Synthesis and Structures of Zirconium and Hafnium Alkyl Complexes That Contain $[H_3CC(2\text{-}C_5H_4N)(CH_2NAr)_2]^{2-}$ ($[ArNpy]^{2-}$; Ar = Mesityl, Triisopropylphenyl) Ligands

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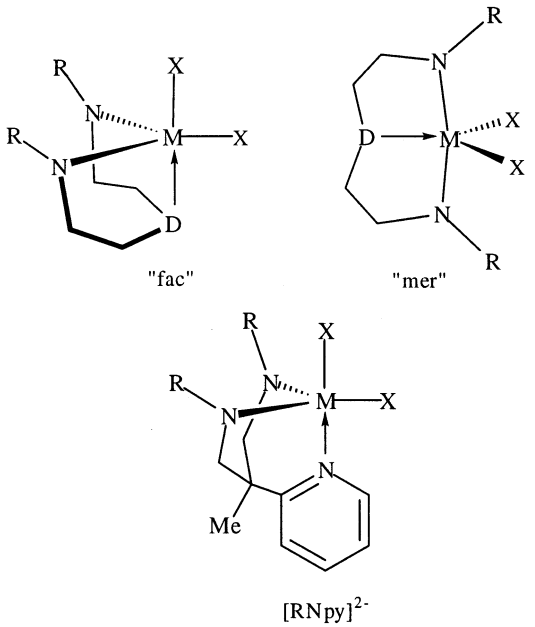
We report the synthesis of the arylated diamidopyridine ligands $[H_3CC(2\text{-}C_5H_4N)(CH_2NAr)_2]^{2-}$ ($[ArNpy]^{2-}$; Ar = 2,4,6-$Me_3C_6H_2$ (Mes), 2,4,6-(i-Pr)$_3C_6H_2$ (Trip)). [ArNpy]M$(NMe_2)_2$ (M = Zr, Hf) complexes were prepared by treating $M(NMe_2)_4$ with H_2[ArNpy], while [ArNpy]MCl_2 was prepared in a reaction between [ArNpy]$M(NMe_2)_2$ and Me_3SiCl. Zirconium dialkyl complexes that were prepared include [MesNpy]ZrR_2 (R = methyl, benzyl, neopentyl, isobutyl), [MesNpy]Zr(THF)Me_2, [Li(Et$_2$O)]{[MesNpy]ZrMe_3}, and [TripNpy]Zr-(i-Bu)$_2$. Hafnium [MesNpy]HfR_2 complexes are relatively stable, even when β-protons are present in R (R = Me, Et, n-Pr, n-Bu, i-Bu, i-Pr). Monoalkyl monochloro hafnium complexes that were prepared include [MesNpy]Hf(i-Pr)Cl and [MesNpy]Hf(t-Bu)Cl. X-ray studies were carried out for [MesNpy]$ZrMe_2$, [MesNpy]Zr(THF)Me_2, [Li(Et$_2$O)]{[MesNpy]ZrMe_3}, [TripNpy]Zr(i-Bu)$_2$, [MesNpy]Hf(i-Pr)Cl, and [MesNpy]Hf(i-Pr)$_2$.

Introduction

In the past decade, a great deal of metal chemistry has appeared in which two or three amido ligands have "supported" chemistry at the metal center.[1] Polydentate multiamido ligands have the advantage of not being lost from the metal as readily as monodentate amido ligands and the potential to sterically and electronically define the remaining coordination sites.[2] Diamido/donor ligands, in which the donor occupies a position between the two amido functionalities, have emerged as a relatively useful class of polydentate multiamido ligands.[2] Five-coordinate and six-coordinate species are usually encountered. In the most common version of a diamido/donor ligand the two "arms" contain two atoms (usually two carbon atoms or one carbon and one silicon atom) and both arms are connected directly to the donor in the middle. These ligands adopt either a "*mer*" arrangement of the two amido nitrogens and the donor atom or a "*fac*" arrangement, as illustrated in Chart 1 for two generic five-coordinate $[(RNCH_2CH_2)_2D]MX_2$ species (where D = donor, e.g., O, S, or NR′). An exception is the diamido/donor ligand $[H_3CC(2\text{-}C_5H_4N)(CH_2NAr)_2]^{2-}$ ($[RNpy]^{2-}$) developed by Gade, in which a pyridyl is the donor functionality, the arms are not directly attached to the donor atom, and R = trimethylsilyl.[2−5] In this case the geometry is restricted to *fac* if the pyridyl donor remains bound to the metal.

In the past 5 years we have been interested in exploring the chemistry of group 4 complexes that contain diamido/donor ligands[6] with the goal of developing new olefin polymerization catalysts[7] and, in particular, living polymerization catalysts.[8,9] Although our first successful living polymerization systems involved ligands of the type $[(t\text{-}BuN\text{-}o\text{-}C_6H_5)_2O]^{2-}$ bound to

Chart 1



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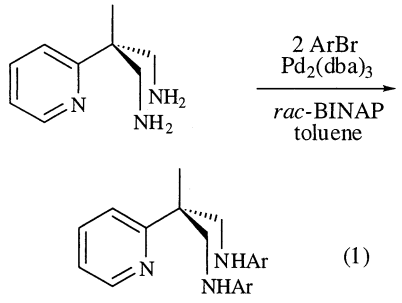
zirconium,[6b,c,e] we have become interested most recently in the potential advantage of a ligand that can coordinate to a metal in only a *fac* manner, namely the $[RNpy]^{2-}$ ligand. However, in our opinion silated amido ligands, with rare exceptions, are not likely to be stable toward side reactions in the cationic complexes that are employed for olefin polymerization.[10] Therefore, we have largely employed aryl substituents on the amido nitrogens in diamido/donor ligands that contain saturated arms and, in particular, 2,6-disubstituted aryl groups. We have hoped that this approach will allow us to probe in detail the characteristics of catalyst systems for the living polymerization of ordinary olefins.

In two preliminary communications we have reported zirconium[11] and hafnium[12] complexes that contain a $[ArNpy]^{2-}$ ligand, where Ar = 2,4,6-trimethylphenyl (Mes), and their use for the polymerization of 1-hexene. It turns out that $\{[MesNpy]Hf(alkyl)\}[B(C_6F_5)_4]$ complexes are readily prepared in wide variety and are well-behaved catalysts for the living polymerization of 1-hexene below 10 °C in chlorobenzene.[12] Systems of this type are believed to be deactivated once β-hydride elimination takes place, thereby limiting the number of polymer chains to one per metal. Most importantly, however, because of the living characteristics of these catalysts under the conditions we have employed, and because we believe that no polymer chain is regenerated after β-elimination under the conditions employed, we have had the opportunity to carry out NMR and direct kinetic studies on a variety of cationic alkyl complexes. In contrast, the many questions that have been posed in other single-site olefin polymerization systems in the past, activated metallocenes in particular,[13] could only be addressed "indirectly" through polymer analysis. (See, however, recent quantitative work by Landis on an ionic metallocene system.[14,15]) We also have come to believe that the $\{[MesNpy]Hf(alkyl)\}^+$ systems are relatively "open", a characteristic that may accentuate the role played by a weakly coordinating anion such as $[B(C_6F_5)_4]^-$.

In this paper we report the preparation of zirconium and hafnium alkyl complexes that we will employ in polymerization studies to be reported in subsequent papers. Stable dialkyl complexes are required for the synthesis of alkyl monocations. As we will show here, hafnium dialkyl complexes are especially stable and isolable, even when the alkyl is a secondary alkyl such as isopropyl.

Results

Synthesis of Zirconium Dialkyl Complexes. The parent diamine $H_3CC(2\text{-}C_5H_4N)(CH_2NH_2)_2$ was synthesized in four steps from 2-ethylpyridine in the manner reported by Gade et al.[4] The aryl groups subsequently were attached to the amine nitrogens using a coupling reaction developed by Buchwald (eq 1).[16,17] A 1% catalyst loading (Pd_2(dibenzylideneacetone)$_3$ plus BINAP) was used for the preparation of both H_2[MesNpy] and H_2[TripNpy]. The synthesis of H_2[MesNpy] was complete



(1)

H_2[ArNpy]; Ar = Mes or Trip

after 1−2 days at 100 °C, whereas synthesis of H_2[TripNpy] required at least 8 days in refluxing toluene to go to completion. H_2[MesNpy] can be recrystallized readily from pentane, while H_2[TripNpy] could be obtained only as a waxy solid.

We have found that the most reproducible approach to zirconium or hafnium dialkyl complexes which contain a $[ArNpy]^{2-}$ ligand is that shown in Scheme 1. Complexes $[MesNpy]Zr(NMe_2)_2$ and $[MesNpy]ZrCl_2$ could be prepared in ~90% yield. The $[MesNpy]ZrMe_2$ complex has a pronounced tendency to coordinate THF and also to form an "ate" complex with the methylating agent. However, $[MesNpy]ZrMe_2$ can be synthesized in moderate yields if the reaction conditions are strictly controlled: i.e., no THF is present in the drybox atmosphere and the Grignard reagent has been carefully titrated. Exposure of $[MesNpy]ZrMe_2$ to even small quantities of THF yields the THF adduct $[MesNpy]Zr(THF)Me_2$, while addition of methyllithium to $[MesNpy]ZrMe_2$ leads to a complex with the formula $[Li(Et_2O)]\{[MesNpy]ZrMe_3\}$ (eq 2). The preferred preparation of the THF adduct is a "direct" method in which $ZrCl_4$ in ether is treated with H_2[MesNpy] followed by 4 equiv of MeMgCl in THF. In systems such as $[(MesNCH_2CH_2)_2NMe]ZrMe_2$[6j] and $[(t\text{-}BuN\text{-}o\text{-}C_6H_5)_2O]ZrMe_2$,[6c] ether

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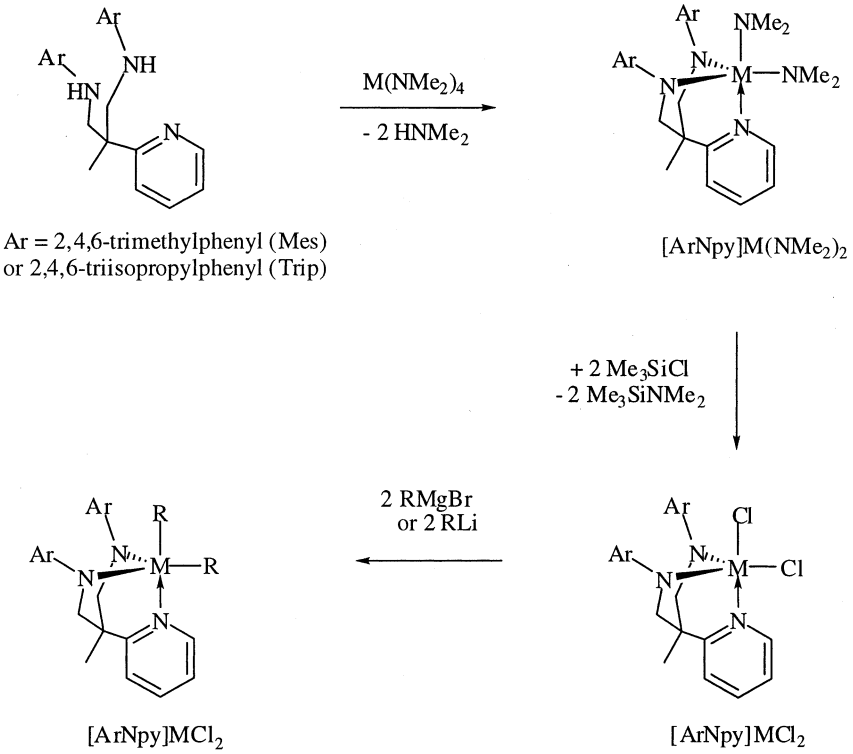
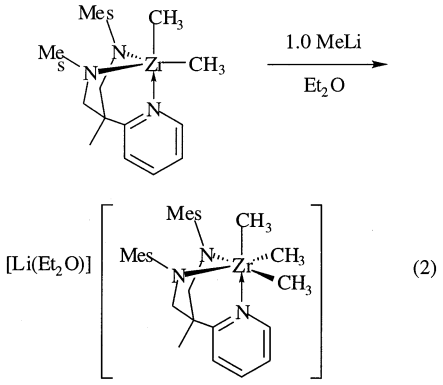
Scheme 1. Synthesis of Dialkyl Complexes



adducts do not form readily, presumably because such species are sterically more crowded than [MesNpy]-$ZrMe_2$.



A single-crystal X-ray study of [MesNpy]$ZrMe_2$ reveals a trigonal-bipyramidal structure with pseudo-C_s symmetry (Figure 1 and Tables 1 and 3). The ligand is coordinated with a *fac* geometry, as expected. The angle between the two methyl groups (C(28) and C(29)) is 89.1(2)°, and the respective Zr−C bond lengths are 2.294(5) and 2.284(6) Å. The N(1)−Zr(1)−N(2) angle in [MesNpy]$ZrMe_2$ is 102.24(12)°, which is significantly smaller than the angle in analogous complexes where the ligand is coordinated with a *mer* geometry: i.e., 140.5(2) and 139.6(2)° for [$(MesNCH_2CH_2)_2NMe$]$ZrMe_2$[6j] or [2,6-$(2,6\text{-}Et_2C_6H_3NCH_2)_2NC_5H_3$]$ZrMe_2$,[18] respectively. The Zr−N_{donor} bond is only slightly longer than those reported for [$(MesNCH_2CH_2)_2NMe$]$ZrMe_2$[6j] (2.387(7) Å) or [2,6-$(2,6\text{-}Et_2C_6H_3NCH_2)_2NC_5H_3$]$ZrMe_2$ (2.325(4) Å),[18] in which the diamido/donor ligands bind to the metal in a *mer* fashion. The planes of the mesityl rings are virtually perpendicular to the plane of the amido ligands: e.g., the C(13)−N(2)−C plane. This will be true in all complexes whose structures are reported here. An orientation of the aryl plane perpendicular to the amido ligand plane is most reasonable sterically; also, π-bonding to the metal is likely to be more significant than any conjugation with the phenyl π-system.

The X-ray crystal structures of [MesNpy]Zr(THF)Me_2 (Figure 2, Tables 1 and 4) and [Li(Et_2O)]{[MesNpy]-$ZrMe_3$} (Figure 3, Tables 1 and 4) showed them to be pseudo-octahedral complexes, with one molecule of THF in the former coordinated trans to an amido nitrogen (N(2)) and a lithium cation (to which one ether is bound) interacting approximately equally with the methyl groups (Li−C = 2.206, 2.217, and 2.272 Å) in the latter. The differences between these structures and [MesNpy]-$ZrMe_2$ is readily understood in terms of the higher coordination geometry. The main difference is that the N_{amido}−Zr−N_{amido} bond angle in each is ∼10° less than what it is in [MesNpy]$ZrMe_2$. In [Li(Et_2O)]{[MesNpy]-

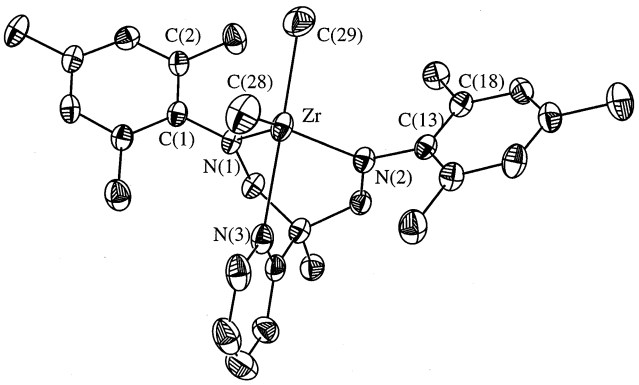


Figure 1. Thermal ellipsoid plot (35% probability level) of the structure of [MesNpy]$ZrMe_2$.

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Table 1. Crystal Data and Structure Refinement Details for [MesNpy]ZrMe$_2$, [MesNpy]Zr(THF)Me$_2$, and [Li(Et$_2$O)]{[MesNpy]ZrMe$_3$}[a]

	[MesNpy]ZrMe$_2$	[MesNpy]Zr(THF)Me$_2$	[Li(Et$_2$O)]{[MesNpy]ZrMe$_3$}
empirical formula	$C_{33}H_{49}N_3OZr$	$C_{33}H_{47}N_3OZr$	$C_{34}H_{52}LiON_3Zr$
fw	594.97	592.96	617.15
temp, K	183(2)	180(2)	183
cryst syst	orthorhombic	monoclinic	orthorhombic
space group	$P2_12_12_1$	$C2/c$	$P2_12_12_1$
unit cell dimens			
a, Å	11.4721(2)	32.739(2)	14.540(6)
b, Å	16.3643(3)	12.6838(7)	15.451(6)
c, Å	17.5024(2)	15.1138(9)	15.504(5)
β, deg		92.890(2)	
V, Å^3	3285.78(9)	6268.0(6)	3483(2)
Z	4	8	3
density (calcd), g/cm^3	1.203	1.257	1.176
abs coeff, mm^{-1}	0.362	0.379	0.343
F(000)	1264	2512	1312
cryst size, mm^3	0.5 × 0.5 × 0.5	0.32 × 0.25 × 0.18	0.3 × 0.3 × 0.3
θ range for data collecn, deg	2.12−23.25	1.25−23.28	2.33−23.39
index ranges	$-12 \le h \le 8$	$-36 \le h \le 36$	$-16 \le h \le 11$
	$-18 \le k \le 18$	$-14 \le k \le 9$	$-17 \le k \le 12$
	$-19 \le l \le 19$	$-15 \le l \le 16$	$-12 \le l \le 13$
no. of rflns collected	13 544	12 617	6715
no. of indep rflns	4674 (R(int) = 0.0361)	4502 (R(int) = 0.0528)	4175 (R(int) = 0.0478)
completeness, % (to θ, deg)	99.9 (23.25)	99.9 (23.28)	85.5 (23.39)
abs cor	empirical	none	empirical
max, min transmission	0.2617, 0.2347	0.9349, 0.8883	0.2731, 0.2158
no. of data/restraints/params	4674/0/344	4502/0/363	4175/0/361
goodness of fit on F^2	1.129	1.263	0.941
final R indices ($I > 2\sigma(I)$)	R1 = 0.0410, wR2 = 0.0990	R1 = 0.0616, wR2 = 0.1346	R1 = 0.0426, wR2 = 0.0842
R indices (all data)	R1 = 0.0462, wR2 = 0.1030	R1 = 0.0718, wR2 = 0.1395	R1 = 0.0745, wR2 = 0.0924
extinction coeff	0.0028(5)	0.00008(8)	−0.04(6)
largest diff peak, hole, e Å^{-3}	0.462, −0.436	0.461, −0.444	0.248, −0.298

[a] In all cases the wavelength was 0.710 73 Å (Mo Kα) and the refinement method was full-matrix least squares on F^2.

Table 2. Crystal Data and Structure Refinement for [TripNpy]Zr(i-Bu)$_2$, [MesNpy]Hf(i-Pr)Cl, and [MesNpy]Hf(i-Pr)$_2$[a]

	[TripNpy]Zr(i-Bu)$_2$	[MesNpy]Hf(i-Pr)Cl	[MesNpy]Hf(i-Pr)$_2$
empirical formula	$C_{47}H_{75}N_3Zr$	$C_{30}H_{40}ClN_3Hf$	$C_{33}H_{47}N_3Hf$
fw	773.32	656.59	664.23
temp, K	293(2)	183(2)	293(2)
cryst syst	triclinic	orthorhombic	orthorhombic
space group	$P\bar{1}$	$Pbca$	$Pbca$
unit cell dimens			
a, Å	12.592(4)	15.4981(9)	15.926(4)
b, Å	12.601(4)	18.3136(11)	18.600(5)
c, Å	17.403(6)	21.0590(13)	20.937(6)
α, deg	69.662(5)		
β, deg	86.747(5)		
γ, deg	64.631(5)		
v, Å^3	2325.6(13)	5977.1(6)	6202(3)
Z	2	8	8
density (calcd), g/cm^3	1.104	1.459	1.423
abs coeff, mm^{-1}	0.268	3.601	3.388
F(000)	836	2640	2704
cryst size, mm^3	0.2 × 0.2 × 0.1	0.26 × 0.20 × 0.10	0.16 0.14 × 0.10
θ range for data collecn, deg	2.54−11.65	2.34−23.27	1.94−23.27
index ranges	$-8 \le h \le 13$	$-16 \le h \le 17$	$-17 \le h \le 17$
	$-13 \le k \le 10$	$-18 \le k \le 20$	$-20 \le k \le 15$
	$-19 \le l \le 13$	$-23 \le l \le 21$	$-23 \le$ l ≤ 21
no. of rflns collected	4637	22 824	24 072
no. of indep rflns	4249 (R(int) = 0.0330)	4288 (R(int) = 0.0499)	4450 (R(int) = 0.0468)
completeness, % (to θ, deg)	63.4 (23.31)	99.8 (23.27)	99.9 (23.27)
abs cor	empirical	empirical	empirical
max, min transmission	0.9291 and 0.6462	0.7147 and 0.4545	0.9848 and 0.6827
no. of data/restraints/params	4249/0/460	4288/0/453	4450/0/346
goodness of fit on F^2	1.020	1.125	1.082
final R indices ($I > 2\sigma(I)$)	R1 = 0.0452, wR2 = 0.1125	R1 = 0.0375, wR2 = 0.0727	R1 = 0.0292, wR2 = 0.0603
R indices (all data)	R1 = 0.0608, wR2 = 0.1217	R1 = 0.0461, wR2 = 0.0758	R1 = 0.0380, wR2 = 0.0634
extinction coeff		0.000000(13)	0.000024(16)
largest diff peak, hole, e Å^{-3}	0.421, −0.309	0.652, −0.983	0.825, −0.667

[a] In all cases the wavelength was 0.71073 Å (MoKα) and the refinement method was full-matrix least-squares on F^2.

ZrMe$_3$} the equatorial Zr−C bonds are now ∼0.1 Å longer than the axial Zr−C bond. A similar interaction between (two) methyl groups and a solvated lithium ion is found in [Li(tmeda)][ZrMe$_6$].[19]

Table 3. Selected Bond Distances (Å) and Angles (deg) in the Five-Coordinate Complexes

	[MesNpy]ZrMe$_2$	[TripNpy]Zr(i-Bu)$_2$	[MesNpy]Hf(i-Pr)Cl	[MesNpy]Hf(i-Pr)$_2$
M−N$_{amido}$(1)	2.027(3)	2.047(4)	1.997(5)	2.032(3)
M−N$_{amido}$(2)	2.034(3)	2.047(4)	2.031(5)	2.035(3)
M−N(py)	2.444(4)	2.483(4)	2.339(5)	2.412(3)
M−C$_{ax}$	2.284(6)	2.253(5)	2.252(7)	2.297(4)
M−L$_{eq}$[a]	2.294(5)	2.258(7)	2.445(2)	2.268(5)
N$_{amido}$(1)−M−N$_{amido}$(2)	102.24(12)	98.46(16)	97.35(18)	98.94(14)
N$_{amido}$(1)−M−C$_{ax}$	102.2(2)	102.31(17)	108.0(2)	105.57(15)
N$_{amido}$(2)−M−C$_{ax}$	101.2(2)	104.35(18)	97.4(2)	97.72(15)
N$_{amido}$(1)−M−L$_{eq}$	125.55(19)	130.2(3)	118.49(14)	122.75(17)
N$_{amido}$(2)−M−L$_{eq}$	127.74(19)	125.0(3)	139.98(15)	134.62(17)
C$_{ax}$−M−L$_{eq}$	89.1(2)	90.4(2)	87.98(19)	88.24(18)
N$_{amido}$(1)−M−N(py)	80.81(14)	80.03(13)	83.78(18)	81.14(12)
N$_{amido}$(2)−M−N(py)	80.58(14)	81.18(14)	82.08(18)	81.34(13)
C$_{ax}$−M−N(py)	175.96(19)	173.46(18)	168.1(2)	173.28(14)
L$_{eq}$−M−N(py)	86.9(2)	83.5(2)	84.96(13)	87.73(16)

[a] L$_{eq}$ is an alkyl or (for [MesNpy]Hf(i-Pr)Cl) a chloride ligand.

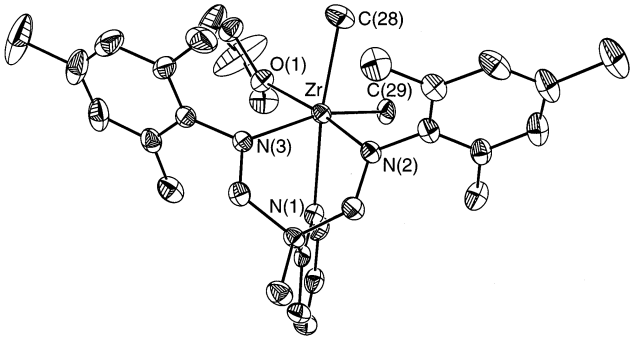

Figure 2. Thermal ellipsoid plot (35% probability level) of the structure of [MesNpy]Zr(THF)Me$_2$.

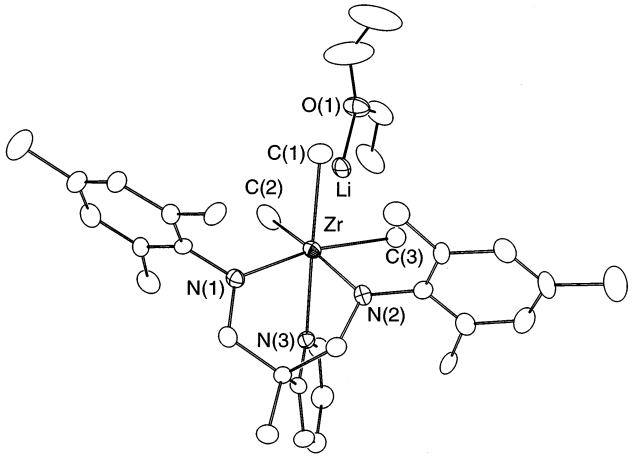

Figure 3. Thermal ellipsoid plot (35% probability level) of the structure of [Li(Et$_2$O)]{[MesNpy]ZrMe$_3$}.

Dimethyl complexes of the bulkier [TripNpy]$^{2-}$ ligand could also be prepared by similar methods. [TripNpy]ZrMe$_2$ is easier to synthesize and isolate than [MesNpy]ZrMe$_2$, since complications due to solvent coordination or zirconate formation are minimized, presumably because of the greater steric demand of the [TripNpy]$^{2-}$ ligand versus the [MesNpy]$^{2-}$ ligand.

Dimethyl complexes that contain a ^{13}C label in the methyl groups also have been prepared in good yield and were used in many labeling and NMR studies to be discussed below and in future papers.

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Table 4. Selected Bond Distances (Å) and Angles (deg) in the Six-Coordinate Complexes

	[MesNpy]-Zr(THF)Me$_2$	[Li(OEt$_2$)]-{[MesNpy]ZrMe$_3$}
M−N$_{amido}$(1)	2.063(4)	2.113(5)
M−N$_{amido}$(2)	2.115(4)	2.101(5)
M−N(py)	2.471(4)	2.399(5)
M−C$_{ax}$	2.288(6)	2.319(6)
M−C$_{eq}$	2.361(5)	2.461(6)
M−L$_{eq}$[a]	2.387(4)	2.421(7)
N$_{amido}$(1)−M−N$_{amido}$(2)	90.73(16)	91.48(18)
N$_{amido}$(1)−M−N(py)	79.93(15)	80.44(17)
N$_{amido}$(1)−M−L$_{eq}$	173.81(14)	165.7(2)
N$_{amido}$(1)−M−C$_{ax}$	99.4(2)	105.5(2)
N$_{amido}$(1)−M−C$_{eq}$	100.70(18)	87.39(19)
N$_{amido}$(2)−M−N(py)	76.66(15)	79.74(18)
N$_{amido}$(2)−M−L$_{eq}$	84.23(14)	94.3(2)
N$_{amido}$(2)−M−C$_{ax}$	111.3(2)	105.6(2)
N$_{amido}$(2)−M−C$_{eq}$	154.26(19)	167.1(2)
N(py)−M−L$_{eq}$	95.35(13)	87.8(2)
N(py)−M−C$_{ax}$	172.1(2)	171.62(18)
N(py)−M−C$_{eq}$	82.69(18)	87.40(18)
L$_{eq}$−M−C$_{ax}$	85.84(18)	85.4(2)
L$_{eq}$−M−C$_{eq}$	82.56(16)	84.1(2)
C$_{ax}$−M−C$_{eq}$	89.7(2)	87.0(2)

[a] L$_{eq}$ is an alkyl or (for [MesNpy]Zr(THF)Me$_2$) a THF ligand.

NMR Studies of Zirconium Methyl Complexes. The ^{1}H and ^{13}C{^{1}H} NMR spectra of [MesNpy]ZrMe$_2$ show significant solvent and temperature dependence. In C$_6$D$_6$ at 20 °C, the ^{1}H NMR spectrum of [MesNpy]ZrMe$_2$ shows a singlet at 0.56 ppm corresponding to six Zr−C*H*$_3$ protons, while the ^{13}C{^{1}H} NMR spectrum shows one broad resonance at 36.5 ppm for the Zr−*C*H$_3$ carbons. In C$_6$D$_5$Br at 20 °C and a concentration of 0.01 M in [MesNpy]ZrMe$_2$, the ^{1}H NMR spectrum shows two broad singlets at 0.22 and 0.32 ppm (Figure 4), while the ^{13}C{^{1}H} NMR spectrum shows two resonances at 35.46 and 36.65 ppm. At −25 °C two relatively sharp resonances are observed, corresponding to the axial and equatorial methyl groups (Figure 4). As the temperature is raised, the peaks broaden and finally coalesce to a broad singlet at 90 °C, indicating an exchange of methyl groups. At temperatures above 70 °C [MesNpy]ZrMe$_2$ starts to decompose to yield methane (0.15 ppm in the ^{1}H NMR spectrum) as well as unidentified zirconium products. At a concentration of 0.1 M the 20 °C spectrum shows a single resonance for the two methyl groups at 0.26 ppm. All data are consistent with a significant intermolecular component to the methyl exchange process. Since two alkyl groups are observed at 22 °C and

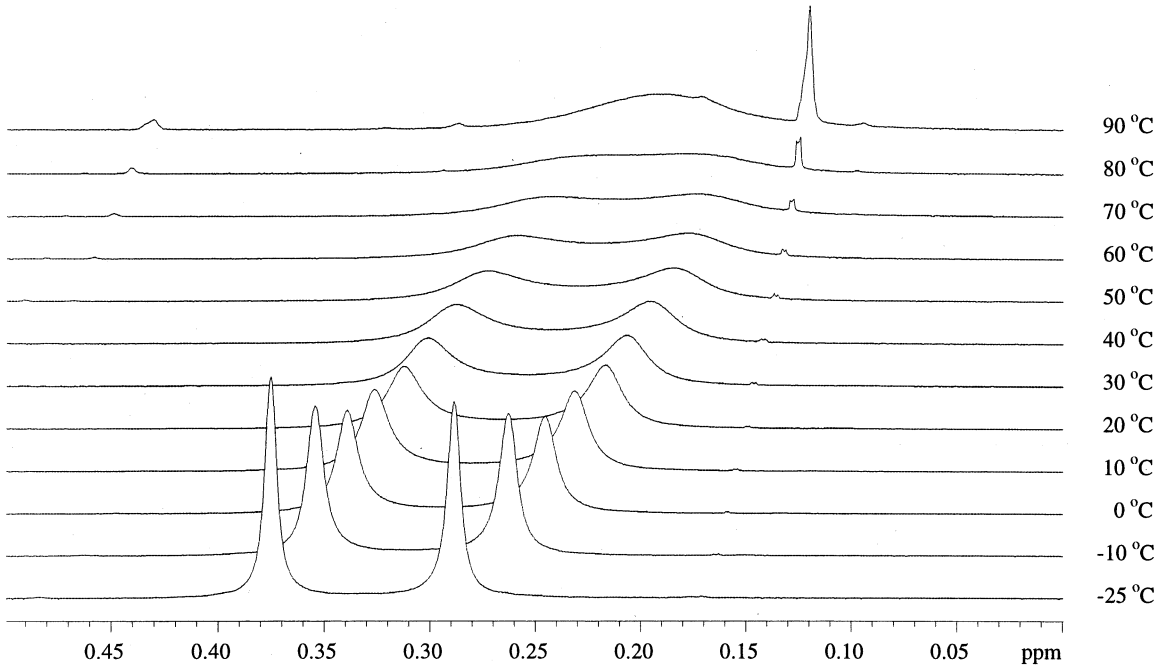


Figure 4. Variable-temperature ^{1}H NMR spectra (500 MHz, C_6D_5Br, $ZrCH_3$) of [MesNpy]$ZrMe_2$ (0.010 M).

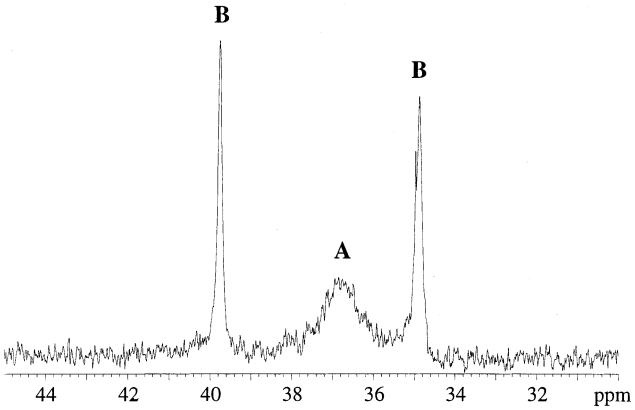


Figure 5. Exchange of methyl groups between [TripNpy]-$Zr^{13}Me_2$ (**B**) and [MesNpy]$ZrMe_2$ (**A**) (20 °C, C_6D_6, 0.018 M) to give partially labeled **B** and **A**.

concentrations of ~0.01 M in compounds of zirconium and hafnium in which the alkyl groups are large relative to methyl, we believe that exchange of two alkyl groups may be exclusively intermolecular and, therefore, fast only for methyl.

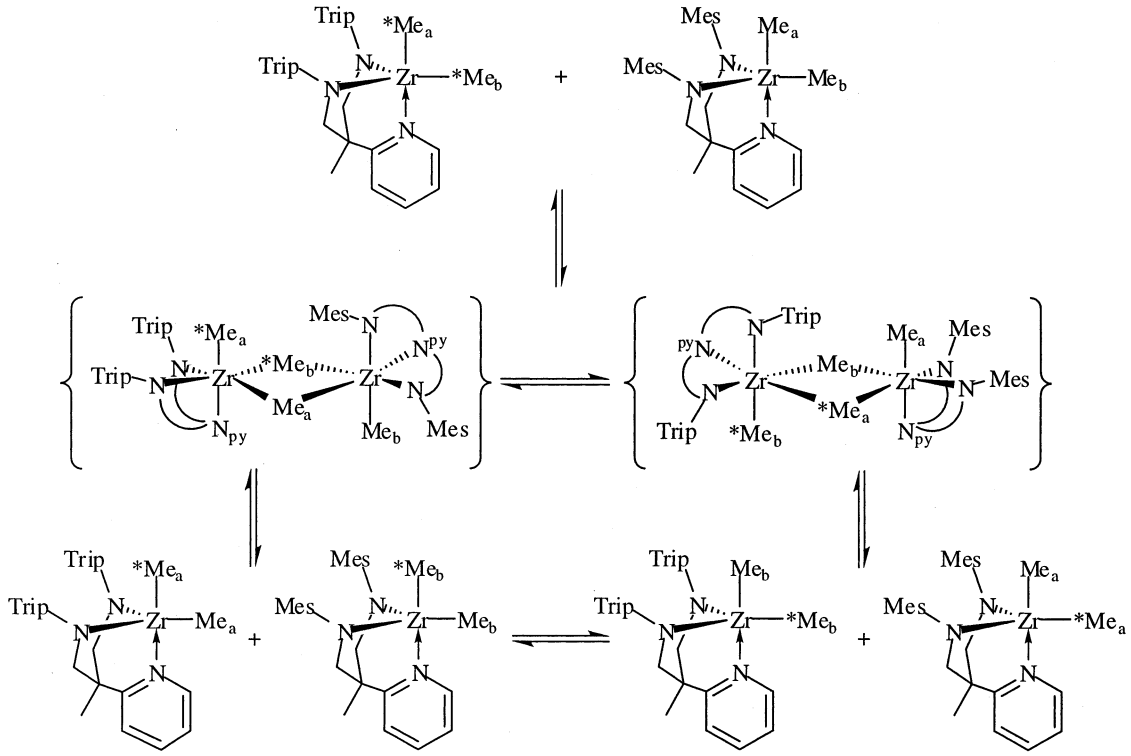
Exchange of the methyl groups is slower in [TripNpy]-$ZrMe_2$, as shown by the presence of two resonances for the two zirconium methyl groups at room temperature in benzene at 0.53 and 0.61 ppm, consistent with the greater steric demand of the [TripNpy]$^{2-}$ ligand. The $^{13}C\{^1H\}$ NMR spectrum of [TripNpy]$Zr^{13}Me_2$ shows two resonances for $Zr-CH_3$ carbons at 34.2 and 38.3 ppm. The pattern observed for the isopropyl group resonances are also consistent with slow rotation about the Trip−N bond in the sterically more crowded environment.

A double-labeling study revealed that methyl groups transfer rapidly on the chemical time scale between [MesNpy]$ZrMe_2$ and [TripNpy]$Zr^{13}Me_2$. For example, as shown in Figure 5, $^{13}C\{^1H\}$ NMR spectra (20 °C, C_6D_6) of mixtures of [MesNpy]$ZrMe_2$ and [TripNpy]$Zr(^{13}Me)_2$ show resonances at 39.8 and 34.9 ppm corresponding to the two methyl groups in (partially) ^{13}C-labeled [TripNpy]$ZrMe_2$, along with a broad singlet at 36.9 ppm that corresponds to (partially) ^{13}C-labeled [MesNpy]-$ZrMe_2$. We propose that the intermediates in such intermolecular exchanges contain two bridging methyl groups, as shown in Scheme 2, on the basis of ready formation of six-coordinate species, especially [Li(Et_2O)]-{[MesNpy]$ZrMe_3$}. There is always a possibility that the pyridyl group can dissociate from the metal at some point during an exchange process, since a dissociated pyridyl donor has been observed in certain imido complexes that contain the [TMSNpy]$^{2-}$ ligand that have been reported in the literature.[3]

The ^{1}H NMR spectrum (20 °C, C_6D_6) of [MesNpy]Zr-(THF)Me_2 shows a singlet at 0.54 ppm which corresponds to six $Zr-CH_3$ protons, along with resonances for 1 equiv of THF, while the $^{13}C\{^1H\}$ spectrum shows a broad signal at 35.8 ppm. The ^{1}H NMR spectrum (C_6D_6, 20 °C) of [Li(Et_2O)]{[MesNpy]$ZrMe_3$} shows a singlet at −0.06 ppm corresponding to nine $Zr-CH_3$ protons along with resonances that correspond to 1 equiv of diethyl ether. Two resonances are observed for the ortho methyl groups on the mesityl rings, consistent with restricted rotation of the aryl groups. Zirconium−methyl group exchange may be more complex in [MesNpy]Zr(THF)Me_2 and [Li(Et_2O)]{[MesNpy]$ZrMe_3$} than in [MesNpy]$ZrMe_2$. However, we presume that [MesNpy]-$ZrMe_2$ is readily accessible in each of the octahedral systems and that methyl groups exchange intermolecularly.

Other Zirconium Dialkyl Complexes. Several other zirconium dialkyl compounds could be prepared by alkylation of dichloride complexes. The dibenzyl compound [MesNpy]$ZrBz_2$ was isolated easily in 83% yield and was found to be quite robust, as is typically the case for benzyl complexes (e.g., $ZrBz_4$) compared to methyl or other alkyl analogues, in which the alkyl contains a β-proton. The ^{1}H NMR spectrum (21 °C, C_6D_6) showed one broad resonance at 2.5 ppm corre-

Scheme 2. Proposed Mechanism for Methyl Exchange between between [TripNpy]Zr^{13}Me$_2$ and [MesNpy]ZrMe$_2$



sponding to the four Zr−CH_2 protons of the two benzyl groups. At −40 °C in $C_6D_5CD_3$, the peak at 2.5 ppm splits into two separate resonances for two distinct sets of Zr−CH_2 protons at 2.92 and 3.44 ppm, respectively. The dineopentyl complex [MesNpy]ZrNp$_2$ could also be isolated readily from the reaction between [MesNpy]-ZrCl$_2$ and 2 equiv of neopentyllithium. (Similar reactions with neopentylmagnesium chloride were unsuccessful.) The ^{1}H NMR spectrum (20 °C, C_6D_6) of [MesNpy]ZrNp$_2$ showed two resonances for the *tert*-butyl protons at 1.10 and 1.36 ppm and another set of signals for the Zr−CH_2 groups at 1.27 and 1.46 ppm. Presumably intermolecular alkyl exchange is slow in [MesNpy]ZrNp$_2$, at least on the NMR time scale.

Dialkylzirconium complexes in which β-protons are present in the alkyl group have limited stability. [MesNpy]Zr(i-Bu)$_2$ can be prepared, although light must be avoided in order to realize good yields (>90%). Different isobutyl resonances are observed, but a single broad resonance is observed for the ortho methyl groups in the proton NMR spectrum at 2.29 ppm at room temperature, consistent with rotation of the mesityl rings on the NMR time scale. Although [MesNpy]ZrEt$_2$ appeared to form as a product of the reaction between [MesNpy]ZrCl$_2$ and EtMgBr in diethyl ether, it was not stable enough to be isolated readily in pure form. Proton NMR spectra at 22 °C were consistent with the proposed composition, although decomposition was rapid at room temperature (minutes).

Synthesis and isolation of [TripNpy]Zr(i-Bu)$_2$ was more straightforward than that of [MesNpy]Zr(i-Bu)$_2$. Two isobutyl groups were observed in the NMR spectrum, and rotation about the Trip−N bonds was slow on the NMR time scale at room temperature. An X-ray study of [TripNpy]Zr(i-Bu)$_2$ revealed the structure shown in Figure 6. (See also Tables 2 and 3.) The ligand is bound in a *fac* manner with the alkyl groups in axial and equatorial positions, as found for other dialkyl complexes in this category mentioned so far. The structural features are similar to those of [MesNpy]-ZrMe$_2$. The Zr−C(5)−C(6) and Zr−C(1)−C(2) bond angles are 130.3 and 135.5°, respectively.

Synthesis of Hafnium Dialkyl Complexes. Hafnium complexes, [MesNpy]Hf(NMe$_2$)$_2$ and [MesNpy]HfCl$_2$, can be prepared readily by a procedure analogous to that shown in Scheme 1. Alkylation of [MesNpy]HfCl$_2$ leads to relatively stable [MesNpy]HfR$_2$ species, even when β protons are present in R. Dialkyl complexes have been isolated for R = Me, Et, n-Pr, i-Pr, n-Bu, and i-Bu. NMR spectra of [MesNpy]HfMe$_2$ and its ^{13}C-labeled analogue are entirely analogous to those for [MesNpy]-ZrMe$_2$. NMR spectra of other dialkyls are straightforward, with different resonances for axial and equatorial alkyl groups and broad resonances for the ortho methyl

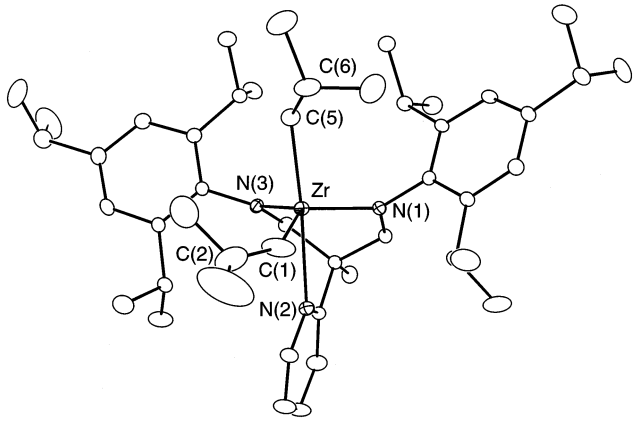


Figure 6. Thermal ellipsoid plot (35% probability level) of [TripNpy]Zr(i-Bu)$_2$.

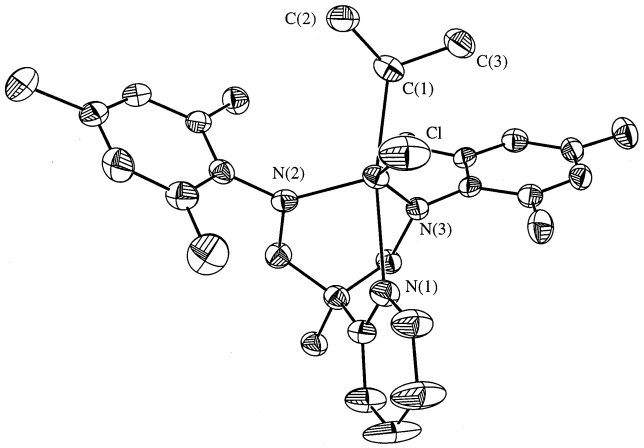


Figure 7. Thermal ellipsoid plot (35% probability level) of the structure of [MesNpy]Hf(i-Pr)Cl.

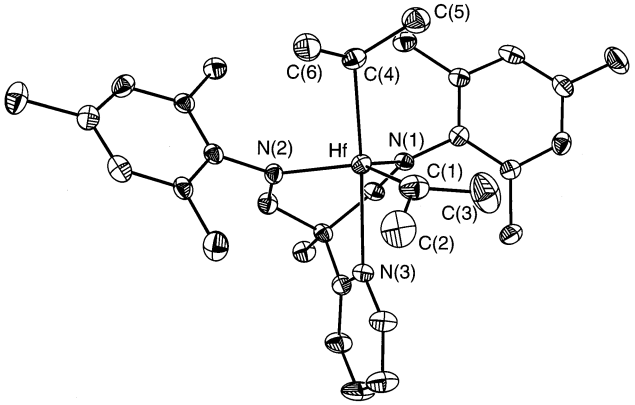


Figure 8. Thermal ellipsoid plot (35% probability level) of the structure of [MesNpy]Hf(i-Pr)$_2$.

groups in the mesityl rings being observed. (All data can be found in the Experimental Section.) The preparation and isolation of relatively stable [TripNpy]Hf(i-Bu)$_2$ is also straightforward.

Addition of only 1 equiv of i-PrMgCl to [MesNpy]HfCl$_2$ led to isolation of [MesNpy]Hf(i-Pr)Cl. Only one isomer was observed, according to NMR spectra of this compound. Treatment of [MesNpy]Hf(i-Pr)Cl with 1.2 equiv of MeMgBr led to two major products, which we presume to be isomers that contain the isopropyl group either in an axial or in an equatorial position, i.e., [MesNpy]Hf(i-Pr)$_{eq}$Me$_{ax}$ and [MesNpy]HfMe$_{eq}$(i-Pr)$_{ax}$. Minor amounts of [MesNpy]HfMe$_2$ and [MesNpy]Hf(i-Pr)$_2$ are also present in solution, presumably as a consequence of some alkyl exchange between hafnium and magnesium compounds. Treatment of [MesNpy]HfCl$_2$ with 2 equiv of (t-Bu)MgCl resulted in the formation of [MesNpy]Hf(t-Bu)Cl in 48% yield. The ^{1}H NMR spectrum (22 °C, C_6D_6) showed a resonance at 0.98 ppm corresponding to nine Hf−C(CH_3)$_3$ protons. The ^{13}C{^{1}H} NMR spectrum showed only one signal for the Hf−*C*(CH$_3$)$_2$ carbon at 70.6 ppm.

The X-ray crystal structure of [MesNpy]Hf(i-Pr)Cl (Figure 7, Tables 2 and 3) reveals that the isopropyl group is located in the axial position of a trigonal-bipyramidal structure that overall is similar to the structure of other five-coordinate species discussed here. However, the Cl−Hf−N$_{amido}$ angles (118.49(14) and 139.98(15)°) are significantly different, and this structure therefore is distorted significantly compared to other five-coordinate species reported here. On the basis of this structure we assume that the *tert*-butyl group in [MesNpy]Hf(t-Bu)Cl is also located in the axial position.

An X-ray study of [MesNpy]Hf(i-Pr)$_2$ (Figure 8, Tables 2 and 3) revealed, as expected, that the structure of [MesNpy]Hf(i-Pr)$_2$ is similar to that of the other dialkyl complexes. The TBP geometry is slightly distorted with N(1)−Hf−C(1) = 122.75(17)° and N(2)−Hf−C(1) = 134.62(17)°. The Hf−C(1)−C(2) angle is 135.1(4)°, but the Hf−C(1)−C(3) angle is only 107.9(3)°. (The Hf−C(4)−C(5) and Hf−C(4)−C(6) angles are 118.6(3) and 111.7(3)°, respectively.) We could find no evidence (e.g., an agostic interaction) that would lead to an explanation of the difference between the Hf−C(1)−C(2) and Hf−C(1)−C(3) angles.

Discussion

The complexes reported here further establish that [ArNpy]$^{2-}$ ligands (Ar = Mes, Trip, 3,5-Cl$_2$C$_6$H$_3$[20]) enforce formation of complexes in which the ligand is bound in a *fac* manner to the metal, as has been observed in several group 4 complexes that contain the [TMSNpy]$^{2-}$ ligand.[3,4] Since the plane of an amido ligand approximately bisects the C$_{ax}$−M−C$_{eq}$ angle in five-coordinate dialkyl complexes, it is not apparent, in the absence of calculations, whether one or two metal−nitrogen (amido) π-bonds can form efficiently and, therefore, whether a five-coordinate species has a 12- or a 14-electron count. In a variety of other amido complexes of early metals[1] the σ- and π-electron-donating ability of nitrogen in nitrogen-based ligands in general almost certainly decreases the electrophilicity of the metal and consequently the polarity of metal−carbon bonds in general, thereby leading to electron-deficient dialkyl complexes that are relatively stable toward intermolecular or intramolecular β-hydride abstraction reactions. The ability of nitrogen in amido complexes to delocalize positive charge from the metal out onto the amido nitrogens clearly also will be even more important in cationic complexes.

The increased stability of hafnium dialkyls versus zirconium dialkyls toward β-hydride processes is relatively well documented in the literature.[21−23] For example, Cp$_2$MEt$_2$ is relatively stable only when M = Hf. Even Cp$_2$Hf(t-Bu)Cl is known, and it reacts with butyllithium to give isolable Cp$_2$Hf(t-Bu)(n-Bu).[24] However, several dialkylzirconocenes in which the alkyl contains a β-hydrogen are also known.[22,25] Amido ligands appear to produce more stable dialkyl complexes, as demonstrated by Andersen some time ago.[26,27] In our research on diamido/donor complexes we have found many examples of relatively stable dialkyls in which the alkyl contains a β-hydrogen, e.g., diisobutyl complexes that

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contain $[(t\text{-BuN-}o\text{-}C_6H_5)_2O]^{2-}$ or $[(i\text{-PrN-}o\text{-}C_6H_5)_2O]^{2-}$ ligands.[6b,c,h] In one case even a titanium diisobutyl complex ($[(i\text{-PrN-}o\text{-}C_6H_4)_2O]Ti(i\text{-Bu})_2$) was stable at room temperature.[6c] Recently Sita[28−33] published several examples of stable acetamidinate complexes of the type Cp*Zr(acetamidinate)R(Cl) and Cp*Zr(acetamidinate)-R_2, including an example of a Cp*Zr(acetamidinate)-(t-Bu)(Cl) species. Therefore, nitrogen-based ligands in general appear to stabilize group 4 monoalkyl and dialkyl complexes against facile β-hydride elimination or abstraction. If a stable dialkyl complex is to be prepared, then clearly the supporting ligand must be large enough to prevent any intermolecular decomposition of a monoalkyl intermediate or the dialkyl product, but not so large as to prevent formation of a dialkyl complex or to induce a β-hydride abstraction reaction in a dialkyl complex to give an olefin complex. Therefore, the fact that [MesNpy]Hf(i-Pr)$_2$ is stable toward β-hydride abstraction is not especially surprising, nor is the stability of [MesNpy]Hf(t-Bu)Cl. (We could find no example of a diisopropyl complex that contains a group 4 metal.)

In future publications we will employ many of the Zr or Hf dialkyl complexes reported here as precursors to monoalkyl monocations. We have shown that {[MesNpy]-HfR}$[B(C_6F_5)_4]$ species are stable below 10 °C in chlorobenzene or bromobenzene and will serve as catalysts for the living polymerization of up to 600 equiv of 1-hexene without any detectable β-hydride elimination.[12] The rigidity of the $[ArNpy]^{2-}$ ligand and the ability to vary the size of the substituent on the amido nitrogen will both help define the degree of steric crowding in the resulting ion pair more definitively than has been possible in other diamido/donor ligand systems that we have employed in past studies.[6]

Experimental Section

General Procedures. All manipulations, with the exception of the synthesis of ligand precursors, were performed under N_2 in a glovebox or using standard Schlenk procedures. Solvents were dried using conventional procedures.[34] Chlorobenzene (HPLC grade) and deuterated solvents were degassed and stored over and distilled from CaH_2. Commercial reagents were used without further purification. NMR spectra were recorded on a Varian INOVA 500 spectrometer. ^{1}H NMR chemical shifts are given in ppm versus residual protons in the deuterated solvents as follows: δ 7.16, C_6D_6; δ 2.09, toluene-d_8 (methyl); δ 7.29, C_6D_5Br (most downfield resonance). $^{13}C\{^1H\}$ NMR chemical shifts are given in ppm versus residual ^{13}C in the solvents as follows: δ 128.39, C_6D_6; δ 20.4, toluene-d_8 (methyl); δ 122.25, C_6D_5Br (most upfield resonance). Some aryl resonances in ^{1}H and $^{13}C\{^1H\}$ spectra are not given.

Elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. The Grignard reagents $^{13}CH_3MgI$ and $(CH_3)_2CH^{13}CH_2MgBr$ were prepared from $^{13}CH_3I$ and $(CH_3)_2CH^{13}CH_2Br$, respectively, and Mg turnings in diethyl ether according to standard procedures. All others were purchased from Aldrich. All Grignard reagents were carefully titrated with 2-butanol in the presence of 1,10-phenanthroline prior to use. $H_2[H_3CC(2\text{-}C_5H_4N)(CH_2NAr)_2]$,[4] $Zr(NMe_2)_4$,[35] and $Hf(NMe_2)_4$[35] were prepared according to previously reported methods.

The reaction between $^{13}CO_2$ and i-PrMgBr in diethyl ether followed by in situ reduction with $LiAlH_4$ and quenching of the reaction mixture with water yielded $(CH_3)_2CH^{13}CH_2OH$. The alcohol was separated from diethyl ether by careful and repeated distillations. The alcohol was treated with PBr_3 at 0 °C, followed by refluxing at 90 °C for 2 h, to yield $(CH_3)_2CH^{13}CH_2Br$, which was distilled (80−84 °C, 30 mTorr) and dried over $MgSO_4$.

H_2[MesNpy]. A Schlenk flask was charged with $H_3CC(2\text{-}C_5H_4N)(CH_2NH_2)_2$ (5.00 g, 30 mmol), mesityl bromide (11.74 g, 59 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.419 g, 0.45 mmol), *rac*-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (0.717 g, 1.15 mmol), sodium *tert*-butoxide (8.75 g, 91 mmol), and toluene (200 mL). The reaction mixture was stirred and heated to 110 °C under a stream of N_2. The reaction was complete after 1 day, with H_2[MesNpy] being the only significant product in the reaction mixture. The hot solution was filtered through Celite to remove NaBr and washed with pentane. The solvent was removed in vacuo, and the red residue was dissolved in refluxing pentane (200 mL) and filtered while hot. Clear, colorless crystals of H_2[MesNpy] were obtained from pentane: yield 7.5 g (63%); ^{1}H NMR (500 MHz, $CDCl_3/C_6D_6$, 295 K) δ 1.71/1.59 (s, 3H, C*H*$_3$), 2.16/2.21 (s, 12H, *o*-C*H*$_3$), 2.21/2.19 (s, 6H, *p*-C*H*$_3$), 3.17/3.25 (d, 2H, C*H*$_2$), 3.45/3.49 (d, 2H, C*H*$_2$), 3.45/3.70 (s, 2H, N*H*), 6.79/6.79 (s, 4H, C*H*), 7.22/6.63 (m, 1H, py C*H*), 7.49/7.06 (m, 1H, py C*H*), 7.71/7.07 (m, 1H, py C*H*), 8.69/8.41 (m, 1H, py *o*-C*H*); $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 295 K) δ 18.86 (s, *o*-*C*H$_3$), 21.17 (s, *p*-*C*H$_3$), 23.31 (s, *C*H$_3$), 46.97 (s, *C*R$_4$), 57.97 (s, *C*H$_2$), 121.76 (s, Ar *C*), 122.00 (s, Ar *C*), 130.25 (s, Ar *C*), 130.83 (s, Ar *C*), 131.59 (s, Ar *C*), 136.65 (s, Ar *C*), 144.99 (s, Ar *C*), 149.25 (s, Ar *C*), 165.77 (s, Ar *C*); HRMS (EI, 70 eV) *m*/*z* calcd for $C_{27}H_{35}N_3$ 401.283 098, found 401.2840 (12).

H_2[TripNpy]. A Schlenk flask was charged with $H_3CC(2\text{-}C_5H_4N)(CH_2NH_2)_2$ (5.16 g, 31.2 mmol), triisopropylphenyl bromide (17.25 g, 60.9 mmol), tris(dibenzylideneacetone)-dipalladium(0) (0.429 g, 0.468 mmol), *rac*-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (0.603 g, 0.968 mmol), sodium *tert*-butoxide (9.06 g, 94.3 mmol), and toluene (400 mL). The reaction mixture was refluxed under a stream of dinitrogen. The reaction was complete after 8 days, with H_2[TripNpy] being the only significant product in the reaction mixture. The solvent was removed in vacuo and the purple residue taken up in diethyl ether (100 mL). The solution was washed with H_2O (4 × 100 mL) and saturated NaCl (3 × 100 mL). The organic phase was dried over $MgSO_4$. Evaporation of the solvent gave a red solid which was used without further purification: yield 14.4 g (81%); ^{1}H NMR (500 MHz, $CDCl_3/C_6D_6$, 295 K) δ 1.13/1.23 (d, 12H, CH_3), 1.90/1.25 (d, 12H, C*H*$_3$), 1.23/1.30 (d, 12H, C*H*$_3$), 1.77/1.76 (s, 3H, C*H*$_3$), 2.83/2.84 (m, 2H, C*H*), 3.03/3.27 (d/m, 2H, C*H*$_2$), 3.14/3.42 (m, 4H, C*H*), 3.43/3.63 (d/m, 2H, C*H*$_2$), 3.26/3.67 (s/m, 2H, N*H*), 6.91/7.10 (s, 4H, C*H*), 7.22/6.68 (m, 1H, py C*H*), 7.51/7.10 (m, 1H, py C*H*), 7.70/7.10 (m, 1H, py C*H*), 8.68/8.50 (m, 1H, py *o*-C*H*); $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 295 K) δ 23.08 (s, *C*H$_3$), 24.80 (s, *C*H$_3$), 24.94 (s, *C*H$_3$), 28.18 (s, *C*H$_3$), 34.96 (s, *C*H), 35.15 (s, *C*H), 47.15 (s, *C*R$_4$), 61.55 (s, *C*H$_2$), 121.77 (s, Ar *C*), 122.00 (s, Ar *C*), 122.91 (s, Ar *C*), 122.77 (s, Ar *C*), 128.68 (s, Ar *C*), 136.63 (s, Ar *C*), 142.47 (s, Ar *C*), 143.56 (s, Ar *C*), 144.55 (s, Ar *C*), 149.27 (s, Ar *C*), 165.89 (s, Ar *C*); HRMS (EI, 70 eV) *m*/*z* calcd for $C_{39}H_{59}N_3$ 569.4704, found 569.4708.

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[MesNpy]Zr(NMe$_2$)$_2$. Zr(NMe$_2$)$_4$ (2.00 g, 7.48 mmol) and H$_2$[MesNpy] (3.16 g, 7.86 mmol) were dissolved in pentane (60 mL). The reaction mixture was stirred at room temperature for 16 h. The mixture was filtered, and the solvent was evaporated from the filtrate to yield an orange solid: yield 3.90 g (86%). [MesNpy]Zr(NMe$_2$)$_2$ can be recrystallized from pentane at −30 °C to yield yellow-orange crystals: ^{1}H NMR (500 MHz, C$_6$D$_6$, 295 K) δ 1.07 (s, 3H, CH_3), 2.20 (s, 6H, *p*-CH_3), 2.30 (s, 12H, *o*-CH_3), 2.83 (d, 2H, CH_2), 2.99 (s, 6H, N(CH_3)$_2$), 3.00 (s, 6H, N(CH_3)$_2$), 4.12 (d, 2H, CH_2), 6.68 (m, 1H, py C*H*), 6.87 (m, 1H, py C*H*), 6.89 (s, 4H, C*H*), 7.09 (m, 1H, py C*H*), 8.69 (m, 1H, py *o*-C*H*); ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 295 K) δ 19.68 (s, *o*-*C*H$_3$), 21.28 (s, *p*-*C*H$_3$), 25.29 (s, *C*H$_3$), 42.53 (s, N(*C*H$_3$)$_2$), 45.14 (s, N(*C*H$_3$)$_2$), 47.01 (s, *C*R$_4$), 67.03 (s, *C*H$_2$), 120.65 (s, Ar *C*), 122.18 (s, Ar *C*), 130.07 (s, Ar *C*), 132.12 (s, Ar *C*), 134.14 (s, Ar *C*), 138.92 (s, Ar *C*), 148.63 (s, Ar *C*), 149.96 (s, Ar *C*), 163.94 (s, Ar *C*). Anal. Calcd for C$_{31}$H$_{45}$N$_5$Zr: C, 64.31; H, 7.83; N, 12.10. Found: C, 64.39; H, 7.76; N, 11.94.

[MesNpy]ZrCl$_2$. To a solution of [MesNpy]Zr(NMe$_2$)$_2$ (7.74 g, 13.4 mmol) in diethyl ether (200 mL) was added TMSCl (5.09 mL, 40.0 mmol), and the reaction mixture was stirred at room temperature for 1 h. The resulting white solid was filtered, washed with pentane (3 × 10 mL), and dried in vacuo for 4 h: yield 6.50 g (86%). [MesNpy]ZrCl$_2$ can be recrystallized from toluene at room temperature to yield clear, colorless crystals: ^{1}H NMR (500 MHz, C$_6$D$_6$, 295 K) δ 0.86 (s, 3H, CH$_3$), 1.51 (s, 6H, *o*-CH$_3$), 2.16 (s, 6H, *p*-CH$_3$), 2.76 (d, 2H, CH$_2$), 2.90 (s, 6H, *o*-CH$_3$), 3.83 (d, 2H, CH$_2$), 6.65 (m, 1H, py CH), 6.70 (s, 2H, CH), 6.89 (m, 1H, py CH), 6.90 (s, 2H, CH), 6.98 (m, 1H, py CH), 10.41 (m, 1H, py *o*-CH); ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 295 K) δ 18.63 (s, *o*-CH$_3$), 19.08 (s, *o*-CH$_3$), 19.85 (s, *p*-CH$_3$), 21.30 (s, CH$_3$), 46.89 (s, CR$_4$), 65.82 (s, CH$_2$), some aryl peaks are omitted. Anal. Calcd for C$_{27}$H$_{33}$N$_3$Cl$_2$Zr: C, 57.73; H, 5.92; N, 7.48; Cl, 12.62. Found: C, 57.61; H, 6.11; N, 7.42; Cl, 12.47.

[MesNpy]ZrMe$_2$. A suspension of [MesNpy]ZrCl$_2$ (0.606 g, 1.079 mmol) in diethyl ether (30 mL) was cooled to −30 °C. To the cold solution was added MeMgBr (3.4 M in diethyl ether, 0.666 mL, 2.266 mmol), and the resulting mixture was stirred at room temperature for 15 min until the cloudy suspension became clear. (*Note: correct stoichiometry is very important to the success of the reaction*.) Dioxane (0.216 mL, 2.535 mmol) was added to the solution, and the mixture was filtered through Celite. The filtrate was reduced to ∼5 mL and stored at −30 °C for 1 day to give [MesNpy]ZrMe$_2$ as clear, colorless crystals; yield 0.33 g (59%). The ^{13}C-labeled complex [MesNpy]Zr(^{13}Me)$_2$ was prepared in a similar manner using ^{13}MeMgI. White crystals suitable for a single-crystal X-ray diffraction study were grown by slow crystallization from diethyl ether at −30 °C: ^{1}H NMR (500 MHz, C$_6$D$_6$, 295 K) δ 0.56 (s, 6H, Zr−CH_3), 0.95 (s, 3H, CH_3), 2.18 (s, 6H, *p*-CH_3), 2.27 (s, 12H, *o*-CH_3), 2.73 (d, 2H, CH_2), 4.04 (d, 2H, CH_2), 6.56 (m, 1H, py C*H*), 6.77 (m, 1H, py C*H*), 6.87 (s, 4H, C*H*), 7.02 (m, 1H, py C*H*), 8.77 (m, 1H, py *o*-C*H*); ^{1}H NMR (500 MHz, C$_6$D$_5$Br, 295 K) δ 0.22 (s, 3H, Zr−CH_3), 0.32 (s, 3H, Zr−CH_3), 1.24 (s, 3H, CH_3), 2.16 (s, 12H, *o*-CH_3), 2.18 (s, 6H, *p*-CH_3), 2.74 (d, 2H, CH_2), 4.05 (d, 2H, CH$_2$), 6.80 (s, 4H, CH), 6.97 (m, 1H, py CH), 7.18 (m, 1H, py CH), 7.47 (m, 1H, py CH), 8.83 (m, 1H, py *o*-CH); ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 295 K) δ 19.28 (s, *o*-CH$_3$), 21.31 (s, p-CH$_3$), 25.47 (s, CH$_3$), 36.5 (broad s, Zr−CH$_3$), 46.31 (s, CR$_4$), 66.13 (s, CH$_2$), 120.89 (s, Ar *C*), 122.61 (s, Ar *C*), 130.28 (s, Ar *C*), 134.18 (s, Ar *C*), 135.08 (s, Ar *C*), 139.33 (s, Ar *C*), 145.97 (s, Ar *C*), 147.41 (s, Ar *C*), 162.75 (s, Ar *C*); ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_5$Br, 295 K) δ 19.92 (s, *o*-*C*H$_3$), 21.08 (s, *p*-*C*H$_3$), 25.33 (s, *C*H$_3$), 35.46 (s, Zr−*C*H$_3$), 36.65 (s, Zr−*C*H$_3$), 45.85 (s, *C*R$_4$), 65.42 (s, *C*H$_2$), 120.65 (s, Ar *C*), 122.14 (s, Ar *C*), 131.44 (s, Ar *C*), 133.43 (s, Ar *C*), 134.46 (s, Ar *C*), 139.26 (s, Ar *C*), 145.36 (s, Ar *C*), 146.78 (s, Ar *C*), 162.13 (s, Ar *C*). Anal. Calcd for C$_{29}$H$_{39}$N$_3$Zr: C, 66.87; H, 7.55; N, 8.07. Found: C, 67.02; H, 7.46; N, 7.94.

[MesNpy]ZrBz$_2$. A suspension of [MesNpy]ZrCl$_2$ (0.206 g, 0.367 mmol) in diethyl ether (30 mL) was cooled to −30 °C. To the cold solution was added PhCH$_2$MgCl (1.0 M in diethyl ether, 0.73 mL, 0.73 mmol), and the resulting mixture was stirred at room temperature for 15 min until the cloudy suspension became clear. Dioxane (0.06 mL, 0.73 mmol) was added to the solution, and the mixture was filtered through Celite. The filtrate was reduced to ∼5 mL and stored at −30 °C for 1 day to give [MesNpy]ZrBz$_2$ as yellow crystals: yield 0.21 g (83%); ^{1}H NMR (500 MHz, C$_6$D$_6$, 295 K) δ 0.87 (s, 3H, CH_3), ∼2 (v broad s, 12H, *o*-CH_3), 2.26 (s, 6H, *p*-CH_3), ∼2.5 (broad s, 2H, CH_2Ph), 2.65 (d, 2H, CH_2), 4.01 (d, 2H, CH_2), 6.53 (m, 1H, py C*H*), 6.68 (m, 1H, py C*H*), 6.78 (m, 1H, py C*H*), ∼6.8 (broad s, 4H, C*H*), 6.91 (broad s, 4H, Bn-C*H*), 6.93 (m, 2H, Bn-C*H*), 7.04 (m, 4H, Bn-C*H*), 8.65 (m, 1H, py *o*-C*H*). Anal. Calcd for C$_{41}$H$_{47}$N$_3$Zr: C, 73.17; H, 7.04; N, 6.24. Found: C, 73.25; H, 7.07; N, 6.19.

[MesNpy]ZrNp$_2$. A suspension of [MesNpy]ZrCl$_2$ (1.01 g, 1.80 mmol) in diethyl ether (30 mL) was cooled to −30 °C. To the cold solution was added a solution of NpLi (0.280 g, 3.60 mmol) in diethyl ether at −30 °C, and the resulting mixture was stirred at room temperature for 45 min until the cloudy suspension became clear orange. The mixture was filtered through Celite, and the filtrate was reduced to ∼15 mL and stored at −30 °C for 1 day to give [MesNpy]ZrNp$_2$ as a white powder: yield 0.59 g (52%); ^{1}H NMR (500 MHz, C$_6$D$_6$, 295 K) δ 0.95 (s, 3H, CH_3), 1.10 (s, 9H, Zr−CH$_2$C(CH_3)$_3$), 1.27 (s, 2H, Zr−CH_2C(CH$_3$)$_3$), 1.36 (s, 9H, Zr−CH$_2$C(CH_3)$_3$), 1.46 (s, 2H, Zr−CH_2C(CH$_3$)$_3$), 2.14 (s, 6H, *p*-CH_3), ∼2.3 (v broad s, 12H, *o*-CH_3), 2.75 (d, 2H, CH_2), 4.03 (d, 2H, CH_2), 6.67 (m, 1H, py C*H*), 6.78 (m, 1H, py C*H*), 6.88 (s, 4H, C*H*), 7.05 (m, 1H, py C*H*), 9.17 (m, 1H, py *o*-C*H*); ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 295 K) δ 19.76 (s, *o*-*C*H$_3$), 21.25 (s, *o*-*C*H$_3$), 23.07 (s, *p*-*C*H$_3$), 25.46 (s, *C*H$_3$), 34.40 (s, Zr−CH$_2$*C*(CH$_3$)$_3$), 35.47 (s, Zr−CH$_2$C-(*C*H$_3$)$_3$), 36.26 (s, Zr−CH$_2$*C*(CH$_3$)$_3$), 36.32 (s, Zr−CH$_2$C(*C*H$_3$)$_3$), 46.28 (s, *C*R$_4$), 67.07 (s, *C*H$_2$), 79.61 (s, Zr−*C*H$_2$C(CH$_3$)$_3$), 82.07 (s, Zr−*C*H$_2$C(CH$_3$)$_3$), 120.54 (s, Ar *C*), 122.02 (s, Ar *C*), 128.68 (s, Ar *C*), 134.02 (s, Ar *C*), 139.07 (s, Ar *C*), 147.48 (s, Ar *C*), 148.38 (s, Ar *C*), 163.47 (s, Ar *C*). Anal. Calcd for C$_{37}$H$_{55}$N$_3$Zr: C, 70.20; H, 8.76; N, 6.64. Found: C, 70.08; H, 8.65; N, 6.86.

[MesNpy]Zr(i-Bu)$_2$. *Note: all of the following manipulations were carried out in the absence of light.* A suspension of [MesNpy]ZrCl$_2$ (0.212 g, 0.377 mmol) in diethyl ether (10 mL) was cooled to −30 °C. To the cold solution was added (i-Bu)-MgBr (2.0 M in diethyl ether, 0.377 mL, 0.755 mmol), and the resulting mixture was stirred at room temperature for 10 min until the cloudy suspension became clear. Dioxane (0.080 mL, 0.944 mmol) was added to the solution, and the mixture was filtered through Celite. The solvent was removed in vacuo to give a white powder; yield 0.21 g (92%). [MesNpy]Zr(i-Bu)$_2$ can be recrystallized from diethyl ether at −30 °C to yield clear, colorless crystals: ^{1}H NMR (500 MHz, C$_6$D$_6$, 295 K) δ 0.94 (s, 3H, CH_3), 0.97 (d, 6H, Zr−CH$_2$CH(CH_3)$_2$), 1.04 (m, 4H, Zr−CH_2CH(CH$_3$)$_2$), 1.27 (d, 6H, Zr−CH$_2$CH(CH_3)$_2$), 2.16 (s, 6H, *p*-CH_3), 2.29 (broad s, 12H, *o*-CH_3), 2.35 (m, 1H, Zr−CH$_2$C*H*(CH$_3$)$_2$), 2.52 (m, 1H, Zr−CH$_2$C*H*(CH$_3$)$_2$), 2.72 (d, 2H, CH_2), 4.00 (d, 2H, CH_2), 6.62 (m, 1H, py C*H*), 6.78 (m, 1H, py C*H*), 6.89 (s, 4H, C*H*), 7.02 (m, 1H, py C*H*), 8.87 (m, 1H, py *o*-C*H*); ^{1}H NMR (500 MHz, C$_6$D$_5$Br, 295 K) δ 0.74 (d, 6H, Zr−CH$_2$CH(CH_3)$_2$), 0.81 (d, 2H, Zr−CH_2CH(CH$_3$)$_2$), 0.88 (d, 2H, Zr−CH_2CH(CH$_3$)$_2$), 1.11 (d, 6H, Zr−CH$_2$CH(CH_3)$_2$), 1.22 (s, 3H, CH_3), 2.14 (s, 6H, *p*-CH_3), 2.19 (broad s, 13H, *o*-CH_3, Zr−CH$_2$C*H*(CH$_3$)$_2$), 2.39 (m, 1H, Zr−CH$_2$C*H*(CH$_3$)$_2$), 2.73 (d, 2H, CH_2), 4.02 (d, 2H, CH_2), 6.82 (s, 4H, C*H*), 7.02 (m, 1H, py C*H*), 7.17 (m, 1H, py C*H*), 7.48 (m, 1H, py C*H*), 8.89 (m, 1H, py *o*-C*H*); ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 295 K) δ 19.25 (s, *o*-*C*H$_3$), 21.31 (s, *p*-*C*H$_3$), 25.67 (s, *C*H$_3$), 29.03 (s, Zr−CH$_2$CH-(*C*H$_3$)$_2$), 29.63 (s, Zr−CH$_2$CH(*C*H$_3$)$_2$), 30.51 (s, Zr−CH$_2$*C*H-(CH$_3$)$_2$), 32.72 (s, Zr−CH$_2$*C*H(CH$_3$)$_2$), 46.18 (s, *C*R$_4$), 66.52 (s, *C*H$_2$), 72.59 (s, Zr−*C*H$_2$CH(CH$_3$)$_2$), 74.21 (s, Zr−*C*H$_2$CH(CH$_3$)$_2$), 120.93 (s, Ar *C*), 122.60 (s, Ar *C*), 130.18 (s, Ar *C*), 134.19 (s, Ar *C*), 135.18 (s, Ar *C*), 139.19 (s, Ar *C*), 146.79 (s, Ar *C*), 147.42

(s, Ar *C*), 163.22 (s, Ar *C*). Anal. Calcd for $C_{35}H_{51}N_3Zr$: C, 69.48; H, 8.50; N, 6.95. Found: C, 69.37; H, 8.48; N, 6.86.

[MesNpy]Zr(THF)Me$_2$. $ZrCl_4$ (0.89 g, 3.80 mmol) was added to a cold (−30 °C) solution of H_2[MesNpy] (2.00 g, 3.84 mmol) in diethyl ether (30 mL). The mixture was stirred at room temperature for 1 h to yield a pink-orange solid. The mixture was cooled to −30 °C, and MeMgCl (3.0 M in THF, 5.2 mL, 15.58 mmol) was added. The reaction mixture was stirred for 20 min at room temperature. Dioxane (1.51 g, 17.11 mmol) was added to the mixture, the ensuing white solid filtered through Celite, and the orange filtrate taken to dryness in vacuo. After trituration with pentane (3 × 15 mL), [MesNpy]-Zr(THF)Me_2 was obtained as a yellow powder, which was washed with cold pentane (3 × 10 mL) and dried in vacuo: yield 1.6 g (70%); ^{1}H NMR (C_6D_6, 295 K) δ 0.45 (s, 6H, CH_3), 0.98 (s, 3H, CH_3), 1.21 (m, 4H, O(CH$_2$CH_2)$_2$), 2.15 (s, 6H, *p*-CH_3), 2.23 (s, 12H, *o*-CH_3), 2.76 (d, 2H, CH_2), 3.48 (m, 4, O(CH_2CH$_2$)$_2$), 3.90 (d, 2H, CH_2), 6.62 (m, 1H, py C*H*), 6.84 (s, 4H, C*H*), 6.86 (m, 1H, py C*H*), 7.05 (m, 1H, py C*H*), 8.85 (m, 1H, py C*H*); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 295 K) δ 18.61 (s, *o*-*C*H$_3$), 20.83 (s, *p*-*C*H$_3$), 24.85 (s, *C*H$_3$), 35.04 (s, O(CH$_2$*C*H$_2$)$_2$) 35.8 (broad s, Zr−*C*H$_3$), 46.29 (s, *C*R$_4$), 65.82 (s, *C*H$_2$), 35.04 (s, O(*C*H$_2$CH$_2$)$_2$), 120.67 (s, Ar *C*), 121.83 (s, Ar *C*), 129.63 (s, Ar *C*), 133.09 (s, Ar *C*), 134.86 (s, Ar *C*), 138.51 (s, Ar *C*), 147.05 (s, Ar *C*), 147.98 (s, Ar *C*), 162.87 (s, Ar *C*). Anal. Calcd for $C_{29}H_{39}N_3Zr$: C, 66.84; H, 7.99; N, 7.09. Found: C, 66.69; H, 7.91; N, 6.99.

Yellow crystals suitable for a single-crystal X-ray diffraction study were grown by slow crystallization from diethyl ether at −30 °C.

[Li(Et$_2$O)]{[MesNpy]ZrMe$_3$}. A suspension of [MesNpy]-$ZrMe_2$ (0.092 g, 1.079 mmol) in diethyl ether (5 mL) was cooled to −30 °C. To the cold solution was added MeLi (4.4 M in diethyl ether, 0.126 mL, 1.76 mmol), and the mixture was stirred at room temperature for 10 min. The resulting solution was filtered through Celite, and the filtrate was dried in vacuo to give [Li·OEt$_2$][(MesNpy)ZrMe_3] as a white powder: yield 0.109 g (100%); ^{1}H NMR (500 MHz, C_6D_6, 295 K) δ −0.06 (s, 9H, Zr−CH_3), 1.00 (t, 6H, O−CH$_2$CH_3), 1.12 (s, 3H, CH_3), 1.78 (s, 6H, *o*-CH_3), 2.21 (s, 6H, *p*-CH_3), 2.94 (s, 6H, *o*-CH_3), 3.02 (d, 2H, CH_2), 3.16 (q, 4H, O−CH$_2$CH_3), 3.85 (d, 2H, CH_2), 6.64 (m, 1H, py C*H*), 6.92 (s, 2H, C*H*), 7.02 (m, 1H, py C*H*), 7.07 (s, 2H, C*H*), 7.10 (m, 1H, py C*H*), 9.10 (m, 1H, py *o*-C*H*). Anal. Calcd for $C_{37}H_{52}N_3LiOZr$: C, 66.19; H, 8.50; N, 6.81. Found: C, 66.26; H, 8.43; N, 6.89.

White crystals suitable for a single-crystal X-ray diffraction study were grown by slow crystallization from diethyl ether at −30 °C.

[TripNpy]Zr(NMe$_2$)$_2$. $Zr(NMe_2)_4$ (2.53 g, 9.43 mmol) and H_2[TripNpy] (6.45 g, 11.3 mmol) were dissolved in pentane (80 mL). The reaction mixture was stirred at room temperature for 16 h. The first batch of product was filtered off, and the filtrate was stirred at room temperature for a further 16 h. The solvent was reduced in volume in vacuo to yield more product as a white precipitate. The products were combined and washed with small amounts of cold pentane: yield 1.5 g (60%); ^{1}H NMR (500 MHz, C_6D_6, 295 K) δ 0.67 (d, 6H, CH_3), 1.08 (s, 3H, CH_3), 1.28 (d, 12H, CH_3), 1.33 (d, 6H, CH_3), 1.57 (d, 6H, CH_3), 1.58 (d, 6H, CH_3), 2.86 (m, 4H, C*H*), 2.89 (s, 6H, N(CH_3)$_2$), 3.01 (d, 2H, CH_2), 3.04 (s, 6H, N(CH_3)$_2$), 4.08 (m, 2H, C*H*), 4.19 (d, 2H, CH_2), 6.69 (m, 1H, py C*H*), 6.79 (m, 1H, py C*H*), 7.05 (m, 1H, py C*H*), 7.10 (d, 2H, C*H*), 7.25 (d, 2H, C*H*), 8.71 (m, 1H, py *o*-C*H*); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 295 K) δ 24.81 (s, *C*H$_3$), 24.89 (s, *C*H$_3$), 24.93 (s, *C*H$_3$), 25.50 (s, *C*H$_3$), 26.50 (s, *C*H$_3$), 27.80 (s, *C*H), 29.01 (s, *C*H), 29.71 (s, *C*H), 34.87 (s, *C*H$_3$), 43.29 (s, N(*C*H$_3$)$_2$), 45.04 (s, N(*C*H$_3$)$_2$), 47.75 (s, *C*R$_4$), 70.09 (s, *C*H$_2$), 120.65 (s, Ar *C*), 121.55 (s, Ar *C*), 122.08 (s, Ar *C*), 122.75 (s, Ar *C*), 128.04 (s, Ar *C*), 139.00 (s, Ar *C*), 144.28 (s, Ar *C*), 144.33 (s, Ar *C*), 146.00 (s, Ar *C*), 149.09 (s, Ar *C*). Anal. Calcd for $C_{43}H_{69}N_5Zr$: C, 69.02; H, 9.31; N, 9.43. Found: C, 69.02; H, 9.30; N, 9.43.

[TripNpy]ZrCl$_2$. To a solution of [TripNpy]Zr(NMe$_2$)$_2$ (3.07 g, 4.11 mmol) in diethyl ether (80 mL) was added TMSCl (1.56 mL, 12.3 mmol), and the reaction mixture was stirred at room temperature for 4 h. The resulting white solid was filtered off, washed with pentane (3 × 10 mL) and dried in vacuo for 4 h: yield 2.8 g (93%); ^{1}H NMR (500 MHz, C_6D_6, 295 K) δ 0.63 (d, 6H, CH_3), 0.93 (s, 3H, CH_3), 1.02 (br d, 6H, CH_3), 1.29 (d, 6H, CH_3), 1.32 (d, 6H, CH_3), 1.55 (d, 6H, CH_3), 1.87 (d, 6H, CH_3), 2.31 (br m, 2H, CH), 2.87 (m, 2H, CH), 3.06 (d, 2H, CH_2), 4.03 (d, 2H, CH_2), 4.33 (br m, 2H, C*H*), 6.68 (m, 1H, py C*H*), 6.73 (m, 1H, py C*H*), 6.93 (m, 1H, py C*H*), 6.95 (s, 2H, C*H*), 7.25 (d, 2H, C*H*), 10.24 (m, 1H, py *o*-C*H*).

[TripNpy]ZrMe$_2$. A suspension of [TripNpy]$ZrCl_2$ (1.32 g, 1.81 mmol) in diethyl ether (20 mL) was cooled to −30 °C. To the cold solution was added MeMgBr (3.6 M in diethyl ether, 1.00 mL, 3.62 mmol), and the resulting mixture was stirred at room temperature for 30 min until the cloudy suspension became clear. Dioxane (0.39 mL, 4.5 mmol) was added to the solution, and the mixture was filtered through Celite. The filtrate was reduced to ∼5 mL and stored at −30 °C for 1 day to yield [TripNpy]$ZrMe_2$ as clear, colorless crystals: yield 0.61 g (49%). The ^{13}C-labeled complex, [TripNpy]Zr(^{13}Me)$_2$, was prepared in a similar manner using ^{13}MeMgI: ^{1}H NMR (500 MHz, C_6D_6, 295 K) δ 0.53 (s, 3H, Zr−CH_3), 0.61 (s, 3H, Zr−CH_3), 0.73 (d, 6H, CH_3), 0.95 (s, 3H, CH_3), 1.25 (d, 12H, CH_3), 1.40 (d, 6H, CH_3), 1.55 (d, 6H, CH_3), 1.65 (d, 6H, CH_3), 2.88 (m, 4H, C*H*), 2.89 (d, 2H, CH_2), 4.11 (d, 2H, CH_2), 4.18 (m, 2H, C*H*), 6.61 (m, 1H, py C*H*), 6.75 (m, 1H, py C*H*), 7.05 (m, 1H, py C*H*), 7.12 (s, 2H, C*H*), 7.23 (s, 2H, C*H*), 8.90 (m, 1H, py *o*-C*H*); ^{1}H NMR (500 MHz, C_6D_5Br, 295 K) δ 0.21 (s, 3H, Zr−CH_3), 0.33 (s, 3H, Zr−CH_3), 0.66 (d, 6H, CH_3), 1.21 (s, 3H, CH_3), 1.20 (d, 12H, CH_3), 1.26 (d, 6H, CH_3), 1.45 (d, 6H, CH_3), 1.50 (d, 6H, CH_3), 2.77 (m, 2H, C*H*), 2.83 (m, 2H, C*H*), 2.86 (d, 2H, CH_2), 4.00 (m, 2H, C*H*), 4.06 (d, 2H, CH_2), 7.00 (s, 2H, C*H*), 7.04 (m, 1H, py C*H*), 7.13 (m, 1H, py C*H*), 7.14 (s, 2H, C*H*), 7.45 (m, 1H, py C*H*), 8.92 (m, 1H, py *o*-C*H*); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 295 K) δ 24.82 (s, *C*H$_3$), 25.16 (s, *C*H$_3$), 25.76 (s, *C*H$_3$), 25.93 (s, *C*H$_3$), 27.58 (s, *C*H$_3$), 28.96 (s, *C*H), 29.05 (s, *C*H), 34.86 (s, Zr−*C*H$_3$), 34.96 (s, *C*H$_3$), 39.71 (s, Zr−*C*H$_3$), 46.44 (s, *C*R$_4$), 69.67 (s, *C*H$_2$), 120.82 (s, Ar *C*), 121.97 (s, Ar *C*), 122.57 (s, Ar *C*), 123.08 (s, Ar *C*), 139.62 (s, Ar *C*), 144.84 (s, Ar *C*), 145.28 (s, Ar *C*), 146.03 (s, Ar *C*), 146.46 (s, Ar *C*), 147.62 (s, Ar *C*), 163.04 (s, Ar *C*). Anal. Calcd for $C_{41}H_{63}N_3Zr$: C, 71.45; H, 9.21; N, 6.10. Found: C, 71.33; H, 9.22; N, 6.18.

[TripNpy]Zr(i-Bu)$_2$. A suspension of [TripNpy]$ZrCl_2$ (1.02 g, 1.40 mmol) in diethyl ether (50 mL) was cooled to −30 °C. To the cold solution was added (i-Bu)MgBr (2.3 M in diethyl ether, 1.40 mL, 3.21 mmol), and the resulting mixture was stirred at room temperature for 10 min until the cloudy suspension became clear. Dioxane (0.30 mL, 3.49 mmol) was added to the solution, and the mixture was filtered through Celite. The solvent was removed in vacuo to yield a white powder. [TripNpy]Zr(i-Bu)$_2$ was recrystallized from diethyl ether at room temperature to yield clear, colorless crystals: ^{1}H NMR (500 MHz, C_6D_5Br, 295 K) δ 0.54 (d, 6H, Zr−CH$_2$-CH(CH_3)$_2$), 0.62 (d, 6H, Zr−CH$_2$CH(CH_3)$_2$), 0.75 (d, 2H, Zr−CH_2CH(CH$_3$)$_2$), 0.97 (d, 2H, Zr−CH_2CH(CH$_3$)$_2$), 1.11 (d, 6H, CH_3), 1.21 (d, 6H, CH_3), 1.22 (s, 3H, CH_3), 1.33 (d, 6H, CH_3), 1.46 (d, 6H, CH_3), 1.60 (d, 6H, CH_3), 2.12 (m, 1H, Zr−CH$_2$C*H*(CH$_3$)$_2$), 2.35 (m, 1H, Zr−CH$_2$C*H*(CH$_3$)$_2$), 2.83 (m, 2H, C*H*), 2.95 (d, 2H, CH_2), 3.05 (m, 2H, C*H*), 3.87 (m, 2H, C*H*), 4.07 (d, 2H, CH_2), 7.02 (s, 2H, C*H*), 7.09 (m, 1H, py C*H*), 7.12 (m, 1H, py C*H*), 7.14 (s, 2H, C*H*), 7.45 (m, 1H, py C*H*), 8.98 (m, 1H, py *o*-C*H*); ^{13}C{^{1}H} NMR (125 MHz, C_6D_5Br, 295 K) δ 23.67 (s, *C*H$_3$), 24.32 (s, *C*H$_3$), 24.35 (s, *C*H$_3$), 24.96 (s, *C*H$_3$), 25.70 (s, *C*H$_3$), 27.47 (s, Zr−CH$_2$CH(*C*H$_3$)$_2$), 27.52 (s, Zr−CH$_2$-CH(*C*H$_3$)$_2$), 28.69 (s, Zr−CH$_2$*C*H(CH$_3$)$_2$), 29.28 (s, *C*H), 29.48 (s, *C*H), 32.13 (s, Zr−CH$_2$*C*H(CH$_3$)$_2$), 34.18 (s, *C*H$_3$), 45.85 (s, *C*R$_4$), 68.71 (s, *C*H$_2$), 70.52 (s, Zr−CH$_2$CH(*C*H$_3$)$_2$), 76.18 (s, Zr−*C*H$_2$CH(CH$_3$)$_2$), 120.41 (s, Ar *C*), 121.06 (s, Ar *C*), 121.97 (s, Ar *C*), 122.48 (s, Ar *C*), 139.14 (s, Ar *C*), 144.32 (s, Ar *C*), 144.88

(s, Ar *C*), 145.11 (s, Ar *C*), 145.28 (s, Ar *C*), 146.83 (s, Ar *C*), 162.65 (s, Ar *C*). Anal. Calcd for $C_{47}H_{75}N_3Zr$: C, 73.00; H, 9.78; N, 5.43. Found: C, 73.11; H, 9.71; N, 5.36.

[MesNpy]Hf(NMe$_2$)$_2$. Hf(NMe$_2$)$_4$ (4.00 g, 11.0 mmol) and H$_2$[MesNpy] (4.75 g, 12.0 mmol) were dissolved in pentane (80 mL). The reaction mixture was stirred at room temperature for 16 h and filtered, and the solvent was evaporated to yield the yellow product: yield 7.75 g (95%); ^{1}H NMR (500 MHz, C_6D_6, 295 K) δ 1.02 (s, 3H, CH_3), 2.21 (s, 6H, *p*-CH_3), 2.33 (s, 12H, *o*-CH_3), 2.95 (d, 2H, CH_2), 3.02 (s, 6H, N(CH_3)$_2$), 3.06 (s, 6H, N(CH_3)$_2$), 4.18 (d, 2H, CH_2), 6.67 (m, 1H, py C*H*), 6.83 (m, 1H, py C*H*), 6.91 (s, 4H, C*H*), 7.04 (m, 1H, py C*H*), 8.77 (m, 1H, py *o*-C*H*). Anal. Calcd for $C_{31}H_{45}N_5Hf$: C, 55.89; H, 6.81; N, 10.51. Found: C, 55.96; H, 6.88; N, 10.40.

[MesNpy]HfCl$_2$. To a solution of [MesNpy]Hf(NMe$_2$)$_2$ (7.75 g, 11.0 mmol) in diethyl ether (80 mL) was added TMSCl (4.35 mL, 34.0 mmol), and the reaction mixture was stirred at room temperature for 1 h. The resulting white solid was filtered off, washed with pentane (3 × 10 mL), and dried in vacuo for 4 h: yield 6.82 g (95%); ^{1}H NMR (500 MHz, C_6D_6, 295 K) δ 0.81 (s, 3H, CH_3), 1.59 (s, 6H, *o*-CH_3), 2.20 (s, 6H, *p*-CH_3), 2.97 (d, 2H, CH_2), 2.97 (s, 6H, *o*-CH_3), 4.10 (d, 2H, CH_2), 6.65 (m, 1H, py C*H*), 6.71 (s, 2H, C*H*), 6.89 (m, 1H, py C*H*), 6.89 (m, 1H, py C*H*), 6.94 (s, 2H, C*H*), 10.41 (m, 1H, py *o*-C*H*). Anal. Calcd for $C_{27}H_{33}N_3Cl_2Hf$: C, 49.97; H, 5.13; N, 6.47; Cl, 10.93. Found: C, 49.90; H, 5.08; N, 6.42; Cl, 11.06.

[MesNpy]HfMe$_2$. A suspension of [MesNpy]HfCl$_2$ (1.17 g, 1.80 mmol) in diethyl ether (50 mL) was cooled to −30 °C. To the cold solution was added MeMgBr (3.5 M in diethyl ether, 1.30 mL, 4.55 mmol), and the resulting mixture was stirred at room temperature for 1 h until the cloudy suspension became clear. Dioxane (0.50 mL, 5.87 mmol) was added to the solution, and the mixture was filtered through Celite. The filtrate was reduced to ∼5 mL and stored at −30 °C for 1 day to give [MesNpy]HfMe$_2$ as clear, colorless crystals: yield 1.09 g (64%); ^{1}H NMR (500 MHz, C_6D_5Br, 295 K) δ 0.06 (s, 3H, Hf−CH_3), 0.14 (s, 3H, Hf−CH_3), 1.22 (s, 3H, CH_3), 2.16 (s, 6H, *p*-CH_3), 2.20 (s, 12H, *o*-CH_3), 2.86 (d, 2H, CH_2), 4.15 (d, 2H, CH_2), 6.81 (s, 4H, C*H*), 6.99 (m, 1H, py C*H*), 7.18 (m, 1H, py C*H*), 7.48 (m, 1H, py C*H*), 8.91 (m, 1H, py *o*-C*H*). ^{13}C{^{1}H} NMR (125 MHz, C_6D_5Br, 295 K) δ 18.72 (s, *o*-*C*H$_3$), 20.88 (s, *p*-*C*H$_3$), 24.91 (s, *C*H$_3$), 45.21 (s, Hf−*C*H$_3$), 45.85 (s, *C*R$_4$), 49.36 (s, Hf−*C*H$_3$), 64.98 (s, *C*H$_2$), 120.39 (s, Ar *C*), some aryl signal omitted here, 134.81 (s, Ar *C*), 139.15 (s, Ar *C*). Anal. Calcd for $C_{29}H_{39}N_3Hf$: C, 57.28; H, 6.46; N, 6.91. Found: C, 57.21; H, 6.55; N, 6.84.

The ^{13}C-labeled complex [MesNpy]Hf(^{13}Me)$_2$ was prepared in a similar manner with ^{13}MeMgI.

[MesNpy]HfEt$_2$. A suspension of [MesNpy]HfCl$_2$ (0.210 g, 0.324 mmol) in diethyl ether (50 mL) was cooled to −30 °C. To the cold solution was added EtMgBr (2.0 M in diethyl ether, 0.34 mL, 0.68 mmol), and the resulting mixture was stirred at room temperature for 10 min until the cloudy suspension became clear. Dioxane (0.07 mL, 0.81 mmol) was added to the solution, and the mixture was filtered through Celite. The solvent was removed in vacuo to give a white powder, which was redissolved in 5 mL of diethyl ether and crystallized at −30 °C for 16 h as white crystals: yield 0.098 g (48%); ^{1}H NMR (500 MHz, C_6D_5Br, 255 K) δ 0.53 (m, 4H, Hf−CH_2CH$_3$), 1.19 (s, 3H, CH_3), 1.34 (t, 3H, Hf−CH$_2$CH_3), 1.57 (d, 3H, Hf−CH$_2$CH_3), 2.17 (s, 6H, *p*-CH_3), ∼2.2 (broad s, 12H, *o*-CH_3), 2.83 (d, 2H, CH_2), 4.13 (d, 2H, CH_2), 6.83 (s, 4H, C*H*), 6.99 (m, 1H, py C*H*), 7.12 (m, 1H, py C*H*), 7.45 (m, 1H, py C*H*), 8.81 (m, 1H, py *o*-C*H*); ^{13}C{^{1}H} NMR (125 MHz, C_6D_5Br, 255 K) δ 11.74 (s, Hf−CH$_2$*C*H$_3$), 13.63 (s, Hf−CH$_2$*C*H$_3$), 18.78 (s, *o*-*C*H$_3$), 20.99 (s, *p*-*C*H$_3$), 25.13 (s, *C*H$_3$), 44.91 (s, *C*R$_4$), 57.24 (s, Hf−*C*H$_2$-CH$_3$), 59.39 (s, Hf−*C*H$_2$CH$_3$), 64.97 (s, *C*H$_2$), 120.65 (s, Ar *C*), 121.97 (s, Ar *C*), 122.61 (s, Ar *C*), 131.16 (s, Ar *C*), 132.89 (s, Ar *C*), 139.15 (s, Ar *C*), 146.07 (s, Ar *C*), 146.19 (s, Ar *C*), 162.05 (s, Ar *C*). Anal. Calcd for $C_3H_{43}N_3Hf$: C, 58.53; H, 6.81; N, 6.60. Found: C, 58.40; H, 6.88; N, 6.53.

[MesNpy]Hf(n-Pr)$_2$. A suspension of [MesNpy]HfCl$_2$ (0.312 g, 0.481 mmol) in diethyl ether (50 mL) was cooled to −30 °C. To the cold solution was added (n-Pr)MgCl (2.0 M in diethyl ether, 0.53 mL, 1.06 mmol), and the resulting mixture was stirred at room temperature for 10 min until the cloudy suspension became clear. Dioxane (0.12 mL, 0.14 mmol) was added to the solution, and the mixture was filtered through Celite. The solvent was removed in vacuo to give a white powder, which was redissolved in 5 mL of diethyl ether and crystallized at −30 °C for 16 h and the product isolated as white crystals: yield 0.175 g (55%); ^{1}H NMR (500 MHz, C_6D_5-Br, 295 K) δ 0.82 (m, 2H, Hf−CH_2CH(CH$_3$)$_2$), 0.85 (m, 4H, Hf−CH_2CH(CH$_3$)$_2$), 0.92 (s, 3H, CH_3), 0.95 (d, 6H, Hf−CH$_2$CH-(CH_3)$_2$), 1.27 (d, 6H, Hf−CH$_2$CH(CH_3)$_2$), 2.17 (s, 6H, *p*-CH_3), 2.3 (broad s, 12H, *o*-CH_3), 2.41 (m, 1H, Hf−CH$_2$CH(CH$_3$)$_2$), 2.54 (m, 1H, Hf−CH$_2$CH(CH$_3$)$_2$), 2.84 (d, 2H, CH$_2$), 4.12 (d, 2H, CH$_2$), 6.62 (m, 1H, py CH), 6.78 (m, 1H, py CH), 6.90 (s, 4H, CH), 7.04 (m, 1H, py CH), 8.96 (m, 1H, py *o*-CH); ^{13}C{^{1}H} NMR (125 MHz, C_6D_5Br, 295 K) δ 18.58 (s, *o*-*C*H$_3$), 29.85 (s, Hf−CH(*C*H$_3$)$_2$), 30.41 (s, Hf−CH(*C*H$_3$)$_2$), 21.29 (s, *p*-*C*H$_3$), 25.12 (s, *C*H$_3$), 45.05 (s, *C*R$_4$), 65.70 (s, *C*H$_2$), 68.21 (s, Hf−*C*H(CH$_3$)$_2$), 65.85 (s, Hf−*C*H(CH$_3$)$_2$), 120.80 (s, Ar *C*), 122.83 (s, Ar *C*), 130.15 (s, Ar *C*), 134.13 (s, Ar *C*), 135.70 (s, Ar *C*), 139.27 (s, Ar *C*), 146.92 (s, Ar *C*), 147.40 (s, Ar *C*), 163.40 (s, Ar *C*). Anal. Calcd for $C_{33}H_{47}N_3Hf$: C, 59.67; H, 7.13; N, 6.33. Found: C, 59.67; H, 7.13; N, 6.41.

[MesNpy]Hf(i-Pr)Cl. A suspension of [MesNpy]HfCl$_2$ (0.744 g, 1.15 mmol) in diethyl ether (50 mL) was cooled to −20 °C. To the cold solution was added (i-Pr)MgCl (2.0 M in diethyl ether, 0.60 mL, 1.2 mmol), and the resulting mixture was stirred at room temperature for 1 h until the cloudy suspension became clear. Dioxane (0.15 mL, 1.7 mmol) was added to the solution, and the mixture was filtered through Celite. The solvent was removed in vacuo to yield a white powder, which was redissolved in 5 mL of diethyl ether and crystallized at −20 °C to give the product as white crystals: yield 0.35 g (47%); ^{1}H NMR (500 MHz, C_6D_6, 295 K) δ 0.91 (s, 3H, CH_3), 0.98 (m, 1H, Hf−C*H*(CH$_3$)$_2$), 1.48 (d, 6H, Hf−CH(CH_3)$_2$), 1.92 (s, 6H, *o*-CH_3), 2.15 (s, 6H, *p*-CH_3), 2.66 (s, 6H, *o*-CH_3), 2.82 (d, 2H, CH_2), 4.19 (d, 2H, CH_2), 6.61 (m, 1H, py C*H*), 6.73 (m, 1H, py C*H*), 6.77 (s, 2H, C*H*), 6.95 (s, 2H, C*H*), 7.00 (m, 1H, py C*H*), 9.67 (m, 1H, py *o*-C*H*); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 295 K) δ 18.74 (s, *o*-*C*H$_3$), 19.63 (s, *o*-*C*H$_3$), 21.28 (s, *p*-*C*H$_3$), 22.51 (s, Hf−CH(*C*H$_3$)$_2$), 25.22 (s, *C*H$_3$), 46.28 (s, *C*R$_4$), 65.47 (s, *C*H$_2$), 68.27 (s, Hf−*C*H(CH$_3$)$_2$), 120.57 (s, Ar *C*), 123.04 (s, Ar *C*), 130.14 (s, Ar *C*), 130.50 (s, Ar *C*), 134.89 (s, Ar *C*), 135.92 (s, Ar *C*), 139.70 (s, Ar *C*), 145.02 (s, Ar *C*), 149.20 (s, Ar *C*). Anal. Calcd for $C_{30}H_{40}N_3ClHf$: C, 54.88; H, 6.14; N, 6.40; Cl, 5.40. Found: C, 55.07; H, 6.22; N, 6.34; Cl, 5.32.

[MesNpy]Hf(i-Pr)$_2$. A suspension of [MesNpy]HfCl$_2$ (1.70 g, 2.62 mmol) in diethyl ether (50 mL) was cooled to −30 °C. To the cold solution was added (i-Bu)MgBr (2.0 M in diethyl ether, 2.88 mL, 5.76 mmol), and the resulting mixture was stirred at room temperature for 10 min until the cloudy suspension became clear. Dioxane (0.670 mL, 0.786 mmol) was added to the solution, and the mixture was filtered through Celite. The solvent was removed in vacuo to give a white powder, which was redissolved in 5 mL of diethyl ether and crystallized at −30 °C for 16 h as white crystals: yield 0.098 g (53%); ^{1}H NMR (500 MHz, C_6D_5Br, 295 K) δ 0.088 (m, 1H, Hf−CH_2(CH$_3$)$_2$), 0.51 (m, 1H, Hf−CH_2(CH$_3$)$_2$), 1.19 (s, 3H, CH_3), 1.22 (d, 6H, Hf−CH$_2$(CH_3)$_2$), 1.59 (d, 6H, Hf−CH$_2$(CH_3)$_2$), 2.14 (s, 6H, *p*-CH_3), 2.2 (broad s, 12H, *o*-CH_3), 2.85 (d, 2H, CH_2), 4.14 (d, 2H, CH_2), 6.84 (s, 4H, C*H*), 7.03 (m, 1H, py C*H*), 7.17 (m, 1H, py C*H*), 7.47 (m, 1H, py C*H*), 8.77 (m, 1H, py *o*-C*H*); ^{13}C{^{1}H} NMR (125 MHz, C_6D_5Br, 295 K) δ 18.58 (s, *o*-*C*H$_3$), 20.84 (s, Hf−CH(*C*H$_3$)$_2$), 21.32 (s, *p*-*C*H$_3$), 21.99 (s, Hf−CH-(*C*H$_3$)$_2$), 25.12 (s, *C*H$_3$), 45.05 (s, *C*R$_4$), 65.70 (s, *C*H$_2$), 65.85 (s, Hf−*C*H(CH$_3$)$_2$), 68.21 (s, Hf−*C*H(CH$_3$)$_2$), 120.53 (s, Ar *C*), 121.97 (s, Ar *C*), 132.96 (s, Ar *C*), 138.88 (s, Ar *C*), 146.46 (s, Ar *C*), 147.00 (s, Ar *C*), 162.77 (s, Ar *C*). Anal. Calcd for

$C_{33}H_{47}N_3Hf$: C, 59.67; H, 7.13; N, 6.33. Found: C, 59.76; H, 7.20; N, 6.35.

[MesNpy]Hf(n-Bu)$_2$. A suspension of [MesNpy]$HfCl_2$ (0.265 g, 0.408 mmol) in diethyl ether (10 mL) was cooled to −30 °C. To the cold solution was added (n-Bu)MgBr (2.0 M in diethyl ether, 0.43 mL, 0.81 mmol), and the resulting mixture was stirred at room temperature for 10 min until the cloudy suspension became clear. Dioxane (0.1 mL, 1 mmol) was added to the solution, and the mixture was filtered through Celite. The solvent was removed in vacuo to give a white powder, which was redissolved in 2 mL of diethyl ether and crystallized at −30 °C for 16 h and the product isolated as white crystals: yield 0.14 g (50%); ^{1}H NMR (500 MHz, C_6D_5Br, 295 K) δ 0.52 (m, 4H, Hf−CH_2CH$_2$CH$_2$CH$_3$), 0.73 (t, 3H, Hf−CH$_2$CH$_2$-CH$_2$CH_3), 0.89 (t, 3H, Hf−CH$_2$CH$_2$CH$_2$CH_3), 1.11 (m, 2H, Hf−CH$_2$CH$_2$CH_2CH$_3$), 1.21 (s, 3H, CH_3), 1.40 (m, 2H, Hf−CH$_2$-CH$_2$CH_2CH$_3$), 1.45 (m, 2H, Hf−CH$_2$CH_2CH$_2$CH$_3$), 1.83 (m, 2H, Hf−CH$_2$CH_2CH$_2$CH$_3$), 2.16 (s, 6H, *p*-CH_3), 2.2 (broad s, 12H, *o*-CH_3), 2.87 (d, 2H, CH_2), 4.13 (d, 2H, CH_2), 6.82 (s, 4H, C*H*), 7.02 (m, 1H, py C*H*), 7.18 (m, 1H, py C*H*), 7.49 (m, 1H, py C*H*), 8.90 (m, 1H, py *o*-C*H*); ^{13}C{^{1}H} NMR (125 MHz, C_6D_5Br, 295 K) δ 14.13 (s, Hf−CH$_2$CH$_2$CH$_2$*C*H$_3$), 14.17 (s, Hf−CH$_2$-CH$_2$CH$_2$*C*H$_3$), 18.70 (s, *o*-*C*H$_3$), 20.85 (s, *p*-*C*H$_3$), 25.06 (s, *C*H$_3$), 30.33 (s, Hf−CH$_2$(*C*H$_2$)$_2$CH$_3$), 30.39 (s, Hf−CH$_2$(*C*H$_2$)$_2$CH$_3$), 30.58 (s, Hf−CH$_2$(*C*H$_2$)$_2$CH$_3$), 31.88 (s, Hf−CH$_2$(*C*H$_2$)$_2$CH$_3$), 45.26 (s, *C*R$_4$), 65.22 (s, *C*H$_2$), 66.85 (s, Hf−*C*H$_2$(CH$_2$)$_2$CH$_3$), 69.17 (s, Hf−*C*H$_2$(CH$_2$)$_2$CH$_3$), 120.44 (s, Ar *C*), 122.46 (s, Ar *C*), 129.31 (s, Ar *C*), 129.69 (s, Ar *C*), 131.27 (s, Ar *C*), 134.86 (s, Ar *C*), 139.00 (s, Ar *C*), 146.06 (s, Ar *C*), 146.48 (s, Ar *C*). Anal. Calcd for $C_{35}H_{51}N_3Hf$: C, 60.72; H, 7.43; N, 6.07. Found: C, 60.65; H, 7.37; N, 5.94.

[MesNpy]Hf(i-Bu)$_2$. A suspension of [MesNpy]$HfCl_2$ (1.70 g, 2.62 mmol) in diethyl ether (50 mL) was cooled to −30 °C. To the cold solution was added (i-Bu)MgBr (2.0 M in diethyl ether, 2.88 mL, 5.76 mmol), and the resulting mixture was stirred at room temperature for 10 min until the cloudy suspension became clear. Dioxane (0.670 mL, 0.786 mmol) was added to the solution, and the mixture was filtered through Celite. The solvent was removed in vacuo to yield a white powder, which was redissolved in 5 mL of diethyl ether and crystallized at −30 °C to give the product as white crystals: yield 1.5 g (83%); ^{1}H NMR (500 MHz, C_6D_6, 295 K) δ 0.82 (m, 2H, Hf−CH_2CH(CH$_3$)$_2$), 0.85 (m, 4H, Hf−CH_2CH(CH$_3$)$_2$), 0.92 (s, 3H, CH_3), 0.95 (d, 6H, Hf−CH$_2$CH(CH_3)$_2$), 1.27 (d, 6H, Hf−CH$_2$CH(CH_3)$_2$), 2.17 (s, 6H, *p*-CH_3), 2.3 (broad s, 12H, *o*-CH_3), 2.41 (m, 1H, Hf−CH$_2$C*H*(CH$_3$)$_2$), 2.54 (m, 1H, Hf−CH$_2$C*H*(CH$_3$)$_2$), 2.84 (d, 2H, CH_2), 4.12 (d, 2H, CH_2), 6.62 (m, 1H, py C*H*), 6.78 (m, 1H, py C*H*), 6.90 (s, 4H, C*H*), 7.04 (m, 1H, py C*H*), 8.96 (m, 1H, py *o*-C*H*); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 295 K) δ 19.23 (s, *o*-*C*H$_3$), 21.29 (s, *p*-*C*H$_3$), 25.38 (s, *C*H$_3$), 29.85 (s, Hf−CH$_2$CH(*C*H$_3$)$_2$), 30.41 (s, Hf−CH$_2$CH(*C*H$_3$)$_2$), 30.77 (s, Hf−CH$_2$*C*H(CH$_3$)$_2$), 32.80 (s, Hf−CH$_2$*C*H(CH$_3$)$_2$), 45.84 (s, *C*R$_4$), 66.29 (s, *C*H$_2$), 82.36 (s, Hf−*C*H$_2$CH(CH$_3$)$_2$), 83.88 (s, Hf−*C*H$_2$CH(CH$_3$)$_2$), 120.80 (s, Ar *C*), 122.83 (s, Ar *C*), 130.15 (s, Ar *C*), 134.13 (s, Ar *C*), 135.70 (s, Ar *C*), 139.27 (s, Ar *C*), 146.92 (s, Ar *C*), 147.40 (s, Ar *C*), 163.40 (s, Ar *C*). Anal. Calcd for $C_{35}H_{51}N_3Hf$: C, 60.72; H, 7.43; N, 6.07. Found: C, 60.65; H, 7.51; N, 6.12.

[MesNpy]Hf(^{13}CH$_2$CHMe$_2$)$_2$ was prepared in a similar fashion from Me$_2$CH^{13}CH$_2$MgBr.

[MesNpy]Hf(t-Bu)Cl. A suspension of [MesNpy]$HfCl_2$ (0.243 g, 0.374 mmol) in diethyl ether (15 mL) was cooled to −20 °C. To the cold solution was added (t-Bu)MgCl (2.0 M in diethyl ether, 0.45 mL, 0.90 mmol), and the resulting mixture was stirred at room temperature for 15 min until the cloudy suspension became clear. Dioxane (0.15 mL, 1.7 mmol) was added to the solution, and the mixture was filtered through Celite. The solvent was removed in vacuo to yield a white powder, which was redissolved in 5 mL of diethyl ether and crystallized at −20 °C to give the product as white crystals: yield 0.121 g (48%); ^{1}H NMR (500 MHz, C_6D_6, 295 K) δ 0.93 (s, 3H, CH$_3$), 0.98 (s, 9H, Hf−C(CH$_3$)$_3$), 2.14 (s, 6H, CH$_3$), 2.22 (s, 6H, CH$_3$), 2.65 (s, 6H, *o*-CH$_3$), 2.80 (d, 2H, CH$_2$), 4.38 (d, 2H, CH$_2$), 6.60 (m, 1H, py CH), 6.68 (m, 1H, py CH), 6.76 (s, 2H, CH), 6.90 (s, 2H, CH), 6.97 (m, 1H, py CH), 9.85 (m, 1H, py *o*-CH); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 295 K) δ 20.41 (s, CH$_3$), 20.92 (s, CH$_3$), 21.41 (s, *p*-CH$_3$), 25.79 (s, CH$_3$), 32.10 (s, Hf−C(CH$_3$)$_3$), 46.35 (s, *C*R$_4$), 65.58 (s, *C*H$_2$), 70.59 (s, Hf−*C*(CH$_3$)$_2$), 120.39 (s, Ar *C*), 122.99 (s, Ar *C*), 130.04 (s, Ar *C*), 131.08 (s, Ar *C*), 133.71 (s, Ar *C*), 134.31 (s, Ar *C*), 134.38 (s, Ar *C*), 139.75 (s, Ar *C*), 145.79 (s, Ar *C*), 149.94 (s, Ar *C*), 163.08 (s, Ar *C*). Anal. Calcd for $C_{31}H_{42}N_3ClHf$: C, 54.88; H, 6.14; N, 6.40; Cl, 5.40. Found: C, 55.07; H, 6.22; N, 6.34; Cl, 5.40.

[TripNpy]Hf(NMe$_2$)$_2$. Hf(NMe$_2$)$_4$ (0.66 g, 1.85 mmol) and H_2[TripNpy] (1.06 g, 1.86 mmol) were dissolved in pentane (60 mL). The reaction mixture was stirred at room temperature for 16 h, the residual insoluble precipitate was filtered, and the solution was stirred at room temperature for a further 16 h. The solution was filtered to remove small amounts of solid residue, and the solvent was removed partially in vacuo. The red solution was cooled to −30 °C for 12 h to give a yellow precipitate: yield 0.70 g (45%); ^{1}H NMR (500 MHz, C_6D_6, 295 K) δ 0.66 (d, 6H, CH_3), 1.03 (s, 3H, CH_3), 1.28 (d, 12H, CH_3), 1.33 (d, 6H, CH_3), 1.58 (d, 6H, CH_3), 1.59 (d, 6H, CH_3), 2.86 (m, 2H, C*H*), 2.93 (s, 6H, N(CH_3)$_2$), 3.02 (m, 2H, C*H*), 3.07 (d, 2H, CH_2), 3.10 (s, 6H, N(CH_3)$_2$), 4.12 (m, 2H, C*H*), 4.27 (d, 2H, CH_2), 6.69 (m, 1H, py C*H*), 6.78 (m, 1H, py C*H*), 7.05 (m, 1H, py C*H*), 7.10 (d, 2H, C*H*), 7.27 (d, 2H, C*H*), 8.79 (m, 1H, py *o*-C*H*). Anal. Calcd for $C_{43}H_{69}N_5Hf$: C, 61.89; H, 8.33; N, 8.39. Found: C, 62.01; H, 8.36; N, 8.31.

[TripNpy]HfCl$_2$. To a solution of [TripNpy]Hf(NMe$_2$)$_2$ (0.465 g, 0.567 mmol) in diethyl ether (15 mL) was added TMSCl (0.2 mL, 1.67 mmol), and the reaction mixture was stirred at room temperature for 4 h. The resulting white solid was filtered, washed with pentane (3 × 10 mL), and dried in vacuo for 4 h: yield 0.375 g (82%); ^{1}H NMR (300 MHz, C_6D_6, 295 K) δ 0.67 (d, 6H, CH$_3$), 0.91 (s, 3H, CH$_3$), 1.12 (br d, 6H, CH$_3$), 1.30 (d, 6H, CH$_3$), 1.32 (d, 6H, CH$_3$), 1.59 (d, 6H, CH$_3$), 1.86 (d, 6H, CH$_3$), 2.43 (br m, 2H, CH), 2.88 (m, 2H, CH), 3.16 (d, 2H, CH$_2$), 4.28 (d, 2H, CH$_2$), 4.37 (br m, 2H, CH), 6.68 (m, 2H, py CH), 6.95 (m, 1H, py CH), 7.00 (s, 2H, CH), 7.28 (d, 2H, CH), 10.17 (m, 1H, py *o*-CH).

[TripNpy]Hf(i-Bu)$_2$. A suspension of [TripNpy]$HfCl_2$ (0.600 g, 0.734 mmol) in diethyl ether (20 mL) was cooled to −30 °C. To the cold solution was added (i-Bu)MgBr (2.0 M in diethyl ether, 0.92 mL, 1.83 mmol), and the resulting mixture was stirred at room temperature for 1 h until the cloudy suspension became clear. Dioxane (0.20 mL, 2.2 mmol) was added to the solution, and the mixture was filtered through Celite. The solvent was removed in vacuo to yield a white powder, which was redissolved in 5 mL of diethyl ether and crystallized at −30 °C to yield the product as white crystals: yield 0.44 g (70%); ^{1}H NMR (500 MHz, C_6D_5Br, 295 K) δ 0.51 (d, 6H, Hf−CH$_2$CH(CH$_3$)$_2$), 0.55 (d, 2H, Hf−CH$_2$CH(CH$_3$)$_2$), 0.60 (d, 6H, Hf−CH$_2$CH(CH$_3$)$_2$), 0.72 (d, 2H, Hf−CH$_2$CH(CH$_3$)$_2$), 1.11 (d, 6H, *o*-CH_3), 1.20 (s, 3H, CH_3), 1.21 (d, 12H, *p*-CH_3), 1.32 (d, 6H, *o*-CH_3), 1.47 (d, 6H, *o*-CH_3), 1.61 (d, 6H, *o*-CH_3), 2.17 (m, 1H, Hf−CH$_2$C*H*(CH$_3$)$_2$), 2.36 (m, 1H, Hf−CH$_2$C*H*(CH$_3$)$_2$), 2.83 (m, 1H, C*H*), 3.05 (d, 2H, CH_2), 3.09 (m, 1H, C*H*), 3.90 (d, 1H, C*H*), 4.20 (d, 2H, CH_2), 7.01 (s, 2H, C*H*), 7.11 (m, 1H, py C*H*), 7.12 (m, 1H, py C*H*), 7.16 (s, 2H, C*H*), 7.46 (m, 1H, py C*H*), 9.07 (m, 1H, py *o*-C*H*); ^{13}C{^{1}H} NMR (125 MHz, C_6D_5Br, 295 K) δ 23.47 (s, *C*H$_3$), 24.38 (s, *C*H$_3$), 24.08 (s, *C*H$_3$), 25.42 (s, C*H*), 25.82 (s, *C*H$_3$), 27.47 (s, *C*H$_3$), 27.90 (s, C*H*), 28.42 (s, *C*H$_3$), 28.72 (s, *C*H), 29.84 (s, *C*H), 29.46 (s, *C*H$_3$), 32.21 (s, *C*H), 34.15 (s, *C*H$_3$), 45.50 (s, *C*R$_4$), 68.44 (s, *C*H$_2$), 81.68 (s, Hf−*C*H$_2$CH(CH$_3$)$_2$), 83.04 (s, Hf−*C*H$_2$CH(CH$_3$)$_2$), some aryl resonances are omitted. Anal. Calcd for $C_{47}H_{75}N_3Hf$: C, 65.59; H, 8.78; N, 4.88. Found: C, 65.43; H, 8.71; N, 4.95.

[TripNpy]Hf(^{13}CH$_2$CHMe$_2$)$_2$ was prepared in a similar fashion from Me$_2$CH^{13}CH$_2$MgBr.

X-ray Diffraction Experiments. All single-crystal X-ray diffraction experiments were carried out using a Bruker three-circle platform diffractometer equipped with a CCD detector. A standard hemisphere of data was collected at 183 K. The structures were solved using direct methods and difference Fourier techniques utilizing the SHELXTL suite of programs.[36] In each case, all non-hydrogen atoms were modeled anisotropically, while hydrogen atoms were placed in calculated positions. Absolute configurations were confirmed by analysis of the Flack parameters[37] following refinement. For [MesNpy]-$ZrMe_2$ the Flack parameter was −0.02(5), and for $[Li(Et_2O)]$-{[MesNpy]$ZrMe_3$} it was −0.04(6).

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(36) SHELXTL; Bruker Analytical X-ray Solutions, Madison, WI.
(37) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876−881.

Supporting Information Available: Fully labeled thermal ellipsoid drawings and tables of crystal data and structure refinement details, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for [MesNpy]Zr(THF)Me_2, [Li·OEt_2]{[MesNpy]-$ZrMe_3$}, [TripNpy]Zr(i-Bu)$_2$, [MesNpy]Hf(i-Pr)Cl, and [MesNpy]Hf(i-Pr)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org. Supporting data for the X-ray structure of [MesNpy]$ZrMe_2$ were provided in ref 11.

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