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Terminal vs Bridging Imido Ligation in Complexes of Zirconium(IV) and Hafnium(IV): Structural Characterization of a μ-[$\eta^1(N)$:$\eta^2(N,C)$] Imido Ligand

David J. Arney, Michael A. Bruck, Susan R. Huber, and David E. Wigley*

Carl S. Marvel Laboratories of Chemistry, Department of Chemistry, University of Arizona, Tucson, Arizona 85721

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The reaction of 4 equiv of LiNHAr (Ar = $2,6\text{-}C_6H_3{}^iPr_2$) with a solution of $ZrCl_4(THF)_2$ in THF/pyridine yields $Zr({=}NAr)(NHAr)_2(py)_2$ (**1**) in high yield. $Zr({=}NAr)(NHAr)_2(py)_2$ reacts with 1 and 2 equiv of Me_3SiCl in THF/pyridine to provide $Zr({=}NAr)(NHAr)Cl(py)_2$ (**2**) and $Zr({=}NAr)Cl_2(py)_3$ (**3**), respectively. $ZrCl_4(THF)_2$ reacts with 4 equiv of LiNHAr, followed by 2 equiv of Me_3SiCl (in THF), to afford $Zr({=}NAr)Cl_2(THF)_2$ (**4**) in a high-yield, one-pot synthesis. $Hf({=}NAr)Cl_2(THF)_2$ (**5**) is prepared similarly. $Zr({=}NAr)(NHAr)Cl(py)_2$ reacts with 1 equiv of $K[N(SiMe_3)_2]$ in THF to provide $Zr({=}NAr)(NHAr)[N(SiMe_3)_2](py)_2$ (**6**), which could not be converted into a bis(imido) species. Both $Hf({=}NAr)Cl_2(THF)_2$ and $Zr({=}NAr)Cl_2(THF)_2$ react with $K_2(C_8H_8)$ to provide $[(\eta^8\text{-}C_8H_8)Zr({=}NAr)]_2$ (**7**) and $[(\eta^8\text{-}C_8H_8)Hf({=}NAr)]_2$ (**8**) in high yield. $Zr({=}NAr)Cl_2(THF)_2$ reacts with 1 equiv of $Li(C_5H_4Me)$ in THF to provide $[(\eta^5\text{-}C_5H_4Me)Zr({=}NAr)Cl]_2$ (**9**) in moderate yield. An X-ray structural determination of this compound reveals a dimeric structure with bridging imido ligands. $[(\eta^5\text{-}C_5H_4Me)Zr({=}NAr)Cl]_2$ (**9**) crystallizes in the orthorhombic space group *Pbca* with $a = 16.591$ (1) Å, $b = 20.173$ (2) Å, $c = 21.469$ (2) Å, and $V = 7185$ (1) Å^3 with $Z = 8$ and $\rho_{calcd} = 1.41$ g cm^{-3}. This complex exhibits an unusual (μ-[$\eta^1(N)$:$\eta^2(N,C)$]) imido ligand in which C_{ipso} of the μ-NAr ligand is within bonding distance of one of the Zr atoms. $(\eta^5\text{-}C_5Me_5)ZrCl_3$ reacts with 3 equiv of LiNHAr in THF to provide the imide–amide–amine complex $(\eta^5\text{-}C_5Me_5)Zr({=}NAr)(NHAr)(NH_2Ar)(THF)$ (**10**) in high yield. Complex **10** reacts with pyridine to form dimeric $[(\eta^5\text{-}C_5Me_5)Zr({=}NAr)(NHAr)(py)]_2$ (**11**). When $(\eta^5\text{-}C_5Me_5)ZrCl_3$ reacts with 3 equiv of LiNHAr (in THF/pyridine), followed by the addition of 1 equiv of Me_3SiCl, golden yellow crystals of $(\eta^5\text{-}C_5Me_5)Zr({=}NAr)Cl(py)_2$ (**12**) are formed in high yield. Complex **12** crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.827$ (5) Å, $b = 16.687$ (5) Å, $c = 17.631$ (9) Å, $\beta = 101.04$ (5)°, and $V = 3126.6$ (2) Å^3 with $Z = 4$ and $\rho_{calcd} = 1.26$ g cm^{-3}. In the solid state, this compound is characterized by a Zr–N distance of 1.876 (4) Å and Zr–N–C_{ipso} angle of 164.5 (3)°.

Introduction

Organoimido complexes of the transition metals[1] have received considerable recent attention, in part, from their presumed involvement in catalytic processes such as propylene ammoxidation,[2] nitrile reduction,[3] and, recently, hydrodenitrogenation catalysis.[4] Terminal imido complexes of the group 4 metals, viz. $L_nTi{=}NR$,[5-10] $L_nZr{=}NR$,[11-13] and $L_nHf{=}NR$,[14] have only recently been discovered and remain comparatively scarce. Of the reports of such compounds, transient species of the form $({}^tBu_3SiNH)_2Ti({=}NSi{}^tBu_3)$,[7] $({}^tBu_3SiNH)_2Zr({=}NSi{}^tBu_3)$[11], and $(\eta^5\text{-}C_5H_5)_2Zr({=}NR)$[12] are of particular interest since their imido ligands can serve as sites for C–H bond activation and cycloaddition chemistry.

To provide for systematic studies of such compounds, we set out to develop general, high-yield routes to terminal imido species of zirconium and hafnium. In this paper, we report the preparation and properties of mono(imido) complexes of zirconium(IV) and hafnium(IV) and their reactions with carbocyclic ligands in which both terminal and bridging imido ligation has been uncovered. As a part of this study, the solid-state structures of the terminal imido complex $(\eta^5\text{-}C_5Me_5)Zr(NAr)Cl(NC_5H_5)_2$ and the bridging imido species $[(\eta^5\text{-}C_5H_4Me)Zr(NAr)Cl]_2$ (Ar = $2,6\text{-}C_6H_3{}^iPr_2$) have been determined. The latter species is characterized by an unusual μ-[$\eta^1(N)$:$\eta^2(N,C)$] imido binding mode in one of its bridging imido ligands.

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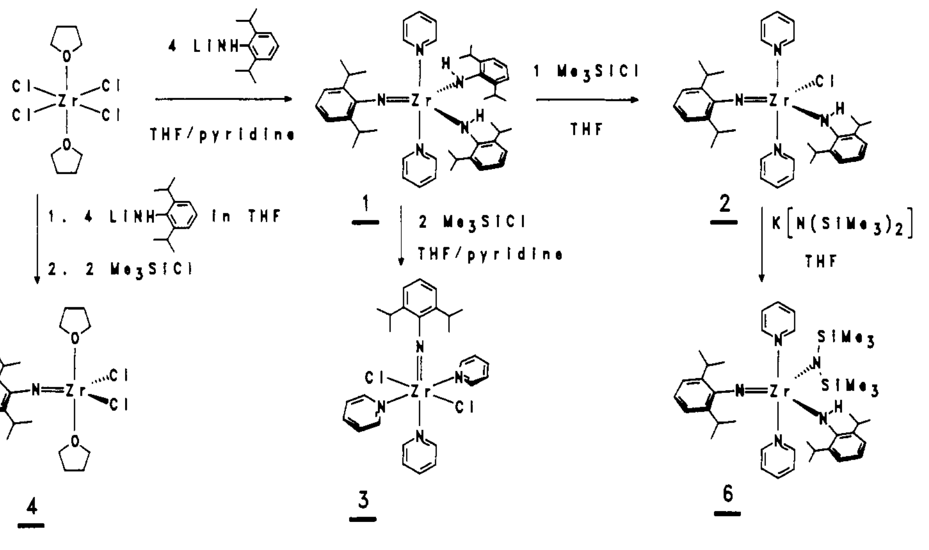
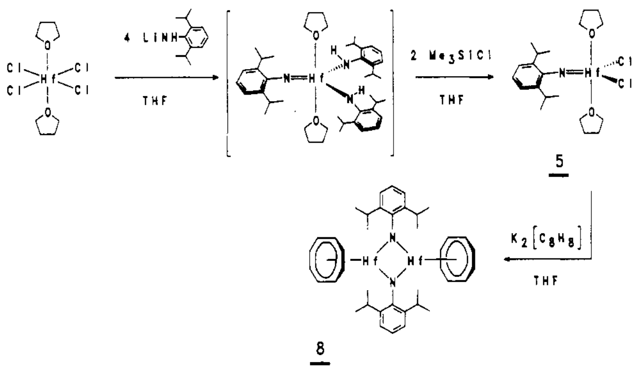
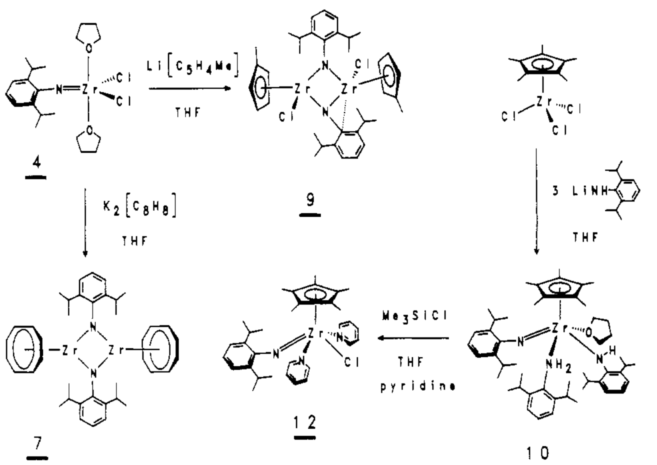
Scheme I



Scheme II



Scheme III



Results

Schemes I–III summarize the reactions reported in this study, while the compounds' spectroscopic and analytical data are recorded in the Experimental Section. Throughout this paper, Ar = 2,6-$C_6H_3{}^iPr_2$.

Terminal Imido Complexes of Zirconium(IV) and Hafnium(IV). Syntheses of terminal imido complexes of group 4 have been effected by the following: (i) α-H abstraction reactions from a primary amide by alkyl or amido ligands;[6a,9,11–14] (ii) N═N bond cleavage of an azobenzene;[6,8] (iii) the reaction of a $(Me_3Si)_2NR$ reagent with a metal tetrahalide;[5] (iv) reductive coupling of nitrile ligands;[8] (v) electrocyclic rearrangements;[10] (vi) *possibly* via intermolecular deprotonation of an amide with a carbanion equivalent.[7] In an effort to develop the most direct route to new imido complexes, the reactions of metal halides with LiNHAr were examined. Thus, the reaction of $ZrCl_4(THF)_2$ with 4 equiv of LiNHAr in THF/pyridine affords yellow, microcrystalline $Zr({=}NAr)(NHAr)_2(py)_2$ (**1**) along with 1 equiv of H_2NAr (Scheme I). Solution molecular weight measurements of **1** were precluded by its slow decomposition; however, we formulate $Zr({=}NAr)(NHAr)_2(py)_2$ as a monomer from the structural precedent provided by recently reported $Zr({=}NAr)(NHAr)_2L_2$ (L = 4-pyrrolidinopyridine).[13] On the basis of its NMR spectra, **1** is proposed to be approximately TBP with axial pyridine ligands and overall C_{2v} symmetry, consistent with related five-coordinate, d^0 imido complexes.[2c,6,9,13,15] In the absence of pyridine, the reaction of $ZrCl_4(THF)_2$ with 4 equiv of LiNHAr (in THF) affords nonstoichiometric $Zr({=}NAr)(NHAr)_2(THF)_x$ ($x = 2$–3) as a pale yellow oil which is virtually impossible to obtain free from byproduct H_2NAr.[16]

$Zr({=}NAr)(NHAr)_2(py)_2$ (**1**) reacts smoothly with 1 and 2 equiv of Me_3SiCl to provide high yields of the imido chloride complexes $Zr({=}NAr)(NHAr)Cl(py)_2$ (**2**) and $Zr({=}NAr)Cl_2(py)_3$ (**3**), respectively, along with $Me_3SiNHAr$ (Scheme I). This reaction is consistent with the notion of an amido ligand being more susceptible to electrophilic attack than the imido ligand in the same molecule.[17] We believe the structure of **2** is related to that of **1**, while **3** is proposed to be analogous to Roesky's titanium complex $Ti({=}NP(S)Ph_2)Cl_2(py)_3$,[5] i.e. with trans chlorides (Scheme I). Attempts to prepare **2** or **3** from $ZrCl_4(THF)_2$ with 2 or 3 equiv of LiNHAr (in THF/pyridine) did not yield tractable products.

Electrophilic attack of Me_3SiCl on the amido ligands in $Zr({=}NAr)(NHAr)_2(THF)_x$, generated in situ, affords a convenient, one-pot preparation of the imido halide compound $Zr({=}NAr)Cl_2(THF)_2$ (**4**). Thus, the reaction of $ZrCl_4(THF)_2$ with 4 equiv of LiNHAr (THF solution), followed by the addition of 2 equiv of Me_3SiCl, affords yellow, microcrystalline $Zr({=}NAr)Cl_2(THF)_2$ (**4**) in greater than 85% yield (Scheme I). The analogous reaction starting with $HfCl_4(THF)_2$ yields $Hf({=}NAr)Cl_2(THF)_2$

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(16) The preparation of the analogous hafnium complex was only moderately successful. Thus, $Hf({=}NAr)(NHAr)_2(py)_2$ can be isolated from the reaction of $HfCl_4(THF)_2$ with 4 equiv of LiNHAr in THF/pyridine as a nearly colorless, oily solid in only ca. 20% yield but is also extremely difficult to obtain free of aniline byproducts.

(17) See, for example: (a) Maatta, E. A.; Wentworth, R. A. D. *Inorg. Chem.* **1979**, *18*, 2409. (b) Maatta, E. A.; Haymore, B. L.; Wentworth, R. A. D. *Ibid.* **1980**, *19*, 1055. (c) Edwards, D. S.; Biondi, L. V.; Ziller, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* **1983**, *2*, 1505.

(**5**) as a light yellow solid in 60% yield (Scheme II). Compounds **4** and **5** are also formulated as monomeric, TBP complexes with axial THF ligands related to compounds **1** and **2**.

The recent interest in multiple imido complexes[1,15] prompted our attempts to prepare a bis(phenylimido) complex of zirconium, either from an α-H abstraction reaction of $Zr({=}NAr)(NHAr)_2(py)_2$ (**1**) or by a dehydrohalogenation of $Zr({=}NAr)(NHAr)Cl(py)_2$ (**2**) in the presence of pyridine. All such attempts proved unsuccessful in our hands. Thus, thermolyzing $Zr({=}NAr)(NHAr)_2(py)_2$ (**1**) in the presence of pyridine (110 °C) resulted only in the formation of intractable decomposition products. Moreover, the attempted deprotonation of $Zr({=}NAr)(NHAr)Cl(py)_2$ (**2**) with 1 equiv of $K[N(SiMe_3)_2]$ resulted in the formation of $Zr({=}NAr)(NHAr)[N(SiMe_3)_2](py)_2$ (**6**), which also did not give tractable elimination products upon thermolysis (110 °C) in the presence of excess pyridine or PMe_3 (Scheme II). The NMR spectra of **6** suggest the structure presented in Scheme II, i.e. with the π donor ligands in the equatorial plane of a TBP.

Imido Complexes of Zirconium(IV) and Hafnium(IV) Containing Cyclooctatetraenyl Ligands. An intriguing contrast within the group 8 metals has arisen in the structures of their imido species of the form (η^6-arene)$M({=}NR)$, which have recently been reported. Michelman, Andersen, and Bergman discovered[18] that the osmium complexes (η^6-arene)$Os({=}NR)$ (arene = *p*-cymene or C_6Me_6) are discrete monomers, while Schrock and co-workers have shown[19] the ruthenium complexes $[(\eta^6\text{-}C_6H_6)Ru({=}NR)]_2$ to be dimeric with bridging imido ligands.

In the designing of a group 4 congener of these group 8 (carbocycle)$M({=}NR)$ compounds, the group 4 metal center must formally acquire four additional electrons from its η^n-C_nH_n ligand. We therefore set out to prepare species of the form $(\eta^8\text{-}C_8H_8)Zr({=}NR)$ and $(\eta^8\text{-}C_8H_8)Hf({=}NR)$ (Schemes II and III). Thus, $Zr({=}NAr)Cl_2(THF)_2$ (**4**) and $Hf({=}NAr)Cl_2(THF)_2$ (**5**) react readily with $K_2(C_8H_8)$ in THF to afford $[(\eta^8\text{-}C_8H_8)Zr({=}NAr)]_2$ (**7**) and $[(\eta^8\text{-}C_8H_8)Hf({=}NAr)]_2$ (**8**) in high yield. CI mass spectral data and the solubility properties of **7** and **8** suggest their formulation as dimers which are most likely imido bridged on the basis of structurally characterized group 4 species such as $[(\eta^5\text{-}C_5H_5)_2Zr({=}NC_6H_4\text{-}4\text{-}{}^tBu)]_2$.[12] Neither compound **7** nor **8** reacts with PPh_2Me or PMe_3 in refluxing toluene. Thus, while the mechanism of dimer formation is unclear, it seems likely that **7** and **8** are formed via monomeric $(\eta^8\text{-}C_8H_8)M({=}NAr)(THF)$, which dimerizes with loss of THF. Attempts to trap a transient monomeric imido species by generating it in the presence of excess 3-hexyne[12] proved unsuccessful as the only isolable products from these reactions were dimers **7** and **8**.

$[(\eta^8\text{-}C_8H_8)Zr({=}NAr)]_2$ (**7**) is also formed from other monomeric precursors, viz. by the reactions of (i) $Zr({=}NAr)Cl_2(py)_3$ (**3**) with $K_2(C_8H_8)$ and (ii) $(\eta^8\text{-}C_8H_8)ZrCl_2(THF)$[20] with 2 equiv of LiNHAr (both in THF). Thus, the Lewis acidity of the metal in a purported intermediate $(\eta^8\text{-}C_8H_8)M({=}NAr)L_n$ must constitute a powerful driving force for dimerization via imido bridges. In a final effort to prepare a monomeric analog of **7**, the reaction of $(\eta^8\text{-}C_8H_8)ZrCl_2(THF)$[20] with 2 equiv of the relatively bulky imide $LiNHSiPh_3$ again provided a dimer $[(\eta^8\text{-}C_8H_8)Zr({=}NSiPh_3)]_2$ in very low yield.[21] While the nature of the dimeric structure is of interest, all attempts to grow crystallographic quality crystals of **7** and **8** were unsuccessful.

Preparation and Structure of $[(\eta^5\text{-}C_5H_4Me)Zr({=}NAr)Cl]_2$ Containing a μ-[$\eta^1(N)$:$\eta^2(N,C)$] Imido Ligand. Cyclopentadienyl–imido complexes of group 4 are of particular interest since the imido moiety in transient $(\eta^5\text{-}C_5H_5)_2Zr{=}NR$ constitutes a reactive site toward cycloaddition or C–H bond activation chemistry.[12] We have found that $Zr({=}NAr)Cl_2(THF)_2$ (**4**) reacts with 1 equiv of $Li(C_5H_4Me)$ in THF to afford lemon yellow crystals of $[(\eta^5\text{-}C_5H_4Me)Zr({=}NAr)Cl]_2$ (**9**) in moderate yield. The solubility properties and stoichiometry of **9** suggest that this complex is a dimer, presumably with bridging imido ligands like its titanium analog $[(\eta^5\text{-}C_5H_5)Ti({=}NPh)Cl]_2$.[22] The X-ray structural determination of **9** confirms this assignment.

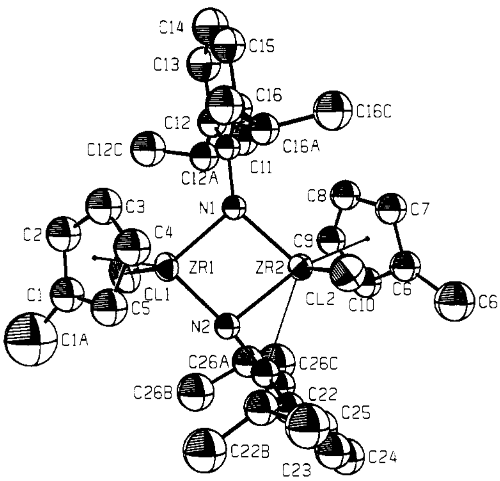

Figure 1. Molecular structure of $[(\eta^5\text{-}C_5H_4Me)Zr(NAr)Cl]_2$ (**9**, Ar = 2,6-$C_6H_3{}^iPr_2$) with atoms shown as 50% probability ellipsoids.

Table I. Details of the X-ray Diffraction Study for $[(\eta^5\text{-}C_5H_4Me)Zr(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)Cl]_2$ (**9**) and $(\eta^5\text{-}C_5Me_5)Zr(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)Cl(NC_5H_5)_2$ (**12**)

molecular formula	$C_{36}H_{48}Cl_2N_2Zr_2$ (**9**)	$C_{32}H_{42}ClN_3Zr$ (**12**)
M_r	762.14	595.38
cryst color	yellow	golden yellow
space group	*Pbca* (No. 61)	$P2_1/n$ (No. 14)
unit cell vol, Å^3	7185 (1)	3126.6 (2)
a, Å	16.591 (1)	10.827 (5)
b, Å	20.173 (2)	16.687 (5)
c, Å	21.469 (2)	17.631 (9)
β, deg	90.0	101.04 (5)
Z	8	4
calcd density, g cm^{-3}	1.41	1.26
cryst dimens, mm	0.25 × 0.25 × 0.17	0.38 × 0.45 × 0.45
data collcn temp, °C	23 ± 1	21 ± 1
Mo Kα radiation λ, Å	0.710 73	0.710 73
monochromator	graphite	graphite
abs coeff, cm^{-1}	7.5	4.5
2θ range, deg	2–50	2–50
tot. no. of reflns measd	6433 (6302 unique)	5745 (5487 unique)
no. of reflns measd with $I > 3\sigma(I)$	2191	3787
scan type	ω–2θ	ω–2θ
scan speed, deg min^{-1}	1–7	1–7
params refined	189	334
R	0.052	0.048
R_w	0.057	0.059

Figure 1 presents the molecular structure of **9**, while Tables I and II summarize crystal and structural data. On the basis of the structural precedent provided by $[(\eta^5\text{-}C_5H_5)Ti({=}NPh)Cl]_2$,[22] $[Zr({=}N^tBu)(NMe_2)_2]_2$,[23] $[Ti({=}N^tBu)(NMe_2)_2]_2$,[24] and $[(\eta^5\text{-}C_5H_5)_2Zr({=}NC_6H_4\text{-}4\text{-}{}^tBu)]_2$,[12] as well as theoretical studies,[24a] compound **9** was expected to exhibit symmetrically bridging phenylimido ligands and approximate C_2 symmetry. Although the

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(21) ^{1}H NMR data for $[(\eta^8\text{-}C_8H_8)Zr({=}NSiPh_3)]_2$ ($CDCl_3$): δ 7.68 (m, 6 H, H_o), 7.48 (m, 9 H, H_m and H_p), 5.60 (s, 8 H, C_8H_8). Mass spectrum (EI): m/z = 832, $[(C_8H_8)Zr_2(NSiPh_3)_2]^-$ (i.e. $[M - C_8H_8]^-$).

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Table II. Selected Bond Distances (Å) and Bond Angles (deg) in $[(\eta^5\text{-}C_5H_4Me)Zr(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)Cl]_2$ (**9**)[a,b]

	Bond Distances		
Zr(1)–N(1)	2.081 (9)	Zr(1)–Zr(2)	3.087 (2)
Zr(1)–N(2)	1.951 (9)	Zr(1)–C(1)	2.53 (1)
Zr(1)–Cp'_{cent}	2.237 (1)	Zr(1)–C(2)	2.57 (1)
Zr(1)–Cl(1)	2.419 (3)	Zr(1)–C(3)	2.52 (1)
Zr(2)–N(1)	2.054 (9)	Zr(1)–C(4)	2.48 (1)
Zr(2)–N(2)	2.171 (9)	Zr(1)–C(5)	2.51 (1)
Zr(2)–C(21)	2.58 (1)	Zr(2)–C(6)	2.59 (1)
Zr(2)–Cp'_{cent}	2.226 (1)	Zr(2)–C(7)	2.57 (1)
Zr(2)–Cl(2)	2.411 (3)	Zr(2)–C(8)	2.49 (1)
N(1)–C(11)	1.42 (1)	Zr(2)–C(9)	2.45 (1)
N(2)–C(21)	1.41 (1)	Zr(2)–C(10)	2.50 (1)
	Bond Angles		
Zr(1)–N(1)–Zr(2)	96.6 (4)	N(2)–Zr(1)–Cl(1)	102.7 (3)
Zr(1)–N(2)–Zr(2)	96.9 (4)	Cp'_{cent}–Zr(1)–N(1)	118.0 (2)
Zr(1)–N(1)–C(11)	124.9 (8)	Cp'_{cent}–Zr(1)–N(2)	126.4 (2)
Zr(2)–N(1)–C(11)	138.5 (8)	Cp'_{cent}–Zr(1)–Cl(1)	109.9 (1)
Zr(1)–N(2)–C(21)	173.2 (8)	N(1)–Zr(2)–Cl(2)	106.0 (3)
Zr(2)–N(2)–C(21)	89.8 (7)	N(2)–Zr(2)–Cl(2)	104.8 (3)
Zr(2)–C(21)–N(2)	57.2 (6)	Cp'_{cent}–Zr(2)–N(1)	111.8 (2)
N(1)–Zr(1)–N(2)	85.6 (3)	Cp'_{cent}–Zr(2)–N(2)	140.8 (2)
N(1)–Zr(2)–N(2)	80.8 (3)	Cp'_{cent}–Zr(2)–Cl(2)	106.65 (9)
N(1)–Zr(1)–Cl(1)	111.6 (3)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Cp'_{cent} represents the average of the *x*, *y*, and *z* coordinates of the η^5-C_5H_4Me ring carbons bound to the specified zirconium atom.

structure is somewhat imprecise,[25] the $Zr_2(\mu\text{-}NAr)_2$ portion of the structure is well-behaved. Unexpectedly, the $Zr_2(\mu\text{-}NAr)_2$ core displays considerable asymmetry in *one* of its Zr–N–Zr bridges (viz. N(2)), both in the Zr–N(2) distances and in the distortion which brings the imido $C(21)_{ipso}$ to within η^2-bonding distance of Zr(2). Thus, the Zr–N(2)–Zr bridge shows considerably more localization (Zr(1)–N(2) = 1.951 (9) Å vs Zr(2)–N(2) = 2.171 (9) Å) than the Zr–N(1)–Zr bridge (Table II).

The unusual μ-[η^1(*N*):η^2(*N*,*C*)] bonding mode exhibited by the N(2) phenylimide ligand includes the following structural features: (i) the $Zr(2)\text{–}C(21)_{ipso}$ distance of 2.58 (1) Å is in the range of Zr–C π bonding distances in both Zr–(η^5-C_5H_4Me) interactions (range: 2.45 (1)–2.59 (1) Å); (ii) the "short" Zr(1)–N(2) bond of 1.951 (9) Å is just within an upper limit of 1.974 (6) Å for terminal Zr═NR bond distances in the complex $Zr({=}NSi^tBu_3)(NHSi^tBu_3)_2(THF)$;[11a,26] (iii) the nearly linear $Zr(1)\text{–}N(2)\text{–}C(21)_{ipso}$ bond angle of 173.2 (8)° leads to an acute $Zr(2)\text{–}N(2)\text{–}C(21)_{ipso}$ angle of 89.8 (7)° and contrasts with the symmetric Zr–N(1)–Zr bridge where the $Zr\text{–}N(1)\text{–}C(11)_{ipso}$ angles are 124.9 (8) and 138.5 (8)°. The μ-[η^1(*N*):η^2(*N*,*C*)]-NAr structure could not be frozen out in low-temperature NMR studies. Although a new compound is observed to form as the temperature is lowered to 233 K (THF-d_8), this species was surmised to be the THF adduct $[(\eta^5\text{-}C_5H_4Me)Zr({=}NAr)Cl(THF)]_2$ on the basis of its spectroscopic similarities to dimeric $[(\eta^5\text{-}C_5Me_5)Zr({=}NAr)(NHAr)(py)]_2$; vide infra. Thus, we may envisage a rapid μ-[η^1(*N*):η^1(*N*)] ⇄ μ-[η^1(*N*):η^2(*N*,*C*)] process in solution in which the C_{ipso} reversibly coordinates to a zirconium, perhaps rocking back and forth between both Zr(1) and Zr(2), but a donor solvent competes effectively with C_{ipso} for coordination to the metal. In the solid state, crystal packing forces may induce the tilt of the NAr ring and allow isolation of the μ-[η^1(*N*):η^2(*N*,*C*)]-NAr structure, which is stabilized by the Lewis acidity of the zirconium.

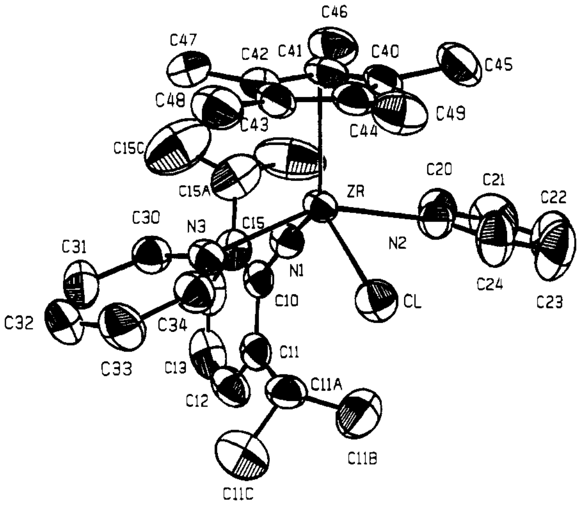

Figure 2. Molecular structure of $(\eta^5\text{-}C_5Me_5)Zr(NAr)Cl(NC_5H_5)_2$ (**12**, Ar = 2,6-$C_6H_3{}^iPr_2$) with atoms shown as 50% probability ellipsoids.

Bridging vs Terminal Imido Ligation in η^5-C_5Me_5 Complexes of Zirconium(IV): Structural Characterization of $(\eta^5\text{-}C_5Me_5)Zr({=}NAr)Cl(py)_2$. While the reactions of $Zr({=}NAr)Cl_2(THF)_2$ (**4**) with $Li(C_5Me_5)$ or $(C_5Me_5)MgCl{\cdot}THF$ did not provide the (η^5-C_5Me_5)–imido complexes, starting with a η^5-C_5Me_5 precursor did afford these species. Thus, the reaction of $(\eta^5\text{-}C_5Me_5)ZrCl_3$[27] with 3 equiv of LiNHAr in THF produced the *extremely* air- and moisture-sensitive, monomeric $(\eta^5\text{-}C_5Me_5)Zr({=}NAr)(NHAr)(NH_2Ar)(THF)$ (**10**) in moderate isolated yield. However, the in situ generation of **10**, followed by its reaction with pyridine, afforded red-orange crystals of $[(\eta^5\text{-}C_5Me_5)Zr({=}NAr)(NHAr)(py)]_2$ (**11**) in high yield. Compound **11** is formulated as dimeric on the basis of its stoichiometry and solubility properties[28] and is *presumed* to contain bridging imido ligands like **9**.

The amido ligand in $[(\eta^5\text{-}C_5Me_5)Zr({=}NAr)(NHAr)(py)]_2$ (**11**), like that in $Zr({=}NAr)(NHAr)_2(THF)_x$ (vide infra), is susceptible to electrophilic attack. Thus, **11** reacts with 1 equiv of Me_3SiCl in THF/pyridine to afford red-orange, crystalline $(\eta^5\text{-}C_5Me_5)Zr({=}NAr)Cl(py)_2$ (**12**) in high yield. Both ^1H and ^{13}C NMR data for **12** are consistent with a solution structure with a molecular plane of symmetry, i.e. with mutually trans pyridine ligands in a four-legged piano stool geometry, and the solid-state structure of $(\eta^5\text{-}C_5Me_5)Zr({=}NAr)Cl(py)_2$ bears out this prediction.

Crystals of $(\eta^5\text{-}C_5Me_5)Zr({=}NAr)Cl(py)_2$ (**12**) were obtained from a diethyl ether/pyridine solution at −35 °C. Figure 2 presents the molecular structure of **12**, and Tables I and III summarize crystal and structural data. $(\eta^5\text{-}C_5Me_5)Zr({=}NAr)Cl(py)_2$ may be described as a four-legged piano stool with trans pyridine ligands. The trans pyridine N(2)–Zr–N(3) angle of 151.6 (1)° is considerable more obtuse than the trans imido and chloride angle (N(1)–Zr–Cl = 117.1 (1)°) as the imide and chloride are moved further away from the bulky C_5Me_5 moiety. The nearly linear phenylimido linkage (Zr–N(1)–C(10) = 164.5 (3)°) and the short Zr–N(1) bond (1.876 (4) Å) are in the range of previously observed terminal Zr═NR linkages[26b] and are consistent with a Zr–N bond order somewhat greater than two, i.e. with 4-electron donation from the imide to the metal thereby making **12** a *formal* 18 valence electron species.

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(25) The best crystal of **9** suitable for X-ray structural studies diffracted weakly and most of the data collected were "unobserved" thereby limiting the refinement to isotropic values, except for the Zr and Cl atoms. Refer to the supplementary material for a full discussion of the structure solution.

(26) (a) As reported in footnote 16 of ref 13. (b) Other terminal Zr═NR bond distances (Å): $(\eta^5\text{-}C_5H_5)_2Zr({=}N^tBu)(THF)$, 1.826 (4), ref 12; $Zr({=}NAr)(NHAr)_2L_2$ (L = 4-pyrrolidinopyridine), 1.868 (3), ref 13; $Zr({=}NPh)(O\text{-}2,6\text{-}C_6H_3{}^tBu_2)_2L_2$ (L = 4-pyrrolidinopyridine), 1.844 (9), ref 13.

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(28) Compound **11** slowly decomposes in solution at room temperature over 3–4 days; therefore, molecular weight measurements by vapor pressure equilibration are inconclusive.

Table III. Selected Bond Distances (Å) and Bond Angles (deg) in $(\eta^5\text{-}C_5Me_5)Zr(N\text{-}2,6\text{-}C_6H_3{}^iPr_2)Cl(NC_5H_5)_2$ (**12**)[a,b]

Bond Distances			
Zr–N(1)	1.876 (4)	Zr–C(42)	2.525 (5)
Zr–Cl	2.504 (1)	Zr–C(43)	2.596 (5)
Zr–N(2)	2.435 (4)	Zr–C(44)	2.650 (5)
Zr–N(3)	2.414 (4)	Zr–Cp^*_{cent}	2.286 (4)
Zr–C(40)	2.601 (5)	N(1)–C(10)	1.377 (6)
Zr–C(41)	2.533 (5)		
Bond Angles			
Cl–Zr–N(1)	117.1 (1)	Zr–N(1)–C(10)	164.5 (3)
Cl–Zr–N(2)	79.6 (1)	Cp^*_{cent}–Zr–Cl	114.27 (4)
Cl–Zr–N(3)	81.9 (1)	Cp^*_{cent}–Zr–N(2)	104.3 (1)
N(1)–Zr–N(2)	86.3 (2)	Cp^*_{cent}–Zr–N(1)	128.6 (1)
N(1)–Zr–N(3)	83.3 (1)	Cp^*_{cent}–Zr–N(3)	102.86 (9)
N(2)–Zr–N(3)	151.6 (1)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Cp^*_{cent} represents the average of the *x*, *y*, and *z* coordinates of the $\eta^5\text{-}C_5Me_5$ ring carbons.

Discussion

Although theoretical[24a] studies and structural precedent[12,22–24] suggested that $[(\eta^5\text{-}C_5H_4Me)Zr({=}NAr)Cl]_2$ (**9**) would contain symmetrically bridging imido ligands, this complex is characterized by the unusual $\mu\text{-}[\eta^1(N){:}\eta^2(N,C)]$ interaction in the solid state. This interaction is reminiscent of the homoleptic benzyl complex $Zr(CH_2Ph)_4$ in which the β carbons (phenyl C_{ipso}) are a mean 2.74 Å from the metal,[29] and like this compound, we attribute the distortions in **9** to a weak interaction between the $p(\pi)$ orbital on C_{ipso} and the d^0 metal. In **9**, the C_{ipso}–Zr distance (2.58 (1) Å) is significantly closer than the average C_{ipso}–Zr distance in $Zr(CH_2Ph)_4$. We formulate the μ-NAr interaction as $\eta^2(N,C)$ bonding to Zr(2) rather than an η^3 interaction involving N(2)–C(21)–C(26) (even though the phenyl ring tilts toward Zr(2)) on the basis of the Zr(2)–C(22) and Zr(2)–C(26) distances of 3.30 (1) and 3.24 (1) Å, respectively. Another zirconium compound which possesses a relevant structure is the $\mu\text{-}(2\text{-}\eta^1{:}1\text{-}2\text{-}\eta^2\text{-naphthyl})$ complex $[(\eta^5\text{-}C_5H_5)_2Zr]_2(\mu\text{-}H)(\mu\text{-}C_{10}H_7)$ in which one ring carbon bonds η^1 to one metal and two carbons interact η^2 to the other in an asymmetric bridge.[30] Perhaps most similar to **9** in the asymmetry and the *selective* interaction observed in only one bridging ligand is the structure of $[(\eta^5\text{-}C_5H_5)_2Zr({=}NN{=}CHPh)]_2$, which contains one symmetrically bridged and one $\eta^2\text{-}(NN{=}CHPh)$ unit in the same molecule.[31] The structure of **9** does *not* indicate a difference between the N–C_{ipso} bond distances in the two μ-NAr ligands nor is the aromaticity of the aryl ring of the N(2)Ar ligand disrupted as in the π interaction of an aryl group in the μ-diarylmethylene compounds $Cp_2Mo_2(CO)_4(CR_2)$ (R = Ph or *p*-tolyl).[32]

Compound **9** may constitute a relevant structural model for industrial hydrodenitrogenation (HDN) catalysis.[33] The most difficult step in HDN is generally regarded as the scission of C–N bonds.[4] Since both heterocyclic (e.g. pyridine and quinoline derivatives) and nonheterocyclic (aliphatic amines and anilines) nitrogen compounds contaminate petroleum and coal and are subject to HDN catalysis,[33,34] the $\mu\text{-}[\eta^1(N){:}\eta^2(N,C)]$-NAr ligand in **9** could represent a model substrate → catalyst interaction on the way to C–N bond scission in the HDN of anilines.

Both the $\eta^5\text{-}C_5R_5^-$ and the NAr^{2-} moieties have been described as "$\sigma + 2\pi$" donor ligands;[35] therefore, one might expect analogies in the structures of their compounds. Thus, $(\eta^5\text{-}C_5Me_5)Zr({=}NAr)Cl(py)_2$ (**12**) is formally related to $Ta({=}NAr)_2Cl(py)_2$,[15a] which leads to an alternative (perhaps preferred) description of its structure. Like $Ta({=}NAr)_2Cl(py)_2$, $(\eta^5\text{-}C_5Me_5)Zr({=}NAr)Cl(py)_2$ (**12**) is perhaps best described as an approximate TBP structure with axial σ donor pyridines and equatorial π donor ligands (C_5Me_5 and NAr). As seen in Table III, the "axial" pyridines are situated with N(2)–Zr–N(3) = 151.6 (1)°, while the "equatorial" interligand angles range from 114.27 (4) to 128.6 (1)°. Such an analogy has been useful in relating the structures of bis(imido) complexes of W(IV) to their group 4 bis(cyclopentadienyl) analogues.[35]

Unlike the terminal imido complexes of zirconium reported by the Bergman group[12] and by Wolczanski and co-workers,[11] the compounds reported in this study were unreactive at their imido ligands. This observation most likely reflects the stability of these complexes arising from the coordination of additional bases (THF, pyridine) which not only coordinatively saturate the metal but also diminish its electrophilicity. Future efforts will focus on the formation of transient M=NR moieties which are generated via intramolecular α-H abstraction from an amide by an adjacent alkyl ligand in the absence of such donor ligands.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere either by standard Schlenk techniques[36] or in a Vacuum Atmospheres HE-493 drybox at room temperature (unless otherwise indicated). Solvents were distilled under N_2 from an appropriate drying agent[37] and were transferred to the drybox without exposure to air. The "cold" solvents used to wash isolated solid products were typically cooled to ca. −30 °C before use. NMR solvents were passed down a short (5–6 cm) column of activated alumina prior to use. In all preparations Ar = $2,6\text{-}C_6H_3{}^iPr_2$, py = NC_5H_5, COT = $C_8H_8^{2-}$, Cp′ = $C_5H_4Me^-$, and Cp* = $C_5Me_5^-$.

Starting Materials. Zirconium(IV) chloride and hafnium(IV) chloride were purchased from Cerac and resublimed (185 °C, 10^{-4} Torr) before use. Chlorotrimethylsilane was purchased from Petrarch and used as received. 2,6-Diisopropylaniline was obtained from Aldrich and was vacuum distilled before use. $ZrCl_4(THF)_2$,[38] $HfCl_4(THF)_2$,[38] LiNHAr,[39] $K_2(C_8H_8)$,[40] $K[N(SiMe_3)_2]$,[41] and $(\eta^5\text{-}C_5Me_5)ZrCl_3$[27a] were prepared from the literature procedures. (*Caution*: *Solid $K_2(C_8H_8)$ explodes violently upon contact with air!*) $Li(C_5H_4Me)$ was prepared by the reaction of freshly cracked Cp′H with ${}^nBuLi$ in pentane for 18 h (initiated at 0 °C and then warmed to room temperature) followed by solvent removal and washing of the resulting solid with pentane and drying in vacuo.

Physical Measurements. ^1H (250 MHz) and ^{13}C (62.9 MHz) NMR spectra were recorded at probe temperature (unless otherwise specified) on a Brucker WM-250 spectrometer in C_6D_6, $CDCl_3$, or toluene-d_8 solvent. Chemical shifts are referenced to protio impurities (δ 7.15, C_6D_6; δ 7.24, $CDCl_3$; δ 2.09, toluene-d_8) or solvent ^{13}C resonances (δ 128.0, C_6D_6; δ 77.0, $CDCl_3$; δ 20.4, toluene-d_8) and are reported downfield of Me_4Si. Molecular weight measurements were determined as previously described.[42] Chemical ionization mass spectra were recorded to m/z = 999 on a Hewlett-Packard 5988A instrument in both positive ion (isobutane reagent) and negative ion (methane reagent) modes. Microanalytical samples were handled under N_2 and were combusted with WO_3 (Texas Analytical Laboratories, Inc., Stafford, TX).

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Preparations. Zr(NAr)(NHAr)$_2$(py)$_2$ (1). A solution of LiNHAr (1.49 g, 8.22 mmol) in 5 mL of THF was added dropwise to a rapidly stirred, cold (–35 °C) solution of ZrCl$_4$(THF)$_2$ (0.75 g, 1.99 mmol) in 20 mL of THF. The best yields of **1** were obtained by allowing this reaction to stir at room temperature for 4 h and then adding dropwise ca. 1.5 mL of pyridine to the pale yellow-orange solution. Upon pyridine addition, the solution immediately became clear, bright orange in color. After being stirred at room temperature for an additional 12 h, the solvent was removed in vacuo yielding a cloudy, orange oil. The oil was extracted with 30 mL of toluene and filtered through Celite, and toluene was removed from the filtrate in vacuo. The resulting yellow-orange oil was dissolved in 10 mL of diethyl ether and cooled to –35 °C for 24 h over which time the product precipitated as mustard yellow flakes. These flakes were filtered off, washed with minimal cold pentane, and dried in vacuo, yield 1.34 g (1.73 mmol) or 87%. Analytically pure samples were obtained by recrystallization from diethyl ether at –35 °C. ^{1}H NMR (C$_6$D$_6$): δ 9.05 (d, 4 H, H$_o$, py), 7.23–6.81 (m, 11 H, H$_{aryl}$ and N*H*Ar), 6.71 (m, 2 H, H$_p$, py), 6.29 (m, 4 H, H$_m$, py), 3.51 (spt, 4 H, C*H*Me$_2$, NHAr), 3.41 (spt, 2 H, C*H*Me$_2$, NAr), 1.24 (d, 24 H, CH*Me*$_2$, NHAr), 1.00 (d, 12 H, CH*Me*$_2$, NAr). ^{13}C NMR (C$_6$D$_6$): δ 155.4 (C$_{ipso}$, NAr), 152.7 (C$_o$, py), 149.8 (C$_{ipso}$, NHAr), 139.7 (C$_o$, NAr), 138.9 (C$_p$, py), 135.7 (C$_o$, NHAr), 124.0 (C$_m$, py), 123.8 (C$_m$, NHAr), 122.2 (C$_m$, NAr), 117.8 (C$_p$, NHAr), 116.8 (C$_p$, NAr), 30.2 (*C*HMe$_2$, NHAr), 28.7 (*C*HMe$_2$, NAr), 24.4 (CH*Me*$_2$, NHAr), 23.7 (CH*Me*$_2$, NAr). Anal. Calcd for $C_{46}H_{63}N_5Zr$: C, 71.08; H, 8.17; N, 9.01. Found: C, 70.88; H, 8.23; N, 9.12.

Zr(NAr)(NHAr)Cl(py)$_2$ (2). A THF solution of Me$_3$SiCl (0.06 g, 0.58 mmol, in 5 mL of THF) was added dropwise to a rapidly stirred solution of Zr(NAr)(NHAr)$_2$(py)$_2$ (**1**, 0.50 g, 0.64 mmol) in 20 mL of THF at –35 °C. The reaction was stirred at room temperature for 48 h after which time the solvent was removed in vacuo to afford a clear, pale orange oil. Upon trituration of the oil with a cold (ca. –20 °C) mixture of diethyl ether/pentane (1:1 by volume), the yellow orange compound was obtained as a fine powder (0.30 g, 0.47 mmol, 81%), which was filtered off and dried in vacuo. Analytically pure samples were obtained by recrystallization from toluene/diethyl ether at –35 °C. ^{1}H NMR (C$_6$D$_6$): δ 9.04 (d, 4 H, H$_o$, py), 8.71 (s, 1 H, N*H*Ar), 7.16–6.83 (A$_2$B mult, 6 H, H$_{aryl}$), 6.68 (m, 2 H, H$_p$, py), 6.35, (m, 4 H, H$_m$, py), 4.39 (spt, 2 H, C*H*Me$_2$, NAr), 3.24 (spt, 2 H, C*H*Me$_2$, NHAr), 1.31 (d, 12 H, CH*Me*$_2$, NHAr), 1.27 (d, 12 H, CH*Me*$_2$, NAr). ^{13}C NMR (C$_6$D$_6$):δ 153.7 (C$_{ipso}$, NAr), 151.2 (C$_o$, py), 149.2 (C$_{ipso}$, NHAr), 141.6 (C$_o$, NAr), 138.3 (C$_p$, py), 133.9 (C$_o$, NHAr), 124.2 (C$_m$, py), 123.7 (C$_m$, NHAr), 122.3 (C$_m$, NAr), 119.2 (C$_p$, NHAr), 118.7 (C$_p$, NAr), 31.4 (*C*HMe$_2$, NHAr), 28.7 (*C*HMe$_2$, NAr), 24.2 and 24.0 (CH*Me*$_2$, NAr and NHAr). Anal. Calcd for $C_{34}H_{45}ClN_4Zr$: C, 64.17; H, 7.13; N, 8.80. Found: C, 63.98; H, 7.21; N, 8.83.

Zr(NAr)Cl$_2$(py)$_3$ (3). A solution of Zr(NAr)(NHAr)$_2$(py)$_2$ (**1**, 0.50 g, 0.64 mmol) in 20 mL of THF and 1.5 mL of pyridine was prepared in an ampule (Teflon stopcock). This solution was rapidly stirred (room temperature) while a Me$_3$SiCl/THF solution (0.146 g, 1.34 mmol in 5 mL of THF) was added dropwise. The reaction was stirred for 2 h at ambient temperature in the sealed ampule and then heated to 65 °C for 18 h over which time it developed a yellow-orange color. The solvent was removed in vacuo yielding a pale orange, oily solid which upon trituration with pentane afforded the product as a pale orange powder. The product was filtered off, washed with pentane, and dried in vacuo, yield 0.35 g (0.61 mmol, 95%). Analytically pure samples were obtained by recrystallization at –35 °C from minimal toluene with 3–4 drops of pyridine added. ^{1}H NMR (CDCl$_3$): δ 8.91 (m, 6 H, H$_o$, py), 7.70 (m, 3 H, H$_p$, py), 7.24 (m, 6 H, H$_m$, py), 6.86–6.52 (A$_2$B mult, 3 H, H$_{aryl}$), 4.23 (spt, 2 H, C*H*Me$_2$), 0.96 (d, 12 H, CH*Me*$_2$). ^{13}C NMR (CDCl$_3$): δ 151.6 (C$_{ipso}$), 151.0 (C$_o$, py), 143.8 (C$_o$, NAr), 138.4 (C$_p$, py), 124.1 (C$_m$, py), 121.6 (C$_m$, NAr), 118.3 (C$_p$, NAr), 27.1 (*C*HMe$_2$), 24.0 (CH*Me*$_2$).

Zr(NAr)Cl$_2$(THF)$_2$ (4). A solution of 0.75 g (1.99 mmol) of ZrCl$_4$(THF)$_2$ in 20 mL of THF was prepared and cooled to –35 °C. A solution of LiNHAr (1.49 g, 8.22 mmol, in 5 mL of THF) was added dropwise to the rapidly stirred ZrCl$_4$(THF)$_2$ solution, which resulted in an immediate color change to pale yellow followed by a slower change to light orange. The reaction was stirred at room temperature for 18 h after which time the solvent was removed in vacuo to afford a pale orange oil. This oil was dissolved in toluene (20 mL) and filtered through Celite, and the filtrate was stripped in vacuo to provide a clear orange oil free of lithium salts. This sample was dissolved in 30 mL of THF, and the solution was added to an ampule (Teflon stopcock) along with 0.45 g (4.17 mmol) of Me$_3$SiCl. The solution was heated to 65 °C for 12 h over which time a lemon yellow color developed. The reaction volatiles were removed in vacuo yielding an oily solid which provided 0.82 g (1.70 mmol, 85%) of lemon yellow, microcrystalline solid upon trituration with pentane. The product was filtered off, washed with pentane, and dried in vacuo. Analytically pure samples were obtained by recrystallization from THF at –35 °C. ^{1}H NMR (CDCl$_3$): δ 7.00–6.80 (A$_2$B mult, 3 H, H$_{aryl}$), 4.55 (spt, 2 H, C*H*Me$_2$), 3.66 (br, 8 H, H$_\alpha$, THF), 1.61 (br, 8 H, H$_\beta$, THF), 1.19 (d, 12 H, CH*Me*$_2$). ^{13}C NMR (CDCl$_3$): δ 147.0 (C$_{ipso}$), 141.7 (C$_o$), 124.1 (C$_m$), 123.3 (C$_p$), 72.1 (C$_\alpha$, THF), 27.1 (*C*HMe$_2$), 26.4 (C$_\beta$, THF), 25.2 (CH*Me*$_2$). Anal. Calcd for $C_{20}H_{33}Cl_2NO_2Zr$: C, 49.88; H, 6.91; N, 2.91. Found: C, 49.74; H, 7.02; N, 2.95.

Hf(NAr)Cl$_2$(THF)$_2$ (5). HfCl$_4$(THF)$_2$ (0.75 g, 1.61 mmol) and LiNHAr (1.20 g, 6.60 mmol) were reacted as described for the preparation of the zirconium analog Zr(NAr)Cl$_2$(THF)$_2$ (**4**), except that this reaction was stirred for 48 h (at room temperature) and the reaction with Me$_3$SiCl (0.37 g, 3.39 mmol) was carried out (at 65 °C) for 18 h. Upon removal of the solvent (in vacuo) from the Me$_3$SiCl reaction, a brown, oily solid was obtained which afforded 0.45 g (0.79 mmol, 49%) of pale yellow powder upon trituration with 15 mL of cold diethyl ether. This product was filtered off and washed with minimal cold pentane. Analytically pure samples were obtained by recrystallization from THF at –35 °C. ^{1}H NMR (CDCl$_3$): δ 6.98–6.77 (A$_2$B mult, 3 H, H$_{aryl}$), 4.63 (spt, 2 H, C*H*Me$_2$), 3.66 (br, 8 H, H$_\alpha$, THF), 1.60 (br, 8 H, H$_\beta$, THF), 1.20 (d, 12 H, CH*Me*$_2$). ^{13}C NMR (CDCl$_3$): δ 146.8 (C$_{ipso}$), 141.8 (C$_o$), 123.8 (C$_m$), 122.3 (C$_p$), 72.4 (C$_\beta$, THF), 26.8 (coincident *C*HMe$_2$ and C$_\beta$ THF), 25.1 (CH*Me*$_2$). Anal. Calcd for $C_{20}H_{33}Cl_2HfNO_2$: C, 42.23; H, 5.85; N, 2.46. Found: C, 41.68; H, 5.95; N, 2.40.

Zr(NAr)(NHAr)[N(SiMe$_3$)$_2$](py)$_2$ (6). A solution of K[N(SiMe$_3$)$_2$] (0.156 g, 0.78 mmol) in 3 mL of THF was added dropwise to a rapidly stirred solution of Zr(NAr)(NHAr)Cl(py)$_2$ (**2**, 0.50 g, 0.79 mmol) in 20 mL of THF at –35 °C. The reaction was allowed to stir at room temperature for 18 h over which time it became cloudy and developed a yellow orange color. The solvent was removed in vacuo to afford a yellow orange oil from which the product was extracted with 30 mL of toluene. The extract was filtered through Celite, the solvent was removed from the filtrate in vacuo, and trituration of the resulting oil with cold pentane yielded the bright yellow microcrystalline product (0.55 g, 0.72 mmol, 92%). Analytically pure product was obtained by recrystallization from diethyl ether at –35 °C. ^{1}H NMR (C$_6$D$_6$): δ 9.26 (d, 4 H, H$_o$, py), 7.29–6.77 (A$_2$B mult, 8 H, H$_{aryl}$ and H$_p$, py), 6.54 (m, 4 H, H$_m$, py), 5.44 (s, 1 H, N*H*Ar), 3.89 (spt, 2 H, C*H*Me$_2$, NAr), 3.36 (spt, 2 H, C*H*Me$_2$, NHAr), 1.19 (d, 12 H, CH*Me*$_2$, NHAr), 0.91 (d, 12 H, CH*Me*$_2$, NAr), 0.61 and 0.58 (br, 9 H each, Si*Me*$_3$). ^{13}C NMR (C$_6$D$_6$): δ 154.7 (C$_{ipso}$, NAr), 152.2 (C$_o$, py), 150.2 (C$_{ipso}$, NHAr), 140.6 (C$_o$, NAr), 138.7 (C$_p$, py), 136.1 (C$_o$, NHAr), 124.3 (C$_m$, py), 123.7 (C$_m$, NHAr), 122.3 (C$_m$, NAr), 118.2 (C$_p$, NAr), 117.7 (C$_p$, NHAr), 28.3 (*C*HMe$_2$, NHAr), 28.0 (*C*HMe$_2$, NAr), 24.0 and 24.5 (CH*Me*$_2$, NHAr and NAr), 7.2 and 4.8 (SiMe$_3$). Anal. Calcd for $C_{40}H_{63}N_5Si_2Zr$: C, 63.10; H, 8.34; N, 9.20. Found: C, 62.28; H, 8.34; N, 9.26.

[(η^8-C$_8$H$_8$)Zr(NAr)]$_2$ (7). Zr(NAr)Cl$_2$(THF)$_2$ (**4**, 0.50 g, 1.04 mmol) was dissolved in 20 mL of THF and cooled to –35 °C. To this cold, rapidly stirred solution was added a THF solution of K$_2$(C$_8$H$_8$) (0.19 g, 1.04 mmol in 3 mL of THF) dropwise over 1 min. This mixture was stirred for 18 h at room temperature over which time it became red-orange in color and formed a precipitate. The solvent was removed in vacuo yielding a brick red, oily solid from which the product was extracted with 40 mL of toluene. The extract was filtered through Celite and the toluene removed from the filtrate (in vacuo) to afford to product as a microcrystalline, red orange solid. This product was washed with minimal cold pentane, filtered off, and dried in vacuo; yield 0.35 g (0.47 mmol) or 91%. Analytically pure samples were obtained by recrystallization from toluene at –35 °C. ^{1}H NMR (CDCl$_3$): δ 7.08–6.83 (A$_2$B mult, 3 H, H$_{aryl}$), 6.23 (s, 8 H, C$_8$*H*$_8$), 2.63 (spt, 2 H, C*H*Me$_2$), 1.48 (d, 12 H, CH*Me*$_2$). ^{13}C NMR (CDCl$_3$): δ 156.0 (C$_{ipso}$), 135.8 (C$_o$), 123.3 (C$_m$), 120.0 (C$_p$), 95.3 (C$_8$H$_8$), 28.3 (CH*Me*$_2$), 25.9 (*C*HMe$_2$). Anal. Calcd for $C_{40}H_{50}N_2Zr_2$: C, 64.81; H, 6.80; N, 3.78. Found: C, 64.58; H, 6.88; N, 3.69.

[(η^8-C$_8$H$_8$)Hf(NAr)]$_2$ (8). Hf(NAr)Cl$_2$(THF)$_2$ (0.50 g, 0.88 mmol) was dissolved in 20 mL of THF and cooled to –35 °C. To this cold, rapidly stirred solution was added a THF solution of K$_2$(C$_8$H$_8$) (0.17 g, 0.88 mmol in 3 mL of THF) dropwise over 1 min. This mixture was stirred for 18 h at room temperature over which time it became red-orange in color and formed a precipitate. The solvent volume was reduced to ca. 5 mL in vacuo, 30 mL of toluene was added, and this solution was filtered through Celite. Removing the solvent from the filtrate in vacuo afforded the product as a microcrystalline, light yellow solid, yield 0.37 g (0.40 mmol) or 91%. Analytically pure samples were prepared by recrystallization from toluene at –35 °C. ^{1}H NMR (CDCl$_3$): δ 7.05–6.70 (A$_2$B mult, 3 H, H$_{aryl}$), 6.23 (s, 8 H, C$_8$*H*$_8$), 2.70 (spt, 2 H, C*H*Me$_2$), 1.47 (d, 12 H, CH*Me*$_2$). ^{13}C NMR (CDCl$_3$): δ 154.6 (C$_{ipso}$), 136.8 (C$_o$), 123.1 (C$_m$), 119.8 (C$_p$), 93.7 (C_8H_8), 27.8 (*C*HMe$_2$), 26.4 (CH*Me*$_2$). Anal. Calcd for $C_{40}H_{50}Hf_2N_2$: C, 52.46; H, 5.50; N, 3.06. Found: C, 52.14; H, 5.61; N, 2.88.

[(η^5-C$_5$H$_4$Me)Zr(NAr)Cl]$_2$ (9). A solution of Li(C$_5$H$_4$Me) (0.089 g, 1.04 mmol) in 3 mL of THF was added dropwise to a rapidly stirred, cold (−35 °C) solution of Zr(NAr)Cl$_2$(THF)$_2$ (**4**, 0.50 g, 1.04 mmol) in 20 mL of THF. The reaction was allowed to stir at room temperature for 17 h over which time a light yellow color developed. The solvent was removed in vacuo to provide an oily, yellow-orange solid from which the product was extracted with 20 mL of toluene. Filtration of the extract through Celite, followed by removal of the solvent from the filtrate (in vacuo) and trituration of the resulting orange oil with cold pentane, afforded the product as a light yellow solid. The product was filtered off, washed with pentane, and dried in vacuo, yield 0.21 g (0.55 mmol, 53%). Analytically pure samples were obtained by recrystallization from THF at −35 °C. ^{1}H NMR (C$_6$D$_6$): δ 7.10–6.97 (A$_2$B mult, 3 H, H$_{aryl}$), 6.15 and 5.82 (m, 2 H each, C$_5$*H*$_4$Me), 3.78 (spt, 2 H, C*H*Me$_2$), 1.94 (s, 3 H, C$_5$H$_4$*Me*), 1.31 and 1.27 (d, 6 H each, CH*Me*$_2$). ^{13}C NMR (C$_6$D$_6$): δ 147.9 (C$_o$), 142.7 (C$_{ipso}$), 126.6 (C$_p$), 124.4 (C$_m$), 117.0 (CH, Cp′), 115.0 (*C*Me, Cp′), 112.3 (CH, Cp′), 29.1 (*C*HMe$_2$), 26.1 and 24.3 (CH*Me*$_2$), 14.6 (C$_5$H$_4$*Me*). Anal. Calcd for $C_{36}H_{48}Cl_2N_2Zr_2$: C, 56.73; H, 6.35; N, 3.68. Found: C, 56.58; H, 6.42; N, 3.60.

(η^5-C$_5$Me$_5$)Zr(NAr)(NHAr)(NH$_2$Ar)(THF) (10). A solution of LiNHAr (0.54 g, 2.93 mmol) in 3 mL of THF was added dropwise to a rapidly stirred, cold (−35 °C) solution of (η^5-C$_5$Me$_5$)ZrCl$_3$ (0.315 g, 0.95 mmol) in 15 mL of THF. The reaction was stirred at room temperature for 18 h after which time the solvent was removed in vacuo yielding a light orange oil. The product was extracted from this oil into 30 mL of toluene, the solution was filtered through Celite, and the toluene was removed from the filtrate in vacuo to afford a pale yellow, waxy solid. Trituration of the solid with 10 mL of cold pentane gave a pale yellow powder, which was filtered off and dried in vacuo, yield 0.35 g (0.42 mmol, 44%). Analytically pure samples were obtained by recrystallization from pentane/diethyl ether at −35 °C. ^{1}H NMR (C$_6$D$_6$): δ 7.20–6.79 (m, 10 H, H$_{aryl}$ and N*H*Ar), 4.01 (spt, 2 H, C*H*Me$_2$, NAr), 3.59 (s, 2 H, N*H*$_2$Ar), 3.35 (spt, 2 H, C*H*Me$_2$, NHAr), 2.91 (m, 4 H, H$_\alpha$, THF), 2.69 (spt, 2 H, C*H*Me$_2$, NH$_2$Ar), 1.97 (s, 15 H, C$_5$Me$_5$), 1.47–1.26 (overlapping d, 24 H, CH*Me*$_2$, NAr and NHAr), 1.09 (d, 12 H, CH*Me*$_2$, NH$_2$Ar), 0.99 (m, 4 H, H$_\beta$, THF). ^{13}C NMR (C$_6$D$_6$): δ 152.5 (C$_{ipso}$, NAr), 149.3 (C$_{ipso}$, NHAr), 141.2 (C$_o$, NAr), 139.9 (C$_{ipso}$, NH$_2$Ar), 137.6 (C$_o$, NHAr), 132.7 (C$_o$, NH$_2$Ar), 122.9, 123.1 and 123.3 (C$_m$; NAr, NHAr, and NH$_2$Ar), 119.8, 119.5 and 118.8 (C$_p$; NAr, NHAr, and NH$_2$Ar), 119.1 (*C*$_5$Me$_5$), 68.2 (C$_\alpha$, THF), 28.1 (C$_\beta$, THF), 29.4, 27.2, 25.4, 25.0, 24.7, 23.8 and 22.7 (*C*HMe$_2$ and CH*Me*$_2$; NAr, NHAr, and NH$_2$Ar), 11.1 (C$_5$*Me*$_5$). Anal. Calcd for $C_{50}H_{77}N_3OZr$: C, 72.58; H, 9.38; N, 5.08. Found: C, 72.36; H, 9.47; N, 5.02.

[(η^5-C$_5$Me$_5$)Zr(NAr)(NHAr)(py)]$_2$ (11). A solution of LiNHAr (0.88 g, 4.78 mmol) in 3 mL of THF was added dropwise to a rapidly stirred, cold (−35 °C) solution of (η^5-C$_5$Me$_5$)ZrCl$_3$ (0.51 g, 1.54 mmol) in 15 mL of THF. The reaction was stirred at room temperature for 6 h over which time it developed a canary yellow color. Pyridine (0.13 g, 1.64 mmol) was then added dropwise (inducing a slight orange color), and this mixture was stirred for an additional 10 h. The reaction volatiles were removed in vacuo to afford a yellow oil. The product was extracted with 50 mL of toluene and filtered through Celite, and the toluene was removed in vacuo to afford an oily, red-orange solid. Trituration with diethyl ether afforded red-orange microcrystals, which were filtered off, washed with diethyl ether, and dried in vacuo, yield 0.85 g (1.29 mmol, 84%). Analytically pure samples were obtained by recrystallization from pyridine/diethyl ether at −35 °C. ^{1}H NMR (CDCl$_3$): δ 8.88 (m, 2 H, H$_o$, py), 7.99 (m, 1 H, H$_p$, py), 7.60 (m, 2 H, H$_m$, py), 6.93–6.52 (A$_2$B mult, 6 H, H$_{aryl}$), 6.28 (s, 1 H, N*H*Ar), 3.52 (spt, 2 H, C*H*Me$_2$), 3.35 (spt, 2 H, C*H*Me$_2$), 1.98 (s, 15 H, C$_5$Me$_5$), 1.03–0.92 (overlapping d, 24 H total, CH*Me*$_2$). ^{13}C NMR (CDCl$_3$): δ 152.5 (C$_{ipso}$, NAr), 150.9 (C$_o$, py), 150.4 (C$_{ipso}$, NHAr), 140.7 (C$_o$, NAr), 140.0 (C$_p$, py), 136.7 (C$_o$, NHAr), 125.2 (C$_m$, py), 122.6 (C$_m$, NHAr), 121.2 (C$_m$, NAr), 118.5 (C$_p$, NHAr), 117.5 (C$_p$, NAr), 115.9 (*C*$_5$Me$_5$), 29.1 (*C*HMe$_2$, NHAr), 27.4 (*C*HMe$_2$, NAr), 24.5, 24.1, 23.7, and 23.1 (CH*Me*$_2$), 11.0 (C$_5$*Me*$_5$). Anal. Calcd for $C_{39}H_{55}N_3Zr$: C, 71.30; H, 8.44; N. 6.39. Found: C, 71.02; H, 8.49; N, 6.42.

(η^5-C$_5$Me$_5$)Zr(NAr)Cl(py)$_2$ (12). A THF solution of Me$_3$SiCl (0.06 g, 0.58 mmol, in 5 mL of THF) was added dropwise to a rapidly stirred, cold (−35 °C) solution of [(η^5-C$_5$Me$_5$)Zr(NAr)(NHAr)(py)]$_2$ (**11**, 0.38 g, 0.29 mmol of dimer) in 20 mL of THF and 1 mL of pyridine. The reaction was stirred at room temperature for 24 h over which time the solution became clear yellow. The solvent was then removed in vacuo to afford a clear, pale yellow-orange oil. Upon trituration of the oil with pentane (ca. −20 °C) the mustard yellow compound was obtained as a fine powder (0.28 g, 0.47 mmol, 81%), which was filtered off and dried in vacuo. Analytically pure samples were obtained by recrystallization from pyridine/ether at −35 °C. ^{1}H NMR (toluene-*d*$_8$, 313 K): δ 8.94 (m, 4 H, H$_o$, py), 7.13–6.69 (m, 5 H, H$_p$, py; H$_{aryl}$), 6.62 (m, 4 H, H$_m$, py), 4.62 (spt, 2 H, C*H*Me$_2$), 1.81 (s, 15 H, C$_5$Me$_5$), 1.15 (d, 12 H total, CH*Me*$_2$). ^{13}C NMR (toluene-*d*$_8$; 313 K): δ 164.0 (C$_{ipso}$, NAr), 159.4 (C$_o$, NAr), 144.4 (C$_o$, py), 130.0 (C$_m$, py), 125.4 (C$_m$, NAr), 117.1 (C$_p$, NAr), 116.9 (*C*$_5$Me$_5$), 36.1 (CH*Me*$_2$, NAr), 33.4 (CH*Me*$_2$, NAr), 18.6 (C$_5$*Me*$_5$). Anal. Calcd for $C_{32}H_{42}ClN_3Zr$: C, 64.56; H, 7.11; N, 7.06. Found: C, 64.34; H, 7.20; N, 7.01.

Structural Determinations. General Methods. Preliminary examinations and data collection were performed at ambient temperature with Mo Kα radiation (λ = 0.710 73 Å) on an Enraf-Nonius CAD4 computer-controlled, κ axis diffractometer equipped with a graphite crystal incident beam monochromator. Crystal color and dimensions are recorded in Table I. As a check on crystal and electronic stability, two representative reflections were measured after 1 h of data collection. Only those reflections having intensities $I \geq 3\sigma(I)$ were used in the refinements. Hydrogen atoms were placed in calculated positions and included in the refinement. Lorentz–polarization and empirical absorption (Walker and Stuart[43]) corrections were applied to the data for both compounds. All calculations were performed on a VAX computer uxing MolEN/VAX.[44]

[(η^5-C$_5$H$_4$Me)Zr(N-2,6-C$_6$H$_3{}^i$Pr$_2$)Cl]$_2$ (9). A yellow, irregular crystal of **9** crystallized from THF (−35 °C) and was mounted in a glass capillary in a random orientation. From the systematic absences of $hk0$, $h = 2n + 1$, $h0l$, $l = 2n + 1$, and $0kl$, $k = 2n + 1$, and from the subsequent least-squares refinement, the space group was determined to be orthorhombic *Pbca* (No. 61). A total of 6433 reflections were collected in the $+h,+k,+l$ octant (6302 unique) in the range $2° \leq \theta \leq 50°$, with 2191 reflections having $I \geq 3\sigma(I)$. The intensities of the check reflection standards remained constant within experimental error throughout data collection, so no decay correction was required. The structure was solved by direct methods and refined by full-matrix least-squares techniques for a final $R = 0.052$ and $R_w = 0.057$. The largest peak in the final difference Fourier was 0.62 (11) e/Å^3. Lorentz–polarization and empirical absorption (from 0.83 to 1.00 on I) corrections were applied to the data.

(η^5-C$_5$Me$_5$)Zr(N-2,6-C$_6$H$_3{}^i$Pr$_2$)Cl(NC$_5$H$_5$)$_2$ (12). A golden yellow, irregular block crystal of **12** was obtained from pyridine solution (at −35 °C) by layering on diethyl ether and was mounted in a glass capillary in a random orientation. From the systematic absences of $h0l$, $h + l = 2n + 1$ and $0k0$, $k = 2n + 1$, and from subsequent least-squares refinement, the space group was determined to be $P2_1/n$ (No. 14). A total of 5745 reflections were collected in the $+h,+k,\pm l$ octants (5487 unique) in the range $2° \leq \theta \leq 50°$, with 3787 reflections having $I \geq 3\sigma(I)$. The check reflection standards showed a decrease in intensity over time, with a total loss in intensity of 7.9%. Therefore, a linear decay correction was applied. The correction factors on I ranged from 1.000 to 1.042 with an average value of 1.020. The structure was solved by the Patterson method and refined in full-matrix least squares for a final $R = 0.048$ and $R_w = 0.059$. The largest peak in the final difference Fourier was 1.11 (8) e/Å^3. Lorentz–polarization, empirical absorption (from 0.75 to 1.00 on I), reflection averaging (agreement on I = 1.9%), and linear decay corrections (from 1.000 to 1.042 on I) were applied to the data.

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Supplementary Material Available: Text and tables giving full details of the structure solution and crystallographic details for [(η^5-C$_5$H$_4$Me)Zr(NAr)Cl]$_2$ (**9**) and (η^5-C$_5$Me$_5$)Zr(NAr)Cl(py)$_2$ (**12**), tables of atomic positional and thermal parameters, bond distances and angles, least-squares planes, and dihedral angles, and ORTEP figures (30 pages); tables of observed and calculated structure factor amplitudes (32 pages). Ordering information is given on any current masthead page.

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