Intramolecular Benzylation of an Imino Group of Tridentate 2,5-Bis(N-aryliminomethyl)pyrrolyl Ligands **Bound to Zirconium and Hafnium Gives Amido-Pyrrolyl Complexes That Catalyze Ethylene Polymerization**

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Amido-pyrrolyl complexes of zirconium (3a-d) and hafnium (4a-f) were prepared by the reaction of tetrabenzyl-zirconium and -hafnium with 2,5-bis(N-aryliminomethyl)pyrrole ligands (2a-e), respectively. During the course of the reaction, one of two imino moieties of the ligand was selectively benzylated to give unique dianionic tridentate ligands, which stabilized dibenzyl complexes of zirconium and hafnium. The coordinative unsaturation around the metal center was compensated by not only the donation of the imino moiety but also by the η^2 -coordination of one of the two benzyl ligands, as confirmed by spectral data together with X-ray analysis of 3b and 3c. The zirconium complexes 3b and 3c bearing bulky substituents at the nitrogen atoms of the ligand exhibited high catalytic activities (**3b**, 131 (kg PE)(mol cat)⁻¹ h⁻¹ at 60 °C; **3c**, 458 (kg PE)(mol cat)⁻¹ h⁻¹ at 75 °C) upon combining with 1000 equiv of MMAO. Lewis-base-free cationic alkyl complexes 5b, 5c, 6b, and **6c** were prepared by alkyl abstruction from the corresponding dibenzyl complexes of zirconium **3b**,**c** and hafnium **4b**,**c**, and the resulting cationic complexes **5c** and **6c** were found to catalyze the ethylene polymerization without MMAO.

Introduction

Recent development of well-defined single site transition metal catalysts enables us to precisely control not only catalytic activity for α -olefin polymerization but also microstructure of polymers.¹⁻³ The nitrogen-based polydentate ligands such as phenoxyimine,4-7 2,6-bis-

(*N*-aryliminomethyl)pyridine,⁸ and α -diimine⁹ derivatives, which serve the polymerization catalysts as supporting ligands, have attracted particular interest in terms of their advantageous feasibility and flexibility in design to introduce sterically and electronically demanding features on the ligand.^{10,11} Despite these merits, the catalysts supported by these ligands have been found to be occasionally deactivated by the alkylation of the C=N bond of the ligand. Scott et al. recently reported that titanium and zirconium dibenzyl complexes **A** having a bridged phenoxyimine ligand (\mathbb{R}^3 = H) were decomposed by an intramolecular benzylation. The migratory insertion of the benzyl group into the C=N bond gave thermally unstable products **B** (eq 1),

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resulting in no catalytic activity for ethylene polymerization, whereas protection against ligand alkylation by introducing the bulky substituents at R^3 positions of the ligand rendered complexes **A** stable, providing active catalysts.¹²



On the contrary, nitrogen-based ligands, in some cases, have been alkylated to be anionic ligands that support some alkyl complexes. A reaction of AlMe₃ with bis(imino)pyridine ligand afforded an aluminum complex C.¹³ During the course of the reaction, one of two imino moieties was selectively methylated. The same methylated tridentate ligand was utilized for preparing dialkyl complexes of lutetium (**D**).¹⁴ Furthermore, the anionic tridentate ligand stabilized cationic alkyl complexes of aluminum and lutetium, derived from the reactions of **C** and **D** with $B(C_6F_5)_3$, respectively. Additionally, Gambarotta et al. reported that a tridentate anionic ligand derived from the ring C=N bond methylation of 2,6-bis[1-(N-arylimino)ethyl]pyridine was used to prepare a vanadium complex E, which exhibited catalytic activity for ethylene polymerization upon activation with MAO.15



The alkylation of the C=N moiety of the nitrogenbased ligand was thus anticipated to have the capability to stabilize a cationic alkyl species that catalyzes polymerization of ethylene. We already reported that an intramolecular benzylation of the imino moiety of bidentate iminopyrrolyl ligands afforded an amidopyrrolyl complex **1**, and it exhibited better catalytic activity for ethylene polymerization compared to the corresponding bis(iminopyrrolyl) dichloro complexes of zirconium.^{16a,b} For understanding the polymerization mechanism of **1** as a catalyst precursor, we tried to isolate cationic derivatives of **1**; however, we were not able to detect any cationic species due to their thermal instability.



We thus turned our attention to tridentate 2,5-bis-(*N*-aryliminomethyl)pyrrole ligands $(2\mathbf{a}-\mathbf{e})$,¹⁷ which were expected to be better supporting ligands of cationic alkyl species owing to the presence of an additional nitrogen donor moiety.



Here we report unique benzylation of one of two imino groups of the tridentate bis(imino)pyrrolyl ligand, by the reaction of **2** with M(CH₂Ph)₄ (M = Zr, Hf), giving complexes **3a**-**c** and **4a**-**e**, which were characterized by spectral data along with X-ray analysis of **3b** and **3c**. We found that these zirconium and hafnium complexes became catalyst precursors for ethylene polymerization. Moreover, cationic monobenzyl complexes **5b**, **5c**, **6b**, and **6c** were prepared by treating the corresponding dibenzyl complexes of **3b**, **3c**, **4b**, and **4c** with [Ph₃C][B(C₆F₅)₄], and **5c** and **6c** were found to catalyze ethylene polymerization in the absence of Al-cocatalyst.



Results and Discussion

Synthesis and Characterization of Zirconiumand Hafnium-Benzyl Complexes. The reaction of Zr- $(CH_2Ph)_4$ with 1 equiv of tridentate 2,5-bis(*N*-aryliminomethyl)pyrrolyl ligands 2a-c in toluene afforded the

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corresponding dibenzyl complexes of zirconium (3a-c) along with the release of 1 equiv of toluene (eq 2). In contrast, reaction with 1 equiv of *p*-substituted pyrrolyl ligands **2d** and **2e** resulted in a complicated mixture, from which no products were isolated. Complexes **3a**-c were air- and moisture-sensitive and were characterized by spectral data, and X-ray analysis of 3b and 3c (vide infra).



The ¹H NMR spectra of 3a-c essentially displayed the same pattern, clearly indicating that one of two imino groups was selectively benzylated. The most informative spectral data were three sets of benzyl signals: methylene protons of a benzyl group attached to the carbon adjacent to the nitrogen group appeared as an ABX pattern, while those of the other two benzyl groups bound to the zirconium atom were observed as an ABq pattern. In the ¹³C NMR spectra, two carbon resonances due to two ZrCH₂Ph groups were displayed around δ 70, while a signal due to *C*H₂Ph of the ligand appeared at higher field (around δ 42). It is noteworthy that one of two methylene carbons bound to the zirconium atom had a large J_{C-H} value (132–136 Hz for **3a**– **c**), which was compatible with that (132 Hz) of the η^2 benzyl complexes $[Cp_2Zr(\eta^2-CH_2Ph)][B(C_6F_5)_4]$. On the other hand, the J_{C-H} value (120–122 Hz for 3a-c) of another $Zr CH_2Ph$ was comparable to that ($J_{C-H} = 119$ Hz) reported for a typical η^1 -bonding mode of zirconocene dibenzyl complexes.¹⁸

The pyrrolyl ring protons were observed in the olefinic region, indicating that the pyrrolyl anion was attached in an η^1 -*N*-coordination mode to the zirconium atom. The resonance of the imine proton of **3a**-**c** was shifted to higher field and the imine carbon signal appeared in lower field compared to those of the corresponding free ligand, suggesting that the imino nitrogen atom was also coordinated to the zirconium atom.

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Figure 1. Molecular structure of complex 3b. All hydrogen atoms are omitted for clarity.



Figure 2. Molecular structure of complex 3c. All hydrogen atoms are omitted for clarity.

Table 1.	Selected Bond Distances and Angles i	in
	Complexes 3b and 3c	

	3b	3 c		
	Bond Distances (Å)			
Zr-N1	2.1408(11)	2.1317(12)		
Zr-N2	2.0867(12)	2.0827(12)		
Zr-N3	2.3932(12)	2.4228(13)		
Zr-C41	2.2860(14)	2.2691(17)		
Zr-C42	2.6588(13)	2.7806(17)		
Zr-C51	2.2916(15)	2.2900(16)		
N2-C5	1.4904(17)	1.4854(18)		
N3-C6	1.3189(18)	1.312(2)		
	Bond Angles (deg)			
N1-Zr-N2	71.22(4)	71.26(5)		
N1-Zr-N3	67.43(4)	67.46(5)		
N2-Zr-N3	138.12(4)	138.15(5)		
Zr-C41-C42	87.18(9)	93.78(11)		
Zr-C51-C52	113.19(10)	112.62(10)		
N2-C5-C1	106.06(11)	105.97(11)		
N3-C6-C4	116.64(12)	117.49(14)		

Figures 1 and 2 show crystal structures of **3b** and **3c**, respectively, and their selected bond distances and angles are summarized in Table 1. The zirconium atom of **3b** adopts a distorted trigonal bipyramidal geometry, where an amido nitrogen atom (N(2)) and an imine nitrogen atom (N(3)) occupy the axial positions, and two benzyl groups and the nitrogen atom (N(1)) of the pyrrolyl moiety are placed at equatorial positions. In complex **3b**, the distance (2.1408(11) Å) of Zr-N(1) is

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comparable to that $(2.14-2.35 \text{ Å})^{16a,b,17,19}$ found for zirconium-pyrrolyl complexes. The distance (2.0867(12) Å) of Zr-N(2) is much shorter than that of Zr-N(1) and is comparable to that of metal-amido complexes.²⁰ Although the distance (2.3932(12) Å) of Zr-N(3) is longer than others, it is short enough to interact with the metal center. The angle (138.12(4)°) of N(2)-Zr-N(3) significantly deviates from 180°, but is reasonable as a complex with a meridional tridentate ligand.²¹ The short distance (2.6588(13) Å) of Zr-C(42) and the acute angle (87.18(9)°) of Zr-C(41)-C(42) clearly show the η^2 coordination of the benzyl ligand, consistent with the structure depicted by NMR spectral data. The coordinatively unsaturation around the metal center in **3b** is thus compensated by not only the coordination of the imino group but also the coordination of the ipso carbon of the benzyl group. The other benzyl moiety is normal: the Zr-C(52) distance is 3.187 Å and the Zr-C(51)-C(52) angle is 113.19(10)°. The structural features of 3c are essentially the same as 3b. A notable difference is that complex **3c** has a longer distance (2.7806(17) Å) of Zr-C(42) and larger angle (93.78(11)°) of Zr-C(41)-C(42) than those of **3b** owing to bulky ortho-diisopropyl substituents on the phenyl groups of 3c.

The reaction of tetrabenzyl hafnium with 1 equiv of 2a-e gave the corresponding hafnium complexes 4a-e as air- and moisture-sensitive yellow solids (eq 3). In contrast to the reaction of tetrabenzyl zirconium, reactions with less bulky *p*-substituted pyrrolyl ligands 2d and 2e afforded 4d and 4e, respectively, presumably due to the general tendency that hafnium alkyl complexes are more stable toward an insertion of the imine into the Hf-carbon bond than the corresponding zirconium alkyl complexes.²² Complexes 4a - e have the same structure as 3a-c. The ¹H NMR spectra of 4a-e displayed three sets of benzyl signals (one ABX signal and two ABq signals). The 13 C NMR spectrum of the complexes $4\mathbf{a} - \mathbf{c}$ showed that one of two methylene carbons, HfCH₂Ph, has a large J_{C-H} value (134–138 Hz), suggesting that one benzyl group coordinated in an η^2 -mode to the hafnium atom, while the other with a small J_{C-H} value (117–119 Hz) adopts an η^1 -benzyl coordination mode. Complexes 4d and 4e have two benzyl groups coordinating in an η^1 -fashion to the hafnium atom as judged by the J_{C-H} values of benzyl methylene carbons (124 and 126 Hz for 4d; 118 and 125

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Table 2. Ethylene Polymerization Catalyzed by Zirconium (3a–d) and Hafnium Complexes (4a–f)^a

cat.	amount of cat. (µmol)	yield PE (mg)	activity (kg PE) (mol cat.) $^{-1}$ h $^{-1}$
3a	9.6	134	14
3b	7.6	395	52
3c	2.1	103	49
4a	8.6	11	1.3
4b	3.5	22	6.4
4 c	8.7	50	5.7
4d	17.0	1.7	0.1
4e	4.9	0.5	0.1

^{*a*} Conditions: cocatalyst = 1000 equiv of MMAO, ethylene pressure 1 atm, reaction 2 h at rt, [cat.] = 1.0-1.3 mM in toluene.

Hz for **4e**), although a sterically less demanding environment of **4d** and **4e** might be expected to require the contribution of the η^2 -mode of the benzyl group. Thus, it is likely assumed that the less hindered substituent on the ligand increased the donation of the imino moiety to the metal center.



Catalytic Performance of the Benzyl Complexes for Ethylene Polymerization. The zirconium and hafnium pyrrolyl complexes 3a-c and 4a-e were used as catalyst precursors for ethylene polymerization under atomspheric pressure of ethylene in the presence of excess amounts of MMAO (1000 equiv), and the results are summarized in Table 2. Zirconium complexes are superior in activity to the corresponding hafnium complexes. The higher catalytic activities were achieved when zirconium complexes 3b and 3c, bulky 2,6dialkylphenyl derivatives, were used as catalyst precursors. Temperature dependence of the polymerization activity for complexes 3b and 3c was further investigated (Table 3). In the case of the complex 3c, the highest polymerization activity was obtained at 75 °C, whose activity was 10 times higher than that operated at room temperature, indicating that at room temperature the insertion of ethylene into the metal-carbon bond of catalytically active cationic species was prevented, to some extent, by steric bulkiness of the imino and amido moieties. Similarly, complex 3b showed the highest activity of the polymerization at 60 °C. The polyethylenes obtained by using 3b and 3c at various temperature have rather broad M_w/M_n values (26.7-51.4 for **3b**; 17.5-43.2 for **3c**), due to the thermal instability of the catalytically active species under the polymerization condition. These observations imply that the coordination of the imino group as the third N-donor was required to stabilize an active cationic spicies, but lowered the catalytic activity at room temperature.

Formation of Cationic Benzyl Complexes and Their Reactions to α**-Olefins.** Cationic complexes **5b**,

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5c, 6b, and 6c were prepared by treatment of complexes **3b**, **3c**, **4b**, and **4c** with $[Ph_3C][B(C_6F_5)_4]$, respectively (eq 4). Monitoring the reaction of 3c and $[Ph_3C]$ - $[B(C_6F_5)_4]$ in bromobenzene- d_5 by ¹H NMR spectroscopy showed the quantitative formation of a cationic complex 5c and Ph₃CCH₂Ph. The ¹H NMR spectrum of 5c displayed an ABq signal attributed to $\text{ZrC}H_aH_b\text{Ph}$ (δ 2.31 and 2.95 with a coupling constant of 9.1 Hz). In the ¹³C NMR spectrum of complex **5c**, the carbon signal of Zr*C*H₂Ph was observed at δ 83.5 with a large J_{C-H} value (140 Hz), indicating the large contribution of the η^2 -coordination of the benzyl moiety, due to a stronger Lewis acidic nature and coordinative unsaturation of the cationic zirconium center. The other three complexes **5b**, **6b**, and **6c** have almost the same spectral pattern. The ¹H NMR spectra of **5b**, **5c**, **6b**, and **6c** additionally showed temperature-dependence. The ortho-protons of the benzyl phenyl group bound to the zirconium atom of **5c** were observed as two doublets (δ 5.14 and 5.44) at -25 °C, which became one broad signal at room temperature. This process can be rationalized by the restricted rotation of the MCH₂-Ph bond through the η^1 -coordination mode,²³ the ΔG^{\ddagger} value being estimated to be 14.7 kcal/mol (coalesced at 32.5 °C). For the other three complexes, the ΔG^{\ddagger} value was found to be 13.4 kcal/mol for 5b (coalesced at 10 °C), 13.7 kcal/mol for 6b (coalesced at 10 °C), and 14.3 kcal/mol for 6c (coalesced at 20 °C).

We observed that complexes **5b** and **6b** with the 2,6xylyl-substituted ligand gradually decomposed within a few hours, probably through the C–H activation of an ortho-methyl group of the ligand.²⁴ The characterization of the decomposed products was hampered by their poor solubility in organic solvents such as toluene and bromobenzene.



Cationic complexes are catalytically active for ethylene polymerization without aluminum cocatalyst. A solution of **5c** or **6c** in C_6H_5Br was exposed to atmospheric pressure of ethylene at room temperature for 1 h to give trace amounts of polyethylene, suggesting that

Table 3. Temperature Effect on the Performanceof Ethylene Polymerization Catalyzed by 3a and $3b^a$

entry	cat.	time (min)	temp (°C)	activity (kg PE) (mol cat) ⁻¹ h^{-1}
1	3a	360	0	1.2
2	3a	90	r.t.	28
3	3a	60	45	71
4	3a	90	60	131
5	3a	30	75	68
6	3a	90	90	50
7	3b	600	0	1.5
8	3b	60	r.t.	57
9	3b	30	45	88
10	3b	20	60	258
11	3b	20	75	447
12	3b	60	90	75

 a Conditions: cocatalyst = 1000 equiv of MMAO, ethylene pressure 1 atm, [cat.] = 0.25 mM in toluene.

the catalyst systems involve cationic alkyl complexes as key intermediates in ethylene polymerization.

We further examined the reactions of 5c and 6c with 1-hexene in C₆D₅Br, and the reactions were monitored by ¹H NMR spectroscopy. The ¹H NMR spectrum of the mixture of 5c and 1-hexene displayed no signal due to ZrCH₂Ph of 5c, indicating that 1-hexene inserted into the Zr-benzyl bond. The reaction solution was then quenched by adding 1 N HCl. The resulting organic product was collected and analyzed by using GC-MS to be CH₃CH(ⁿBu)CH₂Ph, which is a product of insertion of one molecule of 1-hexene into the metal-benzyl bond. No oligomer or polymer of 1-hexene was obtained. The insertion of 1 equiv of 1-hexene stabilized the cationic species and prevented further insertion of the monomer, presumably due to the interaction between the phenyl ring of the hydrocarbyl group bound to the metal and the cationic metal center via an η^6 -coordination. This was supported by the observation that the phenyl protons of the benzyl group shifted to higher field compared with complexes 5c and 6c. Such an insertion of only 1 equiv of α -olefin into the metal-benzyl bond has been revealed by the η^6 -coordination of the phenyl ring at the chain end to the cationic center, as evident from the shift of the phenyl protons to lower field after the reaction.^{21f,25}

Conclusion

We have demonstrated that the reactions of 2,5-bis-(*N*-aryliminomethyl)pyrrole (**2**) with tetrabenzyl-zirconium and -hafnium afforded the corresponding amidopyrrolyl complexes by the unique intramolecular benzylation of one of two imino moieties of the tridentate ligands. The resulting dianionic ligands not only stabilized dibenzyl complexes of zirconium and hafnium but also enhanced the catalytic activity. The high unsaturation around the metal center was found to be compensated by contributions through the donation of the imino nitrogen atom and the η^2 -coordination of one of two benzyl groups bound to the metal center. These complexes upon activation by excess amounts of MMAO

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showed catalytic activity for ethylene polymerization, and complexes **3b** and **3c** with the bulky substituents on the ligand were found to be better catalyst precursors among them. The Lewis-base-free cationic alkyl species **5b**, **5c**, **6b**, and **6c** were respectively prepared by reaction of **3b**, **3c**, **4b**, and **4c** with $[Ph_3C][B(C_6F_5)_4]$, and **5c** and **6c** were tested as catalysts for ethylene polymerization without the aluminum cocatalyst. We also found that 1 equiv of 1-hexene inserted into the metal–benzyl bond of the cationic complexes **5c** and **6c**, but the successive insertion was prevented by the coordinative interaction of the phenyl moiety of the chain end to the cationic metal center.

Experimantal Section

General Procedures. All manipulations involving air- and moisture-sensitive organometallic compounds were performed using standard Schlenk techniques under argon. Complexes Zr(CH₂Ph)₄ and Hf(CH₂Ph)₄ were prepared according to the literature.^{26,27} Tridentate ligands 2a-e were prepared according to the literature.^{17b} [Ph₃C][B(C₆F₅)₄] was prepared according to the literature.²⁸ Hexane, THF, toluene, and ether were dried and deoxygenated by distillation over sodium benzophenone ketyl under argon. Benzene- d_6 and THF- d_8 were distilled from P₂O₅ and thoroughly degassed by trap-to-trap distillation before use. Bromobenzene and bromobenzene- d_5 were distilled over CaH₂ and then degassed. Methylalminoxane (MMAO-3A, Tosoh-finechem) was used as received. Ethylene (Sumitomo Seika Chemicals Co.) was dried by passing through a drycolumn (Nikka Seiko Co., DC-3A) and a gas-clean column (Nikka Seiko Co., GC-RX) before use. The 1H (300 MHz) and ¹³C (75 Hz) NMR spectra were measured on a Varian-Unity-Inova-300 spectrometer. 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 argon atmosphere.

(DIP₂-pyr-CH₂Ph)Zr(CH₂Ph)₂ (3c). In a Schlenk tube, Zr-(CH₂Ph)₄ (525 mg, 1.15 mmol) and 1c (494 mg, 1.12 mmol) were placed, and then toluene (40 mL) was added at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. All volatiles were removed under reduced pressure. The resulting yellow oil was dissolved in a small amount of hexane and stored at room temperature. The yellow crystals were formed and then dried under vacuum to give 3c as yellow crystals (857 mg, 95% yield), mp 155-162 °C (dec). ¹H NMR (300 MHz, C₆D₆, 35 °C): δ 1.03 (d, ³J_{H-H} = 6.8 Hz, 3H, CH₃), 1.12 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, CH₃), 1.20 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, CH₃), 1.25 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, CH₃), 1.26 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, CH₃), 1.32 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, CH₃), 1.38 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, CH₃), 1.49 (d, ${}^{3}J_{H-H} =$ 6.8 Hz, 3H, CH₃), 1.83 (s, 2H, ZrCH₂Ph), 1.89 (dd, ²J_{H-H} = 12.5 Hz, ${}^{3}J_{H-H} = 11.5$ Hz, 1H, CHC*H*HPh), 2.09 and 2.18 (ABq, $_{3}J_{H-H} = 10.1$ Hz, 2H, ZrC*HH*Ph), 2.92 (dd, $^{2}J_{H-H} = 12.5$ Hz, ${}^{3}J_{H-H} = 4.7$ Hz, 1H, CHCH*H*Ph), 3.40 (sep, ${}^{3}J_{H-H} = 6.8$ Hz, 1H, $CH(CH_3)_2$), 3.64 (sep, ${}^{3}J_{H-H} = 6.8$ Hz, 1H, $CH(CH_3)_2$), 3.69 (sep, ${}^{3}J_{H-H} = 6.8$ Hz, 1H, CH(CH₃)₂), 3.74 (sep, ${}^{3}J_{H-H} = 6.8$ Hz, 1H, $CH(CH_3)_2$), 5.11 (dd, ${}^3J_{H-H} = 11.5$ and 4.7 Hz, 1H, CH-N), 5.29 (d, ${}^{3}J_{H-H} = 3.5$ Hz, 1H, pyrrole ring), 5.97 (d, ${}^{3}J_{\rm H-H} = 6.9$ Hz, 2H, *o*-Ph of ZrCH₂Ph), 6.59 (d, ${}^{3}J_{\rm H-H} = 3.5$ Hz, 1H, pyrrole ring), 6.9-7.4 (m, 19H, aromatic protons), 7.81 (s, 1H, N=CH). ¹³C NMR (75 MHz, C₆D₆, 35 °C): δ 22.4 (CH-(CH₃)₂), 22.7 (CH(CH₃)₂), 24.2 (CH(CH₃)₂), 26.2(CH(CH₃)₂), 26.7 (CH(CH₃)₂), 27.2 (CH(CH₃)₂), 27.6 (CH(CH₃)₂), 28.1 (CH(CH₃)₂), 29.1 (CH(*C*H₃)₂), 29.2 (2C, *C*H(CH₃)₂), 29.6 (*C*H(CH₃)₂), 42.2 (t, ${}^{1}J_{C-H} = 130$ Hz, CH*C*H₂Ph), 68.1 (t, ${}^{1}J_{C-H} = 120$ Hz, Zr*C*H₂Ph), 73.1 (t, ${}^{1}J_{C-H} = 132$ Hz, Zr*C*H₂Ph), 78.0 (d, ${}^{1}J_{C-H} = 137$ Hz, *C*HCH₂Ph), 111.4 (d, ${}^{1}J_{C-H} = 173$ Hz, pyrrole ring), 122.0 (d, ${}^{1}J_{C-H} = 169$ Hz, pyrrole ring), 164.7 (d, ${}^{1}J_{C-H} = 166$ Hz, N=CH), 122–163 (aromatic carbons). Anal. Calcd for C₅₁H₅₉N₃-Zr₁: C, 76.07; H, 7.38; N, 5.22. Found: C, 76.05; H, 7.58; N, 4.82.

Similarly, zirconium complexes 3a and 3b were prepared. {(o-TOL)₂-pyr-CH₂Ph}Zr(CH₂Ph)₂ (3a): 96% yield, mp 145-160 °C (dec). ¹H NMR (300 MHz, C₆D₆, 35 °C): δ 1.54 and 1.60 (ABq, ${}^{2}J_{H-H} = 12.1$ Hz, 2H, ZrC*HH*Ph), 1.96 and 2.23 $(ABq, {}^{2}J_{H-H} = 8.7 \text{ Hz}, 2H, ZrCHHPh), 1.97 (s, 3H, CH_3), 2.06$ $(dd, {}^{2}J_{H-H} = 12.8 \text{ Hz}, {}^{3}J_{H-H} = 10.9 \text{ Hz}, 1H, CHCHHPh), 2.34$ (s, 3H, CH₃), 2.78 (dd, ${}^{2}J_{H-H} = 12.8$ Hz, ${}^{3}J_{H-H} = 4.7$ Hz, 1H, CHCH*H*Ph), 5.27 (dd, ${}^{3}J_{H-H} = 10.9$ and 4.7 Hz, 1H, CH–N), 5.38 (d, ${}^{3}J_{H-H} = 7.2$ Hz, 2H, *o*-Ph of ZrCH₂Ph), 5.43 (d, ${}^{3}J_{H-H}$ = 3.5 Hz, 1H, pyrrole ring), 6.56 (d, ${}^{3}J_{H-H}$ = 3.5 Hz, 1H, pyrrole ring), 6.8–7.3 (m, 19H, aromatic protons and N=CH). ¹³C NMR (75 MHz, C₆D₆, 35 °C): δ 18.7 (q, ¹J_{C-H} = 126 Hz, 2C, CH₃), 42.2 (t, ${}^{1}J_{C-H} = 131$ Hz, CH*C*H₂Ph), 65.6 (t, ${}^{1}J_{C-H} = 122$ Hz, Zr*C*H₂Ph), 66.8 (t, ${}^{1}J_{C-H} = 136$ Hz, Zr*C*H₂Ph), 73.6 (d, ${}^{1}J_{C-H} = 138$ Hz, *C*HCH₂Ph), 111.2 (d, ${}^{1}J_{C-H} = 172$ Hz, pyrrole ring), 122.7 (d, ${}^{1}J_{C-H} = 169$ Hz, pyrrole ring), 164.8 (d, ${}^{1}J_{C-H}$ = 168 Hz, N=CH), 122-163 (aromatic carbones).

(XYL₂-pyr-CH₂Ph)Zr(CH₂Ph)₂ (3b): 92% yield, mp 151-156 °C (dec). ¹H NMR (300 MHz, C₆D₆, 35 °C): δ 1.00 and 1.64 (ABq, ${}^{2}J_{H-H} = 12.4$ Hz, 2H, ZrC*HH*Ph), 1.97 (s, 2H, ZrC H_2 Ph), 2.09 (s, 3H, CH₃), 2.09 (dd, ${}^2J_{H-H} = 12.4$ Hz, ${}^3J_{H-H}$ = 11.5 Hz, 1H, CHCHHPh), 2.21 (s, 3H, CH₃), 2.32 (s, 3H, CH₃), 2.48 (s, 3H, CH₃), 2.71 (dd, ${}^{2}J_{H-H} = 12.4$ Hz, ${}^{3}J_{H-H} = 4.8$ Hz, 1H, CHCH*H*Ph), 5.04 (dd, ${}^{3}J_{H-H} = 11.5$ and 4.8 Hz, 1H, CH–N), 5.33 (d, ${}^{3}J_{H-H} = 3.6$ Hz, 1H, pyrrole ring), 5.68 (d, ${}^{3}J_{H-H} = 6.6$ Hz, 2H, o-Ph of ZrCH₂Ph), 6.58 (d, ${}^{3}J_{H-H} = 3.6$ Hz, 1H, pyrrole ring), 6.8–7.3 (m, 19H, aromatic protons and N=CH). ¹³C NMR (75 MHz, C₆D₆, 35 °C): δ 19.5 (q, ¹J_{C-H} = 127 Hz, CH₃), 19.7 (q, ${}^{1}J_{C-H} = 126$ Hz, CH₃), 20.1 (q, ${}^{1}J_{C-H} =$ 127 Hz, CH₃), 21.4 (q, ${}^{1}J_{C-H} = 124$ Hz, CH₃), 42.4 (t, ${}^{1}J_{C-H} = 132$ Hz, CH*C*H₂Ph), 68.9 (t, ${}^{1}J_{C-H} = 120$ Hz, Zr*C*H₂Ph), 69.7 (t, ${}^{1}J_{C-H} = 136$ Hz, Zr*C*H₂Ph), 77.4 (d, ${}^{1}J_{C-H} = 136$ Hz, *C*HCH₂-Ph), 111.4 (pyrrole ring), 122.0 (pyrrole ring), 165.5 (d, ¹*J*_{C-H} = 167 Hz, N=CH), 122-163 (aromatic carbones). Anal. Calcd for C₄₃H₄₃N₃Zr₁: C, 74.52; H, 6.25; N, 6.06. Found: C, 73.98; H, 6.26; N, 6.15.

Preparation of (DIP₂-pyr-CH₂Ph)Hf(CH₂Ph)₂ (4c). To a solution of $Hf(CH_2Ph)_4$ (110 mg, 0.20 mmol) and $\boldsymbol{1c}$ (90 mg, 0.20 mmol) at -78 °C was added toluene (30 mL). The reaction mixture was allowed to warm to room temperature. After stirring for 1 h at 50 °C, all volatiles were removed under reduced pressure. The resulting yellow-brown oil was dissolved in toluene to give yellow crystals of 4c: (174 mg, 97% yield), mp 165–176 °C (dec). ¹H NMR (300 MHz, C₆D₆, 35 °C): δ 1.03 $(d^{3}_{H-H} = 6.8 \text{ Hz}, 3H, CH_{3}), 1.14 (d^{3}_{H-H} = 6.8 \text{ Hz}, 3H, CH_{3}),$ 1.23 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, CH₃), 1.27 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, CH₃), 1.28 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, CH₃), 1.33 (d, ${}^{3}J_{H-H} =$ 6.8 Hz, 3H, CH₃), 1.40 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, CH₃), 1.48 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, CH₃), 1.79 (dd, ${}^{2}J_{H-H} = 12.5$ Hz, ${}^{3}J_{H-H} =$ 11.7 Hz, 1H, CHC*H*HPh), 1.83 and 1.94 (ABq, ${}^{2}J_{H-H} = 13.9$ Hz, 2H, HfC*HH*Ph), 1.94 and 2.06 (ABq, ${}^{2}J_{H-H} = 10.9$ Hz, 2H, HfC*HH*Ph), 2.94 (dd, ${}^{2}J_{H-H} = 12.6$ Hz, ${}^{3}J_{H-H} = 4.6$ Hz, 1H, CHCH*H*Ph), 3.45 (sep, ${}^{3}J_{H-H} = 6.8$ Hz, 1H, C*H*(CH₃)₂), 3.65 (sep, ${}^{3}J_{H-H} = 6.8$ Hz, 1H, CH(CH₃)₂), 3.76 (sep, ${}^{3}J_{H-H} = 6.8$ Hz, 1H, $CH(CH_3)_2$), 3.87 (sep, ${}^{3}J_{H-H} = 6.8$ Hz, 1H, $CH(CH_3)_2$), 5.24 (dd, ${}^{3}J_{H-H} = 11.7$ and 4.6 Hz, 1H, CH–N), 5.27 (d, ${}^{3}J_{H-H}$ = 3.5 Hz, 1H, pyrrole ring), 6.01 (d, ${}^{3}J_{H-H}$ = 6.9 Hz, 2H, *o*-Ph of HfCH₂Ph), 6.55 (d, ${}^{3}J_{H-H} = 3.5$ Hz, 1H, pyrrole ring), 6.8– 7.4 (m, 19H, aromatic protons), 8.00 (s, 1H, N=CH). ¹³C NMR (75 MHz, C₆D₆, 35 °C): δ 22.5 (CH(CH₃)₂), 22.7 (CH(CH₃)₂), 24.5 (CH(CH₃)₂), 26.5 (CH(CH₃)₂), 26.7 (CH(CH₃)₂), 27.3 (CH-(CH₃)₂), 27.6 (CH(CH₃)₂), 27.7 (CH(CH₃)₂), 28.9 (CH(CH₃)₂), 29.1 (CH(CH₃)₂), 29.1 (CH(CH₃)₂), 29.8 (CH(CH₃)₂), 42.6 (t,

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 $^1J_{C-H}=132$ Hz, CH CH_2 Ph), 76.0 (t, $^1J_{C-H}=117$ Hz, Hf CH_2 Ph), 77.2 (t, $^1J_{C-H}=138$ Hz, Hf CH_2 Ph), 82.1 (d, $^1J_{C-H}=126$ Hz, $CHCH_2$ Ph), 112.1 (d, $^1J_{C-H}=173$ Hz, pyrrole ring), 123.1 (d, $^1J_{C-H}=169$ Hz, pyrrole ring), 165.3 (d, $^1J_{C-H}=168$ Hz, N=CH), 122–163 (aromatic carbons). Anal. Calcd for $C_{51}H_{59}N_3$ -Hf_1: C, 68.63; H, 6.66; N, 4.71. Found: C, 68.39; H, 6.83; N, 4.74.

Similarily, hafnium complexes **4a**, **4b**, **4d**, and **4e** were prepared.

{(*o***TOL)₂-pyr-CH₂Ph}Hf(CH₂Ph)₂ (4a):** 93% yield, mp 145–156 °C (dec). ¹H NMR (300 MHz, C₆D₆, 35 °C): δ 1.51 (s, 2H, HfCH₂Ph), 1.78 and 2.15 (ABq, ²J_{H-H} = 10.2 Hz, 2H, HfCHHPh), 2.00 (s, 3H, CH₃), 2.06 (dd, ²J_{H-H} = 12.7 Hz, ³J_{H-H} = 11.2 Hz, 1H, CHCHHPh), 2.38 (s, 3H, CH₃), 2.84 (dd, ²J_{H-H} = 12.7 Hz, ³J_{H-H} = 4.4 Hz, 1H, CHCHHPh), 5.40 (d, ³J_{H-H} = 3.6 Hz, 1H, pyrrole ring), 5.44 (dd, ³J_{H-H} = 11.2 and 4.4 Hz, 1H, CH–N), 5.50 (d, ³J_{H-H} = 7.4 Hz, 2H, *o*-Ph of HfCH₂Ph), 6.50 (d, ³J_{H-H} = 3.6 Hz, 1H, pyrrole ring), 6.8–7.3 (m, 22H, aromatic protons and N=CH). ¹³C NMR (75 MHz, C₆D₆, 35 °C): δ 18.6 (q, ¹J_{C-H} = 126 Hz, 2C, CH₃), 42.5 (t, ¹J_{C-H} = 130 Hz, CH*C*H₂Ph), 72.4 (t, ¹J_{C-H} = 119 Hz, Hf*C*H₂Ph), 72.8 (t, ¹J_{C-H} = 138 Hz, Hf*C*H₂Ph), 74.7 (d, ¹J_{C-H} = 131 Hz, *C*HCH₂-Ph), 111.9 (pyrrole ring), 123.3 (pyrrole ring), 165.2 (d, ¹J_{C-H} = 168 Hz, N=CH), 122–163 (aromatic carbons).

(XYL₂-pyr-CH₂Ph)Hf(CH₂Ph)₂ (4b): 87% yield, mp 168-184 °C (dec). ¹H NMR (300 MHz, C₆D₆, 35 °C): δ 0.98 and 1.49 (ABq, ${}^{2}J_{H-H} = 13.5$ Hz, 2H, HfC*HH*Ph), 1.77 and 1.92 $(ABq, {}^{2}J_{H-H} = 10.3 \text{ Hz}, 2H, HfCHHPh), 2.00 (dd, {}^{2}J_{H-H} = 12.6$ Hz, ${}^{3}J_{H-H} = 11.3$ Hz, 1H, CHC*H*HPh), 2.13 (s, 3H, CH₃), 2.25 (s, 3H, CH₃), 2.40 (s, 3H, CH₃), 2.51 (s, 3H, CH₃), 2.75 (dd, ${}^{2}J_{H-H} = 12.6$ Hz, ${}^{3}J_{H-H} = 4.9$ Hz, 1H, CHCH*H*Ph), 5.19 (dd, ${}^{3}J_{H-H} = 11.3$ and 4.9 Hz, 1H, CH–N), 5.30 (d, ${}^{3}J_{H-H} = 3.3$ Hz, 1H, pyrrole ring), 5.76 (d, ${}^{3}J_{H-H} = 7.1$ Hz, 2H, *o*-Ph of HfCH₂-Ph), 6.54 (d, ${}^{3}J_{H-H} = 3.3$ Hz, 1H, pyrrole ring), 6.9–7.5 (m, aromatic protons and N=CH). ¹³C NMR (75 MHz, C₆D₆, 35 °C): δ 19.5 (CH₃), 19.7 (CH₃), 20.1 (CH₃), 21.4 (CH₃), 42.9 (t, ${}^{1}J_{C-H} = 131$ Hz, CH*C*H₂Ph), 74.5 (t, ${}^{1}J_{C-H} = 119$ Hz, Hf*C*H₂-Ph), 76.4 (d, ${}^{1}J_{C-H} = 138$ Hz, *C*HCH₂Ph), 76.9 (t, ${}^{1}J_{C-H} = 134$ Hz, Hf*C*H₂Ph), 112.0 (d, ${}^{1}J_{C-H} = 173$ Hz, pyrrole ring), 123.0 (d, ${}^{1}J_{C-H} = 169$ Hz, pyrrole ring), 165.9 (d, ${}^{1}J_{C-H} = 168$ Hz, N=CH), 122-163 (aromatic carbons).

{(p-ANI)₂-pyr-CH₂Ph}Hf(CH₂Ph)₂ (4d): 90% yield, mp 129-140 °C (dec). ¹H NMR (300 MHz, C₆D₆, 35 °C): δ 1.91 and 2.20 (ABq, ${}^{2}J_{H-H} = 11.5$ Hz, 2H, HfC*HH*Ph), 2.05 and 2.32 (ABq, ${}^{2}J_{H-H} = 12.2$ Hz, 2H, HfC*HH*Ph), 2.53 (dd, ${}^{2}J_{H-H} = 13.3$ Hz, ${}^{3}J_{H-H} = 9.8$ Hz, 1H, CHC*H*HPh), 3.08 (dd, ${}^{2}J_{H-H} = 13.3$ Hz, ${}^{3}J_{H-H} = 4.1$ Hz, 1H, CHCH*H*Ph), 3.38 (s, 3H, OCH₃), 3.50 (s, 3H, OCH₃), 5.54 (d, ${}^{3}J_{H-H} = 3.5$ Hz, 1H, pyrrole ring), 5.61 (dd, ${}^{3}J_{H-H} = 9.8$ and 4.1 Hz, 1H, CH–N), 6.39 (d, ${}^{3}J_{H-H} = 7.1$ Hz, 2H, *o*-Ph of HfCH₂Ph), 6.45 (d, ${}^{3}J_{H-H} = 3.5$ Hz, 1H, pyrrole ring), 6.7-7.3 (m, 19H, aromatic protons), 7.43 (s, 1H, N=CH). ¹³C NMR (75 MHz, C₆D₆, 35 °C): δ 42.0 (t, ¹J_{C-H} = 130 Hz, CH*C*H₂Ph), 55.7 (q, ${}^{1}J_{C-H} = 143$ Hz, 2C, OCH₃), 73.0 (d, ${}^{1}J_{C-H}$ = 138 Hz, CHCH₂Ph), 76.8 (t, ${}^{1}J_{C-H}$ = 124 Hz, HfCH₂Ph), 78.5 (t, ${}^{1}J_{C-H} = 126$ Hz, Hf*C*H₂Ph), 111.6 (d, ${}^{1}J_{C-H} = 172$ Hz, pyrrole ring), 123.2 (d, $^1J_{\rm C-H}=$ 175 Hz, pyrrole ring), 160.8 (d, $^1J_{\rm C-H}$ = 168 Hz, N=CH), 115-163 (aromatic carbones).

{(*p***-TOL)₂-pyr-CH₂Ph}Hf(CH₂Ph)₂ (4e):** 92% yield, mp 82–98 °C. ¹H NMR (300 MHz, C₆D₆, 35 °C): δ 1.98 and 2.18 (AB*q*, ²*J*_{H-H} = 12.0 Hz, 2H, HfC*HH*Ph), 2.16 (s, 3H, CH₃), 2.22 and 2.48 (AB*q*, ²*J*_{H-H} = 12.1 Hz, 2H, HfC*HH*Ph), 2.32 (s, 3H, CH₃), 2.58 (dd, ²*J*_{H-H} = 13.2 Hz, ³*J*_{H-H} = 9.3 Hz, 1H, CHC*H*HPh), 3.09 (dd, ²*J*_{H-H} = 13.2 Hz, ³*J*_{H-H} = 9.3 Hz, 1H, CHC*HH*Ph), 5.55 (d, ³*J*_{H-H} = 3.6 Hz, 1H, pyrrole ring), 5.66 (dd, ³*J*_{H-H} = 9.3 and 4.1 Hz, 1H, CH–N), 6.42 (d, ³*J*_{H-H} = 3.6 Hz, 1H, pyrrole ring), 6.51 (d, ³*J*_{H-H} = 7.1 Hz, 2H, *o*-Ph of HfCH₂Ph), 6.7–7.4 (m, aromatic protons), 7.47 (s, 1H, N=CH). ¹³C NMR (75 MHz, C₆D₆, 35 °C): δ 21.3 (q, ¹*J*_{C-H} = 126 Hz, 2C, CH₃), 41.5 (t, ¹*J*_{C-H} = 128 Hz, CH*C*H₂Ph), 70.5 (d, ¹*J*_{C-H} = 138 Hz, *C*HCH₂Ph), 79.0 (t, ¹*J*_{C-H} = 118 Hz, Hf*C*H₂Ph), 80.6 (t, ¹*J*_{C-H} = 125 Hz, Hf*C*H₂Ph), 111.9 (d, ¹*J*_{C-H} = 171 Hz, pyrrole ring), 123.8 (d, ${}^{1}J_{C-H} = 170$ Hz, pyrrole ring), 159.7 (d, ${}^{1}J_{C-H} = 167$ Hz, N=CH), 119–162 (aromatic carbones). Anal. Calcd for C₄₁H₃₉N₃O₂Hf₁: C, 65.46; H, 5.23; N, 5.59. Found: C, 64.71; H, 5.22; N, 5.73.

Formation of [(DIP₂-pyr-CH₂Ph)Zr(CH₂Ph)][B(C₆F₅)₄] (5c). A solution of 3c (39.2 mg, 49 μ mol) and [Ph₃C][B(C₆F₅)₄] (46.4 mg, 50 μ mol) in C₆D₅Br (0.60 mL) was sealed in a NMR tube. The color of the solution gradually turned red-brown at room temperature. The ¹H NMR spectrum of the solution at 35 °C revealed the quantitative formation of [(DIP₂-pyr-CH₂-Ph) $Zr(CH_2Ph)$][B(C₆F₅)₄] and Ph₃CCH₂Ph (CH₂ at 3.84 ppm). ¹H NMR (300 MHz, C₆D₅Br, 35 °C): δ 0.85 (d, ³J_{H-H} = 6.4 Hz, 3H, CH₃), 0.88 (d, ${}^{3}J_{H-H} = 6.4$ Hz, 3H, CH₃), 0.94 (d, ${}^{3}J_{H-H}$ = 6.8 Hz, 3H, CH₃), 0.98 (d, ${}^{3}J_{H-H}$ = 6.7 Hz, 3H, CH₃), 1.15 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, CH₃), 1.20 (d, ${}^{3}J_{H-H} = 6.3$ Hz, 3H, CH₃), 1.22 (d, ${}^{3}J_{H-H} = 6.7$ Hz, 3H, CH₃), 1.35 (d, ${}^{3}J_{H-H} = 6.3$ Hz, 3H, CH₃), 1.58 (br t, $J_{H-H} = 11.9$ Hz, 1H, CHC*H*HPh), 2.31 and 2.95 (ABq, ${}^{2}J_{H-H} = 9.1$ Hz, 2H, ZrC*HH*Ph), 2.49 (m, 1H, $CH(CH_3)_2$), 2.57 (dd, ${}^2J_{H-H} = 12.5$ Hz, ${}^3J_{H-H} = 4.2$ Hz, 1H, CHCHHPh), 2.88 (m, 1H, CH(CH3)2), 3.10 (m, 1H, CH(CH3)2), 3.45 (m, 1H, CH(CH₃)₂), 5.05 (d, ${}^{3}J_{H-H} = 3.5$ Hz, 1H, pyrrole ring), 5.20 (br, 2H, o-Ph of ZrCH₂Ph), 5.60 (br d, $J_{H-H} = 7.7$ Hz, 1H, CH–N), 6.57 (d, ${}^{3}J_{H-H} = 3.5$ Hz, 1H, pyrrole ring), 6.7-7.4 (aromatic protons), 7.87 (s, 1H, N=CH). ¹³C NMR (75 MHz, C₆D₅Br, 23 °C): δ 21.9 (CH(CH₃)₂), 21.9 (CH(CH₃)₂), 22.2 (CH(CH₃)₂), 23.1 (CH(CH₃)₂), 24.2 (CH(CH₃)₂), 24.9 (CH(CH₃)₂), 25.9 (CH(CH₃)₂), 26.9 (CH(CH₃)₂), 27.9 (CH(CH₃)₂), 29.4 (CH- $(CH_3)_2$), 29.4 ($CH(CH_3)_2$), 29.4 ($CH(CH_3)_2$), 41.1 (t, ${}^{1}J_{C-H} = 132$ Hz, CHCH₂Ph), 77.7 (d, ${}^{1}J_{C-H} = 142$ Hz, CHCH₂Ph), 83.5 (t, ${}^{1}J_{C-H} = 140$ Hz, Zr*C*H₂Ph), 112.1 (d, ${}^{1}J_{C-H} = 180$ Hz, pyrrole ring), 166.1 (d, ${}^{1}J_{C-H} = 170$ Hz, N=CH), 122–163 (aromatic and pyrrolyl carbones).

Similarly, [(XYL₂-pyr-CH₂Ph)Zr(CH₂Ph)][B(C₆F₅)₄] (**5b**) was generated in situ and characterized by its ¹H NMR spectrum. Stirring a solution of **5b** at room temperature for a few hours afforded microcrystals, which did not dissolve in toluene and C₆H₅Br. ¹H NMR (300 MHz, C₆D₅Br, 25 °C): δ 1.32 (br, 1H, CHC*H*HPh), 1.77 (s, 3H, CH₃), 2.11 (s, 6H, CH₃), 2.15 (overrapped with other resonances, 1H, ZrC*HH*Ph), 2.25 (m, 1H, CHCH*H*Ph), 2.54 (d, ²J_{H-H} = 8.8 Hz, 1H, ZrC*HH*Ph), 5.06 (d, ³J_{H-H} = 3.7 Hz, 1H, pyrrole ring), 5.12 (br, 2H, *o*-Ph of ZrCH₂Ph), 5.22 (dd, ³J_{H-H} = 4.1 and 11.5 Hz, 1H, CH-N), 6.54 (d, ³J_{H-H} = 3.7 Hz, 1H, pyrrole ring), 6.6–7.2 (aromatic protons and N=CH).

Cationic hafnium complexes **6b** and **6c** were prepared in a similar procedure.

[(XYL₂-pyr-CH₂Ph)Hf(CH₂Ph)][B(C₆F₅)₄] (6b): ¹H NMR (300 MHz, C₆D₅Br, 25 °C): \delta 1.15 (t, J_{H-H} = 12.0 Hz, 1H, CHC*H***HPh), 1.77 (s, 3H, CH₃), 1.85 and 2.41 (AB***q***, ²J_{H-H} = 9.9 Hz, 1H, HfC***HH***Ph), 2.11 (s, 3H, CH₃), 2.14 (s, 3H, CH₃), 2.29 (dd, ²J_{H-H} = 12.9 Hz, ³J_{H-H} = 4.1 Hz, 1H, CHCH***H***Ph), 2.47 (s, 3H, CH₃), 5.07 (d, ³J_{H-H} = 3.6 Hz, 1H, pyrrole ring), 5.10 (br, 2H,** *o***-Ph of HfCH₂Ph), 5.56 (dd, ³J_{H-H} = 4.1 and 11.3 Hz, 1H, CH–N), 6.54 (d, ³J_{H-H} = 3.6 Hz, 1H, pyrrole ring), 6.8–7.3 (aromatic protons), 7.53 (s, 1H, N=CH).**

[(DIP₂-pyr-CH₂Ph)Hf(CH₂Ph)][B(C₆F₅)₄] (6c): ¹H NMR (300 MHz, C₆D₅Br, 25 °C): δ 0.87 (d, ${}^{3}J_{H-H} = 6.3$ Hz, 3H, CH₃), 0.95 (m, 9H, CH₃), 0.98 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, CH₃), 1.16 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, CH₃), 1.21 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, CH₃), 1.26 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, CH₃), 1.31 (t, J = 12.1 Hz, 1H, CHC*H*HPh), 1.47 (d, ${}^{3}J_{H-H} = 6.8$ Hz, 3H, CH₃), 2.07 and 2.86 (ABq, ${}^{2}J_{H-H} = 10.2$ Hz, 2H, HfC*HH*Ph), 2.52 (sep, ${}^{3}J_{H-H} = 6.3$ Hz, 1H, CH(CH₃)₂), 2.55 (dd, ${}^{2}J_{H-H} = 12.8$ Hz, ${}^{3}J_{H-H} = 4.1$ Hz, 1H, CHCH*H*Ph), 2.97 (sep, ${}^{3}J_{H-H} = 6.8$ Hz, 1H, C*H*(CH₃)₂), 3.20 (sep, ${}^{3}J_{H-H} = 6.8$ Hz, 1H, CH(CH₃)₂), 3.51 (sep, ${}^{3}J_{H-H} =$ 6.8 Hz, 1H, CH(CH₃)₂), 5.06 (d, ${}^{3}J_{H-H} = 3.6$ Hz, 1H, pyrrole ring), 5.45 (br, 2H, o-Ph of HfCH₂Ph), 5.92 (dd, ${}^{3}J_{H-H} = 4.1$ and 11.8 Hz, 1H, CH–N), 6.58 (d, ${}^{3}J_{H-H} = 3.6$ Hz, 1H, pyrrole ring), 6.7-7.3 (aromatic protons), 8.13 (s, 1H, N=CH). ¹³C NMR (75 MHz, C₆D₅Br, 25 °C): δ 21.4 (CH(CH₃)₂), 21.7 (CH-(CH₃)₂), 23.0 (CH(CH₃)₂), 24.4 (CH(CH₃)₂), 25.5 (CH(CH₃)₂),

26.4 (CH(*C*H₃)₂), 26.5 (CH(*C*H₃)₂), 27.2 (*C*H(CH₃)₂), 28.6 (*C*H-(CH₃)₂), 28.8 (2C, *C*H(CH₃)₂), 29.4 (CH(*C*H₃)₂), 41.4 (t, ${}^{1}J_{C-H}$ = 129 Hz, CH*C*H₂Ph), 75.1 (d, ${}^{1}J_{C-H}$ = 139 Hz, *C*HCH₂Ph), 82.4 (t, ${}^{1}J_{C-H}$ = 138 Hz, Hf*C*H₂Ph), 112.2 (d, ${}^{1}J_{C-H}$ = 177 Hz, pyrrole ring), 166.2 (d, ${}^{1}J_{C-H}$ = 172 Hz, N=CH), 122–163 (aromatic and pyrrolyl carbons).

Formation of [(DIP₂-pyr-CH₂Ph)Zr(CH₂CH("Bu)-**CH₂Ph**][**B**(**C**₆**F**₅)₄] (7c). To a solution of 3c (10.7 mg, 15.1 μ mol) in C₆D₅Br (0.20 mL) was added a solution of [Ph₃C]- $[B(C_6F_5)_4]$ (14.2 mg, 15.3 µmol) and 1-hexene (23.5 µmol) in C_6D_5Br (0.30 mL) at -30 °C, and then it was sealed in a NMR tube. The ¹H NMR spectrum of the solution at 35 °C revealed the quantitative formation of [(DIP₂-pyr-CH₂Ph)Zr(CH₂CH(ⁿ-Bu)Ph)][B(C₆F₅)₄] and Ph₃CCH₂Ph (CH₂ at 3.84 ppm). ¹H NMR (300 MHz, C₆D₅Br, 35 °C): δ 0.14 (t, $J_{H-H} = 12.4$ Hz, 1H, ZrC*H*H), 0.8–1.3 (aliphatic), 1.36 (d, ${}^{3}J_{H-H} = 6.6$ Hz, 3H, CH- $(CH_3)_2$), 1.48 (d, ${}^{3}J_{H-H} = 5.8$ Hz, 3H, $CH(CH_3)_2$), 2.2–3.6 (aliphatic), 5.05 (d, ${}^{3}J_{H-H} = 3.6$ Hz, 1H, pyrrole ring), 5.51 (t, ${}^{3}J_{H-H} = 7.7$ Hz, 1H, *m*-Ph of ZrCH₂CH(^{*n*}Bu)CH₂Ph), 6.07 (dd, ${}^{3}J_{H-H} = 4.4$ and 12.4 Hz 1H, CH–N), 6.21 (t, ${}^{3}J_{H-H} = 7.4$ Hz, 1H, *m*-Ph of HfCH₂CH(*ⁿ*Bu)CH₂*Ph*), 6.41 (d, ${}^{3}J_{H-H} = 3.6$ Hz, 1H, pyrrole ring), 6.65 (overlapping with Ph₃CCH₂Ph resonance, 1H, o-Ph of ZrCH₂CH("Bu)CH₂Ph), 6.8-7.3 (aromatic protons), 7.35 (t, ${}^{3}J_{H-H} = 7.1$ Hz, 1H, *p*-Ph of ZrCH₂CH(${}^{n}Bu$)-CH₂*Ph*), 7.46 (s, 1H, N=CH).

Reaction of 1-hexene with cationic hafnium complex ${\bf 6c}$ was carried out in a similar procedure.

[(DIP₂-pyr-CH₂Ph)Hf(CH₂CH(ⁿBu)CH₂Ph)][B(C₆F₅)₄] (8c): ¹H NMR (300 MHz, C₆D₅Br, 35 °C): δ 0.03 (t, $J_{H-H} =$ 12.9 Hz, 1H, HfC*H*H), 2.24, 2.80, and 3.17 (m, 4H, α , β , and γ protons of HfCH₂CH(ⁿBu)CH₂Ph), 0.86 (m, 3H, CH₃ of ⁿBu), 0.94 (d, ${}^{3}J_{H-H} = 6.9$ Hz, 3H, CH₃), 0.97 (d, ${}^{3}J_{H-H} = 6.6$ Hz, 3H, CH₃), 1.16 (d, ${}^{3}J_{H-H} = 6.6$ Hz, 3H, CH₃), 1.20 (m, 6H, CH₂) of ^{*n*}Bu), 1.27 (d, ${}^{3}J_{H-H} = 6.6$ Hz, 3H, CH₃), 1.33 (d, ${}^{3}J_{H-H} = 6.6$ Hz, 6H, CH₃), 1.37 (d, ${}^{3}J_{H-H} = 6.9$ Hz, 3H, CH₃), 1.48 (d, ${}^{3}J_{H-H}$ = 6.6 Hz, 3H, CH₃), 2.45 (sep, ${}^{3}J_{H-H}$ = 6.6 Hz, 1H, CH(CH₃)₂), 2.46 (t, $J_{H-H} = 12.9$ Hz, 1H, NCHC*H*HPh), 2.64 (dd, ${}^{2}J_{H-H} =$ 13.4 Hz, ${}^{3}J_{H-H} = 4.4$ Hz, 1H, NCHCH*H*Ph), 2.80 (sep, ${}^{3}J_{H-H}$ = 6.9 Hz, 1H, CH(CH₃)₂), 3.13 (sep, ${}^{3}J_{H-H}$ = 6.6 Hz, 1H, $CH(CH_3)_2$), 3.23 (sep, ${}^{3}J_{H-H} = 6.6$ Hz, 1H, $CH(CH_3)_2$), 5.04 (d, ${}^{3}J_{H-H} = 3.6$ Hz, 1H, pyrrole ring), 5.70 (m, 1H, *m*-Ph of HfCH₂-CH("Bu)CH2Ph), 6.25 (m, 2H, CH-N and m-Ph of HfCH2CH- $(^{n}Bu)CH_{2}Ph$), 6.40 (d, $^{3}J_{H-H} = 3.6$ Hz, 1H, pyrrole ring), 6.65 (overlapping with Ph₃CCH₂Ph resonance, 1H, o-Ph of HfCH₂-CH(^{*n*}Bu)CH₂*Ph*), 6.8–7.3 (aromatic protons), 7.38 (t, ${}^{3}J_{H-H} =$ 7.4 Hz, 1H, *p*-Ph of HfCH₂CH(n Bu)CH₂Ph), 7.66 (s, 1H, N= CH).

Ethylene Polymerization. In a typical experiment, to a solution of **3c** (1.7 mg, 2.1 μ mol) in toluene (0.4 mL) was added a toluene solution of MMAO (1.66 mol/L, 1.3 mL, 1000 equiv) under ethylene atmosphere. The solution was stirred for 1 h, and then the polymerization reaction was quenched with acidic methanol. The solid polymer was collected and washed with HCl (1.2 M) and MeOH. The polymer was dried in vacuo for a few days to give constant weight polyethylene.

Al-Cocatalyst-Free Ethylene Polyemrization. Lewisbase-free cationic alkyl complexes **5c** and **6c** were generated from the reaction of the dibenzyl complexes **3c** and **4c** with $[Ph_3C][B(C_6F_5)_4]$, respectively. The solution was then degassed, and ethylene gas was introduced. The solution was stirred for 1 h, and the polymer was formed.

Crystallographic Data Collection and Structure Determination of 3b and 3c. Crystals of **3b** and **3c** suitable for the X-ray diffraction study were mounted on glass fibers. All measurements were made on a Rigaku R-AXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71069$). Indexing was performed from two oscillations. The camera radius was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. A symmetry-

Table 4. Crystal Data and Data CollectionParameters of 3b and 3c

	3b	3c
formula	C43H43N3Zr	C ₅₁ H ₅₉ N ₃ Zr
fw	693.05	805.27
cryst syst	triclinic	monoclinic
space group	P1 (No. 2)	$P2_1/c$ (No. 14)
a, Å	11.3951(11)	15.3212(3)
<i>b</i> , Å	12.6564(11)	13.2839(3)
<i>c</i> , Å	14.1142(11)	22.0592(4)
α, deg	83.967(3)	90.0
β , deg	71.381(4)	98.9295(4)
γ , deg	69.055(3)	90.0
V, Å ³	1801.5(3)	4435.2(2)
no. of reflns for cell determ (θ range)	57 686 (3.06-30.54°)	90 209 (2.05–27.50°)
Z, D_{calcd} , g/cm ⁻³	2, 1.278	4, 1.206
F(000)	724	1704
μ [Mo K α], mm ⁻¹	0.339	0.284
diffractometer	R-AXIS RAPID	R-AXIS RAPID
Т, К	153(1)	153(1)
cryst size, mm	$0.46 \times 0.43 \times 0.31$	$0.61 \times 0.59 \times 0.34$
no. of images	180	120
total oscillation angles, deg	540.0	360
exposure time, min per deg	2.00	0.83
$2\theta_{\rm max}$, deg	61.0	55.0
no. of refins measd	53 865	65 053
no. of unique data (R_{int})	10 842 (0.0429)	10 168 (0.0562)
completeness to $\theta = 30.43, \%$	99.2	99.9
no. of observations	9125	8806
max. and min. transmn	0.953840, 0.909887	0.9728, 0.9446
no. of variables	596	496
R1, wR2 (all data)	0.0463, 0.0756	0.0398, 0.0810
R1, wR2 $(I > 2.0\sigma(I))$	0.0335, 0.0726	0.0321, 0.0768
GOF on F^2	1.024	1.064
$\Delta \rho$, e Å ⁻³	0.474, -0.557	0.532, -0.335

related absorption correction using the program ABSCOR was applied. The data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods (SIR97)²⁹ and refined on F^2 by full-matrix least-squares methods, using SHELXL-97.30 The non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. All hydrogen atoms of 3b were isotropically refined, and those of 3c were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $\sum w(F_0^2)$ $(W = 1/[\sigma^2(F_0^2) + (aP)^2 + bP])$, where $P = (Max(F_0^2, 0))$ $+ 2F_{c}^{2}$ /3 with $\sigma^{2}(F_{o}^{2})$ from counting statistics. The functions **R1** and w**R2** were $(\sum ||F_0| - |F_c||) / \sum |F_0|$ and $[\sum w (F_0^2 - F_c^2)^2 / E_0]$ $\sum (wF_0^4)^{1/2}$. All calculations of least-squares refinements were performed with SHELXL-97 programs on a Silicon Graphics Inc. Origin 3400 computer at the Research Center for Structural Biology Institute for Protein Research, Osaka University. Structural parameters and X-ray structure analyses for 3b and **3c** are summarized in Table 4. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers CCDC 230760 for 3b and CCDC 230759 for 3c.

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Intramolecular Benzylation of an Imino Group

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