Zirconium and Hafnium Complexes that Contain the Electron-Withdrawing Diamido/Donor Ligands $[(2,6\text{-}X_2C_6H_3NCH_2)_2C(2\text{-}C_5H_4N)(CH_3)]^{2-}$ (X = Cl or F). An Evaluation of the Role of Ortho Halides in 1-Hexene Polymerization

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Received July 11, 2003

The pyridyldiamines $[(2,6\text{-}X_2C_6H_3NHCH_2)_2C(CH_3)(2\text{-}C_5H_4N)]$ (X = Cl or F) can be prepared in good yield through the Pd-catalyzed coupling between 2,6-dihalobromobenzene and $(H_2\text{-}NCH_2)_2C(CH_3)(2\text{-}C_5H_4N)$. Zirconium and hafnium complexes that contain these ligands were prepared through traditional routes; they include $[Ar_{Cl2}Npy]M(NMe_2)_2$ (M = Zr or Hf), $[Ar_{Cl2}\text{-}Npy]MCl_2$, $[Ar_{Cl2}Npy]MMe_2$, $[Ar_{Cl2}Npy]Hf(i\text{-}Bu)_2$, $[Ar_{F2}Npy]Hf(i\text{-}Bu)_2$, and $[Ar_{F2}Npy]HfMe_2$. Attempts to prepare $[Ar_{F2}Npy]Hf(NMe_2)_2$ in a reaction between $Hf(NMe_2)_4$ and free ligand led to compounds in which one or two dimethylamino groups had been exchanged with one or two ortho fluorides on the 2,6-difluorophenyl rings. Compounds whose structures were determined in X-ray studies include $[Ar_{Cl2}Npy]Hf(i\text{-}Bu)_2$, $[Ar_{F2}Npy]Hf(i\text{-}Bu)_2$, and $[Ar_{(FNMe2)2}\text{-}Npy]Hf(F)Cl$, a compound that contains 2-fluoro-6-dimethylaminophenyl rings. In the first compound one chloride is weakly bonded to the metal, in the second two fluorides are weakly bonded to the metal, and in the third two dimethylamino groups are strongly bonded to the metal. Activation of dimethyl species with $[Ph_3C][B(C_6F_5)_4]$ in bromobenzene led initially to the formation of dimeric monocations such as $\{[Ar_{X2}Npy]_2M_2Me_3\}[B(C_6F_5)_4]$, which are inactive for polymerization of 1-hexene. The $\{[Ar_{X2}Npy]_2M_2Me_3\}[B(C_6F_5)_4]$ compounds react further with $[Ph_3C][B(C_6F_5)_4]$ to give $\{[Ar_{X2}Npy]MMe\}[B(C_6F_5)_4]$ species, which are active for polymerization of 1-hexene. Activation of $[Ar_{X2}Npy]Hf(i\text{-}Bu)_2$ complexes with $[Ph_3C]\text{-}[B(C_6F_5)_4]$ in bromobenzene led to the formation of $\{[Ar_{X2}Npy]Hf(i\text{-}Bu)\}[B(C_6F_5)_4]$ species that are also active for the polymerization of 1-hexene. The rate of consumption of 1-hexene followed a first-order dependence on 1-hexene (and hafnium), although the rates were substantially slower compared to those for the known catalyst with mesityl substituents on the amido nitrogens and slower when X = F than when X = Cl. The ease of preparation of the cations also followed the order aryl = mesityl > $2,6\text{-}Cl_2C_6H_3$ > $2,6\text{-}F_2C_6H_3$. Finally, the quality of the polymerization, in terms of its living characteristics, deteriorated markedly when the aryl was $2,6\text{-}F_2C_6H_3$. We conclude that the introduction of ortho chlorides or fluorides decreases the rate of polymerization and also encourages β hydride elimination and formation of shorter polymer chains, therefore compromising the living characteristics of the polymerization.

Introduction

Recent activity in the area of Ziegler−Natta catalysis has centered on the development of well-behaved, nonmetallocene systems for the polymerization of ordinary α-olefins.[1−12] Our attention recently has focused on zirconium and hafnium dialkyl complexes containing diamido/donor ligands that can be activated to yield cationic initiators for the living polymerization of ordinary olefins.[3,11−15] We have recently explored catalysts

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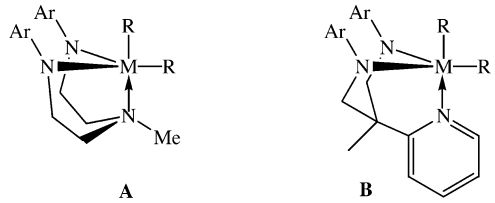
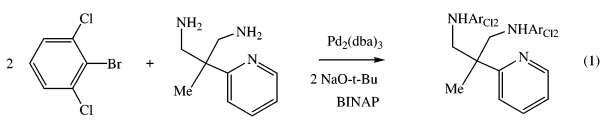
10.1021/om0305364 CCC: $25.00
Publication on Web 10/31/2003

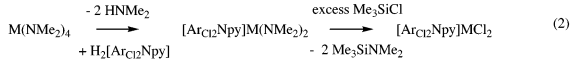
containing $[(ArNCH_2)_2C(CH_3)(2\text{-}C_5H_4N)]^{2-}$ ($[ArNpy]^{2-}$; see structure **B** below),[3,15,16] which is an arylated version of the trimethylsilyl-substituted ligand developed by Gade.[17] Cationic zirconium and hafnium complexes formed from complexes of type **B** (Ar = mesityl) are relatively stable toward CH activation during the polymerization of up to 600 equiv of 1-hexene at 0 °C in bromobenzene or chlorobenzene.[3,15] In contrast, cationic zirconium complexes formed from complexes of type **A** (Ar = mesityl)[4,18] are deactivated via aryl ortho-methyl CH activation. Since we found that 2,6-$Cl_2C_6H_3$ substituents were viable alternatives to mesityl groups in catalysts derived from complexes of type **A**,[4] we became interested in the possibility of preparing catalysts of type **B** that contain 2,6-$X_2C_6H_3$ groups (X = Cl or F). We hoped to compare the catalytic activity of complexes that contain 2,6-$X_2C_6H_3$ aryl groups on the amido nitrogens with those that contain 2,4,6-$Me_3C_6H_2$ (mesityl) groups on the amido nitrogens. The results of this study are reported here.



Results

Preparation of $[(2,6\text{-}Cl_2C_6H_3NCH_2)_2C(CH_3)(2\text{-}C_5H_4N)]^{2-}$ ($[Ar_{Cl2}Npy]^{2-}$) Complexes. The palladium-catalyzed coupling reaction[19,20] between 2,6-dichlorobromobenzene and $(H_2NCH_2)_2C(CH_3)(2\text{-}C_5H_4N)$ produces $H_2[Ar_{Cl2}Npy]$ in good yield (65%, eq 1). Impurities arising from what is believed to be competitive coupling at the 2 and 6 positions of 2,6-dichlorobromobenzene (5%) cannot be eliminated, however, and impure $H_2[Ar_{Cl2}Npy]$ must be employed to prepare zirconium and hafnium complexes. As shown in eq 2, $[Ar_{Cl2}Npy]MCl_2$ is synthesized via a method analogous to that employed to prepare zirconium and hafnium complexes bearing $[MesNpy]^{2-}$ ligands.[3,15,16] Alkylation of the $[Ar_{Cl2}Npy]MCl_2$ complexes with Grignard reagents proceeds smoothly to yield $[Ar_{Cl2}Npy]MR_2$ complexes, where M = Zr and R = Me, or M = Hf and R = Me or i-Bu. $[Ar_{Cl2}Npy]Zr(i\text{-}Bu)_2$ is unstable at room temperature and therefore could not be isolated. Impurities formed as a consequence of competitive coupling in the ligand synthesis are removed by recrystallization of either the $[Ar_{Cl2}Npy]M(NMe_2)_2$ or $[Ar_{Cl2}Npy]MR_2$ complexes.





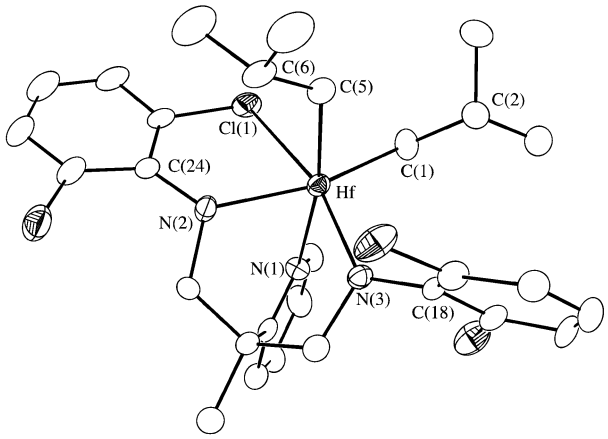


Figure 1. Thermal ellipsoid drawing of $[Ar_{Cl2}Npy]Hf(i\text{-}Bu)_2$.

The X-ray structure of $[Ar_{Cl2}Npy]Hf(i\text{-}Bu)_2$ (Figure 1, Table 1) features a distorted octahedral species in which one ortho chloride (Cl(1)) interacts weakly with the metal (Hf−Cl(1) = 2.760(3) Å). (Selected bond distances and angles can be found in Table 2.) The Hf−C and Hf−N distances are not unusual for a complex of this type, and the magnitudes of the Hf−C−C angles (125.7(9)° and 116.4(9)°) do not suggest any agostic interaction[21] between the β alkyl protons and the metal. It is interesting to note that the Hf−N(2)−C(24) and Hf−N(3)−C(18) angles are essentially identical (131.0(7)° and 128.9(7)°, respectively). Therefore the interaction between Cl(1) and the metal must take place simply by rotation of the aryl ring into the Hf−N(2)−C(24) plane. The Hf−Cl interaction apparently is not strong enough to permit the formation of a sterically congested seven-coordinate complex with two coordinating aryl ortho chlorides.

Room-temperature NMR spectra of $[Ar_{Cl2}Npy]Hf(i\text{-}Bu)_2$ feature separate resonances for axial and equatorial alkyl groups and mirror symmetry consistent with a TBP structure rather than an octahedral structure. Therefore the Hf−Cl interaction does not persist in solution at room temperature. ^{1}H-NOESY experiments exhibited a cross-peak between the equatorial bound alkyl methylene and the pyridyl ortho proton (H_o), showing that the methylene resonance for the equatorial alkyl group is found at lower field than the methylene resonance for the axial alkyl group. In the zirconium dimethyl species, the ^{1}H NMR methyl resonances appear as two broadened singlets, characteristic of exchange of axial and equatorial methyl groups on the NMR time scale. Upon mixing $[Ar_{Cl2}Npy]Hf^{13}Me_2$ and $[Ar_{Cl2}Npy]ZrMe_2$ in benzene at 22 °C, the methyl groups scrambled between the two metals within seconds. Therefore we believe that the broad methyl resonances can be ascribed to rapid intermolecular exchange.[16] In contrast, the i-Bu resonances are sharp because intermolecular exchange is relatively slow on the NMR time scale due to steric constraints.

A second dynamic process that can be observed in these compounds is restricted rotation of the aryl

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Table 1. Crystal Data and Structure Refinement for [Ar_{Cl2}Npy]Hf(i-Bu)$_2$, [$Ar_{(FNMe2)2}$Npy]Hf(F)Cl, and [Ar_{F2}Npy]Hf(i-Bu)$_2$

	[Ar_{Cl2}Npy]Hf(i-Bu)	[$Ar_{(FNMe2)2}$Npy]Hf(F)Cl	[Ar_{F2}Npy]Hf(i-Bu)$_2$
empirical formula	$C_{29}H_{35}Cl_4HfN$	$C_{25}H_{29}ClF_3HfN_5$	$C_{29}H_{35}F_4HfN_3$
fw	745.92	670.47	680.09
temperature (K	293(2)	293(2)	273(2)
cryst syst, space group	monoclinic, *P*2(1)/*n*	monoclinic, *P*2(1)	monoclinic, *C*2/*c*
unit cell dimens	$a = 15.562(3)$ Å	$a = 8.4334(14)$ Å	$a = 15.2329(9)$ Å
	$b = 12.314(3)$ Å	$b = 17.106(3)$ Å	$b = 12.1484(7)$ Å
	$c = 16.897(5)$ Å	$c = 9.2935(16)$ Å	$c = 29.4719(17)$ Å
	$\alpha = 90°$	$\alpha = 90°$	$\alpha = 90°$
	$\beta = 109.925(15)°$	$\beta = 111.336(3)°$	$\beta = 96.2770(10)°$
	$\gamma = 90°$	$\gamma = 90°$	$\gamma = 90°$
volume (Å^3)	3044.0(13)	1248.8(4)	5421.2(5)
Z, calcd density (Mg/m^3)	4, 1.628	2, 1.78	8, 1.667
abs coeff (mm^{-1})	3.801	4.330	3.899
F(000)	148	660	2704
θ range for data collection (deg)	2.19 to 23.34	2.35 to 20.98	2.48 to 28.31
limiting indices	$-17 \le h \le 11$, $-10 \le k \le 6$, $-12 \le l \le 18$	$-8 \le h \le 8$, $-14 \le k \le 17$, $-9 \le l \le 9$	$-18 \le h \le 18$, $-16 \le k \le 7$, $-39 \le l \le 37$
no. of reflns collected/unique	5603	4017	14 787
no. of indep reflns	3585 [*R*(int) = 0.0431]	1398 [*R*(int) = 0.0536]	6180 [*R*(int) = 0.0735]
completeness to θ max	81.2%	99.8%	91.8%
no. of data/restraints/params	3585/0/33	1398/0/178	6180/0/340
goodness-of-fit on F^2	1.056	1.263	1.020
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0645, wR2 = 0.150	R1 = 0.0540, wR2 = 0.1152	R1 = 0.0367, wR2 = 0.0898
R indices (all data)	R1 = 0.0770, wR2 = 0.159	R1 = 0.0574, wR2 = 0.1166	R1 = 0.0498, wR2 = 0.0945
largest diff peak and hole (e Å^{-3})	2.149 and −3.583	1.533 and −2.586	2.496 and −1.215

[a] In each case the wavelength was 0.71073 Å and the refinement method was full-matrix least-squares on F^2. No absorption correction was applied.

Table 2. Selected Bond Distances (Å) and Angles (deg) in [Ar_{Cl2}Npy]Hf(i-Bu)$_2$

Hf−N(1)	2.416(9)	N(2)−Hf−C(5)	97.4(4)
Hf−N(2)	2.112(9)	N(2)−Hf−Cl(1)	70.2(3)
Hf−N(3	2.048(8	N(3)−Hf−C(1)	106.6(4)
Hf−C(1)	2.261(11)	N(3)−Hf−C(5	104.2(4)
Hf−C(5	2.222(12)	N(3)−Hf−Cl(1)	161.8(3)
Hf−Cl(1	2.760(3	C(1)−Hf−Cl(1)	79.1(3)
N(1)−Hf−N(2)	75.2(3)	C(1)−Hf−C(5	96.8(5)
N(1)−Hf−N(3)	83.2(4	C(5)−Hf−Cl(1)	92.0(3)
N(1)−Hf−C(1)	86.7(4)	C(24)−N(2)−Hf	131.0(7)
N(1)−Hf−C(5	170.4(4)	C(18)−N(3)−Hf	128.9(7)
N(1)−Hf−Cl(1)	79.8(2	C(6)−C(5)−Hf	125.7(9)
N(2)−Hf−N(3)	99.1(3)	C(2)−C(1)−H	116.4(9)
N(2)−Hf−C(1)	146.5(4)		

groups, as indicated by the inequivalence of the meta protons in the 2,6-dichlorophenyl ring. The barrier toward aryl ring rotation is slightly larger in [Ar_{Cl2}Npy]Hf(i-Bu)$_2$ than in [Ar_{Cl2}Npy]HfMe_2; that is, the barrier is higher in the more crowded complexes. The coalescence temperatures (at 400 mHz), respectively, are −67 and −90 °C, with activation energies at the coalescence temperature of ∼40 and ∼35 kJ mol^{-1}, respectively. A higher barrier toward ring rotation in more crowded circumstances would be expected as a consequence of a straightforward steric effect.

Preparation of [(2,6-$F_2C_6H_3NCH_2)_2C(CH_3)$(2-C_5H_4N)]$^{2-}$ ([Ar_{F2}Npy]$^{2-}$) Complexes. The coupling reaction between 1-bromo-2,6-difluorobenzene and (H_2-$NCH_2)_2$C(Me)(2-py) proceeded at a much slower rate than the coupling reaction to give H_2[Ar_{Cl2}Npy], affording H_2[Ar_{F2}Npy] in only 37% yield. In contrast to the 24 h reaction time required to prepare H_2[Ar_{Cl2}Npy], temperatures up to 120 °C for 4 to 5 days still failed to convert all of the monoarylated intermediate to the desired H_2[Ar_{F2}Npy]. Ultimately H_2[Ar_{F2}Npy] was obtained free from impurities by column chromatography, in contrast to H_2[Ar_{Cl2}Npy], which could not be separated from impurities in this manner.

H_2[Ar_{F2}Npy] reacted readily with Hf(NMe_2)$_4$; however, the primary product was [$Ar_{F2;FNMe2}$Npy]HfF(NMe_2) (**3**, Scheme 1), with [Ar_{F2}Npy]Hf(NMe_2)$_2$ (**1**, Scheme 1) formed only in trace quantities (≤5%). In **3** one of the four ortho fluorides has been replaced by a dimethylamido group, and the fluoride transferred to the metal. The ^{1}H NMR and ^{19}F NMR spectra at 22 °C are indicative of an asymmetric complex with the aryl NMe_2 moiety coordinating strongly to the metal and the 2,6-difluoro aryl ring rotating freely. Two separate singlets, each representing three hydrogens, are observed for the donor NMe_2 group, while a singlet representing six hydrogens is observed for the covalently bound NMe_2 ligand. This type of exchange of a dimethylamido group for an ortho aryl fluoride has been documented in a related molybdenum system.[22]

The ^{19}F NMR spectrum of **3** consists of three resonances representing a total of four fluorides. Two resonances at −128.6 and −122.0 ppm show fine structure as a consequence of coupling with aryl hydrogens (J_{FH} = 6 Hz). The resonance at −122.0 ppm (representing two fluorides) is further split into a doublet by the fluoride covalently bound to the metal (J_{FF} = 32.9 Hz). Conversely, the Hf−F resonance appears as a triplet (J_{FF} = 32.9 Hz) at 28.5 ppm, which is in the expected range for a metal-bound fluoride.[23−27] Observation of only one doublet for the two fluorides in the 2,6-$F_2C_6H_3$ ring confirms that the 2,6-$F_2C_6H_3$ ring

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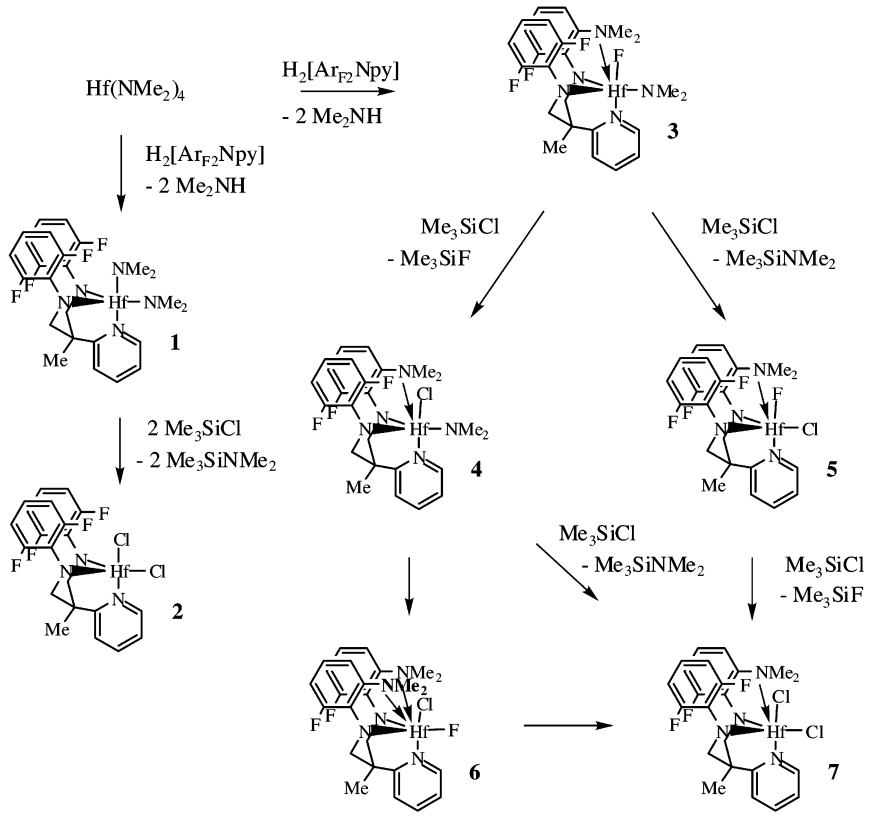
Scheme 1. Reactions Leading to Products 1−7



rotates freely on the NMR time scale, as noted in proton NMR spectra.

The presence of $[Ar_{F2}Npy]Hf(NMe_2)_2$ (**1**) as a product of the reaction between $Hf(NMe_2)_4$ and $H_2[Ar_{F2}Npy]$ was overlooked initially. Compound **1** can be identified by a pyridyl H_o resonance at 8.42 ppm. (The H_o resonance in free ligand is found at 8.35 ppm.) $[Ar_{F2}Npy]Hf(NMe_2)_2$ is more soluble in both ether and pentane than **3**, and therefore is removed easily upon recrystallization of the crude product from ether, and identified more easily in the residue obtained from the mother liquor. The ^{19}F NMR spectrum of **1** gives rise to one singlet at −125.1 ppm with fine structure (J_{FH} = 6.8 Hz) characteristic of aryl fluorides in a mirror symmetric species with two 2,6-$F_2C_6H_3$ rings that rotate freely on the NMR time scale at 22 °C. Subsequent reaction of the crude product with Me_3SiCl led to formation of small amounts of $[Ar_{F2}Npy]HfCl_2$ (**2**). NMR spectra of **2** are also consistent with the presence of a plane of symmetry on the NMR time scale and freely rotating aryl rings.

The reaction of pure **3** with excess Me_3SiCl afforded $[Ar_{F2;FNMe2}Npy]HfCl_2$ (**7**, Scheme 1) in good yield; that is, both the Hf−F and Hf−NMe_2 groups are replaced by chlorides upon reaction with excess Me_3SiCl. Addition of 1 equiv of Me_3SiCl to **3** yields $[Ar_{F2;FNMe2}Npy]HfCl(NMe_2)$ (**4**) according to NMR experiments. This result suggests that **4** is a more likely intermediate than $[Ar_{F2;FNMe2}Npy]Hf(F)Cl$ (**5**); that is, the fluoride bound to hafnium is replaced more readily than the dimethylamido group. The ^{19}F spectrum of **7** contained a resonance for two fluorides at −120.9 ppm and a resonance for one fluoride at −129.7 ppm. No resonance was observed downfield characteristic of a fluoride on the metal. Compound **7** is relatively insoluble in toluene and therefore could be isolated cleanly by filtration. In a typical reaction, several products remained in solution in addition to **7**. One was $[Ar_{F2}Npy]HfCl_2$ (**2**), the presence of which confirmed that $[Ar_{F2}Npy]Hf(NMe_2)_2$ was present in the sample of crude **3**. Another compound that was identified in the toluene solution was $[Ar_{(FNMe2)2}Npy]Hf(F)Cl$ (**6**), a species with mirror symmetry in which a second ortho fluoride has been exchanged with an amido group to give a compound in which two aryl NMe_2 groups are coordinating to hafnium. Compound **6** could be derived directly from **4** as a result of dimethylamido/fluoride exchange.

Recrystallization of a sample of **7** from ether led to a product that we initially assumed to be a purer sample of **7**. Three successive recrystallizations were required to obtain X-ray quality yellow-orange, single crystals. In fact the recrystallization process had succeeded in concentrating and purifying the least soluble component of the crude reaction, which turned out to be **6** (Scheme 1). The ^{19}F NMR spectrum of **6** contains a resonance at −127.5 ppm for two equivalent ortho aryl fluorides (J_{FH} = 6.3 Hz) and a resonance at 45.8 ppm for a single fluoride on the metal (J_{FH} = 6.3 Hz).

The X-ray structure of $[Ar_{(FNMe2)2}Npy]Hf(F)Cl$ (**6**) is shown in Figure 2. (See also Tables 1 and 3.) In this seven-coordinate species the aryl NMe_2 donors are coordinated to the metal at a distance of 2.459(11) Å, while the pyridine donor is bound at a distance of 2.355(14) Å. The Hf−N_{donor} bond length (2.459(11) Å) is significantly longer than the covalent Hf−N bond lengths (2.136(10) Å). Also notable is the Hf−N(2)−C(8) bond angle of 119.6(7)°, which is smaller than in $[Ar_{Cl2}Npy]Hf(i\text{-}Bu)_2$ as a consequence of strong coordination of the *o*-NMe_2 group. In a closely related molybdenum difluoride complex in which the substituents on the amido nitrogens are *o*-dimethylamidotetrafluorophenyls

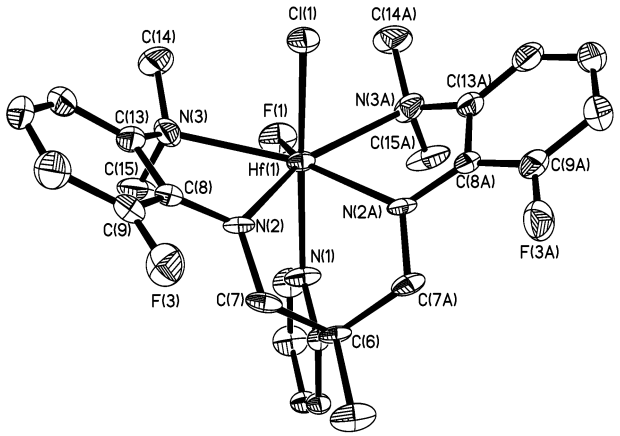


Figure 2. Thermal ellipsoid drawing of [$Ar_{(FNMe2)2}$Npy]-Hf(F)Cl (**6**).

Table 3. Bond Lengths (Å) and Angles (deg) for [$Ar_{(FNMe2)2}$Npy]Hf(F)Cl.

Hf−F(1)	1.989(9	Hf−N(2)	2.136(10)
Hf−Cl(1	2.440(4)	Hf−N(3)	2.459(11)
Hf−N(1)	2.355(14)	Hf−N(2)−C(8)	119.6(7)
F(1)−Hf−Cl(1)	108.0(4)	Cl(1)−Hf−N(3)	81.5(3)
F(1)−Hf−N(1)	79.8(5)	N(1)−Hf−N(2)	79.9(3)
F(1)−Hf−N(2)	132.1(3)	N(1)−Hf−N(3)	101.2(3)
F(1)−Hf−N(3)	72.8(3)	N(2)−Hf−N(3)	154.0(4)
Cl(1)−Hf−N(1)	172.2(4)	N(2)−Hf−N(2A)	85.5(5)
Cl(1)−Hf−N(2)	94.4(3)	N(3)−Hf−N(3A)	134.3(5)

(Ar′ in [(Ar′$NCH_2CH_2)_2$NMe]HfF_2)[22] the NMe_2 donors are coordinated to the metal at distances of 2.482(5) and 2.440(5) Å, the amine donor is bound at a distance of 2.330(5) Å, and the covalent Mo−N bond lengths are 2.008(5) and 2.013(5) Å. The M−F bond lengths in the two compounds are 1.989(9) Å (Hf) and 1.968(3) Å (Mo).

The reaction between **7** and 2.1 equiv of i-BuMgCl resulted in formation of [$Ar_{F2;FNMe2}$Npy]HfCl(i-Bu). As expected, no metal-bound fluoride could be found in the ^{19}F NMR spectrum. Further substitution of the chloride to give [$Ar_{F2;FNMe2}$Npy]Hf(i-$Bu)_2$ did not occur, most likely because [$Ar_{F2;FNMe2}$Npy]HfCl(i-Bu) is much more crowded than **7** and the metal is not as electrophilic. However, **7** reacted with 2 equiv of MeMgBr in 1 h at room temperature to give [$Ar_{F2;FNMe2}$Npy]$HfMe_2$ according to NMR spectra. Activation of [$Ar_{F2;FNMe2}$Npy]$HfMe_2$ with [Ph_3C][$B(C_6F_5)_4$] yielded a monomethyl cationic species that did not react readily with 1-hexene under the conditions used in similar experiments described later.

Because $Hf(NMe_2)_4$ could not be employed in the synthesis of [Ar_{F2}Npy]HfR_2 complexes, the synthesis of [Ar_{F2}Npy]Hf(i-$Bu)_2$ was attempted "directly" from $HfCl_4$ by forming a complex between $HfCl_4$ and the ligand prior to the addition of 4.1 equiv of i-BuMgCl. After several experiments in ether and toluene, we found that dichloromethane was a suitable solvent for forming the initial adduct. In order for the reaction to succeed, complete dissolution of $HfCl_4$ in the presence of ligand is essential. After 36 h, the solvent was removed in vacuo to afford the adduct between H_2[Ar_{F2}Npy] and $HfCl_4$ as a yellow powder. Isobutylmagnesium chloride (4.1 equiv) was then added to a suspension of this adduct in ether that had been cooled to −30 °C. After filtering the mixture through Celite, the ether-soluble portion was concentrated in vacuo and the product

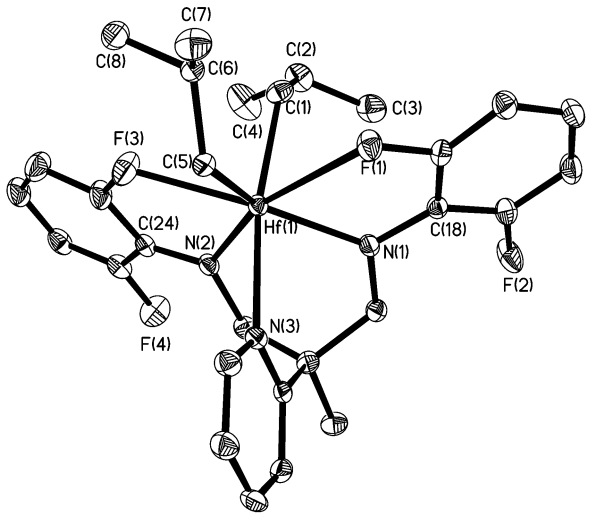


Figure 3. Thermal ellipsoid drawing of [Ar_{F2}Npy]Hf(i-$Bu)_2$.

Table 4. Bond Lengths (Å) and Angles (deg) for [Ar_{F2}Npy]Hf(i-$Bu)_2$.

Hf−N(2	2.103(3)	N(1)−Hf−F(3)	162.34(13)
Hf−N(1	2.117(4)	N(1)−Hf−N(2)	96.38(14)
Hf−C(1)	2.261(5)	F(1)−Hf−C(5)	67.16(13)
Hf−C(5	2.277(4)	F(1)−Hf−C(1)	78.37(15)
Hf−N(3)	2.442(4)	F(1)−Hf−F(3)	130.41(9)
Hf−F(3	2.443(3)	F(1)−Hf−N(2)	161.59(12)
Hf−F(1)	2.674(3)	C(5)−Hf−C(1)	99.06(16)
N(3)−Hf−N(1)	76.36(13)	C(5)−Hf−F(3)	71.33(14)
N(3)−Hf−F(1)	96.09(11)	C(5)−Hf−N(2)	129.16(15)
N(3)−Hf−C(5)	85.48(14)	C(1)−Hf−N(2)	104.23(16)
N(3)−Hf−C(1)	170.66(15)	C(1)−Hf−F(3)	82.65(16)
N(3)−Hf−F(3)	106.59(12)	N(2)−Hf−F(3)	67.76(13)
N(3)−Hf−N(2)	78.67(13)	C(18)−N(1)−Hf	125.2(3)
N(1)−Hf−F(1)	65.22(11)	C(24)−N(2)−Hf	124.8(3)
N(1)−Hf−C(5)	126.28(15)	C(2)−C(1)−Hf	129.3(4)
		C(6)−C(5)−Hf	120.4(3)

recrystallized from a mixture of ether and pentane (1:4) to give [Ar_{F2}Npy]Hf(i-$Bu)_2$ in 52% yield. When equivalent amounts of H_2[Ar_{F2}Npy] and $HfCl_4$ were used, free ligand (<5%) was present as an impurity and could not be removed easily. When a slight excess of $HfCl_4$ was employed, however, clean [Ar_{F2}Npy]Hf(i-$Bu)_2$ was obtained without successive recrystallization. Although this is not a high-yield route to [Ar_{F2}Npy]Hf-(i-$Bu)_2$, it is the only one available thus far.

The X-ray structure of [Ar_{F2}Npy]Hf(i-$Bu)_2$ is shown in Figure 3. (See also Table 1 for crystal and structure refinement data and Table 4 for selected bond lengths and angles.) Two ortho fluorides in the 2,6-difluorophenyl rings are interacting weakly with the metal at distances of 2.443(3) and 2.674(3) Å to form a sterically congested seven-coordinate complex. The pyridine donor is bound at a distance of 2.442(4) Å, and the covalent Hf−N bond lengths are 2.103(3) and 2.117(4) Å, which are similar to those found in the analogous compound that contains 2,6-dichlorophenyl substituents. The Hf−N(2)−C(24) and Hf−N(3)−C(18) angles are smaller than those in [Ar_{Cl2}Npy]Hf(i-$Bu)_2$ (124.8° and 125.2°, respectively, compared to 131.0° and 128.9°, respectively), but larger than those in **6** (119.6°). We propose that two fluorides are interacting in this complex (versus only one chloride in [Ar_{Cl2}Npy]Hf(i-$Bu)_2$) as a consequence of the more electron-poor nature of the metal and the smaller size of a fluoride versus a chloride.

The synthesis of $[Ar_{F2}Npy]HfMe_2$ was also successful through the direct route. The initial yield was much higher (89%); however, the reaction was not as clean as in the case of $[Ar_{F2}Npy]Hf(i\text{-}Bu)_2$, with an unidentifiable impurity being formed (~10%). This impurity could be removed through recrystallization, leading to pure $[Ar_{F2}Npy]HfMe_2$ in a yield of 43%.

Attempts to prepare $[Ar_{Cl2}Npy]Hf(i\text{-}Bu)_2$ in a similar direct manner failed. Only trace amounts of $[Ar_{Cl2}Npy]Hf(i\text{-}Bu)_2$ were observed. The synthesis of $[Ar_{Cl2}Npy]HfMe_2$ in this manner was more promising, although clean $[Ar_{Cl2}Npy]HfMe_2$ could be obtained in a yield of only about 10%.

Activation of $[(2,6\text{-}Cl_2C_6H_3NCH_2)_2C(CH_3)(2\text{-}C_5H_4N)]^{2-}$ ($[Ar_{Cl2}Npy]^{2-}$) Complexes. Addition of $[Ph_3C][B(C_6F_5)_4]$ to the $[Ar_{Cl2}Npy]MMe_2$ complexes (M = Zr or Hf) resulted in formation of dimeric monocations, $\{[Ar_{Cl2}Npy]_2M_2Me_3\}^+$; that is, $\{[Ar_{Cl2}Npy]MMe\}^+$ is formed and captured rapidly by $[Ar_{Cl2}Npy]HfMe_2$, as shown in eq 3. Therefore only 0.5 equiv of $[Ph_3C][B(C_6F_5)_4]$ is consumed. Proton and carbon NMR spectra of this hafnium species show a broad resonance for the methyl group at ~1.3 ppm in the proton NMR spectrum and ~42.9 ppm in the carbon NMR spectrum. In the zirconium species these resonances are found at 1.13 and 44.64 ppm ($^1J_{CH}$ = 109.5 Hz), respectively, and are not as broad as in the hafnium case. Variable-temperature ^{13}C NMR studies of the hafnium species showed that the broad methyl resonance splits into two at 52.2 (3 protons) and 38.0 (6 protons) at −60 °C, consistent with two types of methyl groups being present in the dimer. These observations are similar to those made for $\{[ArNpy]_2Zr_2Me_3\}^+$ (Ar = mesityl or 2,4,6-i-$Pr_3C_6H_2$) species.[28] A dimeric monocation of this general type, but with the $[(MesNCH_2CH_2)_2NMe]^{2-}$ ligand, was shown in an X-ray study to contain one bridging methyl group.[14] In the analogous $\{[MesNpy]_2M_2Me_3\}^+$ species, it was proposed that three bridging methyl groups are present in the ratio of 2:1 by virtue of the mirror plane of symmetry. The same is proposed to be the case in $\{[Ar_{Cl2}Npy]_2M_2Me_3\}^+$, as shown in eq 3. The mechanism by which the three methyl groups average intramolecularly is not known. We cannot discount the possibility that the pyridyl donor dissociates from the metal at one or both metal centers, thereby leading to a five-coordinate metal center that can rearrange by a pseudorotation or turnstile mechanism.

The $\{[Ar_{Cl2}Npy]_2M_2Me_3\}^+$ cations are slowly converted into monomeric monocations in the presence of $[Ph_3C][B(C_6F_5)_4]$. In the zirconium system the conversion requires a few minutes at 20 °C at the concentrations employed (12−17 mM), while more than 2 h is required in the hafnium system under similar conditions. We propose that the dimeric monocation dissociates to a small extent to give the monomethyl cation $\{[Ar_{Cl2}Npy]MMe\}^+$ and the (unobservable) dimethyl species $[Ar_{Cl2}Npy]MMe_2$. Trityl then reacts with the dimethyl species in competition with recombination of $[Ar_{Cl2}Npy]MMe_2$ with $\{[Ar_{Cl2}Npy]MMe\}^+$; we do not believe that $[Ph_3C][B(C_6F_5)_4]$ reacts with the dimeric monocation itself. In contrast, in the mesityl system $\{[MesNpy]_2Zr_2Me_3\}^+$ dissociates into $\{[MesNpy]ZrMe\}^+$ and $[MesNpy]ZrMe_2$ significantly more slowly,[28] and therefore pure $\{[MesNpy]ZrMe\}[B(C_6F_5)_4]$ species could not be prepared. We propose that the ortho chlorides assist in breaking up the $\{[Ar_{Cl2}Npy]_2M_2Me_3\}^+$ cation by coordinating weakly to the metal and perhaps also by stabilizing $\{[Ar_{Cl2}Npy]MMe\}^+$, thereby making $[Ar_{Cl2}Npy]MMe_2$ available in a high enough concentration to react with $[Ph_3C][B(C_6F_5)_4]$ at a practical rate. The methyl resonances in the $\{[Ar_{Cl2}Npy]MMe\}^+$ species are found in the proton NMR spectra at 0.88 ppm (Zr) and 0.63 ppm (Hf) in bromobenzene at room temperature, while the carbon resonances in the ^{13}C-labeled compounds are found at 60.32 ppm (J_{CH} = 115 Hz) in the hafnium complex. It is clear on the basis of proton NMR spectra that these cations are not formed quantitatively and/or that they decompose slowly at 22 °C in bromobenzene over a period of hours. The decomposition products have not been identified.

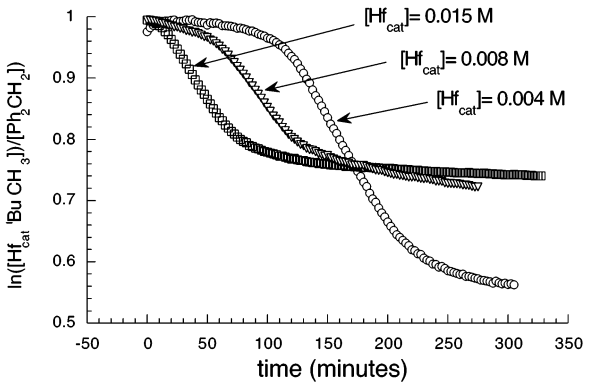


Figure 4. Decomposition of $\{[Ar_{Cl2}Npy]Hf(i\text{-}Bu)\}\{B(C_6F_5)_4\}$ (formed by trityl activation of $[Ar_{Cl2}Npy]Hf(i\text{-}Bu)_2$) at 0 °C by following the disappearance of the isobutyl methyl resonances in the ^1H NMR spectrum.

Addition of 1.0 equiv of $[Ph_3C][B(C_6F_5)_4]$ to $[Ar_{Cl2}Npy]Hf(i\text{-}Bu)_2$ in bromobenzene yielded $\{[Ar_{Cl2}Npy]Hf(i\text{-}Bu)\}\{B(C_6F_5)_4\}$, triphenylmethane, and isobutene quantitatively in seconds (eq 4). The decomposition of $\{[Ar_{Cl2}Npy]Hf(i\text{-}Bu)\}\{B(C_6F_5)_4\}$ at 0 °C has been monitored by observing the disappearance of the isobutyl methyl resonance (0.77 ppm) in the proton NMR spectrum compared to the Ph_3CH standard as a function of time for varying concentrations of catalyst (Figure 4). In the 0.0075 M sample (and in many other similar runs) the catalyst initially displayed first-order decomposition with a $k_{decomp} \approx 0.0005\ min^{-1}$. The rate of decomposition then accelerated to a rate approximately 6 times faster than that for $\{[MesNpy]Hf(i\text{-}Bu)\}\{B(C_6F_5)_4\}$ ($k_{decomp} \approx$

(28) Mehrkhodavandi, P.; Pryor, L. L.; Schrock, R. R. *Organometallics* **2003**, *22*, 4569.

0.003 min^{-1} for Ar = Ar_{Cl2}, $k_{decomp} \approx 0.00055$ min^{-1} for Ar = Mes[28]) before decreasing again after 2 h to a value roughly comparable to the initial value. We have not been able to determine the origin of this strange behavior, although it appears to be linked in some way to the polymerization of any isobutene that is present and possibly also to the presence of traces of $[Ph_3C][B(C_6F_5)_4]$. Isobutene is polymerized in the presence of traces of Ph_3C^+, not by the cationic hafnium complex itself, as found in the parent system that contains the mesityl-substituted ligand.[28] Purification of the reactants through recrystallization did not alter the results. Similar observations have been made for the decomposition of $\{[MesNpy]Hf(i\text{-}Bu)\}\{B(C_6F_5)_4\}$ at 22 °C, although at 0 °C the decomposition followed first-order kinetics.[28]

Activation of $[(2,6\text{-}F_2C_6H_3NCH_2)_2C(CH_3)(2\text{-}C_5H_4N)]^{2-}$ ($[Ar_{F2}Npy]^{2-}$) Complexes. $[Ar_{F2}Npy]HfMe_2$ may be activated with trityl to yield $\{[Ar_{F2}Npy]HfMe\}\{B(C_6F_5)_4\}$ (~70% pure) and Ph_3CCH_3. The dissociation of the $\{[Ar_{X2}Npy]_2M_2Me_3\}^+$ dimer required only 15 min at room temperature when X = F compared to 2.5 h when X = Cl. This lends further evidence that the halides assist in breaking up the dimer by coordinating to hafnium, with X = F being more efficient than X = Cl.

Activation of $[Ar_{F2}Npy]Hf(i\text{-}Bu)_2$ with $[Ph_3C][B(C_6F_5)_4]$ at 0 °C in bromobenzene-d_5 did not produce $\{[Ar_{F2}Npy]Hf(i\text{-}Bu)\}\{B(C_6F_5)_4\}$ as cleanly as $\{[Ar_{Cl2}Npy]Hf(i\text{-}Bu)\}\{B(C_6F_5)_4\}$. Several very small resonances for impurities were observed, none of them amounting to more than 8% of the initial dialkyl; however, in combination they comprised nearly 20% of the monocationic initiator. Decomposition of $\{[Ar_{F2}Npy]Hf(i\text{-}Bu)\}\{B(C_6F_5)_4\}$ is also more rapid than the decomposition of $\{[Ar_{Cl2}Npy]Hf(i\text{-}Bu)\}\{B(C_6F_5)_4\}$, a trend that was most apparent at room temperature. After 20 min at room temperature, nearly 65% of the initial $\{[Ar_{F2}Npy]Hf(i\text{-}Bu)\}\{B(C_6F_5)_4\}$ decomposed, whereas only ~20% of the initial $\{[Ar_{Cl2}Npy]Hf(i\text{-}Bu)\}\{B(C_6F_5)_4\}$ decomposed. At 0 °C approximately 38% of $\{[Ar_{F2}Npy]Hf(i\text{-}Bu)\}\{B(C_6F_5)_4\}$ decomposed in 270 min, which is about 1.5 times faster than $\{[Ar_{Cl2}Npy]Hf(i\text{-}Bu)\}\{B(C_6F_5)_4\}$ in the same time. For comparison, after 270 min at 0 °C only ~5% of the $\{[MesNpy]Hf(i\text{-}Bu)\}\{B(C_6F_5)_4\}$ initiator had decomposed. It is clear that the stabilities of the $\{[ArNpy]Hf(i\text{-}Bu)\}\{B(C_6F_5)_4\}$ species follow the order Ar = mesityl > Ar_{Cl2} > Ar_{F2}, even though the decompositions are not smooth and the rates are not reproducible.

Polymerization of 1-Hexene by $[Ar_{Cl2}Npy]^{2-}$ Cationic Alkyls. It is possible to prepare $\{[Ar_{Cl2}Npy]HfMe\}\{B(C_6F_5)_4\}$ and use it as an initiator in 1-hexene polymerization, although 2.5 h is required to form it at room temperature, and some impurities are present. A plot of ln([1-hexene]/[standard]) versus time at 0 °C is curved before becoming linear after 10 min, a trend that suggests a slower initiation than propagation. We ascribe the slower initiation rate to either a tighter binding of the anion to the methyl cation than to the propagating cation formed upon 1,2-insertion and/or to an interaction of an ortho chloride in the aryl substituent that is stronger in the methyl cation than the propagating cation. At 0 °C the observed rate constant for propagation was found to be 0.024 min^{-1} at a catalyst concentration of 15 mM, or $k_p = 0.027$ M^{-1} s^{-1}. A second run produced a value of $k_p = 0.031$ M^{-1} s^{-1}. If the initiator is prepared at 30 °C, only 45 min is required in order to produce a maximum yield. In a polymerization with the initiator prepared in this manner, $k_p = 0.034$ M^{-1} s^{-1}. These values for k_p are ~60% of those obtained with the analogous isobutyl initiator (see below), suggesting that ~40% of the metal that is present is not available to polymerize 1-hexene. The problem is that although $\{[Ar_{Cl2}Npy]_2Hf_2Me_3\}\{B(C_6F_5)_4\}$ loses $[Ar_{Cl2}Npy]HfMe_2$ slowly and therefore $\{[Ar_{Cl2}Npy]_2Hf_2Me_3\}\{B(C_6F_5)_4\}$ can be converted into $\{[Ar_{Cl2}Npy]HfMe\}\{B(C_6F_5)_4\}$, $\{[Ar_{Cl2}Npy]HfMe\}\{B(C_6F_5)_4\}$ begins to decompose slowly to unknown products before $\{[Ar_{Cl2}Npy]_2Hf_2Me_3\}\{B(C_6F_5)_4\}$ is completely consumed.

Table 5. Kinetic Data for Polymerization of 1-Hexene by $\{[Ar_{Cl2}Npy]Hf(i\text{-}Bu)\}\{B(C_6F_5)_4\}$ and $\{[Ar_{F2}Npy]Hf(i\text{-}Bu)\}\{B(C_6F_5)_4\}$

initiator	temp (°C)	[Hf] (M)	equiv 1-hexene	k_p (M^{-1} s^{-1})
Ar_{Cl2}	20	0.012	100	0.12, 0.15
Ar_{Cl2}	10	0.012	100	0.080
Ar_{Cl2}	10	0.006	100	0.088
Ar_{Cl2}	0	0.015	50	0.032
Ar_{Cl2}	0	0.012	100	0.049, 0.050, 0.052
Ar_{Cl2}	0	0.012	300	0.047, 0.056, 0.039
Ar_{Cl2}	0	0.012	400	0.055
Ar_{Cl2}	−5	0.015	50	0.023
Ar_{Cl2}	−10	0.015	50	0.018
Ar_{F2}	20	0.012	100	0.028
Ar_{F2}	10	0.012	100	0.016
Ar_{F2}	0	0.012	50	0.0007
Ar_{F2}	0	0.012	100	0.0007

As reported previously, addition of 1.0 equiv of trityl to $[Ar_{Cl2}Npy]Hf(i\text{-}Bu)_2$ at −40 °C followed by warming to 0 °C afforded $\{[Ar_{Cl2}Npy]Hf(i\text{-}Bu)\}\{B(C_6F_5)_4\}$, triphenylmethane, and isobutene. Addition of 1-hexene then led to a smooth consumption of 1-hexene at 0 °C at a rate that was first order in 1-hexene and first order in hafnium. The polymerization of 1-hexene was followed until consumption of 1-hexene was essentially complete (>98%), and k_p values were obtained from plots of ln([1-hexene]/[standard]) versus time. At 0 °C (see Table 5), the average k_p value was 0.049 M^{-1} s^{-1}, demonstrating that the $\{[Ar_{Cl2}Npy]Hf(CH_2R)\}\{B(C_6F_5)_4\}$ catalyst system polymerizes 1-hexene at half the rate of the $\{[MesNpy]Hf(CH_2R)\}\{B(C_6F_5)_4\}$ system, for which k_p was found to be 0.10 M^{-1} s^{-1} at 0 °C.[28] Plots of ln[1-hexene] versus time at 10 and 20 °C also were linear (Figure 5). An Eyring plot of the rate constants between 0 and 20 °C gave $\Delta H^{\ddagger} = 7.23$ kcal/mol and $\Delta S^{\ddagger} = -37.9$ cal/mol K (at [Hf] = 1 M). This should be compared with polymerization of 1-hexene by $\{[MesNpy]Hf(i\text{-}Bu)\}[B(C_6F_5)_4]$ in C_6D_5Br, where $\Delta H^{\ddagger} = 10.82$ kcal and $\Delta S^{\ddagger} = -23.0$ cal mol^{-1} K^{-1} (at [Hf] = 1 M).

Despite the linearity of the plots of ln([1-hexene]/[standard]) versus time over more than 5 half-lives, significant β-H elimination was observed to occur by ^1H NMR. A broad vinylidene resonance corresponding to the olefinic product of 1,2 β-H elimination in bromobenzene-d_5 grew in at 4.86 ppm[28,29] in the ^1H NMR spectrum as 1-hexene was consumed at 0 °C (to approximately 15% of $[Hf_{cat}]_i$ after ~98% consumption of

(29) Liu, Z.; Somsook, E.; White, C. B.; Rosaaen, K. A.; Landis, C. R. *J. Am. Chem. Soc.* **2001**, *123*, 11193.

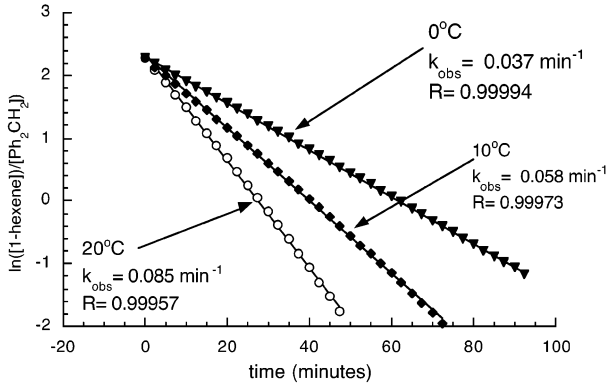


Figure 5. Polymerization of 100 equiv of 1-hexene by 0.012 M {[Ar_{Cl2}Npy]Hf(i-Bu)}{$B(C_6F_5)_4$} (formed by trityl activation of [Ar_{Cl2}Npy]Hf(i-$Bu)_2$).

Table 6. β-Hydride Elimination Associated with the Polymerization of 1-Hexene Catalyzed by {[Ar_{X2}Npy]Hf(i-Bu)}{$B(C_6F_5)_4$} in C_6D_5Br

	T (°C)	equiv 1-hexene	% complete	β-$H_{1,2}$	β-$H_{2,1}$	β-$H_{1,2}$ (48 h)
Cl	0	100	100	0.1−0.2	∼0.05	0.7
Cl	10	100	100	0.5−0.8	∼0.05	0.8
Cl	20	100	100	1.0−1.1	∼0.05	1.1
Cl	0	300	100	0.1−0.2	0.1−0.3	1.0
F	0	50	93	0.2	0.2	0.6
F	0	50	77	0.2	0.2	0.8
F	0	100	77	0.4	0.2	0.9
F	10	100	77	0.6	0.4	
F	10	100	98	1.3	0.6	
F	20	100	77	1.4	1.5	1.9

1-hexene) and continued to grow after the polymerization was complete (to about 70% $[Hf_{cat}]_i$ after 48 h). (Landis found vinylidene resonances due to 1,2 β-H elimination at 4.68 and 4.76 ppm in toluene.[29]) The ratio of the 1,2 β-H elimination product to the initial hafnium concentration was obtained by comparing the integration of the olefinic product peak to a known Ph_2CH_2 standard concentration. (Integrations are not highly accurate under these conditions, and the product of β elimination from a 1,2 insertion product, like isobutene, may be polymerized itself in the presence of trityl under these conditions.) These details are listed in Table 6 for reference. Under the conditions of 1-hexene polymerization employed here the half-life for the consumption of 1-hexene is ∼40 min (for [Hf] = 0.012 M), so consumption is complete in ∼200 min. During this time 10−20% of chain termination by β elimination from a 1,2 insertion product has taken place.

When 300 equiv of 1-hexene was polymerized at 0 °C, vinylene resonances due to β-H elimination after a 2,1 insertion grew between 5.36 and 5.40 ppm and integrated to about 0.1−0.2 equiv of $[Hf_{cat}]_i$. (Landis reported the shifts of the vinylene resonances due to 2,1 β-H elimination to be at 5.3 ppm in toluene.[29]) In runs where 100 equiv of 1-hexene was employed at 0 °C, however, only 0.05 equiv of β-2,1 elimination was observed. Since the resonance due to the β-2,1 elimination product was not observed to grow after all of the 1-hexene had been consumed, it appears that a β-2,1 elimination product forms only when 1-hexene is present in high enough concentrations.

On the basis of olefinic peak integration alone we cannot say in this case whether the metal-containing product of β hydride elimination (assumed to be a hydride) reacts with 1-hexene to generate a new polymer chain or whether the product of β hydride elimination is inactive even in the presence of 1-hexene. However, the linearity of the plots of ln([1-hexene]/[standard]) versus time over more than 5 half-lives would suggest that the Hf hydride byproduct of 1,2 or 2,1 β-H elimination may still be active for polymerization in the presence of a high enough concentration of 1-hexene. A plot of the expected molecular weight versus equivalents of 1-hexene added for a series of experiments run at 0 °C in bromobenzene with the {[Ar_{Cl2}Npy]Hf(i-Bu)}{$B(C_6F_5)_4$} initiator yielded linear plots, with molecular weight values being ∼90% of the expected molecular weight values for a perfect living system (Figure 6). Polydispersities (M_w/M_n) also were quite low, ranging from 1.01 to 1.05. We believe that these data accurately show that a small amount of 1,2 β-H elimination takes place during the polymerization reaction and that the product of that decomposition reacts with more 1-hexene to form polymer. However, the amount of 1,2 β-H elimination apparently is not great enough to affect the polydispersity values to any significant degree.

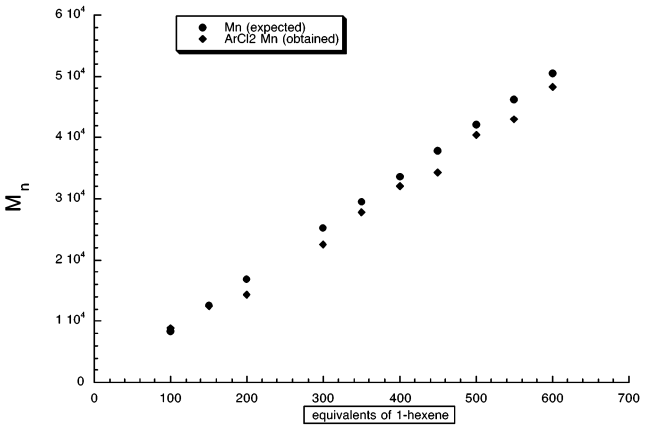


Figure 6. Molecular weight measurements for poly(1-hexene) obtained with {[Ar_{Cl2}Npy]Hf(i-Bu)}{$B(C_6F_5)_4$} as the initiator at 0 °C in C_6D_5Br.

Polymerization of 1-Hexene by $[Ar_{F2}Npy]^{2-}$ Cationic Alkyls. Although the reaction of [Ar_{F2}Npy]$HfMe_2$ with trityl to give {[Ar_{F2}Npy]HfMe}{$B(C_6F_5)_4$} at 0 °C was the most rapid as a consequence of the greater ease of dissociation of intermediate {[Ar_{F2}Npy]$_2Hf_2Me_3$}{$B(C_6F_5)_4$} into {[Ar_{F2}Npy]HfMe}{$B(C_6F_5)_4$} and [Ar_{F2}Npy]$HfMe_2$, {[Ar_{F2}Npy]HfMe}{$B(C_6F_5)_4$} was not formed quantitatively before {[Ar_{F2}Npy]$_2Hf_2Me_3$}{$B(C_6F_5)_4$} was consumed due to concomitant decomposition of {[Ar_{F2}Npy]HfMe}{$B(C_6F_5)_4$} and perhaps also formation of side products during the activation process. At 0 °C, k_p was found to be 0.002(1) M^{-1} s^{-1} for {[Ar_{F2}Npy]HfMe}{$B(C_6F_5)_4$} prepared in this manner. This value was lower than that for {[Ar_{F2}Npy]Hf(i-Bu)}{$B(C_6F_5)_4$} (see below) as a consequence of formation of inactive side products during polymerization and perhaps also as a consequence of a slower initiation relative to propagation. Approximately 50% of the {[Ar_{F2}Npy]HfMe}{$B(C_6F_5)_4$} initiator remained in solution after the consumption of 50 equiv of 1-hexene.

Polymerization of 1-hexene by {[Ar_{F2}Npy]Hf(i-Bu)}{$B(C_6F_5)_4$} led to plots of ln([1-hexene]/[standard]) versus time that were linear throughout the reaction for

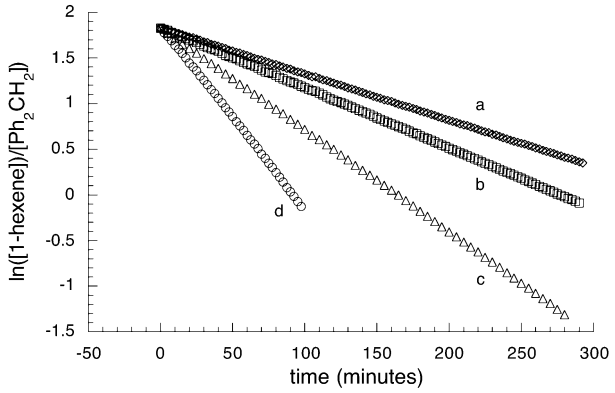


Figure 7. Plots of ln([1-hexene]/[Ph_2CH_2]) versus time for the consumption of 1-hexene by {[Ar_{F2}Npy]Hf(i-Bu)}{$B(C_6F_5)_4$}: (a) [Hf_{cat}] = 0.012 M, 0 °C, 50 equiv 1-hexene, k_p = 0.0070 M^{-1} s^{-1}; (b) [Hf_{cat}] = 0.015 M, 0 °C, 100 equiv 1-hexene, k_p = 0.0073 M^{-1} s^{-1}; (c) [Hf_{cat}] = 0.012 M, 10 °C, 100 equiv 1-hexene, k_p = 0.0155 M^{-1} s^{-1}; (d) [Hf_{cat}] = 0.012 M, 20 °C, 100 equiv 1-hexene, k_p = 0.028 M^{-1} s^{-1}.

temperatures ranging from 0 to 20 °C (Figure 7). At 0 °C for 50 and 100 equiv of 1-hexene, k_p was found to be 0.007 M^{-1} s^{-1}. This should be compared with k_p = 0.10 M^{-1} s^{-1} for {[MesNpy]Hf(i-Bu)}{$B(C_6F_5)_4$} and 0.049 M^{-1} s^{-1} for {[Ar_{Cl2}Npy]Hf(i-Bu)}{$B(C_6F_5)_4$}. Both 1,2 and 2,1 β-H elimination also were more prominent in the {[Ar_{F2}Npy]Hf(CH_2R)}{$B(C_6F_5)_4$} catalyst system than in the {[Ar_{Cl2}Npy]Hf(CH_2R)}{$B(C_6F_5)_4$} catalyst system. The vinylidene resonance corresponding to the 1,2 β-H elimination product was again found at 4.86 ppm, and the vinylene resonances corresponding to the 2,1 β-H elimination products were found between 5.36 and 5.40 ppm and also at 5.48 ppm. For the polymerization of 50 equiv of 1-hexene at 0 °C, the 1,2 β-H elimination product peak (representing 2 protons) integrated to 0.2 equiv of [Hf_{cat}]$_i$ after approximately 77% consumption of 1-hexene was observed (the polymerization was stopped after 77% polymerization due to time restraints). At 20 °C, the 1,2 β-H elimination product peak (representing 2 protons) integrated to 1.4 equiv of the [Hf_{cat}]$_i$ after 77% of the 1-hexene was consumed and grew to 1.9 equiv after a period of 48 h. 2,1 β-H elimination was also more prominent in this system, with the 2,1 β-H elimination product peaks growing to a total of 1.5 equiv at 20 °C.

Virtually all of the propagating catalyst decomposed after a period of 48 h at 0 °C to give one or more unidentifiable metal complexes. If the metal-containing product of β hydride elimination (assumed to be a hydride) decomposes before it can react with 1-hexene, then the amount of β hydride elimination product from 1,2 insertion cannot be greater than the amount of initiator initially present unless the hydride is able to react with 1-hexene to start a new polymer chain. Since the total equivalents of β-H elimination product was significantly greater than the amount of catalyst present initially at 20 °C, it seems probable that new polymer chains can be generated at this temperature when 1-hexene is present. Molecular weights for polymerization reactions run at 0 °C were much lower than expected (~50% of theory; Figure 8), suggesting that the decomposition product may indeed react with 1-hexene to re-form poly(1-hexene), thus leading to the observed first-order kinetics. The polydispersities varied between

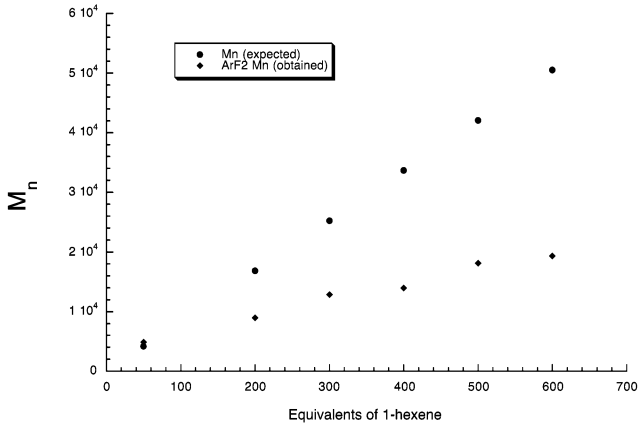


Figure 8. Molecular weight measurements for poly(1-hexene) obtained with {[Ar_{F2}Npy]Hf(i-Bu)}{$B(C_6F_5)_4$} as the initiator at 0 °C in C_6D_5Br.

1.1 and 1.4, consistent with less than perfect characteristics for a living polymerization reaction.

Discussion

The main goal of this work was to determine the behavior of {[2,6-$X_2C_6H_3$Npy]Hf(i-Bu)}{$B(C_6F_5)_4$} (X = Cl or F) initiators in 1-hexene polymerization and to compare their behavior with the system in which 2,4,6-$Me_3C_6H_2$ (mesityl) groups are present on the amido nitrogens. We found that the catalytic activity steadily decreases in the order aryl = mesityl > 2,6-$Cl_2C_6H_3$ > 2,6-$F_2C_6H_3$. Three explanations for this effect are plausible. First, the electron-withdrawing effect of the halides increases the strength of anion binding to the cationic metal center. The resulting stronger interaction between cation and anion lowers the metal's electrophilicity and hinders olefin binding to the metal and insertion into the M−carbon bond. The second possibility is that Cl or F coordinates to the cationic metal center, again competing with olefin binding. Metal−halide binding is not strong enough to observe readily by NMR methods, in contrast to binding of an ortho dimethylamino group, but it may be detected in terms of a decrease in polymerization rate. A third possibility is some hydrogen bonding between the ortho chloride, or especially the ortho fluoride, and α or β protons in the alkyl in cationic monoalkyl species. There is some evidence gathering in the literature that interactions between fluorides and α[30] or β protons[31] can significantly alter olefin polymerization pathways. However, we believe there is considerably more evidence that ortho fluorides in aryl rings can coordinate to early transition metals such as Zr[24,32] or Ta[33] (in addition to the structure reported here) and therefore favor one of the first two explanations. We can think of no way to differentiate between these explanations in the actual cationic intermediates in 1-hexene polymerization.

Initially we had entertained the possibility that a halide in the ortho position would coordinate to the

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metal and in fact stabilize a cationic alkyl against β-$H_{1,2}$ (β hydride elimination from a 1,2 insertion product), while reactivity toward insertion would be maintained or possibly increased as a consequence of the electron-withdrawing ability of the halide. Instead we find that the isobutyl initiators decompose more readily by β hydride elimination, and the propagating species in 1-hexene polymerization are less stable toward β-$H_{1,2}$. Again there appear to be three possible explanations. The first is that the metal is more electrophilic as a consequence of the electron-withdrawing ability of the halides, and β hydride elimination is faster if the metal center is more electrophilic. The second possible explanation is that interaction of the halide with the metal accelerates the rate of β hydride elimination. The third is that any hydrogen-bonding interactions between ortho halides and α or β protons in the alkyl in cationic monoalkyl species promotes more rapid β-$H_{1,2}$ processes. This last explanation would be in contrast with recent evidence that such a hydrogen-bonding interaction between a fluoride and a β proton in the alkyl *stabilizes* a Ti system against β-$H_{1,2}$ processes and therefore allows a polymerization at room temperature to be living.[31] Again it is difficult to differentiate between these possible explanations.

The third intriguing result is that more β-$H_{2,1}$ is observed in the order aryl = mesityl < 2,6-$Cl_2C_6H_3$ < 2,6-$F_2C_6H_3$, assuming that β-$H_{2,1}$ gives rise to the hexene-dependent resonances at 5.36−5.40 ppm. The fact that β-$H_{2,1}$ appears only in the presence of 1-hexene can be explained if β-$H_{2,1}$ takes place a significant percentage of the time that there is a 2,1 "misinsertion".[29] Much more work is needed in order to elucidate the origin of an increase in the amount of β-$H_{2,1}$ and to quantitate it. Unfortunately, the precise reason may be difficult to pin down, for reasons that we have already alluded to above.

We conclude that substitution of chlorides or fluorides (especially the latter) in the ortho positions of the aryl groups attached to the amido nitrogens in $[ArylNpy]^{2-}$ complexes in place of methyl groups is detrimental to the development of living olefin polymerization catalysts of this general type. Not only do 1-hexene polymerization reactions slow down, but during polymerization more β hydride elimination from both 1,2 and 2,1 insertion products is observed. Even without detailed knowledge about the stability of the putative "hydride" that is formed as a consequence of a β hydride elimination, it is clear that the living nature of the polymerization is compromised. We plan to explore the behavior of catalysts with other groups in the 2 and 6 positions of the aryl rings (e.g., isopropyl groups[16]) or with electron-withdrawing or electron-donating groups in positions other than ortho positions in the aryl substituents on the amido nitrogens.

Experimental Procedures

General Details. All reactions were conducted under an atmosphere of dinitrogen in a Vaccum Atmospheres drybox or using standard Schlenk techniques, and catalyst activation was performed in an inert atmosphere (dinitrogen) box free of ether, THF, or other coordinating solvents. Nondeuterated solvents were sparged with nitrogen for 45 min followed by passage through a 1 gallon column of activated alumina as described in the literature.[34] Bromobenzene and deuterated solvents were stirred over CaH_2 for 48 h, vacuum-transferred, and stored over 4 Å molecular sieves. Commercial reagents were used without further purification. The parent pyridyl diamine $(NH_2CH_2)_2C(CH_3)(2\text{-}C_5H_4N)$),[35,36] $Hf(NMe_2)_4$, and $Zr(NMe_2)_4$[37] were synthesized according to reported methods. Ordinary Grignard reagents were bought from Aldrich and titrated prior to use with 4-cumylphenol or 1-propanol using 1,10-phenanthroline as an indicator. $^{13}CH_3MgI$ was prepared from $^{13}CH_3I$ (purchased from Cambridge Isotopes) and Mg as an etheral solution. NMR data were recorded using Varian Inova-500, Bruker AVANCE-400, Varian Unity-300, or Varian Mercury-300 spectrometers. Chemical shifts are reported in parts per million (ppm), and coupling constants are reported in hertz. The residual protons or ^{13}C atoms of the deuterated solvents were used as internal references. ^{19}F NMR chemical shifts were referenced to the external standard C_6F_6. Elemental analyses (C, H, N, Cl) were done by Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

GPC analyses were conducted using a system equipped with two Jordi-Gel DVB mixed bed columns (250 mm length × 10 mm inner diameter) in series and a Wyatt Technology mini Dawn light scattering detector coupled with a Knauer differential refractometer. A Knauer 64 HPLC pump was used to supply HPLC grade THF at a flow rate of 1.0 mL/min. The auxiliary constant of the apparatus (5.9×10^{-4}) was calibrated using a polystyrene standard ($M_n = 2.2 \times 10^5$), and M_n and M_w values for poly(1-hexene) were obtained using dn/dc = 0.076 mL/gr (Wyatt Technology). Data analysis was carried out using Astrette 1.2 software (Wyatt Technology).

$[(2,6\text{-}Cl_2C_6H_3NHCH_2)_2C(CH_3)(2\text{-}C_5H_4N)]$ ($H_2[Ar_{Cl2}Npy]$). BINAP (566 mg, 0.91 mmol) was added to 30 mL of toluene, and the mixture was heated until the BINAP dissolved. To this solution was added 416 mg (0.45 mmol) of $Pd_2(DBA)_3$. The reaction was stirred for 15 min and filtered through a glass frit. The parent diamine (5.00 g, 30.3 mmol) was dissolved in 30 mL of toluene. To this solution were added NaO-t-Bu 6.7 g (70 mmol) and 1-bromo-2,6-dichlorobenzene (13.69 g, 60.6 mmol), and the total volume was brought to 200 mL. The sealed Schlenk flask was then heated for 1 day at 95 °C. The hot mixture was filtered, and the toluene was removed from the filtrate in vacuo. The residue was extracted with 300 mL of ether, and the ether solution was washed with water (400 mL total) and saturated NaCl solution (200 mL). The combined water extracts were then washed with ether (200 mL total). The combined ether extracts were concentrated to about 30 mL, and pentane (10 mL) was added. A solid precipitated and was filtered off and discarded. The solvent was removed from the filtrate to yield a brown oil; yield 8.9 g (19.7 mmol, 65%). ^1H NMR ($CDCl_3$): δ 1.5 (3H, s, CH_3), 3.65 (2H, dd, J = 12.2 and 7.3, CH*H*), 3.79 (2H, dd, J = 12.2 and 7.3, C*H*H), 4.68 (2H, t, J = 7.3, NH), 6.62 (2H, t, J = 8.4, arom. p-H), 7.05 (4H, d, J = 8.4, arom. m-H), 7.06 (1H, t, J = 4.2, py-H), 7.35 (1H, t, J = 8.4, py-H), 7.57 (1H, t, J = 8.4, py-H), 8.55 (1H, d, J = 4.2, py-H_o). HRMS (ESI): calcd for $C_{21}H_{19}N_3Cl_4$ $[M]^+$ 453.0328, found $[M]^+$ 453.0328. The product was estimated to be ~95% pure according to its ^1H NMR spectrum.

$[Ar_{Cl2}Npy]Zr(NMe_2)_2$. To a solution of $Zr(NMe_2)_4$ (1.5 g, 7.48 mmol) in 60 mL of pentane was added 2.55 g (7.48 mmol) of $H_2[Ar_{Cl2}Npy]$. The mixture was stirred at room temperature for 16 h. The solvent was removed in vacuo, and the resulting orange solid was washed with 20 mL of pentane; yield 3.05 g (86%). ^1H NMR (toluene-d_8): δ 1.22 (3H, s, CH_3), 3.18 (6H, s,

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$N(CH_3)_2$), 3.28 (2H, d, J = 9.6, CH*H*), 3.33 (6H, s, $N(CH_3)_2$), 4.63 (2H, d, J = 9.6, C*H*H), 6.35 (2H, t, J = 8.6, arom. p-H), 6.68 (1H, t, J = 5.2, py-H), 6.92 (1H, d, J = 8.6, py-H), 7.05 (1H, t, J = 8.6, py-H), 7.12 (4H, d, J = 8.6, arom. m-H), 8.75 (1H, d, J = 5.2, o-py-H_o). The product was estimated to be ~95% pure according to its ^{1}H NMR spectrum.

[Ar_{Cl2}Npy]ZrCl$_2$. To a solution of 1.69 g (2.67 mmol) of [Ar_{Cl2}Npy]Zr(NMe_2)$_2$ in 30 mL of ether was added 1.16 g (10.67 mmol) of Me_3SiCl. After 6 h the resulting pale yellow solid was filtered off, washed with pentane, and dried in vacuo; yield 1.15 g (70%). ^{1}H NMR (toluene-d_8): δ 0.89 (3H, s, CH_3), 2.95 (2H, d, J = 12.0, CH*H*), 4.35 (2H, d, J = 12.0, C*H*H), 6.1 (2H, t, J = 7.2, arom. p-H), 6.35 (1H, t, J = 2.4, py-H), 6.54 (1H, d, J = 4.8, py-H), 6.75 (4H, d, J = 7.2, arom. m-H), 6.75 (1H, t, py-H), 9.4 (1H, d, J = 2.4, py-H_o). The product was estimated to be ~95% pure according to its ^{1}H NMR spectrum.

[Ar_{Cl2}Npy]ZrMe$_2$. [Ar_{Cl2}Npy]$ZrCl_2$ (0.3 g, 0.488 mmol) was suspended in 10 mL of diethyl ether. The mixture was cooled to −30 °C, and MeMgCl (0.34 mL, 3 M in THF) was added. The reaction mixture was stirred for 1 h at room temperature. Dioxane (0.090 g) was then added, and after 5 min the reaction mixture was filtered through Celite. The filtrate's volume was reduced to 3 mL, and the solution was stored at −30 °C for one week. White microcrystals were filtered off and dried in vacuo; yield 158 mg (56%). ^{1}H NMR (toluene-d_8): δ 0.88 (3H, s, $HfCH_3$), 3.1 (2H, d, J = 11.7, CH*H*), 4.24 (2H, d, J = 11.7, C*H*H), 6.1 (2H, t, J = 8.3, arom. p-H), 6.3 (1H, t, J = 5.0, py-H), 6.5 (1H, d, J = 8.3, py-H), 6.68 (1H, t, J = 8.3, py-H), 6.84 (4H, d, J = 8.3, arom. m-H), 8.51 (1H, d, J = 5.0, py-H_o). Anal. Calcd for $C_{23}H_{23}N_3Cl_4Zr$: C, 48.09; H, 4.04; N, 7.31; Cl, 24.68. Found: C, 47.88; H, 3.92; N, 7.24; Cl, 24.63.

[Ar_{Cl2}Npy]Hf(NMe_2)$_2$. $Hf(NMe_2)_4$ (2 g, 5.64 mmol) was suspended in 60 mL of pentane, and 2.57 g (5.64 mmol) of H_2[Ar_{Cl2}Npy] was added. The reaction mixture was stirred at room temperature for 16 h. The solvent was removed in vacuo, and the resulting orange solid was washed with 20 mL of pentane and dried in vacuo; yield 3.52 g (87%). ^{1}H NMR (toluene-d_8): δ 1.15 (3H, s, CH_3), 3.3 (6H, s, $N(CH_3)_2$), 3.35 (6H, s, $N(CH_3)_2$), 3.42 (2H, d, J = 10.6, CH*H*), 4.6 (2H, d, J = 10.6, C*H*H), 6.32 (2H, t, J = 7.8, arom. p-H), 6.7 (1H, t, J = 7.0, py-H), 6.85 (1H, d, J = 7.8, py-H), 7.05 (1H, t, J = 7.8, py-H), 7.15 (4H, d, J = 7.8, arom. m-H), 8.75 (1H, d, J = 7.0, py-H_o). The product was estimated to be ~95% pure according to its ^{1}H NMR spectrum.

[Ar_{Cl2}Npy]HfCl_2. [Ar_{Cl2}Npy]Hf(NMe_2)$_2$ (1.763 g, 2.45 mmol) was dissolved in 25 mL of toluene, and 1.064 g (9.8 mmol) of Me_3SiCl was added. The Schlenk flask was then sealed and heated at 85 °C for 16 h. The mixture was cooled to room temperature, and the volatile compounds were removed in vacuo. The pale yellow-brown solid was washed with pentane (2 times 10 mL) and dried in vacuo; yield 1.5 g (87%). ^{1}H NMR (toluene-d_8): δ 1.57 (3H, s, CH_3), 3.34 (2H, d, J = 11.8, CH*H*), 4.55 (2H, d, J = 11.8, C*H*H), 6.8 (2H, t, J = 8.5, arom. p-H), 7.18 (4H, d, J = 8.5, arom. m-H), 7.47 (1H, t, J = 6.8, py-H), 7.53 (1H, d, J = 8.5, py-H), 7.97 (1H, t, J = 8.5, py-H), 9.36 (1H, d, J = 6.8, py-H_o). The product was estimated to be ~95% pure according to its ^{1}H NMR spectrum.

[Ar_{Cl2}Npy]HfMe$_2$. [Ar_{Cl2}Npy]$HfCl_2$ (200 mg, 0.285 mmol) was suspended in 10 mL of ether, and the mixture was stored at −30 °C for 1 h. MeMgBr (0.2 mL, 0.598 mmol, 3 M in ether) was added, and the mixture was stirred for 1 h while it warmed to room temperature. The mixture was filtered, and the solvent was removed from the filtrate in vacuo. The resulting residue was triturated with pentane until a powder was obtained. This crude material was then recrystallized from a mixture of benzene and pentane (1:2); yield 116 mg (62%). ^{1}H NMR (toluene-d_8): δ 0.33 (3H, s, Hf-CH_3), 0.45 (3H, s, Hf−CH_3), 0.85 (3H, s, ligand CH_3), 3.1 (2H, d, CH*H*), 4.23 (2H, d, C*H*H), 6.11 (2H, t, arom. p-H), 6.38 (1H, t, meta py-H), 6.50 (1H, d, meta py-H), 6.75 (1H, t, para py-H), 6.8 (4H, d, arom. m-H), 8.65 (1H, d, py-H_o). Anal. Calcd for $C_{23}H_{23}N_3Cl_4Hf$: C, 43.95; H, 3.37; N, 6.11; Cl, 20.62. Found: C, 44.08; H, 3.31; N, 6.11; Cl, 20.49.

[Ar_{Cl2}Npy]Hf(i-Bu)$_2$. [Ar_{Cl2}Npy]$HfCl_2$ (460 mg, 0.655 mmol) was suspended in 20 mL of ether, and the mixture was cooled to −30 °C. A solution of i-BuMgBr (0.69 mL, 1.375 mmol, 2 M in ether) was then added. The reaction mixture was stirred for 1 h at room temperature. The mixture was filtered, and the solvent was removed from the filtrate in vacuo. The resulting light yellow powder is about 95% pure. Pure product was obtained by recrystallization from a mixture of benzene and pentane (1:1); yield 283 mg (58%). ^{1}H NMR (toluene-d_8): δ 0.80 (2H, d, ax CH_2CH(CH_3)$_2$), 0.85 (3H, s, CH_3), 0.95 (6H, d, ax CH_2CH(CH_3)$_2$), 0.98 (2H, d, eq CH_2CH(CH_3)$_2$), 1.15 (6H, d, eq CH_2CH(CH_3)$_2$), 2.34 (1H, m, CH_2C*H*(CH_3)$_2$), 2.45 (1H, m, CH_2C*H*(CH_3)$_2$), 3.1 (2H, d, ligand CH*H*), 4.23 (2H, d, ligand C*H*H), 6.11 (2H, t, arom. p-H), 6.38 (1H, t, meta py-H), 6.50 (1H, d, meta py-H), 6.75 (1H, t, para py-H), 6.8 (4H, d, arom. m-H), 8.65 (1H, d, py-H_o). Anal. Calcd for $C_{29}H_{35}N_3Cl_4Hf$: C, 46.70; H, 4.73; N, 5.63; Cl, 19.01. Found: C, 46.58; H, 4.65; N, 5.56; Cl, 19.10.

[(2,6-$F_2C_6H_3NHCH_2$)$_2$C(CH_3)(2-C_5H_4N)] (H_2[Ar_{F2}Npy]). BINAP (0.113 g, 0.181 mmol) was added to 25 mL of toluene, and the resulting suspension was heated until the BINAP dissolved. $Pd(DBA)_3$ (0.083 g, 0.091 mmol) was added, and the solution was heated until the reaction turned orange. The solution was filtered through Celite and combined with the parent diamine (1.00 g, 6.05 mmol), 1-bromo-2,6-difluorobenzene (2.34 g, 12.1 mmol), and NaO-t-Bu (1.34 g, 0.0139 mmol) in 40 mL of toluene. The reaction was heated at 95 °C for 5 days under N_2 in a sealed Schlenk flask. The hot reaction mixture was filtered, and toluene was removed in vacuo. The product was extracted into ether, and the solution was treated as described above for H_2[Ar_{Cl2}Npy]. The volume of the combined ether extracts was reduced to 6 mL, and pentane (10 mL) was added. A brown precipitate was filtered off through a bed of packed Celite. The filtrate was collected, and the solvent was removed in vacuo to yield a brown oil, which was purified via column chromatography (silica gel, ethyl acetate solvent) to give a red-brown oil; yield 1.20 g (37%). ^{1}H NMR ($CDCl_3$): δ 1.43 (3H, s, CH_3), 3.79 (4H, m, CH*H*), 4.60 (2H, s, NH), 6.63 (2H, m, arom. p-H), 6.77 (4H, m, arom. m-H), 7.16 (1H, dd, py-H), 7.42 (1H, d, py-H), 7.67 (1H, t, py-H), 8.62 (1H, d, py-H). ^{1}H NMR (C_6D_6): δ 1.42 (3H, s, CH_3), 3.78 (4H, m, CH*H*), 4.98 (2H, s, NH), 6.22, 6.98, 6.55 (9H total, 3 py H, 6 arom. H), 8.35 (1H, d, py-H_o). ^{19}F NMR (C_6D_6): δ −130.0 (4F, s, arom. *o*-F). HRMS (ESI): calcd for $C_{21}H_{19}N_3F_4$ [M + Na] 412.1407, found [M + Na] 412.1402.

[$Ar_{F2;FNMe2}$Npy]Hf(F)(NMe_2) (3). H_2[Ar_{F2}Npy] (0.852 g, 2.19 mmol) and $Hf(NMe_2)_4$ (0.739 g, 2.08 mmol) were dissolved in a mixture of pentane (30 mL) and benzene (5 mL). After 20 h the solvent was removed in vacuo to yield a brown powder that was recrystallized from ether at −30 °C to yield yellow crystals; yield 1.189 g (87%), ^{1}H NMR (C_6D_6): δ 1.15 (3H, s, CH_3), 2.07 (3H, s, $ArNCH_3$), 2.82(3H, s, $ArNCH_3$), 2.94 (6H, s, $HfNCH_3$), 3.20 (1H, d, CH*H*), 3.55 (1H, dd, CH*H*), 4.58 (1H, d, C*H*H), 4.91 (1H, dd, CH*H*), 6.2−7.0 (9H, complex, 3 py-H, 6 arom. H), 9.19 (1H, d, py-H_o). ^{19}F NMR (C_6D_6): δ −128.6 (1F, s, arom. uncoord. o-F, J_{FH} = 5.9), −122.0 (2F, d, J_{FF} = 32.9, arom. o-F, J_{FH} = 6.5), 28.5 (1F, t, J_{FF} = 32.9, Hf-F). Anal. Calcd for $C_{25}H_{29}N_5F_4Hf$: C, 45.91; H, 4.47; N, 10.71. Found: C, 46.08; H, 4.41; N, 10.64.

[Ar_{F2}Npy]Hf(NMe_2)$_2$ (1). This compound is the byproduct of the synthesis of **3**, identified in solution only; yield ≤5%. ^{1}H NMR (C_6D_6): δ 1.18 (3H, s, CH_3), 2.89 (6H, s, $N(CH_3)_2$), 3.07 (6H, s, $N(CH_3)_2$), 3.39 (2H, d, CH*H*), 4.35 (2H, d, J = 10.6, C*H*H), 6.1−7.0 (6H, arom. protons), 8.42 (1H, d, py-H_o). ^{19}F NMR (C_6D_6): δ −125.1 (4F, s, arom. o-F, J_{FH} = 6.84).

[$Ar_{F2;FNMe2}$Npy]Hf(Cl)(NMe_2) (4). [$Ar_{F2;FNMe2}$Npy]Hf(F)-NMe_2 (**3**, 0.300 g, 0.465 mmol) and Me_3SiCl (0.050 g, 0.465 mmol) were dissolved in toluene (7 mL), and the solution was stirred for 30 h. The reaction was filtered through Celite and

the solvent removed in vacuo from the filtrate to afford a yellow powder. The product was recrystallized from ether in order to remove unreacted [$Ar_{F2;FNMe2}$Npy]Hf(F)(NMe_2); yield = 0.126 g (41%). ^{1}H NMR (C_6D_6): δ 1.07 (3H, s, CH_3), 2.05 (3H, s, $ArNCH_3$), 2.85 (3H, s, $ArNCH_3$), 2.91 (6H, s, $HfNCH_3$), 3.43 (1H, d, CH*H*), 3.57 (1H, dd, C*H*H), 3.70 (1H, d, CH*H*), 4.95 (1H, dd, C*H*H), 6.2−7.0 (9H, multiplets, 3 py-H, 6 arom. H), 9.19 (1H, d, py-H_o). ^{19}F NMR (C_6D_6): δ −127.9 (1F, s, arom. uncoord. o-F, J_{FH} = 5.9), −119.3 (2F, d, J_{FF} = 32.9, arom. o-F, J_{FH} = 6.5).

[$Ar_{F2;FNMe2}$Npy]$HfCl_2$ (7). [$Ar_{F2;FNMe2}$Npy]Hf(F)NMe_2 (**3**, 0.771 g, 1.18 mmol) and Me_3SiCl (0.767 g, 7.07 mmol) were dissolved in toluene (25 mL), and the solution was stirred for 30 h. The yellow precipitate was filtered off and washed with ether (10 mL) and pentane (10 mL); yield 0.634 g (83%). ^{1}H NMR (C_6D_6): δ 0.93 (3H, s, CH_3), 2.32 (3H, s, $ArNCH_3$), 3.03 (1H, d, CH*H*), 3.07, (3H, s, $ArNCH_3$), 3.63 (1H, dd, C*H*H), 4.05 (1H, d, CH*H*), 4.55 (1H, dd, C*H*H), 6.3−6.9 (9H, ms, 3 py-H, 6 arom. H), 9.44 (1H, d, py-H_o). ^{19}F NMR (C_6D_6): δ −129.7 (1F, s, arom. uncoord. o-F, J_{FH} = 6.3), −120.9 (2F, s, arom. o-F, J_{FH} = 6.3). Anal. Calcd for $C_{23}H_{23}N_4F_3HfCl_2$: C, 41.74; H, 3.5; N, 8.47; Cl, 10.71. Found: C, 41.50; H, 3.43; N, 8.43; Cl, 10.71.

[$Ar_{F2;FNMe2}$Npy]HfCl(i-Bu). A suspension of [$Ar_{F2;FNMe2}$Npy]-$HfCl_2$ (0.600 g, 0.907 mmol) in ether (25 mL) was cooled to −30 °C, and i-BuMgCl (0.228 g, 1.952 mmol, 2.7 M in ether) was added. The mixture was stirred at room temperature for 24 h and filtered off through Celite. The solvent was removed in vacuo from the filtrate, and the resulting residue was triturated thoroughly with pentane to give a yellow powder; yield 0.203 g (33%). ^{1}H NMR (C_6D_6): δ 0.72 (1H dd, CH*H*CH-$(CH_3)_2$), 0.90 (3H, d, $CH_2CH(CH_3)_2$), 0.94 (3H, s, CH_3), 1.06 (3H, dd, C*H*HCH$(CH_3)_2$), 1.17 (3H, d, $CH_2CH(CH_3)_2$), 2.02 (3H, s, $ArNCH_3$), 2.24 (1H, sept, $CH_2CH(CH_3)_2$), 3.02 (3H, s, $ArNCH_3$), 3.05 (1H, d, CH*H*), 3.45 (1H, dd, C*H*H), 4.12 (1H, d, CH*H*), 4.93 (1H, dd, C*H*H), 6.3−7.0 (9H, ms, 3 py-H, 6 arom. H), 9.29 (1H, d, py-H_o). ^{19}F NMR (C_6D_6): δ −127.3 (1F, s, arom. uncoord. o-F, J_{FH} = 6.12), −119.2 (2F, s, arom. o-F, J_{FH} = 6.10). Anal. Calcd for $C_{27}H_{32}N_4F_3Cl_1Hf$: C, 47.48; H, 4.65; N, 8.12; Cl, 5.25. Found: C, 47.45; H, 4.72; N, 8.2; Cl, 5.19.

[$Ar_{F2;FNMe2}$Npy]$HfMe_2$. A suspension of [$Ar_{F2;FNMe2}$Npy]-$HfCl_2$ (0.100 g, 0.151 mmol) in ether (5 mL) was cooled to −30 °C, and MeMgBr (0.038 g, 0.317 mmol, 3.45 M in ether) was added. The mixture was stirred at room temperature for 1 h, and the mixture was filtered through a bed of Celite. The solvent was removed in vacuo from the filtrate, and the resulting residue was triturated thoroughly with pentane to yield a pale yellow powder; yield 0.043 g (46%). ^{1}H NMR (C_6D_6): δ 0.28 (3H, m, $HfCH_3$), 0.57 (3H, m, $HfCH_3$), 1.04 (3H, s, CH_3), 2.14 (3H, s, $ArNCH_3$), 2.75 (3H, s, $ArNCH_3$), 3.27 (1H, d, CH*H*), 3.59 (1H, dd, C*H*H), 4.17 (1H, d, CH*H*), 4.77 (1H, dd, CH*H*), 6.2−7.0 (9H, ms, 3 py-H, 6 arom. H), 8.66 (1H, d, py-H_o).

[$Ar_{(FNMe2)2}$Npy]Hf(F)Cl (6). This compound was a byproduct of the synthesis of [$Ar_{F2;FNMe2}$Npy]$HfCl_2$ (≤5%). It was identified only by its NMR spectrum. ^{1}H NMR (C_6D_6): δ 1.10 (3H, s, CH_3), 2.22 (3H, s, $ArNCH_3$), 3.10, (3H, s, $ArNCH_3$), 3.39 (2H, dd, CH*H*), 4.90 (2H, dd, C*H*H), 6.2−7.0 (9H, complex, 3 py-H, 6 arom. H), 9.11 (1H, d, py-H_o). ^{19}F NMR (C_6D_6): δ −127.5 (2F, s, arom. uncoord. o-F, J_{FH} = 6.28), 45.8 (1F, s, Hf-F, J_{FH} = 6.26).

[Ar_{F2}Npy]$HfCl_2$. This compound was the byproduct of failed direct method reaction. ^{1}H NMR (C_6D_6): δ 0.84 (3H, s, CH_3), 3.26 (2H, d, CHH), 4.39 (2H, d, CHH), 6.18 (2H, m, ArF_2 p-H), 6.36 (1H, t, py-H), 6.52 (4H, m, ArF_2 m-H), 6.61 (1H, d, py-H), 6.80 (1H, t, py-H), 9.52 (1H, d, py-H_o). ^{19}F NMR (C_6D_6): δ −118.7 (4F, s, arom. o-F, J_{FH} = 6.03).

[Ar_{F2}Npy]Hf(i-Bu)$_2$. $HfCl_4$ (0.428 g, 1.34 mmol) and H_2-[Ar_{F2} Npy] (0.496 g, 1.27 mmol) were dissolved in dichloromethane (150 mL), and the reaction was stirred at room temperature for 36 h. Dichloromethane was removed in vacuo to afford a yellow powder, which was suspended in ether (100 mL). The mixture was cooled to −30 °C, i-BuMgCl (0.631 g, 5.40 mmol) was added, and the reaction was stirred at room temperature for 1 h. A white precipitate was filtered off through Celite, and the solution was concentrated in vacuo to afford an orange residue, which was washed with pentane (25 mL). The resulting yellow powder was recrystallized in a 1:4 mixture of ether and pentane; yield 0.488 g (52%). ^{1}H NMR (C_6D_6): δ 0.09 (2H, m, $CH_2CH(CH_3)_2$), 0.96 (3H, s, CH_3), 1.05 (6H, d, $CH_2CH(CH_3)_2$), 1.12 (2H, m, $CH_2CH(CH_3)_2$), 1.48 (6H, d, $CH_2CH(CH_3)_2$), 2.31 (1H, p, $CH_2CH(CH_3)_2$), 2.93 (1H, p, $CH_2CH(CH_3)_2$), 3.56 (2H, d, ligand CH*H*), 4.47 (2H, d, ligand C*H*H), 6.12 (2H, m, ArF_2 p-H), 6.37 (1H, t, py-H), 6.68 (4H, m, ArF_2 m-H), 6.69 (1H, d, py-H), 6.83 (1H, t, py-H), 8.69 (1H, d, py-H_o). ^{19}F NMR (C_6D_6): δ −117.4 (4F, s, arom. o-F). Anal. Calcd for $C_{29}H_{35}N_3F_4Hf$: C, 51.22; H, 5.19; N, 6.18. Found: C, 51.31; H, 5.14; N, 6.06.

[Ar_{F2}Npy]$HfMe_2$. $HfCl_4$ (0.229 g, 0.715 mmol) and H_2[Ar_{F2}-Npy] (0.265 g, 0.681 mmol) were dissolved in dichloromethane (150 mL), and the reaction was stirred at room temperature for 36 h. Dichloromethane was removed in vacuo to give a yellow powder, which was suspended in ether (150 mL). The mixture was cooled to −30 °C, MeMgBr (0.337 g, 2.83 mmol) was added, and the reaction mixture was stirred at room temperature for 1 h. A white precipitate was filtered off through Celite, and the resulting solution was concentrated in vacuo to afford a brown residue. This residue was triturated with pentane (20 mL) to afford a brown powder. The resulting brown powder was dissolved in pentane. The solution was filtered and cooled to −30 °C to afford yellow crystals; yield 0.172 g (43%). ^{1}H NMR (C_6D_6Br): δ 0.08 (3H, m, $HfCH_3$), 0.68 (3H, m, $HfCH_3$), 1.23 (3H, s, CH_3), 3.55 (2H, d, CH*H*), 4.38 (2H, d, C*H*H), 6.26 (2H, m, arom. p-H), 6.76 (4H, m, arom. m-H), 6.80 (1H, t, py-H), 7.09 (1H, d, py-H), 7.36 (1H, t, py-H), 8.67 (1H, d, py-H_o). ^{19}F NMR (C_6D_6Br): δ −114.6 (4F, s, arom. o-F). Anal. Calcd for $C_{23}H_{23}N_3F_4Hf$: C, 46.36; H, 3.89; N, 7.05. Found: C, 46.42; H, 3.95; N, 6.88.

General Procedure for Kinetic Studies of 1-Hexene Polymerization. Suspensions of [Ph_3C][$B(C_6F_5)_4$] (0.0036−0.0139 g; 0.004−0.015 mmol) and an equimolar amount of [Ar_{X2}Npy]HfR_2 in equal volumes of bromobenzene-d_5 (total solution volume, including 1-hexene = 1 mL) were cooled to −40 °C and mixed along with the internal standard Ph_2CH_2 (∼0.005 g, 0.030 mmol, R = i-Bu) or hexamethylbenzene (∼0.005 g, 0.031 mmol, R = Me). The dimethyl complexes were stirred at room temperature for 10 min with M = Zr and 3 h with M = Hf, or at 30 °C with M = Hf for 45 min. Activation of the diisobutyl complexes occurred immediately for both M = Zr and M = Hf and was marked by a change in color from an orange to a yellow solution. The activated complex was transferred to a J-Young NMR tube and cooled to −40 °C. To this solution was added the appropriate volume of 1-hexene. The NMR tube was shaken immediately, brought out of the glovebox, and frozen in liquid nitrogen. The frozen sample was brought to the NMR machine, which was precooled to a defined temperature. The sample was warmed until it was liquid again and then placed into the NMR machine, and the reaction was monitored by standard NMR measurement. Disappearance of the olefinic signals of the 1-hexene was measured against the internal standard.

General Procedure for the Preparative Polymerization of 1-Hexene at 0 °C. Suspensions of [Ph_3C][$B(C_6F_5)_4$] (0.0221 g, 0.024 mmol) and an equimolar amount of [Ar_{Cl2}]Hf-$(i\text{-}Bu)_2$ in equal volumes of bromobenzene (total solution volume, including 1-hexene = 3 mL) were cooled to −40 °C and mixed. The activated complex was again cooled to −40 °C and transferred to a reaction bomb to which 1-hexene was added. The reaction bomb was sealed with a Teflon screw cap, shaken, removed from the glovebox, and cooled in an ice bath for the length of the polymerization. Methanol was added to the reaction after 6 h for the {[Ar_{Cl2}Npy]Hf(i-Bu)}{$B(C_6F_5)_4$} system and after 9 h for the {[Ar_{F2}Npy]Hf(i-Bu)}{$B(C_6F_5)_4$}

system. After stirring the solution at room temperature for 1 min, all volatiles were removed in vacuo and the polymer was extracted into pentane. The pentane solution was filtered through silica gel and Celite, and the pentane was then removed in vacuo to afford a colorless viscous oil, which was used for further NMR and GPC studies.

Activation of $[Ar_{X2}Npy]HfR_2$ with $[Ph_3C][B(C_6F_5)_4]$. (i) To Give $\{[Ar_{Cl2}Npy]Hf(i\text{-}Bu)\}\{B(C_6F_5)_4\}$, Ph_3CH, and Isobutene. ^{1}H NMR (C_6D_5Br): δ 0.77 (6H, d, $CH_2CH(CH_3)_2$), 1.03 (2H, d, $CH_2CH(CH_3)_2$), 1.26 (3H, s, CH_3), 1.62 (6H, s, isobutene), 2.09 (1H, p, CH_2CHMe_2), 3.64 (2H, d, CH*H*), 4.13 (2H, d, C*H*H), 4.70 (2H, s, isobutene), 5.45 (1H, s, Ph_3CH) 6.61−7.59 (aromatics), 8.29 (1H, d, py-H_o).

(ii) To Give $\{[Ar_{Cl2}Npy]ZrMe\}\{B(C_6F_5)_4\}$ and Ph_3CCH_3. ^{1}H NMR (C_6D_5Br): δ 0.88 (3H, s, Zr-CH_3), 1.30 (3H, s, CH_3), 2.09 (3H, s, Ph_3CCH_3), 3.06 (2H, d, CH*H*), 4.54 (2H, d, C*H*H), 6.69 (2H, arom. p-H), 7.25 (1H, d, m-py-H), 7.63 (1H, t, p-py-H), 8.25 (1H, d, py-H_o).

(iii) To Give $\{[Ar_{Cl2}Npy]HfMe\}\{B(C_6F_5)_4\}\}$ and Ph_3CCH_3. ^{1}H NMR (C_6D_5Br): δ 0.63 (3H, s, Hf-CH_3), 1.33 (3H, s, CH_3), 2.09 (3H, s, Ph_3CCH_3), 3.45 (2H, d, CH*H*), 4.45 (2H, d, C*H*H), 6.64 (2H, t, arom. p-H), 7.27 (1H, d, m-py-H), 7.64 (1H, t, p-py-H), 8.25 (1H, d, py-H_o). ^{13}C NMR: δ 60.32 (s, Hf-CH_3).

(iv) To Give $\{[Ar_{F2}Npy]Hf(i\text{-}Bu)\}\{B(C_6F_5)_4\}$, Ph_3CH, and Isobutene. ^{1}H NMR (C_6D_5Br): δ 0.97 (6H, d, $CH_2CH(CH_3)_2$), 1.09 (2H, q, $CH_2CH(CH_3)_2$), 1.22 (3H, s, CH_3), 1.62 (6H, s, isobutene), 2.31 (1H, p, CH_2CHMe_2), 3.67 (2H, d, ligand CH*H*), 4.02 (2H, d, ligand C*H*H), 4.70 (2H, s, isobutene), 5.45 (1H, s, Ph_3CH), 6.48−7.66 (aromatics), 8.35 (1H, d, py-H_o). ^{19}F NMR (C_6D_6): δ −117.2 (4F, s, arom. o-F).

(v) To Give $\{[Ar_{F2}Npy]HfMe\}\{B(C_6F_5)_4\}$ and Ph_3CCH_3. ^{1}H NMR (C_6D_6Br): δ 0.44 (3H, s, Hf-CH_3), 1.23 (3H, s, ligand CH_3), 2.09 (3H, s, Ph_3CCH_3), 3.78 (2H, d, CH*H*), 3.94 (2H, d, C*H*H), 6.40−7.80 (aromatics), 8.26 (1H, d, o-py-H). ^{19}F NMR (C_6D_6): δ −116.1 (4F, s, arom. o-F).

(vi) To Give $\{[Ar_{F2;FNMe2}Npy]HfMe\}\{B(C_6F_5)_4\}$ and Ph_3CCH_3. ^{1}H NMR (C_6D_6Br): δ 0.38 (3H, s, Hf-CH_3), 1.25 (3H, s, CH_3), 2.09 (3H, s, Ph_3CCH_3), 2.13 (3H, s, $ArNCH_3$), 2.78 (3H, s, $ArNCH_3$), 3.35 (1H, d, CH*H*), 3.39 (1H, dd, C*H*H), 3.97 (1H, d, CH*H*), 4.23 (1H, dd, C*H*H), 6.3−7.6 (aromatics), 8.20 (1H, d, py-H_o).

Acknowledgment. We thank the Department of Energy (DE-FG02-86ER13564) for supporting this research, and Dr. William M. Davis for assistance with X-ray studies. K.R. thanks the Deutsche Forschungsgemeinschaft for partial support in the form of a postdoctoral fellowship.

Supporting Information Available: Fully labeled thermal ellipsoid drawing, crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for $[Ar_{Cl2}Npy]Hf(i\text{-}Bu)_2$, $[Ar_{(FNMe2)2}Npy]Hf(F)Cl$, and $[Ar_{F2}Npy]Hf(i\text{-}Bu)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0305364