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Fluorinated Diarylamido Complexes of Lithium, Zirconium, and Hafnium

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Deprotonation of *N*-(2-fluorophenyl)-2,6-diisopropylaniline (H[^{i}PrAr-NF]) with 1 equiv of *n*-BuLi in toluene at –35 °C produced cleanly [^{i}PrAr-NF]Li. Subsequent recrystallization of [^{i}PrAr-NF]Li in diethyl ether generated the bis(ether) adduct [^{i}PrAr-NF]Li(OEt$_2$)$_2$. An X-ray study of [^{i}PrAr-NF]Li(OEt$_2$)$_2$ showed it to be a four-coordinate species with the coordination of the fluorine atom to the lithium center. The reactions of [^{i}PrAr-NF]Li with MCl$_4$(THF)$_2$ (M = Zr, Hf), regardless of the stoichiometry employed, afforded the corresponding dichloride complexes [^{i}PrAr-NF]$_2$MCl$_2$ (M = Zr, Hf). Alkylation of [^{i}PrAr-NF]$_2$MCl$_2$ with a variety of Grignard reagents generated [^{i}PrAr-NF]$_2$MR$_2$ (M = Zr, Hf; R = Me, *i*-Bu, CH$_2$Ph). The X-ray structures of [^{i}PrAr-NF]$_2$ZrCl$_2$, [^{i}PrAr-NF]$_2$HfCl$_2$, [^{i}PrAr-NF]$_2$ZrMe$_2$, [^{i}PrAr-NF]$_2$Zr(*i*-Bu)$_2$, and [^{i}PrAr-NF]$_2$Hf(CH$_2$Ph)$_2$ are all indicative of the coordination of the fluorine atoms to these group 4 metals, leading to a C_2-symmetric, distorted octahedral geometry for these molecules.

Introduction

Amido complexes of group 4 metals continue to constitute an active area of exploratory research.[1–22] Much recent attention has been paid to the development of well-defined catalysts for homogeneous olefin polymerization.[23–28] It has been shown that variations of bi- and tridentate amido ligands such as $[RN(CH_2)_3NR]^{2-}$ (R = 2,6-^{i}Pr$_2$C$_6$H$_3$, 2,6-Me$_2$C$_6$H$_3$)[29] and $[(^tBuN\text{-}o\text{-}C_6H_4)_2O]^{2-}$,[30] respectively, are capable of stabilizing the catalytically active species of group 4 metals for polymerization of α-olefins in a living manner. Modifications of chelating amido ligands in this regard are of current interest.[31–38]

We are currently exploring coordination chemistry of chelating amido ligands involving both early and late transition metals.[39–49] A number of metal complexes that contain *o*-phenylene-derived amido phosphine ligands have shown markedly thermal stability while generating intriguing reactivity.[50–53] During our investigation involving diarylamido phosphine complexes, we became interested in their fluorine analogues due primarily to the potentials of the weakly coordinating nature of the fluorine atom that may play an important role in stabilizing and activating the reactive species upon fluorine association and dissociation, respectively.[12,13,54,55] To this end, we have set out to prepare metal complexes of *ortho*-fluorinated diarylamides and examine their coordination chemistry. In this contribution, we describe the preparation and structural characterization of lithium, zirconium, and hafnium complexes derived from *N*-(2-fluorophenyl)-2,6-diisopropylanilide ([^{i}PrAr-NF]$^-$). The coordination characteristics of the *ortho*-fluorine atom with respect to these electrophilic metals are discussed.

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(1) Schrock, R. R. *Acc. Chem. Res.* **1997**, *30*, 9–16.
(2) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Organometallics* **1992**, *11*, 1452–1454.
(3) Schrock, R. R.; Cummins, C. C.; Wilhelm, T.; Lin, S.; Reid, S. M.; Kol, M.; Davis, W. M. *Organometallics* **1996**, *15*, 1470–1476.
(4) Tonzetich, Z. J.; Lu, C. C.; Schrock, R. R.; Hock, A. S.; Bonitatebus, P. J. *Organometallics* **2004**, *23*, 4362–4372.
(5) Agapie, T.; Diaconescu, P. L.; Mindiola, D. J.; Cummins, C. C. *Organometallics* **2002**, *21*, 1329–1340.
(6) Johnson, A. R.; Davis, W. M.; Cummins, C. C. *Organometallics* **1996**, *15*, 3825–3835.
(7) Cummins, C. C.; Schaller, C. P.; Vanduyne, G. D.; Wolczanski, P. T.; Chan, A. W. E.; Hoffmann, R. *J. Am. Chem. Soc.* **1991**, *113*, 2985–2994.
(8) Cummins, C. C.; Vanduyne, G. D.; Schaller, C. P.; Wolczanski, P. T. *Organometallics* **1991**, *10*, 164–170.
(9) Tsuie, B.; Swenson, D. C.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1997**, *16*, 1392–1400.
(10) Uhrhammer, R.; Black, D. G.; Gardner, T. G.; Olsen, J. D.; Jordan, R. F. *J. Am. Chem. Soc.* **1993**, *115*, 8493–8494.
(11) Manke, D. R.; Nocera, D. G. *Inorg. Chem.* **2003**, *42*, 4431–4436.
(12) Findeis, B.; Schubart, M.; Gade, L. H.; Moller, F.; Scowen, I.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1996**, 125–132.
(13) Memmler, H.; Walsh, K.; Gade, L. H.; Lauher, J. W. *Inorg. Chem.* **1995**, *34*, 4062–4068.
(14) Hagadorn, J. R.; Arnold, J. *Organometallics* **1998**, *17*, 1355–1368.
(15) Hagadorn, J. R.; Arnold, J. *J. Am. Chem. Soc.* **1996**, *118*, 893–894.
(16) Duncan, A. P.; Mullins, S. M.; Arnold, J.; Bergman, R. G. *Organometallics* **2001**, *20*, 1808–1819.
(17) Ackermann, L.; Bergman, R. G. *Org. Lett.* **2002**, *4*, 1475–1478.
(18) Patel, S.; Li, Y.; Odom, A. L. *Inorg. Chem.* **2007**, *46*, 6373–6381.

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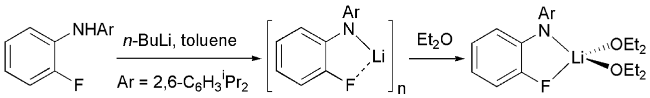
Scheme 1



Results and Discussion

Addition of 1 equiv of *n*-BuLi to a toluene solution of H[^{i}PrAr-NF][45] at –35 °C produced cleanly [^{i}PrAr-NF]Li as an off-white solid. The lithium complex is sparingly soluble in pentane but fairly soluble in arenes such as benzene and toluene. The ^{1}H and ^{13}C NMR spectra of [^{i}PrAr-NF]Li in C_6D_6 indicate C_s symmetry for this molecule. The room-temperature ^{19}F{^{1}H} and ^{7}Li{^{1}H} NMR spectra reveal a singlet resonance at –148.5 and 1.6 ppm, respectively, for the fluorine and the lithium atoms. The ^{7}Li signal broadens significantly upon cooling to temperatures lower than −70 °C (in toluene-d_8), but no ^{19}F−^{7}Li coupling is observed. Similar phenomenon was also found in a variable-temperature ^{19}F{^{1}H} NMR study. These results are consistent with a fluxional exchange process that involves rapid association and dissociation of the fluorine donor with respect to the lithium atom. Given the high electrophilic nature of the hard lithium cation, [^{i}PrAr-NF]Li is likely an oligomeric aggregate (Scheme 1). In accord with this postulation, [^{i}PrAr-NF]Li adopts readily 2 equiv of diethyl ether upon recrystallization from a diethyl ether solution to give colorless crystals of [^{i}PrAr-NF]Li(OEt_2)$_2$. Similar to [^{i}PrAr-NF]Li, [^{i}PrAr-NF]Li(OEt_2)$_2$ displays solution C_s symmetry on the NMR time scale as evidenced by the ^{1}H and ^{13}C NMR spectra, and no ^{19}F−^{7}Li coupling is observed even at −80 °C (in toluene-d_8).

The solid-state structure of [^{i}PrAr-NF]Li(OEt_2)$_2$ was confirmed by X-ray diffraction analysis. Crystallographic data are summarized in Table 1. As depicted in Figure 1, [^{i}PrAr-NF]Li(OEt_2)$_2$ is a four-coordinate species with the lithium center being coordinated with a bidentate [^{i}PrAr-NF]$^-$ and two diethyl ether molecules. The coordination geometry of [^{i}PrAr-NF]Li(OEt_2)$_2$ is best described as a distorted tetrahedron with the dihedral angles of N−Li−F and O−Li−O being 64.0°. The bond angles about the lithium center range from 80.6(2) to 131.0(2)°, with the most acute being associated with the [^{i}PrAr-NF]$^-$ ligand. The lithium atom lies perfectly on the N−phenylene−F plane, a result that is in sharp contrast to that of its phosphine analogue [Me-NP]Li(THF)$_2$ ([Me-NP]$^-$ =*N*-(2-diphenylphosphinophenyl)-2,6-dimethylanilide) in which the lithium atom is displaced significantly from the N−phenylene−P plane by 0.5954 Å.[42] Such discrepancy likely highlights the increased hardness and the small size of the fluorine atom in [^{i}PrAr-NF]$^-$ as compared to the diphenyl-substituted phosphorus donor in [Me-NP]$^-$, although the former carries a larger aryl substituent at the amido nitrogen. The *N*-aryl ring is perpendicular to the N−phenylene−F plane. The F−Li distance of 2.150(4) Å in [^{i}PrAr-NF]Li(OEt_2)$_2$ is comparable to those found in $Li_4(LH)_2(THF)_6$ (L = 2,4,6-tris(2-fluoroanilido)-1,3,5-triazene) (2.15(2) Å)[56] and [HC{SiMe$_2$N(2-FC$_6$H$_4$)}$_3$Sn(Li)] (1.984 Å average).[57] The fluorine donor, however, is likely to dissociate readily from the lithium center in solution as suggested by the NMR spectroscopic studies. This phenomenon is consistent with the weakly coordinating

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(19) Basuli, F.; Bailey, B. C.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 6052–6053.

(20) Bai, G.; Wei, P.; Stephan, D. W. *Organometallics* **2006**, *25*, 2649–2655.

(21) Swartz, D. L., II; Odom, A. L. *Organometallics* **2006**, *25*, 6125–6133.

(22) Ramanathan, B.; Odom, A. L. *J. Am. Chem. Soc.* **2006**, *128*, 9344–9345.

(23) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 429–447.

(24) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283–315.

(25) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169–1203.

(26) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236–2257.

(27) Murtuza, S.; Casagrande, O. L.; Jordan, R. F. *Organometallics* **2002**, *21*, 1882–1890.

(28) Domski, G. J.; Rose, J. M.; Coates, G. W.; Bolig, A. D.; Brookhart, M. *Prog. Polym. Sci.* **2007**, *32*, 30–92.

(29) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008–10009.

(30) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830–3831.

(31) Tonzetich, Z. J.; Schrock, R. R.; Hock, A. S.; Muller, P. *Organometallics* **2005**, *24*, 3335–3342.

(32) Schrock, R. R.; Adamchuk, J.; Ruhland, K.; Lopez, L. P. H. *Organometallics* **2005**, *24*, 857–866.

(33) Liang, L.-C.; Schrock, R. R.; Davis, W. M. *Organometallics* **2000**, *19*, 2526–2531.

(34) Liang, L.-C.; Schrock, R. R.; Davis, W. M.; McConville, D. H. *J. Am. Chem. Soc.* **1999**, *121*, 5797–5798.

(35) Mehrkhodavandi, P.; Bonitatebus, P. J.; Schrock, R. R. *J. Am. Chem. Soc.* **2000**, *122*, 7841–7842.

(36) Mehrkhodavandi, P.; Schrock, R. R. *J. Am. Chem. Soc.* **2001**, *123*, 10746–10747.

(37) Guerin, F.; McConville, D. H.; Vittal, J. J. *Organometallics* **1997**, *16*, 1491–1496.

(38) Oakes, D. C. H.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **2006**, *45*, 3476–3477.

(39) Liang, L.-C. *Coord. Chem. Rev.* **2006**, *250*, 1152–1177.

(40) Liang, L.-C.; Chien, P.-S.; Huang, Y.-L. *J. Am. Chem. Soc.* **2006**, *128*, 15562–15563.

(41) Lee, W.-Y.; Liang, L.-C. *Dalton Trans.* **2005**, 1952–1956.

(42) Liang, L.-C.; Lee, W.-Y.; Yin, C.-C. *Organometallics* **2004**, *23*, 3538–3547.

(43) Liang, L.-C.; Huang, M.-H.; Hung, C.-H. *Inorg. Chem.* **2004**, *43*, 2166–2174.

(44) Liang, L.-C.; Lin, J.-M.; Hung, C.-H. *Organometallics* **2003**, *22*, 3007–3009.

(45) Liang, L.-C.; Lee, W.-Y.; Hung, C.-H. *Inorg. Chem.* **2003**, *42*, 5471–5473.

(46) Lee, P.-Y.; Liang, L.-C. *Inorg. Chem.* **2007**, 46.

(47) Liang, L.-C.; Lee, P.-Y.; Lan, W.-L.; Hung, C.-H. *J. Organomet. Chem.* **2004**, *689*, 947–952.

(48) Liang, L.-C.; Yang, C.-W.; Chiang, M. Y.; Hung, C.-H.; Lee, P.-Y. *J. Organomet. Chem.* **2003**, *679*, 135–142.

(49) Chien, P.-S.; Liang, L.-C. *Inorg. Chem.* **2005**, *44*, 5147–5151.

(50) Liang, L.-C.; Lin, J.-M.; Lee, W.-Y. *Chem. Commun.* **2005**, 2462–2464.

(51) Liang, L.-C.; Chien, P.-S.; Lin, J.-M.; Huang, M.-H.; Huang, Y.-L.; Liao, J.-H. *Organometallics* **2006**, *25*, 1399–1411.

(52) Liang, L.-C.; Chien, P.-S.; Huang, M.-H. *Organometallics* **2005**, *24*, 353–357.

(53) Huang, M.-H.; Liang, L.-C. *Organometallics* **2004**, *23*, 2813–2816.

(54) Memmler, H.; Kauper, U.; Gade, L. H.; Scowenb, I. J.; McPartlin, M. *Chem. Commun.* **1996**, 1751–1752.

(55) Schneider, A.; Gade, L. H.; Breuning, M.; Bringmann, G.; Scowen, I. J.; McPartlin, M. *Organometallics* **1998**, *17*, 1643–1645.

(56) Rivals, F.; Steiner, A. *Chem. Commun.* **2001**, 2104–2105.

(57) Lutz, M.; Haukka, M.; Pakkanen, T. A.; McPartlin, M.; Gade, L. H. *Inorg. Chim. Acta* **2003**, *345*, 185–189.

Table 1. Crystallographic Data for [^{i}PrAr-NF]Li(OEt$_2$)$_2$, [^{i}PrAr-NF]$_2$ZrCl$_2$, [^{i}PrAr-NF]$_2$HfCl$_2$, [^{i}PrAr-NF]$_2$ZrMe$_2$, [^{i}PrAr-NF]$_2$Zr(i-Bu)$_2$, and [^{i}PrAr-NF]$_2$Hf(CH$_2$Ph)$_2$

compound	[^{i}PrAr-NF]Li(OEt$_2$)$_2$	{[^{i}PrAr-NF]$_2$ZrCl$_2$}(OEt$_2$)
formula	$C_{26}H_{41}FLiNO_2$	$C_{40}H_{52}Cl_2F_2N_2OZr$
Fw	425.54	776.96
crystal size (mm^3)	0.55 × 0.4 × 0.25 mm^3	0.66 × 0.38 × 0.28
D_{calc} (Mg/m^3)	1.067	1.283
crystal syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (Å)	16.3699(5)	12.4422(2)
b (Å)	9.5320(3)	13.03410(10)
c (Å)	17.0844(6)	14.8695(2)
α (deg)	90	64.6730(10)
β (deg)	96.353(2)	86.7590(10)
γ (deg)	90	68.3530(10)
V (Å^3)	2649.44(15)	2011.15(4)
Z	4	2
T (K)	200(2)	200(2)
radiation, λ (Å)	0.71073	0.71073
$2\theta_{max}$ (deg)	50.72	55.02
index ranges (h;k;l)	−16,19;−9,11;−20,20	−16,16;−16,16;−18,19
total no. of reflns	14501	30725
no. of indep reflns	4820	9209
R_{int}	0.0712	0.0529
absorp coeff (mm^{-1})	0.070	0.447
no. of data/restraints/parameters	4820/0/281	9209/0/424
goodness of fit	1.042	1.142
final R indices ($I > 2\sigma(I)$)	$R1 = 0.0654$, $wR2 = 0.1586$	$R1 = 0.0429$, $wR2 = 0.1110$
R indices (all data)	$R1 = 0.1216$, $wR2 = 0.1955$	$R1 = 0.0551$, $wR2 = 0.1258$
residual density (e/Å^3)	−0.342 to 0.297	−0.665 to 0.720

compound	[^{i}PrAr-NF]$_2$HfCl$_2$	[^{i}PrAr-NF]$_2$ZrMe$_2$
formula	$C_{36}H_{42}Cl_2F_2HfN_2$	$C_{38}H_{48}F_2N_2Zr$
Fw	790.11	662.00
crystal size (mm^3)	0.45 × 0.4 × 0.2	0.45 × 0.4 × 0.22
D_{calc} (Mg/m^3)	1.509	1.260
crystal syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.18380(10)	12.7396(2)
b (Å)	13.6568(2)	16.7097(3)
c (Å)	16.0542(3)	17.8080(4)
α (deg)	67.0810(10)	105.5730(10)
β (deg)	77.9100(10)	105.8670(10)
γ (deg)	70.2950(10)	91.7950(10)
V (Å^3)	1738.88(5)	3490.07(11)
Z	2	4
T (K)	200(2)	200(2)
radiation, λ (Å)	0.71073	Mo Kα, 0.71073
$2\theta_{max}$ (deg)	52.04	50.76
index ranges (h;k;l)	−11,11;−16,16;−19,19	−15,15;−20,20;−21,21
total no. of reflns	24897	35399
no. of indep reflns	6845	12304
R_{int}	0.0529	0.0690
absorp coeff (mm^{-1})	3.190	0.353
no. of data/restraints/parameters	6845/0/389	12304/0/775
goodness of fit	0.924	0.826
final R indices ($I > 2\sigma(I)$)	$R1 = 0.0328$, $wR2 = 0.0833$	$R1 = 0.0600$, $wR2 = 0.1593$
R indices (all data)	$R1 = 0.0391$, $wR2 = 0.0993$	$R1 = 0.0895$, $wR2 = 0.1910$
residual density (e/Å^3)	−1.990 to 1.577	−0.797 to 1.910

compound	[^{i}PrAr-NF]$_2$Zr(i-Bu)$_2$	[^{i}PrAr-NF]$_2$Hf(CH$_2$Ph)$_2$
formula	$C_{44}H_{60}F_2N_2Zr$	$C_{50}H_{56}F_2HfN_2$
Fw	746.16	901.46
crystal size (mm^3)	0.24 × 0.2 × 0.08	0.24 × 0.2 × 0.08
D_{calc} (Mg/m^3)	1.198	1.407
crystal syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a (Å)	18.4614(4)	11.06020(10)
b (Å)	12.6894(3)	11.73110(10)
c (Å)	19.2483(5)	18.4898(3)
α (deg)	90	74.8510(10)
β (deg)	113.4910(10)	86.3970(10)
γ (deg)	90	66.8840(10)
V (Å^3)	4135.47(17)	2127.60(4)
Z	4	2
T (K)	200(2)	200(2)
radiation, λ (Å)	0.71073	0.71073

Table 1. Continued

compound	[^{i}PrAr-NF]$_2$Zr(i-Bu)$_2$	[^{i}PrAr-NF]$_2$Hf(CH$_2$Ph)$_2$
$2\theta_{max}$ (deg)	50.72	50.76
index ranges (h;k;l)	−22,22;-15,15;-23,21	−13,13;-14,14;-22,22
total no. of reflns	31134	29927
no. of indep reflns	7545	7798
R_{int}	0.0922	0.0593
absorp coeff (mm^{-1})	0.305	2.496
no. of data/restraints/parameters	7545/0/443	7798/0/497
goodness of fit	1.124	1.111
final R indices ($I > 2\sigma(I)$)	$R1 = 0.0691$, $wR2 = 0.1595$	$R1 = 0.0317$, $wR2 = 0.0844$
R indices (all data)	$R1 = 0.1134$, $wR2 = 0.1977$	$R1 = 0.0416$, $wR2 = 0.1115$
residual density (e/Å^3)	−1.046 to 0.869	−1.702 to 0.762

nature of the fluorine atom but somewhat surprising in view of the hardness of both donor and acceptor. The Li−N and Li−O distances are both well within the expected values.

The reactions of [^{i}PrAr-NF]Li with MCl$_4$(THF)$_2$ (M = Zr, Hf),[58] irrespective of the molar ratio, in toluene or diethyl ether at –35 °C afforded the corresponding dichloride complexes [^{i}PrAr-NF]$_2$ZrCl$_2$ and [^{i}PrAr-NF]$_2$HfCl$_2$ in high isolated yield. Attempts to spectroscopically observe or isolate the transient 1:1 products from reactions employing 1 equiv of [^{i}PrAr-NF]Li were not successful. Instead, [^{i}PrAr-NF]$_2$ZrCl$_2$ and [^{i}PrAr-NF]$_2$HfCl$_2$ were generated exclusively. These results are notably different from what has been reported for the phosphine analogue *N*-(2-diphenylphosphinophenyl)-2,6-diisopropylanilide ([^{i}Pr-NP]$^-$), which reacts with 1 equiv of MCl$_4$(THF)$_2$ (M = Zr, Hf) to produce successfully the corresponding [^{i}Pr-NP]MCl$_3$(THF)[49] under similar conditions. The unsuccessful observation or isolation of the presumed [^{i}PrAr-NF]MCl$_3$(THF) is ascribable to the steric unsaturation of this transient molecule due to the lack of substituent at the fluorine donor.

The fluorine atoms in [^{i}PrAr-NF]$_2$ZrCl$_2$ and [^{i}PrAr-NF]$_2$HfCl$_2$ appear as a singlet resonance in the ^{19}F{^{1}H} NMR spectra at −115.6 and −118.5 ppm, respectively. These ^{19}F chemical shifts are relatively downfield as compared to those of H[^{i}PrAr-NF] (−138.3 ppm),[45] [^{i}PrAr-NF]Li (−148.5 ppm), and [^{i}PrAr-NF]Li(OEt$_2$)$_2$ (−149.0 ppm). The ^{1}H NMR spectra of [^{i}PrAr-NF]$_2$ZrCl$_2$ and [^{i}PrAr-NF]$_2$HfCl$_2$ at room temperature reveal one septet resonance for isopropylmethine and two doublet resonances for isopropylmethyl groups. These results are indicative of an intramolecular symmetry for the two [^{i}PrAr-NF]$^-$ ligands in [^{i}PrAr-NF]$_2$ZrCl$_2$ and [^{i}PrAr-NF]$_2$HfCl$_2$ on the NMR time scale. In principle, four possible stereoisomers (and their corresponding enantiomers) can be deduced for the solution structures of these dichloride complexes on the basis of the NMR investigation, assuming that both molecules contain coordinated fluorine atoms in an octahedral core (Figure 2). A variable-temperature ^{1}H NMR study of [^{i}PrAr-NF]$_2$ZrCl$_2$ (in toluene-d_8) showed that the isopropyl methine and methyl signals become broadening at −20 °C and resolve to give two sets of signals at a temperature lower than −50 °C, consistent with a rapid rotation of the 2,6-diisopropylphenyl groups about the N−Ar bonds at room temperature.[59] As a result, the two arylated amido nitrogen donors in [^{i}PrAr-NF]$_2$MCl$_2$ (M = Zr, Hf) are likely *trans* to each other, given the significant steric bulk imposed by the diisopropylphenyl groups. Stereoisomers II and III are thus more possible than I and IV. In view of the *trans* influence order of the formally anionic chlorides and the neutral fluorine atoms, stereoisomer III seems more likely than II.

Colorless crystals of [^{i}PrAr-NF]$_2$ZrCl$_2$ and [^{i}PrAr-NF]$_2$HfCl$_2$ suitable for X-ray diffraction analysis were grown from a concentrated diethyl ether solution at –35 °C. As depicted in Figures 3 and 4, both structures are C_2-symmetric and correspond to the stereoisomer III in which the two amido nitrogen donors are virtually *trans* to each other (N−M−N angles of 145.44(7)° for Zr and 144.9(1)° for Hf) and the two fluorine donors (and the two chloride ligands) are *cis*, consistent with what is deduced from the solution NMR studies. The severe distortion from the ideal octahedron is ascribed to the acute bite angles of 70.16° (average) for [^{i}PrAr-NF]$_2$ZrCl$_2$ and 71.14° (average) for [^{i}PrAr-NF]$_2$HfCl$_2$, leading to markedly wide Cl−M−Cl angles of 105.34(3)° for the former and 104.63(5)° for the latter. The C_2 axis lies

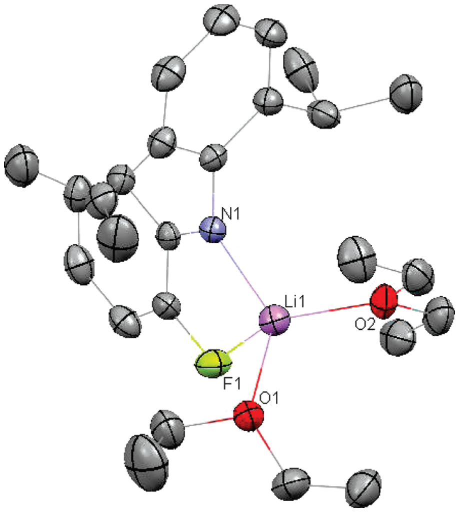

Figure 1. Molecular structure of [^{i}PrAr-NF]Li(OEt$_2$)$_2$ with thermal ellipsoids drawn at the 35% probability level. Selected bond distances (Å) and angles (deg): F(1)−Li(1) 2.150(4), O(1)−Li(1) 2.000(4), O(2)−Li(1) 1.962(4), N(1)−Li(1) 1.959(4), N(1)−Li(1)−O(2) 115.3(2), N(1)−Li(1)−O(1) 131.0(2), O(2)−Li(1)−O(1) 108.1(2), N(1)−Li(1)−F(1) 80.6(2), O(2)−Li(1)−F(1) 128.7(2), O(1)−Li(1)−F(1) 89.8(2).

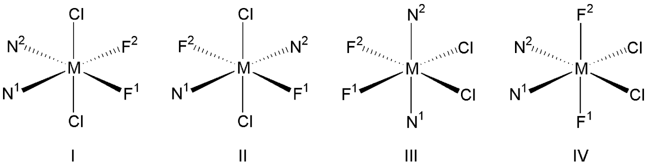

Figure 2. Possible stereoisomers for [^{i}PrAr-NF]$_2$MCl$_2$, where N^{x}F^x (x = 1, 2) represents the chelating *o*-fluorinated diarylamido ligands.

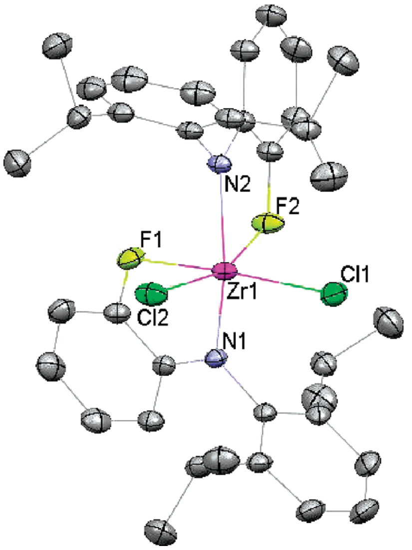

Figure 3. Molecular structure of $[^i\text{PrAr-NF}]_2\text{ZrCl}_2$ with thermal ellipsoids drawn at the 35% probability level. Selected bond distances (Å) and angles (deg): Zr(1)−N(2) 2.1159(19), Zr(1)−N(1) 2.1298(18), Zr(1)−F(1) 2.3474(14), Zr(1)−Cl(1) 2.3491(7), Zr(1)−Cl(2) 2.3648(7), Zr(1)−F(2) 2.3796(14), N(2)−Zr(1)−N(1) 145.44(7), N(2)−Zr(1)−F(1) 83.19(6), N(1)−Zr(1)−F(1) 70.60(6), N(2)−Zr(1)−Cl(1) 102.67(5), N(1)−Zr(1)−Cl(1) 96.84(5), F(1)−Zr(1)−Cl(1) 162.29(4), N(2)−Zr(1)−Cl(2) 97.83(5), N(1)−Zr(1)−Cl(2) 104.19(5), F(1)−Zr(1)−Cl(2) 90.16(4), Cl(1)−Zr(1)−Cl(2) 105.34(3), N(2)−Zr(1)−F(2) 69.72(6), N(1)−Zr(1)−F(2) 81.51(6), F(1)−Zr(1)−F(2) 74.35(6), Cl(1)−Zr(1)−F(2) 91.84(5), Cl(2)−Zr(1)−F(2) 160.88(4).

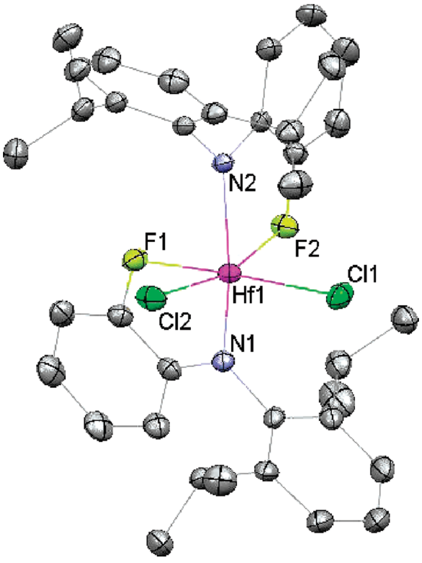

Figure 4. Molecular structure of $[^i\text{PrAr-NF}]_2\text{HfCl}_2$ with thermal ellipsoids drawn at the 35% probability level. Selected bond distances (Å) and angles (deg): Hf(1)−N(2) 2.114(3), Hf(1)−N(1) 2.117(3), Hf(1)−F(1) 2.311(2), Hf(1)−F(2) 2.312(2), Hf(1)−Cl(1) 2.3340(11), Hf(1)−Cl(2) 2.3358(11), N(2)−Hf(1)−N(1) 144.89(13), N(2)−Hf(1)−F(1) 82.64(11), N(1)−Hf(1)−F(1) 70.95(11), N(2)−Hf(1)−F(2) 71.32(11), N(1)−Hf(1)−F(2) 81.25(11), F(1)−Hf(1)−F(2) 79.56(10), N(2)−Hf(1)−Cl(1) 102.62(9), N(1)−Hf(1)−Cl(1) 97.94(9), F(1)−Hf(1)−Cl(1) 164.57(8), F(2)−Hf(1)−Cl(1) 88.32(8), N(2)−Hf(1)−Cl(2) 97.36(9), N(1)−Hf(1)−Cl(2) 104.63(9), F(1)−Hf(1)−Cl(2) 88.86(8), F(2)−Hf(1)−Cl(2) 164.63(8), Cl(1)−Hf(1)−Cl(2) 104.63(5).

on the mean MF_2Cl_2 plane and bisects the Cl−M−Cl angle. The chirality of the molecules shown in Figures 3 and 4is Λ. We suggest that possible stereoisomers other than conformation III and its enantiomer be virtually not present in the reaction mixture on the basis of the nearly quantitative isolated yield and the solution NMR studies that display only one set of signals for the reaction aliquots. The stereoisomeric preference of $[^i\text{PrAr-NF}]_2\text{ZrCl}_2$ and $[^i\text{PrAr-NF}]_2\text{HfCl}_2$ is notably different from that of their phosphorus analogues such as $[\text{Me-NP}]_2\text{ZrCl}_2$,[49] $[\text{Me-NP}]_2\text{HfCl}_2$,[49] and $\text{ZrCl}_2[\eta^2\text{-N(SiMe}_2\text{CH}_2\text{PMe}_2)_2]_2$,[60] whose solid-state structures correspond instead to that analogous to stereoisomer I (with phosphorus donors in the place of the fluorine atoms). The Zr−N and Hf−N distances in $[^i\text{PrAr-NF}]_2\text{MCl}_2$ are comparable to the expected values for a six-coordinate Zr(IV) and Hf(IV) species; however, the Zr−Cl and Hf−Cl distances of 2.3570 (average) and 2.3349 Å (average), respectively, are relatively shorter than those of $[\text{Me-NP}]_2\text{ZrCl}_2$ (2.4502 Å average),[49] $[\text{Me-NP}]_2\text{HfCl}_2$ (2.4170 Å average),[49] $\text{ZrCl}_2(\eta^2\text{-N(SiMe}_2\text{CH}_2\text{PMe}_2)_2]_2$ (2.4599 Å average),[60] and $\text{MLCl}_2(\mu\text{-Cl})_2\text{Li(OEt}_2)_2$ (L = 5-*tert*-butyl-2-[(2,6-diisopropylphenyl)aldimino]pyrrolide; M = Zr, 2.4505 Å average; M = Hf, 2.4397 Å average).[48] The M−F distances in $[^i\text{PrAr-NF}]_2\text{ZrCl}_2$ (2.3635 Å average) and $[^i\text{PrAr-NF}]_2\text{HfCl}_2$ (2.312 Å average) are notably shorter than the corresponding values found for $[\text{C}_6\text{F}_5\text{NCH}_2\text{CH}_2\text{CH}_2\text{NC}_6\text{F}_5]\text{Zr(CH}_2\text{Ph)}_2$(2.511(1)Å),[61] $\text{HC}\{\text{SiMe}_2\text{N(2-FC}_6\text{H}_4)\}_3\text{ZrCl}_2\text{Li(OEt}_2)_2$ (2.535(5) Å),[13] $[cis,cis\text{-1,3,5-(C}_6\text{F}_5\text{N)}_3\text{C}_6\text{H}_9]\text{ZrCH(SiMe}_3)_2$ (2.559 Å average),[62] $\text{HC}\{\text{SiMe}_2\text{N(2-FC}_6\text{H}_4)\}_3\text{Zr(S}_2\text{C)Fe(CO)}_2(\delta\text{-C}_5\text{H}_5)$ (2.563(8) Å),[54] $\{\text{K(C}_7\text{H}_8)_2\}\{\text{ZrCl}_2[\text{N(C}_6\text{F}_5)_2]_3\}$ (2.602(2) Å),[63] $\text{HC}\{\text{SiMe}_2\text{N(2-FC}_6\text{H}_4)\}_3\text{Zr(SCNPh)Fe(CO)}_2(\delta\text{-C}_5\text{H}_5)$ (2.703(11) Å),[64] and $[(2,6\text{-F}_2\text{C}_6\text{H}_3\text{NCH}_2)_2\text{C(CH}_3)(2\text{-C}_5\text{H}_4\text{N)}]\text{Hf(}i\text{-Bu)}_2$ (2.559 Å average).[65] The relatively short distances of M−Cl and M−F bonds in $[^i\text{PrAr-NF}]_2\text{ZrCl}_2$ and $[^i\text{PrAr-NF}]_2\text{HfCl}_2$ are reflective of the highly electrophilic nature of these group 4 complexes. Similar to what has been found for $[^i\text{PrAr-NF}]\text{Li(OEt}_2)_2$, the group 4 metals in $[^i\text{PrAr-NF}]_2\text{ZrCl}_2$ and $[^i\text{PrAr-NF}]_2\text{HfCl}_2$ lie virtually on the mean N−phenylene−F planes and the *N*-aryl rings are approximately perpendicular to the corresponding N−phenylene−F planes.

Alkylation of $[^i\text{PrAr-NF}]_2\text{ZrCl}_2$ or $[^i\text{PrAr-NF}]_2\text{HfCl}_2$ with a variety of Grignard reagents in diethyl ether at –35 °C generated the corresponding dialkyl complexes $[^i\text{PrAr-NF}]_2\text{MR}_2$ (M = Zr, Hf; R = Me, *i*-Bu, CH$_2$Ph; Scheme 2) in high isolated yield. Reminiscent to what has been observed for $[^i\text{PrAr-NF}]_2\text{MCl}_2$, these dialkyl complexes display solution C_2 symmetry on the NMR time scale. The $^{19}\text{F}\{^1\text{H}\}$ NMR spectra exhibit a singlet resonance at ca. −120 ppm. The *ortho*-isopropyl substituents on the *N*-aryl rings are observed in the ^{1}H NMR spectra as one septet resonance for the methine and two doublet resonances for the methyl groups. A variable-temperature ^{1}H NMR study of $[^i\text{PrAr-NF}]_2\text{ZrMe}_2$

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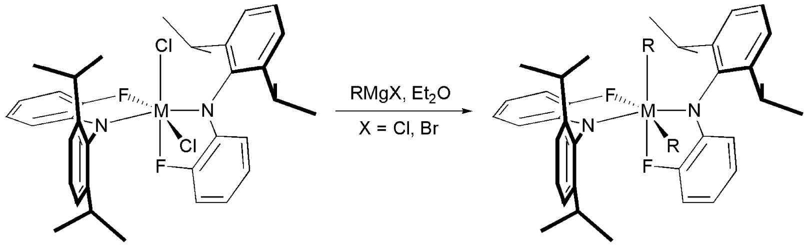
(58) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135–140.
(59) Guerin, F.; McConville, D. H.; Payne, N. C. *Organometallics* **1996**, *15*, 5085–5089.
(60) Fryzuk, M. D.; Williams, H. D.; Rettig, S. J. *Inorg. Chem.* **1983**, *22*, 863–868.
(61) Ziniuk, Z.; Goldberg, I.; Kol, M. *Inorg. Chem. Commun.* **1999**, *2*, 549–551.
(62) Turculet, L.; Tilley, T. D. *Organometallics* **2002**, *21*, 3961–3972.
(63) Giesbrecht, G. R.; Gordon, J. C.; Clark, D. L.; Hijar, C., A.; Scott, B. L.; Watkin, J. G. *Polyhedron* **2003**, *22*, 153–163.
(64) Gade, L. H.; Memmler, H.; Kauper, U.; Schneider, A.; Fabre, S.; Bezougli, I.; Lutz, M.; Galka, C.; Scowen, I. J.; McPartlin, M. *Chem.*−*Eur. J.* **2000**, *6*, 692–708.
(65) Schrock, R. R.; Adamchuk, J.; Ruhland, K.; Lopez, L. P. H. *Organometallics* **2003**, *22*, 5079–5091.

Scheme 2



[^{i}PrAr-NF]$_2$MCl$_2$

[^{i}PrAr-NF]$_2$MR$_2$
M = Zr, Hf
R = Me, *i*-Bu, CH$_2$Ph

(toluene-d_8) revealed that these signals do not tend to broaden at temperatures higher than −80 °C, implying a rapid rotation of the *N*-aryl rings about the N−Ar bonds.[59] The ^{1}H and ^{13}C{^{1}H} NMR spectra exhibit only one set of resonances corresponding to the Zr- or Hf-bound alkyl ligands. The triplet resonances found for the Cα atoms ($^2J_{C\alpha F}$ = ca. 14 Hz) in the ^{13}C{^{1}H} NMR spectra of these dialkyl species are indicative of the coordination of the two *o*-fluorine atoms in these molecules. The stereochemistry of [^{i}PrAr-NF]$_2$MR$_2$ is thus presumably analogous to that of their dichloride precursors.

Single crystals of [^{i}PrAr-NF]$_2$ZrMe$_2$, [^{i}PrAr-NF]$_2$Zr(*i*-Bu)$_2$, and [^{i}PrAr-NF]$_2$Hf(CH$_2$Ph)$_2$ suitable for X-ray diffraction analysis were grown from a concentrated diethyl ether solution at –35 °C. As depicted in Figures 5−7, these dialkyl complexes are six-coordinate species with core structures analogous to those of the dichloride derivatives. These results are consistent with those determined by NMR spectroscopic studies. It is interesting to note that these C_2-symmetric group 4 dichloride and dialkyl complexes featuring two mutually *cis*-chloride or alkyl ligands, respectively, fall into the territory of the popular motifs for the development of nonmetallocene catalysts for stereospecific polymerization of α-olefins.[66–72] The chirality of [^{i}PrAr-NF]$_2$ZrMe$_2$ shown in Figure 5 is Δ, whereas that of [^{i}PrAr-NF]$_2$Zr(*i*-Bu)$_2$ and [^{i}PrAr-NF]$_2$Hf(CH$_2$Ph)$_2$ illustrated in Figures 6 and 7, respectively, is Λ. The M−F distances in [^{i}PrAr-NF]$_2$ZrMe$_2$ (2.446 Å average), [^{i}PrAr-NF]$_2$Zr(*i*-Bu)$_2$ (2.454 Å average), and [^{i}PrAr-NF]$_2$Hf(CH$_2$Ph)$_2$ (2.411 Å average) are all slightly longer than those of the corresponding dichloride complexes, consistent with the greater *trans* influence of an alkyl than a chloride. The discrepancy in M−F distances is also ascribable to the somewhat more electrophilic metals of the dichloride complexes than those of the dialkyl counterparts (electronegativity: Cl 3.16, C 2.55).[73] The benzyl ligands in [^{i}PrAr-NF]$_2$Hf(CH$_2$Ph)$_2$ adopt an α^1-coordination mode as evidenced by the Hf−C distances and the Hf−C−C angles.

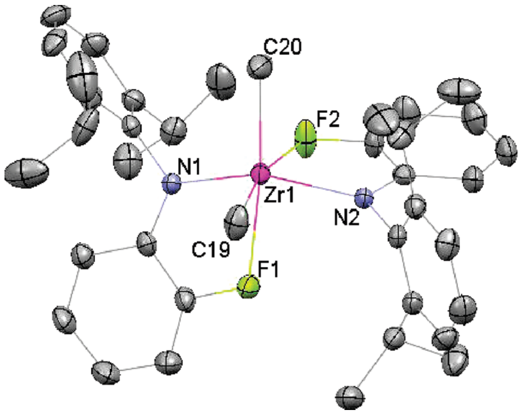


Figure 5. Molecular structure of [^{i}PrAr-NF]$_2$ZrMe$_2$ with thermal ellipsoids drawn at the 35% probability level. The asymmetric unit cell contains two independent molecules; only one is shown for clarity. Selected bond distances (Å) and angles (deg): Zr(1)−N(1) 2.134(3), Zr(1)−N(2) 2.151(3), Zr(1)−C(19) 2.216(5), Zr(1)−C(20) 2.228(5), Zr(1)−F(2) 2.418(3), Zr(1)−F(1) 2.473(3), N(1)−Zr(1)−N(2) 139.62(13), N(1)−Zr(1)−C(19) 104.13(17), N(2)−Zr(1)−C(19) 98.91(17), N(1)−Zr(1)−C(20) 101.98(17), N(2)−Zr(1)−C(20) 103.84(18), C(19)−Zr(1)−C(20) 104.3(2), N(1)−Zr(1)−F(2) 82.75(12), N(2)−Zr(1)−F(2) 69.56(11), C(19)−Zr(1)−F(2) 167.19(16), C(20)−Zr(1)−F(2) 84.4(2), N(1)−Zr(1)−F(1) 68.69(11), N(2)−Zr(1)−F(1) 81.85(11), C(19)−Zr(1)−F(1) 83.22(18), C(20)−Zr(1)−F(1) 169.48(17), F(2)−Zr(1)−F(1) 89.42(12).

Conclusions

In summary, we have prepared and characterized a series of *o*-fluorinated diarylamido complexes of lithium, zirconium, and hafnium. The solution- and solid-state structures of these complexes have been established by multinuclear NMR spectroscopy and X-ray crystallography, respectively. Consistent with its weakly coordinating nature, the fluorine donor in [^{i}PrAr-NF]Li and [^{i}PrAr-NF]Li(OEt$_2$)$_2$seems to dissociate readily from the lithium atom in solution. With the coordination of the *o*-fluorine atoms, the group 4 complexes reported herein are all six-coordinate species that adopt selectively a C_2-symmetric structure with the two chlorides or alkyls having *cis* orientation. This result is of particular interest as no internal symmetry is inherently imposed by the ligands employed. The C_2-symmetric structure found for [^{i}PrAr-NF]$_2$MX$_2$ (M = Zr, Hf; X = Cl, alkyl) in this study is

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(66) Tshuva, E. Y.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2000**, *122*, 10706–10707.

(67) Cohen, A.; Yeori, A.; Goldberg, I.; Kol, M. *Inorg. Chem.* **2007**, *46*, 8114–8116.

(68) Segal, S.; Goldberg, I.; Kol, M. *Organometallics* **2005**, *24*, 200–202.

(69) Yeori, A.; Goldberg, I.; Shuster, M.; Kol, M. *J. Am. Chem. Soc.* **2006**, *128*, 13062–13063.

(70) Capacchione, C.; Proto, A.; Ebeling, H.; Mulhaupt, R.; Moller, K.; Spaniol, T. P.; Okuda, J. *J. Am. Chem. Soc.* **2003**, *125*, 4964–4965.

(71) Capacchione, C.; De Carlo, F.; Zannoni, C.; Okuda, J.; Proto, A. *Macromolecules* **2004**, *37*, 8918–8922.

(72) Beckerle, K.; Manivannan, R.; Spaniol, T. P.; Okuda, J. *Organometallics* **2006**, *25*, 3019–3026.

(73) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 93.

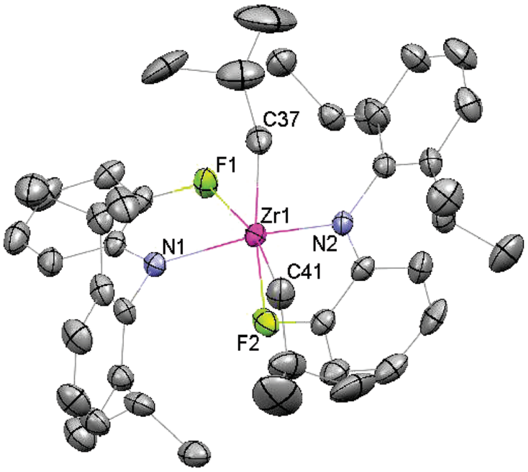

Figure 6. Molecular structure of [^{i}PrAr-NF]$_2$Zr(i-Bu)$_2$ with thermal ellipsoids drawn at the 35% probability level. Selected bond distances (Å) and angles (deg): Zr(1)−N(2) 2.159(4), Zr(1)−N(1) 2.159(4), Zr(1)−C(37) 2.203(5), Zr(1)−C(41) 2.211(5), Zr(1)−F(2) 2.438(3), Zr(1)−F(1) 2.470(3), N(2)−Zr(1)−N(1) 139.00(14), N(2)−Zr(1)−C(37) 97.88(17), N(1)−Zr(1)−C(37) 109.36(17), N(2)−Zr(1)−C(41) 108.44(17), N(1)−Zr(1)−C(41) 99.20(18), C(37)−Zr(1)−C(41) 95.1(2), N(2)−Zr(1)−F(2) 68.60(12), N(1)−Zr(1)−F(2) 78.53(11), C(37)−Zr(1)−F(2) 163.97(17), C(41)−Zr(1)−F(2) 97.32(17), N(2)−Zr(1)−F(1) 81.24(11), N(1)−Zr(1)−F(1) 68.74(12), C(37)−Zr(1)−F(1) 90.67(17), C(41)−Zr(1)−F(1) 167.83(16), F(2)−Zr(1)−F(1) 79.07(10).

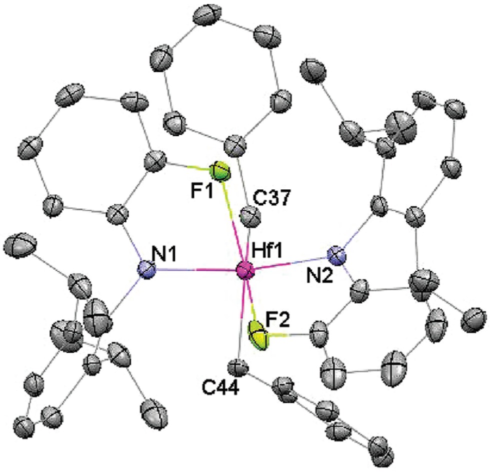

Figure 7. Molecular structure of [^{i}PrAr-NF]$_2$Hf(CH$_2$Ph)$_2$ with thermal ellipsoids drawn at the 35% probability level. Selected bond distances (Å) and angles (deg): Hf(1)−N(2) 2.130(4), Hf(1)−N(1) 2.147(4), Hf(1)−C(44) 2.220(4), Hf(1)−C(37) 2.221(5), Hf(1)−F(1) 2.367(3), Hf(1)−F(2) 2.454(3), N(2)−Hf(1)−N(1) 138.91(14), N(2)−Hf(1)−C(44) 110.63(16), N(1)−Hf(1)−C(44) 92.67(16), N(2)−Hf(1)−C(37) 103.73(16), N(1)−Hf(1)−C(37) 106.12(16), C(44)−Hf(1)−C(37) 97.72(19), N(2)−Hf(1)−F(1) 84.31(12), N(1)−Hf(1)−F(1) 70.14(12), C(44)−Hf(1)−F(1) 162.77(15), C(37)−Hf(1)−F(1) 86.49(15), N(2)−Hf(1)−F(2) 68.87(11), N(1)−Hf(1)−F(2) 83.63(12), C(44)−Hf(1)−F(2) 79.38(16), C(37)−Hf(1)−F(2) 170.03(14), F(1)−Hf(1)−F(2) 99.09(11)

conceptually analogous to that of ansa-metallocenes and their noncyclopentadienyl alternatives. Studies directed to delineate the reactivity of these molecules are currently underway.

Experimental Section

General Procedures. Unless otherwise specified, all experiments were performed under nitrogen using standard Schlenk or glovebox techniques. All solvents were reagent grade or better and purified by standard methods. The NMR spectra were recorded on Varian Unity or Bruker AV instruments. Chemical shifts (δ) are listed as parts per million downfield from tetramethylsilane, and coupling constants (J) and peak widths at half-height ($\Delta\upsilon_{1/2}$) are in hertz. ^{1}H and ^{13}C NMR spectra are referenced using the residual solvent peak at δ 7.16 and 128.39, respectively, for C$_6$D$_6$. The assignment of the carbon atoms is based on the DEPT ^{13}C NMR spectroscopy. ^{19}F and ^{7}Li NMR spectra are referenced externally using CFCl$_3$ in CHCl$_3$ at δ 0, respectively. Routine coupling constants are not listed. All NMR spectra were recorded at room temperature in specified solvents unless otherwise noted. Elemental analysis was performed on a Heraeus CHN-O rapid analyzer.

Materials. Compounds N-(2-fluorophenyl)-2,6-diisopropylaniline (H[^{i}PrAr-NF])[45] and MCl$_4$(THF)$_2$ (M = Zr, Hf)[58] were prepared according to the literature procedures. All other chemicals were obtained from commercial vendors and used as received.

X-ray Crystallography. Table 1 summarizes the crystallographic data for [^{i}PrAr-NF]Li(OEt$_2$)$_2$, [^{i}PrAr-NF]$_2$ZrCl$_2$, [^{i}PrAr-NF]$_2$HfCl$_2$, [^{i}PrAr-NF]$_2$ZrMe$_2$, [^{i}PrAr-NF]$_2$Zr(i-Bu)$_2$, and [^{i}PrAr-NF]$_2$Hf(CH$_2$Ph)$_2$. Data were collected on a Bruker-Nonius Kappa CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.7107 Å). Structures were solved by direct methods and refined by full matrix least-squares procedures against F^2 using WinGX crystallographic software package or SHELXL-97. All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions.

Synthesis of Lithium N-(2-Fluorophenyl)-2,6-diisopropylanilide, [^{i}PrAr-NF]Li, and Its Diethyl Ether Adduct, [^{i}PrAr-NF]Li(OEt$_2$)$_2$. Compound H[^{i}PrAr-NF] (1.007 g, 3.71 mmol) was dissolved in toluene (10 mL) and cooled to −35 °C. To this was added n-BuLi (2.32 mL, 1.6 M in hexane, Aldrich, 3.71 mmol) dropwise. The reaction solution was stirred at room temperature for 3 h and evaporated to dryness under reduced pressure. The red, viscous residue was triturated with pentane (10 mL) to afford the product as an off-white solid, which was isolated, washed with pentane (5 mL × 2), and dried in vacuo: yield 798.4 mg (78%); ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ 7.06 (s, 3, Ar), 6.95 (dd, 1, Ar), 6.79 (t, 1, Ar), 6.26 (q, 1, Ar), 6.14 (t, 1, Ar), 3.03 (septet, 2, CHMe$_2$), 1.03 (d, 6, CHMe_2), 0.74 (d, 6, CHMe_2); ^{7}Li{^{1}H} NMR (C$_6$D$_6$, 194 MHz) δ 1.64 ($\upsilon_{1/2}$ = 8.97 Hz); ^{19}F NMR (C$_6$D$_6$, 188.15 MHz) δ −148.51; ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.5 MHz) δ 156.63 (d, J_{CF} = 214.10, CF), 147.75 (d, J_{CF} = 8.16, C), 145.72 (s, C), 14.99 (s, C), 127.01 (s, CH), 125.50 (s, CH), 125.17 (s, CH), 115.88 (d, J_{CF} = 6.40, CH), 113.99 (d, J_{CF} = 21.96, CH), 111.71 (d, J_{CF} = 9.16, CH), 27.93 (s, CHMe$_2$), 25.11 (s, CHMe_2), 24.79 (s, CHMe_2). Anal. Calcd for C$_{18}$H$_{21}$FLiN: C, 77.93; H, 7.64; N, 5.05. Found: C, 77.60; H, 8.07; N, 4.69. Recrystallization of the off-white solid [^{i}PrAr-NF]Li from a concentrated diethyl ether solution at –35 °C gave colorless crystals of [^{i}PrAr-NF]Li(OEt$_2$)$_2$ suitable for X-ray diffraction analysis: ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ 7.35 (d, 2, Ar), 7.23 (t, 1, Ar), 7.03 (dd, 1, Ar), 6.89 (t, 1, Ar), 6.32 (dd, 1, Ar), 6.15 (q, 1, Ar), 3.60 (septet, 2, CHMe$_2$), 3.06 (q, 8, OCH_2CH$_3$), 1.31 (d, 6, CHMe_2), 1.22 (d, 6, CHMe_2), 0.83 (d, 12, OCH$_2$CH_3); ^{7}Li{^{1}H} NMR (C$_6$D$_6$, 194 MHz) δ 1.12 ($\upsilon_{1/2}$ = 7.68 Hz); ^{19}F NMR (C$_6$D$_6$, 188.15 MHz) δ −148.97; ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.5 MHz) δ 157.00 (d, J_{CF} = 214.10, CF), 150.53 (s, C), 149.73 (d, J_{CF} = 8.16, C), 145.15 (s, C), 127.21 (s, CH), 124.30 (s, CH), 122.84 (s, CH), 114.83 (d, J_{CF} = 6.78, CH), 113.23 (d, J_{CF} = 20.71, CH), 106.39 (d, J_{CF} = 9.16, CH), 66.28 (s, OCH$_2$CH$_3$), 28.52 (s, CHMe$_2$), 25.53 (s, CHMe_2), 25.23 (s, CHMe_2), 14.92 (s, OCH$_2$$CH_3$). Anal. Calcd for C$_{26}H_{41}$FLiNO$_2$: C, 73.35; H, 9.72; N, 3.29. Found: C, 73.35; H, 9.31; N, 3.77.

Synthesis of [^{i}PrAr-NF]$_2$ZrCl$_2$. Solid ZrCl$_4$(THF)$_2$ (204 mg, 0.54 mmol) was suspended in toluene (5 mL) and cooled to –35 °C. To this was added dropwise a prechilled solution of [^{i}PrAr-NF]Li (300 mg, 1.08 mmol, 2 equiv) in toluene (5 mL) at –35 °C.

Upon addition, the reaction solution became pale yellow in color and the suspended $ZrCl_4(THF)_2$ dissolved gradually. The reaction mixture was stirred at room temperature overnight and evaporated to dryness in vacuo. The solid residue was dissolved in diethyl ether (15 mL), and the ether solution was filtered through a pad of Celite, which was further washed with diethyl ether (1 mL × 2). The filtrates were combined, concentrated under reduced pressure to ca. 2 mL, and cooled to –35 °C to afford the product as colorless crystals suitable for X-ray diffraction analysis: yield 312.1 mg (82%); ^1H NMR (C_6D_6, 500 MHz) δ 7.26 (m, 6, Ar), 6.65 (q, 2, Ar), 6.61 (t, 2, Ar), 6.22 (m, 2, Ar), 6.05 (m, 2, Ar), 3.63 (septet, 4, C*H*Me$_2$), 1.48 (d, 12, CH*Me*$_2$), 1.07 (d, 12, CH*Me*$_2$); ^{19}F NMR (C_6D_6, 188.15 MHz) δ −115.61; $^{13}C\{^1H\}$ NMR (C_6D_6, 125.679 MHz) δ 159.03 (dd, $^1J_{CF}$ = 226.47, $^3J_{CF}$ = 7.04, CF), 146.35 (s, C), 142.11 (s, C), 141.74 (m, C), 128.75 (s, CH), 127.47 (s, CH), 125.81 (s, CH), 118.81 (t, J_{CF} = 6.03, CH), 116.73 (s, CH), 113.07 (dd, J_{CF} = 13.07, 8.04, CH), 28.59 (s, *C*HMe$_2$), 26.40 (s, CH*Me*$_2$), 25.00 (s, CH*Me*$_2$). Anal. Calcd for $C_{36}H_{42}Cl_2F_2N_2Zr$: C, 61.50; H, 6.03; N, 3.99. Found: C, 61.08; H, 6.10; N, 3.86.

Synthesis of [^{i}PrAr-NF]$_2$HfCl$_2$. Solid $HfCl_4(THF)_2$ (251 mg, 0.54 mmol) was suspended in toluene (5 mL) and cooled to –35 °C. To this was added dropwise a prechilled solution of [^{i}PrAr-NF]Li (300 mg, 1.08 mmol, 2 equiv) in toluene (5 mL) at –35 °C. Upon addition, the reaction mixture became pale green in color and the suspended $HfCl_4(THF)_2$ dissolved gradually. The reaction mixture was stirred at room temperature overnight. All volatiles were removed in vacuo. The solid residue was dissolved in diethyl ether (15 mL). The ether solution was filtered through a pad of Celite, which was further washed with diethyl ether (1 mL × 2). The filtrates were combined, concentrated under reduced pressure to ca. 2 mL, and cooled to −35 °C to afford the product as colorless crystals suitable for X-ray diffraction analysis: yield 330.8 mg (77%); ^1H NMR (C_6D_6, 500 MHz) δ 7.27 (s, 6, Ar), 6.62 (m, 4, Ar), 6.16 (m, 2, Ar), 6.07 (m, 2, Ar), 3.63 (septet, 4, C*H*Me$_2$), 1.47 (d, 12, CH*Me*$_2$), 1.09 (d, 12, CH*Me*$_2$); ^{19}F NMR (C_6D_6, 188.15 MHz) δ −118.53; $^{13}C\{^1H\}$ NMR (C_6D_6, 125.679 MHz) δ 159.79 (dd, $^1J_{CF}$ = 222.45, $^3J_{CF}$ = 7.54, CF), 146.73 (s, C), 142.25 (s, C), 142.21 (m, C), 128.68 (s, CH), 127.73 (s, CH), 124.64 (s, CH), 120.50 (t, d, J_{CF} = 10.04, CH), 117.62 (s, CH), 112.91 (m, CH), 28.45 (s, *C*HMe$_2$), 26.35 (s, CH*Me*$_2$), 25.06 (s, CH*Me*$_2$). Anal. Calcd for $C_{36}H_{42}Cl_2F_2HfN_2$: C, 54.70; H, 5.36; N, 3.55. Found: C, 54.44; H, 5.39; N, 3.44.

Synthesis of [^{i}PrAr-NF]$_2$ZrMe$_2$. Solid [^{i}PrAr-NF]$_2$ZrCl$_2$ (100 mg, 0.14 mmol) was dissolved in diethyl ether (3 mL) and cooled to –35 °C. To this was added MeMgBr (0.09 mL, 3 M in diethyl ether, Aldrich, 0.27 mmol, 1.93 equiv) dropwise. The reaction mixture was naturally warmed to room temperature and stirred overnight. The reaction solution was filtered through a pad of Celite, concentrated under reduced pressure to ca. 3 mL, and cooled to –35 °C to afford the product as colorless crystals: yield 85.0 mg (90%); ^1H NMR (C_6D_6, 500 MHz) δ 7.29 (s, 6, Ar), 6.68 (t, 4, Ar), 6.27 (m, 2, Ar), 6.18 (m, 2, Ar), 3.72 (septet, 4, ArC*H*Me$_2$), 1.34 (d, 12, CH*Me*$_2$), 1.12 (d, 12, CH*Me*$_2$), 0.81 (s, 6, ZrC*H*$_3$); ^{19}F NMR (C_6D_6, 188.15 MHz) δ −123.14; $^{13}C\{^1H\}$ NMR (C_6D_6, 125.68 MHz) δ 157.45 (dd, J_{CF} = 226.64 and 5.02, CF), 147.10 (s, C), 143.15 (dd, J_{CF} = 7.03 and 3.01, C), 141.65 (s, C), 128.03 (s, CH), 126.76 (s, CH), 125.70 (s, CH), 117.32 (t, J_{CF} = 4.02, CH), 116.96 (s, CH), 113.52 (dd, J_{CF} = 13.11 and 7.03, CH), 56.62 (t, $^2J_{CF}$ = 13.58, Zr*C*H$_3$), 28.53 (s, *C*HMe$_2$), 26.57 (s, CH*Me*$_2$), 24.92 (s, CH*Me*$_2$).

Synthesis of [^{i}PrAr-NF]$_2$HfMe$_2$. Solid [^{i}PrAr-NF]$_2$HfCl$_2$ (50 mg, 0.063 mmol) was dissolved in diethyl ether (3 mL) and cooled to –35 °C. To this was added MeMgBr (0.042 mL, 3 M in diethyl ether, Aldrich, 0.126 mmol, 2 equiv) dropwise. The reaction mixture was naturally warmed to room temperature and stirred overnight. The reaction solution was filtered through a pad of Celite, concentrated under reduced pressure to ca. 3 mL, and cooled to –35 °C to afford the product as colorless crystals: yield 32.7 mg (69%); ^1H NMR (C_6D_6, 500 MHz) δ 7.29 (s, 6, Ar), 6.68 (t, 4, Ar), 6.22 (m, 2, Ar), 6.17 (m, 2, Ar), 3.72 (septet, 4, ArC*H*Me$_2$), 1.35 (d, 12, CH*Me*$_2$), 1.12 (d, 12, CH*Me*$_2$), 0.58 (s, 3, HfCH$_3$); ^{19}F NMR (C_6D_6, 188.15 MHz) δ −123.21; $^{13}C\{^1H\}$ NMR (C_6D_6, 125.68 MHz) δ 158.03 (dd, J_{CF} = 224.21 and 5.40, C), 147.28 (s, C), 143.50 (dd, J_{CF} = 6.28 and 3.64, C), 141.88 (s, C), 127.90 (s, CH), 127.02 (s, CH), 125.69 (s, CH), 117.65 (s, CH), 117.07 (t, J_{CF} = 4.52, CH), 113.45 (dd, J_{CF} = 12.80 and 7.28, CH), 63.79 (t, $^2J_{CF}$ = 13.68, Hf*C*H$_3$), 28.39 (s, *C*HMe$_2$), 26.58 (s, CH*Me*$_2$), 24.95 (s, CH*Me*$_2$).

Synthesis of [^{i}PrAr-NF]$_2$Zr(*i*-Bu)$_2$. Solid [^{i}PrAr-NF]$_2$ZrCl$_2$ (104.9 mg, 0.15 mmol) was dissolved in diethyl ether (3 mL) and cooled to –35 °C. To this was added ^{i}BuMgCl (0.15 mL, 2 M in diethyl ether, Aldrich, 0.30 mmol, 2 equiv) dropwise. The reaction mixture was naturally warmed to room temperature and stirred overnight. The reaction solution was filtered through a pad of Celite, concentrated under reduced pressure to ca. 3 mL, and cooled to –35 °C to afford the product as colorless crystals suitable for X-ray diffraction analysis: yield 99.7 mg (90%); ^1H NMR (C_6D_6, 500 MHz) δ 7.33 (m, 6, Ar), 6.77 (dd, 2, Ar), 6.65 (t, 2, Ar), 6.26 (dd, 2, Ar), 6.18 (m, 2, Ar), 3.85 (septet, 4, ArC*H*Me$_2$), 1.81 (septet, 2, ZrCH$_2$C*H*Me$_2$), 1.48 (d, 12, CH*Me*$_2$), 1.44 (d, 4, ZrC*H*$_2$CHMe$_2$), 1.15 (d, 12, CH*Me*$_2$), 0.67 (d, 12, CH*Me*$_2$); ^{19}F NMR (C_6D_6, 188.15 MHz) δ –122.97; $^{13}C\{^1H\}$ NMR (C_6D_6, 125.679 MHz) δ 157.08 (dd, $^1J_{CF}$ = 223.46, $^3J_{CF}$ = 2.76, CF), 146.75 (s, C), 143.55 (t, J_{CF} = 4.52, C), 127.62 (s, CH), 126.61 (s, CH), 125.69 (s, CH), 117.79 (s, CH), 117.00 (t, J_{CF} = 5.53, CH), 113.48 (dd, J_{CF} = 13.70, J_{CF} = 6.41, CH), 94.53 (t, $^2J_{CF}$ = 14.20, ZrCH$_2$), 30.73 (s, *C*HMe$_2$), 28.57 (s, *C*HMe$_2$), 27.83 (s, CH*Me*$_2$), 26.91 (s, CH*Me*$_2$), 24.63 (s, CH*Me*$_2$).

Synthesis of [^{i}PrAr-NF]$_2$Hf(*i*-Bu)$_2$. Solid [^{i}PrAr-NF]$_2$HfCl$_2$ (50 mg, 0.063 mmol) was dissolved in diethyl ether (3 mL) and cooled to –35 °C. To this was added ^{i}BuMgCl (0.063 mL, 2 M in diethyl ether, Aldrich, 0.126 mmol, 2 equiv) dropwise. The reaction mixture was naturally warmed to room temperature and stirred overnight. The reaction solution was filtered through a pad of Celite, concentrated under reduced pressure to ca. 3 mL, and cooled to –35 °C to afford the product as colorless crystals: yield 48.9 mg (93%); ^1H NMR (C_6D_6, 500 MHz) δ 7.33 (m, 6, Ar), 6.78 (q, 2, Ar), 6.65 (t, 2, Ar), 6.22 (q, 2, Ar), 6.16 (t, 2, Ar), 3.85 (septet, 4, ArC*H*Me$_2$), 1.90 (m, 2, HfCH$_2$C*H*Me$_2$), 1.49 (d, 12, CH*Me*$_2$), 1.14 (d, 12, CH*Me*$_2$), 1.10 (d, 4, *J* = 6.5, HfC*H*$_2$CHMe$_2$), 0.69 (d, 12, CH*Me*$_2$); ^{19}F NMR (C_6D_6, 188.15 MHz) δ –122.49; $^{13}C\{^1H\}$ NMR (C_6D_6, 125.5 MHz) δ 157.73 (dd, $^1J_{CF}$ = 222.07, $^3J_{CF}$ = 2.76, CF), 147.10 (s, C), 143.73 (dd, J_{CF} = 7.34 and 2.26, C), 143.40 (s, C), 127.62 (s, CH), 126.85 (s, CH), 125.70 (s, CH), 118.49 (s, CH), 116.85 (t, J_{CF} = 4.52, CH), 113.40 (dd, J_{CF} = 13.68 and 5.90, CH), 99.22 (t, $^2J_{CF}$ = 14.68, Hf*C*H$_2$), 30.29 (s, *C*HMe$_2$), 28.80 (s, CH*Me*$_2$), 28.46 (s, *C*HMe$_2$), 26.98 (s, CH*Me*$_2$), 24.60 (s, CH*Me*$_2$).

Synthesis of [^{i}PrAr-NF]$_2$Zr(CH$_2$Ph)$_2$. Solid [^{i}PrAr-NF]$_2$ZrCl$_2$ (100 mg, 0.14 mmol) was dissolved in diethyl ether (3 mL) and cooled to –35 °C. To this was added PhCH$_2$MgCl (0.28 mL, 1 M in diethyl ether, Aldrich, 0.28 mmol, 2 equiv) dropwise. The reaction mixture was naturally warmed to room temperature and stirred overnight. The reaction solution was filtered through a pad of Celite, concentrated under reduced pressure to ca. 3 mL, and cooled to –35 °C to afford the product as colorless crystals: yield 103.1 mg (89%); ^1H NMR (C_6D_6, 500 MHz) δ 7.31 (m, 6, Ar), 6.88 (t, 4, Ar), 6.70 (t, 2, Ar), 6.56 (td, 2, Ar), 6.52 (m, 6, Ar), 6.25 (q, 2, Ar), 6.01 (t, 2, Ar), 3.52 (septet, 4, ArC*H*Me$_2$), 2.94 (s, 4, ZrC*H*$_2$Ph), 1.23 (d, 12, CH*Me*$_2$), 0.99 (d, 12, CH*Me*$_2$); ^{19}F NMR (C$_6$D$_6$, 188.15 MHz) δ 116.17; ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.68 MHz) δ 157.06 (d, $^1J_{CF}$ = 221.88, CF), 147.17 (s, C), 145.04 (s, C), 143.18 (d, J_{CF} = 10.17, C), 142.67 (s, C), 128.66 (s, CH), 128.04 (s, CH), 126.89 (s, CH), 126.23 (s, CH), 125.84 (s, CH), 122.60 (s, CH), 118.03 (s, CH), 117.63 (dd, J_{CF} = 4.58 and 3.77, CH), 113.88 (dd, J_{CF} = 19.70 and 7.78, CH), 84.29 (t, $^2J_{CF}$ = 15.06, Zr*C*H$_2$Ph), 29.03 (s, Ar*C*HMe$_2$), 27.02 (s, ArCH*Me*$_2$), 24.24 (s, ArCH*Me*$_2$).

Synthesis of [^{i}PrAr-NF]$_2$Hf(CH$_2$Ph)$_2$. Solid [^{i}PrAr-NF]$_2$HfCl$_2$ (100 mg, 0.127 mmol) was dissolved in diethyl ether (3 mL) and cooled to –35 °C. To this was added PhCH$_2$MgCl (0.254 mL, 1 M in diethyl ether, Aldrich, 0.254 mmol, 2 equiv) dropwise. The reaction mixture was naturally warmed to room temperature and stirred overnight. The reaction solution was filtered through a pad of Celite, concentrated under reduced pressure to ca. 3 mL, and cooled to –35 °C to afford the product as pale yellow crystals: yield 89.4 mg (78%); ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ 7.34 (m, 6, Ar), 6.87 (t, 4, Ar), 6.66 (t, 2, Ar), 6.59 (t, 2, Ar), 6.49 (dd, 2, Ar), 6.29 (d, 4, Ar), 6.20 (q, 2, Ar), 6.07 (t, 2, Ar), 3.69 (m, 4, ArC*H*Me$_2$), 2.61 (s, 4, HfC*H*$_2$Ph), 1.24 (d, 12, CH*Me*$_2$), 1.05 (d, 12, CH*Me*$_2$); ^{19}F NMR (C$_6$D$_6$, 188.15 MHz) δ 117.92; ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125.5 MHz) δ 157.75 (d, J_{CF} = 220.00, CF), 147.39 (s, C), 144.96 (s, C), 143.43 (d, J_{CF} = 9.66, C), 142.90 (s, C), 128.32 (s, CH), 127.94 (s, CH), 127.25 (s, CH), 126.62 (s, CH), 125.97(s, CH), 122.69 (s, CH), 118.54 (s, CH), 117.42 (t, J_{CF} = 4.52, CH), 113.64 (dd, J_{CF} = 10.04 and 4.64, CH), 89.45 (t, $^2J_{CF}$ = 15.06, Hf*C*H$_2$Ph), 28.82 (s, *C*HMe$_2$), 27.04 (s, CH*Me*$_2$), 24.19 (s, CH*Me*$_2$).

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Supporting Information Available: X-ray crystallographic data in CIF format for [^{i}PrAr-NF]Li(OEt$_2$)$_2$, [^{i}PrAr-NF]$_2$ZrCl$_2$, [^{i}PrAr-NF]$_2$HfCl$_2$, [^{i}PrAr-NF]$_2$ZrMe$_2$, [^{i}PrAr-NF]$_2$Zr(*i*-Bu)$_2$, and [^{i}PrAr-NF]$_2$Hf(CH$_2$Ph)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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