Synthesis of Titanium, Zirconium, and Hafnium Complexes that Contain Diamido Donor Ligands of the Type $[(t\text{-BuN-}o\text{-}C_6H_4)_2O]^{2-}$ and an Evaluation of Activated Versions for the Polymerization of 1-Hexene

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Titanium, zirconium, and hafnium dialkyl complexes that contain the $[(t\text{-Bu-}d_6\text{-N-}o\text{-}C_6H_4)_2O]^{2-}$ ($[t\text{-BuNON}]^{2-}$) ligand have been prepared. Only $[t\text{-BuNON}]TiMe_2$ could be isolated, but $[t\text{-BuNON}]ZrR_2$ and $[t\text{-BuNON}]HfR_2$ complexes could be isolated in which (for example) R = Me, Et, or i-Bu. X-ray studies showed $[t\text{-BuNON}]MMe_2$ structures (M = Ti or Zr) to be of the "twisted *fac*" variety in which two amido nitrogens occupy equatorial positions in a distorted trigonal bipyramid. However, in solution all such species show equivalent alkyl groups on the NMR time scale as a consequence of formation of an intermediate *mer* structure that contains a planar oxygen donor. In analogous complexes that contain the $\{[Me(CD_3)_2CNC_6H_4][Me(CD_3)_2CN\text{-}2,4\text{-}Me_2C_6H_2]O\}^{2-}$ or $\{[Me(CD_3)_2CNC_6H_4][Me(CD_3)_2N\text{-}2\text{-}EtC_6H_3]O\}^{2-}$ ligand the two metal alkyl groups are inequivalent on the NMR time scale. Addition of trimethylphosphine to $[t\text{-BuNON}]Zr(CH_2CH_3)_2$ yields structurally characterized, pseudooctahedral $[t\text{-BuNON}]Zr(\eta^2\text{-}C_2H_4)(PMe_3)_2$. Addition of $B(C_6F_5)_3$ to $[t\text{-BuNON}]ZrMe_2$ yields structurally characterized $\{[t\text{-BuNON}]ZrMe\}[MeB(C_6F_5)_3]$, while addition of $[PhNMe_2H][B(C_6F_5)_4]$ to $[t\text{-BuNON}]ZrMe_2$ in bromobenzene-d_5 generates "$\{[t\text{-BuNON}]ZrMe(PhNMe_2)\}[B(C_6F_5)_4]$", which is an active catalyst for the polymerization of up to 500 equiv of 1-hexene in a living manner at 0 °C. The analogous hafnium systems are not as well behaved, since the dimethylaniline is insufficiently labile. No polymerization activity is observed for activated titanium dialkyl complexes. Polymerization activity is quenched upon addition of THF or dimethoxyethane to the cationic complexes. An X-ray structure of $\{[t\text{-BuNON}]ZrMe(THF)_2\}[B(C_6F_5)_4]$ shows it to be a pseudooctahedral species in which the $[t\text{-BuNON}]^{2-}$ ligand adopts a "twisted *mer*" geometry, while the X-ray structure of $\{[t\text{-BuNON}]ZrMe(MeOCH_2CH_2OMe)\}[B(C_6F_5)_4]$ was found to be of the "twisted *fac*" variety. In the case of hafnium, pseudooctahedral cationic bis-THF or DME complexes can be isolated even when the anion is $[B(C_6H_5)_4]^-$; like all complexes that contain THF or DME they are essentially inactive for polymerization of 1-hexene.

Introduction

For more than forty years[1−4] group 4 metallocene complexes have been targeted as catalysts for the polymerization of ethylene or monosubstituted olefins.[5−8] The active species in such circumstances is now widely regarded to be a metal cation.[9−16] In the last fifteen years research has focused largely on the development of variations, in particular chiral metallocenes for controlling tacticity,[8] anions (e.g., $[B(C_6F_5)_4]^-$)[16,17] that are relatively weakly associated with the metal cation,[14,18−22] alkylalumoxanes (e.g., MAO[23−25]) as alkyl acceptors, and catalysts that contain only one cyclopentadienyl ring.[26−28]

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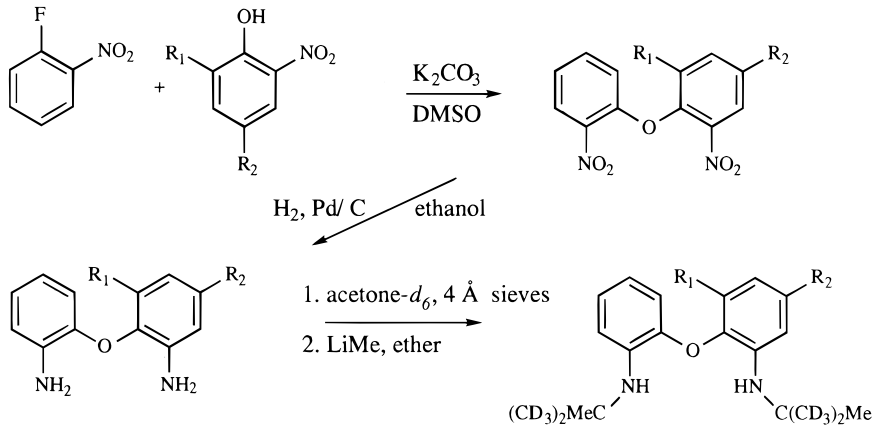
Scheme 1



$R_1 = R_2 = H$; H_2[t-BuNON]
$R_1 = R_2 = Me$; H_2[t-BuNONMe$_2$]
$R_1 = Et$, $R_2 = H$; H_2[t-BuNONEt]

Most recently group 4 metal catalysts that have no cyclopentadienyl ring bound to the metal have been actively sought.[29] One of the most intriguing discoveries was that titanium dialkyl complexes containing propylene-bridged aryl-substituted diamido ligands such as $[ArNCH_2CH_2CH_2NAr]^{2-}$ (Ar = 2,6-$R_2C_6H_3$, R = Me, i-Pr) would promote the living polymerization of essentially neat 1-hexene when activated by $B(C_6F_5)_3$, as long as the concentration of 1-hexene remained high.[30,31] We had been exploring the chemistry of triamidoamine complexes, largely of Mo or W,[32] and considered the possibility of increasing reactivity by employing related *di*amido/donor ligands and in particular the possibility of employing complexes containing such ligands for the polymerization of olefins. That quest was successful, as we reported in a preliminary fashion; zirconium catalysts that contain the $[(t\text{-Bu-}d_6\text{-N-o-}C_6H_4)_2O]^{2-}$ ([t-BuNON]$^{2-}$) ligand were shown to polymerize 1-hexene in a living fashion, even after a given quantity of 1-hexene had been consumed.[33] We have also reported some ^{13}C-labeling studies that support the proposal that the polymerization is a living process and that the olefin inserts into the metal−alkyl bond primarily (>95%) in a 1,2-fashion.[34] We now report the full version of the synthesis and structure of [t-BuNON]$^{2-}$ complexes of Ti, Zr, and Hf, some polymerization chemistry employing Zr and Hf initiators, and X-ray structures of two (catalytically inactive) Zr cations that contain the [t-BuNON]$^{2-}$ ligand.

Results

Synthesis of Ligands. 2,2′-Dinitrodiphenyl ether was prepared by the known nucleophilic aromatic substitution using 2-nitrophenol and 2-fluoronitrobenzene (Scheme 1).[35] A derivative that bears methyl groups ortho and para to the phenol oxygen can be synthesized in an analogous fashion in ∼80% yield (Scheme 1; $R_1 = R_2 = Me$). However, larger substituents ortho to the phenolic oxygen slow the nucleophilic substitution. For example, 2-ethyl-2′,6-dinitrodiphenyl ether (R_1 = Et, R_2 = H) can be prepared in only moderate yield overall. All derivatives can be hydrogenated in high yield employing Pd on C.[36] The proton NMR spectrum of H_2[t-BuNONEt] revealed that the ethyl's methylene protons are diastereotopic on the NMR time scale as a consequence (we propose) of hindered rotation of one phenyl ring past the other.

Schiff bases are formed quantitatively in a reaction between the dianilines and acetone-d_6 in the presence of molecular sieves as the dehydrating reagent. The condensation can be monitored conveniently by ^1H NMR and is complete within 3−7 days. The Schiff bases can be used without purification in a reaction with LiMe to produce the *tert*-butyl-substituted anilines $[Me(CD_3)_2CNHC_6H_4]_2O$ (H_2[t-BuNON]), $[Me(CD_3)_2CNHC_6H_4][Me(CD_3)_2CNH\text{-}2,4\text{-}Me_2C_6H_2]O$ (H_2[t-BuNONMe$_2$]), and $[Me(CD_3)_2CNHC_6H_4][Me(CD_3)_2NH\text{-}2\text{-}EtC_6H_3]O$ (H_2[t-BuNONEt]. The first two compounds can be prepared on a multigram scale and are isolated as pale orange oils in ∼55% overall yield. This synthesis of *tert*-butyl-substituted anilines is analogous to the synthesis of monodentate *tert*-butyl anilines reported by Cummins and co-workers.[37] Similar reactions with acetone itself produced only low yields of the *tert*-butyl-substituted

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Scheme 2

$$Ti(NMe_2)_2Cl_2 \xrightarrow[-25\ °C]{Li_2[t\text{-}BuNON]} [t\text{-}BuNON]Ti(NMe_2)_2$$

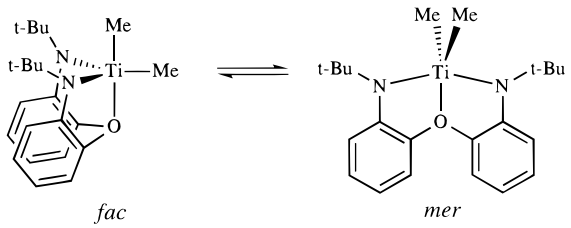
$$\xrightarrow[\text{toluene, 110 °C}]{Me_3SiCl} [t\text{-}BuNON]TiCl_2 \xrightarrow{2\ MeMgCl,\ -25\ °C} [t\text{-}BuNON]TiMe_2$$

anilines. Successful synthesis of the d_6 derivatives is perhaps the consequence of a significant isotope effect that enhances the rate of nucleophilic attack at the imine carbon versus deprotonation of the imine. Proton NMR spectra (500 MHz) of H_2[t-BuNON] show two small upfield shoulders on the *tert*-butyl resonance that amount to ~0.5 H per *tert*-butyl group. These additional resonances are ascribed to methyl protons in partially deuterated methyl groups (CD_2H and CDH_2). Exchange of D for H is believed to originate from base-catalyzed scrambling of NH protons into CD_3 groups, either in acetone-d_6 or at some stage during imine formation. These shoulders are also observed in H_2[t-BuNONMe$_2$] and H_2[t-BuNONEt], as well as all metal complexes reported here that contain diamidoether ligands of this type. The practical consequence is that integrations for *tert*-butyl protons in a [t-BuNON]$^{2-}$ ligand typically amount to ~7 instead of 6.

Synthesis of Titanium Complexes. Addition of 2 equiv of LiBu to a solution of H_2[t-BuNON] in ether, followed by $Ti(NMe_2)_2Cl_2$, yields orange crystalline [t-BuNON]Ti(NMe$_2$)$_2$ in ~55% yield (Scheme 2). Proton NMR spectra of [t-BuNON]Ti(NMe$_2$)$_2$ reveal only one singlet at ~3.1 ppm for the dimethylamide groups. The dichloride complex, [t-BuNON]$TiCl_2$, was prepared in ~80% yield by treating [t-BuNON]Ti(NMe$_2$)$_2$ with Me_3SiCl over a period of several days at 110 °C. [t-BuNON]$TiCl_2$ is a purple-black solid that is moderately soluble in toluene and ether. A dimeric formulation for [t-BuNON]$TiCl_2$ cannot be ruled out, since [t-BuNON]$ZrCl_2$ was shown to be a dimer in the solid state (see below). Reaction of Li_2[t-BuNON] (generated in situ) with $TiCl_4(thf)_2$ led to [t-BuNON]$TiCl_2$ in only low and irreproducible yields. Addition of methylmagnesium chloride to [t-BuNON]$TiCl_2$ gave [t-BuNON]$TiMe_2$ in good yield. The room-temperature ^{1}H NMR spectra of [t-BuNON]$TiMe_2$ show one singlet for the titanium methyl groups and one singlet for the *tert*-butyl groups. Attempts to prepare [t-BuNON]TiR_2 complexes in which one or more β hydrogens are present in the alkyl ligand (e.g., R = Et or i-Bu) were unsuccessful; only apparent decomposition took place upon addition of the Grignard reagent to [t-BuNON]$TiCl_2$.

An X-ray study of [t-BuNON]$TiMe_2$ (Tables 1 and 3; Figure 1a,b) showed it to be a "twisted," approximately trigonal bipyramidal molecule with equatorial amido groups, an axial oxygen donor, and an axial methyl group (C(2)−Ti(1)−(O) = 175.6(2) Å). We call this the "twisted *fac*" form. It is characterized by an angle between the N(1)−Ti−O and N(2)−Ti−O planes of approximately 120° (here 121°) and O−Ti−N(1)−C(17) and O−Ti−N(2)−C(27) dihedral angles of 136−137°. The equatorial methyl group is bent down slightly from the ideal equatorial position (C(1)−Ti(1)−C(2) = 96.0(2)°), while the two amide atoms are bent away from the axial methyl group even further (114.6(2)° and 115.1(2)°), we presume as a consequence of the [t-BuNON]$^{2-}$ ligand's coordination requirements. The Ti−C and Ti−N distances are in the expected range, but the Ti−O bond is relatively long (Ti(1)−O = 2.402(4) Å). The sum of the angles about the oxygen atom (~315.5°) suggests that it is tetrahedral, while the sum of the angles around the amido atoms suggests that they are planar, as expected. The [t-BuNON]$^{2-}$ ligand is twisted to a significant degree, in part, we presume, to minimize the steric interaction of the *tert*-butyl groups with the axial methyl group, but also as a consequence of the rigidity of the planar *o*-phenylene "arm" that connects O to N. The "twisted *fac*" structure has C_1 symmetry, with one *tert*-butyl group (on N(2)) pointing "away" from C(1), and the other (on N(1)) pointing "toward" C(1).

The fact that [t-BuNON]$TiMe_2$ appears to have C_2 or C_{2v} symmetry on the NMR time scale suggests that *fac* forms are interconverting rapidly via a *mer* intermediate form in which Ti, N(1), N(2), and O are in a plane (eq 1). Either there is a molecular plane coincident with the



(1)

Ti/N(1)/N(2)/O plane (C_{2v} symmetry), or the *mer* form is also "twisted" with a C_2 axis bisecting the C−Ti−C angle (C_2 symmetry). In an ideal C_{2v} *mer* form two methyl groups in each *tert*-butyl group would lie on either side of an adjacent phenyl ring, leaving the third to point directly between the methyl groups on titanium. The aryl protons in the backbone *ortho* to oxygen would also point directly toward one another. Therefore a "twisted *mer*" (C_2) form seems more likely and has been observed in two molecules that we will discuss later in this paper. We propose that steric interactions between the *tert*-butyl groups and the $TiMe_2$ groups lead to a further twisting of the ligand, a rotation of the $TiMe_2$ unit in the $OTiMe_2$ plane, and conversion of the twisted *mer* to the more stable twisted *fac* form. We cannot tell if the molecule actually "flips" on the NMR time scale through a C_{2v} form having a planar oxygen donor, or not, as formation of the twisted *mer* (C_2) form is sufficient in order to equilibrate the methyl groups on Ti. A variable-temperature ^{1}H NMR study of [t-BuNON]-$TiMe_2$ in toluene-d_8 down to −80 °C revealed no evidence for any inequivalence of the Ti methyl groups on the NMR time scale.

Synthesis of Zirconium Complexes. Reactions between $Zr(NMe_2)_4$ and H_2[t-BuNON], H_2[t-BuNONMe$_2$], or H_2[t-BuNONEt] proceed smoothly to give bisdimethylamido complexes (Scheme 3; "[NON]" refers to any of the ligands employed in this work). Reactions involving H_2[t-BuNONMe$_2$] and H_2[t-BuNONEt] required 100 °C to proceed readily as a consequence of more significant steric problems. Reaction of the dilithio [t-BuNON]$^{2-}$ salt with $ZrCl_4$ or $ZrCl_4(thf)_2$ yielded only a mixture of unidentified species. Upon treatment with Me_3SiCl in ether or toluene, [t-BuNON]Zr(NMe$_2$)$_2$ complexes are converted in high yield into dichloride

Table 1. Crystal Data and Structure Refinement for [t-BuNON]TiMe$_2$, {[t-BuNON]ZrCl$_2$}$_2$, [t-BuNON]ZrMe$_2$, and [t-BuNON]Zr(η^2-C$_2$H$_4$)(PMe$_3$)$_2$

	[t-BuNON]TiMe$_2$	{[t-BuNON]ZrCl$_2$}$_2$	[t-BuNON]ZrMe$_2$	[t-BuNON]Zr(η^2-C$_2$H$_4$)L$_2$
crystals obtained from	ether/pentane	ether	toluene	ether
formula	$C_{22}H_{32}N_2OTi$	$C_{20}H_{26}Cl_2N_2OZ$	$C_{25.5}H_{36}N_2OZr$	$C_{28}H_{48}N_2OP_2Zr$
fw	388.40	472.55	477.78	581.84
crystal size (mm)	0.34 × 0.34 × 0.20	0.10 × 0.10 × 0.04	0.32 × 0.18 × 0.03	0.23 × 0.15 × 0.12
crystal system	monoclinic	monoclinic	triclinic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$Pbca$
a (Å)	14.376(4)	10.109(3)	9.135(3)	15.85260(10)
b (Å)	9.160(4)	17.174(4)	12.244(4)	19.3138(3)
c (Å)	16.456(7)	12.132(4)	12.529(6)	19.52380(10)
α (deg)	90	90	118.55(3)	90
β (deg)	102.04(3)	97.893(13)	90.55(2)	90
γ (deg)	90	90	91.67(2)	90
V (Å^3)	2119.4(14)	2086.5(10)	1230.0(7)	5977.68(10)
Z	4	4	2	8
density calcd (Mg/m^3)	1.217	1.504	1.290	1.293
μ (mm^{-1})	0.416	0.794	0.465	0.497
F(000)	832	968	502	2464
T (K)	158(2)	183(2)	185(2)	183(2)
θ range (ω scans) (deg)	1.45−23.26	2.03−23.26	1.85−23.25	1.96−23.27
no. of reflns collected	3857	8385	5113	22901
no. of indep reflns	2632	2984	3467	4278
no. of data/restr/params	2632/0/236	2980/0/236	3466/0/281	4277/0/308
goodness-of-fit on F^2	1.182	1.243	0.999	1.048
R1/wR2 [$I > 2\sigma(I)$]	0.0682/0.1482	0.0446/0.0864	0.0445/0.1125	0.0296/0.0675
R1/wR2 (all data)	0.0886/0.1688	0.0567/0.0945	0.0595/0.1331	0.0340/0.0698
extinction coeff	0.0113(13)	0.0013(3)	0.0009(14)	0.00075(11)
max/min peaks (e/Å^3)	0.463/−0.369	0.379/−0.396	0.485/−0.503	0.303/−0.285

Table 2. Crystal Data and Structure Refinement for {[t-BuNON]ZrMe}[MeB(C$_6$F$_5$)$_3$], {[t-BuNON]ZrMe(THF)$_2$}[B(C$_6$F$_5$)$_4$], and {[t-BuNON]ZrMe(DME)}[B(C$_6$F$_5$)$_4$]

	{[t-BuNON]ZrMe}[MeB(C$_6$F$_5$)$_3$]	{[t-BuNON]ZrMe(THF)$_2$}$^+$	{[t-BuNON]ZrMe(DME)}$^+$
crystals obtained from	pentane	THF/pentane	DME/pentane
formula	$C_{40}H_{32}BF_{15}N_2OZr$	$C_{53}H_{45}BF_{20}N_2O_3Zr$	$C_{49}H_{39}BF_{20}N_2O_3Zr$
fw	943.71	1239.94	1185.85
crystal size (mm)	0.33 × 0.29 × 0.22	0.3 × 0.3 × 0.3	0.34 × 0.22 × 0.08
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1$/c	$P\bar{1}$
a (Å)	11.747(5)	12.5537(3)	10.6023(3)
b (Å)	12.321(5)	12.1378(3)	14.3701(5)
c (Å)	16.829(8)	34.1037(9)	16.2272(4)
α (deg)	100.21(3)	90	90.930(1)
β (deg)	98.22(3)	98.470(1)	99.707(1)
γ (deg)	108.06(3)	90	97.771(1)
V (Å^3)	2228(2)	5139.7(2)	2412.61(12)
Z	2	4	2
density calcd (Mg/m^3)	1.407	1.602	1.632
μ (mm^{-1})	0.341	0.333	0.351
F(000)	948	2504	1192
T (K)	153(2)	173(2)	185(2)
θ range (ω scans) (deg)	1.26−20.00	1.21−23.25	1.88−23.25
no. of reflns collected	4425	20491	9796
no. of indep reflns	3722	7365	6704
no. of data/restr/params	3709/0/536	7365/0/721	6704/0/685
goodness-of-fit on F^2	1.068	1.322	1.441
R1/wR2 [$I > 2\sigma(I)$]	0.0890/0.1857	0.0665/0.1153	0.0832/0.1463
R1/wR2 (all data)	0.1077/0.2136	0.0791/0.1191	0.1030/0.1551
extinction coeff	0.0006(4)		
max/min peaks (e/Å^3)	0.817/−0.535	0.410/−0.414	0.612/−0.683

complexes.[38] Even in the presence of excess Me_3SiCl the sterically protected ligand amido nitrogen atoms are not alkylated under the conditions employed. The reaction between [t-BuNON]Zr(NMe$_2$)$_2$ and methyl iodide[39,40] proceeds more slowly than that between [t-BuNON]Zr(NMe$_2$)$_2$ and Me_3SiCl, although upon heating a mixture of [t-BuNON]Zr(NMe$_2$)$_2$ and excess methyl iodide in toluene to ∼50 °C, [t-BuNON]ZrI$_2$ is formed in high yield within 2 days.

In proton NMR spectra of [t-BuNON]Zr(NMe$_2$)$_2$ the NMe$_2$ groups appear as one sharp singlet, consistent with C_2 or C_{2v} symmetry of the molecular core and ligand backbone and free rotation about the Zr−N bond in solution on the NMR time scale. In contrast, proton NMR spectra of [t-BuNONMe$_2$]Zr(NMe$_2$)$_2$ feature two sharp singlets (at 3.15 and 2.82 ppm) for two NMe$_2$ ligands in which rotation about the Zr−N bond is still rapid on the NMR time scale. No coalescence of the NMe$_2$ resonances was observed when a chlorobenzene-

(38) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4045.
(39) Johnson, A. R.; Davis, W. M.; Cummins, C. C. *Organometallics* **1996**, *15*, 3825.
(40) Johnson, A. R.; Wanandi, P. W.; Cummins, C. C.; Davis, W. M. *Organometallics* **1994**, *13*, 2907.

Table 3. Selected Bond Lengths (Å) and Angles (deg) in [t-BuNON]TiMe$_2$, {[t-BuNON]ZrCl$_2$}$_2$, and [t-BuNON]ZrMe$_2$

[t-BuNON]TiMe$_2$		{[t-BuNON]ZrCl$_2$}$_2$		[t-BuNON]ZrMe$_2$	
Ti−O	2.402(4)	Zr−O	2.336(3)	Zr−O	2.418(3)
Ti−N(1)	1.944(4)	Zr−N(1)	2.089(4)	Zr−N(1)	2.096(4)
Ti−N(2)[a]	1.936(4)	Zr−N(2)	2.061(4)	Zr−N(2)	2.087(4)
Ti−C(2)(ax)	2.119(6)	Zr−Cl(2)(ax)	2.4025(13)	Zr−C(2)(ax)	2.280(5)
Ti−C(1)(eq)	2.097(6)	Zr−Cl(1)(eq)	2.5290(14)	Zr−C(1)(eq)	2.235(5)
N(1)−Ti−N(2)	113.5(2)	N(1)−Zr−N(2)	101.88(14)	N(1)−Zr−N(2)	113.19(14)
N(1)−Ti−O	73.9(2)	N(1)−Zr−O	72.69(12)	N(1)−Zr−O	70.74(12)
N(1)−Ti−C(2)	110.0(2)	N(1)−Zr−Cl(2)	98.79(12)	N(1)−Zr−C(2)	113.6(2)
N(1)−Ti−C(1)	115.1(2)	N(1)−Zr−Cl(1)	135.71(10)	N(1)−Zr−C(1)	112.7(2)
N(2)−Ti−O	74.0(2)	N(2)−Zr−O	73.28(12)	N(2)−Zr−O	71.16(12)
N(2)−Ti−C(2)	105.7(2)	N(2)−Zr−Cl(2)	103.20(11)	N(2)−Zr−C(2)	105.4(2)
N(2)−Ti−C(1)	114.6(2)	N(2)−Zr−Cl(1)	135.71(10)	N(2)−Zr−C(1)	111.8(2)
C(2)−Ti−O	175.6(2)	Cl(2)−Zr−O	169.49(8)	C(2)−Zr−O	175.48(14)
C(2)−Ti−C(1)	96.0(2)	Cl(2)−Zr−Cl(1)	110.89(5)	C(2)−Zr−C(1)	99.2(2)
C(1)−Ti−O	80.2(2)	Cl(1)−Zr−O	77.25(8)	C(1)−Zr−O	79.8(2)
C(12)−Ti−C(26)	115.5(4)	C(1)−O−C(7)	115.5(3)	C(11)−O−C(21)	117.2(3)
Ti−N(1)−C(17)	128.0(3)	Zr−N(1)−C(101)	129.0(3)	Zr−N(1)−C(17)	123.1(3)
Ti−N(2)−C(27)	128.0(3)	Zr−N(2)−C(201)	135.3(3)	Zr−N(2)−C(27)	126.6(3)
N(1)/Ti/O/N(2)[b,c]	121	N(1)/Zr/O/N(2)[b,c]	109	N(1)/Zr/O/N(2)[b,c]	124
O−Ti−N(1)−C(17)[c]	137.3	O−Zr−N(1)−C(101)[c]	143.3	O−Zr−N(1)−C(17)[c]	146.1
O−Ti−N(2)−C(27)[c]	136.3	O−Zr−N(2)−C(201)[c]	135.5	O−Zr−N(2)−C(27)[c]	142.9
		Zr−Cl(1A)	2.7944(13)		

[a] In all compounds the *tert*-butyl group on N(2) is turned toward the region between N(1) and N(2). [b] The external angle between the planes. [c] Obtained from Chem 3D model.

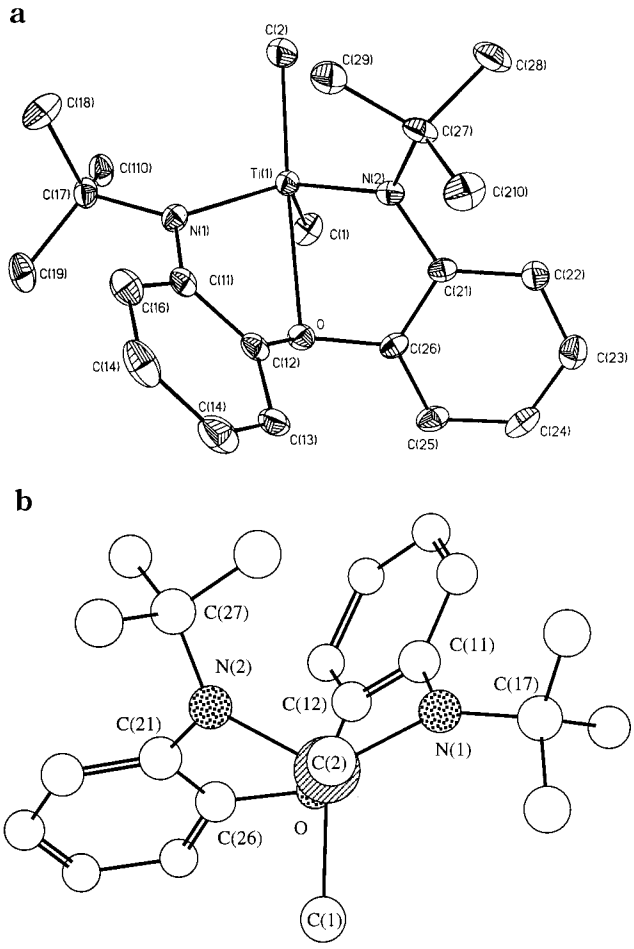
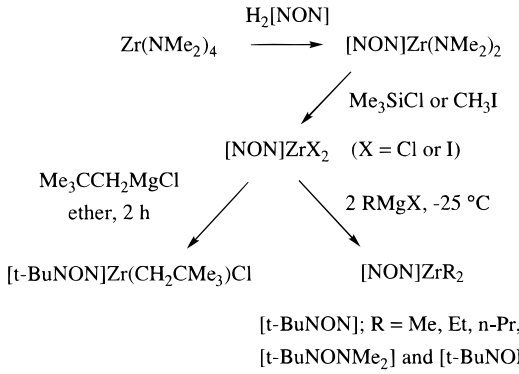


Figure 1. (a) ORTEP diagram (35% probability level) of [t-BuNON]TiMe$_2$. (b) Chem 3D view of [t-BuNON]TiMe$_2$] from the axial position.

d_5 solution of [t-BuNONMe$_2$]Zr(NMe$_2$)$_2$ was heated to 120 °C. We propose that the lowest energy form of [t-BuNONMe$_2$]Zr(NMe$_2$)$_2$ is a twisted *fac* structure and that the phenyl groups cannot pass one another rapidly on the NMR time scale. In this case the molecule must pass through a true C_{2v} transition state in order to interconvert the two dimethylamido ligands; a "twisted *mer*" transition state in which a C_2 axis passes between the two ZrMe$_2$ methyl groups is insufficient. Proton NMR spectra of [t-BuNONEt]Zr(NMe$_2$)$_2$ at room temperature also show two distinct NMe$_2$ resonances.

Scheme 3



The X-ray structure of [t-BuNON]ZrCl$_2$ (Tables 1 and 3, Figure 2) shows it to be a dimer having a crystallographic inversion center. Each zirconium has a distorted trigonal bipyramidal coordination geometry similar to what is found in [t-BuNON]TiMe$_2$, with an axial chloride (Zr−Cl(2) = 2.4025(13)) and an equatorial chloride (Zr−Cl(1) = 2.5290(14)). A chloride that is in an equatorial position with respect to the second zirconium (Cl(1A)) is bonded to the N(2)−Cl(1)−Cl(2) face at a distance of 2.7944(13) Å. (The N(2)−Cl(1)−Cl(2) face is that from which the *tert*-butyl group turns away, i.e., C(201) points toward N(1), thereby providing room for the weakly bound Cl(1A).) For comparison, in {Cl$_2$Zr(NSiHMe$_2$)$_2$}$_2$[41] the Zr−Cl$_{bridge}$ bond lengths are 2.599 and 2.628 Å, respectively. The Zr−O bond length (2.336(3) Å) is approximately what would be expected

(41) Herrmann, W. A.; Huber, N. W.; Behm, J. *Chem. Ber.* **1992**, *125*, 1405.

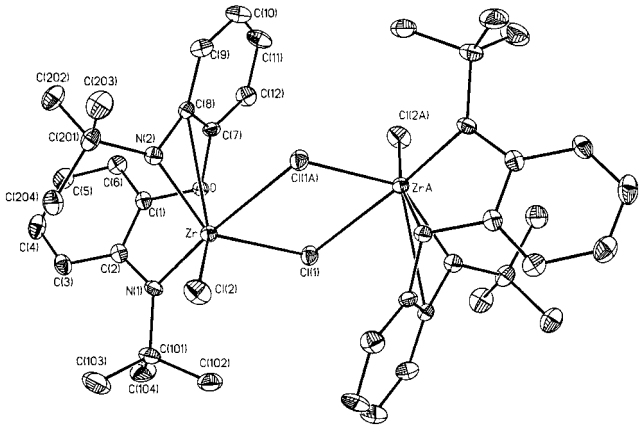


Figure 2. ORTEP diagram (35% probability level) of {[t-BuNON]$ZrCl_2$}$_2$.

for a Zr−O_{donor} bond, and the sum of the angles about the oxygen atom (∼328.5°) suggests that it is tetrahedral. The N(1)−Zr−N(2) angle and the angle between the N(1)−Zr−O and N(2)−Zr−O planes is approximately 10° smaller than the corresponding angles in the other (five-coordinate) species listed in Table 3, consistent with a more crowded pseudo-six-coordinate coordination sphere in {[t-BuNON]$ZrCl_2$}$_2$, while the Zr−N bond lengths (2.061(4) and 2.089(4) Å) are approximately 0.1 Å longer than the corresponding Ti−N bond lengths, as one would expect. An *ipso* carbon atom in one phenyl ring (C(8)) weakly interacts with the zirconium metal center (Zr···C(8) = 2.774(4) Å), as also has been observed in compounds such as [1,2-(NSi-i-Pr_3)$_2$$C_6H_4$]$_2$Zr,[42] where Zr−$C_{ipso}$ ≈ 2.60 Å. It is believed to be a consequence of the [t-BuNON]$^{2-}$ ligand's conformation in a crowded environment, not a determinant of that conformation. For convenience, and since a dimeric formulation was confirmed for only one dichloride complex, all [NON]ZrX_2 (X = Cl or I) complexes will be written as monomers in the text of this paper with the understanding that they almost certainly are dimers in the solid state.

Alkylation of [NON]ZrX_2 precursors with methyl Grignard reagents affords a variety of dimethyl complexes in 50−75% yield (Scheme 3). [t-BuNONMe_2]-$ZrMe_2$ is highly soluble even in pentane and consequently could be isolated in only ∼55% yield as a pale yellow amorphous solid. Proton NMR spectra of [t-BuNON]$ZrMe_2$ are virtually identical to those of [t-BuNON]$TiMe_2$. However, the zirconium methyl groups in [t-BuNONMe_2]$ZrMe_2$ are inequivalent and appear as two distinct singlets. Heating a solution of [t-BuNONMe_2]-$ZrMe_2$ in toluene-d_8 to 70 °C did not lead to significant broadening of the zirconium methyl resonances. At temperatures higher than ∼70 °C the sample decomposed to a mixture of unidentified species. The methylene protons of the ethyl group in [t-BuNONEt]$ZrMe_2$ give rise to two distinct doublets of triplets, as expected since the phenyl rings of the ligand cannot pass one another on the NMR time scale even in the free form of the ligand. At temperatures up to 90 °C, where the sample of [t-BuNONEt]$ZrMe_2$ in toluene-d_8 decomposed, there was no evidence that the methylene protons could interconvert on the NMR time scale.

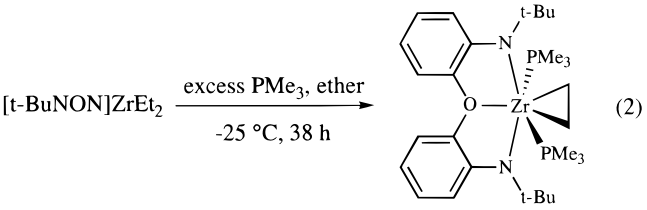
(42) Aoyagi, K.; Gantzel, P. K.; Kalai, K.; Tilley, T. D. *Organometallics* **1996**, *15*, 923.

The X-ray structure of [t-BuNON]$ZrMe_2$ is shown in Figure 3. (See also Tables 1 and 3.) The molecule is a twisted *fac* form in the solid state, similar to [t-BuNON]-$TiMe_2$. The equatorial positions are occupied by the two ligand nitrogen atoms [N(1)−Zr−N(2) = 113.19(14)°] and one methyl group. The other methyl group (containing C(2)) and the oxygen donor are in axial positions [C(2)−Zr−O = 175.48(14)°]. The sum of the angles about oxygen is ∼329°. The only significant structural differences between [t-BuNON]$ZrMe_2$ and [t-BuNON]$TiMe_2$ are the more normal Zr−O distance (Zr−O = 2.418(3) Å) and the slightly larger O−Zr−N−C dihedral angles.

Several dialkyl complexes in which the alkyl contains one or more β hydrogens (R = Et, n-Pr, i-Bu) also can be isolated as highly pentane soluble, pale yellow solids in ∼50% yield. At −25 °C all three can be stored in the solid state for months or in ether solution for several days without decomposition. However, at room temperature in C_6D_6 or ether solution they decompose within several hours to a mixture of unidentified products.

When [t-BuNON]$ZrCl_2$ is treated with 1 or 2 equiv of Me_3CCH_2MgCl, [t-BuNON]$Zr(CH_2CMe_3)Cl$ is obtained, while addition of 2 equiv of $LiCH_2CMe_3$ to [t-BuNON]-$ZrCl_2$ leads to a mixture of unidentified products. Apparently a complex that contains two neopentyl groups is too crowded to form, and some alternative pathway leads to decomposition during its attempted formation. We propose that the neopentyl group in [t-BuNON]$Zr(CH_2CMe_3)Cl$ is located in the sterically more open equatorial position in a *fac* structure, while the chloride occupies the more crowded axial position *trans* to the oxygen donor.

When an ether solution of [t-BuNON]$ZrEt_2$ is allowed to stand at −25 °C in the presence of excess PMe_3, [t-BuNON]$Zr(\eta^2$-$C_2H_4)(PMe_3)_2$ forms over a period of 2 days and can be isolated in ∼80% yield (eq 2). Since



(2)

[t-BuNON]$ZrEt_2$ does not decompose at this temperature in the absence of PMe_3, the β hydrogen abstraction reaction must be induced by coordination of PMe_3 to Zr. According to ^{1}H and ^{31}P NMR studies, the PMe_3 is labile. A variable-temperature ^{31}P NMR study in toluene-d_8 shows a broad signal at −29.9 ppm at 0 °C. At −40 °C this resonance is sharp. The thermal stability of [t-BuNON]$Zr(\eta^2$-$C_2H_4)(PMe_3)_2$ in C_6D_6 is moderate, but is much higher in the presence of additional PMe_3, suggesting that decomposition occurs via initial loss of PMe_3. All attempts to isolate a monophosphine ethylene derivative have failed. Attempts to isolate olefin complexes analogous to [t-BuNON]$Zr(\eta^2$-$C_2H_4)(PMe_3)_2$ via decomposition of [t-BuNON]$ZrPr_2$ or [t-BuNON]$Zr(i$-$Bu)_2$ in the presence of PMe_3 failed, perhaps because the second phosphine is not firmly bound.

An X-ray structure of [t-BuNON]$Zr(\eta^2$-$C_2H_4)(PMe_3)_2$ (Tables 1 and 5, Figure 4) shows that it is a pseudo-octahedral species in which the [t-BuNON]$^{2-}$ ligand is bound in a twisted *mer* manner and the two PMe_3

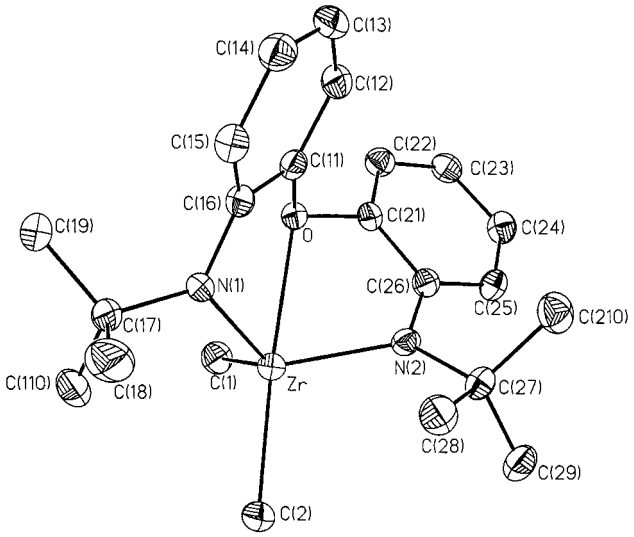


Figure 3. ORTEP diagram (35% probability level) of [t-BuNON]$ZrMe_2$.

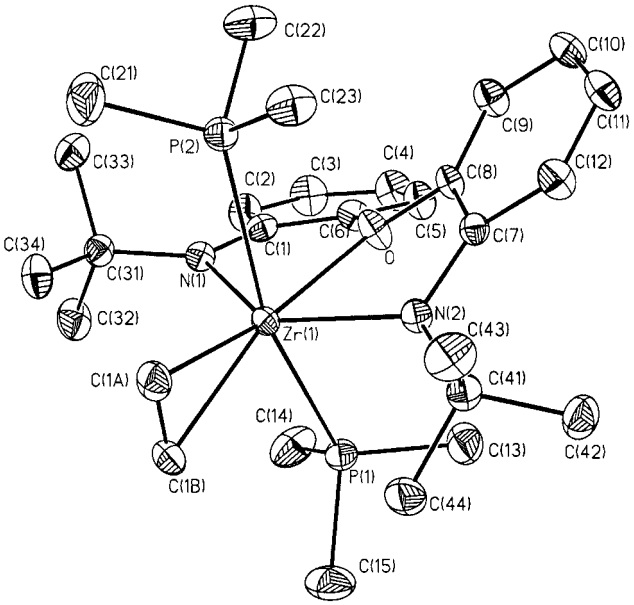


Figure 4. ORTEP diagram (35% probability level) of [t-BuNON]$Zr(\eta^2\text{-}C_2H_4)(PMe_3)_2$.

ligands are *trans* to one another. The external angle between the N(1)−Zr−O and N(2)−Zr−O planes is 177° and the O−Zr−N−C_{t-Bu} dihedral angles are 159° and 165°, both significantly larger than in the twisted *fac* structures. The ligand oxygen donor atom is essentially planar, judging from the sum of the angles around it (359°). The ethylene ligand is trans to the oxygen and lies ∼15° out of the P−O−Zr−P plane. The Zr−CH_2 distances (Zr(1)−C(1A) = 2.285(3) Å, Zr(1)−C(1B) = 2.288(3) Å) are slightly shorter than the zirconium to ethylene carbon distances in $Cp_2Zr(\eta^2\text{-}CH_2CH_2)(PMe_3)$ (Zr−C = 2.354(3) and 2.332(4) Å),[43,44] while the C(1A)−C(1B) bond length (1.469(4) Å) is virtually identical to that in $Cp_2Zr(\eta^2\text{-}CH_2CH_2)(PMe_3)$ (1.449(6) Å). The relatively short Zr−O bond distance (2.295(2) Å) is consistent with a strong interaction, while the Zr−N distances (2.253(2) and 2.256(2) Å), on the other hand, are long relative to what they are in zirconium complexes that contain the *fac* form of the [t-BuNON]$^{2-}$ ligand. The Zr−P bond distances (2.8284(7) and 2.8100(7) Å) are also longer than the Zr−P distance in $Cp_2Zr(\eta^2\text{-}CH_2\text{-}CH_2)(PMe_3)$ (2.695(1) Å). It appears that while the oxygen atom interacts strongly with the metal center, both the Zr−P bonds and the π component of the Zr−N bonds are weakened as a consequence of steric crowding in the pseudo-six-coordinate geometry. The lability of PMe_3 in solution is consistent with the long Zr−P bond. The electron count in [t-BuNON]$Zr(\eta^2\text{-}C_2H_4)(PMe_3)_2$ is 14 if the Zr−N π bond that utilizes the unsymmetric combination of p orbitals on the nitrogen atoms is included.

Synthesis of Hafnium Complexes. The most convenient entry into Hf chemistry is analogous to that shown in Scheme 2 for zirconium complexes. The reaction between H_2[t-BuNON] and $Hf(NMe_2)_4$ in concentrated toluene solution at 100−105 °C for 16 h gave [t-BuNON]$Hf(NMe_2)_2$ in 82% yield. The purity of [t-BuNON]$Hf(NMe_2)_2$ was sufficiently high to use it without further purification in a subsequent reaction with Me_3SiCl. The dimethylamido methyl groups are equivalent on the NMR time scale at room temperature in [t-BuNON]$Hf(NMe_2)_2$ (at 3.01 ppm), as they are in [t-BuNON]$Zr(NMe_2)_2$ and [t-BuNON]$Ti(NMe_2)_2$. The reaction between [t-BuNON]$Hf(NMe_2)_2$ and excess Me_3SiCl in toluene at 100 °C for 5 h gave [t-BuNON]-$HfCl_2$ in 90% yield. [t-BuNON]$HfCl_2$ can be used without purification in subsequent alkylation reactions in diethyl ether at −40 °C with the appropriate Grignard reagent to give dialkyl derivatives [t-BuNON]HfR_2 (R = Me, Et, i-Bu) in 70−80% isolated yields. As in the case of [t-BuNON]$ZrCl_2$, only monoalkylation took place upon addition of Me_3CCH_2MgCl to [t-BuNON]$HfCl_2$ to give [t-BuNON]$Hf(CH_2CMe_3)Cl$ in 87% yield. Addition of 2 equiv of neopentyllithium to [t-BuNON]$HfCl_2$ gave mixtures that appeared to contain crude [t-BuNON]Hf-$(CH_2CMe_3)_2$ (by ^{1}H NMR), but several attempts to isolate [t-BuNON]$Hf(CH_2CMe_3)_2$ in pure form were unsuccessful. However, [t-BuNON]$Hf(CH_2CMe_3)Me$ could be prepared in good yield from the reaction between [t-BuNON]$Hf(CH_2CMe_3)Cl$ and MeMgI. NMR spectra for the symmetric dialkyl derivatives show one set of resonances for the alkyl ligands, suggesting that in solution these complexes are interconverting rapidly between *fac* and *mer* forms. [t-BuNON]$HfEt_2$ and [t-BuNON]$Hf(CH_2CHMe_2)_2$ do not decompose at room temperature in the solid state and at least for several days in solution (C_6D_6, ether, or pentane) at room temperature, in contrast to their less stable Zr analogues.

Observation and Isolation of Cations. When 1 equiv of $B(C_6F_5)_3$ is added to a C_6D_5Br solution of [t-BuNON]$ZrMe_2$, the color changes immediately to bright yellow as {[t-BuNON]ZrMe}[$MeB(C_6F_5)_3$] is formed (Scheme 4). The ^{1}H NMR spectrum of the solution shows one sharp singlet at 0.77 ppm that we assign to the equatorial ZrMe protons and a broad singlet at 2.24 ppm that we assign to the Zr···Me···B protons. (The resonance of the bridging methyl group is broadened due to coupling to boron.) The *tert*-butyl groups are equivalent on the NMR time scale and appear as a singlet at 0.98

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(44) Alt, H. G.; Denner, C. E.; Thewalt, U.; Rausch, M. D. *J. Organomet. Chem.* **1988**, *356*, C83.

Table 4. Selected Bond Lengths (Å) and Angles (deg) in {[t-BuNON]ZrMe}[MeB(C_6F_5)$_3$], {[t-BuNON]ZrMe(THF)$_2$}[B(C_6F_5)$_4$], and {[t-BuNON]ZrMe(DME)}[B(C_6F_5)$_4$]

{[t-BuNON]ZrMe}[MeB(C_6F_5)$_3$]		{[t-BuNON]ZrMe(THF)$_2$}[B(C_6F_5)$_4$]		{[t-BuNON]ZrMe(DME)}[B(C_6F_5)$_4$]	
Zr−O	2.256(8)	Zr−O(1)	2.302(3)	Zr−O(1)	2.458(5)
Zr−N(1)	2.049(10)	Zr−N(1)	2.140(4)	Zr−N(1)	2.061(5)
Zr−N(2)	2.065(10)	Zr−N(2)	2.160(4)	Zr−N(2)	2.096(5)
Zr−C(1)	2.487(12)[a]	Zr−C(1)	2.284(5)	Zr−C(1)	2.238(7)
N(1)−Zr−N(2)	113.8(4)	N(1)−Zr−N(2)	137.20(15)	N(1)−Zr−N(2)	106.1(2)
N(1)−Zr−O	73.5(4)	N(1)−Zr−O(1)	69.37(13)	N(1)−Zr−O(1)	71.58(19)
N(2)−Zr−O	75.2(3)	N(2)−Zr−O(1)	68.72(13)	N(2)−Zr−O(1)	70.90(18)
C(1)−Zr−O	167.3(4)	C(1)−Zr−O(1)	159.58(16)	C(1)−Zr−O(1)	171.1(2)
N(1)−Zr−C(1)	118.6(5)	N(1)−Zr−C(1)	99.33(17)	N(1)−Zr−C(1)	104.3(3)
N(2)−Zr−C(1)	101.2(5)	N(2)−Zr−C(1)	123.27(16)	N(2)−Zr−C(1)	103.5(3)
C(11)−O−C(26)	116.4(11)	C(11)−O−C(12)	125.2(4)	C(11)−O−C(12)	116.4(5)
Zr−N(1)−C(17)	125.8(7)	Zr−N(1)−C(2)	127.5(3)	Zr−N(1)−C(5)	131.5(4)
Zr−N(2)−C(27)	129.3(8)	Zr−N(2)−C(18)	118.9(3)	Zr−N(2)−C(18)	127.6(4)
N(1)/Zr/O/N(2)[b,c]	121	N(1)/Zr/O/N(2)[b,c]	171	N(1)/Zr/O/N(2)[b,c]	115
O−Zr−N(1)−C(17)[c]	140.3	O−Zr−N(1)−C(2)	158.0(4)	O−Zr−N(1)−C(5)	132.2(6)
O−Zr−N(2)−C(27)[c]	125.4	O−Zr−N(2)−C(18)	175.6(4)	O−Zr−N(2)−C(18)	145.4(6)
Zr−C(2)	2.200(13)	Zr−O(2)	2.212(3)	Zr−O(2)	2.259(5)
N(1)−Zr−C(2)	113.8(5)	Zr−O(3)	2.212(3)	Zr−O(3)	2.339(5)
N(2)−Zr−C(2)	115.4(5)	O(2)−Zr−N(1)	96.90(14)	O(2)−Zr−N(1)	130.2(2)
C(2)−Zr−O	79.2(4)	O(2)−Zr−N(2)	84.9814)	O(2)−Zr−N(2)	95.7(2)
C(2)−Zr−C(1)	91.8(5)	O(2)−Zr−O(1)	103.91(12)	O(2)−Zr−O(1)	74.43(17)
B−C(1)	1.69(2)	O(2)−Zr−O(3)	173.48(12)	O(2)−Zr−O(3)	67.89(17)
		O(3)−Zr−N(1)	89.44(14)	O(3)−Zr−N(1)	88.1(2)
		O(3)−Zr−N(2)	91.44(14)	O(3)−Zr−N(2)	163.2(2)
		O(3)−Zr−O(1)	79.75(12)	O(3)−Zr−O(1)	106.52(17)

[a] Methyl group bridging between Zr and B. [b] The external angle between the planes. [c] Obtained from Chem 3D model.

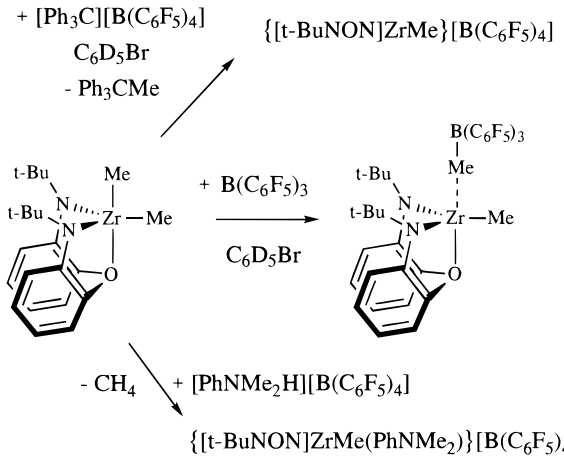
Table 5. Selected Bond Distances (Å) and Angles (deg) in [t-BuNON]Zr(η^2-CH_2CH_2)(PMe_3)$_2$

Distances			
Zr−N(2)	2.253(2)	Zr−N(1)	2.256(2)
Zr−C(1A)	2.285(3)	Zr−C(1B)	2.288(3)
Zr−P(1)	2.8284(7)	Zr−P(2)	2.8100(7)
Zr−O	2.295(2)	C(1A)-C(1B)	1.469(4)

Angles			
N(2)−Zr−N(1)	137.94(7)	C(1A)−Zr−C(1B)	37.48(10)
N(2)−Zr−O	68.53(6)	O−Zr−P(1)	79.05(5)
N(2)−Zr−P(2)	85.34(5)	O−Zr−P(2)	83.65(5)
N(2)−Zr−P(1)	89.57(5)	P(2)−Zr−P(1)	162.65(2)
N(1)−Zr−O	69.50(7)	C(6)−O−C(8)	124.8(2)
N(1)−Zr−P(2)	87.37(5)	C(31)−N(1)−Zr	126.0(2)
N(1)−Zr−P(1)	85.33(5)	C(41)−N(2)−Zr	128.1(2)
N(1)/Zr/O/N(2)[a,b]	177	O−Zr−N(1)−C(31)[b]	165
		O−Zr−N(2)−C(41)[b]	159

[a] The external angle between the planes. [b] Obtained from Chem 3D model.

Scheme 4



ppm. Carbon NMR spectra show two different methyl group resonances, one at 50.90 ppm for the methyl group bound to Zr and another at 29.5 ppm (a broad multiplet) for the methyl group bridging between Zr and B.

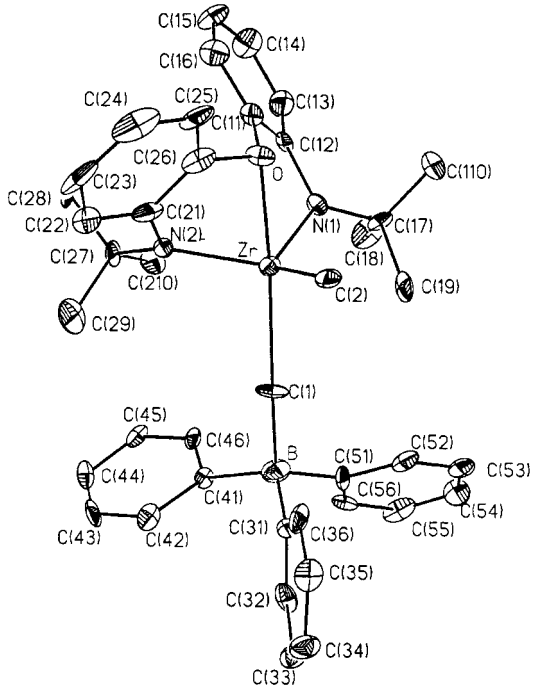


Figure 5. ORTEP diagram (35% probability level) of {[t-BuNON]ZrMe}[MeB(C_6F_5)$_3$].

The reaction between [t-BuNON]ZrMe_2 and B(C_6F_5)$_3$ also takes place in pentane. A solution of {[t-BuNON]-ZrMe}[MeB(C_6F_5)$_3$] forms, from which at −35 °C a yellow crystalline sample could be isolated in ∼46% yield. This isolated sample contains 0.5 equiv of pentane, according to ^{1}H NMR spectra. An X-ray structure (Tables 2 and 4, Figure 5) reveals that the axial methyl group has been partially abstracted from the zirconium center. The Zr−C(1) bond length (2.487(12) Å) is lengthened by ∼0.2 Å compared to what it is in [t-BuNON]-

$ZrMe_2$. In related metallocene complexes[45,46] Zr···Me bond distances are ~2.549−2.667 Å. The Zr−ligand bond lengths otherwise are contracted only slightly from what they are in [t-BuNON]$ZrMe_2$, most noticeably in the Zr−O bond length (2.256(8) Å), consistent with the developing cationic charge on zirconium.

[t-BuNON]$ZrMe_2$ reacts with 1 equiv of [$PhNMe_2H$]-[$B(C_6F_5)_4$] in C_6D_5Br to give what we propose is {[t-BuNON]ZrMe($PhNMe_2$)}[$B(C_6F_5)_4$] (Scheme 4). The ^{1}H NMR spectrum in C_6D_5Br shows a singlet for the zirconium methyl group at 0.95 ppm. For comparison, in C_6D_5Br the methyl groups of [t-BuNON]$ZrMe_2$ appear at 0.66 ppm. At 25 °C the methyl resonances for coordinated dimethyl aniline (at 2.74 ppm) and added free dimethyl aniline (at 2.65 ppm) are broadened, suggesting that dimethyl aniline is bound to Zr but exchanging readily. Upon cooling this solution to −30 °C, the dimethylaniline methyl resonances sharpen. The *tert*-butyl groups are equivalent. The ^{13}C NMR spectrum of {[t-BuNON]Zr($^{13}CH_3$)($PhNMe_2$)}[$B(C_6F_5)_4$] showed a single resonance for the zirconium methyl group at 55.88 ppm. Solutions of {[t-BuNON]ZrMe($PhNMe_2$)}-[$B(C_6F_5)_4$] in C_6D_5Br can be heated briefly to 50 °C, although at that temperature decomposition is relatively rapid. At room temperature {[t-BuNON]ZrMe($PhNMe_2$)}-[$B(C_6F_5)_4$] is stable for at least ~1 h in solution. Unfortunately, we have not yet been able to isolate a solid sample of {[t-BuNON]ZrMe($PhNMe_2$)}[$B(C_6F_5)_4$]. Solutions of {[t-BuNON]ZrMe($PhNMe_2$)}[$B(C_6F_5)_4$] in C_6H_5Cl or C_6D_5Br are bright yellow and homogeneous, whereas dark orange oils separate out of toluene.

A methyl group also can be abstracted to give "{[t-BuNON]ZrMe}[$B(C_6F_5)_4$]" by treating a C_6D_5Br solution of [t-BuNON]$ZrMe_2$ with [Ph_3C][$B(C_6F_5)_4$]; a sharp singlet for Ph_3CMe appears at 2.01 ppm in the proton NMR spectrum. The ^{1}H NMR resonances of {[t-BuNON]-ZrMe}[$B(C_6F_5)_4$] are similar to those found for {[t-BuNON]ZrMe($PhNMe_2$)}[$B(C_6F_5)_4$]. In the absence of a relatively good donor we propose that the metal is either solvated by C_6D_5Br (by donation through bromide) or forms a tight anion/cation pair. At room temperature the zirconium methyl resonance in {[t-BuNON]ZrMe}-[$B(C_6F_5)_4$] (at 0.72 ppm) is somewhat broader than in {[t-BuNON]ZrMe($PhNMe_2$)}[$B(C_6F_5)_4$], which suggests that {[t-BuNON]ZrMe}[$B(C_6F_5)_4$] in C_6D_5Br may not be as well-defined in terms of the nature of the interaction between the cationic Zr center and the neutral base or anion. The ^{13}C NMR chemical shift of the methyl group in {[t-BuNON]Zr($^{13}CH_3$)}[$B(C_6F_5)_4$] is 53.60 ppm (at 25 °C), compared to 45.2 ppm in [t-BuNON]Zr($^{13}CH_3$)$_2$[34] and 50.90 ppm for the terminal methyl group in the incipient cation in {[t-BuNON]ZrMe}[$MeB(C_6F_5)_3$]. At −30 °C the zirconium methyl group appears as three broad resonances at 53.06, 50.16, and 44.20 ppm, possibly as a consequence of a variety of anion and/or solvent interactions with the cation that have comparable stability. This phenomenon is still under investigation in a variety of cations that contain diamido/donor ligands.

Abstraction of a methyl group from [t-BuNON]Zr-($^{13}CH_3$)$_2$ with [Ph_3C][$B(C_6F_5)_4$] in a 1:1 mixture of diethyl ether and C_6D_6 gave "{[t-BuNON]ZrMe(ether)$_2$}-[$B(C_6F_5)_4$]"; the ^{13}C NMR spectrum consisted of a single zirconium methyl resonance at 54.84 ppm. Multiple attempts to obtain a crystalline product were unsuccessful. The product was obtained as a solid in 92% yield by addition of an ether solution of {[t-BuNON]ZrMe-(ether)$_2$}[$B(C_6F_5)_4$] to cold pentane. The ^{1}H NMR spectrum in C_6D_5Br contained a sharp resonance at 0.96 ppm for the zirconium methyl group and the *tert*-butyl groups appeared as a single resonance at 1.46 ppm. Dissolution of {[t-BuNON]ZrMe(ether)$_2$}[$B(C_6F_5)_4$] in THF or DME yielded {[t-BuNON]ZrMe(THF)$_2$}[$B(C_6F_5)_4$] and {[t-BuNON]ZrMe(DME)}[$B(C_6F_5)_4$], respectively. (See below.)

The THF adduct, {[t-BuNON]ZrMe(THF)$_2$}[$B(C_6F_5)_4$], was prepared by adding 2 equiv of THF to a solution of {[t-BuNON]ZrMe}[$B(C_6F_5)_4$] or {[t-BuNON]ZrMe-(ether)$_2$}[$B(C_6F_5)_4$] in C_6H_5Cl; it was isolated in 72% yield upon addition of pentane to the C_6H_5Cl solution. The DME adduct could be prepared similarly. The ^{1}H NMR spectrum of {[t-BuNON]ZrMe(THF)$_2$}[$B(C_6F_5)_4$] in C_6D_5Br contained a sharp single zirconium methyl resonance at 1.03 ppm and three broadened resonances at 3.9, 1.8, and 1.6 ppm that can be attributed to THF. The ^{13}C NMR spectrum of {[t-BuNON]Zr($^{13}CH_3$)(THF)$_2$}-[$B(C_6F_5)_4$] revealed two broad methyl resonances at 53.4 and 55.6 ppm in a ratio of ~10:1 that we ascribed to isomers of the cation, perhaps *fac* and *mer* isomers analogous to those observed in the Hf system (see below). The ^{1}H NMR spectrum of {[t-BuNON]ZrMe-(DME)}[$B(C_6F_5)_4$] contained a single zirconium methyl resonance at 1.01 ppm. The resonances for the DME appeared as two broadened resonances for methylene protons at 3.62 and 3.86 ppm and a sharp singlet at 3.78 for the apparently equivalent methyl groups. The ^{13}C NMR spectrum of {[t-BuNON]Zr($^{13}CH_3$)(DME)}-[$B(C_6F_5)_4$] consisted of a single resonance at 52.47 ppm, consistent with formation of only one isomer.

Crystals of {[t-BuNON]ZrMe(THF)$_2$}[$B(C_6F_5)_4$] suitable for single-crystal X-ray diffraction were obtained from mixtures of THF and pentane (Tables 2 and 4, Figure 6). The Zr atom is in a pseudooctahedral environment with the [t-BuNON]$^{2-}$ ligand in a twisted *mer* conformation. The twisted *mer* conformation is suggested by the large angle between the N(1)−Zr−O(1) and N(2)−Zr−O(2) planes (171°) and O(1)−Zr−N−C_{t-Bu} dihedral angles of 158° and 176°. These angles are comparable to what are found for the twisted *mer* ligand in [t-BuNON]Zr(η^2-C_2H_4)(PMe_3)$_2$ (Table 5). The ligand oxygen donor atom (O(1)) is essentially planar, judging from the sum of the angles around it (359°), as found also in [t-BuNON]Zr(η^2-C_2H_4)(PMe_3)$_2$. The CH_3 group occupies the position approximately *trans* to the ligand's oxygen donor (C(1)−Zr−O(1) = 159.58(16)°), and the THF donors are mutually *trans*. The Zr−ligand bonds are all somewhat longer than they are in {[t-BuNON]-ZrMe}[$MeB(C_6F_5)_3$], as would be expected in a compound with a higher coordination number.

Crystals of {[t-BuNON]ZrMe(DME)}[$B(C_6F_5)_4$] suitable for single-crystal X-ray diffraction were obtained from mixtures of DME and pentane (Tables 2 and 4, Figure 7). The Zr atom is in a pseudooctahedral environment with the [t-BuNON]$^{2-}$ ligand in a twisted *fac* conformation. The twisted *fac* conformation is charac-

(45) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, K. M. A. *Organometallics* **1994**, *13*, 2235.
(46) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015.

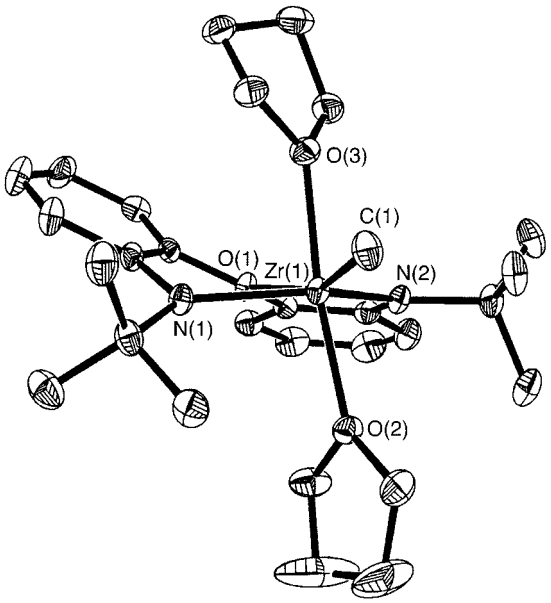


Figure 6. ORTEP drawing (50% probability level) of the structure of $\{[t\text{-BuNON}]Zr(CH_3)(THF)_2\}^+$. (Anion not shown.)

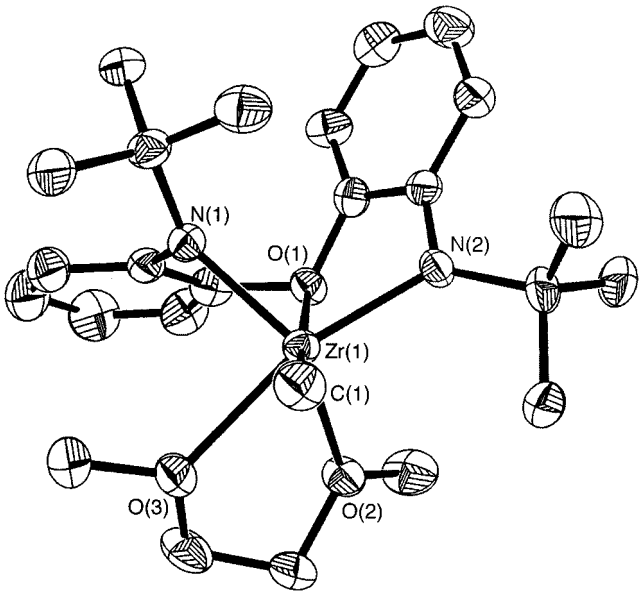
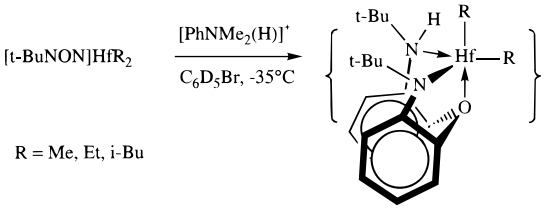


Figure 7. ORTEP drawing (50% probability level) of the structure of $\{[t\text{-BuNON}]Zr(CH_3)(DME)\}^+$. (Anion not shown.)

terized by an angle between the N(1)−Zr−O(1) and N(2)−Zr−O(2) planes of close to 115° and O(1)−Zr−N−C_{t-Bu} dihedral angles similar to those found in $\{[t\text{-BuNON}]ZrMe\}[MeB(C_6F_5)_3]$ (132° and 145°) and $[t\text{-BuNON}]ZrMe_2$ (143° and 146°). The CH_3 group is *trans* to the $[t\text{-BuNON}]^{2-}$ ligand's oxygen donor (O(1)−Zr−C(1) = 171.1(2)°), with the DME coordinated to the Zr atom in the two positions approximately *trans* to the amido nitrogen donors with Zr−O bond distances of 2.259(5) (to O(2)) and 2.339(5) Å (to O(3)). The Zr−O(1) bond length (2.458(5) Å) is the longest of the Zr−O_{NON} bond lengths in the three complexes in Table 4, which we assume to be a consequence of the six-coordinate geometry combined with the greater degree of conformational strain associated with the twisted *fac* ligand relative to a twisted *mer* ligand. It is interesting to note the significant distortion of the six-coordinate core in $\{[t\text{-BuNON}]ZrMe(DME)\}^+$ from octahedral geometry and its strong similarity with the distorted core in $\{[t\text{-BuNON}]ZrCl_2\}_2$ (Figure 2). In $\{[t\text{-BuNON}]ZrCl_2\}_2$ Cl(1) is in a position with respect to Zr(A) (and Cl(1A) with respect to Zr in Figure 2) that is analogous to the position of O(3) in $\{[t\text{-BuNON}]ZrMe(DME)\}^+$; both coordinate to the face on a five-coordinate core that is more "open" as a consequence of the *tert*-butyl group on the amido nitrogen (N(1) in $\{[t\text{-BuNON}]ZrMe(DME)\}^+$) turning toward the other amido ligand, i.e., being twisted in a clockwise direction in the view in Figure 7. (In Figure 2 the twist at Zr(A) is clockwise; the twist at the other Zr center is counterclockwise.) The chloride and oxygen that are bound to this more open face in less than an ideal position have the longer Zr−ligand bond lengths, e.g., Zr−O(2) = 2.259(5) Å, while Zr−O(3) = 2.339(5) Å. On the NMR time scale at room temperature we believe that $\{[t\text{-BuNON}]ZrMe(DME)\}^+$ is oscillating from one twisted *fac* form to the other, thereby yielding equivalent DME methyl (proton or carbon) resonances but still inequivalent methylene proton resonances ("up" and "down").

Addition of 1 equiv of $[PhNMe_2H][B(C_6F_5)_4]$ to a C_6D_5Br solution of $[t\text{-BuNON}]HfMe_2$ at 22 °C produced $\{[t\text{-BuNON}]HfMe(PhNMe_2)\}[B(C_6F_5)_4]$ in high yield, according to NMR spectra. The ^1H NMR spectrum of $\{[t\text{-BuNON}]HfMe(PhNMe_2)\}[B(C_6F_5)_4]$ in C_6D_5Br shows a methyl resonance at 0.89 ppm, a singlet at 2.79 ppm for bound Me_2NPh, and a resonance at 2.66 ppm for a trace of free Me_2NPh. The $^{13}C\{^1H\}$ NMR spectrum of $\{[t\text{-BuNON}]Hf(^{13}CH_3)(PhNMe_2)\}[B(C_6F_5)_4]$ contains a methyl resonance at 64.90 ppm (cf. 56.32 ppm in $[t\text{-BuNON}]HfMe_2$). Addition of approximately 1 equiv of free dimethylaniline yields a resonance at 2.66 ppm for the methyl group in free aniline. These data suggest that exchange of coordinated and free aniline is slow on the NMR time scale at room temperature. When this sample is heated, the methyl resonances for bound and free dimethylaniline broaden and coalesce between 70 and 80 °C. No significant decomposition was observed, even when the sample was held at 80 °C for 10−15 min, and the original spectrum was regenerated when the sample was cooled back to room temperature. The analogous Zr compound will not survive this treatment, as noted earlier.

Protonation of $[t\text{-BuNON}]HfMe_2$ with 1 equiv of $[PhNMe_2H][B(C_6F_5)_4]$ in C_6D_5Br at −40 °C led to the rapid dissolution of the sparingly soluble ammonium reagent, but there was no obvious evolution of methane, as there is in a similar reaction performed at 22 °C. A proton NMR spectrum at −35 °C suggested that two methyl groups were still present in a complex that lacks a plane of symmetry. We propose that one amido nitrogen has been protonated and the unsymmetric dimethyl complex shown in eq 3 has been formed.



(3)

Important spectral features for $\{[t\text{-BuNHC}_6H_4OC_6H_4N\text{-}$

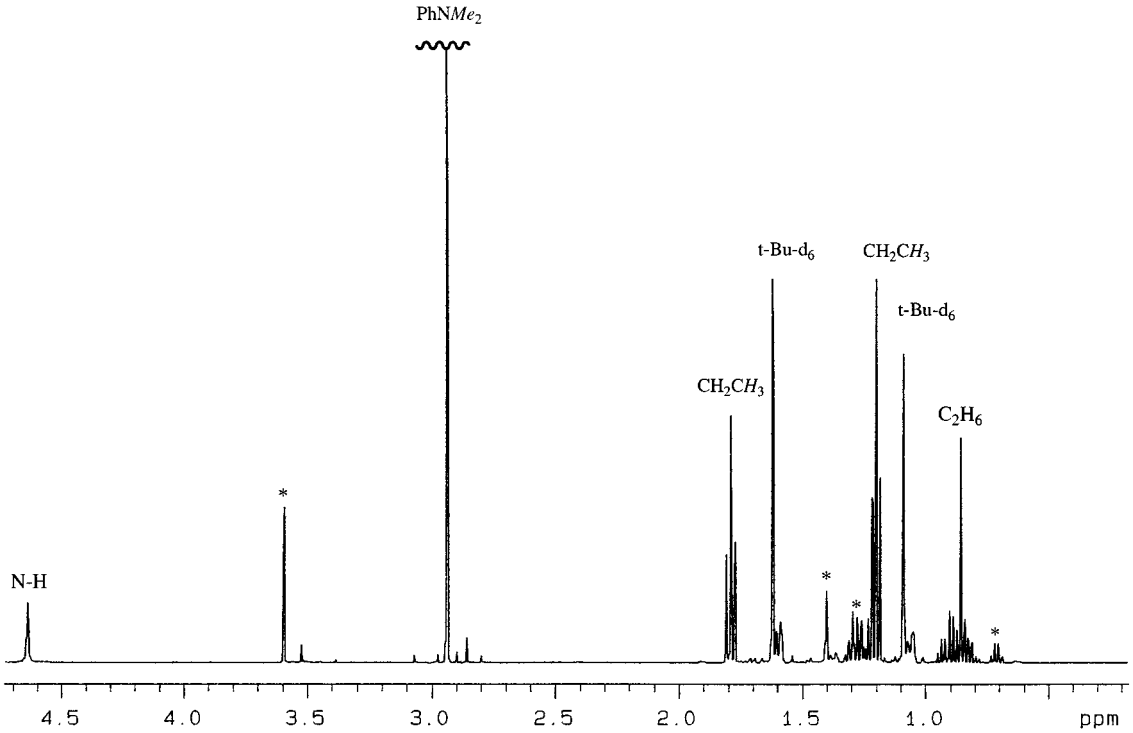


Figure 8. 500 MHz ^{1}H NMR spectrum of $\{[t\text{-}BuNHC_6H_4OC_6H_4N\text{-}t\text{-}Bu]HfEt_2\}^+$ in CD_2Cl_2 at 22 °C. *Resonances for what is proposed to be [t-BuNON]HfCl(Et)(Me_2NPh).

t-Bu]$HfMe_2\}^+$ include two equally intense *tert*-butyl resonances at 1.06 and 1.03 ppm and two hafnium methyl resonances at 0.55 and 0.53 ppm. A slightly broadened singlet at 4.33 ppm with a relative intensity of 1 was assigned to the N−H proton. The solution also contained free Me_2NPh, according to the chemical shift of the *Me*$_2$NPh protons (2.53 ppm at −35 °C). Over the course of several minutes, resonances for {[t-BuNON]-HfMe(PhNMe_2)}$^+$ and methane increased in intensity as those for $\{[t\text{-}BuNHC_6H_4OC_6H_4N\text{-}t\text{-}Bu]HfMe_2\}^+$ gradually disappeared. The generation of $\{[t\text{-}BuNHC_6H_4\text{-}OC_6H_4N\text{-}t\text{-}Bu]HfMe_2\}^+$ was always accompanied by the formation of substantial amounts of {[t-BuNON]HfMe-(PhNMe_2)}$^+$, even when the reaction was performed at −40 °C. The details of how {[t-BuNON]HfMe(PhN-Me_2)}$^+$ forms from $\{[t\text{-}BuNHC_6H_4OC_6H_4N\text{-}t\text{-}Bu]HfMe_2\}^+$ are not known.

Progressively more stable "N−H" species resulted from protonation of [t-BuNON]$HfEt_2$ or [t-BuNON]Hf-(i-Bu)$_2$ by [PhNMe_2H][B(C_6F_5)$_4$] in cold CD_2Cl_2. At 22 °C $\{[t\text{-}BuNHC_6H_4OC_6H_4N\text{-}t\text{-}Bu]HfEt_2\}^+$ persists for hours. The ^{1}H NMR spectrum of $\{[t\text{-}BuNHC_6H_4OC_6H_4N\text{-}t\text{-}Bu]HfEt_2\}^+$ (Figure 8) includes a singlet at 4.64 ppm arising from the N−H moiety and two sets of *tert*-butyl and ethyl resonances. The α-protons on the ethyl ligands are diastereotopic, as indicated by two complex multiplets at 0.87 and 1.23 ppm, as should be the case for the unsymmetric species shown in eq 3. Ethane (δ_H = 0.85 ppm) was liberated gradually and free Me_2NPh consumed over the course of several hours as resonances appear for what we propose to be a monochloride complex [t-BuNON]HfCl(Et)(PhNMe_2), formally the product of chloride abstraction by putative {[t-BuNON]HfEt-(PhNMe_2)}$^+$.

The ^{1}H NMR spectrum of $\{[t\text{-}BuNHC_6H_4OC_6H_4N\text{-}t\text{-}Bu]Hf(CH_2CHMe_2)_2\}^+$ in CD_2Cl_2 at 22 °C showed the N−H resonance at 4.89 ppm and resonances consistent with formation of an unsymmetric species of the type shown in eq 3. The two isobutyl methyne multiplets are well-separated at 2.41 and 1.52 ppm. Slow decomposition of $\{[t\text{-}BuNHC_6H_4OC_6H_4N\text{-}t\text{-}Bu]Hf(CH_2CHMe_2)_2\}^+$ in CD_2Cl_2 over the course of 1 day yielded isobutane and resonances consistent with formation of a monoisobutyl chloride complex.

Several base-stabilized methyl cations could be prepared by oxidation of [t-BuNON]$HfMe_2$ with [Cp′$_2$Fe]-BPh_4 (Cp′ = η^5-C_5H_4Me) in the presence of oxygen donors (THF or 1,2-dimethoxyethane) in toluene. {[t-BuNON]HfMe(THF)$_2$}BPh_4 was obtained in 62% yield as colorless crystals. Proton and carbon NMR spectra in CD_2Cl_2 showed that it is approximately an equimolar mixture of bis-THF adducts, one that has two planes of symmetry (believed to be the *mer* isomer) and one that has one plane of symmetry (believed to be the *fac* isomer) with structures that are analogous to those of *mer*-{[t-BuNON]ZrMe(THF)$_2$}$^+$ and *fac*-{[t-BuNON]-ZrMe(DME)}$^+$, respectively, described above. The methyl resonance in the *mer* isomer is found at 0.72 ppm and in the *fac* isomer at 0.55 ppm. Lowering the temperature to −40 °C did not change the relative intensities of each set of resonances, but in C_6D_5Br the *mer*/*fac* ratio was found to be 2.4. The *fac* resonances could be assigned on the basis of the location of the *tert*-butyl and methyl resonances in the related DME complex, {[t-BuNON]HfMe(DME)}BPh_4, in which the Hf−CH_3 resonance is found at 0.51 ppm. Addition of a slight excess of DME to a dichloromethane solution of {[t-BuNON]HfMe(THF)$_2$}BPh_4 at 22 °C resulted in the quantitative formation of {[t-BuNON]HfMe(DME)}-BPh_4, while dissolution of {[t-BuNON]HfMe(DME)}-BPh_4 in THF and cooling to −40 °C gave back crystalline {[t-BuNON]HfMe(THF)$_2$}BPh_4. Addition of THF or DME to {[t-BuNON]HfMe(PhNMe_2)}[B(C_6F_5)$_4$] in C_6D_5-Br generated spectra for the THF and DME adducts,

Table 6. Data for Poly(1-hexene) Prepared at 0 °C in Chlorobenzene Employing {[t-Bu-NON]ZrMe(PhNMe$_2$)}[B(C$_6$F$_5$)$_4$] as the Initiator[a]

entry	1-hexene (equiv)	initiator (μmol)	M_n(calcd)	M_n(found)	M_w/M_n
1	49	49	4144	4877	1.14
2	179	45	15027	14890	1.08
3	229	52	19306	19520	1.04
4	288	50	24262	24780	1.02
5	343	47	28902	24590	1.05
6	399	52	33593	35820	1.04
7	408	55	34349	28030	1.03
8	517	46	43481	39310	1.03
9	1230	45[b]	103500	102500	1.11
10	1565	46 (3.5 h)	131700	97550	1.20
11	1635	44[b]	137700	124900	1.11

[a] The initiator was prepared in situ and the reaction time was 1 h, unless noted otherwise; see Experimental Section for full details. Polymer yields in each case were essentially quantitative. [b] For 10 h at −10 °C.

respectively, that were identical to the spectra for the isolated BPh_4^- salts, consistent with no coordination or reaction of BPh_4^- with the metal in the BPh_4^- salts.

All attempts to observe a titanium cation in chlorobenzene or bromobenzene prepared by treating [t-BuNON]TiMe$_2$ with [Ph$_3$C][B(C$_6$F$_5$)$_4$] or [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] failed. The appearance of the sample was consistent with decomposition to dark oily materials that could not be identified.

Polymerization of 1-Hexene. We employ the polymerization of 1-hexene as a means of evaluating catalysts for controlled polymerizations, primarily because 1-hexene can be handled easily and because poly(1-hexene) is soluble and easy to characterize by gel permeation chromatography at room temperature. Reactions involving zirconium initiators were run in a batch mode in chlorobenzene at 0 °C with a known amount of initiator and activator, unless otherwise noted. (Polymerization reactions were run at 0 °C in order to avoid a rise in temperature above 30 °C and irreversible decomposition of the catalyst.[34]) Data are shown in Table 6 for the polymerization of 1-hexene by {[t-BuNON]ZrMe(PhNMe$_2$)}[B(C$_6$F$_5$)$_4$]. The yield of poly(1-hexene) in all cases was quantitative.

The poly(1-hexene) has a narrow molecular weight distribution, consistent with a single polymerization site and little or no chain termination or transfer during the course of the polymerization reaction. The number average molecular weights (M_n(found), measured by light scattering) are in good agreement with the expected values (M_n(calcd)). The measured molecular weights appear to deviate from the expected values at higher monomer loadings, although the inherent errors in measuring the molecular weight of poly(1-hexene) are large as a consequence of the small change in refractive index with concentration (dn/dc). (See Experimental Section.) Polymers with the expected molecular weights in excess of 100 000 can be formed at −10 °C. Preparation of higher molecular weight polymers is impractical using simple stirring techniques, as the reaction mixtures become too viscous.

1-Hexene is also polymerized by {[t-BuNON]ZrMe}[B(C$_6$F$_5$)$_4$] (prepared using the trityl method) in chlorobenzene at 0 °C, although characterization of such polymers is not yet complete. Results concerning the use of {[t-BuNON]ZrMe}[B(C$_6$F$_5$)$_4$] and other initiators for 1-hexene and the polymerization of other monomers will be reported in due course elsewhere.

Labeling experiments suggest that an initiator prepared from [t-BuNON]Zr(^{13}CH$_3$)$_2$ and [Ph$_3$C][B(C$_6$F$_5$)$_4$] in bromobenzene-d_5 will polymerize 1-hexene or 1-nonene by a 1,2-insertion process and that living poly(1-hexene) decomposes at ∼40 °C in 10 min to yield largely, but not exclusively, the product expected by β hydride elimination.[34] These results were confirmed here. The poly(1-hexene) had a ^{13}C NMR spectrum essentially identical to that reported by McConville.[30] In C$_6$D$_5$Br the six resonances are found at 41.1 (br), 35.2 (br m), 33.2 (br s), 29.4 (m), 24.2 (∼s), and 15.2 (s) ppm; note that the region between 24.2 and 15.2 contains no resonances. The last two resonances were assigned to C$_5$ and C$_6$ (the methyl group at the end of the side chain), respectively, where the numbers correspond to those in the 1-hexene monomer. The addition of 1 equiv of 1-hexene to {[t-BuNON]Zr(^{13}CH$_3$)}[B(C$_6$F$_5$)$_4$] yielded a solution whose ^{13}C NMR spectrum consisted primarily of several resonances near ∼20 ppm, where one would expect the resonance for a methyl adjacent to a methyne carbon to be found, in addition to resonances near 30.8 and 24.0 ppm that have been assigned to the first and second 1,2-insertion products, respectively.[34] Addition of 5 equiv of 1-hexene to a rapidly stirred solution of activated [t-BuNON]Zr(^{13}CH$_3$)$_2$ resulted in the complete consumption of the zirconium methyl cation, which suggests that k_p/k_i is on the order of 5 or less.[47] The chemical shift for a ^{13}CH$_3$ group bound next to a methylene carbon, which would be the result of a initial 2,1-addition process, would be expected to fall in the area between 10 and 15 ppm.[34] Upon the addition of 5 equiv of 1-hexene to the zirconium methyl cation, a resonance at ∼15 ppm is observed, but this resonance is due to natural abundant ^{13}C in the methyl group in the side chain of poly(1-hexene) (see above) and has an intensity of ∼5% that of the resonances at 20 ppm for the labeled methyl group from the initiator, as expected. The low intensity of any resonance arising from the ^{13}C label in the initial methyl group at a position other than ∼20 ppm leads us to conclude that the percentage of 1,2-insertion in the first step of the polymerization reaction is greater than at least 95%.

Analogous experiments with {[t-BuNON]HfMe(PhNMe$_2$)}[B(C$_6$F$_5$)$_4$] as an initiator in C$_6$D$_5$Br at 22 °C also yielded poly(1-hexene) (Table 7). As indicated by entries 2 and 5, polymers prepared near room temperature had molecular weights 2 to 3 times greater than expected for a well-behaved living polymerization in which k_p is on the same order as k_i. The molecular weights were approximately those expected when polymerizations were performed at 50 °C if no more than 150 equiv of 1-hexene was employed (entries 1, 3, and 4), but M_n(found) dropped below M_n(calcd) in attempts to prepare longer polymers (entries 6 and 7). GPC traces of the polymers revealed unimodal distributions of molecular weights and relatively low polydispersities. No poly(1-hexene) was isolated in polymerizations at 22 °C to which additional Me$_2$NPh (3 equiv) had been added, consistent with tight binding of PhNMe$_2$ to Hf

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Table 7. Data for Poly(1-hexene) Prepared at 0 °C in Chlorobenzene Employing {[t-Bu-NON]HfMe(PhNMe$_2$)}[B(C$_6$F$_5$)$_4$] as the Initiator[a]

entry	1-hexene (equiv)	time[b] (min)	temp (°C)	M_n(calcd)	M_n(found)	PDI
1	50	72	50	4208	7900	1.53
2	100	100	21	8416	24600	1.20
3	150	93	50	12624	14300	1.74
4	150	64	50	12624	10200	1.49
5	200	95	22	16832	35000	1.19
6	250	58	50	21040	13000	1.33
7	400	465	50	33664	10600	1.30

[a] The initiator was prepared in situ and the reaction time was 1 h, unless noted otherwise; see Experimental Section for full details. Polymer yields in each case were essentially quantitative. [b] Time was that required for complete consumption of 1-hexene.

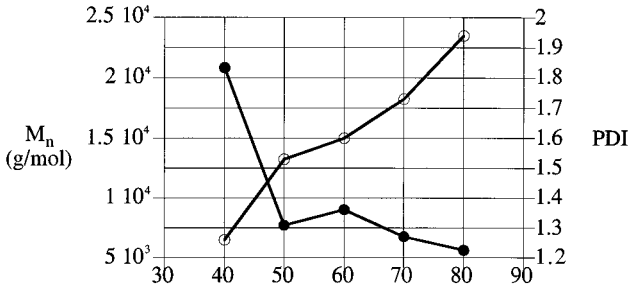

Figure 9. Plot of M_n (●) and PDI (○) for poly(1-hexene) prepared at temperature T with Hf catalyst. (See Experimental Section for experimental details.)

(relative to Zr) and required loss of PhNMe$_2$ in order for an olefin to access the metal.

Averaged values for M_n(found) and PDI for poly(1-hexene) (two runs each) prepared from 100 equiv of 1-hexene at 10 °C intervals between 40 and 80 °C are shown in Figure 9. In each case the yields of poly(1-hexene) were essentially quantitative. The expected value for M_n is 8416 for a well-behaved living polymerization in which k_p is on the same order as k_i. It is clear that at 40 °C M_n(found) is much greater than M_n(calcd), approaches the expected value at temperatures between 50 and 60 °C, and then continues to decrease as the temperature is increased, while the relatively low values for PDI at 40 °C increase to almost 2 at 80 °C. The inherent inaccuracy of determining the M_n for poly(1-hexene) does not allow us to conclude with confidence that M_n actually decreases below the expected value of ~8400, although that seems to be the trend.

The complete consumption of 2 equiv of 1-hexene by {[t-BuNON]Hf(^{13}CH$_3$)(PhNMe$_2$)}[B(C$_6$F$_5$)$_4$] in C$_6$D$_5$Br at 22 °C was confirmed by ^{1}H NMR spectroscopy. The ^{13}C{^{1}H} NMR spectrum of the resulting solution showed that it contained a large amount of unreacted initiator (δCH_3 = 64.91). Several closely spaced resonances centered near 20 ppm were assigned to the terminal ^{13}CH$_3$ end groups next to a methyne carbon, analogous to what is observed in zirconium experiments described above, which suggests that 1-hexene inserts into the Hf(^{13}CH$_3$) bond primarily in a 1,2 manner. The ^{13}C{^{1}H} NMR spectra in experiments described here show no resonances between 10 and 15 ppm when only 1 equiv of 1-hexene was employed. After addition of 20 more equivalents of 1-hexene to the same sample, the ^{13}C{^{1}H} NMR spectrum still showed the presence of unreacted initiator and more intense resonances arising from poly(1-hexene). Therefore it appears that the rate of propagation is significantly greater than the rate of initiation, *if* we assume that 1-hexene mixes completely with the initiator before much is polymerized. Resonances that could be assigned to the first and second insertion products, which was possible in the Zr system,[34] were not observed, consistent with a much larger ratio of k_p to k_i in the Hf system than in the Zr system. Unfortunately, detailed kinetic investigations that might yield definitive values for k_p and k_i were prevented by the fact that unreacted initiator persisted even after the consumption of 200 equiv of 1-hexene, at which point solutions were prohibitively viscous for NMR analyses. One possible explanation of the observed results is that dimethylaniline is much more strongly bound in the initiator (which has the smallest alkyl group) than in the propagating species.

In view of the failure to observe a titanium cation in chlorobenzene or bromobenzene upon treating [t-BuNON]-TiMe$_2$ with [Ph$_3$C][B(C$_6$F$_5$)$_4$] or [PhNMe$_2$H][B(C$_6$F$_5$)$_4$], we were not surprised to find that all attempts to polymerize 1-hexene in a well-behaved fashion using activated [t-BuNON]TiMe$_2$ failed. We also found that none of the zirconium or hafnium cations that contained an external oxygen donor (diethyl ether, THF, DME) was active for the polymerization of 1-hexene and that addition of diethyl ether, THF, or DME to any active system led to an immediate loss of activity. (The ether complex, {[t-BuNON]ZrMe(ether)$_2$}[B(C$_6$F$_5$)$_4$], yielded traces of poly(1-hexene) after 18 h at 60 °C.) Polymerization of 1-hexene by "{[t-BuNON]ZrMe(2,4-lutidine)}-[B(C$_6$F$_5$)$_4$]" (prepared by adding 1 equiv of 2,4-lutidine to {[t-BuNON]ZrMe(PhNMe$_2$)}[B(C$_6$F$_5$)$_4$]) at 0 °C also failed.

Discussion

It has been known for some time that titanium alkyl complexes that contain amido ligands are more stable than simple chlorides.[48−51] Even (R′$_2$N)$_3$TiR complexes in which R contains one or more β protons (e.g., Et, Pr, i-Pr) were found to be stable at temperatures up to 0 °C, which at the time was an unusually high stability for titanium alkyl species containing a β proton.[48,52] The extensive work of Bürger revealed that decomposition of dialkylamido titanium complexes often involved an N−C bond cleavage[49] or abstraction of a proton α to nitrogen.[53] Bürger also noticed that trimethylsilyl-substituted amido complexes were much more stable than dialkylamido complexes,[54] a fact that he attributed to the lower basicity of nitrogen atoms that have a silyl substituent. Andersen prepared a variety of diamido group 4 metal dialkyl complexes,[55,56] especially those in

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which the amide was $[(Me_3Si)_2N]^-$. He found (inter alia) that $[(Me_3Si)_2N]_2TiMe_2$ was significantly more stable than the analogous $(Me_2N)_2TiMe_2$ compounds prepared by Bürger. Andersen also showed that complexes of the type $[(Me_3Si)_2N]_2ZrR_2$ were relatively stable not only for R = Me but for R = Et and documented decompositions that involved double CH bond activation in a TMS group.[55] The greater stability of the sterically protected TMS complexes, along with the ease of synthesizing TMS-substituted amines, is presumably part of the reason many explorations of group 4 amido chemistry since then have employed TMS-substituted amido complexes. (Notable exceptions are recently reported complexes of the type $(Cy_2N)_2TiR_2$, in which R is neopentyl, trimethylsilylmethyl, and other alkyls that do not contain a β proton.[57,58]) This is unfortunate, at least as far as the search for olefin polymerization catalysts are concerned, since TMS-substituted amido complexes in general do not appear to be robust enough for chemistry as demanding as that involved in olefin polymerizations. (Complexes in which a dimethylsilyl group connects a cyclopentadienyl ring and an amido nitrogen are notable exceptions.[28]) For example, we have found that although $[(Me_3SiN\text{-}o\text{-}C_6H_4)_2O]ZrMe_2$ can be prepared readily, it cannot be activated to yield well-behaved catalysts for the polymerization of 1-hexene.[59] As Andersen showed, CH activation is always a potential problem with TMS-substituted amido groups, but other reactions such as silyl migrations also might be relatively facile in some circumstances.

The use of bidentate bisamido ligands in group 4 chemistry can be traced back to Bürger,[50] who studied a variety of bidentate diamido titanium complexes, among them complexes that contain relatively simple $[TMSNCH_2CH_2NTMS]^{2-}$ and $[TMSNCH_2CH_2CH_2NTMS]^{2-}$ ligands, and also a variety of spirocyclic bidentate diamido complexes. One might suspect bidentate diamido ligands to be relatively resistant to some forms of decomposition compared to analogues that contain related monodentate amido ligands, although no direct comparisons are possible. Since 1990 a variety of group 4 complexes have been reported that contain bidentate diamido ligands, many of them without Si−N bonds.[19,30,31,33,34,42,60−79] Complexes that contain "diamido/donor" ligands in which the donor is in the central position of a tridentate ligand are of relatively recent vintage,[33,34,60,61,65−67,70−76,80,81] especially those that do not contain Si−N bonds.[33,34,65−67,70,71,80,81]

There is a good deal of evidence in the recent literature that diamido dialkyl group 4 metal complexes can be relatively resistant toward β hydride abstraction reactions in the alkyl groups. The instability of many amido ligands, especially trimethylsilyl-substituted amido ligands, toward reactions such as CH activation perhaps has masked a natural resistance toward β hydride abstraction in amido complexes. Stable dialkyl complexes in which the alkyl contains a β proton have begun to appear in group 4 metal chemistry in complexes that contain at least one metal−amido bond.[82−86] The first stable diisobutyl complex of titanium also was reported recently,[69] and complexes of the type $[C_5H_3N\text{-}2,6\text{-}(CH_2N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)]ZrR_2$ where R = propyl or butyl have been found to be isolable species.[87] An increase in the stability of group 4 dialkyl complexes toward β hydride abstraction as one proceeds from Ti to Zr to Hf that we have noted in this work is typical of what has been found in metallocene chemistry. For example, it is known that Cp_2TiEt_2[88] and Cp_2TiBu_2[89] decompose readily, and in the presence of PMe_3, Cp_2TiEt_2 decomposes to yield $Cp_2Ti(PMe_3)_2$.[43] Cp_2ZrEt_2 is also not isolable, although Cp_2HfEt_2 is isolable.[90] Dialkyl zirconocene complexes (alkyl = Et, Pr, Bu) are known to decompose to yield olefin adducts, which can be trapped as PMe_3 adducts.[43,91] The trend toward greater stabilities of dialkyl zirconocenes as the β protons become more sterically protected and less numerous (Et < Pr < i-Bu) has been documented by Negishi.[90,92]

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A potentially important issue for complexes that contain diamido/donor ligands is the structure of five-coordinate dialkyl complexes, especially when the ligand is flexible and can form more than one type of five-coordinate structure. We have used the structure of *five*-coordinate dialkyl precursors to *four*-coordinate cations as a measure of the degree of steric crowding that might be expected in a four-coordinate cation, using the argument that the anion will be couched on one face of that pseudotetrahedral cation. We have been operating on the theory that when a ligand adopts a *fac* coordination mode rather than a *mer* coordination mode in a five-coordinate dialkyl complex, then pseudotetrahedral *four*-coordinate cationic intermediates in polymerization reactions will be relatively crowded. The failure to prepare dineopentyl complexes, as found here, is actually a good sign that the four-coordinate cation in which the alkyl is a growing poly(1-hexene) chain may be crowded enough to keep the anion further away from the metal than would be the case otherwise.

The $[t\text{-BuNON}]^{2-}$ ligand was chosen on the basis of successful chemistry employing $[d_6\text{-t-BuNAryl}]^-$ ligands in early metal chemistry,[37,93−96] the proposed relatively high stability of the diphenyl ether backbone, and the lack of any readily abstractable protons α to the nitrogen or to the oxygen. The *tert*-butyl group is the largest readily available substituent one could envision placing on the amido nitrogen. The bulk of the *tert*-butyl group, along with the planarity of the *o*-phenylene "arms" and consequent interaction between two aryl protons *ortho* to the oxygen (if the aryl rings lie in the same plane), leads to a natural twisting of the backbone of the $[t\text{-BuNON}]^{2-}$ ligand, so that in five-coordinate species that contain group 4 metals a twisted *fac* conformation is preferred over the twisted *mer* coordination. The $[t\text{-BuNON}]^{2-}$ ligand "predisposes" five-coordinate dialkyl species or cationic monoalkyl species to have a crowded, twisted *fac* geometry. (A five-coordinate yttrium complex that contains the $[t\text{-BuNON}]^{2-}$ ligand in a twisted *mer* coordination has been structurally characterized. It was proposed that in this case the relatively large size of yttrium(3+) allows the $[t\text{-BuNON}]^{2-}$ ligand to adopt the twisted *mer* conformation.[97]) Interestingly, six-coordinate cationic monoalkyl solvated species were isolated in which the ligand had either a twisted *mer* or a twisted *fac* orientation. In a cationic pseudotetrahedral $\{[t\text{-BuNON}]MR\}^+$ complex we propose that the twisted *fac* conformation of the $[t\text{-BuNON}]^{2-}$ ligand becomes even more favorable in view of the likely contraction of the metal−ligand bonds and exacerbation of steric crowding. The importance of the *tert*-butyl group is emphasized by the finding that decreasing the size of the substituent on nitrogen from *tert*-butyl to isopropyl leads to five- and six-coordinate complexes that contain a *mer* form of the ligand and that activated $[i\text{-PrNON}]ZrMe_2$ initiators produce only 1-hexene oligomers.[98] We propose that activated $[i\text{-PrNON}]ZrMe_2$ will only oligomerize 1-hexene for reasons largely traceable to a higher rate of β elimination, possibly from more likely regioerrors (2,1-insertions). It is interesting to note that complexes that contain the analogous $[t\text{-BuNSN}]^{2-}$ ligand are considerably less well-behaved than $[t\text{-BuNON}]^{2-}$ complexes in terms of polymerization activity, even though they are predisposed to a *fac* geometry as a consequence of the relatively constant C−S−C angle (∼105°) and the reluctance of sulfur to become planar, relative to oxygen.[99] At this stage the reason for the instability of $\{[t\text{-BuNSN}]ZrR\}^+$ complexes relative to $\{[t\text{-BuNON}]ZrR\}^+$ complexes is not known.

We propose that the crowded tetrahedral environment in $\{[t\text{-BuNON}]ZrR\}^+$ complexes, where R is the growing poly(1-hexene) chain, most efficiently limits access to the cationic metal center by a bulky, poorly coordinating anion, encourages 1,2-insertion of 1-hexene, and discourages β elimination from an alkyl derived from 1,2-insertion. In $\{[t\text{-BuNON}]Zr(PhNMe_2)Me\}^+$ complexes the base is likely to be less labile than in the product of reaction with 1-hexene, so that k_i will naturally be less than k_p, and evidently significantly so in the case of $\{[t\text{-BuNON}]Hf(PhNMe_2)Me\}^+$. This may also be true of the anion in initiators prepared in the absence of a base but in the presence of a solvent such as chlorobenzene. The more "open" the coordination sphere, the more tightly the anion is likely to be associated with the cation, the greater the probability for 2,1-insertion, and the more opportunity for β elimination in what we *presume* to be a less stable cationic alkyl complex. Polymerization of ethylene by zirconium dimethyl complexes that contain the rigorously planar $[2,6\text{-}(ArylNCH_2)_2(C_5H_3N)]^{2-}$ ligand,[65,66] at least when activated by MAO, was not successful, although the reason is not yet known.[100] The theory that 2,1-regioerrors lead to relatively unstable and unreactive intermediates in propylene polymerizations catalyzed by activated zirconocene alkyls has been discussed in the literature recently.[101−105]

An important feature of cations that contain a diamido/donor ligand is the fact that more than one site for base (or anion) coordination to form a five-coordinate species, and therefore also for olefin attack, is possible. This behavior of pseudotetrahedral cations is unlike that of pseudo-three-coordinate metallocenes, where the resulting pseudotetrahedral transition state is basically of only one type. The possibility of multiple and competitive polymerization sites at a *single* metal center, a circumstance that might also depend on the nature of the olefin in question, is an additional complication in the systems described here that must be taken into account in future studies. Issues surrounding values of

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k_p versus k_i therefore are perhaps more complex than might appear initially.

The thermal stability of the pseudotetrahedral cationic zirconium intermediates in a polymerization of 1-hexene is not high. The greater stability of the Hf cations, at least with dimethylaniline coordinated to the metal, probably can be ascribed to a low concentration of four-coordinate cationic species. However, decomposition probably should not be attributed solely to irreversible β hydride elimination.[34] The two alternative modes of decomposition we favor at this stage are loss of a *tert*-butyl radical or carbonium ion from an amido nitrogen, as has been observed in a related diamido/phosphine ligand system,[106] or cleavage of the ligand backbone, as has been observed in a recent report concerning [i-PrNON]Ti(II) species.[98] However, other possibilities certainly cannot be excluded at this time, for example, "direct" CH activation in a *tert*-butyl group to produce isobutylene and an imido-like nitrogen.

Low-polydispersity polyolefins (as low as PDI = 1.1) have been obtained in the past in several early metal catalyst systems, usually at low temperatures (−60 to −20 °C).[107−110] Molecular weights usually are relatively low, in part as a consequence of the low temperatures that are generally required, and often are consistent with a low percentage of active polymerization sites. Cobalt[111] and nickel[112] catalysts have been discovered recently that contain α-diimine ligands and which appear to polymerize α-olefins in a living fashion, the latter at −10 °C. The pyridine-based α-diimine ligand in the nickel catalysts is strictly planar, and the characteristics of the catalyst are controlled to a significant degree by the steric demands of the 2,6-disubstituted aryl groups on the imine nitrogens. Low polydispersities are characteristic of a high rate of chain propagation relative to chain termination, whereas a polydispersity of 2.0 is characteristic of a polymer that is formed from identical catalyst sites with fixed rates of chain propagation and termination.[113] Polyolefins produced from well-defined "single-site" catalysts such as activated metallocenes typically have polydispersities between 2.0 and 2.5.[8] It often is difficult to prove that a process is living, unless chain initiation and chain growth can be observed and studied directly, e.g., by NMR techniques. That has been possible with the system reported here and Ni[112] and Pd[114] systems that contain pyridine-based α-diimine ligands. In the Ni and Pd systems the olefin often inserts in 2,1-fashion, and isomerizations ("chain-running") of a coordinated olefin are rampant.

So far it appears that diamido/donor ligands do not produce well-behaved titanium catalysts. Conversely, simple arylated diamido ligands that have been successful for titanium chemistry[30,31,64] have not yielded well-behaved zirconium catalysts.[100] The reason for this sharp disparity is not known at this stage. However, as far as diamido complexes of zirconium are concerned, we suspect that a pseudo-three-coordinate cation leaves the larger zirconium much too accessible and the alkyls susceptible to β elimination processes, either from 1,2-insertion products or from regioerrors (2,1-insertions).

We expect to explore some of the issues raised by this work in future studies of $\{[t\text{-BuNON}]MR\}^+$ catalysts and to continue to explore syntheses of other pseudotetrahedral $\{(\text{diamido/donor})MR\}^+$ species in which the steric crowding can be maximized when R is a growing polymer chain and in which 2,1-regioerrors thereby are minimized and the stability toward β hydride elimination processes is maximized.

Experimental Section

General Procedures. Unless otherwise noted all manipulations were performed under rigorous exclusion of oxygen and moisture in a dinitrogen-filled glovebox or using standard Schlenk procedures. Ether, THF, and pentane were sparged with dinitrogen followed by passage through two 1 gallon columns of activated alumina. Toluene and benzene were distilled from benzophenone ketyl. Methylene chloride was distilled from CaH_2. ^1H NMR spectra are referenced (in ppm) versus residual protons in the deuterated solvents as follows: 7.15 (C_6D_6), 7.27 ($CDCl_3$), 2.09 (toluene-d_8 methyl), 7.29 (C_6D_5-Br; most upfield resonance). ^{13}C NMR spectra are referenced as follows: 128.4 (C_6D_6), 77.2 ($CDCl_3$), 137.9 (toluene-d_8), 122.3 (C_{ipso} in C_6D_5Br). ^{31}P NMR spectra are referenced versus an external standard of 85% H_3PO_4 ($\delta = 0$). All NMR spectra were taken at room temperature (~22 °C) in C_6D_6 unless otherwise noted. Aromatic ligand resonances in ^1H and ^{13}C spectra are not assigned. Coupling constants usually are not provided unless necessary for the identification of a compound.

$Zr(NMe_2)_4$,[115] $Hf(NMe_2)_4$,[116] $TiCl_2(NMe_2)_2$,[117] $(2\text{-}NO_2C_6H_4)_2O$,[35] $(2\text{-}NH_2C_6H_4)_2O$,[36] and Me_3CCH_2MgCl[118] were prepared according to literature procedures. 2,4-Dimethyl-6-nitrophenol[119] was prepared according to a procedure reported for 2-*tert*-butyl-4-methylnitrophenol.[120] Zinc dust (97.5%) was purchased from Strem and activated with 5% aqueous HCl prior to use.[121] PMe_3 (Strem) and 1,4-dioxane (anhydrous, Aldrich) were stored under dinitrogen over 4 Å molecular sieves. All other reagents were used as received. C_6D_6 and toluene-d_8 (Cambridge Isotope Laboratories) were degassed with dinitrogen and dried over 4 Å molecular sieves for ~1 day prior to use. CD_2Cl_2 (Cambridge Isotope Laboratories) was stirred over CaH_2 for several days, vacuum transferred, and stored under dinitrogen over 4 Å molecular sieves. C_6D_5Br (Aldrich) was filtered through activated alumina and stored under dinitrogen over 4 Å molecular sieves. Elemental analyses were performed in our laboratories on a Perkin-Elmer 2400 CHN analyzer or at H. Kolbe, Mikroanalytisches Laboratorium (Mühlheim an der Ruhr, Germany).

GPC analyses were carried out on a system equipped with two Alltech columns (Jordi-Gell DVB mixed bed, 250 mm × 10 mm (i.d.)). The solvent was supplied at a flow rate of 1.0

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mL/min with a Knauer HPLC pump 64. HPLC grade CH_2Cl_2 was continuously dried and distilled from CaH_2. Molecular weights were measured using a Wyatt Technology miniDawn three-angle detector operating at 690 nm coupled to a Knauer differential-refractometer. The differential refractive index increment, d*n*/d*c*, was determined assuming that all polymer that was weighed for the run (usually ~5 mg to ±0.1 mg) eluted from the column. To minimize polymer weighing error, the average value for d*n*/d*c* (0.049 mL/g) from 18 runs (0.045−0.053 mL/g) was employed, and the molecular weights were recalculated.

(2-NO_2-C_6H_4)O(2′,4′-Me_2-6′-NO_2-C_6H_2). A 1 L one-neck flask was charged with 2,4-dimethyl-6-nitrophenol (47.5 g, 0.28 mol), 2-fluoronitrobenzene (40.0 g, 0.28 mol), K_2CO_3 (80.0 g, 0.58 mol), and DMSO (500 mL). The reaction mixture was stirred at 100 °C under an atmosphere of dinitrogen for 48 h. The dark red slurry was allowed to cool to room temperature and then poured onto ice/water (1.5 L). A beige solid immediately precipitated from the red solution. The mixture was stirred for 30 min and then filtered. The solid was liberally washed with water and dried in vacuo; yield 68.1 g (83%). The crude product was used for subsequent reactions without further purification. Recrystallization from hot methanol gave analytically pure tan needles: ^{1}H NMR ($CDCl_3$) δ 8.01 (d, 1), 7.71 (s, 1), 7.42 (m, 2), 7.15 (t, 1), 6.63 (d, 1), 2.44 (s, 3, *Me*), 2.22 (s, 3, *Me*); ^{13}C NMR ($CDCl_3$, only 11 aromatic resonances were identified) δ 150.8, 142.9, 142.2, 139.1, 137.5, 137.0, 134.4, 126.2, 124.0, 122.4, 115.7, 20.8, 16.2. Anal. Calcd for $C_{14}H_{12}N_2O_5$: C, 58.33; H, 4.20; N, 9.72. Found: C, 58.53; H, 4.22; N, 9.66.

(2-$NH_2C_6H_4$)O(2′,4′-Me_2-6′-$NH_2C_6H_2$). A Fischer−Porter bottle was charged with (2-$NO_2C_6H_4$)O(2′,4′-Me_2-6′-$NO_2C_6H_2$) (60.7 g, 0.21 mol), Pd/C (3.00 g, 10% Pd), and ethanol (500 mL). The slurry was stirred under dihydrogen (35 psi) at 65 °C for 24 h. The mixture was cooled to room temperature and filtered through Celite. The initially colorless filtrate turned orange upon exposure to air. All volatile components were removed in vacuo, leaving a light orange/brown solid or occasionally an orange oil; yield 46.9 g (98%). The crude product was used for subsequent reactions without further purification. It slowly darkens in air and is therefore best stored under dinitrogen. It may be crystallized as large off-white blocks by slow evaporation of a saturated ether solution: ^{1}H NMR ($CDCl_3$) δ 6.82 (m, 2), 6.59 (dd, 1), 6.47 (m, 3), 4.0 (br s, 2, N*H*$_2$), 3.66 (br s, 2, N*H*$_2$), 2.26 (s, 3, *Me*), 2.07 (s, 3, *Me*); ^{13}C NMR ($CDCl_3$) δ 144.8, 139.5, 138.0, 135.9, 135.3, 131.5, 122.4, 121.5, 118.7, 115.8, 114.9, 112.8, 21.2, 16.1. Anal. Calcd for $C_{14}H_{16}N_2O$: C, 73.66; H, 7.06; N, 12.27. Found: C, 73.69; H, 7.21; N, 12.43.

[2-Me(CD_3)$_2$CNHC_6H_4]$_2$O (H_2[t-BuNON]). (2-$NH_2C_6H_4$)$_2$O (18.8 g, 94 mmol) was dissolved in acetone-d_6 (120 g, 1.87 mol), and activated 4 Å molecular sieves (30 g) were added. After the condensation was complete (3−7 days, as judged by ^{1}H NMR) the molecular sieves were filtered off and rinsed with ether. All volatile components were removed from the ether solution of the ligand in vacuo. The imine dissolved in ether (60 mL) was slowly added to a precooled solution (acetone/dry ice) of methyllithium in ether (270 mL, 0.88 M). The reaction mixture was allowed to warm to room temperature and stirred. After 24 h the reaction mixture was quenched by pouring it slowly into a beaker filled with 500 mL of a mixture of ice and water. The product was extracted into hexane (3 × 100 mL), and the combined organic layers were filtered through a ~35 cm long and 2.5 cm wide alumina column. The solvent was evaporated in vacuo to afford a viscous orange oil; yield 16.7 g (55%): ^{1}H NMR ($CDCl_3$) δ 7.00 (m, 4), 6.68 (m, 4), 4.19 (br s, 2, N*H*), 1.35 (s, 6, C(CD_3)$_2$*Me*); ^{13}C NMR ($CDCl_3$) δ 145.24, 138.34, 123.62, 117.76, 117.30, 115.96, 50.81 (*C*(CD_3)Me), 29.81 (C(CD_3)$_2$*Me*), 29.28 (m, C(*C*D_3)$_2$Me); HRMS (EI) calcd for $C_{20}H_{16}D_{12}N_2O$ 324.295485; found 324.29549. Anal. Calcd for $C_{20}H_{16}D_{12}N_2O$: C, 74.02; H, 8.70; N, 8.63. Found: C, 74.41; H, 8.94; N, 8.30.

[2-Me(CD_3)$_2$CNHC_6H_4]O[2′,4′-Me_2-6′-Me(CD_3)$_2$CNHC_6H_2](H_2[t-BuNONMe_2]). (2-$NH_2C_6H_4$)O(2′,4′-Me_2-6′-$NH_2C_6H_2$) (10.18 g, 44.6 mmol) was dissolved in acetone-d_6 (60 g, 0.94 mol), and activated 4 Å molecular sieves (30 g) were added. After the condensation was complete (3−7 days, as judged by ^{1}H NMR) the molecular sieves were filtered off and rinsed with ether. All volatile components were removed in vacuo. The imine dissolved in ether (80 mL) was slowly added to a precooled solution (acetone/dry ice) of methyllithium in ether (130 mL, 0.86 M). The reaction mixture was allowed to warm to room temperature and stirred. After 24 h the reaction mixture was quenched by pouring it slowly into a beaker filled with 500 mL of a mixture of ice and water. The product was extracted into pentane (3 × 50 mL), and the solvents were evaporated in vacuo. The residue was redissolved in pentane (200 mL) and filtered through a ~40 cm long and 2.5 cm wide alumina column. The product was eluted with more pentane (400 mL). The pentane was evaporated in vacuo to afford a viscous pale yellow oil; yield 8.43 g (54%): ^{1}H NMR ($CDCl_3$) δ 7.01 (d, 1), 6.86 (t, 1), 6.70 (s, 1), 6.54 (t, 1), 6.40 (m, 2), 4.43 (s, 1, N*H*), 3.87 (s, 1, N*H*), 2.30 (s, 3, Ar*Me*), 2.00 (s, 3, Ar*Me*), 1.43 (s, 3, C(CD_3)$_2$*Me*), 1.26 (s, 3, C(CD_3)$_2$*Me*); ^{13}C NMR ($CDCl_3$) δ 146.1, 140.2, 139.3, 136.6, 134.6, 130.9, 122.0, 120.2, 117.6, 116.1, 114.5, 112.6, 51.4 (*C*(CD_3)$_2$Me), 51.0 (*C*(CD_3)$_2$Me), 30.3 (C(CD_3)$_2$*Me*), 30.1 (C(CD_3)$_2$*Me*), 29.9 (m, C(*C*D_3)$_2$Me), 21.8 (Ar*Me*), 16.5 (Ar*Me*); HRMS (EI) calcd for $C_{22}H_{20}D_{12}N_2O$ 352.326785; found 352.32679. Anal. Calcd for $C_{22}H_{20}D_{12}N_2O$: C, 74.94; H, 9.15; N, 7.94. Found: C, 74.91; H, 9.14; N, 7.96.

2-Ethyl-6-nitrophenol. To a cooled (0 °C) and vigorously stirred solution of 34.00 g (0.4 mol) $NaNO_3$ and 1.760 g (4 mmol) of $La(NO_3)_3{\cdot}6H_2O$ in 640 mL of a 1:1 mixture of concentrated HCl and water was added a solution of 48.88 g (0.4 mol) of 2-ethylphenol in 500 mL of diethyl ether over a period of 20 min.[122] The reaction was stirred for 2.5 h at 0 °C until no more starting material could be detected by TLC. The phases were separated, and the aqueous phase was extracted twice with 200 mL of diethyl ether. The combined organic phases were dried with Na_2SO_4, and the diethyl ether was removed in vacuo. The dark yellow oil was subjected to chromatography on silica with hexane first as an eluent, with gradually increasing amounts of CH_2Cl_2. Only the first yellow fraction was collected. All volatile components were removed in vacuo to leave a yellow-orange oil; 26.82 g (0.16 mol, 40%): ^{1}H NMR δ 10.95 (s, 1), 7.97 (d, 1), 7.46 (d, 1), 6.91 (t, 1), 2.75 (q, 2), 1.26 (t, 3); ^{13}C NMR δ 153.5, 136.6, 135.2, 133.5, 122.5, 119.5, 23.0, 13.6.

6-Ethyl-2,2′-dinitrodiphenyl Ether. A mixture of 2-ethyl-6-nitrophenol (16.72 g, 0.1 mol), 2-fluoronitrobenzene (14.11 g, 0.1 mol), and anhydrous K_2CO_3 (27.64 g, 0.2 mol) was heated in 100 mL of DMSO to 100 °C for 48 h. The mixture was poured into 500 mL of ice water. After 2 h the tan precipitate was filtered off and washed with water until the washings were colorless. The residue was dried in vacuo and recrystallized from 30 mL of boiling methanol to give a tan powder; 15.51 g (0.054 mol, 54%): ^{1}H NMR ($CDCl_3$) δ 7.97 (d, 1), 7.63 (d, 1), 7.45−7.38 (m, 2), 7.15 (t, 1), 6.60 (d, 1), 2.64 (q, 2), 1.21 (t, 3): ^{13}C NMR ($CDCl_3$) δ 151.1, 144.2, 143.2, 140.8, 139.1, 135.3, 134.4, 126.8, 126.4, 124.0, 122.6, 115.6, 23.4, 14.1. (Due to impurities, these chemical shifts are not completely reliable.)

6-Ethyl-2,2′-diaminodiphenyl Ether. In a pressure bottle, 15.14 g (52.5 mmol) of 6-ethyl-2,2′-dinitrodiphenyl ether was suspended in 50 mL of degassed ethanol, and 0.75 g of 10% Pd on activated carbon was added. The bottle was purged with N_2 three times and then pressurized with dihydrogen while stirring the solution. The pressure was adjusted to 40 psi, and the bottle was heated to 70 °C for 16 h. After the bottle had

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reached room temperature, the ethanol was removed in vacuo. The residue was dissolved in 75 mL of diethyl ether, and the solution was cooled to −60 °C. A tan precipate formed, which was filtered off using a precooled (−78 °C) frit. The residue was dried in vacuo. The product contains ∼10% of an unidentified impurity that contains one ethyl group; 6.30 g (27 mmol, 53% if pure product): ^{1}H NMR ($CDCl_3$) δ 7.03 (t, 1), 6.83 (dt, 2), 6.70 (dt, 2), 6.63 (dt, 1), 6.44 (d, 1), 4.02 (s, br, 2), 3.70 (s, br, 2), 2.51 (q, 2), 1.15 (t, 3); ^{13}C NMR ($CDCl_3$) δ 151.0, 144.0, 143.1, 140.6, 139.0, 135.4, 134.5, 126.8, 126.2, 123.9, 122.6, 115.5, 23.1, 14.0.

6-Ethyl-2,2′-diaminodiphenyl Ether Acetonediimine-d_6. 6-Ethyl-2,2′-diaminodiphenyl ether (6.30 g, 27 mmol) was dissolved in 20.0 g (310 mmol) of acetone-d_6. Activated 4 Å molecular sieves (15 g) were added, and the mixture was stirred for 16 h. The solution was filtered, and the molecular sieves were thoroughly washed with 150 mL of diethyl ether. The solvents were removed in vacuo to give an orange oil; 7.97 g (25 mmol, 96%): ^{1}H NMR ($CDCl_3$) δ 7.09 (t, 1), 6.98 (d, 1), 6.85 (dt, 1), 6.73−6.61 (m, 2), 6.42 (d, 1), 2.52 (q, 2), 2.19 (m, 1), 1.93 (m, 1), 1.85 (m, 1), 1.73 (m, 1), 1.13 (t, 3).

6-Ethyl-2,2′-bis(d_6-*tert*-butylamino)diphenyl Ether. A solution of 7.97 g (25 mmol) in 25 mL of diethyl ether was slowly added to 100 mL of a 0.7 M solution of methyllithium (obtained by dilution of 50 mL of a 1.4 M solution with 50 mL of diethyl ether) in diethyl ether (70 mmol) at −78 °C. The mixture was allowed to reach room temperature, was stirred for 16 h, and then was poured on 200 mL of ice. The phases were separated, and the aqueous phase was extracted with 150 mL of pentane. The combined organic phases were dried with Na_2SO_4, and the solvents were removed in vacuo. The dark green oil was purified by chromatography on silica with pentane/CH_2Cl_2 mixtures of gradually increasing polarity as the eluent. The first yellow fraction was collected, and the solvents were removed in vacuo to give an orange oil; 3.27 g (10 mmol, 39%): ^{1}H NMR ($CDCl_3$) δ 7.05 (t, 2), 6.89 (t, 2), 6.64 (d, 1), 6.53 (t, 1), 6.42 (d, 1), 4.46 (s, 1), 3.92 (s, 1), 2.44 (dm, 2), 1.45 (s, ∼4), 1.27 (s, ∼4), 1.13 (t, 3); ^{13}C NMR ($CDCl_3$) δ 146.2, 140.7, 140.4, 137.3, 136.5, 125.4, 122.2, 117.6, 116.0, 113.5, 112.6, ≈ 51.2, 30.0, 23.3, 14.7.

[t-BuNON]Ti(NMe$_2$)$_2$. A solution of butyllithium in hexane (4.2 mL, 1.6 M) was added to a solution of H_2[t-BuNON] (1.09 g, 3.36 mmol) in ether (30 mL) at −35 °C. The mixture was warmed to room temperature and stirred for 4 h. A suspension of $TiCl_2(NMe_2)_2$ (696 mg, 3.36 mmol) in ether (20 mL) was added to the solution containing the Li_2[t-BuNON] at −35 °C. The mixture was warmed to room temperature and stirred for 15 h. The mixture was filtered through Celite, and all volatile components were removed from the filtrate in vacuo. The residue was dissolved in a minimum of methylene chloride and layered with pentane. The mixture was cooled to −35 °C to afford an orange crystalline solid; yield 864 mg (56%). An analytically pure sample was obtained by recrystallization from ether: ^{1}H NMR δ 6.92 (m, 6), 6.63 (m, 2), 3.13 (s, 12, N*Me*$_2$), 1.28 (s, 6, C(CD$_3$)$_2$*Me*); ^{13}C NMR δ 150.9, 147.1, 124.37, 123.3, 120.3, 118.6, 60.2 (m, *C*(CD$_3$)$_2$Me), 47.8 (N*Me*$_2$), 32.4 (C(CD$_3$)$_2$*Me*), 31.9 (m, C(*C*D$_3$)$_2$Me). Anal. Calcd for $C_{24}H_{26}D_{12}N_4OTi$: C, 62.86; H, 8.35; N, 12.22. Found: C, 62.85; H, 8.34; N, 12.14.

[t-BuNON]TiCl$_2$. A Schlenk tube was charged with [t-BuNON]Ti(NMe$_2$)$_2$ (379 mg, 0.83 mmol), Me_3SiCl (270 mg, 2.49 mmol), and toluene (10 mL). The solution was heated to 110 °C for 7 days, during which time the solution turned black-purple. The volatile components were removed in vacuo, and the residue was recrystallized from a mixture of methylene chloride and pentane at −35 °C; yield 286 mg (78%): ^{1}H NMR δ 6.84 (m, 4), 6.57 (m, 4), 1.33 (s, 6, C(CD$_3$)$_2$*Me*); ^{13}C NMR δ 147.8, 142.1, 126.7, 124.4, 120.6, 118.9, 64.8 (m, *C*(CD$_3$)$_2$Me), 30.6 (C(CD$_3$)$_2$*Me*), 30.4 (m, C(*C*D$_3$)$_2$Me). Anal. Calcd for $C_{20}H_{14}D_{12}Cl_2N_2OTi$: C, 54.43; H, 5.89; N, 6.35. Found: C, 54.57; H, 5.96; N, 6.13.

[t-BuNON]TiMe$_2$. A solution of MeMgCl in THF (3.0 M, 350 μL) was added to a solution of [t-BuNON]$TiCl_2$ (230 mg, 0.52 mmol) in ether (10 mL) at −35 °C. The color immediately changed from dark purple to orange, and a white solid precipitated. The mixture was stirred for 15 min without further cooling. All volatile components were removed in vacuo, and the residue was extracted with pentane (∼10 mL) over a period of ∼5 min. The mixture was filtered through Celite, and the pentane was removed from the filtrate in vacuo to afford an orange-red solid, which was recrystallized from a mixture of ether and pentane at −35 °C; yield 162 mg (78%): ^{1}H NMR δ 6.87 (m, 6), 6.56 (m, 2), 1.60 (s, 6, Ti*Me*$_2$) 1.42 (s, 6, C(CD$_3$)$_2$*Me*); ^{13}C NMR δ 148.5, 143.5, 126.1, 122.1, 121.4, 119.3, 64.6 (Ti*Me*$_2$), 60.2 (*C*(CD$_3$)$_2$Me), 31.4 (C(CD$_3$)$_2$*Me*), 30.9 (m, C(*C*D$_3$)$_2$Me). Anal. Calcd for $C_{22}H_{20}D_{12}N_2OTi$: C, 65.98; H, 8.05; N, 6.99. Found: C, 66.07; H, 7.94; N, 6.84.

[t-BuNON]Zr(NMe$_2$)$_2$. H_2[t-BuNON] (6.48 g, 20 mmol) and $Zr(NMe_2)_4$ (5.34 g, 20 mmol) were dissolved in pentane (40 mL). Colorless crystals precipitated over a period of 2 days at 22 °C and were filtered off (6.9 g). The supernatant was concentrated and cooled to −35 °C overnight, yielding a second crop of colorless solid (1.15 g); total yield 8.05 g (80%): ^{1}H NMR δ 6.97 (m, 6), 6.55 (m, 2), 2.94 (s, 12, N*Me*$_2$), 1.33 (s, 6, C(CD$_3$)$_2$*Me*); ^{13}C NMR δ 147.8, 145.7, 125.6, 122.4, 118.3, 117.8, 57.0 (*C*(CD$_3$)$_2$Me), 43.6 (N*Me*$_2$), 32.1 (C(CD$_3$)$_2$*Me*), 32.0 (m, C(*C*D$_3$)$_2$Me). Anal. Calcd for $C_{24}H_{26}D_{12}N_4OZr$: C, 57.43; H, 7.57; N, 11.16. Found: C, 57.56; H, 7.76; N, 11.16.

[t-BuNON]ZrCl$_2$. Me_3SiCl (1.5 g, 13.74 mmol) was added to a suspension of [t-BuNON]Zr(NMe$_2$)$_2$ (2.295 g, 4.58 mmol) in ether (50 mL). The reaction mixture was stirred at room temperature for 20 h. All volatile components were removed from the mixture in vacuo, and the yellow solid was washed with pentane (10 mL) and dried; yield 2.06 g (93%). An analytically pure sample was obtained by crystallization from ether. For alkylation reactions the crude material was used without further purification: ^{1}H NMR δ 6.79 (m, 6), 6.54 (m, 2), 1.29 (s, 6H, C(CD$_3$)$_2$*Me*); ^{13}C NMR δ 147.1, 141.0, 127.4, 122.8, 122.4, 118.9, 58.7 (*C*(CD$_3$)$_2$Me), 30.6 (C(CD$_3$)$_2$*Me*), 30.1 (m, C(*C*D$_3$)$_2$Me). Anal. Calcd for $C_{20}H_{14}Cl_2D_{12}N_2OZr$: C, 49.77; H, 5.43; N, 5.80. Found: C, 49.84; H, 5.21; N, 5.68.

[t-BuNON]ZrI$_2$. A Schlenk tube was charged with [t-BuNON]Zr(NMe$_2$)$_2$ (3.5 g, 7.0 mmol), methyl iodide (15 g, 106 mmol), and toluene (100 mL). The pale yellow solution was heated to 50 °C for 2 days, during which time white Me_4NI precipitated from the reaction and the color of the solution turned bright orange. The Me_4NI was filtered off, the solvents were removed from the filtrate in vacuo, and the residue was washed with pentane (10 mL) to afford a yellow solid. The crude product can be recrystallized from toluene layered with pentane, but was used in subsequent reactions without further purification; yield 4.14 g (89%): ^{1}H NMR δ 6.79 (m, 6), 6.56 (m, 2), 1.36 (br s, 6, C(CD$_3$)$_2$C*H*$_3$); ^{13}C NMR (C_6D_6, 70 °C) δ 146.8, 139.4, 127.9, 124.0, 123.3, 119.4, 60.2 (m, *C*(CD$_3$)$_2$CH$_3$), 31.3 (C(CD$_3$)$_2$*C*H$_3$), 30.7 (m, C(*C*D$_3$)$_2$CH$_3$). Anal. Calcd for $C_{20}H_{14}D_{12}I_2N_2OZr$: C, 35.98; H, 3.93; N, 4.20. Found: C, 35.71; H, 3.94; N, 3.88.

[t-BuNONMe$_2$]Zr(NMe$_2$)$_2$. A solution of H_2[t-BuNONMe$_2$] (5.00 g, 14.2 mmol) and $Zr(NMe_2)_4$ (3.79 g, 14.2 mmol) in toluene (40 mL) was heated in a sealed Schlenk tube to 105 °C for 3 days. All volatile components were then removed in vacuo. Recrystallization of the light orange residue from pentane at −25 °C produced pale yellow microcrystalline material in 4 crops; yield 4.97 g (66%): ^{1}H NMR δ 7.13 (d, 1), 6.88 (t, 1), 6.72 (s, 1), 6.62 (d, 1), 6.53 (t, 1), 6.35 (s, 1), 3.15 (s, 6, N*Me*$_2$), 2.82 (s, 6, N*Me*$_2$), 2.21 (s, 3, Ar*Me*), 2.17 (s, 3, Ar*Me*), 1.51 (s, 3, C(CD$_3$)$_2$*Me*), 1.20 (s, 3, C(CD$_3$)$_2$*Me*); ^{13}C NMR δ 149.4, 146.3, 144.2, 143.0, 135.6, 130.4, 124.2, 122.5, 121.4, 120.8, 119.4, 113.3, 57.5 (m, *C*(CD$_3$)$_2$Me), 56.7 (m, *C*(CD$_3$)$_2$Me), 45.3 (N*Me*$_2$), 42.3 (N*Me*$_2$), 32.3 (C(CD$_3$)$_2$*Me*), 32.1 (C(CD$_3$)$_2$*Me*), 31.7 (m, C(*C*D$_3$)$_2$Me), 22.3 (Ar*Me*), 16.6 (Ar*Me*). Anal. Calcd for

$C_{26}H_{30}D_{12}N_4OZr$: C, 58.93; H, 7.99; N, 10.57. Found: C, 59.21; H, 8.10; N, 10.38.

[t-BuNONMe$_2$]ZrCl$_2$. Me_3SiCl (2.55 g, 23.5 mmol) was added to a suspension of [t-BuNONMe$_2$]Zr(NMe$_2$)$_2$ (4.59 g, 8.66 mmol) in ether (60 mL). After stirring the mixture at room temperature for 20 h all volatile components were removed in vacuo, leaving an analytically pure, bright yellow powder (4.31 g, 97%): ^{1}H NMR δ 6.77 (m, 2), 6.52 (s, 1), 6.47 (d, 2), 6.38 (s, 1), 2.18 (s, 3, Ar*Me*), 2.0 (s, 3, Ar*Me*), 1.53 (s, 3, C(CD$_3$)$_2$*Me*), 1.12 (s, 3, C(CD$_3$)$_2$*Me*); ^{13}C NMR δ 149.2, 141.9, 141.0, 139.0, 131.6, 125.8, 125.3, 122.3, 121.9, 120.9, 114.6 (only 11 aroamatic resonances were observed), 59.2 (*C*(CD$_3$)$_2$Me), 58.2 (*C*(CD$_3$)$_2$Me), 30.9 (C(CD$_3$)$_2$*Me*), 30.5 (C(CD$_3$)$_2$*Me*), 30.0 (m, C(*C*D$_3$)$_2$Me), 22.0 (Ar*Me*), 16.9 (Ar*Me*). Anal. Calcd for $C_{22}H_{18}D_{12}Cl_2N_2OZr$: C, 51.54; H, 5.90; N, 5.46. Found: C, 51.88; H, 6.07; N, 5.47.

[t-BuNONEt]Zr(NMe$_2$)$_2$. A 1.763 g (5 mmol) sample of 6-ethyl-2,2′-bis([d$_6$]-*tert*-butylamino)diphenyl ether and 1.334 g (5 mmol) of Zr(NMe$_2$)$_4$ were dissolved in 25 mL, and the mixture was heated in a sealed Schlenk tube at 100 °C for 24 h. The toluene was removed in vacuo, and the residue was recrystallized from pentane to give orange crystals; 1.724 g (3.25 mmol, 65%): ^{1}H NMR δ 7.10 (t, 1), 6.99 (t, 1), 6.87−6.79 (m, 2), 6.61−6.46 (m, 3), 3.12 (s, 6), 2.82 (s, 6), 2.79 (dt, 1), 2.55 (dt, 1), 1.15 (s, ∼4), 1.19 (t, 3), 1.18 (s, ∼4); ^{13}C NMR δ 149.3, 146.8, 144.3, 143.9, 136.9, 126.8, 124.2, 122.7, 120.8, 119.5, 117.9, 113.3, ∼57.3, 45.4, 42.2, 32.2, 23.5, 14.9.

[t-BuNONEt]ZrCl$_2$. A 1.152 g (2.2 mmol) sample of [t-BuNONEt]Zr(NMe$_2$)$_2$ and 0.6 g (5.5 mmol) of Me_3SiCl were dissolved in 10 mL of diethyl ether, and the mixture was stirred for 17 h. All volatile components were removed, and repeated coevaporation with pentane gave a yellow powder; 1.083 g (2.1 mmol, 96%): ^{1}H NMR δ 6.93 (t, 1), 6.82−6.60 (m, 4), 6.45 (m, 2), 2.76 (dt, 1), 2.40 (dt, 1), 1.50 (s, ∼4), 1.21 (t, 3), 1.11 (s, ∼4); ^{13}C NMR δ 148.9, 142.6, 141.7, 139.8, 138.1, 129.3, 125.4, 123.0, 121.9, 121.9, 121.0, 114.6, 58.8, 30.2, 24.3, 14.9.

[t-BuNONEt]ZrMe$_2$. A 1.02 g (2.0 mmol) sample of [t-BuNONEt]ZrCl$_2$ was dissolved in 20 mL of diethyl ether, and 1.33 mL (3 M solution in diethyl ether, 2.0 mmol) of MeMgBr was added. After 10 min all volatile components were removed in vacuo, and the residue was extracted with 20 mL of pentane. The solution was filtered through Celite, and the pentane was removed in vacuo. The residue was recrystallized from 5−7 mL of pentane to give large colorless crystals; 0.738 g (1.5 mmol, 78%): ^{1}H NMR δ 7.03 (t, 1), 6.93−6.79 (m, 3), 6.67 (d, 1), 6.53 (d, 1), 6.43 (d, 1), 2.73 (dt, 1), 2.40 (dt, 1), 1.62 (s, ∼4), 1.15 (t, 3), 1.14 (s, ∼4), 0.88 (s, 3), 0.81 (s, 3); ^{13}C NMR δ 149.4, 144.1, 142.7, 142.4, 138.2, 124.6, 121.8, 121.0, 120.5, 119.6, 114.9, ∼57.0, 45.8, 44.6, 30.7, 24.3, 15.2. Anal. Calcd for $C_{24}H_{24}D_{12}N_2OZr$: C, 61.09; H, 7.69; N, 5.94. Found: C, 61.18; H, 7.76; N, 6.05.

[t-BuNON]ZrMe$_2$. (a) From [t-BuNON]ZrI$_2$. A solution of MeMgI in ether (2.8 M, 2.3 mL) was added to a suspension of [t-BuNON]ZrI$_2$ (2.119 g, 3.17 mmol) in ether (50 mL) at −35 °C. The reaction mixture was allowed to warm to room temperature and was stirred until the yellow solid was replaced by white precipitate (∼30 min). All volatile solvents were then removed in vacuo, and the off-white residue was extracted with pentane (50 mL). The extract was filtered, and the pentane was removed in vacuo. The crude product was recrystallized from a mixture of pentane and ether to afford pale yellow crystals; yield 1.02 g (72%): ^{1}H NMR δ 6.90 (m, 6), 6.53 (m, 2), 1.36 (s, 6, C(CD$_3$)$_2$*Me*), 0.84 (s, 6, Zr*Me*$_2$); ^{13}C NMR δ 148.1, 142.9, 126.5, 122.5, 120.1, 119.3, 57.0 (*C*(CD$_3$)$_2$Me), 45.6 (Zr*Me*$_2$), 31.1 (C(CD$_3$)$_2$*Me*), 30.6 (m, C(*C*D$_3$)$_2$Me). Anal. Calcd for $C_{22}H_{20}D_{12}N_2OZr$: C, 59.54; H, 7.21; N, 6.31. Found: C, 59.81; H, 7.19; N, 6.39.

(b) From [t-BuNON]ZrCl$_2$. A solution of MeMgI in ether (3.0 M, 1.4 mL) was added to a suspension of [t-BuNON]ZrCl$_2$ (1.00 g, 2.07 mmol) in ether (20 mL) at −25 °C. The reaction mixture was stirred for 5 min without further cooling. All volatile solvents were then removed in vacuo, and the residue was extracted with pentane (20 mL) for 15 min. The extract was filtered, and the pentane was removed in vacuo. The residue was recrystallized from ether at −25 °C to produce pale yellow crystals; yield 664 mg (72%).

[t-BuNONMe$_2$]ZrMe$_2$. A solution of MeMgI in ether (3.0 M, 1.3 mL) was added to a suspension of [t-BuNONMe$_2$]ZrCl$_2$ (1.00 g, 1.95 mmol) in ether (20 mL) at −25 °C. The reaction mixture was stirred for 5 min without further cooling. All volatile solvents were then removed in vacuo, and the residue was extracted with pentane (20 mL) for 5 min. The extract was filtered, and the pentane was removed from the filtrate in vacuo. Crystallization of the foamy, very soluble residue from a concentrated solution of ether/pentane (∼1−2 mL) at −25 °C produced analytically pure, pale yellow, somewhat waxy material; yield 503 mg (55%): ^{1}H NMR δ 6.92−6.77 (m, 3), 6.56−6.38 (m, 3), 2.15 (s, 3, Ar*Me*), 2.11 (s, 3, Ar*Me*), 1.63 (s, 3, C(CD$_3$)$_2$*Me*), 1.16 (s, 3, C(CD$_3$)$_2$*Me*), 0.89 (s, 3, Zr*Me*), 0.81 (s, 3, Zr*Me*); ^{13}C NMR δ 149.6, 142.9, 142.5, 141.8, 137.5, 131.6, 124.5, 123.7, 122.4, 120.4, 119.5, 114.9, 57.3 (*C*(CD$_3$)$_2$Me), 56.7 (*C*(CD$_3$)$_2$Me), 45.7 (Zr*Me*), 44.1 (Zr*Me*), 31.5 (C(CD$_3$)$_2$*Me*), 31.1 (m, C(*C*D$_3$)$_2$Me), 30.7 (C(CD$_3$)$_2$*Me*), 22.1 (Ar*Me*), 17.0 (Ar*Me*). Anal. Calcd for $C_{24}H_{24}D_{12}N_2OZr$: C, 61.09; H, 7.69; N, 5.94. Found: C, 61.12; H, 8.06; N, 6.08.

[t-BuNON]ZrEt$_2$. A solution of EtMgBr in ether (3.0 M, 1.4 mL) was added to a suspension of [t-BuNON]ZrCl$_2$ (1.00 g, 2.07 mmol) in ether (20 mL) at −25 °C. The reaction mixture was stirred for 5 min without further cooling. All volatile solvents were then removed in vacuo, and the residue was extracted with cold pentane (20 mL) over a period of 5 min. The extract was filtered through Celite, and the pentane was removed from the filtrate in vacuo. Recrystallization of the residue from ether at −25 °C produced pale yellow crystals; yield 549 mg (56%): ^{1}H NMR δ 6.90 (m, 6), 6.54 (m, 2), 1.60 (t, 6, ZrCH$_2$C*H*$_3$), 1.37 (s, 6, C*Me*(CD$_3$)$_2$), 1.18 (q, 4, ZrC*H*$_2$CH$_3$); ^{13}C NMR δ 148.53, 143.30, 126.43, 122.67, 120.08, 119.45, 59.98, 57.18, 31.16 (C(CD$_3$)$_2$*Me*), 30.59 (m, C(*C*D$_3$)$_2$Me), 13.86 (ZrCH$_2$*C*H$_3$). Anal. Calcd for $C_{24}H_{24}D_{12}N_2OZr$: C, 61.09; H, 7.69; N, 5.94. Found: C, 61.41; H, 7.73; N, 6.02.

[t-BuNON]ZrPr$_2$. A solution of PrMgCl in ether (2.0 M, 2.1 mL) was added to a suspension of [t-BuNON]ZrCl$_2$ (1.00, 2.07 mmol) in ether (20 mL) at −25 °C. The reaction mixture was stirred for 5 min without further cooling. All volatile solvents were then removed in vacuo, and the residue was extracted with cold pentane (20 mL). After 5 min the extract was filtered and the pentane was reduced in volume in vacuo to a pale yellow oil (∼1 mL). Ether (∼1 mL) was added. Cooling this solution to −35 °C overnight yielded 527 mg (51%) of a pale yellow solid. The precise assignment of ^{1}H and ^{13}C resonances is uncertain: ^{1}H NMR δ 6.90 (m, 6), 6.54 (m, 3), 1.93 (m, 4), 1.37 (s, 6, C*Me*(CD$_3$)$_2$), 1.25 (m, 4), 1.08 (t, 6, ZrCH$_2$-CH$_2$C*H*$_3$); ^{13}C NMR δ 148.51, 143.23, 126.45, 122.76, 120.13, 119.48, 72.50 (Zr*C*H$_2$CH$_2$CH$_3$), 57.24, 31.20 (C(CD$_3$)$_2$*Me*), 30.39 (m, C(*C*D$_3$)$_2$Me), 23.96, 21.30. Anal. Calcd for $C_{26}H_{28}D_{12}N_2$-OZr: C, 62.47; H, 8.06; N, 5.60. Found: C, 62.74; H, 8.34; N, 5.65.

[t-BuNON]Zr(i-Bu)$_2$. A solution of i-BuMgCl in ether (2.0 M, 950 μL) was added to a suspension of [t-BuNON]ZrCl$_2$ (462 mg, 954 μmol) in ether (12 mL) at approximately −35 °C. The reaction mixture was stirred for 5 min without further cooling. All volatile solvents were then removed in vacuo, and the off-white residue was extracted with pentane (10 mL). After 5 min two drops of 1,4-dioxane were added. The extract was filtered, and the pentane was reduced in volume in vacuo to a pale yellow oil (∼1 mL). Ether (∼1 mL) was added. This solution was stored at −35 °C overnight and produced 244 mg (49%) of analytically pure pale yellow, waxy solid: ^{1}H NMR (C$_6$D$_5$Br) δ 6.95 (m, 6), 6.63 (m, 2), 2.24 (sept, 2, CH$_2$C*H*(CH$_3$)$_2$) 1.38 (s, 6, C*Me*(CD$_3$)$_2$), 1.18 (d, 4, C*H*$_2$CH(CH$_3$)$_2$), 1.01 (d, 12, CH$_2$CH(C*H*$_3$)$_2$); ^{13}C NMR (C$_6$D$_5$Br) δ 147.52, 142.29, 125.8, 121.9, 119.4, 118.7, 81.5 (*C*H$_2$CHMe$_2$, 56.7 (*C*(CD$_3$)$_2$Me), 30.8 (C(CD$_3$)$_2$*Me*), 30.2 (m, C(*C*D$_3$)$_2$Me), 28.5 (CH$_2$CH*Me*$_2$). The

resonance for CH_2CHMe_2 was not observed. Anal. Calcd for $C_{28}H_{32}D_{12}N_2OZr$: C, 63.70; H, 8.40; N, 5.31. Found: C, 63.92; H, 8.69; N, 5.28.

[t-BuNON]Zr(CH_2CMe_3)Cl. A solution of Me_3CCH_2MgCl in ether (1.35 M, 840 μL) was added to a suspension of [t-BuNON]$ZrCl_2$ (543 mg, 1.12 mmol) in ether (10 mL) at −25 °C. The reaction mixture was allowed to warm to room temperature and stirred for 30 min. All volatile components were removed in vacuo, and the residue was extracted with pentane (20 mL) over a period of 10 min. The extract was filtered, and the filtrate was concentrated to ∼3 mL. Pale yellow microcrystals began to form. The mixture was stored at −25 °C overnight; yield 414 mg (71%): ^{1}H NMR δ 6.87 (m, 4), 6.80 (d, 2), 6.52 (m, 2), 1.64 (s, 2, CH_2CMe$_3$), 1.36 (s, 6, C(CD$_3$)$_2$*Me*), 1.08 (s, 9, CH$_2$C*Me*$_3$); ^{13}C NMR δ 146.7, 142.3, 127.3, 122.6, 120.4, 118.8, 87.9 (*C*H$_2$CMe$_3$), 57.6 (*C*CD$_3$)$_2$Me), 35.3 (CH$_2$*C*Me$_3$), 34.5 (CH$_2$C*Me*$_3$), 31.1 (C(CD$_3$)$_2$*Me*), 30.6 (C(*C*D$_3$)$_2$Me). Anal. Calcd for $C_{25}H_{25}D_{12}ClN_2OZr$: C, 57.71; H, 7.17; N, 5.38. Found: C, 57.88; H, 7.16; N, 5.36.

[t-BuNON]Zr(η^2-C_2H_4)(PMe_3)$_2$. To a solution of [t-BuNON]-$ZrEt_2$ (149 mg, 316 μmol) in ether (2 mL) neat PMe_3 (185 mg, 2.434 mmol) was added. The reaction mixture was shaken for a few seconds and then stored at −25 °C. After 38 h red crystals were separated and dried in vacuo; yield 160 mg (85%): ^{1}H NMR (toluene-d_8) δ 7.23 (d, 2), 6.85 (t, 2), 6.75 (d, 2), 6.37 (t, 2), 1.43 (br s, 2, CH^AH^{B}CH^ACH^B), 1.23 (br s, CH^AH^B-CH^ACH^B), 1.08 (s, 6, C(CD$_3$)$_2$*Me*), 0.87 (d, J_{PH} = 3 Hz, 18, P*Me*$_3$); ^{13}C NMR (toluene-d_8, 0 °C) δ 148.60, 145.22, 124.64, 118.09, 114.03, 112.65, 53.22 (*C*(CD$_3$)$_2$Me), 46.45 (s, C_2H_4), 30.93 (C(CD$_3$)$_2$*Me*), 16.23 (s, P*Me*$_3$); ^{31}P (0 °C) δ −29.9 (br s). Anal. Calcd for $C_{28}H_{36}D_{12}N_2OP_2Zr$: C, 56.62; H, 8.15; N, 4.72. Found: C, 57.01; H, 8.27; N, 4.59.

[t-BuNON]Hf(NMe_2)$_2$. H_2[t-BuNON] (22.87 g, 0.070 mol) and Hf(NMe_2)$_4$ (25.00 g, 0.070 mol) were dissolved in 30 mL of toluene, and the solution was heated slowly. Rapid gas evolution was observed, and a microcrystalline product subsequently precipitated from solution. The resulting mixture was kept at 100−105 °C for 16 h. It was then cooled to 22 °C, and the volatile components were removed in vacuo. The white microcrystalline solid was slurried in 40 mL of pentane, collected on a frit, washed with several portions of pentane, and dried in vacuo; yield 33.90 g (82%): ^{1}H NMR δ 7.06 (m, 2, Ar), 6.97 (m, 2, Ar), 6.90 (m, 2, Ar), 6.56 (m, 2, Ar), 3.01 (s, 12, NMe$_2$), 1.34 (s, 6, t-Bu); ^{13}C{^{1}H} NMR δ 147.73, 145.30, 125.79, 123.28, 118.51, 117.91, 57.18 (*C*(CD$_3$)$_2$CH$_3$), 43.33 (N(*C*H$_3$)$_2$), 32.23 (C(CD$_3$)$_2$*C*H$_3$), 31.69 (m, C(*C*D$_3$)$_2$CH$_3$). Anal. Calcd for $C_{24}H_{26}N_4D_{12}OHf$: C, 48.93; H, 6.50; N, 9.51. Found: C, 49.08; H, 6.54; N, 9.51.

[t-BuNON]$HfCl_2$. [t-BuNON]Hf(NMe_2)$_2$ (33.90 g, 57.54 mmol) and Me_3SiCl (25.00 g, 230.2 mmol) were dissolved in 125 mL of toluene in a 250 mL round-bottom Schlenk flask. The stirred mixture was heated to 100 °C, whereupon all solids dissolved. After 16 h, the solution was cooled to 22 °C and volatile components were removed in vacuo. The pale yellow solid was slurried in 100 mL of pentane, collected by filtration, washed with 2 × 30 mL of pentane, and dried in vacuo; yield 31.445 g (96%). Analytically pure samples were recrystallized from ether at −40 °C: ^{1}H NMR δ 6.80 (m, 6, Ar), 6.53 (m, 2, Ar), 1.31 (s, 6, t-Bu); ^{13}C{^{1}H} NMR δ 146.89 (b), 140.71, 127.58 (b), 123.31 (b), 121.74, 118.81 (b), 57.79 (*C*(CD$_3$)$_2$CH$_3$), 31.01 (C(CD$_3$)$_2$CH$_3$), 30.46 (m, C(*C*D$_3$)$_2$CH$_3$). Anal. Calcd for $C_{20}H_{14}N_2$-$Cl_2D_{12}HfO$: C, 42.00; H, 4.58; N, 4.90; Cl, 12.40. Found: C, 42.16; H, 4.60; N, 4.86; Cl, 12.81.

[t-BuNON]$HfMe_2$. A stirred solution of [t-BuNON]$HfCl_2$ (10.41 g, 18.21 mmol) in 100 mL of ether at −40 °C was treated with MeMgI (38.24 mmol, 3.0 M in ether). The mixture was allowed to warm to 25 °C over 1 h, after which 1,4-dioxane (∼5 mL) was added and the mixture was stirred for an additional 50 min. The mixture was filtered through Celite, and the volatile components were removed from the filtrate in vacuo. The crude material was crystallized from ether at −40 °C as colorless prisms; yield 7.405 g (77%): ^{1}H NMR δ 6.94−6.83 (m, 6, Ar), 6.54 (m, 2, Ar), 1.36 (s, 6, t-Bu), 0.65 (s, 6, Me); ^{13}C{^{1}H} NMR δ 126.66, 123.15, 119.93, 119.15, 57.01. Anal. Calcd for $C_{22}H_{20}N_2D_{12}HfO$: C, 49.76; H, 6.07; N, 5.27. Found: C, 49.62, 49.66; H, 5.97, 5.90; N, 5.18, 5.21.

[t-BuNON]Hf($^{13}CH_3$)$_2$. This complex was prepared in an analogous manner to that employed to prepare [t-BuNON]-$HfMe_2$ from [t-BuNON]$HfCl_2$ (1.43 g, 2.50 mmol) and $^{13}CH_3$-MgI (5.00 mmol, 1.54 M in ether; prepared from equimolar amounts of $^{13}CH_3I$ and Mg in ether) in 17 mL of ether at −40 °C; yield 670 mg (50%): ^{1}H NMR δ 6.94−6.83 (m, 6, Ar), 6.54 (m, 2, Ar), 1.36 (s, 6, t-Bu), 0.65 (d, 6, $^1J_{CH}$ = 112, Me); ^{13}C{^{1}H} NMR δ 56.32 ($^{13}CH_3$).

[t-BuNON]$HfEt_2$. EtMgBr (7.28 mmol, 3.00 M in ether) was added dropwise to a stirred suspension of [t-BuNON]$HfCl_2$ (2.00 g, 3.47 mmol) in 60 mL of ether at −40 °C. The mixture was allowed to warm to 25 °C over 2 h, after which 1,4-dioxane (∼2 mL) was added. The resulting mixture was stirred for an additional 10 min and filtered through Celite, and the filtrate was stripped to dryness in vacuo. The residue was dissolved in ether (7 mL), and the solution was stored at −40 °C. Colorless crystals separated from the mother liquor were collected and washed quickly with pentane and dried in vacuo; yield 1.535 g (79%): ^{1}H NMR δ 7.01−6.80 (m, 6), 6.55 (m, 2), 1.78 (t, 6, CH$_2$CH_3), 1.36 (s, 6, t-Bu), 0.97 (q, 4, CH_2CH$_3$); ^{13}C{^{1}H} NMR δ 148.08, 142.82, 126.59, 123.43, 120.02, 119.30, 70.26 (*C*H$_2$CH$_3$), 56.92, 31.47, 30.02, 14.14 (CH$_2$*C*H$_3$). Anal. Calcd for $C_{24}H_{24}N_2D_{12}HfO$: C, 51.56; H, 8.65; N, 5.01. Found: C, 51.72; H, 6.74; N, 5.35.

[t-BuNON]Hf(CH_2CHMe_2)$_2$. A stirred suspension of [t-BuNON]$HfCl_2$ (3.00 g, 5.20 mmol) in 50 mL of ether at −40 °C was treated with i-BuMgCl (10.400 mmol, 2.0 M in ether). The mixture was allowed to warm to 25 °C over 2 h, after which 1,4-dioxane (∼3 mL) was added and the mixture was stirred for an additional 30 min. The mixture was filtered through Celite, and the filtrate was stripped to dryness. The crude product was dissolved in pentane (30 mL), and the solution was filtered. The filtrate was concentrated in vacuo and stored at −40 °C. Large colorless prisms separated from the mother liquor and were collected and dried in vacuo; yield 2.49 g (78%): ^{1}H NMR δ 7.02−6.85 (m, 6, Ar), 6.56 (m, 2, Ar), 2.43 (m, 2, CH$_2$C*H*C(CH$_3$)$_2$), 1.37 (s, 6, t-Bu), 1.16 (d, 12, CH$_2$-CHC(C*H*$_3$)$_2$, 1.02 (d, 4, CH_2CHC(CH$_3$)$_2$, J_{HH} = 6.9); ^{13}C{^{1}H} NMR δ 148.29, 142.77, 126.64, 123.73, 120.18, 119.48, 92.22, 31.57, 31.35, 30.81 (m, CD$_3$), 29.84. Anal. Calcd for $C_{28}H_{32}N_2D_{12}$-HfO: C, 54.66; H, 7.21; N, 4.55. Found: C, 54.85; H, 7.39; N, 4.48.

[t-BuNON]Hf(CH_2CMe_3)Cl. A stirred suspension of [t-BuNON]$HfCl_2$ (3.28 g, 5.69 mmol) in 50 mL of ether at −40 °C was treated dropwise with Me_3CCH_2MgCl (5.69 mmol, 3.16 M in ether), and the mixture was allowed to warm to room temperature over a period of 2 h. 1,4-Dioxane (∼3 mL) was added, and the mixture was stirred for another 15 min and then filtered through Celite. The filtrate was stripped to dryness, dissolved in a mixture of ether and pentane, and filtered again. The filtrate was stored at −40 °C. Colorless crystals of the product were collected, washed with pentane, and dried in vacuo; yield 3.00 g (87%): ^{1}H NMR δ 6.90 (m, 4), 6.81 (m, 2), 6.51 (m,2), 1.38 (m, 14, t-Bu), 1.34 (s, 2, CH_2C-(CH$_3$)$_3$)), 1.10 (s, 9, CH$_2$C(CH_3)$_3$); ^{13}C{^{1}H} NMR δ 146.31, 141.90, 127.42, 123.11, 120.01, 118.54, 92.13 (*C*H$_2$C(CH$_3$)$_3$), 57.10 (CH$_2$*C*(CH$_3$)$_3$), 56.95 (m, *C*(CD$_3$)$_2$CH$_3$), 35.28 (CH$_2$C-(*C*H$_3$)$_3$), 31.41 (s, C(CD$_3$)$_2$*C*H$_3$), 30.88 (m, C(*C*D$_3$)$_2$CH$_3$). Anal. Calcd for $C_{25}H_{25}N_2ClD_{12}HfO$: C, 49.42; H, 6.14; N, 4.61. Found: C, 49.28; H, 6.25; N, 4.51.

[t-BuNON]Hf(CH_2CMe_3)Me. A stirred solution of [t-BuNON]Hf(CH_2CMe_3)Cl (1.35 g, 2.23 mmol) in 15 mL of ether at −40 °C was treated dropwise with MeMgI (2.34 mmol, 3.0 M in ether), and the mixture was stirred at room temperature for 16 h. 1,4-Dioxane (1 mL) was added, and the mixture was stirred for an additional 30 min and filtered through Celite.

The filtrate was stripped to dryness in vacuo. The crude product was recrystallized from pentane at −40 °C as small white crystals; yield 949 mg (73%): ^{1}H NMR δ 6.95 (m, 4), 6.84 (m,2), 6.54 (m, 2), 1.38 (s, 6, t-Bu), 1.24 (s, 2, CH_2C(CH_3)$_3$), 1.06 (s, 9, CH$_2$C(CH_3)$_3$), 0.82 (s, 3, HfMe); ^{13}C{^{1}H} NMR δ 147.47, 142.81, 126.71, 123.29, 119.78, 119.26, 95.12 (*C*H$_2$C(CH$_3$)$_3$), 62.68 (HfMe), 56.95 (CH$_2$*C*(CH$_3$)$_3$), 56.60 (m, *C*(CD$_3$)$_2$CH$_3$), 35.65 (CH$_2$C(*C*H$_3$)$_3$), 31.43 (C(CD$_3$)$_2$*C*H$_3$), 31.18 (m, C(*C*D$_3$)$_2$CH$_3$).

{**[t-BuNON]ZrMe**}**[MeB(C$_6$F$_5$)$_3$].** A solution of B(C$_6$F$_5$)$_3$ (35 mg, 67 μmol) in pentane (5 mL) that had been cooled to −35 °C was added to a solution of [t-BuNON]ZrMe$_2$ (30 mg, 67 μmol) in pentane (5 mL). The mixture immediately turned bright yellow. A solid precipitated when the B(C$_6$F$_5$)$_3$ solution was added at −35 °C, but it dissolved when the mixture was warmed to room temperature. The slightly cloudy bright yellow solution was stirred at room temperature for 5 min, filtered, and cooled to −35 °C for 2 days. Yellow crystals were filtered off and briefly dried in vacuo; yield 31 mg (47%): ^{1}H NMR (C$_6$D$_5$Br) δ 7.03−6.55 (m, 8), 2.24 (br s, 3, B*Me*), 0.98 (s, 6, C*Me*(CD$_3$)$_2$), 0.77 (s, 3, Zr*Me*); ^{13}C NMR (toluene-d_8, −30 °C) δ 150.24, 147.16, 141.5 (m, *C*$_6$F$_5$), 139.5 (m, *C*$_6$F$_5$), 137.77, 135.8 (m, *C*$_6$F$_5$), 123.54, 59.20, 50.90 (s, Zr*Me*), 29.5 (br m, t-Bu, B-*Me*); ^{19}F NMR (C$_6$D$_6$) δ −133.14 (d, 6, *F*$_o$), −159.35 (br s, 3, F$_p$), −164.27 (t, 6, F$_m$).

Observation of {**[t-BuNON]ZrMe(PhNMe$_2$)**}**[B(C$_6$F$_5$)$_4$]**. Solid [t-BuNON]ZrMe$_2$ (~8 mg, 18 μmol) was added to a suspension of [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (15 mg, 18 μmol) in C$_6$D$_5$Br (1 mL) at −35 °C, and the mixture was stirred for 30 min at room temperature: ^{1}H NMR (C$_6$D$_5$Br) δ 6.94−6.50 (m, 13), 2.74 (s, 6, PhN*Me*$_2$), 1.17 (s, 6, C(CD$_3$)$_2$*Me*), 0.95 (s, 3, Zr*Me*); ^{19}F NMR (C$_6$D$_5$Br) −131.78 (*F*$_o$), −162.11 (t, F$_p$), −165.94 (br m, F$_m$); ^{13}C NMR (C$_6$D$_5$Br) δ 55.88 (Zr*Me*).

{**[t-BuNON]ZrMe(THF)$_2$**}**[B(C$_6$F$_5$)$_4$]**. [Ph$_3$C][B(C$_6$F$_5$)$_4$] (0.230 g, 0.249 mmol) was added to a −35 °C solution of (t-BuNON)ZrMe$_2$ (0.110 g, 0.248 mmol) in 3 mL of C$_6$H$_5$Cl. The solution was allowed to stand for ~5 min or until the [Ph$_3$C][B(C$_6$F$_5$)$_4$] entirely dissolved. To this dark yellow solution was added 0.04 mL (0.493 mmol) of THF. The solution immediately lightened to bright yellow. The product was precipitated as a bright yellow powder by the addition of 10 mL of pentane to the C$_6$H$_5$Cl solution; yield 0.222 g (72%): ^{1}H NMR (C$_6$D$_5$Br) δ 1.03, 1.5−1.8 (br m), 3.9 (br, *THF*); ^{13}C NMR (C$_6$D$_5$Br) δ 53.4, 55.6 (Zr^{13}CH$_3$). When this reaction was repeated in C$_6$D$_5$Br, crystals of [(t-BuNON)ZrMe(THF)$_2$][B(C$_6$F$_5$)$_4$] formed when THF was added. It should be noted that the direct reaction of (t-BuNON)ZrMe$_2$ with [Ph$_3$C][B(C$_6$F$_5$)$_4$] in THF yielded a polymeric product, most likely poly(THF). The addition of [Ph$_3$C][B(C$_6$F$_5$)$_4$] to THF will also produce poly(THF), as will the dissolution of [(t-BuNON)ZrMe(THF)$_2$][B(C$_6$F$_5$)$_4$] in THF, although the latter reaction is much slower.

{**[t-BuNON]ZrMe(DME)**}**[B(C$_6$F$_5$)$_4$]**. In a 10 mL round-bottom flask 0.102 g (0.082 mmol) of [[t-BuNON]ZrMe(ether)$_2$][B(C$_6$F$_5$)$_4$] was dissolved in 1 mL of DME. The bright yellow solution was stirred for 5 min, and then 10 mL of pentane was added. Golden yellow crystals precipitated from solution and were isolated via filtration; yield 0.085 g (87%): ^{1}H NMR (C$_6$D$_5$Br, 500 MHz) δ 1.01 (3, Zr*Me*), 1.58 (~6, t-Bu), 3.62 (2, O*CH$_2$CH$_2$*O), 3.78 (6, CH$_3$O), 3.86 (2, O*CH$_2$CH$_2$*O); ^{13}C NMR (C$_6$D$_5$Br, 125 MHz); δ 52.47 (Zr(*^{13}CH$_3$*)).

Observation of {**[t-BuNON]HfMe(PhNMe$_2$)**}**[B(C$_6$F$_5$)$_4$].** Solid [t-BuNON]HfMe$_2$ (15 mg, 0.028 mmol) and [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (22 mg, 0.028 mmol) were dissolved in 0.7 mL of C$_6$D$_5$Br by stirring for 30 min to give a pale lime-colored solution: ^{1}H NMR (C$_6$D$_5$Br) δ 6.8−7.3 (m, 14, Ar), 2.79 (s, 6, Me$_2$NPh), 1.15 (s, 6, t-Bu), 0.89 (s, 3, HfMe).

{**[t-BuNON]Hf(^{13}CH$_3$)(PhNMe$_2$)**}**[B(C$_6$F$_5$)$_4$]** was prepared in an analogous manner from [t-BuNON]Hf(^{13}CH$_3$)$_2$ (15 mg, 0.028 mmol) and [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (22 mg, 0.028 mmol): ^{1}H NMR (C$_6$D$_5$Br) δ 6.8−7.3 (m, 14, Ar), 2.79 (s, 6, Me$_2$NPh), 1.15 (s, 6, t-Bu), 0.89 (d, 3, HfMe, J_{CH} = 111 Hz); ^{13}C{^{1}H} NMR (C$_6$D$_5$Br) δ 64.91 (HfMe).

{**[t-BuNON]HfMe(THF)$_2$**}**BPh$_4$**. A light blue mixture of [t-BuNON]HfMe$_2$ (700 mg, 1.318 mmol), [Cp′$_2$Fe]BPh$_4$ (703 mg, 1.318 mmol), and THF (209 mg, 2.900 mmol) in 15 mL of toluene was stirred for 16 h. A pale green solid was collected on a fine frit and was washed with 2 × 3 mL toluene followed by 2 × 1 mL of pentane. The crude product was dissolved in THF, and a small amount of white solid was filtered off. The product was crystallized from THF/pentane at −40 °C as an off-white microcrystalline solid, which was washed with pentane and dried in vacuo; yield 805 mg, 62%): ^{1}H NMR (CD$_2$Cl$_2$) δ 7.40−6.70 (m, 8), 7.31 (br, 8, *o*-H), 7.02 (m, 8, *m*-H), 6.89 (m, 4, *p*-H), 4.14/3.80 (bs, 8, THF), 1.76 (m, 8, THF), 1.61 (m, t-Bu$_{mer}$), 1.40 (m, t-Bu$_{fac}$), 0.72 (s, Me$_{mer}$), 0.55 (s, Me$_{fac}$); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 164.46 (q, C$_{ipso}$, J_{CB} = 49 Hz), 147.51 (b), 143.61, 142.72, 136.36 (C$_{meta}$), 127.59 (b), 126.33, 126.07 (C$_{ortho}$), 122.18 (C$_{para}$), 121.68 (b), 120.89, 120.12, 117.97, 113.85, 76.67 (THF), 62.14 (Me$_{fac}$), 60.57 (Me$_{mer}$), 57.43 (br, *C*(CD$_3$)$_2$CH$_3$, *fac*), 56.45 (br, *C*(CD$_3$)$_2$CH$_3$, *mer*), 30.77 (m, C(*C*D$_3$)$_2$*C*H$_3$), 25.99/25.81 (THF). Anal. Calcd for C$_{53}$H$_{53}$N$_2$BD$_{12}$HfO$_3$: C, 64.86; H, 6.68; N, 2.86. Found: C, 64.88; H, 6.80; N, 2.82.

{**[t-BuNON]HfMe(DME)**}**BPh$_4$**. A light blue mixture of [t-BuNON]HfMe$_2$ (1.500 g, 2.824 mmol), [Cp′$_2$Fe]BPh$_4$ (1.506 g, 2.824 mmol), and DME (305 mg, 3.389 mmol) in 50 mL of toluene was stirred for 18 h. An off-white solid was collected on a fine frit and was washed with 3 × 5 mL of toluene followed by 3 × 2 mL of pentane. The crude product was dissolved in 15 mL of CH$_2$Cl$_2$, and a small amount of white solid was filtered off. The product was crystallized from CH$_2$Cl$_2$ at −40 °C as a white microcrystalline solid, which was washed with pentane and dried in vacuo; yield 1.658 g (63%): ^{1}H NMR (CD$_2$Cl$_2$) δ 7.35 (br, 8, *o*-H), 7.24−6.80 (m, 20), 3.57 (s, 6), 3.04 (m, 2), 2.70 (m, 2), 1.34 (s, 6), 0.51 (s, 3, Me); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 164.45 (q, C$_{ipso}$, J_{CB} = 49 Hz), 146.53, 140.70, 136.35 (C$_{meta}$), 127.83, 126.32 (C$_{ortho}$), 122.74, 122.45, 121.87 (C$_{para}$), 119.66, 73.47 (OMe), 67.84 (HfMe), 58.54 (CH$_2$O), 57.67 (m, *C*(CD$_3$)$_2$CH$_3$), 30.65 (C(CD$_3$)$_2$*C*H$_3$), 30.02 (m, C(*C*D$_3$)$_2$CH$_3$). Anal. Calcd for C$_{49}$H$_{47}$N$_2$BD$_{12}$HfO$_3$: C, 63.60; H, 6.43; N, 3.02. Found: C, 63.06; H, 6.54; N, 3.00.

Observation of {**[(t-BuN-*d*$_6$-*o*-C$_6$H$_4$)(*d*$_6$-t-BuNH-*o*-C$_6$H$_4$)O]HfMe$_2$**}**[B(C$_6$F$_5$)$_4$].** A solution of [t-BuNON]HfMe$_2$ (20 mg, 0.038 mmol) in 0.5 mL of C$_6$D$_5$Br at −40 °C was combined with a suspension of [PhNMe$_2$(H)][B(C$_6$F$_5$)$_4$] (30 mg, 0.038 mmol) in 0.5 mL of C$_6$D$_5$Br at 22 °C, whereupon the solids dissolved and the color rapidly turned pale green. The solution was kept at −40 °C for 20 min, then quickly transferred to an NMR tube, which was flame-sealed and kept at −196 °C until placed into an NMR probe precooled to −35 °C: ^{1}H NMR (C$_6$D$_5$Br, −35 °C) δ 7.2 6.0 (m, 13), 4.33 (s, 1, NH), 2.53 (s, 6, Me$_2$NPh), 1.06 (s, 3, t-Bu), 1.03 (s, 3, t-Bu), 0.55 (s, 3, HfMe), 0.53 (s, 3, HfMe). The spectrum also contained resonances for [t-BuNON]HfMe(PhNMe$_2$)][B(C$_6$F$_5$)$_4$] and CH$_4$ (0.16 ppm).

Observation of {**[(t-BuN-*d*$_6$-*o*-C$_6$H$_4$)(*d*$_6$-t-BuNH-*o*-C$_6$H$_4$)O]HfEt$_2$**}**[B(C$_6$F$_5$)$_4$]**. [t-BuNON]HfEt$_2$ (15 mg, 0.027 mmol) and [PhNMe$_2$(H)][B(C$_6$F$_5$)$_4$] (21 mg, 0.027 mmol) were rapidly dissolved in 0.8 mL of CD$_2$Cl$_2$. The solution was transferred rapidly to an NMR tube, which was flame-sealed and then kept at 0 °C until placed into an NMR probe at 22 °C: ^{1}H NMR (CD$_2$Cl$_2$) δ 7.60−6.60 (m, 14), 4.64 (s, 1, NH), 2.93 (s, 6, Me$_2$NPh), 1.78 (t, 3, CH$_2$C*H*$_3$), 1.61 (s, 3, t-Bu), 1.20 (m, 2, C*H*$_2$CH$_3$), 1.19 (t, 3, CH$_2$C*H*$_3$) 1.08 (s, 3, t-Bu), 0.87 (m, 2, C*H*$_2$CH$_3$). The solution also contained C$_2$H$_6$ (δ 0.85) and resonances for [t-BuNON]HfCl(Et)(PhNMe$_2$): δ 7.65 (m, 3), 7.51 (m, 2), 7.17 (m, 6), 6.80 (m, 2), 3.66 (s, 6, Me$_2$NPh), 1.38 (s, 6, t-Bu), 1.28 (t, 3, CH$_2$C*H*$_3$), 0.69 (q, 2, C*H*$_2$CH$_3$).

Observation of {**[(t-BuN-*d*$_6$-*o*-C$_6$H$_4$)(*d*$_6$-t-BuNH-*o*-C$_6$H$_4$)O]Hf(i-Bu)$_2$**}**[B(C$_6$F$_5$)$_4$]**. [t-BuNON]Hf(i-Bu)$_2$ (20 mg, 0.033 mmol) and [PhNMe$_2$(H)][B(C$_6$F$_5$)$_4$] (26 mg, 0.033 mmol) were rapidly dissolved in 0.8 mL of CD$_2$Cl$_2$. The solution was transferred rapidly to an NMR tube, which was flame-sealed and then kept

at 0 °C until placed into an NMR probe at 22 °C: ^{1}H NMR (CD_2Cl_2) δ 7.60−7.07 (m, 10, Ar), 6.80 (m, 3, Ar), 4.49 (s, 1, NH), 2.93 (s, 6, Me_2NPh), 2.41 (m, 1, $CH_2CH(CH_3)_2$), 1.62 (s, 3, t-Bu), 1.52 (m, 1, $CH_2CH(CH_3)_2$), 1.22 (m, 2, $CH_2CH(CH_3)_2$), 1.21 (s, 3, t-Bu), 1.10 (m, 2, $CH_2CH(CH_3)_2$), 1.02 (d, 3), 0.97 (d, 3), 0.81 (d, 3), 0.66 (d, 3). The solution also contained isobutane (δ 0.70 (d, 9), the methyne proton was not located) and a small amount of isobutylene (δ 4.61 (m) and 1.72 (m)). Resonances for [t-BuNON]HfCl(i-Bu)($PhNMe_2$): δ 7.65 (m, 3), 7.51 (m, 2), 7.17 (m, 6), 6.80 (m, 2), 3.66 (s, 6, Me_2NPh), 1.75 (m, $CH_2CH(CH_3)_2$), 1.38 (s, 6, t-Bu), 0.89 (d, 6, $CH_2CHC(CH_3)_2$), 0.80 (d, 2, $CH_2CHC(CH_3)_2$).

Polymerization of 1-Hexene Using {[t-BuNON]ZrMe($PhNMe_2$)}[$B(C_6F_5)_4$]. In a typical experiment varying amounts of hexene (0.3−3.0 mL) were added to a solution of {[t-BuNON]ZrMe($PhNMe_2$)}[$B(C_6F_5)_4$] (∼50 μmol of [$PhNMe_2H$][$B(C_6F_5)_4$] and ∼1.1 equiv of [t-BuNON]$ZrMe_2$) in chlorobenzene at 0 °C). The carefully weighed, limiting reagent was the "activator", [$PhNMe_2H$][$B(C_6F_5)_4$]. It is assumed that the amount of catalyst formed is equal to the amount of activator when it is added to a 10% excess of [t-BuNON]$ZrMe_2$ in chlorobenzene. ([t-BuNON]$ZrMe_2$ itself was found to be inactive.) The total volume of the reaction mixture was always 13.0 mL. The reaction mixture was stirred for 1.5 h and quenched by addition of HCl in diethyl ether (4 mL, 1.0 M). Most solvent was removed at 15 Torr (water aspirator) at 45 °C. The viscous oil was dried at 100 mTorr at 50−60 °C for 20 h. The yields were essentially quantitative (97−100%). The molecular weights and polydispersities were measured by light scattering. The average value for d*n*/d*c* (0.049 mL/g) obtained (assuming total elution) from 18 runs (0.045−0.053 mL/g) was employed and M_n(found) calculated using that basis.

Polymerization of 1-Hexene Using {[t-BuNON]HfMe($PhNMe_2$)}[$B(C_6F_5)_4$]. In a typical experiment varying amounts of 1-hexene (0.3−3.0 mL) were added to a solution of {[t-BuNON]HfMe($PhNMe_2$)}[$B(C_6F_5)_4$] (prepared from ∼75 μmol of [$PhNMe_2H$][$B(C_6F_5)_4$] and ∼1 equiv of [t-BuNON]$HfMe_2$ in chlorobenzene at 22 °C). The reaction mixture was stirred for 1−6 h and quenched by addition of HCl in diethyl ether (3 mL, 1.0 M). Most solvent was removed at 15 Torr (water aspirator) at 60 °C. The viscous oil was dried at 60 mTorr at 80 °C for 20 h. The yields were essentially quantitative (97−100%).

X-ray Crystal Studies. All data were collected on Bruker Platform diffractometer equipped with a CCD area detector and driven by the SMART[123] suite of programs using Mo/Kα radiation, λ = 0.71073 Å. Data reduction was carried out with SAINT,[123] while SHELXTL[123] was used to solve and refine both structures. Patterson methods were employed to locate the heavy atoms in each instance, while subsequent difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. Those atoms were treated as anisotropic scatterers. Hydrogen atoms were placed in calculated positions and were allowed to ride upon their respective non-hydrogen atoms. Crystal data and structure refinement data can be found in Tables 1 and 2.

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Supporting Information Available: Fully labeled ORTEP drawings, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for [t-BuNON]$ZrCl_2$, [t-BuNON]$ZrMe_2$, [t-BuNON]Zr(η^2-C_2H_4)(PMe_3)$_2$, {[t-BuNON]ZrMe(THF)$_2$}[$B(C_6F_5)_4$], and {[t-BuNON]ZrMe(DME)}[$B(C_6F_5)_4$]. (Supporting Information for [t-BuNON]$TiMe_2$ and {[t-BuNON]ZrMe}[$MeB(C_6F_5)_3$] were provided for the preliminary publication of this material.[33]) This material is available free of charge via the Internet at http://pubs.acs.org.

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(123) SMART, SAINT, and SHELXTL are part of the 1995 Bruker Analytical X-ray Systems software, Madison, WI.