR



Scheme 1. The synthetic route of heterogeneous 2,6-bis(imino)pyridyl Fe(II) and Co(II) complexes: (i) EtOH, *conc*. H_2SO_4, 90 °C; (ii)K_2CO_3, allyl bromide, acetone, reflux; (iii) 5N-NaOH, THF, 500 °C; (iv) $SOCl_2$, DMF, 90 °C; (v) CuI(I), MeLi, Et_2O, THF, −78 °C; (vi) 2,6-dimethylaniline or 2,6-diisopropylaniline, EtOH, AcOH, reflux; (vii) $FeCl_2$ or $CoCl_2$, THF, r.t.

(300 MHz, $CDCl_3$) δ1.28 (d, 24H, J = 6.9 Hz), 2.36 (s, 6H), 2.87 (sep, 2H, J = 6.9 Hz), 4.88 (d, 2H, J = 5.4 Hz), 5.48 (d, 1H, J = 10.2 Hz), 5.58 (d, 1H, J = 17.4 Hz), 6.13–6.22 (m, 1H), 7.22 (t, 2H, J = 6.0 Hz), 7.27 (d, 4H, J = 6.6 Hz), 8.17 (s, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ17.44, 23.32, 28.36, 69.08, 108.7, 118.8, 123.0, 123.6, 132.1, 135.8, 146.4, 156.9, 165.7, 166.8. Anal. Calcd for $C_{36}H_{47}N_3O$: C, 80.40; H, 8.81; N, 7.81. Found: C, 80.59; H, 8.90; N, 7.82.

2.3.1. Synthesis of metal complexes

The ligand (1.1 eq.) and the metal salt ($CoCl_2$ or $FeCl_2$) in its hydrated form were added together in a schlenk flask under nitrogen. Stirring was begun and continued for 4 h. Diethylether was added to the reaction mixture to precipitate the complex, and the resultant solids were filtered and washed repeatedly with Et_2O and pentane and dried *in vacuo*. All of the complexes were prepared in high yield (>90%) in this manner.

The iron complexes, [*N*-((*E*)-1-{4-(Allyloxy)-6-[(1*E*)-*N*-(2,6-dimethylphenyl)ethanimidoyl]-2-pyridinyl}ethylidene)-2,6-dimethylaniline]iron(II) chloride ($C_{30}H_{37}Cl_2FeN_3O$: Calcd. C 61.87, H 6.40, N 7.22; Found C 61.99, H 6.51, N 7.17) and [*N*-((*E*)-1-{4-(Allyloxy)-6-[(1*E*)-*N*-(2,6-dimethylphenyl)ethanimidoyl]-2-pyridinyl}ethylidene)-2,6-diisopropylaniline]-iron(II) chloride ($C_{38}H_{53}Cl_2FeN_3O$: Calcd. C 65.71, H 7.69, N 6.05; Found C 65.79, H 7.71, N 6.07) were as a dark blue and blue powders, respectively. The cobalt complexes, [*N*-((*E*)-1-{4-(Allyloxy)-6-[(1*E*)-*N*-(2,6-dimethylphenyl)ethanimidoyl]-2-pyridinyl}ethylidene)-2,6-dimethylaniline]cobalt(II) chloride ($C_{30}H_{37}Cl_2CoN_3O$: Calcd. C 61.54, H 6.37, N 7.18; Found C 61.59, H 6.42, N 7.14) and [*N*-((*E*)-1-{4-(Allyloxy)-6-[(1*E*)-*N*-(2,6-dimethylphenyl)-ethanimidoyl]-2-pyridinyl}ethylidene)-2,6-diisopropylaniline]cobalt(II) chloride ($C_{38}H_{53}Cl_2CoN_3O$: Calcd. C 72.82, H 8.52, N 6.70; Found C 72.79, H 8.60, N 6.77) were isolated as a bright green powder and a gold powder, respectively.

2.4. Synthesis of supported catalysts

The SBA-15 mesoporous material was prepared by using poly(alkylene oxide) block copolymer detergent (average M_n = 5800, Aldrich, P-123) as a template [9]. Tetraethoxysilane (Aldrich, 98%, TEOS), P-123, hydrochloric acid (Daejung, Korea, 35%), and deionized water were mixed to make a reaction mixture with a composition of 1 SiO_2:0.017 P-123:2.9 HCl:203 H_2O. In order to avoid a possible leaching which takes place in many cases by forming covalent bonding between support and metal complexes, we modified the SBA-15 surface as follows: i.e. 0.4 g (5 mmol) of 1,1,3,3-tetramethylsilazane was added to a suspension of 1 g of dehydroxylated SBA-15 (470 °C, 6 h, 2×10^{-4} mbar) in 20 mL of hexane dropwise at room temperature. The resulting suspension was refluxed at 85 °C for 4 h. The solid was isolated by filtration and then washed with hexane (20 mL × 5). The solid was dried *in vacuo* at 30 °C for 30 h.

Hundred milligrams of metal complex was combined with 500 mg of modified silica under nitrogen. On addition of 6 mL of dried THF and 0.1 mL of the Karstedt catalyst (3–3.5 wt% Pt in xylene), the mixture was stirred at 55 °C for 4 days. After finishing reaction, the product was isolated by filtration and then washed with toluene and THF repeatedly. The product was dried *in vacuo* at 50 °C for 24 h.

3. Results and discussion

As illustrated in scheme 1, the pyridyl diimine ligands were prepared by the Schiff-base condensation of 4-(allyloxy)-2,6-diacetylpyridine, prepared by starting from chelidamic acid, with 2,6-dimethylaniline or 2,6-diisopropylaniline. All of the Co(II) and Fe(II) complexes were isolated in high yield (>90%) by reacting the ligand (1.1 eq.) with a suitable metal salt ($CoCl_2$ or $FeCl_2$) in THF at room temperature. For the design of of highly active supported catalysts, we chose the mesoporous SBA-15 material as a supporter [9]. The pore diameter and the surface area of calcined SBA-15 material were determined from its adsorption isotherm of nitrogen to be 99 Å and 594 $m^2\ g^{-1}$, respectively.

A possible leaching of the immobilized metal compound into solution during the polymerization is an important issue for supported catalysts. The formation of covalent bonding between the surface of SBA-15 material and the metal complexes should be a good way to minimize the leaching phenomenon. For this we modified the surface of the SBA-15 material by reacting it with 1,1,3,3-tetramethylsilazane (see scheme 1). This modified SBA-15 was combined with bis(imino)pyridyl iron (**cat-1** and **cat-3**) and cobalt (**cat-2** to **cat-4**) complexes in the presence of Karstedt catalyst [10]. From elemental analyses of the covalently immobilized catalysts, metal loadings of **cat-5**, **cat-6**, **cat-7** and **cat-8** catalysts were calculated to be 0.200, 0.254, 0.169 and 0.129 mmol (based on N) per gram, respectively. These amounts of metal loadings were in good agreement with the results determined using an inductively coupled plasma atomic emission spectroscopy (ICP-AES): i.e. metal loadings of 0.211, 0.248, 0.175 and 0.132 mmol g^{-1} of **cat-5**, **cat-6**, **cat-7** and **cat-8**, respectively. The surface areas of the SBA-15 supported catalysts were 524, 507, 549 and 545 $m^2\ g^{-1}$ for **cat-5**, **cat-6**, **cat-7** and **cat-8**, respectively.

The supported catalysts were tested in slurry polymerization runs at 5.0 atm of ethylene in toluene at temperature between 10 and 50 °C. The active catalysts are generated *in situ* in toluene by the addition of MAO (300 equiv.) to the precursor in the presence of ethylene. A polymerization run time was 30 min. Data for the

polymerizations of ethylene are summarized in table 1. All polymerizations reached maximum rate ($R_{p,max}$) within 5 min and then decayed slowly. Table 1 showed average rate ($R_{p,avg}$) and $R_{p,max}$ values as measures of catalytic activity. All of the catalysts, homogeneous or heterogeneous, convert ethylene to highly linear polyethylene (PE) as determined by both differential scanning calorimetry (T_m values 126.9–136.8 °C, DSC) and NMR spectrum. It was not possible to detect any branching because of sufficiently high molecular weight of polymer obscuring the detection of the methyl end groups [11]. The PE samples produced by the iron and cobalt catalysts have heat of fusion between 160 and 250 J g^{-1} (DSC), demonstrating they are highly crystalline [12].

The polymer molecular weights vary dramatically with modification in ligand and metal. Increasing the steric bulk of the ortho aryl substituents increases molecular weight (compare run no. 1–3 and 2–4 in table 1). Similar results have been reported for Ni(II) and Pd(II) systems and Fe(II) and Co(II) systems [4]. For the Fe systems (**cat-1** and **cat-3**), bimodal curve in the GPC traces is observed. Thus, the peak values of the major high molecular weight fractions provide the most accurate comparisons between different systems [3]. Interestingly such bimodal behavior disappears and molecular weight increases by the immobilization to some degrees. Generally, the iron systems produce higher molecular weight PEs relative to their cobalt analogs for both homogeneous and heterogeneous systems.

It is most desirable that the molecular characteristics of the products produced from heterogeneous catalysts resemble as closely as possible those of their homogeneous counterparts, mirroring or enhancing the catalytic activity, the narrow polydispersity index (PDI) and melting behavior. With a few exceptions, in myriad cases, the activity of the supported catalyst is half to a tenth that of the soluble catalysts not only due to the diffusion limitation of monomer, but may also due to the result of fewer active sites present in the heterogeneous variant [13–16]. In this sense the immobilization method employed in this study seems to be desirable, since molecular weight increases and PDI becomes narrower or remains almost unaffected, and the activity of the supported catalysts mirrors the catalytic activity of corresponding soluble systems. The molecular weight of the polymer produced by supported catalyst is generally higher than that produced by corresponding homogeneous catalyst notwithstanding a decrease of activity (table 1). This suggests that the lower activity of the supported catalyst is due to a reduced number of active centers. If the propagation rate were lower for a supported catalyst, the rate of termination would have to be reduced proportionately or more for theses molecular weight observation to hold. The decrease of the activity of the present heterogeneous catalyst systems over corresponding homogeneous catalyst systems is also induced by a limited accessibility of the MAO cocatalyst into pores of SBA-15. The immobilized active sites are located within the pores of SBA-15, which are hardly accessible to MAO. The metal sites on the outside edges of SBA-15 particles might be the only sites activated with MAO.

If the metal complex is linked to the conventional silica support, different absorptions occur in general. A large part of the metal complexes is also destroyed by acid centers on the silica support. Therefore, the activity

Table 1
Results of ethylene polymerizations over a series of supported pyridyl bis-imine Fe(II) and Co(II) catalysts. Polymerization conditions: 250 mL reactor, 80 mL of toluene, 30 min runs, ethylene pressure of 5 atm, and [MAO]/[Mt] = 300 (Mt = Fe or Co)

Run no.	Cat.	Cat. Amt. μmol	Temp. (°C)	$R_{p,avg} \times 10^{-7}$[a]	$R_{p,max} \times 10^{-7}$[a]	T_m (°C)[b]	Peak mw $\times 10^{-4}$[c]	PDI
1	**cat-1**	3.02	30	18.3	27.5	129.6	2.5	–
2	**cat-5**	5.00	10	14.2	18.5	133.2	4.5	3.4
3			30	17.2	27.5	134.0	2.8	3.7
4			50	19.4	34.2	134.4	2.2	2.6
5	**cat-2**	3.02	30	57.7	83.7	129.3	0.7	2.2
6	**cat-6**	6.35	10	33.0	41.4	131.8	2.3	2.4
7			30	55.5	81.4	131.3	0.9	2.3
8			50	42.1	72.6	129.6	0.6	2.5
9	**cat-3**	3.02	30	26.8	37.5	136.3	15.4	–
10	**cat-7**	4.24	10	19.2	25.0	135.6	38.0	3.1
11			30	25.3	37.4	136.8	17.2	3.6
12			50	29.8	49.4	136.2	13.4	3.2
13	**cat-4**	3.02	30	28.0	39.4	134.2	4.6	2.3
14	**cat-8**	3.23	10	24.0	28.8	135.2	11.8	2.5
15			30	25.8	35.1	133.6	5.4	2.4
16			50	19.6	30.7	131.8	2.5	2.3

[a]Average rate ($R_{p,avg}$) and maximum rate ($R_{p,max}$) of polymerization as (g-PE)(mol-Mt)$^{-1}$ h^{-1} atm^{-1}.
[b]Melting temperature determined by DSC (10 °C min^{-1}).
[c]No 1 and 9 exhibit bimodal MWD (by GPC).

of the supported catalyst is half to a tenth that of the soluble catalyst [8]; however, the immobilization of metal complex on the SBA-15 mesoporous material modified with 1,1,3,3-tetramethyl-silazane employed in this study seems to be a reasonable method, because SBA-15 is not an acidic support. In addition possible leaching of the immobilized metal compound into the toluene solution during the polymerization was minimized. In order to determine whether any leached homogeneous catalyst was present, we filtered the suspended materials after activation and exposing the solution to ethylene. The negligible activity of this solution in further ethylene polymerization demonstrated an absence of the leached active metal compounds in toluene solution. The negligible activity As shown in table 1, the average rate of polymerization of **cat-1** changes from 18.3 to 17.2 (g-PE)(mol-Fe)$^{-1}$ h^{-1} atm^{-1} at 30 °C by immobilization. Similar results were obtained by the other catalysts of this study.

In summary the new heterogeneous Fe(II) and Co(II) catalysts supported on modified SBA-15 mesoporous material were demonstrated to be a reasonable immobilization system since they resemble closely to those of their soluble counterparts, mirroring the activity and the molecular weight behavior. In this sense, the silica-supported late transition metal catalysts of this study are a new family of promising catalysts for the ethylene polymerization.

Acknowledgments

This work is financially supported by the Ministry of Education and Human Resources development (MOE) and the Ministry of Commerce, Industry and Energy (MOCIE) through the fostering project of the Industrial-Academic Cooperation Centered University. The authors are also grateful to the center for Ultramicrochemical Process Systems, the Brain Korea 21 Project, and the National Research Laboratory Program.

References

[1] G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White and D.J. Williams, Chem. Commun. (1998) 849.
[2] A.M.A. Bennett, World Patent Application 98/27124, 1998.
[3] B.L. Small, M. Brookhart and A.M.A. Bennet, J. Am. Chem. Soc. 120 (1998) 4049.
[4] S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169 and references cited therein..
[5] B.L. Small and M. Brookhart, J. Am. Chem. Soc. 120 (1998) 7143.
[6] D.E. De Vos, M. Dams, B.F. Sels and P.A. Jacobs, Chem. Rev. 102 (2002) 3615.
[7] A. Stein, B.J. Melde and R.C. Schroden, Adv. Mater. 12 (2000) 1403.
[8] R. Anwander, Chem. Mater. 13 (2001) 4419.
[9] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrikson, B.F. Chmelka and G.D. Stucky, Science 279 (1998) 548.
[10] Q.J. MiaofcZ.-P. Fang and G.P. Cai, Catal. Commun. 4 (2003) 637.
[11] J.C. Randall, ACS Symp. Ser. 247 (1984) 280.
[12] L. Mandelkern and A.L. Allou, J. Polym. Sci. B 4 (1966) 447.
[13] I. Kim, B.H. Han, J.G. Kim, H.S. Suh and C.-S. Ha, Macromolecules 36 (2003) 6689.
[14] T.R. Boussie, V. Murphy, K.A. Hall, C. Coutard, C. Dales, M. Petro, E. Carlson, H.W. Turner and T.S. Powers, Tetrahedron 55 (1999) 11,699.
[15] P.-P. Peter and M. Brookhart, Macromolecules 35 (2002) 6074.
[16] F.A.R. Kaul, G.T. Puchta, H. Schneider, F. Bielert, D. Mahalios and W.A. Herrmann, Organometallics 21 (2002) 74.