# Synthesis, Characterization, and Activation of Zirconium and Hafnium Dialkyl Complexes that Contain a $C_2$-Symmetric Diaminobinaphthyl Dipyridine Ligand

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The diamine *rac*-$H_2$[MepyN] (*rac*-*N*,*N*′-di(6-methylpyridin-2-yl)-2,2′-diaminobinaphthalene) has been prepared in good yield through reductive amination of *rac*-2,2′-diaminobinaphthalene with 6-methylpyridinecarboxaldehyde. The [MepyN]$^{2-}$ ligand has been employed to prepare a variety of zirconium and hafnium complexes, [MepyN]$MX_2$ (M = Zr, X = $NMe_2$, Cl, $OSO_2CF_3$, $CH_2CHMe_2$, $CH_2Ph$; M = Hf, X = $NMe_2$, $OSO_2CF_3$, $CH_2CHMe_2$). The solid state structures of [MepyN]$Zr(CH_2Ph)_2$, [MepyN]$Zr(NMe_2)Cl$, [MepyN]$Hf(CH_2CHMe_2)_2$, and [MepyN]$Hf(OSO_2CF_3)_2$ have been determined by X-ray diffraction. Activation of [MepyN]-$Zr(CH_2Ph)_2$ and [MepyN]$Hf(CH_2CHMe_2)_2$ with various Lewis acids leads to observable cationic alkyls that are not active toward 1-hexene polymerization.

## Introduction

In the past several years interest in "non-metallocene" early transition metal olefin polymerization catalysts, as well as late metal catalysts (which often contain nitrogen donor ligands), has increased markedly.[1−4] Our laboratory has been exploring the synthesis and activation of dialkyl Zr and Hf complexes that contain diamido/donor ligands, e.g., [(t-BuN-*o*-$C_6H_4)_2O$]$^{2-}$ or [(MesitylN$CH_2)_2C(CH_3)$(2-$C_5H_4N$)]$^{2-}$,[5−9] while a variety of related systems in which the ligand is not a diamido/donor have been explored in other laboratories.[10−27] The most interesting feature of several systems that contain a diamido/donor ligand is that 1-hexene can be polymerized in a living fashion and intermediates in that process can be observed in NMR spectra. Other types of non-metallocene polymerization catalysts are also known that are living to a greater or lesser degree.[17] Living characteristics result largely from a reduced tendency for $\beta$-hydride elimination from (in the case of a terminal olefin) either a 1,2 insertion product or a 2,1 insertion product.

We have been exploring the possibility of preparing asymmetric catalysts that contain a diamido/donor ligand, the ultimate goal being to design a living, stereospecific polymerization process. So far we have not been successful. Therefore we chose to explore the chemistry of asymmetric diamido ligands that contain a relatively rigid and chiral backbone, namely, a $C_2$-symmetric (*rac*) binaphthyl backbone. The rigid biaryl backbone of the binaphthalene provides the desired stereochemical element that can transmit chiral information close to the metal through the amido linkages. A number of reports of biaryl-based amide ligands exist in the literature,[28−34] including some recent work by

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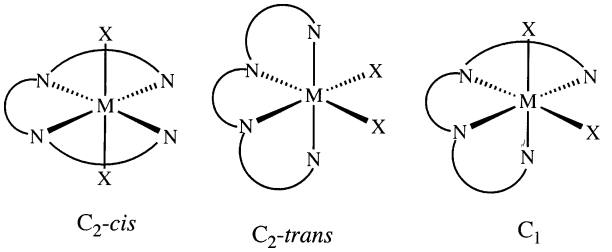
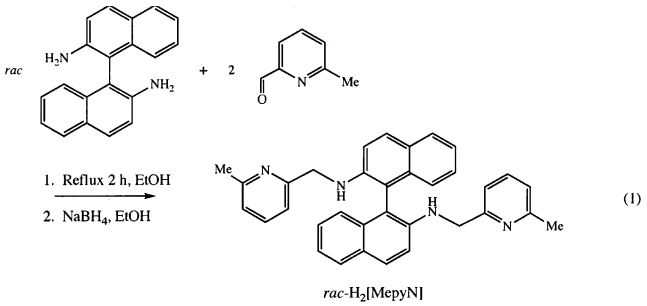
**Scheme 1**




Brintzinger similar to that reported here.[35] In this paper we report zirconium and hafnium dialkyl complexes that contain a new binaphthyl-based diamide ligand and explore activation of the dialkyls.

## Results and Discussion

The diamine *rac*-$H_2$[MepyN] is prepared from *rac*-2,2′-diamino-1,1′-binaphthalene as shown in eq 1. Condensation of *rac*-2,2′-diamino-1,1′-binaphthalene with 6-methyl-2-pyridinecarboxaldehyde followed by reduction with $NaBH_4$ produces the racemic diamine in 80% yield after recrystallization on a scale of 5−10 g. $H_2$[MepyN] is a white crystalline solid that is soluble in aromatic and chlorinated solvents, but is relatively insoluble in alkanes or diethyl ether. The proton NMR spectrum is consistent with it having $C_2$ symmetry; nine aryl resonances can be observed, while the methylene protons appear as a complex multiplet at 4.15 ppm and the methyl group as a singlet at 2.27 ppm in benzene-$d_6$.




(1)

The reaction between $H_2$[MepyN] and $M(NMe_2)_4$ (M = Zr or Hf) proceeds readily to give [MepyN]$M(NMe_2)_2$ complexes in good to excellent yields (eq 2). Proton NMR

$$H_2[\text{MepyN}] + M(NMe_2)_4 \xrightarrow[\text{toluene}]{60\ ^\circ\text{C}} [\text{MepyN}]M(NMe_2)_2 + 2\ HNMe_2 \quad (2)$$

spectra of the [MepyN]$M(NMe_2)_2$ (M = Zr, Hf) complexes are consistent with $C_2$-symmetric structures in solution. Nine aryl resonances can be observed, while the methylene protons give rise to an AB pattern centered around 5.15 ppm in benzene-$d_6$. The methyl groups of the dimethylamide ligands and the pyridine moieties appear as sharp singlets in a 2:1 ratio, as expected. Two of the three possible modes of coordination of the diamido ligand in a [MepyN]$MX_2$ complex (Scheme 1) contain a

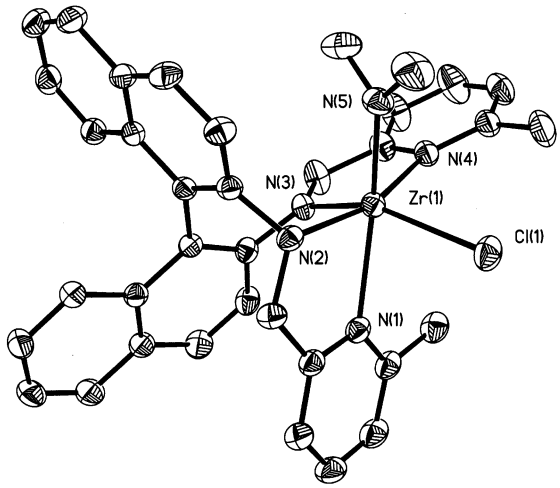



**Figure 1.** Thermal ellipsoid (50%) plot of [MepyN]Zr-$(NMe_2)$Cl. Hydrogen atoms are omitted for clarity.

$C_2$ axis ($C_2$-*cis* and $C_2$-*trans*). Structural characterization of zirconium complexes that contain a related ligand suggest that both $C_2$-*cis* and $C_2$-*trans* coordination are observable.[35] We have no information concerning the correct structure for the [MepyN]$M(NMe_2)_2$ species.

Initial attempts to synthesize [MepyN]$Zr(NMe_2)_2$ led to an unexpected result. Upon addition of $H_2$[MepyN] to $Zr(NMe_2)_4$, a yellow crystalline material was obtained whose $^1$H NMR spectrum showed it to be one diastereomer that has $C_1$ symmetry. Four doublets arise for each of the inequivalent methylene protons of the ligand instead of the AB patterns encountered in $C_2$-symmetric species, while 18 aryl resonances are observed for each proton in the binaphthyl and pyridine residues. A broad peak is also observed that can be assigned to six dimethylamide protons. A crystal structure of the complex revealed it to be [MepyN]$Zr(NMe_2)$Cl (Scheme 2). A rational synthesis of [MepyN]$Zr(NMe_2)$Cl consists of a reaction between [MepyN]$Zr(NMe_2)_2$ and lutidinium chloride in benzene-$d_6$. Recrystallization of $H_2$[MepyN] from non-chlorinated solvents produced samples that yielded exclusively the desired bisdimethylamide complex. Therefore we believe that [MepyN]$Zr(NMe_2)$Cl arises through reaction of [MepyN]$Zr(NMe_2)_2$ (generated in situ) with chloroform that had been retained in the sample of $H_2$[MepyN] that was first employed in the reaction.

The solid state structure of [MepyN]$Zr(NMe_2)$Cl is best described as a distorted octahedron, with the ligand adopting the $C_1$ geometry depicted in Scheme 1 (Figure 1; Tables 1 and 2). In the observed diastereomer, the dimethylamide ligand is bound *trans* to one of the pyridine donors, while the chloride is bound *trans* to an amide. The Zr−N(5) bond length of 2.048(1) Å is within the expected range for a $\pi$-donating amide, as are the Zr−N(2) and Zr−N(3) distances of 2.091(1) and 2.130(1) Å, respectively. The pyridine−zirconium lengths differ to some degree (2.413(1) vs 2.490(1) Å), as might be expected from the asymmetric binding mode of the ligand. The angles around Zr are consistent with a distorted octahedral geometry, with the most acute angles being N(1)−Zr−N(2) (71.91(5)°) and N(3)−Zr−N(4) (71.14(5)°). The broadened dimethylamido resonance is probably the consequence of hindered rotation about the Zr−N(5) bond. The structure of [MepyN]-

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**Scheme 2**

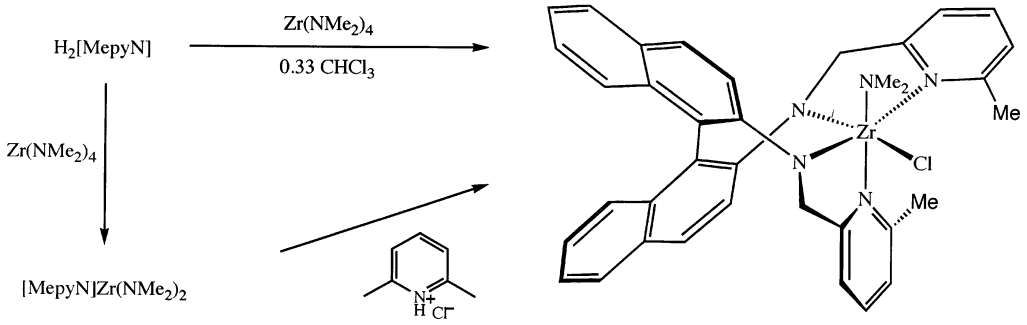



**Table 1. Crystallographic Data, Collection Parameters, and Refinement Parameters[a] for [MepyN]Zr(NMe$_2$)Cl, [MepyN]Hf(OSO$_2$CF$_3$)$_2$, [MepyN]Hf(CH$_2$CHMe$_2$)$_2$, and [MepyN]Zr(CH$_2$Ph)$_2$**

| | [MepyN]Zr(NMe$_2$)Cl | [MepyN]Hf(OSO$_2$CF$_3$)$_2$ | [MepyN]Hf(CH$_2$CHMe$_2$)$_2$ | [MepyN]Zr(CH$_2$Ph)$_2$ |
|---|---|---|---|---|
| empirical formula | $C_{36}H_{34}ClN_5Zr$ | $C_{36}H_{28}F_6N_4O_6S_2Hf$ | $C_{42}H_{46}N_4Hf$ | $C_{48}H_{42}N_4Zr$ |
| fw | 663.366 | 969.241 | 785.331 | 766.098 |
| temperature (K) | 194(2) | 100(2) | 100(2) | 194(2) |
| cryst syst | triclinic | triclinic | triclinic | triclinic |
| space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| unit cell dimens | $a$ = 11.2241(8) Å | $a$ = 11.7762(4) Å | $a$ = 11.228(2) Å | $a$ = 12.3177(4) Å |
| | $b$ = 11.9467(8) Å | $b$ = 12.9221(4) Å | $b$ = 18.140(4) Å | $b$ = 13.2063(5) Å |
| | $c$ = 14.8348(10) Å | $c$ = 17.4473(6) Å | $c$ = 20.381(4) Å | $c$ = 13.8962(5) Å |
| | α = 105.336(1)° | α = 100.366(1)° | α =97.18(3)° | α = 98.643(1)° |
| | $\beta$ = 103.617(1)° | $\beta$ = 104.987(1)° | $\beta$ = 101.92(3)° | $\beta$ = 91.127(1)° |
| | $\gamma$ = 103.295(1)° | $\gamma$ = 112.630(1)° | $\gamma$ = 90.73(3)° | $\gamma$ = 116.507(1)° |
| volume (Å$^3$) | 1771.5(2) | 2247.97(13) | 4026.4(14) | 1990.28(12) |
| $Z$ | 2 | 2 | 4 | 2 |
| density (calcd, g/cm$^3$) | 1.390 | 1.734 | 1.424 | 1.311 |
| absorp coeff (mm$^{-1}$) | 0.424 | 3.550 | 2.629 | 0.316 |
| $F$(000)[b] | 768 | 1157 | 1760 | 817 |
| cryst size (mm) | 0.18 × 0.13 × 0.08 | 0.25 × 0.15 × 0.15 | 0.25 × 0.20 × 0.20 | 0.36 × 0.15 × 0.15 |
| $\theta$ range for data collection (deg) | 1.50 to 28.25 | 1.27 to 26.02 | 1.63 to 26.02 | 1.49 to 28.33 |
| index ranges | $-12 \le h \le 14$ | $-14 \le h \le 13$ | $-13 \le h \le 13$ | $-16 \le h \le 14$ |
| | $-15 \le k \le 11$ | $-15 \le k \le 15$ | $-22 \le k \le 22$ | $-10 \le k \le 17$ |
| | $-17 \le l \le 19$ | $0 \le l \le 21$ | $-24 \le l \le 25$ | $-18 \le l \le 18$ |
| no. of reflns collected | 11 351 | 39 931 | 70 696 | 14 821 |
| no. of indep reflns | 7908 [$R_{int}$ = 0.0146] | 8866 [$R_{int}$ = 0.0280] | 15 780 [$R_{int}$ = 0.0270] | 9789 [$R_{int}$ = 0.0145] |
| absorption corr | empirical | empirical | empirical | empirical |
| no. of data/restraints/params | 7908/0/446 | 8866/849/743 | 15 780/0/955 | 9789/6/502 |
| goodness-of-fit on $F^2$ | 1.046 | 1.059 | 1.017 | 1.095 |
| final $R$ indices [$I>2\sigma(I)$] | $R_1$ = 0.0313 | $R_1$ = 0.0370 | $R_1$ = 0.0268 | $R_1$ = 0.0527 |
| | $wR_2$ = 0.0796 | $wR_2$ = 0.0986 | $wR_2$ = 0.0703 | $wR_2$ = 0.1595 |
| $R$ indices (all data) | $R_1$ = 0.0354 | $R_1$ = 0.0389 | $R_1$ = 0.0295 | $R_1$ = 0.0584 |
| | $wR_2$ = 0.0822 | $wR_2$ = 0.1002 | $wR_2$ = 0.0722 | $wR_2$ = 0.1654 |
| largest diff peak and hole (e·Å$^{-3}$) | 0.434 and −0.295 | 2.143 and −1.553 | 2.231 and −0.659 | 2.178 and −0.474 |

[a] Wavelength = 0.71073 Å; refinement was by full-matrix least squares on $F^2$. [b] The $F$(000) values include solvents, one bromobenzene in the hafnium bistriflate species and one benzene in the hafnium diisobutyl species.

**Table 2. Selected Bond Lengths (Å) and Angles (deg) for [MepyN]Zr(NMe$_2$)Cl, [MepyN]Hf(OSO$_2$CF$_3$)$_2$, [MepyN]Hf(CH$_2$CHMe$_2$)$_2$, and [MepyN]Zr(CH$_2$Ph)$_2$**

| [MepyN]Zr(NMe$_2$)Cl | | [MepyN]Hf(OSO$_2$CF$_3$)$_2$ | | [MepyN]Hf(CH$_2$CHMe$_2$)$_2$ | | [MepyN]Zr(CH$_2$Ph)$_2$ | |
|---|---|---|---|---|---|---|---|
| Zr−N(1) | 2.413(1) | Hf−N(1) | 2.389(4) | Hf−N(1B) | 2.391(2) | Zr−N(1) | 2.518(2) |
| Zr−N(2) | 2.091(1) | Hf−N(2) | 2.047(4) | Hf−N(2B) | 2.111(2) | Zr−N(2) | 2.104(2) |
| Zr−N(3) | 2.130(1) | Hf−N(3) | 2.048(4) | Hf−N(3B) | 2.093(2) | Zr−N(3) | 2.111(2) |
| Zr−N(4) | 2.490(1) | Hf−N(4) | 2.418(4) | Hf−N(4B) | 2.435(3) | Zr−N(4) | 2.540(2) |
| Zr−N(5) | 2.048(1) | Hf-0(1) | 2.087(3) | Hf−C(1B) | 2.308(3) | Zr−C(1) | 2.337(3) |
| Zr−Cl(1) | 2.517(1) | Hf-0(4) | 2.093(4) | Hf−C(5B) | 2.319(3) | Zr−C(8) | 2.311(3) |
| N(1)−Zr−N(4) | 112.81(5) | N(1)−Hf−N(4) | 139.76(14) | N(1B)−Hf−N(4B) | 138.69(9) | N(1)−Zr−N(4) | 135.12(8) |
| N(2)−Zr−N(4) | 159.36(5) | N(2)−Hf−N(4) | 143.76(14) | N(2B)−Hf−N(4B) | 144.26(9) | N(2)−Zr−N(4) | 154.06(8) |
| N(1)−Zr−N(5) | 164.09(6) | N(1)−Hf−N(2) | 72.44(14) | N(1B)−Hf−N(2B) | 72.28(9) | N(1)−Zr−N(2) | 70.62(8) |
| N(1)−Zr−N(3) | 80.64(5) | N(1)−Hf−O(1) | 89.23(14) | N(1B)−Hf−C(1B) | 78.56(10) | C(1)−Zr−C(8) | 132.07(11) |
| N(3)−Zr−Cl(1) | 150.75(4) | Hf−O(1)−S(1) | 152.4(2) | N(1B)−Hf−C(5B) | 88.47(10) | N(1)−Zr−C(1) | 83.86(9) |
| N(2)−Zr−Cl(1) | 101.48(4) | N(2)−Hf−O(1) | 94.80(14) | C(1B)−Hf−C(5B) | 145.31(12) | N(1)−Zr−C(8) | 78.00(9) |
| N(2)−Zr−N(1) | 71.91(5) | O(1)−Hf−O(2) | 132.54(14) | Hf−C(1B)−C(2B) | 125.4(2) | Zr−C(1)−C(2) | 104.97(18) |
| N(3)−Zr-N(4) | 71.14(5) | | | | | | |

Zr(NMe$_2$)Cl illustrates that the [MepyN]$^{2-}$ ligand can adopt a geometry that does not contain *trans*-disposed pyridyl ligands, one of three possible coordination geometries (Scheme 1).

Conversion of [MepyN]Zr(NMe$_2$)$_2$ to [MepyN]ZrCl$_2$ was accomplished by heating [MepyN]Zr(NMe$_2$)$_2$ in toluene or benzene in the presence of 2 equiv of TMSCl at 80 °C for 16 h. The resulting dichloride species is

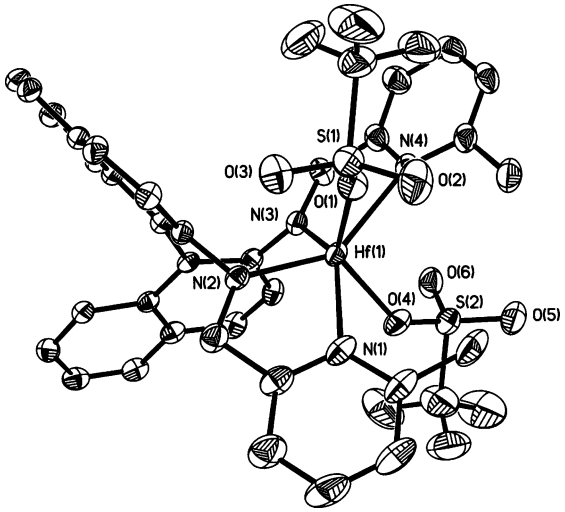



**Figure 2.** Thermal ellipsoid (50%) plot of [MepyN]Hf($OSO_2CF_3$)$_2$. Hydrogen atoms are omitted for clarity.

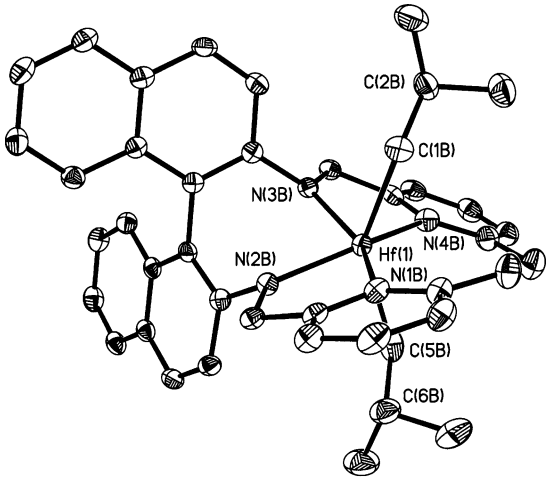



**Figure 3.** Thermal ellipsoid (50%) plot of [MepyN]Hf($CH_2CHMe_2$)$_2$ (one of two chemically equivalent molecules in the asymmetric unit). Hydrogen atoms are omitted for clarity.

relatively insoluble in common solvents, even dichloromethane. Proton NMR spectra of the dichloride complex in $CD_2Cl_2$ is consistent with the structure being $C_2$-symmetric in solution and are overall similar to spectra of [MepyN]Zr($NMe_2$)$_2$. Insolubility of [MepyN]-$ZrCl_2$ hampered efforts to convert it to diakyl complexes by reaction with Grignard reagents. For example, the reaction between [MepyN]$ZrCl_2$ and $Me_2CHCH_2MgBr$ was only successful when conducted in dichloromethane. However, the yield was poor and not reproducible, most likely as a consequence of side reactions involving dichloromethane.

We thought that problems ascribable to insolubility of [MepyN]$ZrCl_2$ might be circumvented if [MepyN]Zr-($OSO_2CF_3$)$_2$ was prepared. Treatment of [MepyN]M-($NMe_2$)$_2$ (M = Zr, Hf) with 2 equiv of trimethylsilyl triflate in benzene proceeded in less than 10 min at room temperature to yield white crystalline [MepyN]M-($OSO_2CF_3$)$_2$ species after crystallization (eq 3). The bistriflate complexes are soluble in benzene and toluene at elevated temperatures and readily dissolve in THF and $CH_2Cl_2$. Proton NMR spectra of [MepyN]M($OSO_2$-$CF_3$)$_2$ species are highly solvent dependent, but in each case the spectra are consistent with a $C_2$-symmetric structure in solution. Upon changing from benzene-$d_6$

$$\text{[MepyN]M(NMe}_2\text{)}_2 + 2\ \text{TMSOSO}_2\text{CF}_3 \xrightarrow[\text{benzene}]{23\ ^\circ\text{C}} \text{[MepyN]M(OSO}_2\text{CF}_3\text{)}_2 + 2\ \text{TMSNMe}_2 \quad (3)$$

to $CD_2Cl_2$ or THF-$d_8$, resonances for the methylene protons between the amide and pyridine donor broaden significantly. Since a solid state structure (see below) reveals that the triflates are monodentate, we speculate that the fluxional process may involve bidentate coordination of one or more triflates with (possibly) accompanying dissociation of a pyridine donor. Solution IR studies did not support the possibility that a triflate is lost in polar solvents to yield a cationic species. In all solvents resonances for the hafnium complex broaden to a greater degree than those for the zirconium species.

The solid state structure of [MepyN]Hf($OSO_2CF_3$)$_2$ was determined by X-ray diffraction (Figure 2; Tables 1 and 2). Crystals of the triflate complex were grown by vapor diffusion of pentane into a bromobenzene solution containing approximately 1 equiv of benzene per hafnium. Due to partial decomposition of [MepyN]-Hf($OSO_2CF_3$)$_2$ in bromobenzene, ~5% of the compound examined contained a bromide in place of one of the triflates. This disorder was modeled successfully. (The reader is directed to the Supporting Information for more details.) The geometry about Hf is a highly distorted octahedron, with the ligand adopting a binding mode that is approximately $C_2$-*cis* (Scheme 1). The triflates are bound in an $\eta^1$ fashion, but the O(1)−Hf−O(2) angle is only 132.54(14)°. The Hf−$N_{amide}$ and Hf−$N_{pyridyl}$ bond lengths are similar to those in [MepyN]Zr-($NMe_2$)Cl. The highly distorted geometry of [MepyN]-Hf($OSO_2CF_3$)$_2$ likely results from steric restraints imposed by the ligand and is similar to distortions found in structures of $C_2$-symmetric dialkyl species discussed below. A search of the Cambridge Structural Database revealed no other example of a structurally characterized hafnium complex that contains one or more triflate ligands.

Attempts to prepare [MepyN]$MMe_2$ by treating either [MepyN]$MCl_2$ or [MepyN]M($OSO_2CF_3$)$_2$ with a variety of methylating agents ($AlMe_3$, MeLi, and $Me_2Mg$) under different conditions in different solvents met with no success. We suspect that methyl nucleophiles may deprotonate the benzyl position of the ligand backbone. In contrast, alkylation was successful with $Me_2CHCH_2$-MgBr to give [MepyN]M($CH_2CHMe_2$)$_2$ (M = Zr, Hf) species. These reactions were found to proceed best in THF. Proton NMR spectra of the zirconium and hafnium isobutyl complexes are almost identical, displaying resonances consistent with $C_2$ symmetry. The isobutyl methine proton appears as a multiplet, while the methyl groups appear as doublets and the methylene protons as doublets of doublets (see Experimental Section). The [MepyN]M($CH_2CHMe_2$)$_2$ complexes are readily soluble in aromatic solvents and THF but insoluble in pentane and diethyl ether.

The structure of [MepyN]Hf($CH_2CHMe_2$)$_2$ was determined in an X-ray study (Figure 3, Tables 1 and 2). The compound crystallizes with both enantiomers in the asymmetric unit, but only one molecule is shown in Figure 3 and listed in Table 2. Like [MepyN]Hf($OSO_2$-

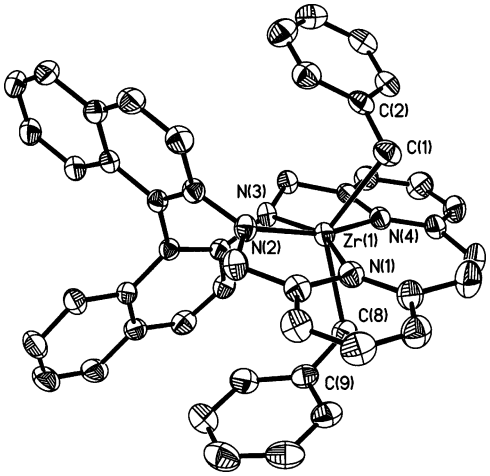



**Figure 4.** Thermal ellipsoid (50%) plot of [MepyN]Zr($CH_2Ph)_2$. Hydrogen atoms are omitted for clarity.

$CF_3)_2$, [MepyN]Hf($CH_2CHMe_2)_2$ is a highly distorted octahedron with the ligand again adopting the $C_2$-*cis* orientation shown in Scheme 1. The bond lengths and angles for the $[MepyN]^{2-}$ ligand are very similar to those of the triflate species. The isobutyl ligands are approximately *trans* to one another (C(1B)−Hf−C(5B) = 145.31(12)°) with relatively long Hf−C bond lengths (Hf−C(1B) = 2.308(3) Å; Hf−C(5B) = 2.319(3) Å), as expected in a relatively crowded six-coordinate complex.

An alternative approach to dialkyl complexes consists of ligand addition to tetraalkyls. Reaction of $H_2$[MepyN] with $Zr(CH_2CMe_3)_4$ did not lead to any observable [MepyN]$Zr(CH_2CMe_3)_2$, even upon heating. At room temperature, no reaction was observed, and at elevated temperatures only decomposition of the tetraalkyl was observed. However, a reaction between $H_2$[MepyN] and $Zr(CH_2Ph)_4$ produced [MepyN]$Zr(CH_2Ph)_2$ in good yield as a yellow-orange crystalline solid. The benzyl complex is considerably less soluble than [MepyN]Zr($CH_2$-$CHMe_2)_2$, although it dissolves readily in dichloromethane. The spectral features of [MepyN]$Zr(CH_2Ph)_2$ are similar to those for [MepyN]$Zr(CH_2CHMe_2)_2$, with the benzyl methylene resonances appearing as a set of doublets at 2.26 and 1.89 ppm in $CD_2Cl_2$. The benzyl resonances appear at relatively low field, with the *ortho* proton resonance appearing at 5.63 ppm. The solid state structure of [MepyN]$Zr(CH_2Ph)_2$ (Figure 4; Tables 1 and 2) shows it to be similar to the isobutyl and bistriflate structures discussed earlier. The ligand once again adopts the $C_2$-*cis* structure shown in Scheme 1. The Zr−C bond lengths and Zr−C−C angles (Table 2) are not consistent with any tendency of a benzyl group to bond in an $\eta^2$ fashion.

Activation of [MepyN]$M(CH_2CHMe_2)_2$ with $B(C_6F_5)_3$, $\{HNMe_2Ph\}\{B(C_6F_5)_4\}$, or $\{Ph_3C\}\{B(C_6F_5)_4\}$ in toluene, benzene, or bromobenzene gave rise in each case to a monoisobutyl cation with concomitant formation of the expected byproducts (eqs 4−6). NMR spectra of the

$$[\text{MepyN}]\text{M}(\text{CH}_2\text{CHMe}_2)_2 \xrightarrow[-\text{Me}_2\text{C=CH}_2]{\text{B}(\text{C}_6\text{F}_5)_3} \{[\text{MepyN}]\text{M}(\text{CH}_2\text{CHMe}_2)\}\{\text{HB}(\text{C}_6\text{F}_5)_3\} \quad (4)$$

cation show the expected asymmetry, with individual resonances visible for each of the protons of the ligand.

$$[\text{MepyN}]\text{M}(\text{CH}_2\text{CHMe}_2)_2 \xrightarrow[-\text{Ph}_3\text{CH} - \text{Me}_2\text{C=CH}_2]{\{\text{Ph}_3\text{C}\}\{\text{B}(\text{C}_6\text{F}_5)_4\}} \{[\text{MepyN}]\text{M}(\text{CH}_2\text{CHMe}_2)\}\{\text{B}(\text{C}_6\text{F}_5)_4\} \quad (5)$$

$$[\text{MepyN}]\text{M}(\text{CH}_2\text{CHMe}_2)_2 \xrightarrow[-\text{Me}_2\text{NPh} - \text{Me}_3\text{CH}]{\{\text{HNMe}_2\text{Ph}\}\{\text{B}(\text{C}_6\text{F}_5)_4\}} \{[\text{MepyN}]\text{M}(\text{CH}_2\text{CHMe}_2)\}\{\text{B}(\text{C}_6\text{F}_5)_4\} \quad (6)$$

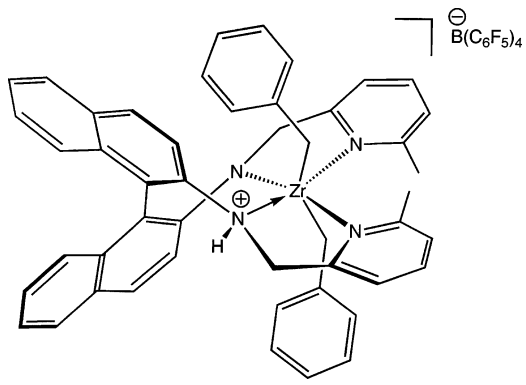
The resonances for the isobutyl ligand are shifted upfield with one of the methylene protons of {[MepyN]-Hf($CH_2CHMe_2$)}$\{HB(C_6F_5)_3\}$ appearing at −1.23 ppm in bromobenzene-$d_5$. An α-agostic interaction is unlikely, however, as the methylene resonances remain sharp in bromobenzene-$d_5$ with splitting patterns similar to those in the neutral dialkyl.

Treatment of any of these species with excess 1-hexene yielded no detectable poly[1-hexene] at either room temperature or 60 °C. Solutions were unchanged for several days at room temperature, although at elevated temperature decompositions to yield some isobutene and unidentifiable metal-containing product(s) were observed after several hours.

A reaction between [MepyN]$Zr(CH_2Ph)_2$ and $\{HNMe_2$-$Ph\}\{B(C_6F_5)_4\}$ in $CD_2Cl_2$ at −30 °C or room temperature occurs quantitatively in seconds. The proton NMR spectrum of the activated species shows resonances consistent with formation of a $C_1$-symmetric species, along with those for dimethylaniline. However, no toluene is formed, while resonances attributable to two benzyl ligands are observed. The proton resonances of the ligand backbone resemble those of the isobutyl cation except for the resonances due to the methylene groups between the amido nitrogens and the pyridine moieties. Unlike the isobutyl cation, only *three* doublets are apparent in the range 3−4 ppm, instead of the expected four. Additionally, a doublet of doublets appears at 2.79 ppm; this type of resonance is not observed in any species discussed so far. The gCOSY spectrum shows a cross-peak between the resonance at 2.79 ppm and a doublet resonance at 5.63 ppm, with an H−H coupling constant of 7.5 Hz, consistent with a three-bond separation. This feature, along with the presence of two benzyl groups, points toward formulation of the species as one that results from protonation of an amido nitrogen, as shown in Scheme 3. As one would expect, this cationic species is not a catalyst for polymerization of 1-hexene.

In a similar experiment, [MepyN]$Zr(CH_2Ph)_2$ was treated with $\{HNMe_2Ph\}Cl$ in $CD_2Cl_2$; free dimethylaniline and toluene were observed, along with a mixture of [MepyN]$Zr(CH_2Ph)_2$, [MepyN]$ZrCl_2$, and [MepyN]-$Zr(CH_2Ph)Cl$. We cannot rule out prior protonation of the amide followed by proton transfer to benzyl. However, the anilinium chloride is not consumed immediately, and monitoring of the reaction mixture does not reveal any intermediate species similar to the one discussed in the preceding paragraph. Solutions of [MepyN]$Zr(CH_2Ph)_2$ activated with $\{HNMe_2Ph\}\{B$-$(C_6F_5)_4\}$ do not yield any monobenzyl cation over a period of days, even at elevated temperatures. This result is somewhat surprising considering the observed tendency for anilinium chloride to protonate the benzyl ligand, and also the possibility that uncoordinated dimethylaniline could move a proton between different

**Scheme 3**




parts of the complex. These observations may be relevant to studies concerning the dibenzyl species reported by Brintzinger, which was inactive toward propene polymerization when activated with anilinium borate.[35]

Treatment of [MepyN]Zr($CH_2Ph$)$_2$ with strong Lewis acids does lead to a monobenzyl cation. Reaction of [MepyN]Zr($CH_2Ph$)$_2$ with B($C_6F_5$)$_3$ or trityl in $CD_2Cl_2$ proceeds to yield the monobenzyl cation cleanly, which can be observed spectroscopically (eqs 7 and 8).

$$[\text{MepyN}]\text{Zr}(\text{CH}_2\text{Ph})_2 \xrightarrow{\text{B}(\text{C}_6\text{F}_5)_3} \{[\text{MepyN}]\text{Zr}(\text{CH}_2\text{Ph})\}\{\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3\} \quad (7)$$

$$[\text{MepyN}]\text{Zr}(\text{CH}_2\text{Ph})_2 \xrightarrow[\text{-PhCH}_2\text{CPh}]{\{\text{Ph}_3\text{C}\}\{\text{B}(\text{C}_6\text{F}_5)_4\}} \{[\text{MepyN}]\text{Zr}(\text{CH}_2\text{Ph})\}\{\text{B}(\text{C}_6\text{F}_5)_4\} \quad (8)$$

The room-temperature proton NMR spectrum of the benzyl cation shows a broadened ligand environment that remains $C_2$-symmetric, as judged from the presence of a broadened singlet for the pyridine methyl resonances. Resonances for the methylene protons of the benzyl ligand appear at 1.53 ppm (sharp doublet) and 0.02 ppm (broad doublet). The aryl protons of the benzyl ligand also remain sharp, as do the peaks corresponding to the $PhCH_2B(C_6F_5)_3$ anion in the case of activation with B($C_6F_5$)$_3$. To further elucidate the nature of the benzyl cation, the $^1$H NMR spectrum was recorded at temperatures down to −70 °C. Upon decreasing the temperature, the resonances of the ligand environment sharpen consistently until at −70 °C they appear in positions close to those observed in the isobutyl cation. At this temperature, two singlets of area three are observed for the pyridine methyl groups, as are four doublets of area one for each of the methylene protons of the ligand. The resonances for the methylene protons of the benzyl group broaden upon decreasing in temperature, then sharpen at −70 °C and appear as a set of doublets of area one with a $^2J_{H-H}$ of 12.5 Hz. One of the methylene protons is significantly shifted upfield (−0.54 ppm), while the other shifts slightly to 1.44 ppm ($CD_2Cl_2$).

Addition of dimethylaniline to solutions of the benzyl cation at room temperature did not reveal any tendency for the cation to form a dimethylaniline adduct. (Zirconium and hafnium alkyl cations that show activity toward 1-hexene polymerization that have been studied in our laboratory form at least a weak adduct with $Me_2$-NPh.) Addition of 1-hexene to the benzyl cation failed to give any detectable poly[1-hexene].

## Conclusion

The chemistry of six-coordinate zirconium and hafnium complexes of the [MepyN]$^{2-}$ ligand offer an opportunity to examine the reactivity of coordinatively more saturated species with well-defined activators such as boranes, carbocations, and proton sources. Activation of dialkyl species, especially [MepyN]M($CH_2CHMe_2$)$_2$, gives rise to asymmetric, cationic, monoalkyl complexes that are readily observable by standard NMR techniques. However, these species will not polymerize 1-hexene. The absence of catalytic activity with these complexes can be ascribed to both their high coordination number and the presence of a sterically encumbering diamidodipyridine ligand which serves to both decrease the Lewis acidity at the metal and hinder olefin approach and binding.

## Experimental Section

**General Comments.** All manipulations of air- and moisture-sensitive materials were performed in oven-dried (200 °C) glassware under an atmosphere of nitrogen on a dual-manifold Schlenk line or in a Vacuum Atmospheres glovebox. NMR measurements were carried out in Teflon-valve sealed J. Young-type NMR tubes. HPLC grade organic solvents were sparged with nitrogen and dried by passage through activated alumina (for diethyl ether, toluene, pentane, THF, and methylene chloride) followed by passage through Q-5 supported copper catalyst (for benzene) prior to use, then stored over 4 Å Linde-type molecular sieves. Benzene-$d_6$, toluene-$d_8$, and THF-$d_8$ were dried over sodium/benzophenone ketyl and vacuum-distilled. Methylene chloride-$d_2$ and bromobenzene-$d_5$ were dried over $CaH_2$, vacuum distilled, and stored over 4 Å Linde-type molecular sieves. NMR spectra were recorded on a Varian 500 or Varian 300 spectrometer. Chemical shifts for $^1$H and $^{13}$C spectra were referenced to the residual $^1$H/$^{13}$C resonances of the deuterated solvent ($^1$H: $C_6D_6$, $\delta$ 7.16; $C_6D_5$-$CD_3$, $\delta$ 2.15; $CD_2Cl_2$, $\delta$ 5.32; $C_6D_5Br$, $\delta$ 7.29; $^{13}$C: $C_6D_6$, $\delta$ 128.39; $CD_2Cl_2$, $\delta$ 54.00) and are reported as parts per million relative to tetramethylsilane. $^{19}$F NMR spectra were referenced externally to fluorobenzene ($\delta$ −113.15 ppm upfield of $CFCl_3$). High-resolution mass spectrometry measurements were performed at the MIT Department of Chemistry Instrument Facility, and elemental analyses were performed by H. Kolbe Microanalytics Laboratory, Mülheim an der Ruhr, Germany.

2,2′-Diamino-1,1′-binaphthalene,[36] Zr($NMe_2$)$_4$,[37] Zr($CH_2$-Ph)$_4$,[38] Hf($NMe_2$)$_4$,[37] and {$HNMe_2Ph$}{B($C_6F_5$)$_4$}[39] were prepared according to published procedures, or slightly modified versions thereof. 6-Methyl-2-pyridinecarboxaldehyde, TMSCl, and i-BuMgBr were purchased from Aldrich Chemical Co. and used as received. Tris(pentafluorophenyl)borane and trimethylsilyl trifluoromethanesulfonate (TMSOTf) were purchased from Strem Chemical Co. and used as received. Trityl tetrakis-(pentafluorophenyl)borate, {$Ph_3C$}{B($C_6F_5$)$_4$}, was obtained as a gift from the Exxon Mobile Corp. and used as received.

**Crystallography.** Low-temperature diffraction data were collected on a Siemens Platform three-circle diffractometer

(36) Brown, K. J.; Berry, M. S.; Murdoch, J. R. *J. Org. Chem.* **1985**, *50*, 4345.
(37) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4030.
(38) Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357.
(39) Tjaden, E. B.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1995**, *14*, 371.

coupled to a Bruker-AXS Smart 1K CCD detector or a Bruker-AXS Apex CCD detector with graphite-monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å), performing $\varphi$- and $\omega$-scans. All structures were solved by direct methods using SHELXS[40] and refined against $F^2$ on all data by full-matrix least squares with SHELXL-97 (Sheldrick, G. M. *SHELXL 97*, Universität Göttingen, Göttingen, Germany, 1997). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of the hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups). The disorders in the structures of [MepyN]Hf($OSO_2CF_3$)$_2$ and [MepyN]Zr($CH_2Ph$)$_2$ were refined with the help of similarity restraints on 1−2 and 1−3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The occupancies for the disordered parts in these two structures were refined freely.

**1-(2-((6-Methylpyridin-2-yl)methylamino)naphthalen-1-yl)-*N*-((6-methylpyridin-2-yl)methyl)naphthalen-2-amine. $H_2$[MepyN].** A two-neck round-bottom flask was charged with 5.71 g (20.1 mmol) of 2,2′-diamino-1,1′-binaphthalene, a magnetic stirbar, and 50 mL of absolute ethanol. The flask was fitted with a reflux condenser and a pressure-equalizing addition funnel. To the addition funnel was added a solution of 5.61 g (46.3 mmol) of 6-methyl-2-pyridinecarboxaldehyde in 20 mL of absolute ethanol. The solution of the pyridine was added dropwise to the suspension of the diamine and then heated at reflux under nitrogen for 90 min, during which time the reaction mixture became a golden yellow solution. The reaction was allowed to cool, and the volatiles were removed in vacuo. An additional 150 mL of absolute ethanol was added, as was 2.28 g (60.3 mmol) of $NaBH_4$. The reaction was heated again under nitrogen at reflux for 20 h. The reaction was cooled to room temperature and quenched by pouring onto 5 g of $NH_4Cl$. The ethanol was removed in vacuo and the resulting residue dissolved in methylene chloride, washed three times with 100 mL of water, dried over $MgSO_4$, and filtered through Celite. The methylene chloride was removed in vacuo and the resulting amber residue dissolved in a minimal amount of hot toluene. Pentane was added until the solution became slightly turbid and was then set aside at −40 °C for 24 h, during which time $H_2$[MepyN] precipitated as off-white crystals. The compound was further purified by repeated crystallization from toluene/pentane; yield 8.13 g (82%): $^1$H NMR ($C_6D_6$) $\delta$ 7.72 (t, 4 Ar*H*), 7.40 (d, 2 Ar*H*), 7.19 (d, 2 Ar*H*), 7.10 (m, 4 Ar*H*), 6.93 (t, 2 Ar*H*), 6.82 (d, 2 Ar*H*), 6.49 (d, 2 Ar*H*), 4.87 (t, 2 N*H*), 4.15 (m, 4 C$H_2$), 2.27 (s, 6 py*Me*); $^{13}$C{$^1$H} NMR ($C_6D_6$) $\delta$ 159.45, 158.206, 144.95, 136.66, 135.18, 130.38, 128.99, 128.76, 127.53, 124.93, 122.65, 121.33, 118.10, 114.85, 113.10, 49.39 (*C*$H_2$), 24.67 (py*Me*); HRMS calcd $[M + H]^+$ 495.2543, found $[M + H]^+$ 495.2551. Anal. Calcd for $C_{34}H_{30}N_4$: C, 82.56; H, 6.11; N, 11.33. Found: C, 82.65; H, 6.04; N, 11.37.

**[MepyN]Zr($NMe_2$)$_2$.** To 1.012 g (2.05 mmol) of $H_2$[MepyN] dissolved in 30 mL of toluene was added a solution of 0.547 g (2.04 mmol) of Zr($NMe_2$)$_4$ in 10 mL of toluene. The solution was heated to 50 °C and stirred for 20 h, during which time it became golden yellow. The toluene was concentrated in vacuo to ∼10 mL, and several volumes of pentane were added. The solution was set aside at −25 °C for several hours, during which time yellow microcrystals precipitated. The crystals were isolated by filtration, washed with pentane, and dried in vacuo; yield 1.343 g (98%): $^1$H NMR ($C_6D_6$) $\delta$ 7.80 (d, 2 Ar*H*), 7.70 (d, 2 Ar*H*), 7.57 (d, 2 Ar*H*), 7.04 (t, 2 Ar*H*), 6.85 (t, 2 Ar*H*), 6.68 (t, 2 Ar*H*), 6.48 (d, 2 Ar*H*), 6.36 (d, 2 Ar*H*), 5.35 (d, 2 C$H_2$, $^2J_{H-H}$ = 18.0 Hz), 5.05 (d, 2 C$H_2$), 2.51 (s, 12 N$Me_2$), 2.26 (s, 6 py*Me*). Anal. Calcd for $C_{38}H_{40}N_6Zr$: C, 67.92; H, 6.00; N, 12.51. Found: C, 67.84; H, 6.09; N, 12.38.

(40) Sheldrick, G. M. *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

**[MepyN]Zr($NMe_2$)Cl.** This compound was prepared in an analogous fashion to [MepyN]Zr($NMe_2$)$_2$ starting with ligand that contained approximately one-third of an equivalent of chloroform (65% yield, on ∼1 g scale): $^1$H NMR ($C_6D_6$) $\delta$ 7.99 (d, 1 Ar*H*), 7.90 (d, 1 Ar*H*), 7.78 (d, 1 Ar*H*), 7.55 (d, 1 Ar*H*), 7.52 (d, 1 Ar*H*), 7.31 (d, 1 Ar*H*), 7.15 (t, 2 Ar*H*), 7.05 (t, 1 Ar*H*), 7.00 (t, 1 Ar*H*), 6.90 (t, 1 Ar*H*), 6.81 (t, 2 Ar*H*), 6.51 (t, 1 Ar*H*), 6.42 (d, 2 Ar*H*), 6.28 (d, 1 Ar*H*), 5.54 (d, 1 Ar*H*), 5.36 (d, 1 C$H_2$, $^2J_{H-H}$ = 20.0 Hz), 4.98 (d, 1 C$H_2$, $^2J_{H-H}$ = 19.0 Hz), 4.49 (d, 1 C$H_2$), 3.88 (d, 1 C$H_2$), 2.95 (s, 3 py*Me*), 2.59 (br s, 6 N$Me_2$), 2.35 (s, 3 py*Me*). Anal. Calcd for $C_{36}H_{34}N_5ClZr$: C, 65.18; H, 5.17; N, 10.56; Cl, 5.34. Found: C, 65.26; H, 5.24; N, 10.44; Cl, 5.25.

Crystals suitable for X-ray diffraction were grown by vapor diffusion of pentane into a saturated benzene solution.

**[MepyN]Zr$Cl_2$.** A solution of 0.900 g (1.36 mmol) of [MepyN]Zr($NMe_2$)$_2$ in 50 mL of toluene was treated with 0.38 mL (3.0 mmol) of TMSCl. The solution was heated to 80 °C and stirred for 24 h, during which time an off-white powder precipitated from solution. The material was collected by filtration, washed with pentane, and dried in vacuo; yield 0.759 g (85%): $^1$H NMR ($CD_2Cl_2$) $\delta$ 7.83 (m, 4 Ar*H*), 7.68 (t, 2 Ar*H*), 7.51 (d, 2 Ar*H*), 7.34 (t, 2 Ar*H*), 7.21 (m, 6 Ar*H*), 7.04 (d, 2 Ar*H*), 5.14 (d, 2 C$H_2$, $^2J_{H-H}$ = 20.5 Hz), 4.73 (d, 2 C$H_2$), 2.99 (s, 6 py*Me*).

**[MepyN]Zr($OSO_2CF_3$)$_2$.** A solution of 1.052 g (1.57 mmol) of [MepyN]Zr($NMe_2$)$_2$ in 50 mL of benzene was treated with 0.70 mL (3.6 mmol) of TMSOTf. The yellow solution was stirred at room temperature for 60 min, during which time the color became lighter. The solution was layered with several volumes of pentane and allowed to stand for 16 h, over which time the compound precipitated as white microcrystals. NMR spectra showed the presence of 1 equiv of benzene, which was confirmed by analysis; yield 0.968 g (68%): $^1$H NMR ($C_6D_6$) $\delta$ 8.15 (d, 2 Ar*H*), 7.78 (d, 2 Ar*H*), 7.63 (d, 2 Ar*H*), 7.55 (d, 2 Ar*H*), 7.15 (t, 2 Ar*H*), 7.04 (t, 2 Ar*H*), 6.52 (t, 2 Ar*H*), 6.24 (d, 2 Ar*H*), 5.75 (d, 2 Ar*H*), 5.10 (d, 2 C$H_2$, $^2J_{H-H}$ = 20.5 Hz), 4.23 (d, 2 C$H_2$), 2.85 (s, 6 py*Me*); $^{19}$F NMR ($C_6D_6$) $\delta$ −77.42 (s, $OSO_2CF_3$). Anal. Calcd for $C_{42}H_{34}N_4F_6O_6S_2Zr$: C, 52.54; H, 3.57; N, 5.84. Found: C, 52.33; H, 3.70; N, 5.62.

**[MepyN]Zr($CH_2C_6H_5$)$_2$.** A reaction vessel was charged with 0.616 g (1.24 mmol) of $H_2$[MepyN] and 0.544 g (1.19 mmol) of Zr($CH_2Ph$)$_4$. Benzene (35 mL) was added, and the resulting orange solution was allowed to stand at room temperature for 20 h. Pentane was added until the solution became turbid. The product precipitated from solution as orange microcrystals over several hours at room temperature; yield 0.675 g (74%): $^1$H NMR ($CD_2Cl_2$) $\delta$ 7.83 (app t, 4 Ar*H*), 7.54 (t, 2 Ar*H*), 7.41 (d, 2 Ar*H*), 7.28 (t, 2 Ar*H*), 7.13 (m, 4 Ar*H*), 7.06 (d, 2 Ar*H*), 6.78 (d, 2 Ar*H*), 6.13 (m, *m* and *p* Bn), 5.63 (d, 4 *o* Bn), 4.75 (d, 2 C$H_2$, $^2J_{H-H}$ = 20.0 Hz), 4.12 (d, 2 C$H_2$), 2.94 (s, 6 py*Me*), 2.26 (d, 2 C$H_2$Ph, $^2J_{H-H}$ = 10.0 Hz), 1.89 (d, 2 C$H_2$Ph); $^{13}$C{$^1$H} NMR ($CD_2Cl_2$) $\delta$ 163.65, 156.87, 153.67, 148.92, 137.92, 134.51, 130.60, 128.46, 128.17, 127.82, 127.31, 126.80, 126.07, 125.67, 124.86, 123.61, 123.31, 119.27, 119.13, 66.58, 61.68, 26.00 (py*Me*). Anal. Calcd for $C_{48}H_{42}N_4Zr$: C, 75.25; H, 5.53; N, 7.31. Found: C, 75.18; H, 5.46; N, 7.22.

Crystals suitable for X-ray diffraction were grown by vapor diffusion of pentane into a saturated methylene chloride solution.

**[MepyN]Zr($CH_2CHMe_2$)$_2$.** A flask was charged with 0.148 g (0.226 mmol) of [MepyN]Zr$Cl_2$, and 15 mL of $CH_2Cl_2$ was added. The suspension was cooled to −25 °C. Once cool, 0.24 mL of (0.58 mmol) i-BuMgBr (2.4 M in $Et_2O$) was added dropwise over the stirring suspension. The reaction was allowed to stir for 10 min at room temperature, during which time it became yellow-orange. 1,4-Dioxane (0.15 mL) was added, at which point a white precipitate formed. The reaction was filtered through Celite and the volatiles were removed in vacuo. The resulting orange residue was dissolved in 2 mL of toluene, and several volumes of pentane were added. The

solution was set aside at −25 °C for several hours, during which time an orange microcrystalline material precipitated. The material was collected by filtration, washed with pentane, and dried in vacuo; yield 70 mg (44%, not optimized): $^1$H NMR ($C_6D_6$) $\delta$ 7.83 (d, 2 Ar*H*), 7.78 (d, 2 Ar*H*), 7.61 (d, 2 Ar*H*), 7.58 (d, 2 Ar*H*), 7.17 (t, 2 Ar*H*), 7.06 (t, 2 Ar*H*), 6.85 (t, 2 Ar*H*), 6.49 (d, 2 Ar*H*), 6.39 (d, 2 Ar*H*), 5.04 (d, C*H*$_2$, $^2J_{H-H}$ = 20.5 Hz), 4.83 (d, C*H*$_2$), 2.81 (s, 6 py*Me*), 1.24 (m, C*H*HC*H*Me$_2$), 0.78 (d, CH$_2$CH*Me*Me), 0.55 (dd, CH*H*CHMe$_2$), 0.41 (d, CH$_2$-CHMe*Me*). Anal. Calcd for $C_{42}H_{46}N_4Zr$: C, 72.26; H, 6.64; N, 8.03. Found: C, 72.14; H, 6.57; N, 7.94.

**[MepyN]Hf(NMe$_2$)$_2$.** This compound was prepared in a fashion similar to that for [MepyN]Zr(NMe$_2$)$_2$ starting from 1.001 g (2.02 mmol) of H$_2$[MepyN] and 0.720 g (2.03 mmol) of Hf(NMe$_2$)$_4$, except that it required heating at 60 °C for 48 h; yield 1.178 g (77%): $^1$H NMR ($C_7D_8$) $\delta$ 7.77 (d, 2 Ar*H*), 7.66 (d, 2 Ar*H*), 7.59 (d, 2 Ar*H*), 7.03 (t, 2 Ar*H*), 6.99 (d, 2 Ar*H*), 6.81 (t, 2 Ar*H*), 6.62 (t, 2 Ar*H*), 6.34 (app d, 4 Ar*H*), 5.32 (d, 2 C*H*$_2$, $^2J_{H-H}$ = 17.5 Hz), 5.01 (d, 2 C*H*$_2$), 2.60 (s, 12 N*Me*$_2$), 2.28 (s, 6 py*Me*); $^{13}$C{$^1$H} NMR ($CD_2Cl_2$) $\delta$ 163.86, 158.18, 152.60, 137.29, 135.69, 129.66, 128.61, 127.82, 127.41, 125,64, 125.54, 122.74, 122.56, 121.97, 119.06, 61.40 (*C*H$_2$), 41.26 (N*Me*$_2$), 23.77 (py*Me*). Anal. Calcd for $C_{38}H_{40}N_6Hf$: C, 60.11; H, 5.31; N, 11.07. Found: C, 60.15; H, 5.40; N, 10.97.

**[MepyN]Hf(OSO$_2$CF$_3$)$_2$.** This compound was prepared in a manner analogous to that used to prepare [MepyN]Zr(OSO$_2$-CF$_3$)$_2$ starting from 1.128 g (1.49 mmol) of [MepyN]Hf(NMe$_2$)$_2$ and 0.60 mL (3.1 mmol) of TMSOTf. One equivalent of benzene was present, as judged by NMR/analysis; yield 1.148 g (74%): $^1$H NMR ($C_6D_6$) $\delta$ 7.90 (br s, 2 Ar*H*), 7.79 (d, 2 Ar*H*), 7.66 (d, 2 Ar*H*), 7.49 (d, 2 Ar*H*), 7.16 (t, 2 Ar*H*), 7.04 (t, 2 Ar*H*), 6.59 (t, 2 Ar*H*), 6.29 (d, 2 Ar*H*), 5.84 (br d, 2 Ar*H*), 5.32 (d, C*H*$_2$, $^2J_{H-H}$ = 19.5 Hz), 4.43 (br d, 2 C*H*$_2$), 2.77 (br s, 6 py*Me*); $^{13}$C{H} NMR ($CD_2Cl_2$) $\delta$ 164.53, 140.63, 134.04, 131.87, 129.85, 128.84, 127.54, 126.43, 125.51, 125.12, 124.75, 120.21, 199.68 (q, OSO$_2$*C*F$_3$, $^1J_{C-F}$ = 318 Hz), 62.66 (br, *C*H$_2$), 23.64 (br, py*Me*). Three of the aromatic carbon peaks could not be unambiguously assigned; however, three very broad peaks appear in the spectrum between 120 and 160 ppm. $^{19}$F NMR ($CD_2Cl_2$) $\delta$ −78.09 (s, OSO$_2$C*F*$_3$). Anal. Calcd for $C_{42}H_{34}N_4F_6O_6S_2Hf$: C, 48.16; H, 3.27; N, 5.35. Found: C, 48.59; H, 3.36; N, 5.10.

Crystals suitable for X-ray diffraction were grown by vapor diffusion of pentane into a concentrated bromobenzene solution.

**[MepyN]Hf(CH$_2$CHMe$_2$)$_2$.** A flask was charged with 0.923 g (0.881 mmol) of [MepyN]Hf(OSO$_2$CF$_3$)$_2$·($C_6H_6$) and 30 mL of THF. The solution was chilled to −25 °C, at which point 0.82 mL (1.8 mmol) of Me$_2$CHCH$_2$MgBr was added dropwise. A precipitate formed immediately upon addition of Grignard. The mixture was allowed to stir at room temperature for 60 min. The THF was removed in vacuo and the residue extracted into toluene and filtered through Celite. The toluene solution was concentrated to ∼10 mL, layered with several volumes of pentane, and set aside at −25 °C for several days, during which time pale yellow crystals formed. The compound could be further purified by multiple recrystallizations from toluene/pentane; yield 0.443 g (64%): $^1$H NMR ($C_6D_6$) $\delta$ 7.85 (d, 2 Ar*H*), 7.79 (d, 2 Ar*H*), 7.63 (d, 2 Ar*H*), 7.57 (d, 2 Ar*H*), 7.18 (t, 2 Ar*H*), 7.07 (d, 2 Ar*H*), 6.85 (t, Ar*H*), 6.47 (d, 2 Ar*H*), 6.38 (d, 2 Ar*H*), 5.16 (d, C*H*$_2$, $^2J_{H-H}$ = 20.5 Hz), 4.86 (d, C*H*$_2$), 2.79 (s, py*Me*), 1.25 (m, 2 CH$_2$C*H*Me$_2$), 1.01 (dd, 2 C*H*HCHMe$_2$), 0.84 (d, 6 CH$_2$CH*Me*Me), 0.39 (d, 6 CH$_2$CHMe*Me*), 0.37 (dd, CH*H*-CHMe$_2$); $^{13}$C{H} NMR ($CD_2Cl_2$) $\delta$ 164.09, 158.03, 153.65, 138.02, 134.26, 130.42, 128.06, 127.90, 127.84, 127.15, 126.95, 125.32, 123.61, 123.35, 119.13, 78.64, 66.81, 31.73, 30.50, 26.44, 25.86. Anal. Calcd for $C_{42}H_{46}N_4Hf$: C, 64.23; H, 5.90; N, 7.13. Found: C, 64.18; H, 5.86; N, 7.05.

Crystals suitable for X-ray diffraction were grown by vapor diffusion of pentane into a concentrated benzene solution.

**{[MepyN]Zr(CH$_2$CH(CH$_3$)$_2$)}{HB(C$_6$F$_5$)$_3$}.** This species was observed spectroscopically by mixing equimolar amounts of [MepyN]Zr(CH$_2$CH(CH$_3$)$_2$)$_2$ and B($C_6F_5$)$_3$ in benzene-$d_6$ at room temperature. $^1$H NMR (20 °C): $\delta$ 8.05 (d, 1 Ar*H*), 7.75 (d, 1 Ar*H*), 7.55 (d, 1 Ar*H*), 7.46 (d, 1 Ar*H*), 7.26 (d, 1 Ar*H*), 7.22 (d, 1 Ar*H*), 7.18 (app t, 2 Ar*H*), 7.01 (m, 3 Ar*H*), 6.89 (m, 2 Ar*H*), 6.84 (d, 1 Ar*H*), 6.56 (m, 4 Ar*H*), 5.17 (d, 1 CH$_2$), 4.97 (d, 1 CH$_2$), 4.51 (d, 1 CH$_2$), 4.24 (d, 1 CH$_2$), 1.56 (br s, 3 py*Me*), 1.40 (s, 3 py*Me*), 0.37 (m, 1 CH$_2$C*H*Me$_2$), 0.129 (d, 3 CH$_2$-CH*Me*Me), −0.12 (dd, 1 CH*H*CHMe$_2$), −0.45 (br d, 3 CH$_2$-CHMe*Me*), −1.01 (br m, 1 C*H*HCHMe$_2$); $^{19}$F NMR $\delta$ −132.71 (d, *o*-Ar*F*), −163.97 (t, *p*-Ar*F*), −166.81 (t, *m*-Ar*F*).

**{[MepyN]Hf(CH$_2$CH(CH$_3$)$_2$)}{A}.** This species was observed spectroscopically by mixing equimolar amounts of [MepyN]Hf(CH$_2$CH(CH$_3$)$_2$)$_2$ and B($C_6F_5$)$_3$, {Ph$_3$C}{B($C_6F_5$)$_4$}, or {HNMe$_2$Ph}{B($C_6F_5$)$_4$} in bromobenzene-$d_5$ at room temperature. The $^1$H NMR (20 °C) shifts for the cation formed by activation with B($C_6F_5$)$_3$ are as follows: $\delta$ 8.13 (d, 1 Ar*H*), 7.89 (d, 1 Ar*H*), 7.67 (d, 1 Ar*H*), 7.56 (d, 1 Ar*H*), 7.47 (t, 1 Ar*H*), 7.35 (m, 2 Ar*H*), 7.15 (m, 5 Ar*H*), 7.03 (m, 3 Ar*H*), 6.81 (d, 1 Ar*H*), 6.75 (d, 1 Ar*H*), 6.38 (d, 1 Ar*H*), 5.61 (d, 1 C*H*$_2$), 5.20 (d, 1 C*H*$_2$), 4.93 (d, 1 C*H*$_2$), 4.58 (d, 1 C*H*$_2$), 1.71 (s, 3 py*Me*), 1.57 (s, 3 py*Me*), 0.39 (m, 1 CH$_2$C*H*CMe$_2$), 0.10 (d, 3 CH$_2$CH*Me*Me), −0.21 (dd, 1 C*H*HCHMe$_2$), −0.53 (d, 3 CH$_2$CHMe*Me*), −1.23 (dd, 1 CH*H*CHMe$_2$).

**{[MepyNNH]Zr(CH$_2$C$_6$H$_5$)$_2$}{B(C$_6$F$_5$)$_4$}.** This species has been observed spectroscopically by mixing equimolar amounts of [MepyN]Zr(CH$_2$C$_6$H$_5$)$_2$ and {HNMe$_2$Ph}{B($C_6F_5$)$_4$} in methylene chloride-$d_2$ at −25 °C followed by warming to room temperature. $^1$H NMR (20 °C): $\delta$ 8.30 (d, 1 Ar*H*), 8.11 (t, 1 Ar*H*), 8.07 (d, 1 Ar*H*), 7.72 (d, 1 Ar*H*), 7.68 (d, 1 Ar*H*), 7.60 (app t, 3 Ar*H*), 7.56 (t, 1 Ar*H*), 7.51 (t, 1 Ar*H*), 7.42 (d, 1 Ar*H*), 7.34 (d, 1 Ar*H*), 7.28 (m, 3 Ar*H*), 7.23 (m, 2 Ar*H*), 7.18 (d, 1 Ar*H*), 7.05 (d, 1 Ar*H*), 6.73 (m, 4 Ar*H*), 6.23 (t, 1 CH$_2$*Ph*), 5.93 (t, 2 CH$_2$*Ph*), 5.63 (d, N*H*, $^3J_{H-H}$ = 7.5 Hz), 5.03 (d, 1 C*H*$_2$), 4.74 (d, 2 CH$_2$*Ph*), 4.21 (d, 1 C*H*$_2$), 4.14 (d, 1 C*H*$_2$), 3.44 (s, 3 py*Me*), 3.11 (d, 1 C*H*$_2$Ph), 2.98 (s, 3 py*Me*), 2.79 (dd, C*H*$_2$), 2.71 (d, 1 C*H*$_2$Ph), 2.51 (d, 1 C*H*$_2$Ph), 1.41 (d, 1 C*H*$_2$Ph); $^{19}$F NMR $\delta$ −131.36 (d, *o*-Ar*F*), −161.90 (t, *p*-Ar*F*), −165.75 (t, *m*-Ar*F*).

**{[MepyN]Zr(CH$_2$C$_6$H$_5$)}{A}.** This species was observed spectroscopically by mixing equimolar amounts of [MepyN]-Zr(CH$_2$C$_6$H$_5$)$_2$ and {Ph$_3$C}{B($C_6F_5$)$_4$} or B($C_6F_5$)$_3$ in methylene chloride-$d_2$ at −25 °C followed by warming to room temperature. The $^1$H NMR (−70 °C) shifts for the complex formed by activation with B($C_6F_5$)$_3$ are as follows: $\delta$ 8.44 (d, 1 Ar*H*), 7.95 (m, 3 Ar*H*), 7.70 (m, 6 Ar*H*), 7.41 (d, 1 Ar*H*), 7.24 (m, 6 Ar*H*), 7.12 (t, 1 Ar*H*), 6.89 (t, 2 *m*-Ar*H* of anion), 6.82 (t, *p*-Ar*H* of anion), 6.66 (d, 2 *o*-Ar*H* of anion), 6.32 (m, *m*/*p*-PhCH$_2$), 5.75 (d, 1 C*H*$_2$), 5.66 (d, 1 C*H*$_2$), 5.46 (d, *o*-PhCH$_2$), 5.33 (d, 1 C*H*$_2$), 5.03 (d, 1 C*H*$_2$), 2.73 (s, C*H*$_2$ of anion), 1.81 (s, 3 py*Me*), 1.73 (s, 3 py*Me*), 1.44 (d, C*H*HPh, $^2J_{H-H}$ = 12.5 Hz), −0.56 (d, CH*H*Ph).

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**Supporting Information Available:** Experimental details, labeled thermal ellipsoid drawings, crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for [MepyN]-Zr(CH$_2$Ph)$_2$, [MepyN]Zr(NMe$_2$)Cl, [MepyN]Hf(CH$_2$CHMe$_2$)$_2$, and [MepyN]Hf(OSO$_2$CF$_3$)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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