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Preparation of Pincer Hafnium Complexes for Olefin Polymerization

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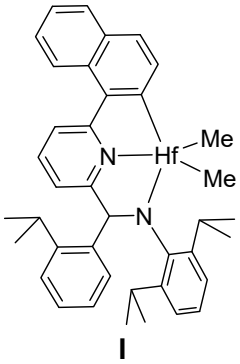
Abstract: Pincer-type [$C^{naphthyl}$, $N^{pyridine}$, N^{amido}]$HfMe_2$ complex is a flagship among the post-metallocene catalysts. In this work, various pincer-type Hf-complexes were prepared for olefin polymerization. Pincer-type [N^{amido}, $N^{pyridine}$, N^{amido}]$HfMe_2$ complexes were prepared by reacting in situ generated $HfMe_4$ with the corresponding ligand precursors, and the structure of a complex bearing 2,6-$Et_2C_6H_3N^{amido}$ moieties was confirmed by X-ray crystallography. When the ligand precursors of [$(CH_3)R_2Si$-C_5H_3N-C(H)PhN(H)Ar (R = Me or Ph, Ar = 2,6-diisopropylphenyl) were treated with in situ generated $HfMe_4$, pincer-type [$C^{silylmethyl}$, $N^{pyridine}$, N^{amido}]$HfMe_2$ complexes were afforded by formation of Hf-CH_2Si bond. Pincer-type [$C^{naphthyl}$, $S^{thiophene}$, N^{amido}]$HfMe_2$ complex, where the pyridine moiety in the flagship catalyst was replaced with a thiophene unit, was not generated when the corresponding ligand precursor was treated with $HfMe_4$. Instead, the [$S^{thiophene}$, N^{amido}]$HfMe_3$-type complex was obtained with no formation of the Hf-$C^{naphthyl}$ bond. A series of pincer-type [$C^{naphthyl}$, $N^{pyridine}$, $N^{alkylamido}$]$HfMe_2$ complexes was prepared where the arylamido moiety in the flagship catalyst was replaced with alkylamido moieties (alkyl = iPr, cyclohexyl, *t*Bu, adamantyl). Structures of the complexes bearing isopropylamido and adamantylamido moieties were confirmed by X-ray crystallography. Most of the complexes cleanly generated the desired ion-pair complexes when treated with an equivalent amount of $[(C_{18}H_{37})_2N(H)Me]^+[B(C_6F_5)_4]^-$, which showed negligible activity in olefin polymerization. Some complexes bearing bulky substituents showed moderate activities, even though the desired ion-pair complexes were not cleanly afforded.

Keywords: pincer complex; hafnium complex; post-metallocene; olefin polymerization

1. Introduction

Transition metal pincer complexes have been prepared to discover applications in various areas, especially in organometallic catalysis [1,2]. The tridentate chelating pincer ligand binds a metal in a meridional fashion to form a coplanar structure with the metal at the center. The ligand-metal interaction is tight and inflexible, which confers high stability. For homogeneous olefin polymerization, the initial zirconium (Zr)-based metallocene catalysts were followed by titanium (Ti)-based half-metallocenes and subsequently post-metallocenes with non-cyclopentadienyl ligands [3–9]. Among the post-metallocenes that have been developed, a pincer-type [$C^{naphthyl}$, $N^{pyridine}$, N^{amido}]$HfMe_2$ complex is a flagship catalyst. The complex was discovered in the early 2000s through high-throughput screening and

has since been extensively explored and applied in a commercial process (**I** in Figure 1) [10,11]. The pincer-type Hf complex **I** is able to incorporate a large amount of α-olefin in ethylene/α-olefin copolymerizations [12], and is capable of controlling the tacticity of propylene polymerization to produce isotactic polypropylene [13–15]. An unique characteristic of **I** is that the β-elimination process, an intrinsic chain transfer reaction that inevitably occurs in the olefin polymerizations performed with the conventional Zr-based metallocene and Ti-based half metallocene catalysts, is completely prevented [14–16]. With these merits, it is possible not only to grow a polyolefin (PO) chain from a Hf-site in a living fashion but also to grow PO chains uniformly from diethylzinc (Et_2Zn) deliberately added in excess as a chain transfer agent. The latter is termed coordinative chain transfer polymerization (CCTP) [17–19]. The CCTP technique is judiciously utilized in the commercial production of olefin block copolymers at the Dow Chemical Company [10,20–22]. By performing anionic polymerization of styrene in a one-pot reaction after CCTP with **I**, it is also possible to synthesize polyolefin-polystyrene block copolymers [23–25]. In this context, many studies have been performed to detail **I** and to improve the catalytic performance by modifying the skeleton of **I** [26–35]. With an aim to develop upgraded catalyst for **I**, we prepared various pincer-type Hf-complexes. The results are presented herein.

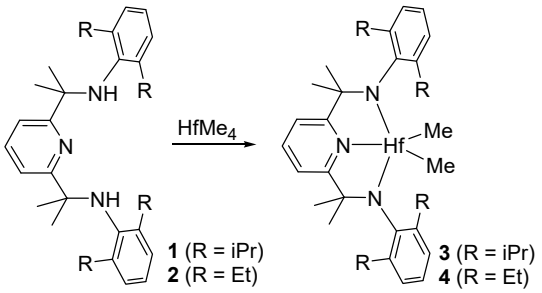


I

Figure 1. A flagship catalyst in the post-metallocenes.

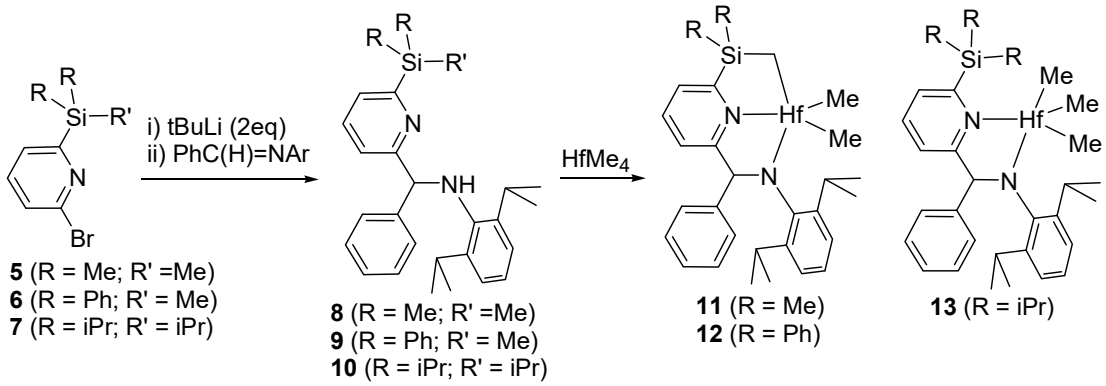
2. Results and Discussion

Pincer-type [N^{amido}, $N^{pyridine}$, N^{amido}]$HfMe_2$ complexes were prepared (**3** and **4** in Scheme 1). Bis(amino)pyridine compounds **1** and **2** were prepared according to the reported method involving the stepwise methylation of the corresponding bis(imino)pyridine compounds with $AlMe_3$ [36]. Zr and Y complexes have been successfully prepared using **1** [36], but the synthesis of its Hf analogue has not been reported. When **1** and **2** were treated with $HfMe_4$ generated by the treatment of $HfCl_4$ with 4 equiv methylmagnesium bromide (MeMgBr) at –30 °C, the desired pincer-type Hf-complexes **3** and **4** were cleanly generated [37]. In ^{1}H NMR spectra of **3** and **4**, $Hf(CH_3)_2$ signals were observed as a singlet at 0.36 and 0.10 ppm, respectively. The structure of **4** was unambiguously confirmed by X-ray crystallography. Metallation of the bis(imino)pyridine compound containing 2,6-$Me_2C_6H_3N$(H)-moieties was unsuccessful under the same reaction conditions.



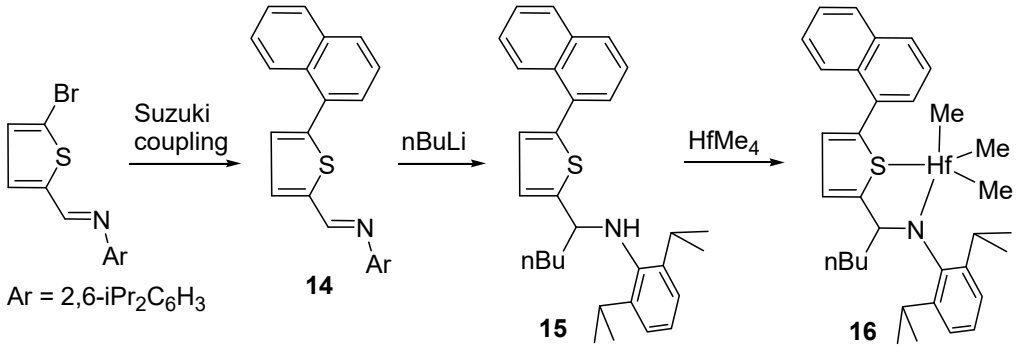
Scheme 1. Synthesis of pincer-type [N^{amido}, $N^{pyridine}$, N^{amido}]$HfMe_2$ complexes.

The prototype complex **I** characteristically contains a Hf-C(aryl) bond. We prepared the related pincer-type [$C^{silylmethyl}$, $N^{pyridine}$, N^{amido}]$HfMe_2$ complexes containing the Hf-CH_2Si bond instead of the Hf-C(aryl) bond (Scheme 2). 2-Br-6-($R_2R'Si$)-pyridines (R = Me, Ph, iPr; R′ = Me, iPr; **5**–**7**) were prepared from 2,6-dibromopyridine by the treatment of *n*BuLi and subsequently Me_3SiCl, $Ph_2(Me)SiCl$, or $iPr_3Si(OSO_2CF_3)$ [38,39]. Compounds **5**–**7** were treated with 2 equiv *t*BuLi to generate 2-Li-6-($R_2R'Si$)-pyridines, which were reacted with imine compound PhC(H)=N(2,6-$iPr_2C_6H_3$) to generate pyridines substituted with the $R_2R'Si$-group and (2,6-$iPr_2C_6H_3$)N(H)C(Ph)(H)-group at the 2- and 6-positions (**8**–**10**). Treatment of **8** and **9** with in situ generated $HfMe_4$ afforded the targeted pincer-type [$C^{silylmethyl}$, $N^{pyridine}$, N^{amido}]$HfMe_2$ complexes containing the Hf-CH_2Si bond (**11** and **12**). The ^{1}H NMR spectrum of **11** distinguished the two diastereotopic protons on HfCH_2Si moiety at 1.31 and 0.24 ppm as doublets with a large geminal coupling constant (J = 12.6 Hz) (Figure S7 in Supporting Information). The two methyl groups attached on Si and the two methyl groups attached on Hf were also diastereotopic, respectively, and four singlet methyl signals were observed at 0.84, 0.42, 0.37, and 0.27 ppm. The same signal pattern was observed in the ^{1}H NMR spectrum of **12**. In contrast, a totally different pattern was observed in the ^{1}H NMR spectrum of the product derived from **10**, which had an iPr_3Si-substituent. Analysis of the spectrum indicated that the $Si(Me)_2$C-Hf bond was not formed, while [$N^{pyridine}$, N^{amido}]$HfMe_3$ complex **13** was generated (Figure S9). The σ-bond metathesis via agostic interaction of SiC-H bond might be a process for the formation of SiC-Hf bond. In the case of iPr_3Si-substituent, steric hindrance might hamper the agostic interaction not to afford the desired pincer-type complex.



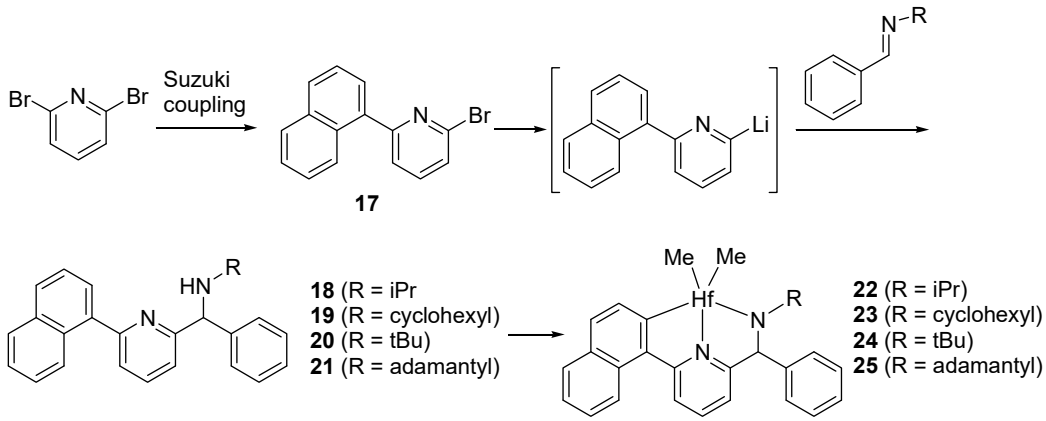
Scheme 2. Synthesis of pincer-type [$C^{silylmethyl}$, $N^{pyridine}$, N^{amido}]$HfMe_2$ complexes.

Synthesis of pincer-type [$C^{naphthyl}$, $S^{thiophene}$, N^{amido}]$HfMe_2$ complex was attempted by replacing the pyridine moiety in **I** with thiophene (Scheme 3). The Suzuki-coupling reaction of 1-naphthylboronic acid with the imine compound constructed with 5-bromo-2-thiophencarboxaldehyde and 2,6-$iPr_2C_6H_3NH_2$ generated the thiophene compound bearing imine (2,6-$iPr_2C_6H_3$N=C(H)-) and naphthyl moieties (**14**). In the synthesis of **I**, 2-$iPrC_6H_4Li$ facilely attacked the imine group to afford the desired ligand precursor. In the case of the reaction between 2-$iPrC_6H_4Li$ and thiophene analogue **14**, the desired ligand precursor was not obtained. However, *n*BuLi readily reacted with **14** to produce the desired thiophene compound **15** substituted with naphthyl and (2,6-$iPr_2C_6H_3$)N(H)C(nBu)(H)-group at the 2- and 5-positions. When **15** was reacted with $HfMe_4$, the Hf-C^{aryl} bond was not formed, which failing to generate the desired [$C^{naphthyl}$, $S^{thiophene}$, N^{amido}]$HfMe_2$ complex. Instead, the [N^{amido}, $S^{thiophene}$]$HfMe_3$ complex **16** was cleanly obtained. S-C-C^{ipso}(naphthyl) angle might be too wide to generate the desired pincer-type complex via formation of Hf-C(naphthyl) bond. A single signal assigned to $Hf(CH_3)_3$ was observed as a singlet at 0.35 ppm in the ^{1}H NMR spectrum (Figure S12).



Scheme 3. Attempt to synthesize pincer-type [$C^{naphthyl}$, $S^{thiophene}$, N^{amido}]$HfMe_2$ complex.

The prototype complex **I** was discovered through the high-throughput screening and a variety of derivatives were prepared for screening [11,40,41]. The starting material for **I** (6-bromo-2-pyridinecarboxaldehyde) is expensive. The naphthyl group is introduced by the Suzuki-coupling reaction with naphthylboronic acid, and the aldehyde group is converted by condensation with aniline derivatives to imine. This group is reactive with 2-isopropylphenyllithium. The imine bond that forms with alkylamine is easily hydrolyzed in the presence of moisture. Therefore, compounds prepared using alkylamine were not included in the screening. In this work, we prepared the derivatives of **I** containing various alkylamido moieties instead of the arylamido moiety in **I**. The synthetic scheme was different from that developed for **I** and the starting material, 2,6-dibromopyridine, was relatively inexpensive (Scheme 4). 2-Bromo-6-naphthylpyridine **17**, which was prepared through the Suzuki-coupling reaction of 2,6-dibromopyridine and 1-naphthylboronic acid [42], was treated with 2 equiv *t*BuLi to generate 2-lithio-6-naphthylpyridine, which was subsequently reacted with the imines generated through the condensation of benzaldehyde and various alkylamines. The resulting alkylamine compounds **18**–**21** were purified by the conventional column chromatography using silica gel. When **18**–**21** were treated with $HfMe_4$, the desired pincer-type [$C^{naphthyl}$, $N^{pyridine}$, $N^{alkylamido}$]$HfMe_2$ complexes **22**–**25** were cleanly generated. ^1H and ^{13}C NMR spectra agreed with the structures (Figures S17–S20) and the structure of **22** and **25** were unambiguously confirmed by X-ray crystallography.



Scheme 4. Synthesis of the derivatives of **I** bearing alkylamino moieties.

2.1. X-ray Crystallographic Studies

The molecular structure of pincer-type [N^{amido}, $N^{pyridine}$, N^{amido}]$HfMe_2$ complexes **4** was confirmed by X-ray crystallography (Figure 2). The geometry around the Hf-center can be defined as a distorted trigonal bipyramid with a basal plane formed by pyridine-N(1), methyl-C(32), and methyl-C(33), with the axial sites occupied with amido N(2) and N(3) atoms. The sum of the bond angles of C(32)-Hf-N(1), C(33)-Hf-N(1), and C(33)-Hf-C(32) is 360°, indicating that the Hf atom is perfectly situated in the basal plane. The N(2)-Hf-N(3) angle is 137.10(6)°, which deviated from the

angle of 180° expected for the ideal trigonal bipyramidal structure. The Hf atom is not situated in a plane formed by the chelating ligand framework (i.e., a plane formed by N(2), C(6), C(1), N(1), C(5), C(19), and N(3) atoms), but rather is situated slightly above the plane (0.46 Å). The sum of the bond angles around the amido N(2) and N(3) atoms is 360°, respectively, indicating that both N atoms adopt an sp^2 hybridization for π-donation from N to Hf-center. Hf-N^{amido} (i.e., Hf-N(2) and Hf-N(3)) distances are significantly shorter than that of Hf-$N^{pyridine}$ (i.e., Hf-N(1)) (2.08 vs. 2.27 Å).

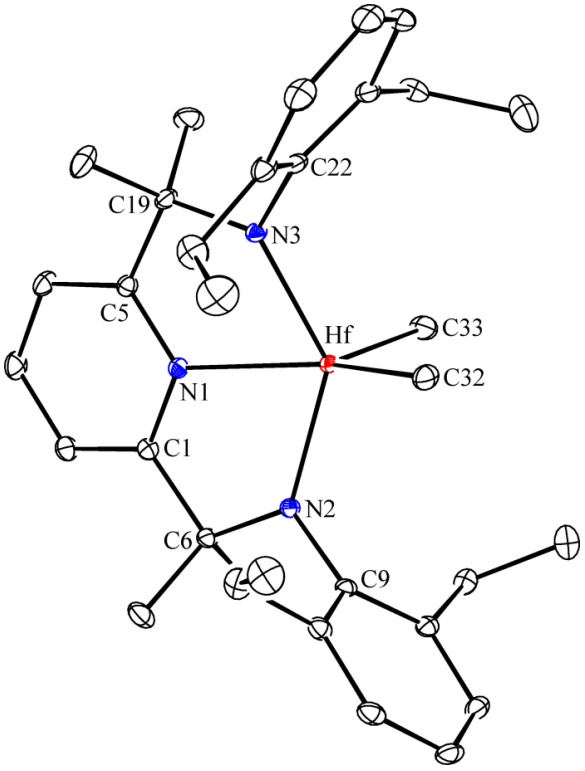


Figure 2. Thermal ellipsoid plot (30% probability level) of **4**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Hf-N(1), 2.267(2); Hf-N(2), 2.084(2); Hf-N(3), 2.088(2); Hf-C(33), 2.233(2); Hf-C(32), 2.248(2); C(32)-Hf-N(1), 147.82(7); C(33)-Hf-N(1), 104.18(7); C(33)-Hf-C(32), 107.98(8); N(2)-Hf-N(3), 137.10(6); C(9)-N(2)-C(6), 114.86(14); C(6)-N(2)-Hf, 125.51(11); C(9)-N(2)-Hf, 119.62(11); C(22)-N(3)-Hf, 119.95(11); C(22)-N(3)-C(19), 115.10(14); C(19)-N(3)-Hf, 124.94(11).

The molecular structure of [$C^{naphthyl}$, $N^{pyridine}$, N^{amido}]$HfMe_2$ complex bearing isopropylamido moiety (**22**) was confirmed by X-ray crystallography (Figure 3a). Geometry around the Hf-center was defined as a distorted trigonal bipyramid with a basal plane formed by pyridine-N(1), methyl-C(26), and methyl-C(27) atoms. The Hf atom is situated in a plane formed by the chelating ligand framework (i.e., a plane formed by N(2), C(16), C(15), N(1), C(11), C(10), and C(1) atoms). Either the naphthalene or the pyridine ring is slightly tilted from the plane formed by the chelating ligand framework (9.5(4)° and 9.6(4)°, respectively). Amido-N(2) atom adopts sp^2 hybridization for π-donation and, accordingly, the *C*H(iPr) atom is almost coplanar with the plane formed by the chelating ligand framework (C(15)-C(16)-N(2)-C(23) torsional angle, 171°). The Hf-C^{aryl} distance is slightly longer than Hf-C^{methyl} distances (2.29 vs. 2.20 or 2.22 Å). Molecular structure of **25** bearing the adamantylamido moiety was also confirmed by X-ray crystallography (Figure 3b). In this structure, N-C-C-N chelating ligand framework and pyridine ring form a plane with the Hf-center, while the naphthalene ring is rather severely tilted from the plane (20.0°). While the Hf-$N^{pyridine}$ distance is almost the same with that in **22**, the Hf-N^{amido} and Hf-$C^{naphthyl}$ distances are longer by 0.01 to 0.03 Å than the corresponding distances in **22**.

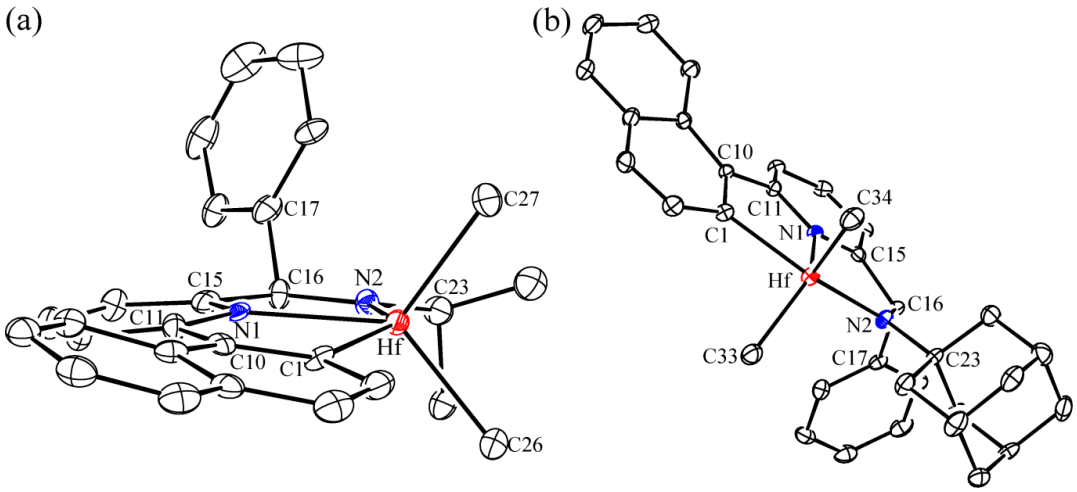


Figure 3. Thermal ellipsoid plot (30% probability level) of **22** (a) and **25** (b). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) in **22** (a): Hf-N(1), 2.296(10); Hf-N(2), 2.065(11); Hf-C(1), 2.285(12); Hf-C(26), 2.203(14); Hf-C(27), 2.223(14); C(27)-Hf-N(1), 122.7(5); C(26)-Hf-N(1), 132.3(5); C(26)-Hf-C(27), 103.9(6); N(2)-Hf-C(1), 139.2(4); C(16)-N(2)-Hf, 127.1(8); C(23)-N(2)-Hf, 121.6(9); C(16)-N(2)-C(23), 110.8(11). In **25** (b): Hf-N(1), 2.295(4); Hf-N(2), 2.089(4); Hf-C(1), 2.302(5); Hf-C(33), 2.231(5); Hf-C(34), 2.212(5); C(33)-Hf-N(1), 133.18(18); C(34)-Hf-N(1), 116.31(18); C(34)-Hf-C(33), 108.4(2); N(2)-Hf-C(1), 140.67(16); C(16)-N(2)-Hf, 123.4(3); C(23)-N(2)-Hf, 122.0(3); C(16)-N(2)-C(23), 114.2(4).

2.2. Activation Reactions

Activation reaction of the prototype complex **I** is complex [43,44]. Reaction with $B(C_6F_5)_3$ results in decomposition through a process involving C_6F_5-transfers. Reaction with $[Ph_3C]^+[B(C_6F_5)_4]^-$ immediately affords the targeted ion-pair complex $\{[N,N,C^{naphthyl}]HfMe\}^+[B(C_6F_5)_4]^-$. However, the complex is unstable. Reaction with $[PhN(H)Me_2]^+[B(C_6F_5)_4]^-$ results in the formation of an undesirable complex. The best activator proved to be the aliphatic amine based Bronsted acid $[(C_{18}H_{37})_2N(H)Me]^+[B(C_6F_5)_4]^-$, which generated the desired ion-pair complex, which is stable in benzene [21].

When **3** was treated with $[(C_{18}H_{37})_2N(H)Me]^+[B(C_6F_5)_4]^-$ in C_6D_6, methide abstraction occurred as was evident from the observation of the methane signal at 0.16 ppm in the ^{1}H NMR spectrum. In the ^{1}H NMR spectrum collected at the early stage of the reaction, two sets of signals corresponding to the ligand framework were observed in a ratio of approximately 10:1 (Figure 4). The major set of signals was unambiguously assigned to the desired ion-pair complex **26** (Scheme 5). In the ^{1}H NMR spectrum of **3**, all four isopropyl groups were equivalent and a single Me_2CH-resonace was observed at 3.65 ppm as a septet. However, in the ^{1}H NMR spectrum of the desired ion-pair complex **26**, Me_2CH-resonances were split as a pair of signals at 3.14 and 2.69 ppm, which was attributed to the persistent coordination of $(C_{18}H_{37})_2NMe$ to the Hf-center. With the persistent coordination of amine, the two protons on an α-methylene of $(C_{18}H_{37})_2NMe$ are diastereotopic to each other, even though the two α-methylene carbons are equivalent. This was reflected as separately observed NCH_2 resonances at 2.39 and 2.13 ppm with a triplet-doublet coupling pattern (J = 13 and 4.2 Hz). Due to the persistent coordination of amine, the NCH_2 signals as well as the NCH_3 signal were sharp. With time, the minor set of signals became more prominent as the set of signals mainly observed at the initial stage became depressed and disappeared by 6 h. The spectrum was assigned to complex **28** generated from the ion-pair complex **26** through C-H bond activation of a H-CH_2(Me)CH-group (i.e., isopropyl group). This unwanted reaction was also observed in the activation reaction of the prototype complex **I** with $[Ph(Me)_2N\text{-}H]^+[B(C_6F_5)_4]^-$. In the ^{1}H NMR spectrum of **28**, three Me_2CH-resonances were observed at 3.67, 3.22, and 2.39 ppm as a septet, while the resonance of the isopropyl group that was engaged in the C-H bond activation process (i.e., Hf-CH_2(Me)CH-signal) was observed at 2.84 ppm as a broad multiplet (Figure 3). In the

case of **4**, which contained ethyl substituents instead of isopropyl, the targeted ion-pair complex **27** was also cleanly generated by the action of $[(C_{18}H_{37})_2N(H)Me]^+[B(C_6F_5)_4]^-$ through methide abstraction. In contrast with **3**, the activated complex was stable in C_6D_6 with no further reaction.

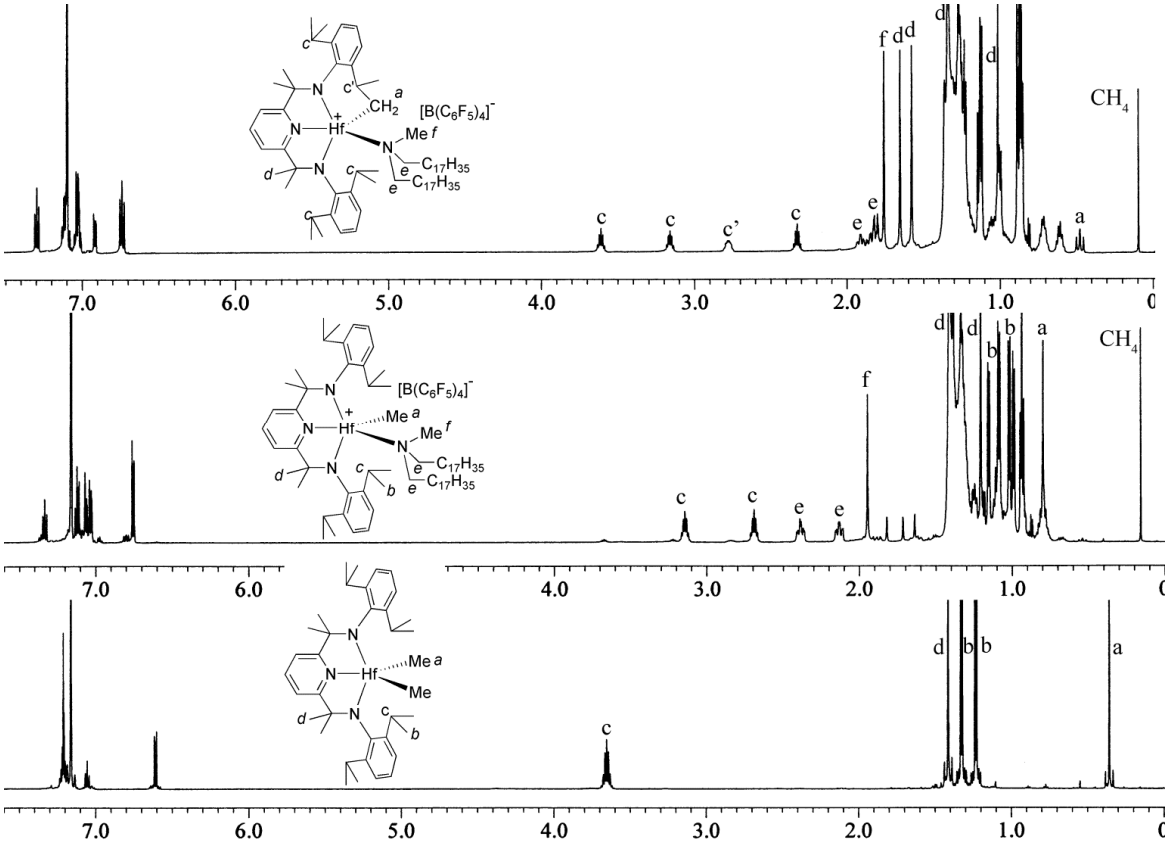
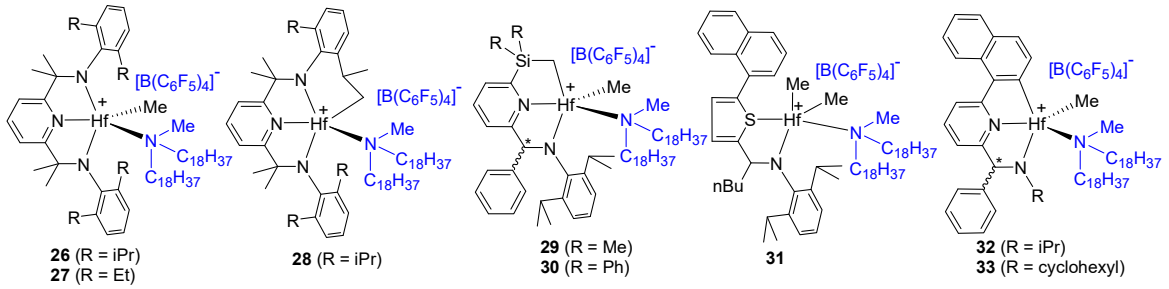


Figure 4. ^{1}H NMR spectra of **3** and its reaction complexes with $[(C_{18}H_{37})_2N(H)Me]^+[B(C_6F_5)_4]^-$ (**26** and **28**).



Scheme 5. Complexes generated by the action of $[(C_{18}H_{37})_2N(H)Me]^+[B(C_6F_5)_4]^-$.

The reaction of $[C^{silylmethyl}, N^{pyridine}, N^{amido}]HfMe_2$ complexes containing the Hf-CH_2Si bond (**11** and **12**) with $[(C_{18}H_{37})_2N(H)Me]^+[B(C_6F_5)_4]^-$ generated the desired ion-pair complexes **29** and **30** with concomitant generation of methane. Due to presence of chiral centers at the ligand framework as well as the Hf-center, two sets of signals were observed. The reaction rate of **11** was slow, requiring approximately 3 h for complete methide abstraction. At this stage of the complete reaction, the ratio of the two diastereomers was approximately 1:1, which slowly changed and ultimately became 1.0:0.60 after an overnight reaction. In the case of **12**, the reaction rate was rapid and efficiently generated two diastereomers at a ratio of 1.0:0.50 within 30 min. Upon an overnight reaction, the ratio also slowly changed to become 1.0:0.85. The change of the ratio indicated that the site epimerization occurred, even though the rate was slow.

[$N^{pyridine}$, N^{amido}]$HfMe_3$-type complex **13** facilely reacted with $[(C_{18}H_{37})_2N(H)Me]^+[B(C_6F_5)_4]^-$ to generate methane. However, the ^1H NMR signals were too complicated to be unambiguously assigned (Figure S24). In contrast, [N^{amido}, $S^{thiophene}$]$HfMe_3$-type complex **16** reacted slowly with $[(C_{18}H_{37})_2N(H)Me]^+[B(C_6F_5)_4]^-$ and a set of signals eventually appeared after 3 days. These were assigned to **31** (Figure S25). Two Hf-CH_3 signals were observed at 0.60 and 0.41 ppm. Reaction of **22** and **23** bearing secondary amido moieties cleanly afforded the targeted ion-pair complexes **32** and **33**, for which two sets of signals were observed, respectively, in ^1H NMR spectra, due to the presence of chiral centers on both the Hf-center and at the ligand framework (Figures S26 and S27). Reaction of **24** and **25** bearing tertiary amido moieties did not cleanly afford the targeted ion-pair complexes (Figures S28 and S29).

2.3. Polymerization Studies

The targeted ion-pair complex **27** derived from [N^{amido}, $N^{pyridine}$, N^{amido}]$HfMe_2$ bearing ethyl substituents (**4**) exhibited moderate activity in ethylene/propylene copolymerization. The activity was approximately 1/7th that of the prototype Dow catalyst **I** (entry 1 vs. 4 in Table 1). All other complexes (i.e., **3**, **11**, **12**, **16**, and **22**–**23**) that showed clean ^1H NMR signals in the activation reaction with $[(C_{18}H_{37})_2N(H)Me]^+[B(C_6F_5)_4]^-$ exhibited negligible activities. Complex **13** and **25** bearing bulky iPr_3Si- and adamantyl group, which did not show clean ^1H NMR signals in the activation reaction, exhibited moderate activities (approximately 1/10th that of **I**; entries 2 and 3). Comonomer incorporation ability was also inferior to that of **I**; 6.7, 0, and 5.1 mol% propylene was incorporated with **4**, **13**, and **25**, respectively, while the propylene content was very high (56 mol%) with **I** under the identical polymerization conditions. [$N^{pyridine}$, N^{amido}]$HfMe_3$ complex **13** bearing bulky iPr_3Si-group generated the relatively high-molecular-weight polymer (M_n, 430 kDa). The prototype Hf catalyst **I** was exceptional in terms of the activity and α-olefin incorporation capability. We also reported various types of Hf-complexes ([N,P]$Hf(CH_2Ph)_3$, [N,P,N]$HfMe_2$, and [N,N]$Hf(CH_2Ph)_3$-type) with tetrahydroquinoline and tetrahydrophenanthroline framework, which were also inferior to **I** in terms of both activity and α-olefin incorporation capability [45–47]. The Hf-C bonding character was significantly ionic when compared to those of Zr-C and Ti-C bonding, and steric congestion around Hf-center might be crucial for the high activity [48]. When steric congestion is not significant, the ionic Hf-C bond becomes strong and the insertion of olefin through the Hf-C bond may be less favorable, leading to lowered activity.

Table 1. Polymerization results [a].

Entry	Complex	Yield (g)	$[C_3H_6]$ [b] (mol%)	T_m	M_n (kDa) [c]	M_w/M_n
1	**4**	2.3	6.7	113–125	10	2.9
2	**13**	1.2	0	119–139	430	2.3
3	**25**	1.7	5.1	91–111	45	1.6
4	**I** (Dow)	16	56	not detected	61	2.6

[a] Polymerization conditions: Hf complex (2.0 μmol), activator ($[(C_{18}H_{37})_2N(H)Me]^+[B(C_6F_5)_4]^-$, 2.0 μmol), scavenger (MMAO, 50 μmol), methylcyclohexane (26 g), ethylene and propylene mixed gas (1:1, 20 bar), 80 °C, 50 min. [b] Propylene content measured by ^1H-NMR spectra. [c] Measured by gel permeation chromatography (GPC) at 160 °C using trichlorobenzene and calculated relative to polystyrene (PS) standards.

3. Materials and Methods

3.1. General Remarks

All manipulations were performed under an inert atmosphere using standard glove box and the Schlenk technique. Toluene, hexane, diethyl ether, THF and C_6D_6 were distilled from benzophenone ketyl. Methylcyclohexane used for the polymerization reactions was purchased from TCI and was purified over a Na/K alloy. Ethylene was purified by contact with molecular sieves and copper at a pressure of 50 bar. ^1H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded using an

ECZ 600 apparatus (JEOL, Tokyo, Japan). Compounds **5** [39], **7** [38], **17** [42], 2-iPrC_6H_4Li [41], and PhC(H)=NCH$(CH_3)_2$ were prepared according to previously reported procedures and conditions [49].

3.2. Complex **3**

MeMgBr (0.400 mL, 1.20 mmol, 3.0 M solution in diethyl ether) was added dropwise at −78 °C to a solution of $HfCl_4$ (93.5 mg, 0.292 mmol) in toluene (2 mL). The resulting solution was stirred at −40 to −35 °C for 1 h to precipitate a white solid. After cooling to −78 °C, a solution of **1** (0.100 g, 0.195 mmol) in toluene was added dropwise. The resulting mixture was stirred at −40 to −35 °C for 2 h and then warmed slowly to room temperature. After stirring overnight, all volatiles were removed using a vacuum line. Toluene (10 mL) was added to extract the product. The extract was collected through filtration over Celite. After the solvent was removed, the residue was triturated with hexane to obtain a pink solid (0.099 g, 70%). The isolated product was contaminated with some amount of chloromethyl-Hf analog, which was converted to the desired dimethyl-Hf complex by treatment with MeLi in toluene. ^{1}H NMR (600 MHz, C_6D_6): δ 7.26–7.19 (m, 6H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.61 (d, *J* = 8.4 Hz, 2H), 3.65 (sept, *J* = 7.2 Hz, 4H, C*H*$(CH_3)_2$), 1.41 (s, 12H, NC$(CH_3)_2$), 1.32 (d, *J* = 7.2 Hz, 12H, CH(C*H*$_3)_2$), 1.22 (d, *J* = 7.2 Hz, 12H, CH(C*H*$_3)_2$), 0.36 (s, 6H, Hf$(CH_3)_2$) ppm. ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 24.38, 25.21, 26.63, 28.44, 32.98, 57.22, 70.38, 116.34, 124.36, 125.71, 127.98, 140.15, 145.67, 148.54, 173.89 ppm. Anal. Calcd. ($C_{37}H_{55}N_3Hf$): C, 61.69; H, 7.70; N, 5.83. Found: C, 61.54; H, 7.62; N, 5.71%.

3.3. Complex **4**

The complex was prepared by the same procedure and conditions as those employed for **3** using $HfCl_4$ (0.158 g, 0.492 mmol), MeMgBr (0.700 mL, 2.08 mmol, 3.0 M solution in diethyl ether), **2** (0.150 g, 0.328 mmol), and toluene (6 mL). A red solid was obtained (0.132 g, 61%). Single crystals suitable for X-ray crystallography were obtained by recrystallization in toluene/hexane cosolvent at −30 °C. ^{1}H NMR (600 MHz, C_6D_6): δ 7.40 (d, *J* = 7.2 Hz, 4H), 7.19 (t, *J* = 7.2 Hz, 2H), 7.11 (t, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 3.13 (quartet, *J* = 7.2 Hz, 4H, C*H*$_2$CH$_3$), 2.85 (quartet, *J* = 7.2 Hz, 4H, C*H*$_2$CH$_3$), 1.38–1.22 (m, 24H, CH$_2$C*H*$_3$, NC$(CH_3)_2$), 0.10 (s, 6H, Hf$(CH_3)_2$) ppm. ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 15.50, 25.82, 31.65, 54.60, 73.10, 117.75, 125.41, 126.36, 139.67, 144.52, 144.97, 173.14 ppm. Anal. Calcd. ($C_{33}H_{47}N_3Hf$): C, 59.67; H, 7.13; N, 6.33. Found: C, 59.86; H, 7.25; N, 6.46%.

3.4. 2-Bromo-6-(dimethylphenylsilanyl)pyridine (**6**)

*n*BuLi (1.70 mL, 4.22 mmol, 2.5 M solution in hexane) was added dropwise at −78 °C to a stirred solution of 2,6-dibromopyridine (1.00 g, 4.22 mmol) in diethyl ether (20 mL). The resulting solution was warmed to −40 °C and stirred for 20 min. After cooling to −78 °C, Ph_2MeSiCl (1.08 g, 4.64 mmol) in diethyl ether (5 mL) was added. After stirring for 3 h, the solution was warmed to room temperature and water (30 mL) was added. The product was extracted with diethyl ether (3 × 10 mL). The collected organic phases were dried over anhydrous $MgSO_4$ and the solvent was removed with a rotary evaporator. The product was purified by column chromatography on silica gel using hexane and ethyl acetate (50:1 *v*/*v*). White solid was obtained (1.05 g, 70%). ^{1}H NMR (600 MHz, C_6D_6): δ 7.58 (d, *J* = 7.2 Hz, 4H), 7.20–7.12 (m, 6H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.53 (t, *J* = 7.2 Hz, 1H), 0.82 (s, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ −3.92, 127.74, 128.34, 129.98, 135.17, 135.71, 136.54, 144.07, 167.94 ppm. IR (neat): ν 478 (C-Br) cm^{-1}. HRMS(FAB): *m*/*z* calcd ([M+H]$^+$ $C_{18}H_{16}$BrNSi) 354.0314. Found: 354.0310.

3.5. (2,6-Diisopropylphenyl)-{[6-(trimethylsilanyl)pyridin-2-yl](phenyl)methyl}amine (**8**)

A solution of *t*BuLi (3.76 mL, 6.39 mmol, 1.7 M in pentane) in hexane (4 mL) was added to a solution of **5** (0.735 g, 3.19 mmol) in THF (15 mL) at −78 °C and the resulting solution was stirred for 2 h. A solution of PhC(H)=N(2,6-i$Pr_2C_6H_3$) (0.763 g, 2.87 mmol) in THF (15 mL) was added. After stirring for 3 h, the resulting solution was warmed slowly to room temperature and stirred overnight. Water

(30 mL) was added and the product was extracted with ethyl acetate (3 × 20 mL). The organic phases were collected and dried over anhydrous $MgSO_4$. The solvent was removed using a rotary evaporator. Purification by column chromatography on silica gel using hexane and toluene (2:1 *v*/*v*) gave a light yellow oil (0.934 mg, 78%). ^{1}H NMR (600 MHz, C_6D_6): δ 7.50 (d, *J* = 7.8 Hz, 2H), 7.15–7.02 (m, 6H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.93 (t, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 6.6 Hz, 1H), 5.69 (br s, 1H, NH), 5.24 (s, 1H, NCH), 3.44 (sept, *J* = 6.6 Hz, 2H, C*H*(CH_3)$_2$)), 1.19 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.09 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 0.30 (s, 9H, CH_3) ppm. ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ −1.76, 24.28, 28.13, 70.17, 121.96, 123.97, 127.07, 127.13, 128.40, 134.42, 142.80, 143.71, 144.39, 162.14, 167.69 ppm. IR (neat): *v* 3361 (N-H) cm^{-1}. HRMS(EI): *m*/*z* calcd ([M$^+$] $C_{27}H_{36}N_2Si$) 416.2648. Found: 416.2650.

*3.6. (2,6-Diisopropylphenyl)-{[6-(dimethylphenylsilanyl)pyridin-2-yl](phenyl)methyl}amine (**9**)*

The compound was prepared by the same procedure and conditions as those employed for **8** using *t*BuLi (1.66 mL, 2.82 mmol, 1.7 M in pentane), **6** (0.500 g, 1.41 mmol), and PhC(H)=N(2,6-i$Pr_2C_6H_3$) (0.337 g, 1.27 mmol). Purification by column chromatography on silica gel using hexane and toluene (2:1 *v*/*v*) produced a white glassy solid (0.186 g, 27%). ^{1}H NMR (600 MHz, C_6D_6): δ 7.63 (t, *J* = 7.8 Hz, 4H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.22–7.00 (m, 13H), 6.86 (t, *J* = 7.2 Hz, 1H), 6.66 (d, *J* = 7.2 Hz, 1H), 5.52–5.40 (br, 1H, NH), 5.32–5.20 (br, 1H, NCH), 3.31 (sept, *J* = 6.0 Hz, 2H, C*H*(CH_3)$_2$), 1.35 (d, *J* = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.09 (d, *J* = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 0.87 (s, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ −3.83, 24.20, 24.45, 28.13, 122.14, 123.94, 127.11, 128.26, 128.42, 129.31, 129.76, 129.81, 134.66, 135.79, 142.72, 143.43, 144.14, 162.61, 164.85 ppm. IR (neat): *v* 3361 (N-H) cm^{-1}. HRMS(EI): *m*/*z* calcd ([M$^+$] $C_{37}H_{40}N_2Si$) 540.2961. Found: 540.2964.

*3.7. (2,6-Diisopropylphenyl)-{[6-(triisopropylsilanyl)pyridin-2-yl](phenyl)methyl}amine (**10**)*

The compound was prepared by the same procedure and conditions as those employed for **8** using *t*BuLi (0.56 mL, 0.954 mmol, 1.7 M in pentane), **7** (0.150 g, 0.477 mmol), and PhC(H)=N(2,6-i$Pr_2C_6H_3$) (0.114 g, 0.429 mmol). Purification by column chromatography on silica gel using hexane and toluene (2:1 *v*/*v*) produced a light yellow oil (0.161 g, 75%). ^{1}H NMR (600 MHz, C_6D_6): δ 7.40 (d, *J* = 7.2 Hz, 2H), 7.15–7.05 (m, 6H), 7.22–7.00 (m, 2H), 6.70 (d, *J* = 8.4 Hz, 1H), 5.34–5.21 (br, 2H, NH, NCH), 3.35 (sept, *J* = 7.2 Hz, 2H, C*H*(CH_3)$_2$), 1.47 (sept, *J* = 7.2 Hz, 3H, SiC*H*(CH_3)$_2$), 1.20–1.10 (m, 30H, CH(C*H*$_3$)$_2$, SiCH(C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 11.17, 18.70, 24.09, 24.38, 28.00, 69.90, 121.38, 123.77, 123.96, 126.87, 129.14, 133.86, 142.84, 143.84, 161.94, 164.65 ppm. IR (neat): *v* 3366 (N-H) cm^{-1}. HRMS(EI): *m*/*z* calcd ([M$^+$] $C_{33}H_{48}N_2Si$) 500.3587. Found: 500.3589.

3.8. Complex **11**

The complex was prepared by the same procedure and conditions as those employed for **3** using $HfCl_4$ (0.230 g, 0.718 mmol), MeMgBr (1.00 mL, 2.94 mmol, 3.0 M solution in diethyl ether), and **8** (0.230 g, 0.552 mmol). A yellow oil was obtained (0.220 g, 60%). ^{1}H NMR (600 MHz, C_6D_6): δ 7.21–7.11 (m, 2H), 7.06 (d, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.98–6.90 (m, 5H), 6.86 (t, *J* = 7.2 Hz, 1H), 6.55 (d, *J* = 9.0 Hz, 1H), 5.96 (s, 1H, NCH), 3.66 (sept, *J* = 6.6 Hz, 1H, C*H*(CH_3)$_2$), 3.26 (sept, *J* = 6.6 Hz, 1H, C*H*(CH_3)$_2$), 1.38 (d, *J* = 7.2 Hz, 3H, CH(C*H*$_3$)$_2$), 1.34 (d, *J* = 7.2 Hz, 3H, CH(C*H*$_3$)$_2$), 1.31 (d, *J* = 12.6 Hz, 1H, $SiCH_2Hf$), 1.24 (d, *J* = 7.2 Hz, 3H, CH(C*H*$_3$)$_2$), 0.84 (s, 3H,$SiCH_3$), 0.42 (s, 3H, $HfCH_3$), 0.37 (s, 3H,$SiCH_3$), 0.35 (d, *J* = 7.2 Hz, 3H, CH(C*H*$_3$)$_2$), 0.27 (s, 3H, $HfCH_3$), 0.24 (d, *J* = 12.6 Hz, 1H, $SiCH_2Hf$) ppm. ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ 11.17, 18.70, 24.09, 24.38, 28.00, 69.90, 121.38, 123.77, 123.96, 126.87, 129.14, 133.86, 142.84, 143.84, 161.94, 164.65 ppm.

3.9. Complex **12**

The complex was prepared by the same procedure and conditions as those employed for **3** using $HfCl_4$ (0.155 g, 0.483 mmol), MeMgBr (0.70 mL, 2.0 mmol, 3.0 M solution in diethyl ether), and **9** (0.174 g, 0.322 mmol). An orange glassy solid was obtained (0.169 g, 84%). ^{1}H NMR (600 MHz, C_6D_6): δ 7.66 (d, *J* = 5.4 Hz, 2H), 7.61–7.52 (m, 2H), 7.27–7.11 (m, 9H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.95–6.86 (m, 5H),

6.79 (t, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 8.4 Hz, 1H), 5.95 (s, 1H, NCH), 3.64 (sept, *J* = 6.6 Hz, 1H, C*H*(CH_3)$_2$), 3.29 (sept, *J* = 6.6 Hz, 1H, C*H*(CH_3)$_2$), 1.69 (d, *J* = 13.2 Hz, 1H, $SiCH_2Hf$), 1.36 (d, *J* = 7.2 Hz, 3H, CH(C*H*$_3$)$_2$), 1.32 (d, *J* = 7.2 Hz, 3H, CH(C*H*$_3$)$_2$), 1.28 (d, *J* = 7.2 Hz, 3H, CH(C*H*$_3$)$_2$), 0.79 (d, *J* = 13.2 Hz, 3H, $SiCH_2Hf$), 0.53 (s, 3H, $HfCH_3$), 0.40 (s, 3H, $HfCH_3$), 0.31 (d, *J* = 7.2 Hz, 3H, CH(C*H*$_3$)$_2$) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 24.22, 25.19, 26.45, 26.59, 28.04, 28.64, 54.40, 62.43, 64.65, 83.14, 127.82, 128.28, 128.40, 128.83, 129.43, 129.62, 129.77, 131.11, 135.49, 135.52, 136.58, 137.46, 139.82, 144.12, 145.66, 146.34, 146.82, 170.02, 172.44 ppm. Anal. Calcd. ($C_{39}H_{44}N_2SiHf$): C, 62.68; H, 5.93; N, 3.75%. Found: C, 62.73; H, 5.97; N, 3.80%.

3.10. Complex **13**

The complex was prepared by the same procedure and conditions as those employed for **3** using $HfCl_4$ (0.071 g, 0.22 mmol), MeMgBr (0.30 mL, 0.91 mmol, 3.0 M solution in diethyl ether), and **10** (0.074 g, 0.15 mmol). Yellow oil was obtained (0.097 g, 91%). ^1H NMR (600 MHz, C_6D_6): δ 7.32 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 2H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.79 (t, *J* = 7.2 Hz, 1H), 6.10 (d, *J* = 7.8 Hz, 1H), 5.56 (s, 1H, NCH), 3.82 (sept, *J* = 6.6 Hz, 1H, C*H*(CH_3)$_2$), 3.63 (sept, *J* = 6.6 Hz, 1H, C*H*(CH_3)$_2$), 1.76 (sept, *J* = 7.2 Hz, 3H, SiC*H*(CH_3)$_2$), 1.43 (d, *J* = 7.2 Hz, 3H, CH(C*H*$_3$)$_2$), 1.42 (d, *J* = 6.6 Hz, 3H, CH(C*H*$_3$)$_2$), 1.36 (d, *J* = 6.6 Hz, 3H, CH(C*H*$_3$)$_2$), 1.15 (d, *J* = 7.8 Hz, 9H, SiCH(C*H*$_3$)$_2$), 1.12 (d, *J* = 7.2 Hz, 9H, SiCH(C*H*$_3$)$_2$), 0.52 (s, 9H, Hf(CH_3)$_3$), 0.43 (d, *J* = 7.8 Hz, 3H, CH(C*H*$_3$)$_2$) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 12.90, 19.25, 19.56, 24.86, 25.45, 25.73, 26.24, 28.38, 28.41, 61.07, 81.25, 123.02, 124.64, 125.02, 126.54, 127.98, 128.86, 129.18, 131.71, 135.31, 143.56, 144.00, 146.32, 147.25 ppm.

*3.11. (2,6-Diisopropylphenyl)-(5-naphthalen-1-ylthiophen-2-ylmethylene)amine (***14***)*

A Schlenk flask was charged with (5-bromothiophen-2-yl)-N-(2,6-diisopropylphenyl)methanimine (1.00 g, 2.86 mmol), 1-naphthylboronic acid (0.491 g, 2.86 mmol), Na_2CO_3 (0.759 g, 7.17 mmol), and toluene (3 mL) under a N_2 atmosphere. Degassed H_2O/EtOH (2 mL, 1:1 *v*/*v*) and a solution of $(Ph_3P)_4Pd$ (9.0 mg, 0.0080 mmol) in toluene (1 mL) was added. The biphasic solution was heated to 70 °C and vigorously stirred overnight. After cooling to room temperature, the organic phase was collected and washed with H_2O (5 mL). The collected organic phase was dried over anhydrous $MgSO_4$ and the solvent was removed with a rotary evaporator. Purification by recrystallization in methanol at −30 °C gave a yellow solid (0.738 g, 65%). ^1H NMR (600 MHz, C_6D_6): δ 8.22 (d, *J* = 8.4 Hz, 1H), 8.03 (s, 1H, NCH), 7.58 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.23–7.16 (m, 3H), 7.15–7.07 (m, 3H), 6.98 (d, *J* = 3.6 Hz, 1H), 6.92 (d, *J* = 3.6 Hz, 1H), 3.24 (sept, *J* = 7.2 Hz, 2H, C*H*(CH_3)$_2$), 1.20 (d, *J* = 6.6 Hz, 12H, CH(C*H*$_3$)$_2$) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 23.63, 28.63, 123.47, 124.83, 125.51, 125.91, 126.40, 127.02, 127.97, 128.53, 128.75, 129.33, 132.03, 132.07, 132.42, 134.44, 138.09, 143.31, 147.29, 149.67, 155.19 ppm. IR (neat): *v* 1619 (C=N) cm^{-1}. HRMS(EI): *m*/*z* calcd ([M^+] $C_{27}H_{27}NS$) 397.1864. Found: 397.1865.

*3.12. (2,6-Diisopropylphenyl)-[1-(5-naphthalen-1-yl-thiophen-2-yl)pentyl]amine (***15***)*

*n*BuLi (0.90 mL, 1.4 mmol, 1.61 M solution in hexane) was added dropwise to a solution of **14** (0.500 g, 1.26 mmol) in toluene (10 mL) at room temperature. After stirring for 1 h, water (10 mL) was added and the product was extracted with toluene (3 × 5 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and the solvent was removed with a rotary evaporator. The analysis with ^1H and ^{13}C NMR spectra indicated that the obtained crude oil was pure and it was used for the next step without further purification (0.573 g, 100%). ^1H NMR (600 MHz, C_6D_6): δ 8.40 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 6.6 Hz, 1H), 7.32–7.22 (m, 2H), 7.22–7.08 (m, 4H), 6.85 (d, *J* = 3.0 Hz, 1H), 6.53 (d, *J* = 3.6 Hz, 1H), 4.35 (q, *J* = 2.4 Hz, 1H, NCH), 3.35 (sept, *J* = 7.2 Hz, 2H, C*H*(CH_3)$_2$), 2.17–2.09 (m, 1H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 2.03–1.94 (m, 1H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.60–1.47 (m, 2H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.32 (sext, *J* = 6.6 Hz, 2H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 1.25 (d, *J* = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 1.18 (d, *J* = 6.0 Hz, 6H, CH(C*H*$_3$)$_2$), 0.87 (t, *J* = 7.2 Hz, 3H, CH$_2$CH$_2$CH$_2$C*H*$_3$) ppm.

$^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 14.23, 23.02, 24.48, 28.22, 29.56, 37.35, 60.88, 123.95 124.37, 125.01, 125.56, 126.21, 126.26, 126.68, 127.28, 128.63, 128.72, 132.38, 133.20, 134.53, 140.61, 141.72, 142.93, 148.43 ppm. IR (neat): *v* 3369 (N-H), 2957 1457, 496, 774 cm^{-1}. IR (neat): *v* 3369 (N-H) cm^{-1}. HRMS(EI): *m/z* calcd ([M^+] $C_{31}H_{35}NS$) 455.2647. Found: 455.2645.

3.13. Complex **16**

The complex was prepared by the same procedure and conditions as those employed for **3** using $HfCl_4$ (0.229 g, 0.716 mmol), MeMgBr (1.00 mL, 2.94 mmol, 3.0 M solution in diethyl ether), and **17** (0.251 g, 0.551 mmol). A yellow oil was obtained (0.293 g, 80%). ^1H NMR (600 MHz, C_6D_6): δ 8.48 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.29–7.08 (m, 6H), 7.01 (d, *J* = 1.8 Hz, 1H), 4.72 (t, *J* = 7.2 Hz, 1H, NCH), 4.04 (sept, *J* = 7.8 Hz, 2H, C*H*$(CH_3)_2$), 3.70 (sept, *J* = 7.2 Hz, 2H, C*H*$(CH_3)_2$), 2.00 (q, *J* = 7.2 Hz, 2H, C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.34 (d, 3H, *J* = 6.0 Hz, CH(C*H*$_3$)$_2$), 1.32 (d, 3H, *J* = 6.6 Hz, CH(C*H*$_3$)$_2$), 1.31 (d, 3H, *J* = 7.2 Hz, CH(C*H*$_3$)$_2$), 1.26 (d, 3H, *J* = 7.2 Hz, CH(C*H*$_3$)$_2$), 1.29–1.20 (m, 1H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.12 (sext, *J* = 7.2 Hz, 2H, CH$_2$CH$_2$C*H*$_2$CH$_3$), 1.07–0.07 (m, 1H, CH$_2$C*H*$_2$CH$_2$CH$_3$), 0.72 (t, *J* = 7.2 Hz, 3H, CH$_2$CH$_2$CH$_2$C*H*$_3$), 0.35 (s, 9H, Hf$(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 14.15, 22.81, 24.92, 25.26, 26.09, 26.33, 27.90, 26.33, 27.90, 28.45, 28.86, 38.31, 63.56, 67.07, 124.99, 125.48, 125.61, 126.06, 126.37, 126.88, 128.37, 128.41, 128.63, 128.80, 128.97, 132.18, 132.59, 134.27, 134.59, 141.84, 146.54, 150.09, 150.70 ppm.

*3.14. Isopropyl[(6-naphthalen-1-yl-pyridin-2-yl)phenylmethyl]amine (***18***)*

The compound was prepared by the same procedure and conditions as those employed for **8** using *t*BuLi (0.79 mL, 1.34 mmol, 1.7 M in pentane), **17** (0.190 g, 0.669 mmol), and PhC(H)=NCH$(CH_3)_2$ (0.108 g, 0.736 mmol). Purification by column chromatograph on silica gel using hexane and triethylamine (100:1 *v*/*v*) gave a colorless oil (0.150 g, 64%). ^1H NMR (600 MHz, C_6D_6): δ 8.32 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.2 Hz, 2H), 7.52 (d, *J* = 6.0 Hz, 1H), 7.34–7.24 (m, 3H), 7.24–7.11 (m, 4H), 7.11–7.04 (m, 2H), 5.23 (s, 1H, NCH), 2.81 (sept, *J* = 6.0 Hz, 1H, C*H*$(CH_3)_2$), 0.11–0.09 (m, 6H, CH(C*H*$_3$)$_2$ ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 23.17, 23.57, 46.43, 66.16, 120.30, 123.12, 125.49, 126.10, 126.46, 126.77, 127.30, 127.85, 128.28, 128.63, 128.72, 129.09, 132.01, 134.58, 136.88, 139.35, 144.40, 159.02, 163.50 ppm. IR (neat): *v* 3311 (N-H) cm^{-1}. HRMS(FAB): *m/z* calcd ([M+H]$^+$ $C_{25}H_{24}N_2$) 353.2018. Found: 353.2015.

*3.15. Cyclohexyl[(6-naphthalen-1-yl-pyridin-2-yl)phenylmethyl]amine (***19***)*

The compound was prepared by the same procedure and conditions as those employed for **8** using *t*BuLi (0.79 mL, 1.34 mmol, 1.7 M in pentane), **17** (0.190 g, 0.669 mmol), and PhC(H)=NC$(CH_3)_3$ (0.119 g, 0.736 mmol). Purification by column chromatograph on silica gel using hexane and triethylamine (100:1 *v*/*v*) gave a colorless oil (0.187 g, 76%). ^1H NMR (600 MHz, C_6D_6): δ 8.34 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.33–7.24 (m, 3H), 7.24–7.12 (m, 4H), 7.11–7.03 (m, 2H), 5.27 (s, 1H, NCH), 1.07 (s, 9H, C$(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 30.25, 51.64, 63.24, 120.46, 122.83, 125.49, 126.42, 126.76, 127.01, 128.69, 129.10, 132.00, 134.61, 136.79, 139.32, 146.89, 158.66, 165.02 ppm. IR (neat): *v* 3302 (N-H) cm^{-1}. HRMS(EI): *m/z* calcd ([M^+] $C_{26}H_{26}N_2$) 366.2096. Found: 366.2098.

*3.16. t-Butyl[(6-naphthalen-1-yl-pyridin-2-yl)phenylmethyl]amine (***20***)*

The compound was prepared by the same procedure and conditions as those employed for **8** using *t*BuLi (1.04 mL, 1.76 mmol, 1.7 M in pentane), **17** (0.250 g, 0.880 mmol), and PhC(H)=NC_6H_{11} (0.181 g, 0.968 mmol). Purification by column chromatograph on silica gel using hexane and triethylamine (*v*/*v*, 100:1) gave a colorless oil (0.238 g, 69%). ^1H NMR (600 MHz, C_6D_6): δ 8.34 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.52 (d, *J* = 6.6 Hz, 1H), 7.36–7.23 (m, 3H), 7.23–7.15 (m, 2H), 7.10–7.04 (m, 2H), 5.32 (s, 1H, NCH), 2.56 (tt, *J* = 9.6, 3.0 Hz, 1H, C_6H_{11}), 1.94 (d, *J* = 12 Hz, 2H, C_6H_{11}), 1.90 (d, *J* = 12.6 Hz, 2H, C_6H_{11}), 1.59 (s, 2H, C_6H_{11}), 1.41 (s, 1H, C_6H_{11}),

1.19–0.98 (m, 5H, C_6H_{11}) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 25.20, 26.62, 33.92, 34.29, 54.33, 65.61, 120.30, 123.12, 125.49, 126.10, 126.44, 126.80, 127.32, 128.63, 128.74, 129.10, 132.02, 134.60, 136.92, 139.36, 144.65 ppm. IR (neat): *v* 3310 (N-H) cm^{-1}. HRMS(FAB): *m*/*z* calcd ($[M+H]^+$ $C_{28}H_{28}N_2$) 393.2096. Found: 393.2329.

*3.17. Adamatyl[(6-naphthalen-1-yl-pyridin-2-yl)phenylmethyl]amine (**21**)*

The compound was prepared by the same procedure and conditions as those employed for **8** using *t*BuLi (1.04 mL, 1.76 mmol, 1.7 M in pentane), **17** (0.250 g, 0.880 mmol), and PhC(H)=$NC_{10}H_{16}$ (0.232 g, 0.968 mmol). Purification by column chromatograph on silica gel using hexane and triethylamine (100:1 *v*/*v*) gave a white glassy solid (0.260 g, 74%). ^1H NMR (600 MHz, C_6D_6): δ 8.38 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.66–7.59 (m, 4H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.37–7.25 (m, 4H), 7.25–7.18 (m, 3H), 7.12–7.05 (m, 2H), 5.45 (s, 1H, NCH), 2.56 (s, 1H, $C_{10}H_{16}$), 1.90 (s, 3H, $C_{10}H_{16}$), 1.67 (t, 6H, *J* = 15 Hz, $C_{10}H_{16}$), 1.51 (dd, 6H, *J* = 19.8, 12 Hz, $C_{10}H_{16}$) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 30.15, 37.03, 44.20, 51.93, 61.16, 120.49, 122.80, 125.49, 126.08, 126.40, 126.87, 126.97, 127.98, 128.39, 128.63, 128.67, 129.10, 132.02, 134.63, 136.79, 139.35 ppm. IR (neat): *v* 3293 (N-H) cm^{-1}. HRMS(EI): *m*/*z* calcd ($[M^+]$ $C_{32}H_{32}N_2$) 444.2565. Found: 444.2563.

3.18. Complex **22**

The complex was prepared by the same procedure and conditions as those employed for **3** using $HfCl_4$ (0.171 g, 0.534 mmol), MeMgBr (0.80 mL, 2.2 mmol, 3.0 M solution in diethyl ether), and **18** (0.126 g, 0.356 mmol). A yellow solid was obtained (0.164 g, 82%). Single crystals suitable for X-ray crystallography were obtained by recrystallization in toluene and hexane at −30 °C. ^1H NMR (600 MHz, C_6D_6): δ 8.64 (d, *J* = 7.2 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 2H), 7.09 (t, *J* = 7.2 Hz, 2H), 7.05 (t, *J* = 7.8 Hz, 1H), 6.73 (t, *J* = 7.8 Hz, 1H), 6.39 (d, *J* = 7.8 Hz, 1H), 5.85 (s, 1H, NCH), 3.98 (sept, *J* = 6.6 Hz, 1H, C*H*$(CH_3)_2$), 1.53 (d, *J* = 3.3 Hz, 3H, CH(CH_3)$_2$), 1.02 (d, *J* = 6.0 Hz, 3H, CH(CH_3)$_2$), 0.81 (s, 3H, $HfCH_3$), 0.77 (s, 3H, $HfCH_3$) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 22.13, 24.04, 46.31, 59.38, 60.35, 75.52, 119.82, 120.11, 124.11, 125.35, 126.86, 129.09, 129.77, 130.01, 130.62, 133.95, 135.70, 140.23, 144.18, 146.38, 164.45, 170.90, 204.71 ppm. Anal. Calcd. ($C_{27}H_{28}N_2Hf$): C, 58.01; H, 5.05; N, 5.01%. Found: C, 58.10; H, 5.16; N, 5.09%.

3.19. Complex **23**

The complex was prepared by the same procedure and conditions as those employed for **3** using $HfCl_4$ (0.131 g, 0.409 mmol), MeMgBr (0.60 mL, 1.7 mmol, 3.0 M solution in diethyl ether), and **19** (0.100 g, 0.272 mmol). A light brown solid was obtained (0.120 g, 79%). ^1H NMR (600 MHz, C_6D_6): δ 8.65 (d, *J* = 7.2 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 7.2 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 2H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.41 (d, *J* = 8.4 Hz, 1H), 5.93 (s, 1H, NCH), 3.56 (tt, *J* = 8.4, 3.6 Hz, 1H, C_6H_{11}), 2.17 (d, *J* = 11.4 Hz, 1H, C_6H_{11}), 2.06 (qd, 1H, *J* = 12, 3.6 Hz, C_6H_{11}), 1.93 (d, 1H, *J* = 12.6 Hz, C_6H_{11}), 1.81 (d, 1H, *J* = 13.8 Hz, C_6H_{11}), 1.61 (d, 1H, *J* = 12 Hz, C_6H_{11}), 1.50 (d, 1H, *J* = 13.2 Hz, C_6H_{11}), 1.25 (qt, 1H, *J* = 12, 3.6 Hz, C_6H_{11}), 1.20–0.97 (m, 3H, C_6H_{11}), 0.84 (s, 3H, $HfCH_3$), 0.80 (s, 3H, $HfCH_3$) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6): δ 26.45, 27.08, 27.49, 33.61, 35.43, 55.83, 59.25, 60.41, 75.78, 119.82, 120.10, 124.12, 125.35, 126.85, 129.08, 129.07, 130.00, 130.61, 134.00, 135.70, 140.22, 144.23, 146.53, 164.46, 170.99, 204.72 ppm. Anal. Calcd. ($C_{30}H_{32}N_2Hf$): C, 60.15; H, 5.38; N, 4.68%. Found: C, 60.32; H, 5.51; N, 4.83%.

3.20. Complex **24**

The complex was prepared by the same procedure and conditions as those employed for **3** using $HfCl_4$ (0.216 g, 0.675 mmol), MeMgBr (1.00 mL, 2.77 mmol, 3.0 M solution in diethyl ether), and **20** (0.165 g, 0.450 mmol). A yellow solid was obtained (0.209 g, 81%). Single crystals suitable for X-ray

crystallography were obtained by recrystallization in toluene and hexane at −30 °C. ^{1}H NMR (600 MHz, C_6D_6): δ 8.65 (d, *J* = 7.8 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.33–7.24 (m, 4H), 7.05 (t, *J* = 7.2 Hz, 3H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.70 (t, *J* = 7.2 Hz, 1H), 6.47 (d, *J* = 7.8 Hz, 1H), 5.88 (s, 1H, NCH), 1.43 (s, 9H, $C(CH_3)_3$), 1.03 (s, 3H, $HfCH_3$), 0.80 (s, 3H, $HfCH_3$) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, C_6D_6): δ 31.10, 55.17, 60.66, 63.223, 75.73, 119.26, 119.42, 124.02, 125.22, 126.78, 127.30, 127.42, 129.15, 129.77, 129.97, 130.55, 134.49, 135.42 ppm. Anal. Calcd. ($C_{28}H_{30}N_2Hf$): C, 58.69; H, 5.28; N, 4.89%. Found: C, 58.81; H, 5.38; N, 4.97%.

3.21. Complex **25**

The complex was prepared by the same procedure and conditions as those employed for **3** using $HfCl_4$ (0.256 g, 0.800 mmol), MeMgBr (1.10 mL, 3.28 mmol, 3.0 M solution in diethyl ether), and **21** (0.237 g, 0.533 mmol). A yellow solid was obtained (0.288 g, 83%). Single crystals suitable for X-ray crystallography were obtained by recrystallization in toluene/hexane cosolvent at −30 °C. ^{1}H NMR (600 MHz, C_6D_6): δ 8.68 (d, *J* = 7.8 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.33–7.25 (m, 2H), 7.08 (t, *J* = 7.8 Hz, 2H), 6.94 (t, *J* = 7.8 Hz, 1H), 6.73 (t, *J* = 7.8 Hz, 1H), 6.54 (d, *J* = 7.8 Hz, 1H), 6.05 (s, 1H, NCH), 2.33 (d, 3H, *J* = 11.4 Hz, $C_{10}H_{16}$), 2.10 (d, 3H, *J* = 10.8 Hz, $C_{10}H_{16}$), 2.02 (s, 3H, $C_{10}H_{16}$), 1.62 (d, 3H, *J* = 12 Hz, $C_{10}H_{16}$), 1.56 (d, 3H, *J* = 11.4 Hz, $C_{10}H_{16}$), 1.10 (s, 3H, $HfCH_3$), 0.86 (s, 3H, $HfCH_3$) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, C_6D_6): δ 30.30, 36.98, 44.25, 56.72, 61.04, 63.92, 73.91, 119.18, 119.44, 124.04, 125.20, 126.76, 127.16, 127.35, 127.98, 129.11, 129.73, 129.95, 130.55, 134.67, 135.42, 140.80, 143.10, 149.16, 164.91, 170.90, 204.57 ppm. Anal. Calcd. ($C_{34}H_{36}N_2Hf$): C, 62.71; H, 5.57; N, 4.30%. Found: C, 62.59; H, 5.44; N, 4.18%.

3.22. Polymerization

A bomb reactor (125 mL) was evacuated at 60 °C for 1 h. After charging with ethylene gas at atmospheric pressure, a solution of Me_3Al (28.8 mg, 200 μmol-Al) in methylcyclohexane (15.5 g) was added to the reactor. The mixture was stirred for 1 h at 100 °C using a mantle, and the solution was subsequently removed using a cannula. The reactor was evacuated once more to remove any residual solvent and was re-charged with ethylene gas at atmospheric pressure. This procedure was performed to clean up any catalyst poisons. The reactor was charged with methylcyclohexane (15.5 g), which contains MMAO (AkzoNobel, 6.7 wt%-Al in heptane, 20 mg, 50 μmol-Al) and the temperature was set to 80 °C. The methylcyclohexane solution (0.30 g) containing the catalyst (2.0 μmol-Hf) that was activated with $[(C_{18}H_{37})_2N(H)Me]^+[B(C_6F_5)_4]^-$ (1.0 eq) in benzene, was injected. Ethylene/propylene mixed gas (10 bar/10 bar, total 20 bar) was charged from a tank into the reactor at 20 bar, and the polymerization was performed for 50 min. The temperature was controlled within the range of 80–90 °C. The remaining ethylene/propylene mixed gas was vented off and the reactor was cooled to 75 °C. The generated polymer was collected and dried in a vacuum oven at 160 °C overnight.

3.23. X-Ray Crystallography

Reflection data for **4**, **22**, and **25** were collected at 100 K on an APEX II CCD area diffractometer (Bruker) using graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å). Specimens of suitable quality and size were selected, mounted, and centered in the X-ray beam using a video camera. The hemisphere of the reflection data was collected as φ and ω scan frames at 0.5 ° per frame and an exposure time of 10 s per frame. The cell parameters were determined and refined by the SMART program. Data reduction was performed using SAINT software. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program. The structures of the compounds were solved by direct methods and refined by full matrix least-squares methods using the SHELXTL package with anisotropic thermal parameters for all non-hydrogen atoms. CCDC 1903714, 1903716, and 1903715 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC,

12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk) Crystallographic data for **4** (CCDC 1903714): $C_{33}H_{47}HfN_3$, M = 664.23, monoclinic, a = 14.1271(3), b = 20.7207(3), c = 20.3386(3) Å, β = 90.4281(8) ° V = 5953.42(18) Å ^{3}, T = 100(2) K, space group C2/c, Z = 8, 6117 unique (R(int) = 0.0152) which were used in all calculations. The final wR_2 was 0.0385 (I >2σ(I)). Data for **22** (CCDC 1903716): $C_{27}H_{28}HfN_2$, M = 559.00, monoclinic, a = 7.4314(3), b = 17.1814(7), c = 35.3369(13) Å, β = 90.1529(18) °, V = 4511.9(3) Å^3, T = 100(2) K, space group $P2_1/_C$, Z = 8, 8305 unique (R(int) = 0.0805) which were used in all calculations. The final wR_2 was 0.1700 (I > 2σ(I)). Data for **25** (CCDC 1903715): $C_{34}H_{36}HfN_2$, M = 651.14, triclinic, a = 9.1883(6), b = 10.9598(7), c = 13.8783(9) Å, α = 75.009(4), β = 83.871(3), γ = 89.949(4) °, V = 1341.77(15) Å^3, T = 100(2) K, space group P-1, Z = 2, 4965 unique (R(int) = 0.0514) which were used in all calculations. The final wR_2 was 0.0696 (I >2σ(I)).

4. Conclusions

Various pincer-type Hf-complexes were prepared mimicking the prototype [$C^{naphthyl}$, $N^{pyridine}$, $N^{arylamido}$]$HfMe_2$ complex **I**. [$N^{arylamido}$, $N^{pyridine}$, $N^{arylamido}$]$HfMe_2$ and [$C^{silylmethyl}$, $N^{pyridine}$, $N^{arylamido}$]$HfMe_2$ pincer complexes, along with a series of [$C^{naphthyl}$, $N^{pyridine}$, $N^{alkylamido}$]$HfMe_2$ complexes where the arylamido moiety in the prototype complex was replaced with alkylamido moieties (alkyl = iPr, cyclohexyl, *t*Bu, and adamantyl), were successfully prepared by the treatment of the corresponding ligand precursors with in situ generated $HfMe_4$. In the case of analogous ligand precursor where the pyridine moiety was replaced with thiophene, the Hf-$C^{naphthyl}$ bond was not formed and the [S, N^{amido}]$HfMe_3$-type complex was generated instead. Most of the prepared complexes cleanly generated the desired ion-pair complex when treated with $[(C_{18}H_{37})_2N(H)Me]^+[B(C_6F_5)_4]^-$. However, the generated ion-pair complexes were inactive in ethylene/propylene copolymerization. Several complexes bearing the bulky iPr_3Si- or adamantyl substituent exhibited moderate activities (approximately 1/10th that of **I**), although the ^{1}H NMR spectra were not clean in the activation reaction with $[(C_{18}H_{37})_2N(H)Me]^+[B(C_6F_5)_4]^-$.

Supplementary Materials: The following are available online, Figures S1–S20: ^{1}H and ^{13}C NMR spectra of **3**, **4**, **6**, **8**, **9**, **10**, **11**, **12**, **13**, **14**, **15**, **16**, **18**, **19**, **20**, **21**, **22**, **23**, **24**, and **25**, Figures S21–S29: ^{1}H NMR spectra of the complexes activated with $[(C_{18}H_{37})_2N(H)Me]^+[B(C_6F_5)_4]^-$.

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Sample Availability: Samples of the compounds **3**, **4**, **22**–**25** are available from the authors.