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Synthesis of Titanium, Zirconium, and Hafnium Complexes That Contain the $[(MesitylN\text{-}o\text{-}C_6H_4)_2O]^{2-}$ Ligand

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$(MesitylNH\text{-}o\text{-}C_6H_4)_2O$ (H_2[MesNON]) has been synthesized in ∼70% yield, and several $[MesNON]^{2-}$ complexes of Ti, Zr, and Hf have been prepared, in particular a variety of dialkyl complexes, $[MesNON]MR_2$ (M = Zr, R = Me, CH_2CMe_3, Ph; M = Hf, R = Me, Et, CH_2CHMe_2, CH_2CMe_3, Ph). $[MesNON]ZrMe_2$ can be activated with $[Ph_3C][B(C_6F_5)_4]$ or $[PhNMe_2H][B(C_6F_5)_4]$, but the resulting cationic species will only oligomerize 1-hexene. We conclude that the sterically bulky *tert*-butyl groups in $[(R'N\text{-}o\text{-}C_6H_4)_2O]^{2-}$ systems are necessary for the success of $[R'NON]^{2-}$ Zr catalyst systems for the living polymerization of 1-hexene.

Introduction

We have been exploring the use of diamido donor ligands for the preparation of early transition metal complexes, in particular cationic group 4 metal complexes that might serve as catalysts for the polymerization of α olefins.[1−13] The first parent diamine of a ligand in this general category that we prepared was $(t\text{-}BuNHC_6H_4)_2O$.[1,6,11] The $[(t\text{-}BuNC_6H_4)_2O]^{2-}$ ($[t\text{-}BuNON]^{2-}$) ligand was placed on Ti, Zr, and Hf, and several dialkyl complexes were prepared. Zirconium dimethyl complexes activated with $[Ph_3C][B(C_6F_5)_4]$ or $[PhNMe_2H][B(C_6F_5)_4]$ were shown to be living catalysts for the polymerization of 1-hexene in chlorobenzene or bromobenzene at 0 °C.[1,6,11] However, simple variations of the $[t\text{-}BuNON]^{2-}$ ligand, namely, $[(CyclohexylNC_6H_4)_2O]^{2-}$,[12] $[(i\text{-}PrNC_6H_4)_2O]^{2-}$,[12] or $[(Me_3SiNC_6H_4)_2O]^{2-}$,[13] were shown to lead to poor Zr-based catalysts for the polymerization of 1-hexene by comparison with the $[t\text{-}BuNON]^{2-}$ zirconium system. Zirconium dialkyl complexes that contain $[i\text{-}PrNON]^{2-}$ or $[CyNON]^{2-}$ ligands gave monomethyl cations that were capable of reacting with 1-hexene, but 1-hexene was oligomerized, rather than polymerized. In contrast, zirconium dialkyl complexes that contain the $[TMSNON]^{2-}$ ligand were found to be relatively unstable, and any significant chemistry, especially well-behaved polymerization activity, was thwarted by CH activation reactions (inter alia). Ligands that contain a saturated two-carbon backbone and 2,6-disubstituted (or 2,4,6-trisubstituted) aryl groups on the amido nitrogen atoms such as $[(ArylNCH_2CH_2)_2O]^{2-}$ [2,3] or $[(MesitylNCH_2CH_2)_2NR]^{2-}$ (R = H or Me)[9] have also been used successfully to prepare polymerization catalysts, although no example as yet has produced poly(1-hexene) with the low polydispersity found for that produced by the $[t\text{-}BuNON]^{2-}$ catalysts. Therefore we became curious as to whether some H_2[ArylNON] diamine could be prepared, and if so, how complexes that contain the $[ArylNON]^{2-}$ ligand would compare with those that contain $[t\text{-}BuNON]^{2-}$ or $[(ArylNCH_2CH_2)_2O]^{2-}$ ligands in terms of the controlled polymerization of 1-hexene. In this contribution we report the synthesis of $(MesitylNHC_6H_4)_2O$ and zirconium and hafnium dialkyl complexes that contain the $[MesNON]^{2-}$ ligand.

Results

H_2[MesNON] can be synthesized in ∼70% yield by the palladium-catalyzed C−N bond-forming reaction between $O(o\text{-}C_6H_4NH_2)_2$[14] and 2 equiv of mesityl bromide under conditions similar to those reported by Buchwald and co-workers.[15,16] The reaction requires more vigorous conditions (6 days in toluene at 95 °C) than the reaction between mesityl bromide and diethylenetriamine, for example.[9] The product was isolated in 66% yield (∼7 g) after purification by passage through alumina.

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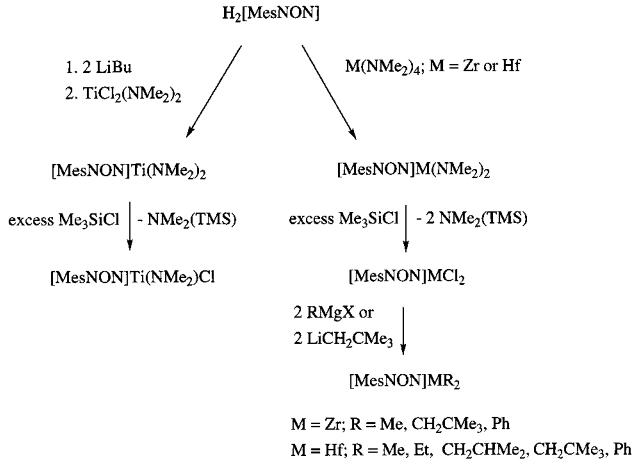
Scheme 1



A suitable entry into titanium chemistry employs $TiCl_2(NMe_2)_2$. Addition of 2 equiv of butyllithium to $H_2[MesNON]$ in diethyl ether followed by addition of $TiCl_2(NMe_2)_2$ led to dark red $[MesNON]Ti(NMe_2)_2$ in good yield (Scheme 1). Proton NMR data for $[MesNON]Ti(NMe_2)_2$ are consistent with a structure that has two planes of symmetry, and the methyl groups in the dimethylamide ligands are equivalent, as is usually the case in dimethylamido complexes in general. Upon heating $[MesNON]Ti(NMe_2)_2$ with excess Me_3SiCl in toluene at 110 °C for 6 days, red, crystalline $[MesNON]TiCl(NMe_2)$ was formed essentially quantitatively. Heating such mixtures to higher temperatures did not appear to yield $[MesNON]TiCl_2$ cleanly. Attempts to synthesize $[MesNON]TiCl_2$ by treating $TiCl_2(NMe_2)_2$ with $H_2[MesNON]$ gave a 1:1 mixture of $H_2[MesNON]$ and $[MesNON]TiCl(NMe_2)$, according to ^1H NMR spectra, while attempts to react $[MesNON]Ti(NMe_2)_2$ with 2 equiv of ethereal HCl led to formation of substantial amounts of $H_2[MesNON]$. The ^1H NMR spectrum of $[MesNON]TiCl(NMe_2)$ exhibits three singlet resonances at 2.37, 2.15, and 1.98 ppm for the mesityl methyl groups and one singlet resonance at 2.58 ppm for the dimethylamide ligand. It is likely that $[MesNON]TiCl(NMe_2)$ contains only one mirror plane, which bisects the $[MesNON]^{2-}$ ligand, and that the mesityl rings in $[MesNON]^{2-}$ do not rotate readily on the NMR time scale, thereby giving rise to inequivalent ortho methyl groups.

The reaction between $H_2[MesNON]$ and $Zr(NMe_2)_4$ in diethyl ether at room temperature gave colorless $[MesNON]Zr(NMe_2)_2$ in quantitative yield. Subsequent reaction of $[MesNON]Zr(NMe_2)_2$ with an excess (∼3 to 4 equiv) of Me_3SiCl in toluene at room temperature gave $[MesNON]ZrCl_2$ in high yield. Analogous hafnium complexes, $[MesNON]Hf(NMe_2)_2$ and $[MesNON]HfCl_2$, were synthesized similarly in two steps in ∼70% overall yield (Scheme 1).

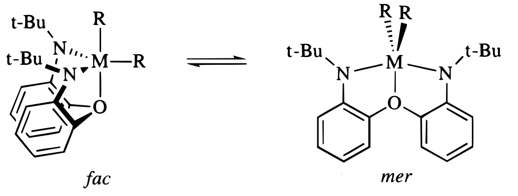
Alkylation of $[MesNON]MCl_2$ (M = Zr of Hf) complexes with magnesium or lithium reagents in diethyl ether or toluene gave the corresponding dialkyl or diphenyl complexes, $[MesNON]MR_2$ (M = Zr, R = Me, CH_2CMe_3, Ph; M = Hf, R = Me, Et, CH_2CHMe_2, CH_2CMe_3, Ph) in 79−95% yields (Scheme 1). Neopentyllithium was employed to prepare neopentyl derivatives; in all other cases Grignard reagents were employed. Variable-temperature ^1H NMR spectra (500 MHz) of $[MesNON]ZrMe_2$ reveal only one sharp singlet resonance for the two methyl ligands at temperatures between −80 and 90 °C and one singlet resonance for ortho mesityl methyl groups. The ^{13}C NMR spectra of $[MesNON]ZrPh_2$ and $[MesNON]HfPh_2$ suggest that the two phenyl ligands are equivalent on the NMR time scale. All other proton and carbon NMR spectra at room temperature were consistent with the presence of a mirror plane on the NMR time scale. The stability of the ethyl and isobutyl complexes toward β abstraction is not surprising, as there are now several examples of diamido donor dialkyl complexes of Zr or (especially) Hf in this category.[11,12]

Table 1. Crystal Data and Structure Refinement for $[MesNON]Hf(CH_2CMe_3)_2$[a]

empirical formula	$C_{40}H_{52}HfN_2O$
fw	755.33
cryst syst	monoclinic
space group	$P2_1/c$
a (Å)	9.82720(10)
b (Å)	20.25430(10)
c (Å)	18.5991(3)
α (deg)	90.0180(10)
β (deg)	100.7380(10)
γ (deg)	90.0000(10)
volume (Å^3)	3637.20(7)
Z	4
density (calcd; Mg/m^3)	1.379
abs coeff (mm^{-1})	2.899
F(000)	1544
crystal size (mm)	0.2 × 0.2 × 0.2
θ range for data collection	1.50−23.26
limiting indices	$-9 \le h \le 10$
	$-18 \le k \le 21$
	$-20 \le l \le 10$
no. of reflns collected	11 381
no. of ind reflns	4935
abs corr	none
no. of data/restraints/params	4931/0/417
goodness-of-fit on F^2	1.276
final R indices [$I > 2\sigma(I)$][b]	R1 = 0.0477, wR2 = 0.0912
R indices (all data)[b]	R1 = 0.0570, wR2 = 0.0970
extinction coeff	0.00069(11)
largest diff peak and hole (e Å^{-3})	0.588 and −1.046

[a] Data were collected at 181(2) K using Mo Kα radiation (0.71073 Å) and refined by full-matrix least-squares on F^2. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)]^{1/2}$.

A single crystal of $[MesNON]Hf(CH_2CMe_3)_2$ was grown from a saturated solution of diethyl ether, benzene, and pentane at −30 °C. An X-ray study (Table 1) shows $[MesNON]Hf(CH_2CMe_3)_2$ to have a structure that is close to a square pyramid with C(1) in the apical position (Figure 1; Table 2), which is approximately halfway between the two "ideal" structures for complexes of this type, the *fac* and *mer* forms as shown in eq 1. The best measure of the core structure is the angle between the O−Hf−N(1) and O−Hf−N(2) planes (145.6°); other angles at the metal are listed in Table 2. For comparison, the corresponding angle in $[t\text{-}BuNON]ZrMe_2$, which has the *fac* structure, is 124°, while in $[(2,6\text{-}i\text{-}Pr_2C_6H_3NCH_2CH_2)_2O]HfEt_2$, the molecule that



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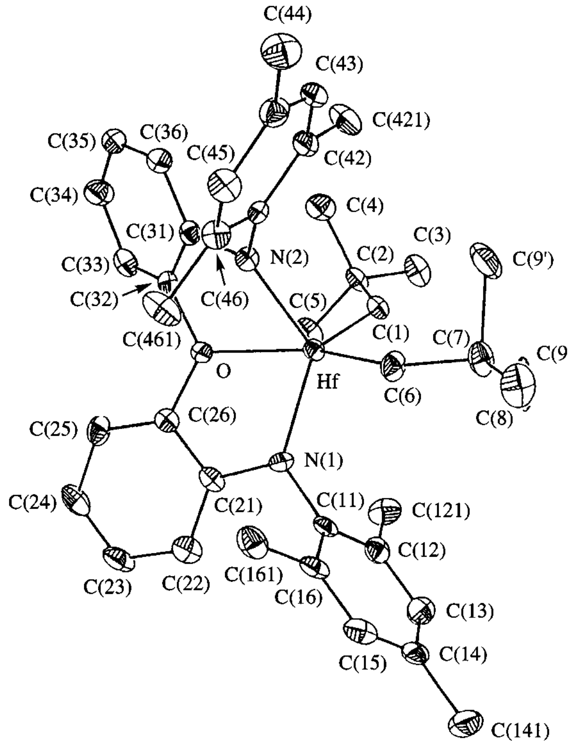

Figure 1. Labeled ORTEP drawing of [MesNON]Hf(CH_2CMe_3)$_2$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in [MesNON]Hf(CH_2CMe_3)$_2$

Bond Lengths			
Hf−N(1)	2.114(6)	Hf−C(1)	2.210(7)
Hf−N(2)	2.093(6)	Hf−C(6)	2.225(7)
Hf−O	2.332(5)		
Bond Angles			
C(1)−Hf−C(6)	107.4(3)	N(1)−Hf−N(2)	127.7(2)
C(1)−Hf−N(1)	110.4(3)	N(1)−Hf−O	69.5(2)
C(1)−Hf−N(2)	107.0(3)	O−Hf−N(2)	70.5(2)
C(1)−Hf−O	97.5(2)	Hf−N(1)−C(11)	122.0(5)
C(6)−Hf−N(1)	101.2(3)	Hf−N(2)−C(41)	125.0(4)
C(6)−Hf−N(2)	101.0(3)	Hf−C(1)−C(2)	133.0(5)
C(6)−Hf−O	155.1(3)	Hf−C(6)−C(7)	132.5(6)
Dihedral Angles			
N(2)/O/Hf/N(1)	145.5	Hf/N(1)/C(11)/C(16)	90.0
C(1)/O/Hf/C(6)	179.0	Hf/N(2)/C(41)/C(42)	89.5

structurally most resembles [MesNON]Hf(CH_2CMe_3)$_2$, it is 160°.[3,8] In a *mer* structure, e.g., [i-PrNON]Zr(CH_2CHMe_2)$_2$,[12] the angle between the planes is 180°. The neopentyl ligands in [MesNON]Hf(CH_2CMe_3)$_2$ are turned so that C(7) points away from N(1) and N(2), while C(2) points away from the *tert*-butyl group containing C(7). In this sense the structure is similar to that of [i-PrNON]Zr(CH_2CHMe_2)$_2$.[12] The two amido nitrogens are sp^2-hybridized, as evidenced by the sum of the angles around them (N(1) = 359.6° and N(2) = 359.8°). The mesityl rings lie perpendicular to the plane of the *o*-phenylene backbone with Hf−N(1)−C(11)−C(16) and Hf−N(2)−C(41)−C(42) dihedral angles of 90.7° and 89.5°, respectively. The Hf−O, Hf−N_{amide}, and Hf−C_α bond distances in [(MesNON]Hf(CH_2CMe_3)$_2$ are all within ~0.02 Å of those in [(2,6-i-$Pr_2C_6H_3NCH_2CH_2$)$_2$O]-HfEt$_2$.[3]

[MesNON]ZrMe$_2$ reacts with [Ph_3C][$B(C_6F_5)_4$] or [$HNMe_2Ph$][$B(C_6F_5)_4$] in C_6D_5Br at 0 °C to yield what we presume are cationic species. These species consume 1-hexene readily. For instance, addition of 60 equiv of 1-hexene to [Ph_3C][$B(C_6F_5)_4$] activated [MesNON]ZrMe$_2$ in C_6D_5Br at 0 °C leads to a complete consumption of 1-hexene in 10 min. However, relatively intense olefinic resonances are observed near 4.9 and 5.5 ppm that can be ascribed to olefinic resonances in β elimination products (Figure 2) on the basis of studies involving propylene end groups in relatively inefficient propylene polymerization catalysts.[17,18] We tentatively ascribe the resonances near 4.9 ppm to 1,1-disubstituted olefins that result from β elimination in a 1,2 insertion product and resonances near 5.5 ppm to internal olefins that result from β elimination in a 2,1 insertion product. The ratio of the olefinic proton resonances suggests that approximately 80% arises from β elimination in a 2,1 insertion product. On the basis of the relative intensity of the aliphatic resonances in the region between 1 and 2 ppm, only ~10 equiv on the average of 1-hexene are present in an oligomeric chain. It should be noted that virtually identical behavior is observed for [CyNON]ZrMe$_2$ activated by [Ph_3C][$B(C_6F_5)_4$] (Figure 2). Similar results are observed for [MesNON]ZrMe$_2$ activated by [$HNMe_2Ph$][$B(C_6F_5)_4$], although the rate of oligomerization is noticeably slower than when [Ph_3C][$B(C_6F_5)_4$] is employed as the activating agent. Although more

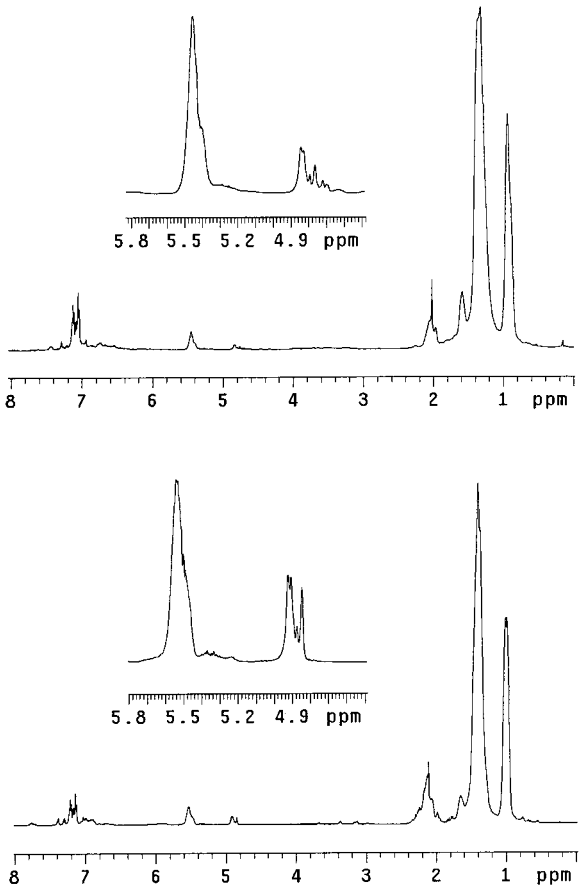

Figure 2. Proton NMR spectra (500 MHz) of the product of the reactions between 1-hexene (60 equiv) and [Ph_3C][$B(C_6F_5)_4$]-activated [CyNON]ZrMe$_2$ (top) or [MesNON]ZrMe$_2$ (bottom) in C_6D_5Br at 0 °C.

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detailed studies will be required in order to positively identify these proposed olefinic products of β elimination, it is clear that activated [CyNON]ZrMe$_2$ and [MesNON]ZrMe$_2$ systems behave similarly and that neither is an efficient 1-hexene polymerization catalyst.

Discussion

Steric crowding in [R′NON]MR$_2$ complexes has been employed in a qualitative sense as some measure of the extent of steric crowding that will develop in {[R′NON]MR}$^+$ species, especially when R is the growing chain that results from polymerization of 1-hexene. [t-BuNON]MR$_2$ species are the only [R′NON]$^{2-}$ species that have a *fac* structure, and the [t-BuNON]$^{2-}$ system is the only one that yields a catalyst for the living polymerization of 1-hexene at 0 °C.[6,11] Steric crowding in pseudotetrahedral {[R′NON]MR}$^+$ is proposed to encourage the insertion of 1-hexene into the M−R bond in a 1,2 manner and to limit the extent to which β hydride elimination can take place from a 1,2 insertion product so formed. Too little steric crowding, i.e., a more “open” and distorted tetrahedral structure, is believed to allow 2,1 insertion to take place and therefore to lead to more facile β elimination. “Smaller” R′ groups (i-Pr, cyclohexyl) apparently simply are not bulky enough to lead to formation of crowded pseudotetrahedral {[R′NON]MR}$^+$ species. It is now clear that mesityl is in the same class as isopropyl and cyclohexyl in [R′NON]$^{2-}$ systems and that any electronic difference between an aryl-substituted [R′NON]$^{2-}$ system and an alkyl-substituted [R′NON]$^{2-}$ system is overshadowed by steric considerations. Only when R′ = t-Bu can a sufficiently crowded pseudotetrahedral structure for {[R′NON]MR}$^+$ be maintained.

The premise that a pseudotetrahedral structure alone is responsible for limiting 2,1 “misinsertions” and facile β elimination is being tested in two ways. One approach is to link the two arms in a [(ArylNCH$_2$CH$_2$)$_2$O]$^{2-}$ ligand system through the two carbon atoms α to the oxygen donor.[10] The oxygen donor now cannot invert and pseudotetrahedral {[R′NON]MR}$^+$ structures are more naturally formed. A second method is to employ a donor that cannot invert when bound to the metal, in particular an amine nitrogen donor.[9] (Diamido donor ligands that contain a central sulfur donor clearly do not invert as readily as those that contain an oxygen donor, but so far controlled polymerization activity with compounds that contain sulfur donor ligands has been disappointing.[8]) A third approach in which the amido substituents are linked to one another is synthetically relatively difficult and in at least one case has been shown to fail.[13] Complexes in which the ligand contains a nitrogen donor are currently showing the most promise, and research therefore is being aimed in that direction.[9,19]

Experimental Section

General Procedures. Unless otherwise specified, all experiments were performed under dinitrogen in a Vacuum Atmospheres glovebox or by using standard Schlenk techniques. All solvents were reagent grade or better. Toluene was distilled from sodium/benzophenone ketyl. Diethyl ether was sparged with nitrogen and passed through two columns of activated alumina. Pentane was sparged with nitrogen, then passed through one column of activated alumina and then through another of activated Q5.[20] All NMR solvents were sparged with nitrogen and dried over activated 4 Å molecular sieves for several days prior to use.

Chemical shifts (δ) are listed as parts per million and coupling constants in hertz. (Routine coupling constants are not listed.) ^{1}H NMR spectra are referenced using the residual solvent peak at δ 7.16 for C$_6$D$_6$, δ 7.29 for C$_6$D$_5$Br (the most upfield resonance), δ 7.27 for CDCl$_3$, and δ 2.09 for toluene-d_8 (the most downfield resonance). ^{13}C NMR spectra are referenced using the residual solvent peak at δ 128.39 for C$_6$D$_6$, δ 77.23 for CDCl$_3$, and δ 137.86 for toluene-d_8 (the most downfield resonance). All NMR spectra were recorded at room temperature unless noted otherwise. Elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

Starting materials (O(o-C$_6$H$_4$NH$_2$)$_2$,[14] TiCl$_2$(NMe$_2$)$_2$,[21] Zr(NMe$_2$)$_4$,[22] Hf(NMe$_2$)$_4$,[23] NpLi,[24] and NpMgCl[25] were prepared as reported in the literature. PhMe$_2$CCH$_2$MgCl was prepared in a manner similar to the preparation of NpMgCl. Zinc dust (97.5%) was activated with 5% aqueous HCl prior to use.[26] HfCl$_4$ (99%, <0.2% Zr) was purchased from Cerac; other metal halides were purchased from Strem. [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] and [Ph$_3$C][B(C$_6$F$_5$)$_4$] were gifts from the Exxon Chemical Corporation. All other chemicals were purchased from commercial suppliers. Pyridine and lutidines were sparged with nitrogen and dried over activated 4 Å molecular sieves prior to use. Mesityl bromide was sparged with nitrogen prior to use. 1-Hexene was refluxed over sodium for 4 days and distilled. All other chemicals were used as received.

H$_2$[MesNON]. A 250 mL Schlenk flask was charged with O(o-C$_6$H$_4$NH$_2$)$_2$ (5.00 g, 25.0 mmol), mesityl bromide (9.94 g, 49.9 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.114 g, 0.125 mmol), rac-BINAP (0.233 g, 0.375 mmol), NaO-t-Bu (6.72 g, 69.9 mmol), and toluene (100 mL). The reaction mixture was stirred with a magnetic stirrer and stir bar at 95 °C for 6 days. All volatile components were removed in vacuo at ∼40 °C, and the resulting dark brown solid residue was dissolved in a mixture of diethyl ether (400 mL) and water (300 mL). The two layers were separated, and the diethyl ether layer was washed with water (3 × 300 mL) and saturated aqueous NaCl solution (300 mL) and dried over MgSO$_4$. The MgSO$_4$ was removed by filtration, and the filtrate was concentrated on a rotary evaporator until the volume was ∼10 mL. The concentrated solution was loaded onto an alumina column (2.5 cm inner diameter × 27 cm height), and the product was eluted with diethyl ether. The first 500 mL of eluent was collected, and the solvent was removed in vacuo to give a pale yellow solid; yield 7.19 g (66%): ^{1}H NMR (C$_6$D$_6$) δ 7.04 (d, 2, Aryl), 6.83 (t, 2, Aryl), 6.80 (s, 4, Aryl), 6.62 (t, 2, Aryl), 6.41 (d, 2, Aryl), 5.69 (s, 2, NH), 2.17 (s, 6, Me$_p$), 2.09 (s, 12, Me$_o$); ^{1}H NMR (CDCl$_3$) δ 6.98 (d, 2, Aryl), 6.95 (s, 4, Aryl), 6.89 (t, 2, Aryl), 6.68 (t, 2, Aryl), 6.27 (d, 2, Aryl), 5.71 (s, 2, NH), 2.32 (s, 6, Me$_p$), 2.16 (s, 12, Me$_o$); ^{13}C NMR (C$_6$D$_6$) δ 144.72 (C$_{Ar}$), 139.05 (C$_{Ar}$), 136.79 (C$_{Ar}$), 136.03 (C$_{Ar}$), 135.94 (C$_{Ar}$), 130.01 (C$_{Ar}$H), 125.28 (C$_{Ar}$H), 119.25 (C$_{Ar}$H), 118.36 (C$_{Ar}$H), 112.99 (C$_{Ar}$H), 21.42 (Me$_p$), 18.58 (Me$_o$); HRMS (EI, 70 eV) calcd for C$_{30}$H$_{32}$N$_2$O 436.25146, found 436.25091.

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[MesNON]Ti(NMe$_2$)$_2$. Butyllithium (0.92 mL, 2.5 M in hexane, 2.3 mmol) was added to a diethyl ether solution (12 mL) of H_2[MesNON] (500 mg, 1.15 mmol) at −30 °C. The solution was stirred at room temperature for 1.5 h and cooled to −30 °C. Solid $TiCl_2(NMe_2)_2$ (237 mg, 1.15 mmol) was added. The reaction mixture was stirred at room temperature overnight (∼14 h). Insoluble materials were removed by filtration through Celite and washed with diethyl ether (5 mL). The filtrate was concentrated in vacuo until the volume was ∼2 mL. Pentane (∼1 mL) was layered on top, and the mixture was cooled to −30 °C to give a dark red needlelike crystalline solid. The supernatant was decanted, and the solid was dried in vacuo; yield 475 mg (73%): ^{1}H NMR (C_6D_6) δ 7.63 (d, 2, Aryl), 6.87 (s, 4, Aryl), 6.86 (t, 2, Aryl), 6.60 (t, 2, Aryl), 6.22 (d, 2, Aryl), 2.77 (s, 12, TiNMe$_2$), 2.20 (s, 6, Me$_p$), 2.16 (s, 12, Me$_o$); ^{13}C NMR (C_6D_6) δ 148.61 (C$_{Ar}$), 147.28 (C$_{Ar}$), 147.14 (C$_{Ar}$), 134.13 (C$_{Ar}$), 133.63 (C$_{Ar}$), 129.68 (C$_{Ar}$H), 126.08 (C$_{Ar}$H), 116.62 (C$_{Ar}$H), 116.24 (C$_{Ar}$H, 113.68 (C$_{Ar}$H), 45.56 (NMe$_2$), 21.31 (Me$_p$), 19.67 (Me$_o$). Anal. Calcd for $C_{34}H_{42}N_4OTi$: C, 71.57; H, 7.42; N; 9.82. Found: C, 71.69; H, 7.48; N, 9.71.

[MesNON]TiCl(NMe$_2$). A toluene solution (5 mL) of [MesNON]Ti(NMe$_2$)$_2$ (104 mg, 0.182 mmol) and Me_3SiCl (0.07 mL, 0.552 mmol) was heated to 105 °C for 6 days in a Teflon-sealed Schlenk tube. All volatile materials were removed in vacuo at ∼40 °C to give a deep red solid, which is pure [MesNON]TiCl(NMe$_2$), according to its ^{1}H NMR spectrum. The solid was recrystallized from a concentrated diethyl ether solution at −30 °C to give blood red crystals; yield 102 mg (100%): ^{1}H NMR (C_6D_6) δ 7.53 (d, 2, Aryl), 6.83 (s, 2, Aryl), 6.79 (t, 2, Aryl), 6.76 (s, 2, Aryl), 6.56 (t, 2, Aryl), 6.02 (d, 2, Aryl), 2.58 (s, 6, TiNMe$_2$), 2.37 (s, 6, Me$_p$), 2.15 (s, 6, Me$_o$), 1.98 (s, 6, Me$_o$); ^{13}C NMR (C_6D_6) δ 149.15 (C$_{Ar}$), 148.17 (C$_{Ar}$), 146.67 (C$_{Ar}$), 135.04 (C$_{Ar}$), 134.70 (C$_{Ar}$), 131.98 (C$_{Ar}$), 130.10 (C$_{Ar}$H), 129.66 (C$_{Ar}$H), 126.23 (C$_{Ar}$H), 118.37 (C$_{Ar}$H), 117.09 (C$_{Ar}$H), 112.30 (C$_{Ar}$H), 46.09 (NMe$_2$), 21.24 (Me$_p$), 19.54 (Me$_o$), 18.81 (Me$_o$). Anal. Calcd for $C_{32}H_{36}ClN_3OTi$: C, 68.39; H, 6.46; N; 7.48. Found: C, 68.48; H, 6.35; N, 7.39.

[MesNON]Zr(NMe$_2$)$_2$. Diethyl ether (10 mL) was added to a solid mixture of H_2[MesNON] (1.03 g, 2.36 mmol) and $Zr(NMe_2)_4$ (0.632 g, 2.36 mmol) at room temperature. The solution was stirred at room temperature overnight (∼13 h). All volatile components were removed in vacuo to give a pale yellow solid, which was pure [MesNON]Zr(NMe$_2$)$_2$, according to its ^{1}H NMR spectrum. Colorless crystals were obtained from a concentrated diethyl ether solution at −30 °C. The crystals were collected by filtration and dried in vacuo; yield 1.43 g (98%): ^{1}H NMR (C_6D_6) δ 7.60 (d, 2, Aryl), 6.89 (s, 4, Aryl), 6.86 (t, 2, Aryl), 6.56 (t, 2, Aryl), 6.25 (d, 2, Aryl), 2.57 (s, 12, Me$_o$), 2.20 (s, 18, containing 6H from Me$_p$ and 12H from ZrNMe$_2$); ^{1}H NMR (toluene-d_8) δ 7.56 (d, 2, Aryl), 6.85 (s, 4, Aryl), 6.79 (t, 2, Aryl), 6.52 (t, 2, Aryl), 6.17 (d, 2, Aryl), 2.54 (s, 12, Me$_o$), 2.17 (s, 6, Me$_p$), 2.16 (s, 12, ZrNMe$_2$); ^{13}C NMR (C_6D_6) δ 147.56 (C$_{Ar}$), 146.57 (C$_{Ar}$), 143.40 (C$_{Ar}$), 135.17 (C$_{Ar}$), 134.08 (C$_{Ar}$), 129.97 (C$_{Ar}$H), 126.60 (C$_{Ar}$H), 116.89 (C$_{Ar}$H), 116.12 (C$_{Ar}$H), 114.35 (C$_{Ar}$H), 41.64 (ZrNMe$_2$), 21.36 (Me$_p$), 18.93 (Me$_o$). Anal. Calcd for $C_{34}H_{42}N_4OZr$: C, 66.52; H, 6.90; N, 9.13. Found: C, 66.64; H, 6.82; N, 9.05.

[MesNON]ZrCl$_2$. Neat Me_3SiCl (0.640 mL, 5.07) was added to a toluene solution (20 mL) of [MesNON]Zr(NMe$_2$)$_2$ (1.04 g, 1.69 mmol) at room temperature. The reaction mixture was stirred at room temperature for 24 h. All volatile components were removed in vacuo at ∼40 °C to give a viscous brown oil. Diethyl ether was added dropwise to the oil to initiate crystallization. A crop of yellow crystalline solid (696 mg) was obtained from ∼5 mL of diethyl ether solution at room temperature. A second crop (225 mg) was obtained by cooling the mother liquor to −30 °C; total yield 921 mg (91%). Diethyl ether (∼0.67 equiv per zirconium) was usually found in the crystalline product, according to ^{1}H NMR spectra: ^{1}H NMR (C_6D_6; ether resonaces excluded) δ 7.34 (d, 2, Aryl), 6.81 (s, 4, Aryl), 6.75 (t, 2, Aryl), 6.52 (t, 2, Aryl), 6.06 (d, 2, Aryl), 2.30 (s, 12, Me$_o$), 2.10 (s, 6, Me$_p$); ^{13}C NMR (C_6D_6) δ 148.29 (C$_{Ar}$), 145.91 (C$_{Ar}$), 139.50 (C$_{Ar}$), 137.64 (C$_{Ar}$), 135.68 (C$_{Ar}$), 130.91 (C$_{Ar}$H), 127.22 (C$_{Ar}$H), 119.50 (C$_{Ar}$H), 116.69 (C$_{Ar}$H), 114.12 (C$_{Ar}$H), 21.37 (Me$_p$), 19.10 (Me$_o$). Anal. Calcd for $C_{30}H_{30}Cl_2N_2OZr(ether)_{0.67}$: C, 60.73; H, 5.72; N, 4.33. Found: C, 60.85; H, 5.86; N, 4.27.

[MesNON]ZrMe$_2$. MeMgI (0.10 mL, 3.0 M in diethyl ether, 0.30 mmol) was added to a diethyl ether solution (4 mL) of [MesNON]ZrCl$_2$ (98 mg, 0.15 mmol) at −30 °C. The reaction mixture was stirred at room temperature for 2.5 h, and the solvent was removed in vacuo. The solid residue was extracted with pentane (10 mL). Insoluble materials were removed by filtration through Celite. The colorless filtrate was concentrated in vacuo until the volume was ∼2 mL and was cooled to −30 °C to give colorless crystals. The supernatant was decanted, and the crystals were dried in vacuo; yield 71 mg (85%): ^{1}H NMR (C_6D_6) δ 7.53 (d, 2, Aryl), 6.92 (s, 4, Aryl), 6.82 (t, 2, Aryl), 6.52 (t, 2, Aryl), 6.20 (d, 2, Aryl), 2.27 (s, 12, Me$_o$), 2.16 (s, 6, Me$_p$), 0.58 (s, 6, ZrMe); ^{1}H NMR (toluene-d_8) δ 7.47 (d, 2, Aryl), 6.87 (s, 4, Aryl), 6.77 (t, 2, Aryl), 6.49 (t, 2, Aryl), 6.12 (d, 2, Aryl), 2.23 (s, 12, Me$_o$), 2.14 (s, 6, Me$_p$), 0.49 (s, 6, ZrMe); ^{1}H NMR (toluene-d_8, −80 °C) δ 7.33 (d, 2, Aryl), 6.73 (s, 4, Aryl), 6.70 (t, 2, Aryl), 6.38 (t, 2, Aryl), 6.11 (d, 2, Aryl), 2.20 (s, 12, Me$_o$), 2.00 (s, 6, Me$_p$), 0.58 (s, 6, ZrMe); ^{1}H NMR (toluene-d_8, 90 °C) δ 7.53 (d, 2, Aryl), 6.91 (s, 4, Aryl), 6.79 (t, 2, Aryl), 6.53 (t, 2, Aryl), 6.13 (d, 2, Aryl), 2.25 (s, 12, Me$_o$), 2.17 (s, 6, Me$_p$), 0.45 (s, 6, ZrMe); ^{13}C NMR (C_6D_6) δ 147.03 (C$_{Ar}$), 146.19 (C$_{Ar}$), 138.43 (C$_{Ar}$), 136.87 (C$_{Ar}$), 136.65 (C$_{Ar}$), 130.75 (C$_{Ar}$H), 126.43 (C$_{Ar}$H), 117.31 (C$_{Ar}$H), 115.18 (C$_{Ar}$H), 113.80 (C$_{Ar}$H), 49.85 (ZrMe), 21.42 (Me$_p$), 19.00 (Me$_o$). Anal. Calcd for $C_{32}H_{36}N_2OZr$: C, 69.14; H, 6.53; N; 5.04. Found: C, 69.26; H, 6.37; N, 5.11.

[MesNON]Zr(CH$_2$CMe$_3$)$_2$. A diethyl ether solution (2 mL) of $LiCH_2CMe_3$ (28 mg, 0.36 mmol) at −30 °C was added to a diethyl ether suspension (4 mL) of [MesNON]ZrCl$_2$ (116 mg, 0.179 mmol) at −30 °C. The reaction mixture was stirred at room temperature for 1 h, and the solvent was removed in vacuo. The solid residue was extracted with pentane (10 mL), and insoluble materials were removed by filtration through Celite. The solvent was removed from the filtrate in vacuo to give a pale yellow solid; yield 100 mg (83%): ^{1}H NMR (C_6D_6) δ 7.60 (d, 2, Aryl), 6.91 (s, 4, Aryl), 6.81 (t, 2, Aryl), 6.55 (t, 2, Aryl), 6.23 (d, 2, Aryl), 2.37 (s, 12, Me$_o$), 2.17 (s, 6, Me$_p$), 1.29 (s, 4, C*H*$_2$CMe$_3$), 0.90 (s, 18, CH$_2$C*Me*$_3$); ^{13}C NMR (C_6D_6) δ 147.24 (C$_{Ar}$), 147.11 (C$_{Ar}$), 141.90 (C$_{Ar}$), 136.37 (C$_{Ar}$), 135.99 (C$_{Ar}$), 130.80 (C$_{Ar}$H), 126.47 (C$_{Ar}$H), 117.58 (C$_{Ar}$H), 116.30 (C$_{Ar}$H), 114.43 (C$_{Ar}$H), 96.57 (Zr*C*H$_2$CMe$_3$), 36.99 (ZrCH$_2$*C*Me$_3$), 34.52 (ZrCH$_2$C*Me*$_3$), 21.32 (Me$_p$), 19.64 (Me$_o$).

[MesNON]ZrPh$_2$. PhMgBr (0.10 mL, 3.0 M in diethyl ether, 0.30 mmol) was added to a diethyl ether suspension (4 mL) of [MesNON]ZrCl$_2$(ether)$_{0.67}$ (97.0 mg, 0.150 mmol) at −30 °C. The color of the suspension changed immediately from green to yellow. The reaction mixture was stirred at room temperature for 1.5 h, and 1,4-dioxane (5 drops) was added. Insoluble materials were removed by filtration through Celite, and the filtrate was concentrated in vacuo until the volume was ∼1 mL. The concentrated solution was cooled to −30 °C overnight to give a yellow crystalline solid. The supernatant was decanted, and the product was dried in vacuo; yield 94 mg (92%): ^{1}H NMR (C_6D_6) δ 7.62 (d, 2, Aryl), 7.52 (m, 4, Aryl), 7.00 (m, 6, Aryl), 6.80 (t, 2, Aryl), 6.75 (s, 4, Aryl), 6.61 (t, 2, Aryl), 6.19 (d, 2, Aryl), 2.15 (s, 6, Me$_p$), 2.05 (s, 12, Me$_o$); ^{13}C NMR (C_6D_6) δ 191.70 (ZrC$_{ipso}$), 147.29 (C$_{Ar}$), 147.08 (C$_{Ar}$), 139.72 (C$_{Ar}$), 136.76 (C$_{Ar}$), 136.67 (C$_{Ar}$), 133.94 (C$_{Ar}$H), 130.59 (C$_{Ar}$H), 129.68 (C$_{Ar}$H), 127.37 (C$_{Ar}$H), 126.62 (C$_{Ar}$H), 118.15 (C$_{Ar}$H), 116.17 (C$_{Ar}$H), 114.04 (C$_{Ar}$H), 21.31 (Me$_p$), 19.17 (Me$_o$). Anal. Calcd for $C_{42}H_{40}N_2OZr$: C, 74.18; H, 5.93; N; 4.12. Found: C, 74.08; H, 6.05; N, 4.18.

[MesNON]Hf(NMe$_2$)$_2$ and [MesNON]HfCl$_2$. Diethyl ether (20 mL) was added to a solid mixture of H_2[MesNON] (1.30 g, 2.98 mmol) and $Hf(NMe_2)_4$ (1.06 g, 2.98 mmol) at room temperature. The reaction was monitored by ^{1}H NMR spectroscopy, which showed that [MesNON]Hf(NMe$_2$)$_2$ had been formed quantitatively after 6 h. All volatile components were removed in vacuo to give [MesNON]Hf(NMe$_2$)$_2$ as an off-white solid; yield 2.09 g (100%): ^{1}H NMR (C$_6$D$_6$) δ 7.57 (d, 2, Aryl), 6.90 (s, 4, Aryl), 6.85 (t, 2, Aryl), 6.55 (t, 2, Aryl), 6.26 (d, 2, Aryl), 2.62 (s, 12, HfNMe$_2$), 2.22 (s, 12, Me$_o$), 2.19 (s, 6, Me$_p$).

Neat Me$_3$SiCl (1.40 mL, 11.93 mmol) was added to a toluene solution (5 mL) of [MesNON]Hf(NMe$_2$)$_2$ at room temperature. After 22 h all volatile components were removed in vacuo at ~45 °C, and the off-white solid was washed with pentane (~20 mL) and dried in vacuo; yield 1.45 g (71%): ^{1}H NMR (C$_6$D$_6$) δ 7.28 (d, 2, Aryl), 6.82 (s, 4, Aryl), 6.77 (t, 2, Aryl), 6.47 (t, 2, Aryl), 6.11 (d, 2, Aryl), 2.13 (s, 12, Me$_o$), 2.11 (s, 6, Me$_p$); ^{13}C NMR (C$_6$D$_6$) δ 148.05 (C$_{Ar}$), 145.98 (C$_{Ar}$), 140.41 (C$_{Ar}$), 137.06 (C$_{Ar}$), 135.68 (C$_{Ar}$), 130.82 (C$_{Ar}$H), 127.61 (C$_{Ar}$H), 119.09 (C$_{Ar}$H), 117.05 (C$_{Ar}$H), 115.14 (C$_{Ar}$H), 21.32 (Me$_p$), 19.01 (Me$_o$). Anal. Calcd for C$_{30}$H$_{30}$Cl$_2$HfN$_2$O: C, 52.68; H, 4.42; N; 4.10. Found: C, 52.83; H, 4.50; N, 4.29.

[MesNON]HfMe$_2$. MeMgI (0.10 mL, 3.0 M in diethyl ether, 0.30 mmol) was added to a diethyl ether suspension (8 mL) of [MesNON]HfCl$_2$ (102 mg, 0.149 mmol) at −30 °C. The reaction mixture was stirred at room temperature for 40 min, and 1,4-dioxane (5 drops) was added. Insoluble materials were removed by filtration through Celite. The filtrate was concentrated in vacuo until the volume was ~0.5 mL. The concentrated solution was kept at −30 °C overnight to give a colorless crystalline solid. The supernatant was decanted, and the solid was washed with pentane (1 mL) and dried in vacuo; yield 84 mg (88%): ^{1}H NMR (C$_6$D$_6$) δ 7.50 (d, 2, Aryl), 6.91 (s, 4, Aryl), 6.81 (t, 2, Aryl), 6.50 (t, 2, Aryl), 6.21 (d, 2, Aryl), 2.28 (s, 12, Me$_o$), 2.16 (s, 6, Me$_p$), 0.40 (s, 6, HfMe); ^{13}C NMR (C$_6$D$_6$) δ 147.24 (C$_{Ar}$), 146.73 (C$_{Ar}$), 138.86 (C$_{Ar}$), 136.74 (C$_{Ar}$), 136.34 (C$_{Ar}$), 130.73 (C$_{Ar}$H), 126.74 (C$_{Ar}$H), 117.26 (C$_{Ar}$H), 115.66 (C$_{Ar}$H), 114.67 (C$_{Ar}$H), 60.18 (HfMe), 21.40 (Me$_p$), 18.97 (Me$_o$). Anal. Calcd for C$_{32}$H$_{36}$HfN$_2$O: C, 59.76; H, 5.64; N; 4.36. Found: C, 59.86; H, 5.73; N, 4.26.

[MesNON]HfEt$_2$. EtMgBr (0.1 mL, 3 M in diethyl ether, 0.3 mmol, 2 equiv) was added to a diethyl ether suspension (3 mL) of [MesNON]HfCl$_2$ (103 mg, 0.151 mmol) at −30 °C. The reaction mixture was stirred at room temperature for 1 h, and 1,4-dioxane (5 drops) was added. Insoluble materials were removed by filtration through Celite. The pale yellow filtrate was concentrated in vacuo until the volume was ~1 mL to give a colorless crystalline solid. The solution was cooled to −30 °C for several hours to allow for the completion of crystallization. The supernatant was decanted, and the crystals were dried in vacuo; yield 89 mg (88%): ^{1}H NMR (C$_6$D$_6$) δ 7.50 (d, 2, Aryl), 6.91 (s, 4, Aryl), 6.84 (t, 2, Aryl), 6.51 (t, 2, Aryl), 6.23 (d, 2, Aryl), 2.30 (s, 12, Me$_o$), 2.17 (s, 6, Me$_p$), 1.28 (t, 6, HfCH$_2$C*H*$_3$), 0.77 (q, 4, HfC*H*$_2$CH$_3$); ^{13}C NMR (C$_6$D$_6$) δ 147.15 (C$_{Ar}$), 147.04 (C$_{Ar}$), 139.06 (C$_{Ar}$), 136.71 (C$_{Ar}$), 136.18 (C$_{Ar}$), 130.66 (C$_{Ar}$H), 126.67 (C$_{Ar}$H), 117.34 (C$_{Ar}$H), 116.13 (C$_{Ar}$H), 114.81 (C$_{Ar}$H), 73.34 (Hf*C*H$_2$CH$_3$), 21.36 (Me$_p$), 18.94 (Me$_o$), 12.05 (HfCH$_2$*C*H$_3$). Anal. Calcd for C$_{34}$H$_{40}$HfN$_2$O: C, 60.84; H, 6.01; N; 4.17. Found: C, 60.69; H, 5.92; N, 4.21.

[MesNON]Hf(CH$_2$CHMe$_2$)$_2$. IsobutylMgBr (0.15 mL, 2.0 M in diethyl ether, 0.30 mmol) was added to a diethyl ether suspension (3 mL) of [MesNON]HfCl$_2$ (103 mg, 0.151 mmol) at −30 °C. The reaction mixture was stirred at room temperature for 30 min. The solvent was removed in vacuo, and the solid residue was extracted with pentane (8 mL). The extract was filtered through Celite, and pentane was removed in vacuo to give a colorless oil. The oil was cooled to −30 °C overnight to give a colorless, waxy solid. The solid was washed with pentane (0.5 mL) and dried in vacuo; yield 86 mg (79%): ^{1}H NMR (C$_6$D$_6$) δ 7.55 (d, 2, Aryl), 6.92 (s, 4, Aryl), 6.83 (t, 2, Aryl), 6.52 (t, 2, Aryl), 6.22 (d, 2, Aryl), 2.34 (s, 12, Me$_o$), 2.17 (s, 6, Me$_p$), 2.02 (septet, 2, HfCH$_2$C*H*Me$_2$), 0.82 (d, 4, HfC*H*$_2$CHMe$_2$), 0.81 (d, 12, HfCH$_2$CH*Me*$_2$); ^{13}C NMR (C$_6$D$_6$) δ 147.32 (C$_{Ar}$), 147.15 (C$_{Ar}$), 139.95 (C$_{Ar}$), 136.47 (C$_{Ar}$), 136.22 (C$_{Ar}$), 130.72 (C$_{Ar}$H), 126.75 (C$_{Ar}$H), 117.45 (C$_{Ar}$H), 116.16 (C$_{Ar}$H), 114.98 (C$_{Ar}$H), 94.96 (Hf*C*H$_2$CHMe$_2$), 30.22 (HfCH$_2$*C*HMe$_2$), 29.03 (HfCH$_2$CH*Me*$_2$), 21.32 (Me$_p$), 19.17 (Me$_o$). Anal. Calcd for C$_{38}$H$_{48}$HfN$_2$O: C, 62.75; H, 6.65; N; 3.85. Found: C, 62.84; H, 6.53; N, 3.77.

[MesNON]Hf(CH$_2$CMe$_3$)$_2$. A diethyl ether solution (2 mL) of LiCH$_2$CMe$_3$ (23 mg, 0.30 mmol) at −30 °C was added to a diethyl ether suspension (4 mL) of [MesNON]HfCl$_2$ (100 mg, 0.146 mmol) at −30 °C. The reaction mixture was stirred at room temperature for 80 min, and all insoluble solids were removed by filtration through Celite. The solvent was removed in vacuo to give an off-white solid product; yield 103 mg (93%): ^{1}H NMR (C$_6$D$_6$) δ 7.56 (d, 2, Aryl), 6.92 (s, 4, Aryl), 6.81 (t, 2, Aryl), 6.50 (t, 2, Aryl), 6.22 (d, 2, Aryl), 2.37 (s, 12, Me$_o$), 2.17 (s, 6, Me$_p$), 0.96 (s, 4, HfC*H*$_2$CMe$_3$), 0.93 (s, 18, HfCH$_2$C*Me*$_3$); ^{13}C NMR (C$_6$D$_6$) δ 147.43 (C$_{Ar}$), 147.24 (C$_{Ar}$), 142.39 (C$_{Ar}$), 136.19 (C$_{Ar}$), 136.12 (C$_{Ar}$), 130.77 (C$_{Ar}$H), 126.82 (C$_{Ar}$H), 117.47 (C$_{Ar}$H), 116.40 (C$_{Ar}$H), 115.29 (C$_{Ar}$H), 104.97 (Hf*C*H$_2$CMe$_3$), 37.09 (HfCH$_2$*C*Me$_3$), 35.26 (HfCH$_2$C*Me*$_3$), 21.31 (Me$_p$), 19.61 (Me$_o$). Anal. Calcd for C$_{40}$H$_{52}$HfN$_2$O: C, 63.60; H, 6.94; N, 3.71. Found: C, 63.46; H, 6.84; N, 3.78.

[MesNON]HfPh$_2$. PhMgBr (0.1 mL, 3 M in diethyl ether, 0.3 mmol, 2 equiv) was added to a diethyl ether suspension (4 mL) of [MesNON]HfCl$_2$ (103 mg, 0.151 mmol) at −30 °C. The reaction mixture was stirred at room temperature for 1 h, and 1,4-dioxane (5 drops) was added. Insoluble materials were removed by filtration through Celite. The yellow filtrate was concentrated in vacuo until the volume was ~1 mL. The solution was cooled to −30 °C overnight to give a pale yellow crystalline solid. The supernatant was decanted, and the solid was dried in vacuo; yield 110 mg (95%): ^{1}H NMR (C$_6$D$_6$) δ 7.58 (d, 2, Aryl), 7.52 (d, 4, Aryl), 7.10 (t, 4, Aryl), 6.99 (t, 2, Aryl), 6.81 (t, 2, Aryl), 6.76 (s, 4, Aryl), 6.55 (t, 2, Aryl), 6.20 (d, 2, Aryl), 2.15 (s, 6, Me$_p$), 2.09 (s, 12, Me$_o$); ^{13}C NMR (C$_6$D$_6$) δ 205.28 (HfC$_{ipso}$), 147.47 (C$_{Ar}$), 147.35 (C$_{Ar}$), 139.75 (C$_{Ar}$), 137.00 (C$_{Ar}$), 136.52 (C$_{Ar}$), 136.48 (C$_{Ar}$H), 130.57 (C$_{Ar}$H), 129.61 (C$_{Ar}$H), 127.76 (C$_{Ar}$H), 126.95 (C$_{Ar}$H), 118.08 (C$_{Ar}$H), 116.45 (C$_{Ar}$H), 115.07 (C$_{Ar}$H), 21.29 (Me$_p$), 19.14 (Me$_o$). Anal. Calcd for C$_{42}$H$_{40}$HfN$_2$O: C, 65.75; H, 5.25; N, 3.65. Found: C, 65.55; H, 5.20; N, 3.59.

Reaction between 1-Hexene and [MesNON]ZrMe$_2$ Activated with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]. A C$_6$D$_5$Br solution (0.3 mL) of [MesNON]ZrMe$_2$ (5 mg, 9 μmol) at −30 °C was added to a C$_6$D$_5$Br solution (0.4 mL) of [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (7 mg, 8.7 μmol) at −30 °C. The solution color changed immediately from colorless to light yellow. The reaction mixture was briefly warmed to 20 °C to allow for the dissolution of the anilinium salt and kept at 0 °C. 1-Hexene (60 equiv) was added to the solution at 0 °C. The reaction was monitored by ^{1}H NMR spectroscopy, which showed ~50% consumption of 1-hexene in 4 h.

Reaction between 1-Hexene and [MesNON]ZrMe$_2$ Activated with [Ph$_3$C][B(C$_6$F$_5$)$_4$]. A C$_6$D$_5$Br solution (0.3 mL) of [MesNON]ZrMe$_2$ (10 mg, 18 μmol) at −30 °C was added to a C$_6$D$_5$Br solution (0.4 mL) of [Ph$_3$C][B(C$_6$F$_5$)$_4$] (16 mg, 17 μmol) at −30 °C. The orange solution was kept at 0 °C. 1-Hexene (60 equiv) was added at 0 °C. The reaction was monitored by ^{1}H NMR spectroscopy, which showed complete consumption of 1-hexene in 10 min.

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Supporting Information Available: Fully labeled ORTEP drawings, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for [MesNON]Hf(CH$_2$CMe$_3$)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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