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Introduction

Well-defined organometallic complexes of group 4 metals as single-site olefin polymerization catalysts have undergone continuous development over the last three decades with regard to precise manipulations of the microstructures of polyolefins, including branching, polydispersity, and stereochemistry, features that directly define the physical properties of the polymers.¹ Among these tunable factors, stereoregularities of polyolefins are most straightforwardly associated with the design of the ligand architecture. In general, for ansa-type metallocene complexes, C_2 - and C_s -symmetric complexes afford isotactic and syndiotactic polypropylenes, respectively, whereas C_1 -symmetric complexes give variable stereoregular polyolefins, such as atactic, hemiisotactic, and isotactic polymers.² The development of non-metallocene precatalysts allows for more versatile and flexible design access to the stereoregularity of poly(olefin)s. Notable efforts in the last decade were targeted toward C2-symmetric complexes. Kol reported titanium and zirconium complexes with

Isospecific polymerization of 1-hexene by C₁-symmetric half-metallocene dimethyl complexes of group 4 metals with bidentate N-substituted iminomethylpyrrolyl ligandst

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Non-bridged half-metallocene dimethyl complexes of group 4 metals 2a-4a with an N-4-methoxyphenyl-(iminomethyl)pyrrolyl ligand 1a were synthesized and characterized by NMR spectroscopy and X-ray analysis. Upon activation with $[Ph_3C][B(C_6F_5)_4]$, these complexes became active catalysts for the polymerization of 1-hexene. A series of hafnium complexes with various N-substituents on the imine group of ligands 1b-1g were also prepared and applied as catalysts for 1-hexene polymerization. The activation parameters for the exchange process between the two methyl groups bound to the metal for Cp*MMe₂(R-pyr) complexes were estimated by NMR shape analysis at various temperatures. The findings indicated that the transition state of the ligand flipping process might be associated with the isoselectivity of the polymerization reaction.

> a tetradentate diamine bis(phenolate) ligand that catalyze the highly isoselective polymerization of 1-hexene.³ Coates⁴ and Fujita⁵ independently reported that titanium complexes bearing two phenoxy-imine ligands produce isotactic polypropylene via enantiomorphic site-control, while titanium complexes having phenoxy-imine ligands with ortho-fluorinated N-aryl groups or bulky ortho-phenol substituents yield highly syndiotactic polypropylene via chain-end control, and nickel complexes supported by an α -diimine ligand with a bulky substituent at the o-position of the phenyl group produce isotactic poly(olefin)s.⁶

> Of particular interest are the C_1 -symmetric metallocene catalysts, which mediate different types of stereoselectivities due to the differentiation of two coordination sites.⁷⁻⁹ Conceptually, migratory insertion at each site during the polymerization propagation step provides different stereoselectivity of the backbone of the polymer with or without site epimerization.¹⁰ In fact, the same enantioface preference of the olefin monomer or rapid-site epimerization that is faster than the propagation results in the isoselective polymerization of α -olefins. An intriguing example is the C₁-symmetric halfmetallocene complexes of zirconium and hafnium with an asymmetrical amidinate ligand reported by Sita et al. as catalysts for the living, isoselective polymerization of 1-hexene, in which the migratory insertion of the monomer followed by the rapid-site shift of the polymer chain end to the less bulky site results in successive insertion of the monomer through the same coordination site and the same enantioface

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[†]Electronic supplementary information (ESI) available: NMR spectra for complex 4e and cationic species 5a were included. CCDC 903413 (2a), 903414 (3a), 903415 (4c), and 903416 (4g). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32481d

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Fig. 1 C_1 -Symmetric half-metallocene complexes of group 4 metals for stereo-specific α -olefin polymerization.

preference (Fig. 1a).¹¹ Accordingly, the high isotactic polymerization achieved using such C_1 -symmetric half-metallocene complexes requires that the monomer insertion rate is much faster than the epimerization rate around the metal center through a bidentate ligand flipping process.

As part of our ongoing interest in the catalytic performance of group 4 metal complexes bearing various 2-iminomethylpyrrolyl ligands as olefin polymerization precatalysts,^{12–15} we reported that some half-metallocene dimethyl complexes of hafnium, upon activation with $[Ph_3C][B(C_6F_5)_4]$, became unique initiators of living and isoselective 1-hexene polymerization.^{13e} These hafnium complexes are the second example of isoselective polymerization precatalysts with a C_1 -symmetric half-metallocene fragment (Fig. 1b). Herein, we report the full details of the synthesis and structural characterization of halfmetallocene complexes of titanium, zirconium and hafnium with various iminopyrrolyl ligands and their catalytic performance for 1-hexene polymerization, as well as studies of the correlation between isospecific polymerization and site fluxionality of the dimethyl precursors.

Results and discussion

Syntheses of half-metallocene dimethyl complexes of group 4 metals bearing a 2-{*N*-(4-methoxyphenyl)iminomethyl}-pyrrolyl ligand

We previously reported the synthesis of Cp*HfMe₂(R-pyr) (4a: R-pyr = 4-MeOC₆H₄-N=CH-pyr) by treating Cp*HfMe₃ $(Cp^* = \eta^5 - C_5 Me_5)$ with 2-{N-(4-methoxyphenyl)iminomethyl}pyrrole (1a).^{13e} We conducted the same protocol to prepare the corresponding titanium complex 2a and zirconium complex 3a by reactions of Cp^*TiMe_3 and Cp^*ZrMe_3 with 1a (eqn (1)). These newly prepared complexes 2a and 3a were characterized by NMR spectral data, combustion analysis, and X-ray analyses. The ¹H NMR spectra of 2a and 3a displayed essentially the same pattern as that of 4a. The singlet resonance due to the imine proton shifted upfield from that of free ligand 1a, suggesting that the imine nitrogen atom is coordinated to the metal in solution. Two singlet resonances (δ 1.07 and 1.27) were shifted downfield from that (δ 0.73) of Cp*TiMe₃¹⁶ due to the diastereotopic methyl groups bound to the titanium atom of 2a at 35 °C, consistent with the C_1 -symmetric fourlegged piano stool structure. In contrast, broad singlet resonances of two methyl groups bound to the zirconium atom of **3a** and the hafnium atom of **4a** were shifted downfield (δ 0.61



Fig. 2 Transition states of the ligand flipping process.

Table 1 Activation parameters for the exchange process of dimethyl complexes 2a, 3a, and 4a

Complex	$T_{\rm c}$ (K)	ΔG^{\dagger}_{c} (kcal mol ⁻¹)	ΔH^{\ddagger} (kcal mol ⁻¹)	ΔS^{\ddagger} (cal mol ⁻¹)	Mode
2a	353	17.4	24.9 ± 0.4	21.2 ± 1.2	В
3a	233	11.2	9.0 ± 0.3	-9.2 ± 1.2	Α
4a	268	13.0	12.4 ± 0.7	-3.4 ± 2.6	Α

for **3a**; δ 0.38 for **4a**) compared with the corresponding trimethyl complexes Cp*ZrMe₃ (δ 0.23)¹⁷ and Cp*HfMe₃ (δ 0.07).¹⁸ The broadening of the signals at 35 °C indicated racemization *via* a rapid ligand flipping process over the NMR time scale (Fig. 2). Consistent with these ¹H NMR spectral data, the ¹³C NMR spectral data of **2a**, **3a**, and **4a** at 35 °C displayed two resonances at δ 73.2 and 74.3 for **2a** due to two diastereotopic methyl carbons, and one resonance each was observed for **3a** (δ 50.5) and **4a** (δ 56.3).



The activation parameters for the exchange process between the two methyl groups bound to the metal in complexes **2a–4a** were estimated by NMR shape analysis at various temperatures and are summarized in Table 1, because such parameters could be directly associated with stereoregularity during 1-hexene polymerization. The ΔG^{\dagger}_{c} values for **3a** and **4a** complexes were lower than that (17.4 kcal mol⁻¹) of **2a**, presumably due to differences in the fluxional process (*vide infra*)

caused by the disparity of the ionic radii between the titanium atom and others, indicating that the steric hindrance around the metal increased the barrier of the exchange process. The ΔG_{c}^{\dagger} value of 2a was 2–3 kcal mol⁻¹ higher than that $(14-15 \text{ kcal mol}^{-1})$ of the reported titanium complexes bearing a dissymmetric amidinate ligand, Cp*TiMe₂[R¹NC(CH₃)NR²],¹⁹ suggesting that the steric repulsion between the Cp* ligand and the bidentate ligand increased as the chelate ring size increased. Two possible fluxionalities can explain the ligand flipping process: one is a distorted trigonal bipyramidal transition state (mode A), in which the ΔS^{\dagger} value is negative or small, while the other is a tetrahedral transition state (mode **B**), in which the ΔS^{\dagger} value is positive and the ΔH^{\dagger} value should be large because it requires the release of the imino moiety from the metal.²⁰ The observed positive value of ΔS^{\ddagger} as well as the large value of ΔH^{\dagger} for **2a** confirmed that titanium complex 2a preferred the tetrahedral transition state B. In contrast, the negative values of ΔS^{\ddagger} for **3a** and **4a** were due to the ring-flipping process through the distorted trigonal bipyramidal transition state A, in which the rather larger atomic radius resulted in adapting the trigonal bipyramidal transition state A.

Fig. 3 shows the ORTEP drawings of complexes **2a** and **3a**, and their selected bond distances and angles are summarized in Table 2. Both complexes adopt the C_1 -symmetric fourlegged piano stool geometry. The imine nitrogen atom and the pyrrolyl nitrogen atom coordinate in a chelating manner to the metal and consequently two methyl groups occupy the *cis*-positions of the four legs. The Ti–N1 [2.096(5) Å] and Ti–N2 [2.295(4) Å] distances of **2a** are slightly longer than those of



Fig. 3 ORTEP drawings of the molecular structures of Cp*MMe₂(R-pyr) (M = Ti, Zr) complexes **2a** and **3a**.

Table 2	Bond distances	(Å) and	angles (°)) of	complexes	2a and 3a	
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	2a	3a
M-C11	2.136(5)	2.2543(17)
M-C12	2.110(5)	2.2656(18)
M-N1	2.096(5)	2.2529(15)
M-N2	2.295(4)	2.3897(14)
C11-M-C12	83.8(2)	87.89(7)
N1-M-N2	74.77(16)	70.97(5)
C11-M-N2	83.04(18)	85.02(6)
C12-M-N1	82.59(19)	82.87(6)

the bis(iminopyrrolyl)titanium dichloride complex, TiCl₂(Ph-N=CH-pyr)₂ [Ti-N_{pvr}: 2.043(2) and 2.033(2) Å; Ti-N_{imine}: 2.215(2) and 2.185(2) Å].^{14a} The Ti–C11 [2.136(5) Å] and Ti–C12 [2.110(5) Å] distances of 2a are normal and comparable to those [2.154(3) and 2.116(3) Å] of a half-titanocene dimethyl amidinate complex, $Cp*TiMe_2[RNC(Me)NR]$ [R = CH(Me)(Ph)].^{19a} The N1-Ti-N2 bite angle [74.77(16)°] of 2a is comparable to the mean bite angle [72.50(6)° and 76.22(6)°] in TiCl₂(Ph-N=CH-pyr)₂,^{14a} but larger than that $[61.27(8)^{\circ}]$ of Cp*Ti- $Me_2[RNC(Me)NR] [R = CH(Me)(Ph)]$.^{19a} For complex 3a, the Zr-N1 [2.2529(15) Å] and Zr–N2 [2.3897(14) Å] bond distances are ca. 0.15 Å longer than those of 2a, a difference that can be rationalized by taking into account the difference in the ionic radii, and longer than that of a bis(iminopyrrolyl) complex, $ZrCl_2(Ar-N=CH-pyr)_2$ [Ar = 4-MeOC₆H₄: Zr-N_{pvr}: 2.191(5) Å; Zr-N_{imine}: 2.280(4) Å].^{13*a*} The Zr-C11 [2.2543(17) Å] and Zr-C12 [2.2656(18) Å] bond lengths are also ca. 0.15 Å longer than those of 2a. The N1-Zr-N2 bite angle [70.97(5)°] of 3a is smaller than that of 2a, confirming that the steric hindrance around zirconium complex 3a is less than that of titanium complex 2a. The bond lengths and angles around the zirconium atom in 3a are quite similar to those of the hafnium complex 4a, whose structural features were discussed in our previous communication.13e

Observation of cationic species by NMR spectroscopy

The addition of 1 equivalent of $[Ph_3C][B(C_6F_5)_4]$ to complexes **2a**, **3a**, and **4a** in C_6D_5Br was monitored by ¹H NMR spectroscopy, which revealed the immediate formation of Ph_3CCH_3 in all reactions. The cationic monomethyl complex **5a** was cleanly formed and stable at room temperature for a few hours, although the cationic complexes of titanium and zirconium decomposed immediately at room temperature. The resonance due to a methyl group bound to the cationic metal center was observed as a sharp singlet (**5a**: δ 0.72), and shifted downfield from that of the corresponding neutral dimethyl complexes (**4a**: δ 0.38) (Scheme 1).

1-Hexene polymerization by complexes 2a, 3a, and 4a

With a series of complexes of group 4 metals in hand, the role of the central metals was exemplified by polymerization of 1-hexene using a mixture of dimethyl complexes and 1 equivalent of $[Ph_3C][B(C_6F_5)_4]$ in chlorobenzene, and the results are summarized in Table 3. Titanium complex **2a** showed very low activity, yielding atactic poly(1-hexene). Because **2a** produced a



Scheme 1 Generation of cationic monomethyl species.

 Table 3
 1-Hexene polymerization by complexes 2a, 3a, and 4a at 25 °C^a

Run	Cat.	Time (h)	Activity (g mol ^{-1} h)	$M_{\rm n}^{\ b} \left(\times 10^3 \right)$	$M_{ m w}^{\ \ b} \left(imes 10^3 ight)$	$M_{ m w}{}^b/M_{ m n}$	$[mmmm]^{c}$ (%)	Mode
1	2a	1.5	350	113.2	174.3	1.5	Atactic	В
3	3a 4a	3	5700	13.0	19.0	1.5	65	A

^{*a*} Conditions: [cat.]:[Ph₃C][B(C₆F₅)₄]:[1-hexene] = 0.020: 0.020: 10 (mmol) in C₆H₅Cl (2.75 mL) at 25 °C. ^{*b*} Determined by GPC analysis at 40 °C in THF. ^{*c*} Determined by ¹³C NMR measurement. ^{*d*} Bimodal molecular weight distribution.

very high molecular weight polymer, the initiation efficiency of 2a was estimated to be quite low. The zirconium 3a and hafnium 4a complexes had higher activities than the titanium complex 2a. The molecular weight distribution of poly-(1-hexene) obtained by using 3a was bimodal, indicating that there were two active species under the polymerization conditions, presumably due to the thermal instability of the catalytically active species. It is notable that atactic poly(1-hexene) was yielded by the zirconium complex, while the hafnium analogous complex 4a afforded isotactic rich poly(1-hexene) [[mmmm] = 65%). Consequently, we selected hafnium as the best metal for polymerizing 1-hexene in terms of the catalytic activity and stereospecificity.

Syntheses of half-metallocene dimethyl complexes of hafnium bearing various iminopyrrolyl ligands

Because hafnium complex **4a** exhibited isospecific polymerization for 1-hexene,^{13e} its derivatives were prepared to finetune the catalytic activity as well as the isoselectivity of hafnium precatalysts. Complexes **4b** and **4f**, together with **4a**, were reported previously, and other hafnium complexes **4c–e**, and **4g** were synthesized and characterized following the same procedure as for **4a** (eqn (2)). All complexes were characterized by NMR spectroscopy and combustion analyses together with X-ray analyses for **4c** and **4g**.



The activation parameters of the methyl group exchange for hafnium complexes **4** were determined by NMR shape analysis at various temperatures and are summarized in Table 4. The barriers for the methyl group exchange of **4c** were too low to determine the activation parameters. Interestingly, in contrast to our presumption that the bulky substituent on the *ortho* position of the aromatic ring made the ligand-flipping barrier high, hafnium complex **4d** had a low ΔG^{\dagger} value and a positive ΔS^{\dagger} value, consistent with the transition state **B**. On the other hand, complexes **4e–4g** with an alkyl substituent at the imine

 Table 4
 Activation parameters of the methyl group exchange process

Complex	$T_{\rm c}$ (K)	ΔG^{\dagger}_{c} (kcal mol ⁻¹)	ΔH^{\ddagger} (kcal mol ⁻¹)	ΔS^{\ddagger} (cal mol ⁻¹)	Mode
4a	268	13.0	12.4 ± 0.7	-3.4 ± 2.6	Α
4b	266	12.9	12.8 ± 0.7	-0.3 ± 2.7	Α
4c	218	ND	ND	ND	
4d	228	10.5	11.0 ± 0.4	2.4 ± 1.4	В
4e	298	14.2	14.1 ± 0.3	-0.3 ± 1.1	Α
4 f	313	15.1	15.2 ± 0.4	0.7 ± 1.4	Α
4g	328	16.0	21.0 ± 0.4	15.9 ± 1.2	В
0					



Fig. 4 ORTEP drawings of the molecular structures of Cp*HfMe_2(R-pyr) complexes 4c and 4g.

Table 5 Bond distances (Å) and angles (°) of complexes 4c and 4g

	4 c	4g
Hf-C11	2,255(3)	2.296(4)
Hf-C12	2.224(3)	2.248(4)
Hf–N1	2.238(3)	2.216(3)
Hf–N2	2.374(3)	2.430(3)
C11-Hf-C12	87.87(14)	83.92(14)
N1-Hf-N2	70.20(10)	71.76(10)
C11-Hf-N2	80.56(11)	90.39(12)
C12-Hf-N1	85.16(12)	81.99(13)

nitrogen had a higher barrier in the order of $CH_2Ph < Cy < {}^tBu$. Complex **4g** exhibited a large positive ΔS^{\dagger} value, suggesting that complex **4g** adopted a tetrahedral transition state **B** after releasing the imine moiety, presumably due to the steric repulsion between the tBu group and the two Me groups bound to the hafnium atom.

The crystal structures of complexes 4c and 4g are shown in Fig. 4 and selected bond distances and angles are summarized in Table 5. These complexes also adopt a C_1 -symmetric four-

legged piano stool geometry and the structural features are almost the same as those of **2a–4a**.

1-Hexene polymerization by hafnium complexes bearing various iminopyrrolyl ligands

In the presence of 1 equivalent of $[Ph_3C][B(C_6F_5)_4]$, hafnium complexes **4b–g** became catalysts for 1-hexene polymerization and the results are summarized in Table 6 together with the results of **4a**. The steric hindrance around the metal suppressed the catalytic activity: hafnium complexes bearing iminopyrrole ligands having *ortho*-substituted aromatic rings or bulky alkyl groups on the imine nitrogen had lower activities and yielded atactic polymers (runs 5 and 6). Furthermore, the polymers yielded by **4c** and **4d** had a trimodal molecular weight distribution, implying that the decomposition of cationic species led to unexpected catalytic species.

Because the catalytically active species were thermally unstable and decomposed at room temperature, polymerization of 1-hexene was conducted at -20 °C. As shown in Table 6, the isoselectivities of complexes 4a, 4b, and 4f increased, whereas their activities decreased at -20 °C. In complex 4e, isoselectivity was slightly decreased ([mmmm] = 25%), although the catalytic activity, which reflected its propagation rate, and the barrier for ligand flipping were higher than those of 4a and 4b (runs 7 and 8). The isoselectivity of complex 4f was higher than that of 4e although the activity of 4f was much lower than that of 4e, indicating that the higher barrier for the ligand flipping of 4f led to increased isoselectivity. It is noteworthy that the isospecific polymerization of 1-hexene was associated with the fluxional nature of catalyst precursors. Dimethyl complexes adopting mode A exhibited two adjacent sites in the C_1 -symmetric structure differentiated by the iminopyrrolyl ligand that play a pivotal role in controlling the stereochemistry of the polymer microstructure.

Conclusion

The synthesis and characterization of half-metallocene complexes of group 4 metals bearing various *N*-substituted iminopyrrole ligands, and their catalytic performance for polymerization of 1-hexene are reported. The ligand flipping process of the bidentate iminopyrrolyl ligand was clarified by VT-NMR studies, which revealed that the ligand flipping proceeded through a distorted trigonal bipyramidal (mode **A**) or a tetrahedral transition state (mode **B**). The dimethyl complexes of group 4 metals became catalysts for 1-hexene polymerization by the addition of 1 equivalent of $[Ph_3C][B(C_6F_5)_4]$. The high isoselectivity in 1-hexene polymerization was associated with the flipping process of the bidentate iminopyrrolyl ligand attached to the half-metallocene fragments.

Experimental section

General procedures

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under an atmosphere of argon using the standard Schlenk techniques. Complexes Cp^*TiCl_3 ,²¹ Cp^*ZrCl_3 ,¹⁷ Cp^*TiMe_3 ,¹⁶ Cp^*HfCl_3 ,²² Cp^*HfMe_3 ,¹⁸ and $Cp^*HfMe_2(R-pyr)$ complexes, **4a**, **4b**, and **4f**^{13e} were prepared according to the literature. Bidentate iminopyrrole ligands were prepared by condensation of the 2-formylpyrrole with the corresponding aniline derivatives. $[Ph_3C][B(C_6F_5)_4]$ was prepared according to the literature.²³ Hexane, THF, toluene, and diethyl ether were dried and deoxygenated by distillation over sodium benzophenone ketyl under argon. 1-Hexene was distilled from sodium benzophenone ketyl and then distilled from CaH₂ by trap-to-trap distillation before use for polymerization. Chlorobenzene and bromobenzene were distilled from CaH₂ and then distilled from CaH₂ by trap-to-

 Table 6
 1-Hexene polymerization by hafnium complexes⁴

Run	Cat.	Time (h)	Temp (°C)	Activity (g mol ^{-1} h)	$M_{\rm n}^{\ b} (\times 10^3)$	$M_{ m w}^{\ \ b}$ (×10 ³)	$M_{\rm w}{}^b/M_{\rm n}$	$[mmmm]^{c}$ (%)	Mode
1	4a	3	25	570	13.0	19.0	1.5	65	Α
2	4a	6	-20	1600	23.5	25.1	1.1	90	Α
3	4b	3	25	7000	9.1	12.7	1.4	45	Α
					0.6	0.7	1.1		
4	4b	6	-20	1200	22.5	24.1	1.1	90	Α
5	4c	6	25	310	178.4	260.4	1.5	Atactic	_
					18.7	27.6	1.5		
					0.9	1.0	1.1		
6	4d	3	25	830	82.4	128.1	1.6	Atactic	В
					17.1	19.0	1.1		
					0.9	1.1	1.1		
7	4e	3	25	1410	7.9	16.7	2.1	30	Α
					1.0	1.1	1.1		
8	4e	6	-20	1900	41.4	73.4	1.8	25	Α
9	4f	3	25	3000	5.9	8.4	1.4	40	Α
10	4f	6	-20	480	9.0	9.7	1.1	75	A
11	49	3	25	1400	16.0	28.2	1.8	Atactic	В

^{*a*} Conditions: [cat.]:[Ph₃C][B(C₆F₅)₄]:[1-hexene] = 0.020: 0.020: 10 (mmol) in C₆H₅Cl (2.75 mL) at 25 °C. ^{*b*} Determined by GPC analysis at 40 °C in THF. ^{*c*} Determined by ¹³C NMR measurement.

trap distillation before use for polymerization. Benzene- d_6 and toluene- d_8 were distilled from P_2O_5 and thoroughly degassed by trap-to-trap distillation before use. Bromobenzene- d_5 was distilled from CaH₂ and degassed.

The ¹H NMR (300 MHz), ¹³C NMR (75 MHz), and ¹⁹F NMR (282 MHz) spectra were measured on a VARIAN-UNITY-I-NOVA-300 Spectrometer. Assignments for ¹H and ¹³C NMR peaks for some of the complexes were aided by 2D ¹H-¹H COSY, 2D ¹H-¹H NOESY, 2D ¹H-¹³C HETCOR spectra. The elemental analyses were recorded by using a Perkin Elmer 2400 at the Faculty of Engineering Science, Osaka University. All melting points were measured in sealed tubes under an argon atmosphere, and were not corrected.

The gel permeation chromatographic analysis of poly-(1-hexene) was carried out at 40 °C by using a Shimadzu LC-10A liquid chromatograph system and a RID 10A refractive index detector, equipped with a Shodex KF-806L column, which was calibrated *versus* commercially available polystyrene standards.

Synthesis of Cp*TiMe₂[*p*-ANI-pyr] (2a)

In a Schlenk tube, Cp*TiMe₃ (240 mg, 1.05 mmol) was dissolved in toluene (5 mL). Ligand 1a (211 mg, 1.05 mmol) was added to the solution at room temperature, and then the solution was stirred overnight. After removal of solvent in vacuo, the resulting red oil was added to a small amount of hexane and dried under vacuum to give 2a as a brown powder (451 mg, 1.09 mmol, quantitative yield). Mp 121 °C (dec.). ¹H NMR (300 MHz, C₆D₆, 35 °C): δ 1.07 (s, 3H, Ti-CH₃), 1.27 (s, 3H, Ti-CH₃), 1.76 (s, 15H, Cp*), 3.35 (s, 3H, -OCH₃), 6.44 (dd, ${}^{3}J_{H-H} = 1.9$ Hz, ${}^{3}J_{H-H} = 3.6$ Hz, 1H, 4-pyr), 6.70 (d, ${}^{3}J_{H-H} =$ 9.1 Hz, 2H, C₆ H_4), 6.74 (d, ${}^{3}J_{H-H}$ = 3.4 Hz, 1H, 3-pyr), 6.92 (d, ${}^{3}J_{H-H} = 9.1$ Hz, 2H, C₆H₄), 7.00 (m, 1H, 5-pyr), 7.53 (s, 1H, N=CH). ¹³C NMR (75 MHz, C₆D₆, 35 °C): δ 13.0 (q, ¹J_{C-H} = 126.7 Hz, $C_5(CH_3)_5$), 55.5 (q, ${}^1J_{C-H}$ = 143.4 Hz, OCH_3), 73.2 (q, ${}^{1}J_{C-H} = 123.8$ Hz, Ti-*C*H₃), 74.3 (q, ${}^{1}J_{C-H} = 121.5$ Hz, Ti-*C*H₃), 114.3 (d, ${}^{1}J_{C-H}$ = 160.9 Hz, *m*-*C*₆H₄), 114.3 (d, ${}^{1}J_{C-H}$ = 168.1 Hz, 4-pyr), 119.7 (d, ${}^{1}\!J_{C-H}$ = 168.1 Hz, 3-pyr), 125.7 (d, ${}^{1}J_{C-H} = 160.6$ Hz, $o-C_{6}H_{4}$), 125.8 (s, $C_{5}(CH_{3})_{5}$), 138.4 (s, 2-pyr), 140.4 (d, ${}^{1}J_{C-H}$ = 179.6 Hz, 5-pyr), 147.1 (s, *ipso-C*₆H₄), 158.4 (s, $p-C_6H_4$), 160.1 (d, ${}^{1}J_{C-H} = 163.5$ Hz, N=CH). Anal. calcd for C₂₄H₃₂N₂OTi: C, 69.90; H, 7.82; N, 6.79. Found: C, 69.88; H, 8.04; N, 6.80.

Synthesis of Cp*ZrMe₂[*p*-ANI-pyr] (3a)

This compound was prepared from Cp*ZrCl₃ (944 mg, 2.84 mmol), MeLi (7.2 mL, 8.6 mmol, 3.0 equiv., 1.20 M in diethyl ether) and **1a** (514 mg, 2.57 mmol, 0.91 equiv.) in diethyl ether by the same procedure described for **2a**. Recrystallization from toluene–hexane yielded yellow crystals of **3a** (483 mg, 1.06 mmol, 41% yield). Mp 114 °C (dec.). ¹H NMR (300 MHz, C₆D₆, 35 °C): δ 0.61 (s, 6H, Zr-CH₃), 1.80 (s, 15H, Cp*), 3.35 (s, 3H, -OCH₃), 6.44 (dd, ³J_{H-H} = 1.9 Hz, ³J_{H-H} = 3.6 Hz, 1H, 3-pyr), 6.91 (d, ³J_{H-H} = 9.1 Hz, 2H, *m*-C₆H₄), 7.19 (m, 1H, 5-pyr), 7.49 (s, 1H, N=CH). ¹³C NMR

(75 MHz, C₆D₆, 35 °C): δ 11.6 (q, ¹J_{C-H} = 127 Hz, C₅(*C*H₃)₅), 50.5 (q, ¹J_{C-H} = 115 Hz, Zr-*C*H₃), 55.0 (q, ¹J_{C-H} = 143 Hz, OCH₃), 114.0 (d, ¹J_{C-H} = 160 Hz, *m*-C₆H₄), 114.7 (d, ¹J_{C-H} = 169 Hz, 4-pyr), 121.2 (s, C₅(CH₃)₅), 121.4 (d, ¹J_{C-H} = 168 Hz, 3-pyr), 124.7 (d, ¹J_{C-H} = 160 Hz, *o*-C₆H₄), 138.6 (s, 2-pyr), 141.0 (d, ¹J_{C-H} = 180 Hz, 5-pyr), 144.9 (s, *ipso*-C₆H₄), 158.1 (s, *p*-C₆H₄), 160.6 (d, ¹J_{C-H} = 164 Hz, N=*C*H). Anal. calcd for C₂₄H₃₂N₂OZr: C, 63.25; H, 7.08; N, 6.15. Found: C, 62.84; H, 6.68; N, 5.85.

Synthesis of Cp*HfMe₂[XYL-pyr] (4c)

This compound was prepared from Cp*HfMe₃ (177 mg, 0.493 mmol) and 2-{N-(2,6-dimethylphenyl)iminomethyl}pyrrole 1c (97.5 mg, 0.492 mmol) in toluene by the same procedure described above. 4c (91.7 mg, 0.169 mmol, 34%). ¹H NMR (300 MHz, C_6D_6 , 35 °C): δ 0.08 (s, 6H, Hf–CH₃), 1.92 (s, 15H, Cp*), 2.17 (s, 6H, Ar–CH₃), 6.42 (dd, 1H, ${}^{3}J_{H-H} =$ 3.6 Hz, ${}^{3}J_{H-H}$ = 1.9 Hz, 4-pyr), 6.69 (dd, 1H, ${}^{3}J_{H-H}$ = 3.6 Hz, ${}^{4}J_{H-H}$ = 1.1 Hz, 3-pyr), 6.96 (m, 3H, Ar), 7.08 (dd, 1H, ${}^{3}J_{H-H}$ = 1.9 Hz, ${}^{3}J_{H-H} = 1.1$ Hz, 5-pyr), 7.18 (s, 1H, N=CH). ${}^{13}C$ NMR (75 MHz, C₆D₆, 35 °C): δ 12.3 (q, ${}^{1}J_{C-H}$ = 126 Hz, C₅(CH₃)₅), 20.1 (q, ${}^{1}J_{C-H}$ = 127 Hz, Ar– CH_{3}), 55.7 (q, ${}^{1}J_{C-H}$ = 112 Hz, Hf-*C*H₃), 115.3 (d, ${}^{1}J_{C-H}$ = 164 Hz, 4-pyr), 119.9 (s, $C_{5}(CH_{3})_{5}$), 121.4 (d, ${}^{1}J_{C-H}$ = 167 Hz, 3-pyr), 123.1 (d, ${}^{1}J_{C-H}$ = 150 Hz, *m*-Ar), 128.0 (d, ${}^{1}J_{C-H}$ = 157 Hz, *p*-Ar), 131.4 (s, *o*-Ar), 138.2 (s, 2-pyr), 142.1 (d, ${}^{1}J_{C-H}$ = 179 Hz, 5-pyr), 151.3 (s, *ipso*-Ar), 164.7 (d, ${}^{1}J_{C-H}$ = 165 Hz, N=CH). Anal. calcd for C₂₅H₃₄N₂Hf: C, 55.50; H, 6.33; N, 5.18. Found: C, 54.81; H, 6.02; N, 5.28.

Synthesis of Cp*HfMe₂[DIP-pyr] (4d)

This compound was prepared from Cp*HfMe₃ (383 mg, 1.07 mmol) and 1d (272 mg, 1.07 mmol) in toluene by the same procedure described above. 4d (374 mg, 0.626 mmol, 59%). ¹H NMR (300 MHz, C₆D₆, 35 °C): δ 0.08 (s, 6H, Hf-CH₃), 1.02 (d, 6H, ${}^{3}J_{H-H} = 6.9$ Hz, CH(CH₃)₂), 1.35 (d, 6H, ${}^{3}J_{H-H} =$ 6.9 Hz, CH(CH₃)₂), 1.95 (s, 15H, Cp*), 3.20 (sep, 2H, ${}^{3}J_{H-H} =$ 6.9 Hz, $CH(CH_3)_2$, 6.43 (dd, 1H, ${}^{3}J_{H-H} = 1.9$ Hz, ${}^{3}J_{H-H} = 3.6$ Hz, 4-pyr), 6.71 (dd, 1H, ${}^{3}J_{H-H}$ = 3.6 Hz, ${}^{4}J_{H-H}$ = 1.1 Hz, 3-pyr), 7.09 (m, 1H, 5-pyr), 7.10–7.14 (m, 3H, Ar), 7.73 (s, 1H, N=CH). ¹³C NMR (75 MHz, C_6D_6 , 35 °C): δ 12.1 (q, ${}^1J_{C-H}$ = 126.1Hz, $C_5(CH_3)_5$, 23.1 (q, ${}^{1}J_{C-H}$ = 126 Hz, $CH(CH_3)_2$), 26.0 (q, ${}^{1}J_{C-H}$ = 126 Hz, $CH(CH_3)_2$), 29.3 (d, ${}^{1}J_{C-H}$ = 124 Hz, $CH(CH_3)_2$), 56.0 (q, ${}^{1}J_{C-H} = 113$ Hz, Hf-*C*H₃), 115.7 (d, ${}^{1}J_{C-H} = 168$ Hz, pyr), 120.0 (s, $C_5(CH_3)_5$), 121.4 (d, ${}^{1}J_{C-H}$ = 168 Hz, pyr), 123.6 (d, ${}^{1}J_{C-H}$ = 157 Hz, m- C_6 H₃), 126.7 (d, ${}^{1}J_{C-H}$ = 159 Hz, p- C_6 H₃), 137.4 (s, 2-pyr), 142.1 (s, $o-C_6H_3$), 142.3 (d, ${}^{1}J_{C-H}$ = 179 Hz, 5-pyr), 149.2 $(s, ipso-C_6H_3)$, 164.7 (d, ${}^{1}J_{C-H}$ = 165 Hz, N=CH). Anal. calcd for C₂₉H₄₂N₂Hf: C, 58.33; H, 7.09; N, 4.69. Found: C, 58.00; H, 7.23; N, 4.76.

Synthesis of Cp*HfMe₂[Bn-pyr] (4e)

This compound was prepared from $Cp*HfMe_3$ (367 mg, 1.02 mmol) and 2-{*N*-benzyliminomethyl}pyrrole **1e** (188 mg, 1.02 mmol) in toluene by the same procedure described above to give **4e** (382 mg, 0.724 mmol, 71%). ¹H NMR (300 MHz,

Table 7 Crystal data and data collection parameters for 2a, 3a, 4c, and 4g

	2a	3a	4c	4g
Empirical formula	C ₂₄ H ₃₂ N ₂ O ₁ Ti ₁	C ₂₄ H ₃₂ N ₂ O ₁ Zr ₁	$C_{25}H_{34}N_2Hf_1$	C ₂₁ H ₃₄ N ₂ Hf ₁
Formula weight	412.42	455.74	541.03	492.99
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	8.9587(7)	9.1395(4)	15.6422(9)	14.6866(9)
b (Å)	14.3777(13)	9.5693(4)	8.9096(5)	8.3103(4)
c (Å)	17.7595(14)	14.4498(6)	16.7840(7)	17.7682(10)
α (°)	73.418(3)	103.4010(10)	_	_ ``
β (°)	81.473(3)	97.5500(10)	90.262(3)	109.942(3)
γ (°)	81.371(3)	110.7440(10)	_ ``	_
$V(A^3)$	2154.1(3)	1117.55(8)	2339.1(2)	2038.6(2)
Z, D_{calcd} (g/cm ⁻³)	4, 1.272	2, 1.354	4, 1.536	4, 1.606
F(000)	880	476	1080	984
μ [Mo-K α] (mm ⁻¹)	0.414	0.508	4.471	5.122
T(K)	120	120	120	120
Crystal size (mm)	0.41 imes 0.26 imes 0.12	0.50 imes 0.30 imes 0.20	0.50 imes 0.40 imes 0.25	0.40 imes 0.30 imes 0.20
$2\theta_{\rm max}(\circ)$	55	54.9	61.0	65.2
No. of reflections measured	40 235	31 628	77 116	93 855
Unique data (R_{int})	9829 (0.0622)	5096 (0.0216)	7135 (0.0642)	7412 (0.0749)
No. of observations	9829	5096	7135	7412
No. of variables	505	253	253	227
R_1 , $^a w R_2^b$ (all data)	0.1394, 0.1785	0.0245, 0.0789	0.0380, 0.0869	0.0426, 0.0982
R_{1}^{a}, WR_{2}^{b} $(I > 2.0\sigma(I))$	0.0530, 0.1492	0.0231, 0.0754	0.0309, 0.0843	0.0369, 0.0949
GOF on F^2	1.038	1.177	1.181	1.141
$\Delta ho ext{ (e Å}^{-3})$	0.392, -0.648	0.445, -0.328	1.912, -1.988	2.884, -2.495
${}^{a}R_{1} = (\Sigma F_{o} - F_{c})/(\Sigma F_{o}). {}^{b}WR_{2}$	$_{2} = \left[\left\{ \Sigma w (F_{o}^{2} - F_{c}^{2})^{2} \right\} / \left\{ \Sigma w (F_{o}^{4}) \right\} \right]$	1/2.		

C₆D₆, 35 °C): δ 0.28 (br, 6H, Hf−C*H*₃), 1.93 (s, 15H, Cp*), 4.34 (br, 2H, C*H*₂), 6.36 (dd, 1H, ${}^{3}J_{HH}$ = 3.6 Hz, ${}^{3}J_{H-H}$ = 1.9 Hz, 4-pyr), 6.47 (m, 1H, pyr), 7.04–7.16 (m, 6H, C₆*H*₅ and pyr), 7.48 (s, 1H, N=C*H*). 13 C NMR (75 MHz, C₆D₆, 35 °C): δ 11.5 (q, ${}^{1}J_{C-H}$ = 127 Hz, C₅(CH₃)₅), 54.0 (q, ${}^{1}J_{C-H}$ = 113 Hz, Hf−C*H*₃), 59.0 (t, ${}^{1}J_{C-H}$ = 142 Hz, CH₂), 114.7 (d, ${}^{1}J_{C-H}$ = 169 Hz, 4-pyr), 119.5 (d, ${}^{1}J_{C-H}$ = 168 Hz, 3-pyr), 119.9 (s, C₅(CH₃)₅), 127.7 (d, ${}^{1}J_{C-H}$ = 160 Hz, Ph), 128.9 (Ph), 129.0 (Ph), 138.1 (*ipso*-Ph or 2-pyr), 138.6 (*ipso*-Ph or 2-pyr), 140.5 (d, ${}^{1}J_{C-H}$ = 163 Hz, N=CH). Elemental analysis did not give a satisfactory result, and the 1 H and 13 C NMR spectra were shown in ESI.†

Synthesis of Cp*HfMe₂[^tBu-pyr] (4g)

This compound was prepared from Cp*HfMe₃ (413 mg, 1.15 mmol) and 2-{*N*-(*tert*-butyl)iminomethyl}pyrrole (**1g**, 173 mg, 1.15 mmol) in diethyl ether by the same procedure described for **4g** (400 mg, 0.811 mmol, 70% yield). ¹H NMR (300 MHz, C₆D₆, 35 °C): δ 0.34 (brs, 3H, Hf-CH₃), 0.58 (brs, 3H, Hf-CH₃), 1.13 (s, 9H, C(CH₃)₃), 1.93 (s, 15H, Cp*), 6.45 (m, 1H, 4-pyr), 6.67 (m, 1H, 3-pyr), 7.05 (m, 1H, 5-pyr), 7.96 (s, 1H, N=CH). ¹³C NMR (75 MHz, C₆D₆, 35 °C): δ 12.0 (q, ¹*J*_{C-H} = 126 Hz, C₅(CH₃)₅), 31.7 (q, ¹*J*_{C-H} = 126 Hz, C(CH₃)₃), 55.5 (q, ¹*J*_{C-H} = 113 Hz, Hf-CH₃), 56.6 (q, ¹*J*_{C-H} = 113 Hz, Hf-CH₃), 59.5 (s, *C*(CH₃)₃), 114.6 (d, ¹*J*_{C-H} = 168 Hz, 4-pyr), 119.7 (d, ¹*J*_{C-H} = 166 Hz, 3-pyr), 120.5 (s, *C*(CH₃)₅), 136.5 (s, 2-pyr), 139.4 (d, ¹*J*_{C-H} = 180 Hz, 5-pyr), 158.3 (d, ¹*J*_{C-H} = 160 Hz, N=CH). Anal. calcd for C₂₁H₃₄N₂Hf: C, 51.16; H, 6.95; N, 5.68. Found: C, 51.24; H, 7.29; N, 5.59.

Observation of cationic species (5a)

In a glove box, hafnium complex 4a (10 µmol) and [Ph₃C]-[B(C₆F₅)₄] (10 µmol) were added into an NMR tube and then C₆D₅Br (0.6 mL) was added at -30 °C. The reaction mixture was observed by ¹H NMR and ¹⁹F NMR spectroscopy at 35 °C. ¹H NMR (300 MHz, C₆D₅Br, 35 °C): δ 0.72 (s, 3H, Hf-CH₃), 1.74 (s, 15H, C₅(CH₃)₅), 2.04 (3H, s, Ph₃CCH₃), 3.56 (s, 3H, OCH₃), 6.39 (dd, 1H, ³J_{H-H} = 3.7 Hz, ³J_{H-H} = 1.9 Hz, 4-pyr), 6.63 (d, 2H, ³J_{H-H} = 8.8 Hz, C₆H₄), 6.81 (d, 2H, 8.8 Hz, C₆H₄), 6.92 (m, 1H, 3-pyr), 6.96 (m, 1H, 5-pyr), 7.01–7.16 (m, 15H, (C₆H₅)₃CCH₃), 7.91 (s, 1H, N=CH). ¹⁹F NMR (282 MHz, C₆D₅Br, 35 °C): δ –167.7 (br t, ³J_{F-F} = 18 Hz, *m*-C₆F₅), –163.9 (t, ³J_{F-F} = 21 Hz, *p*-C₆F₅), –133.4 (br, 8F, *o*-C₆F₅).

1-Hexene polymerization

In a glove box, a solution of $[Ph_3C][B(C_6F_5)_4]$ (20 µmol) in C_6H_5Cl was added to a solution of precatalyst (20 µmol) in C_6H_5Cl (2.75 mL) and 1-hexene (10 mmol). The reaction mixture was stirred and then quenched with 1 N HCl in MeOH. The polymer was extracted with hexane and then washed with MeOH and dried under vacuum. The *isotacticity* of the poly(1-hexene) was determined by the ¹³C NMR measurement.²⁴

Determination of the activation parameters for the exchange process

The ¹H NMR spectra of Cp*MMe₂(R-pyr) complexes were measured between 218 K and 353 K, and curve fitting of the resonances of M–CH₃ protons afforded $\nu_{1/2}$ values. Subtraction of the natural line width, obtained at the high temperature limit, from observed $\nu_{1/2}$ values at each temperature gave the corrected values, $\Delta\nu_{1/2}$. In the fast exchange limit, only one line appears and the following approximation, derived from the Bloch equations, holds: $\Delta t = (2\Delta\nu_{1/2})/{\pi(\delta\nu)^2}$, where $\delta\nu$ is the separation between the lines in the slow exchange case. The first order rate constant *k* is obtained as an inverse of the conformer lifetime, $k = 1/\Delta t$. Activation parameters, ΔH^{\dagger} and ΔS^{\dagger} were determined by linear regression analysis of plots of $\log(k/T)$ vs. 1/T.

Crystallographic data collection and structure determination

Crystals of **2a**, **3a**, **4c**, and **4g** suitable for X-ray measurement were mounted on glass fibers or fixed inside of CryoLoop (Hampton Research Corp.), and placed in a nitrogen stream. All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-K α radiation. Crystal data and structure refinement parameters are summarized in Table 7. Indexing was performed from 3 oscillations which were exposed for an appropriate time for each crystal. The camera radius was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. For the data collection, reflections were measured at a temperature of 120(1) K.

The structures of complexes **3a**, **4c**, and **4g** were solved by direct methods (SIR92),²⁵ and the structure of complex **2a** solved by direct methods (SIR97).²⁶ All structures were refined on F^2 by full-matrix least-squares methods, using SHELXL-97.²⁷ The non-hydrogen atoms were refined anisotropically and all hydrogen atoms were included in the refinement on their carrier atoms. The function minimized was $[\Sigma w-(F_o^2 - F_c^2)^2]$ (w = $1/[\sigma^2(F_o^2) + (aP)^2 + bP]$), where $P = (Max(F_o^2, 0) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The function R_1 and wR_2 were $(\Sigma ||F_o| - |F_c||)/\Sigma |F_o|$ and $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma (wF_o^4)]^{1/2}$, respectively. The ORTEP-III program was used to draw the molecule.²⁸ CCDC 903413 (**2a**), 903414 (**3a**), 903415 (**4c**), and 903416 (**4g**) contain the supplementary crystallographic data for this paper.

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