Polymerization of α-Olefins with Pyridylamidohafnium Catalysts: Living Behavior and Unexpected Isoselectivity from a C_s-Symmetric Catalyst Precursor

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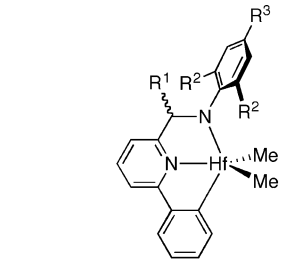
Received December 9, 2006
Revised Manuscript Received February 12, 2007

Introduction

One of the primary goals of polymer synthesis is to control the stereochemistry, molecular weight, and polydispersity of the resultant polymer. There are numerous heterogeneous and homogeneous olefin polymerization catalysts that exhibit exquisite control over the stereochemistry of polymerization.[1] For homogeneous catalysts, the coordination environment about the metal center, which is enforced by the ancillary ligand and the growing polymer chain, dictates the stereoselectivity of coordination/insertion. Control over molecular weight and polydispersity can be achieved by employing a living polymerization catalyst.[2] To date, relatively few examples of catalysts that are stereoselective, especially isoselective, and living for olefin polymerization have been reported.[3a−n] A particularly promising new class of stereoselective olefin polymerization catalysts has been developed through a successful collaborative effort by researchers at Dow and Symyx. Adopting a high-throughput parallel screening approach, researchers at Symyx identified C_1-symmetric dialkyl pyridylamidohafnium complexes (e.g., *rac*-**2**, Figure 1) as catalyst precursors for the high-temperature, isoselective polymerization of propylene and for the copolymerization of various vinyl monomers.[4a−h] The isoselectivity of these catalysts was proposed to result from the conformation imposed on the active species by the bulky substituent on the bridge joining the pyridine and amido moieties.[4a] Researchers at Dow have begun to use these catalysts for industrial scale production of various polyolefins.[5a−f] They have recently reported the preparation of blocky ethylene/1-octene copolymers via chain shuttling polymerization in which the ability of pyridylamidohafnium catalysts to undergo chain transfer via transmetalation was cleverly exploited.[6a−d]

We have recently developed a facile synthetic route for the preparation of chiral anilines via the acid-catalyzed electrophilic aromatic substitution of styrene derivatives on *p*-toluidine.[7] By incorporating these chiral aniline moieties into the α-diimine ligand framework of Ni(II) catalysts, significant levels of isoselectivity for olefin polymerization have been achieved.[3k,8] Seeking to expand the utility of these chiral anilines to other catalyst systems, we set out to incorporate them into the pyridylamine ligand framework. We postulated that by placing the chiral influence nearer the active site higher levels of isoselectivity could be achieved, thereby obviating the necessity of substitution on the carbon adjacent to the amino nitrogen. Additionally, if optically pure chiral anilines were employed in the ligand synthesis, one could easily access enantiomerically pure pyridylamidohafnium precatalysts. Herein we report the results of our initial investigations into the olefin polymerization behavior of pyridylamidohafnium catalysts bearing a methylene bridge between the pyridine and amido ligand components.



1: R^1 = H, R^2 = ^{i}Pr, R^3 = H
rac-**2**: R^1 = Ph, R^2 = ^{i}Pr, R^3 = H
rac-**3**: R^1 = H, R^2 = 1-(4-*t*Bu-C_6H_4)Et, R^3 = Me

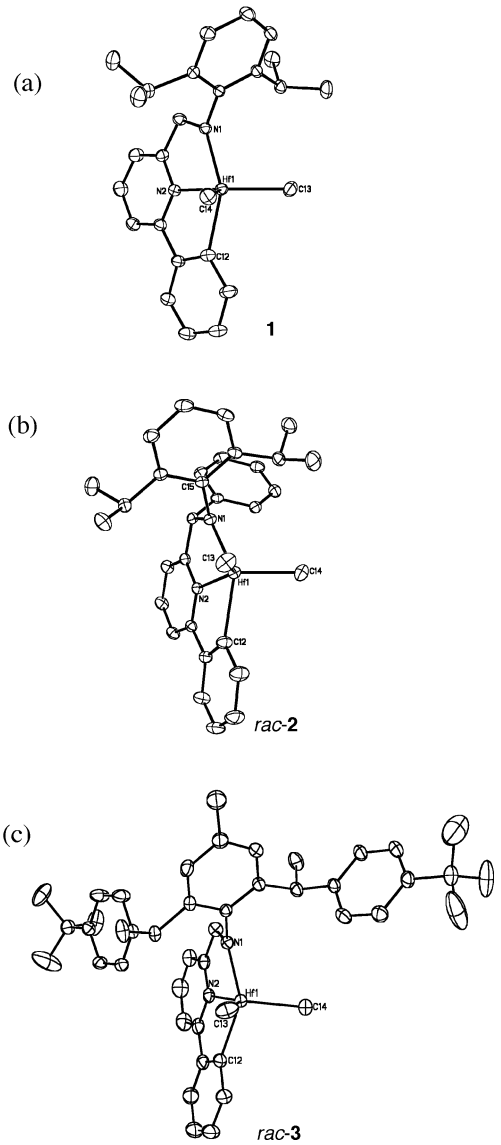


Figure 1. ORTEP diagrams of **1** (toluene molecule of crystallization omitted), *rac*-**2**, and *rac*-**3**. Hydrogen atoms are omitted for clarity and probability ellipsoids are drawn at the 40% probability level. The unlabeled atoms are carbon.

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10.1021/ma062824s CCC: $37.00
Published on Web 04/07/2007

Table 1. Data for 1-Hexene Polymerization Using 1, *rac*-2, and *rac*-3[a]

entry	cat.	activator	t_{age}[b] (min)	t_{rxn} (h)	T_{rxn} (°C)	yield (g)	conv (%)	M_n[c] (g/mol)	M_n^{theo} (g/mol)	M_w/M_n[c]
1	**1**	$B(C_6F_5)_3$	360	2.0	25	0	0	n.a.[d]	n.a.[d]	n.a.[d]
2	**1**	$B(C_6F_5)_3$	60	2.0	25	0.03	2.2	106 000	30 000	4.52
3	**1**	$B(C_6F_5)_3$	5	2.0	25	1.34	99	284 300	134 000	1.09
4	**1**	$B(C_6F_5)_3$	0	2.0	25	1.34	99	152 000	134 000	1.15
5	**1**	$B(C_6F_5)_3$	0	0.5	0	0.13	9.6	51 200	13 000	1.20
6	**1**	$B(C_6F_5)_3$	0	0.5	25	1.13	83	133 200	113 000	1.07
7	**1**	$B(C_6F_5)_3$	0	0.5	50	1.05	77	150 800	105 000	1.18
8	**1**	$[Ph_3C][B(C_6F_5)_4]$	0	2.0	25	1.33	98	267 000	133 000	1.33
9	**1**	$[Ph_3C][B(C_6F_5)_4]$	0	0.5	0	1.29	95	520 300	129 000	1.51
10	*rac*-**2**	$B(C_6F_5)_3$	0	0.5	25	1.33	98	148 600	133 000	1.51
11	*rac*-**3**	$B(C_6F_5)_3$	0	24	25	0.05	3.7	153 800	5 000	1.61

[a] Polymerization conditions: Hf = 10 μmol, [Hf]/[B] = 1.0, 8.0 mL toluene, 2.0 mL 1-hexene. [b] t_{age} = period that precatalyst and activator were in contact prior to introduction of the monomer. [c] Determined using gel permeation chromatography in 1,2,4-$C_6H_3Cl_3$ at 140 °C vs polystyrene standards. [d] n.a. = not applicable.

Experimental Section

Synthesis of 1. The desired compound was prepared following the general procedure described by Coalter et al.[5b] 2,6-Diisopropyl-*N*-((6-phenylpyridin-2-yl)methyl)aniline (see Supporting Information) (0.629 g, 1.83 mmol) was dissolved in the minimum amount of dry toluene and cooled to 0 °C. BuLi (1.20 mL of a 1.6 M solution in hexanes) was added to the ligand solution under N_2. Upon addition of the BuLi solution a yellow precipitate formed. After 1 h, the volatiles were removed in vacuo. The resulting residue was slurried in hexane, the supernatant was removed via cannula, and the resultant yellow powder was dried in vacuo. Fresh toluene was added to the ligand salt, and the resulting slurry was transferred via cannula to a slurry of $HfCl_4$ (0.529 g, 1.65 mmol) in toluene. The resulting mixture was heated to 110 °C, resulting in a color change from yellow to orange. After 3 h, the reaction mixture was cooled to room temperature, and 1.92 mL of 3.0 M MeMgBr in Et_2O was added. The reaction mixture turned from orange to red. After 12 h the volatiles were removed in vacuo. The residue was extracted with toluene, the extracts were filtered through Celite, and the volatiles were removed in vacuo to give a white crystalline solid. Recrystallization from toluene at −35 °C yielded orange, single crystals (0.57 g, 63% yield) suitable for X-ray diffraction. ^{1}H NMR (C_6D_6, 500 MHz): δ 8.34 (dd, J_{HH} = 5.37 Hz, 1.47, 1H, Ar*H*), 7.45 (d, J_{HH} = 7.81 Hz, 1H, Ar*H*), 7.38 (td, J_{HH} = 6.15 Hz, 0.98 Hz, 1H, Ar*H*), 7.26−7.17 (m, 4H, Ar*H*), 6.94 (d, 1H, Ar*H*), 6.88 (t, J_{HH} = 7.81 Hz, 1H, Ar*H*), 6.31 (d, J_{HH} = 7.81 Hz, 1H, Ar*H*), 5.07 (s, 2H, CH_2N), 3.73 (q, J_{HH} = 6.84 Hz, 2H, C*H*$(CH_3)_2$), 1.37 (d, J_{HH} = 6.84 Hz, 6H, CH(CH_3)$_2$), 1.21 (d, J_{HH} = 6.84 Hz, 6H, CH(CH_3)$_2$), 0.68 (s, 6H, Hf−CH_3). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): δ 166.54, 164.99, 148.18, 147.65, 141.04, 139.03, 131.13, 128.88, 128.79, 126.97, 124.88, 124.46, 123.46, 118.07, 115.58, 68.67, 64.85, 28.75, 28.34, 24.37. Elemental analysis: Calcd for $C_{26}H_{32}HfN_2$: C, 56.67%; 5.84%; N, 5.08%. Found: C, 56.42%; H, 5.84%; N, 5.18%.

General Procedure for 1-Hexene Polymerization. In the glovebox, the catalyst precursor was weighed into an oven-dried scintillation vial. The vial was equipped with a stir bar, and the catalyst was dissolved in 5 mL of toluene. To this solution was added 2 mL of 1-hexene. In a separate vial, $B(C_6F_5)_3$ was dissolved in 3 mL of toluene, this solution was added to the catalyst precursor/1-hexene solution, and the reaction was allowed to proceed with vigorous stirring for the desired period of time. The polymerization was quenched with 5 mL of MeOH, and after stirring for at least 6 h, the polymer was isolated by decanting the supernatant and drying to constant weight in vacuo at 60 °C.

Results and Discussion

The pyridylimine ligand precursors were prepared via a Schiff base condensation[9] between 6-phenyl-2-pyridine carboxaldehyde[10] and the aniline. Reduction of the pyridylimines with $LiAlH_4$ or $NaBH_3CN$ gave the pyridylamine ligands in yields from 82 to 90%. The dimethylpyridylamidohafnium complexes **1** and *rac*-**3** were prepared by reacting the pyridylamidolithium salt with $HfCl_4$ to form the trichloropyridylamidohafnium compounds in situ.[5b] Treatment of the trichloropyridylamidohafnium intermediates with 3.5 equiv of MeMgBr led to alkylation and subsequent ortho metalation furnishing the desired compounds in yields from 56 to 63%. In order to investigate the effect of substitution at the carbon adjacent to the amino nitrogen on polymerization behavior, *rac*-**2** was prepared following published procedures.[4d,5b] Single crystals of suitable quality for structural determination via X-ray diffraction were obtained for **1**, *rac*-**2**, and *rac*-**3** (Figure 1). The molecular structure of the bis(dimethylamido) analogue of *rac*-**2** has been reported by Murphy and co-workers.[4a] The X-ray crystal structure of **1** revealed that the molecule is nearly C_s-symmetric in the solid state. The *N*-aryl ring is slightly canted as evidenced by the slight displacement (0.15 Å) of the ipso carbon (C(15)) from the plane defined by N(1), N(2), Hf(1), and C(12). As expected, *rac*-**2** and *rac*-**3** were shown to possess C_1-symmetry. The degree of canting was more pronounced for *rac*-**2** and *rac*-**3**, the ipso carbons exhibiting displacements of 0.75 and 0.64 Å, respectively. The presence of a singlet for the Hf−CH_3 protons in the ^{1}H NMR spectrum of **1** indicates that the complex possesses C_s-symmetry in solution. The isopropyl methyl groups give rise to two doublets, indicating that rotation about the N(1)−C(15) bond is slow on the NMR time scale. The ^{13}C{^{1}H} NMR spectrum for **1** exhibited a resonance at 64.85 ppm which was assigned to Hf−CH_3. ^{1}H and ^{13}C{^{1}H} NMR

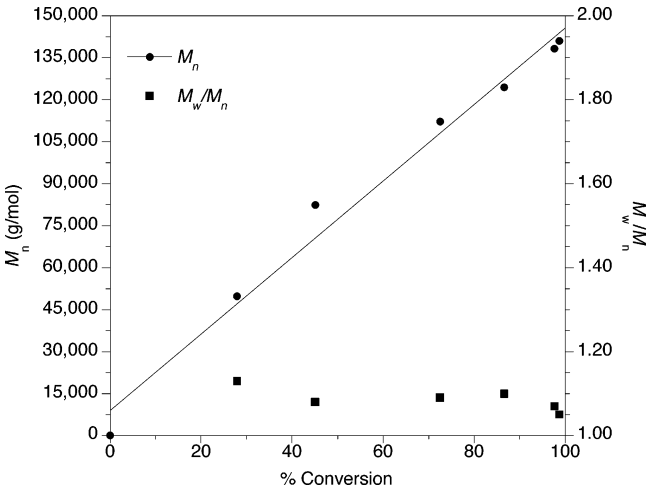

Figure 2. Plot of poly(1-hexene) M_n (●) and M_w/M_n (■) vs percent conversion using **1**/$B(C_6F_5)_3$ at 25 °C. M_n and M_w/M_n values were determined by gel permeation chromatography at 140 °C (polystyrene standards).

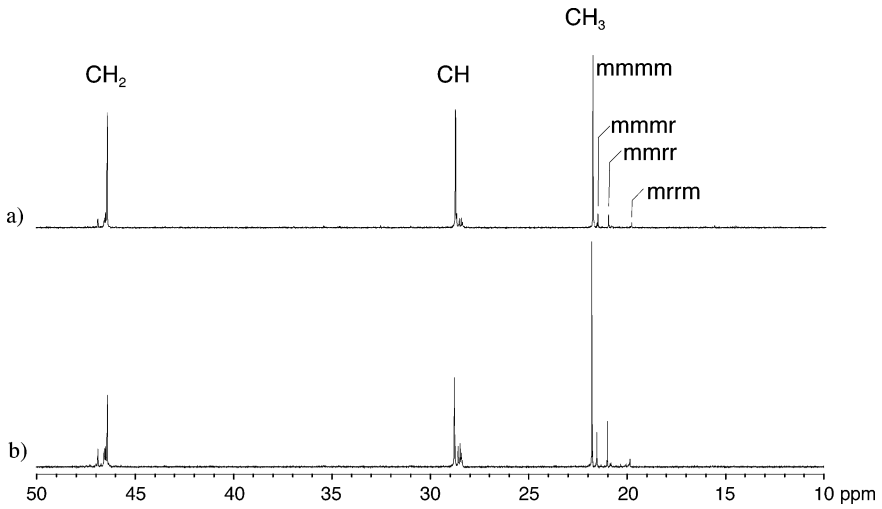

Figure 3. $^{13}C\{^1H\}$ NMR spectra of *iso*-PPs in 1,1,2,2-tetrachloroethane-d_2, 125 MHz, 135 °C, formed by (a) *rac*-**2**/$B(C_6F_5)_3$ and (b) **1**/$B(C_6F_5)_3$ at 20 °C under 30 psig of propylene.

spectroscopy revealed that the C_1-symmetries of *rac*-**2** and *rac*-**3** are retained in solution as expected. The ^1H NMR spectra of *rac*-**2** and *rac*-**3** reveal two singlets corresponding to the Hf−CH_3 protons, which are consistent with the proposed C_1-symmetry.

With several dimethylpyridylamidohafnium complexes in hand, we proceeded to investigate their polymerization behavior. The results of 1-hexene polymerization by catalysts derived from **1**, *rac*-**2**, and *rac*-**3** are presented in Table 1. When **1** is treated with $B(C_6F_5)_3$ in the absence of 1-hexene, rapid catalyst decomposition occurs. With increased catalyst aging time (t_{age}: the period for which **1** and $B(C_6F_5)_3$ are in contact prior to the introduction of monomer) a decrease in percent conversion is observed along with a concomitant increase in the relative disparity between the theoretical molecular weight (M_n^{theo}) calculated on the basis of the assumption of one chain per hafnium center and the experimentally determined M_n (entries 1−3). However, when **1** is activated with $B(C_6F_5)_3$ at room temperature in the presence of 1-hexene, an active polymerization catalyst is formed, and the resultant polymer possesses a narrow polydispersity index (PDI) and an M_n which is in good agreement with M_n^{theo} (entries 4 and 6). These observations suggest that **1**/$B(C_6F_5)_3$ is a living catalyst for 1-hexene polymerization at room temperature. The living character of 1-hexene polymerization catalyzed by **1**/$B(C_6F_5)_3$ is further exemplified by the observation that M_n increases linearly with monomer conversion (Figure 2). To the best of our knowledge, this is the first report of living α-olefin polymerization catalyzed by a pyridylamido-ligated catalyst. At 0 °C, the PDI of the polymer produced by **1**/$B(C_6F_5)_3$ broadens slightly, and the M_n is greater than that expected (entry 5), suggesting that activation is incomplete or slower at lower temperatures. At 50 °C, the PDI remains narrow and the M_n is in fairly good agreement with the expected value (entry 7), suggesting that living behavior is maintained even at elevated temperatures. Interestingly, upon activation of **1** with $[Ph_3C][B(C_6F_5)_4]$, the living character of 1-hexene polymerization is lost as evidenced by the relatively broad PDIs of the resultant polymers (entries 8 and 9). One possible explanation for the observed loss of living behavior may be due to a dramatic increase in the rate of propagation relative to the rate of initiation when the less-coordinating $[B(C_6F_5)_4]^-$ anion is employed.[11] It is noteworthy that polymerization of 1-hexene at 25 °C by *rac*-**2**/$B(C_6F_5)_3$ furnishes poly(1-hexene) with a relatively broad PDI (entry 10). Disappointingly, *rac*-**3**/$B(C_6F_5)_3$ displays very low activity for 1-hexene polymerization (entry 11).[12] The low activity and apparent incomplete initiation of *rac*-**3**/$B(C_6F_5)_3$ may be due to η^6-binding of the 4-*tert*-butylphenyl group by the cationic hafnium center which precludes monomer binding.[13] The poly(1-hexene)s produced by catalysts derived from **1**, *rac*-**2**, and *rac*-**3** are all isoenriched as evidenced by the ^{13}C NMR spectra (see Supporting Information). While the poly(1-hexene) furnished by **1**/$B(C_6F_5)_3$ was only moderately isotactic, it is noteworthy that the catalyst derived from a C_s-symmetric catalyst precursor exhibited any degree of isoselectivity.[1,14]

Since the resolution of the ^{13}C NMR spectra for the poly(1-hexene)s produced was insufficient for detailed statistical analysis, we examined the microstructure of polypropylene (PP) formed by **1**/$B(C_6F_5)_3$ using ^{13}C NMR spectroscopy in order to determine the mechanism of stereocontrol for α-olefin polymerization by this catalyst (Figure 3**)**. Propylene polymerization by **1**/$B(C_6F_5)_3$ and *rac*-**2**/$B(C_6F_5)_3$ was achieved at 20 °C under 30 psig of propylene for 30 min (see Supporting Information). The PP produced by **1**/$B(C_6F_5)_3$ has M_n = 68 600 g/mol and is isoenriched as evidenced by the prominent peak at 21.82 ppm ($[m^4]$ = 56%). The polymer exhibits a narrow PDI (M_w/M_n = 1.05) consistent with living polymerization.[15] Integration of the resonances due to stereoerrors reveals a 2:2:1 ratio of [*mmmr*]:[*mmrr*]:[*mrrm*] sequences which is consistent with an enantiomorphic site control mechanism of isoselective monomer enchainment.[1b] This is an extremely rare example of site-controlled isoselectivity by a C_s-symmetric catalyst precursor.[16] One possible explanation for the observed isoselectivity is an in situ ligand modification brought about by insertion of propylene into the Hf−C_{Aryl} bond; previous work by Hustad et al. supports this hypothesis.[17] In the case of *rac*-**2**, insertion of propylene into the Hf−C_{Aryl} bond would give rise to a mixture of diastereomeric active species leading to a multimodal molecular weight distribution for the resultant polymer. The PDI of the polypropylene produced by *rac*-**2**/$B(C_6F_5)_3$ is relatively broad (M_w/M_n = 2.44), which is consistent with this hypothesis. An intramolecular ligand modification pathway involving C−H activation of the isopropyl group is another possible explanation for the observed isoselectivity.[18] The ^{13}C NMR spectrum for PP produced by *rac*-**2**/$B(C_6F_5)_3$ is included for comparison. The PP is isotactic ($[m^4]$ = 86%), which is consistent with reports by Murphy and co-workers.[4a] Again, the ratio of stereoerrors is indicative of an enantiomorphic site controlled mechanism for isoselective monomer enchainment.

Conclusion

We have shown that, upon activation with $B(C_6F_5)_3$ at room temperature, **1** behaves as a living 1-hexene polymerization catalyst. Under the same conditions *rac*-**2**/$B(C_6F_5)_3$ produces poly(1-hexene) with a relatively broad PDI indicative of a nonliving polymerization. Unexpectedly, **1**/$B(C_6F_5)_3$ was shown to produce isoenriched poly(1-hexene)s and polypropylene. The isoselectivity for propylene polymerization (and presumably 1-hexene polymerization) results from an enantiomorphic site control mechanism, which is highly unusual in light of the generally accepted symmetry rules for olefin polymerization catalysts.[1,14] Efforts to rigorously establish the cause for the site controlled isoselectivity of **1**/$B(C_6F_5)_3$ as well as catalyst optimization through ligand modification are underway.

Acknowledgment. G.W.C. gratefully acknowledges support from the Packard and Sloan Foundations as well as support from Mitsubishi Chemicals. This research made use of the Cornell Center for Materials Research Shared Experimental Facilities supported through the NSF MRSEC program (DMR-0520404).

Supporting Information Available: Catalyst synthesis and characterization, X-ray data for **1**, *rac*-**2**, and *rac*-**3**, polymerization procedures, GPC data, $^{13}C\{^1H\}$ NMR spectra of poly(1-hexene)s, and propylene polymerization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA062824S