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Synthesis, Structure, and Reactivity of Zirconium Alkyl Complexes Bearing Ancillary Pyridine Diamide Ligands

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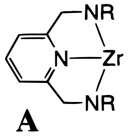
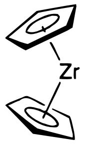
Zirconium alkyl complexes bearing a linked pyridine diamide ligand $[2,6\text{-}(RNCH_2)_2NC_5H_3]^{2-}$ (R = 2,6-diisopropylphenyl, **a**, (BDPP); R = 2,6-diethylphenyl, **b**, (BDEP); R = 2,6-dimethylphenyl, **c**, (BDMP)) have been synthesized. The bis(benzyl) derivatives (**2a**−**c**) undergo an η^1-, η^2-benzyl flip, which is likely a result of the electrophilic nature of the zirconium metal center. The bis(trimethylsilylmethyl) derivative $(BDPP)Zr(CH_2SiMe_3)_2$ (**3a**) is also fluxional; however, this behavior is attributable to the steric crowding in this complex. In contrast, the analogous compounds bearing the less bulky BDEP and BDMP ligands do not show fluxional behavior. The butadiene complexes $(BDPP)Zr(C_4H_6)$ (**5a**) (determined by X-ray crystallography), $(BDEP)Zr(C_4H_6)$ (**5b**), and $(BDMP)Zr(C_4H_6)$ (**5c**) adopt an s-cis bent metallacyclo-3-pentene structure with significant π-donation from the double bond. Consistent with the rigid nature of these complexes, no insertion chemistry is observed below 90 °C. Alkenes and alkynes react (>90 °C) via insertion into the Zr−C σ-bond to give σ,π-allyl products.

Introduction

The organometallic chemistry of zirconium in the +4 oxidation state has been dominated by complexes supported by cyclopentadienyl ligands.[1,2] Within this class of compounds, cationic metallocene derivatives[3,4] of the type $[Cp_2ZrR]^+$ exhibit high activity for the polymerization of ethylene and α-olefins.[5−7] The bent Cp_2Zr framework restricts coordination of olefins to a site cis to the Zr−R bond, while the formally 14-electron count results in a highly electrophilic metal center. Studies in this area have been concerned with the way in which the stereoregularity, catalytic activity, and comonomer incorporation can be altered with changes to the Cp ligand(s). In an effort to develop new families of catalysts with similar structural and/or electronic features, we are exploring the organometallic and polymerization chemistry of zirconium[8,9] and titanium[10,11] complexes supported by chelating diamide ligands. We have previously[8] shown that the pyridine diamide zirconium fragment $[2,6\text{-}(RNCH_2)_2NC_5H_3]Zr$ (**A**, R = aryl) can be viewed as an electron-deficient analogue of Cp_2Zr (**B**).



A



B

In addition, the sterics of the pyridine diamide ligand can be altered readily by varying the size of the substituents at nitrogen. Herein, we report the synthesis, reactivity, and fluxional behavior of a number of mono and bis(alkyl) derivatives of zirconium bearing pyridine diamide ligands of varying steric bulk. The similarities and differences between these compounds and their Cp_2Zr congeners will be presented.

Results and Discussion

We have reported[8] the synthesis of the zirconium pyridine diamide complexes $[2,6\text{-}(RNCH_2)_2NC_5H_3]ZrCl_2$ (**1a**, R = 2,6-$^iPr_2C_6H_3$, $(BDPP)ZrCl_2$; **1b**, R = 2,6-$Et_2C_6H_3$, $(BDEP)ZrCl_2$; **1c**, R = 2,6-$Me_2C_6H_3$, $(BDMP)ZrCl_2$). The reaction of the dichlorides **1a**−**c** with 2 equiv of $BrMgCH_2Ph$ in ether at 23 °C affords the bis(benzyl) derivatives **2a**−**c** in good yield (Scheme 1).

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(1) Jubb, J.; Song, J.; Richeson, D.; Gambarotta, S. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Ed.; Elsevier Science Ltd.: New York, 1995; Vol. 4.

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(11) Guérin, F.; McConville, D. H.; Payne, N. C. *Organometallics* **1996**, *15*, 5085.

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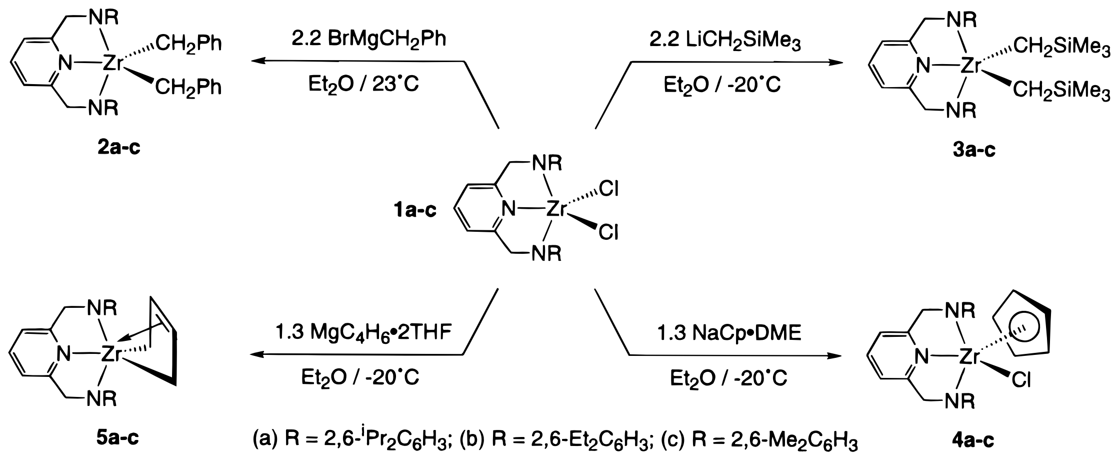
Scheme 1



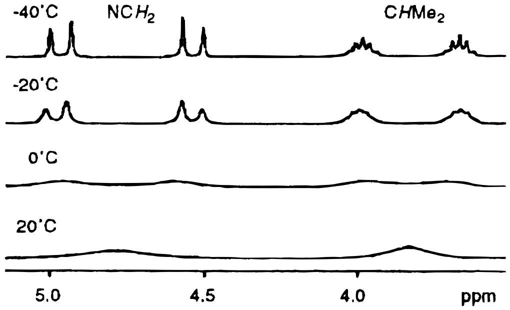


Figure 1. The ligand methylene and methine region of the variable-temperature NMR spectra of compound **2a**.

Compounds **2a** and **2c** are isolated as crystalline solids from CH_2Cl_2, while complex **2b**, which bears ethyl groups in the 2,6-position of the aryl substituents, is isolated as an oily solid due to its high solubility in pentane. The proton NMR spectrum of compound **2a** is broad and featureless at room temperature (Figure 1). The low-temperature (−40 °C) limiting spectrum of **2a** displays resonances for a species with C_s symmetry; in particular, two isopropyl methine resonances ($CHMe_2$) and an AB quartet pattern (NCH_2) are observed for the BDPP ligand, indicating asymmetry about the ligand N_3 plane. In addition, a high-field resonance (5.90 ppm) is observed for the ortho protons of a single benzyl group. These low-temperature proton NMR features are consistent with an η^1-, η^2-benzyl formulation[12] which is supported by the solid-state structure[13] of **2a** (Figure 2). The above resonances coalesce at 10 °C, yielding a barrier to "benzyl flipping" of $\Delta G^{\ddagger} = 13.5(5)$ kcal mol^{-1}. At higher temperatures (>40 °C) the benzyl ligands exchange rapidly, leading to a species with C_{2v} symmetry (Scheme 2).

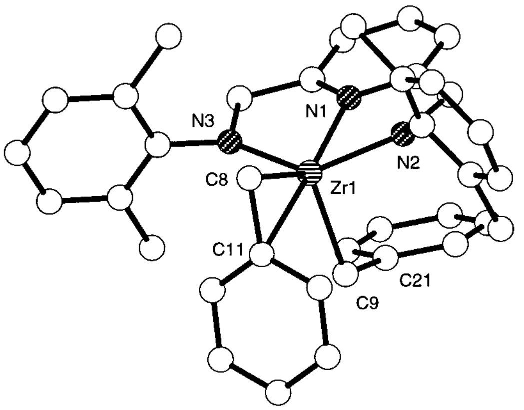
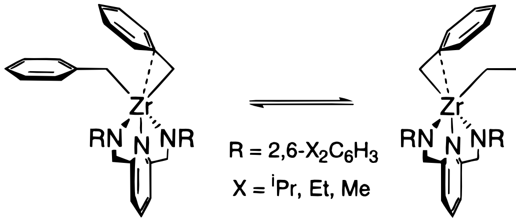


Figure 2. Chem 3D representation of the molecular structure of compound **2a** (the isopropyl methyl groups have been removed for clarity). Only connectivity could be established.

Scheme 2



In contrast to complex **2a**, the room-temperature ^1H NMR spectra of compounds **2b** and **2c** display sharp resonances for species with C_{2v} symmetry. However, upon cooling, both compounds show resonances consistent with both η^1- and η^2-benzyl ligands (**2b**, $T_c = -20$ °C, $\Delta G^{\ddagger} = 11.5(5)$ kcal mol^{-1}; **2c**, $T_c = -30$ °C, $\Delta G^{\ddagger} = 11.2(5)$ kcal mol^{-1}). Interestingly, the low-temperature (−80 °C) limiting spectrum of compound **2c** displays resonances for inequivalent aryl methyl groups, consistent with restricted rotation of the $N-C_{ipso}$ bond at this temperature (similarly, **2a** displays inequivalent isopropyl methyl groups and **2b** shows diastereotopic methylene protons in the aryl ethyl groups). The room-temperature proton NMR spectrum[14] of the metallocene bis(benzyl) derivative $Cp_2Zr(CH_2Ph)_2$ shows no evidence of η^2-benzyl ligands. In contrast, the structurally

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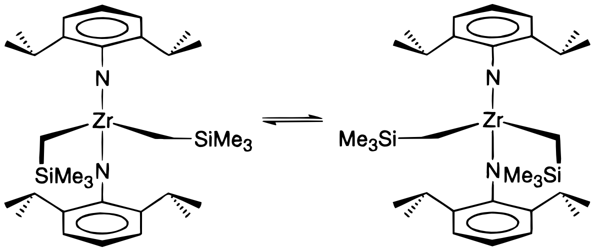
[12] Bei, X.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 3282.

[13] X-ray data for **2a** were collected at 25 °C on a Siemens P4 diffractometer using graphite-monochromated Mo Kα radiation. A total of 3654 reflections were collected in the θ range 1.88−21.0° with significant crystal decay (26.3%), resulting in a low data-to-parameter ratio (6.3:1). Therefore only the connectivity has been established. Crystal data: $C_{45}H_{55}N_3Zr$; MW = 849.29; monoclinic; space group $P2_1/n$; $a = 12.535(11)$ Å, $b = 21.683(21)$ Å, $c = 14.543(18)$ Å, $\beta = 90.28(1)°$; $V = 3952(7)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.223$ g cm^{-3}. In the final least-squares refinement cycles on F, the model converged at $R = 0.0972$, $wR = 0.1077$, and GoF = 1.62 for 989 observations with $F_o = 4\sigma(F_o)$ and 156 parameters (see Supporting Information).

[14] Fachinetti, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1972**, 654.

Scheme 3



characterized cationic benzyl derivative $[Cp_2Zr(\eta^2\text{-}CH_2Ph)(N{\equiv}CMe)]^+\{BPh_4\}^-$ and the spectroscopically identified base-free complex $[(\eta^5\text{-}C_5H_4Me)_2Zr(\eta^2\text{-}CH_2Ph)]^+\text{-}\{BPh_4\}^-$ [15] clearly show the presence of an η^2-benzyl moiety.

The dichlorides **1a**−**c** react with 2 equiv of $LiCH_2SiMe_3$ in ether to afford the bis(trimethylsilylmethyl) derivatives in excellent isolated yield (Scheme 1). Compounds **3a**−**c** are isolated as bright yellow crystalline solids from hexanes. The proton NMR spectra of compounds **3b** and **3c** show resonances for species with C_{2v} symmetry at temperatures between −80 and +80 °C. In contrast, the room-temperature ^1H NMR spectrum of complex **3a**, which bears isopropyl groups in the 2,6-position of the aryl substituents, is broad and featureless. The high-temperature (+70 °C) limiting spectrum shows resonances for the expected C_{2v}-symmetric product, including a $Zr-CH_2SiMe_3$ signal at 0.65 ppm. The low-temperature limiting spectrum displays sharp signals for a species with C_s symmetry; for example, an AB quartet at 4.80 ppm and two isopropyl methines at 4.26 and 3.36 ppm result from asymmetry about the ligand N_3 plane. The absence of fluxionality in compounds **3b** and **3c** suggests that the origin of this behavior in compound **3a** is steric and not electronic. Hence, we propose that the bulk of the isopropyl substituents in compound **3a** prevents both trimethylsilyl groups from simultaneously residing adjacent to these substituents, in other words, to point outward (Scheme 3).

The above resonances coalesce at 20 °C, yielding a barrier to "Zr−C bond rotation" of $\Delta G^\ddagger = 13.4(5)$ kcal mol^{-1}. In the solid-state structure of $Cp_2Zr(CH_2SiMe_3)_2$,[16] the trimethylsilylmethyl groups are arranged in the least sterically hindered position, that is, with both trimethylsilyl moieties directed outward.

Compounds **1a**−**c** react cleanly with NaCp·DME (DME = dimethoxyethane) in ether at −20 °C to give the white crystalline mono(cyclopentadienyl) derivatives **4a**−**c** in good yield (Scheme 1). All three compounds display proton and carbon resonances consistent with molecular C_s symmetry. It has been proposed[17] that the tris(methylcyclopentadienyl) derivative $(C_5H_4Me)_3ZrCl$ contains two η^5-coordinated MeCp rings and one η^1-coordinated ring. We see no evidence of an η^1-Cp ligand in the low-temperature proton NMR spectrum of compound **4a**.

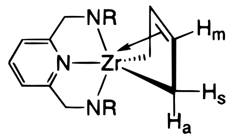
Table 1. Selected Crystallographic Data for Compound 5a[a]

empirical formula	$C_{35}H_{47}N_3Zr{\cdot}0.35Et_2O$
fw	616.49
cryst dimens (mm)	0.20 × 0.10 × 0.10
cryst syst	tetragonal
space group	*I*-42*d*
$a = b$ (Å)	16.155(3)
c (Å)	26.847(3)
$\alpha = \beta = \gamma$ (deg)	90
V (Å^3)	7007(2)
Z	8
ρ (calc) (g/mol)	1.169
collection temp (K)	298(2)
F_{000}	2612
Mo Kα	graphite (monochromated)
total no. of unique reflns	2019 (R(int) = 0.2999)
no. of variable params	244
R1	0.0765
wR2	0.1635
goodness of fit (GoF)	1.029

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$; $GoF = [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (where n is the number of reflections and p is the number of parameters refined).

The dichlorides **1a**−**c** react with $Mg(C_4H_6){\cdot}2THF$ in ether at −20 °C to give the zirconium diene derivatives **5a**−**c** in excellent isolated yield (Scheme 1). The proton NMR spectra of compounds **5a**−**c** display characteristic resonances for species with C_s symmetry; however, the mirror symmetry is in the plane of the meridionally coordinated pyridine diamide ligand; the ^1H NMR spectrum of the diene derivative **5c** shows two ligand methylene (NCH_2) signals which are not coupled. The diene fragment in all three complexes adopts an s-cis bent metallacyclo-3-pentene structure[18,19] with significant π-donation from the cyclopentene double bond; for example, the proton NMR spectrum of compound **5c** displays signals at 4.98, 3.42, and 0.17 ppm for H_m, H_a, and H_s, respectively (**C**).

C



The C_s symmetry of compound **5a** is retained to +80 °C, and we see no evidence of syn/anti proton exchange, consistent with rigid coordination of the diene fragment to the highly electrophilic zirconium center. The zirconocene derivative $Cp_2Zr(\eta^4\text{-}C_4H_6)$ exists in two isomeric forms, having the butadiene coordinated in either the s-cis or s-trans configuration.[19] The s-trans complex is considerably more reactive than the s-cis isomer (vide infra).[20]

The solid-state structure of **5a** was determined by X-ray crystallography (Table 1). The molecular structure of complex **5a** can be found in Figure 3 and relevant bond distances and angles in Table 2. The amide− and pyridine−zirconium bond distances are statistically the same as those found in $(BDEP)ZrMe_2$.[8] The long−short−long bond alternation in the diene fragment coupled with the short Zr−C(17) and long Zr−C(18) bonds confirms the s-cis bent metallacyclo-3-pentene

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(16) Jeffery, J.; Lappert, M. F.; Luong-Thi, N. T.; Webb, M.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1981**, 1593.

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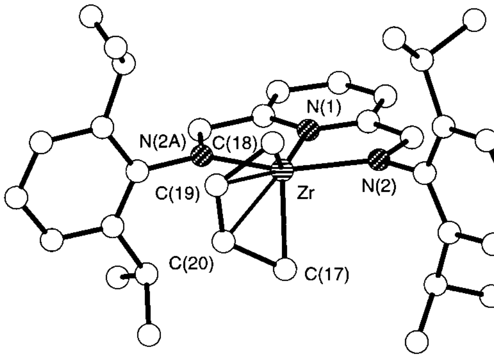
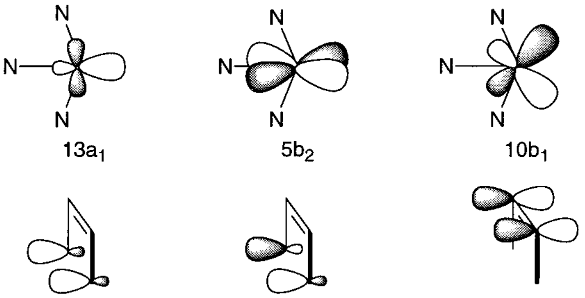


Figure 3. Chem 3D representation of the molecular structure of compound **5a**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 5a

Bond Distances			
Zr−N(1)	2.307 (13)	Zr−C(18)	2.47 (2)
Zr−N(2)	2.111 (8)	Zr−C(19)	2.47 (2)
Zr−N(2A)	2.111 (8)	C(17)−C(18)	1.56 (3)
Zr−C(17)	2.36 (2)	C(18)−C(19)	1.36 (3)
Zr−C(20)	2.33 (2)	C(19)−C(20)	1.55 (3)
Bond Angles			
N(2)−Zr−N(2A)	140.0 (4)	Zr−C(20)−C(19)	37.5 (7)
N(1)−Zr−C(17)	133.3 (6)	C(17)−C(18)−C(19)	126 (2)
N(1)−Zr−C(20)	141.4 (7)	C(20)−C(19)−C(18)	121 (2)
Zr−C(17)−C(18)	37.7 (7)	N(2)−Zr−N(1)	70.0 (2)

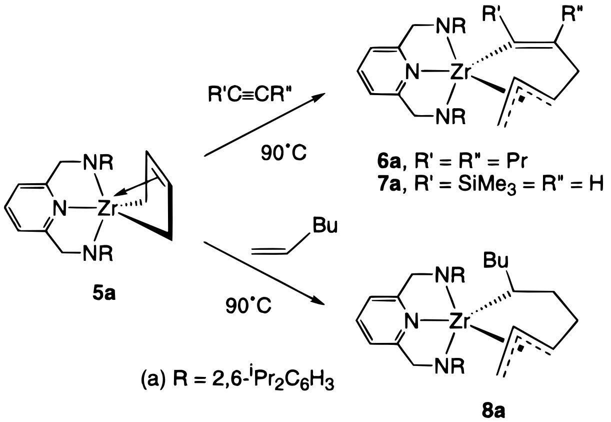
formulation. Overlap of the $5b_2$ and $13a_1$ frontier molecular orbitals[8] of the (BDPP)Zr fragment with the sp^3-hybrids on carbons C(17) and C(20) accounts for the σ-bonds between Zr and these carbons.[21] Presumably, the π-donation from carbons C(18) and C(19) is mainly into the empty $10b_1$ orbital on zirconium.



The diene complex **5a** does not react with unsaturated substrates over several days at 23 °C; however, upon heating to 90 °C in benzene products derived from insertion into the Zr−C σ-bond are observed (Scheme 4).

The σ,π-allyl formulation for compounds **6a**, **7a**, and **8a** is based on characteristic proton[22,23] and carbon[24,25] resonances for the Zr-allyl functional group and the observed C_1 symmetry for all three complexes. The ^{1}H NMR spectrum for compound **6a** displays two AB quartets for the ligand methylene (NCH_2) protons, four isopropyl methine, and eight isopropyl methyl resonances. We see no evidence for syn/anti proton exchange in the allyl group to 80 °C, suggesting that this moiety is firmly coordinated to the electrophilic zirconium center. In an analogous fashion, $Cp_2Zr(\eta^4$-isoprene) reacts with 2-butyne to give a σ,π-allyl derivative.[23] The reaction of compound **5a** with HC≡CSiMe$_3$ affords a single isomer (**7a**) derived from 2,1-insertion of the acetylenic unit into the Zr−C bond. The substitution pattern of complex **7a** was established on the basis of ^{1}H NMR spectroscopy, ^{1}H COSY, and NOE experiments. For example, irradiation of the low-field vinylic resonance (δ 8.02 ppm) results in a strong enhancement of the metallacycle C═CH−CH_2 protons. The reaction of complex **5a** with excess 1-hexene also affords a 2,1-insertion type product. The presence of two AB quartets for the ligand methylene protons (NCH_2) is consistent with a complex with C_1 symmetry. The 2,1-insertion of the olefin was confirmed by a combination of ^{1}H,^{13}C COSY, and ^{13}C-APT and experiments; in particular, an inverted peak is observed for the carbon attached to the zirconium (42.49 ppm), characteristic of a tertiary carbon. In contrast, most 1-alkenes (1-butene, 1-octene, etc.) react with Cp_2Zr(diene) in a 1,2 fashion.[22−24]

Scheme 4



Conclusions

A series of alkyl derivatives stabilized by a linked pyridine diamide ligand have been prepared. The bis(benzyl) derivatives undergo an η^1-, η^2-benzyl flip, which is likely a result of the electrophilic nature of the zirconium metal center. The bis(trimethylsilylmethyl) derivative (BDPP)Zr(CH$_2$SiMe$_3$)$_2$ is also fluxional; however, this behavior is attributable to the steric crowding in this complex. The butadiene complexes **5a**−**c** adopt an s-cis bent metallacyclo-3-pentene structure with significant π-donation from the double bond. Consistent with the rigid nature of these complexes, no insertion chemistry is observed below 90 °C. Alkenes and alkynes react (>90 °C) via insertion into the Zr−C σ-bond to give σ,π-allyl products. The fluxionality and reactivity of the pyridine diamide derivatives detailed herein are consistent with the electron deficiency of these compounds as compared to their metallocene analogues.

Experimental Section

General Details. All experiments were performed under a dry dinitrogen atmosphere using standard Schlenk tech-

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(21) Calculations were performed on an appropriate model using CAChe Scientific Inc. software.

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(23) Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N.; Mashima, K.; Nagasuna, K.; Yasuda, H.; Nakamura, A. *Chem. Lett.* **1982**, 1979.

(24) Erker, G.; Berg, K.; Krüger, C.; Müler, G.; Angermund, K.; Benn, R.; Schroth, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 455.

(25) Temme, B.; Karl, J.; Erker, G. *Chem. Eur. J.* **1996**, *2*, 919.

niques or in an Innovative Technology Inc. glovebox. Solvents were distilled from sodium/benzophenone ketyl (DME, THF, hexanes, diethyl ether, and benzene) or molten sodium (toluene) under argon and stored over activated 4 Å molecular sieves. Zirconium(IV) chloride was purchased from Alfa and used as received. The 4-octyne, trimethylsilylacetylene, and 1-hexene were purchased from Aldrich and distilled prior to use. The compounds (BDPP)$ZrCl_2$ (**1a**), (BDEP)$ZrCl_2$ (**1b**), and (BDMP)$ZrCl_2$ (**1c**) were synthesized by literature procedures.[8] Unless otherwise specified, proton (300 MHz) and carbon (75.46 MHz) NMR spectra were recorded in C_6D_6 at approximately 22 °C on a Varian Gemini-300 or 300-XL spectrometer. The proton chemical shifts were referenced to internal C_6D_5H ($\delta = 7.15$ ppm) and the carbon resonances to C_6D_6 ($\delta = 128.0$ ppm). Elemental analyses were performed using sealed tin cups on a Fisons Instruments model 1108 elemental analyzer by Mr. Peter Borda of this department or by Oneida Research Services Inc., Whitesboro, NY.

(BDPP)Zr(CH_2Ph)$_2$ (2a). To a diethyl ether (25 mL) suspension of compound **1a** (0.100 g, 0.162 mmol) was added 2.2 equiv of $PhCH_2MgBr$ (0.32 mL, 1.13 M, 0.36 mmol) at 23 °C. The suspension was stirred for 12 h. The solvent was removed in vacuo. The resulting solid was extracted with toluene (3 × 10 mL) and filtered through Celite to give a bright-yellow solution. The solvent was removed in vacuo, and the solid was dissolved in a minimum amount of dichloromethane and cooled to −30 °C for 12 h. Yellow crystalline **2a** was isolated by filtration and dried under vacuum (0.093 g, 0.128 mmol, 79%). ^1H NMR (toluene-d_8, 23 °C): δ 6.90−7.30 (m, Ar and CH_2Ph), 6.82 (t, 1H, py), 6.35 (d, 2H, py), 4.82 (br, 4H, NCH_2), 3.85 (br, 4H, $CHMe_2$), 1.92 (br, 4H, CH_2Ph), 1.45 (br, 12H, $CHMe_2$), 1.21 (d, 12H, $CHMe_2$). ^1H NMR (toluene-d_8, −40 °C): δ 6.90−7.30 (m, 6H, Ar and CH_2Ph), 6.82 (m, 4H, *m* Ph), 6.75 (t, 1H, py), 6.51 (m, 2H, *p* Ph), 6.23 (d, 2H, py), 5.90 (d, 2H, *o* Ph), 4.81 (AB quartet, $^2J_{HH} = 20.2$ Hz, 4H, NCH_2), 4.03 (sept, 2H, $CHMe_2$), 3.71 (sept, 2H, $CHMe_2$), 2.10 (s, 2H, CH_2Ph), 1.64 (s, 2H, CH_2Ph), 1.51 (d, 6H, $CHMe_2$), 1.40 (d, 6H, $CHMe_2$), 1.38 (d, 6H, $CHMe_2$),1.08 (d, 6H, $CHMe_2$). Partial $^{13}C\{^1H\}$ NMR (toluene-d_8, 23 °C): δ 68.87 (NCH_2). Anal. Calcd for $C_{45}H_{55}N_3Zr{\cdot}{}^1/_4CH_2Cl_2$: C, 72.43; H, 7.45; N, 5.60. Found: C, 72.65; H, 7.62; N, 5.59.

(BDEP)Zr(CH_2Ph)$_2$ (2b). The preparation of compound **2b** is identical to that for complex **2a**. Compound **1b** (0.300 g, 0.534 mmol) and $PhCH_2MgBr$ (1.42 mL, 1.13M, 1.60 mmol) gave a yellow oily solid **2b**. The crude yield of **2b** is >90%; however, the compound is exceedingly soluble, which precludes its isolation. ^1H NMR: δ 6.5−7.4 (m, 15H, py, Ar and Ph), 6.35 (d, 4H, Ph), 4.55 (s, 4H, NCH_2), 2.89 (q, 8H, CH_2Me), 1.61 (s, 4H, $ZrCH_2Ph$), 1.26 (t, 12H, CH_2Me). $^{13}C\{^1H\}$ NMR: δ 162.74, 149.81, 141.59, 137.76, 129.59, 126.83, 126.18, 125.79, 122.01, 117.17, 65.69, 60.95, 24.66, 15.15.

(BDMP)Zr(CH_2Ph)$_2$ (2c). The preparation of compound **2c** is identical to that for complex **2a**. Compound **1c** (0.075 g, 0.148 mmol) and $PhCH_2MgBr$ (0.29 mL, 1.13 M, 0.33 mmol) gave yellow crystalline **2c** (0.089 g, 0.144 mmol, 97%). ^1H NMR: δ 7.08 (m, 4H, Ar), 6.98 (m, 2H, Ar), 6.87 (m, 4H, Ph), 6.84 (t, 1H, py), 6.67 (m, 2H, Ph), 6.36 (m, 4H, Ph), 6.34 (d, 2H, py), 4.42 (s, 4H, NCH_2), 2.37 (s, 12H, Me), 1.66 (s, 4H, $ZrCH_2Ph$). $^{13}C\{^1H\}$ NMR: δ 162.85, 150.76, 137.59, 136.25, 129.64, 126.69, 125.40, 121.94, 117.13, 64.12, 60.62, 60.57, 19.62. Anal. Calcd for $C_{37}H_{39}N_3Zr$: C, 72.03; H, 6.37; N, 6.81. Found: C, 71.89; H, 6.65; N, 6.82.

(BDPP)Zr(CH_2SiMe_3)$_2$ (3a). To a diethyl ether (25 mL) suspension of compound **1a** (0.100 g, 0.178 mmol) was added 2.2 equiv of Me_3SiCH_2Li (0.037 g, 0.393 mmol) at −20 °C. The suspension was stirred for 12 h. The solvent was removed in vacuo. The resulting solid was extracted with toluene (3 × 10 mL) and filtered through Celite to give a bright-yellow solution. The solvent was removed in vacuo, and the solid was dissolved in a minimum amount of hexanes and cooled to −30 °C for 12 h. Yellow crystalline **3a** was isolated by filtration and dried under vacuum (0.109 g, 0.156 mmol, 88%). ^1H NMR: δ 7.24 (b, 6H, Ar), 6.86 (t, 1H, py), 6.40 (d, 2H, py), 5.0 (br, 4H, NCH_2), 1.52 and 1.28 (br, 12H each, $CHMe_2$), −0.13 (br, 18H, $SiMe_3$). ^1H NMR (toluene-d_8, 70 °C): δ 7.20−7.25 (m, 6H, Ar), 6.98 (t, 1H, py), 6.54 (d, 2H, py), 4.96 (s, 4H, NCH_2), 3.91 (br, 4H, $CHMe_2$), 1.49 and 1.26 (d, 12H each, $CHMe_2$), 0.65 (s, 4H, $ZrCH_2Si$), −0.18 (s, 18H, $SiMe_3$). $^{13}C\{^1H\}$ NMR: δ 146.13, 127.38, 124.68, 117.32, 67.78, 28.18, 27.46, 24.25, 2.82. Anal. Calcd for $C_{39}H_{63}N_3Si_2Zr$: C, 64.94; H, 8.80; N, 5.83. Found: C, 64.94; H, 8.77; N, 5.95.

(BDEP)Zr(CH_2SiMe_3)$_2$ (3b). The preparation of compound **3b** is identical to that for complex **3a**. Compound **1b** (0.100 g, 0.178 mmol) and Me_3SiCH_2Li (0.037 g, 0.393 mmol) gave yellow crystalline **3b** (0.109 g, 0.156 mmol, 88%). ^1H NMR: δ 7.15−7.25 (m, 6H, Ar), 6.88 (t, 1H, py), 6.43 (d, 2H, py), 4.77 (s, 4H, NCH_2), 3.05 (m, 8H, CH_2Me), 1.33 (t, 12H, CH_2Me), 0.54 (s, 4H, $ZrCH_2Si$), −0.13 (s, 18H, $SiMe_3$). $^{13}C\{^1H\}$ NMR: δ 163.33, 149.42, 141.39, 138.43, 126.75, 125.84, 117.58, 66.60, 58.79, 24.57, 15.75, 2.99.

(BDMP)Zr(CH_2SiMe_3)$_2$ (3c). The preparation of compound **3c** is identical to that for complex **3a**. Compound **1c** (0.100 g, 0.198 mmol) and Me_3SiCH_2Li (0.041 g, 0.435 mmol) gave yellow crystalline **3c** (0.103 g, 0.169 mmol, 85%). ^1H NMR: δ 7.15 (d, 4H, Ar), 7.03 (m, 2H, Ar), 6.91 (t, 1H, py), 6.47 (d, 2H, py), 4.64 (s, 4H, NCH_2), 2.48 (s, 12H, Me), 0.61 (s, 4H, $ZrCH_2Si$), −0.13 (s, 18H, $SiMe_3$). $^{13}C\{^1H\}$ NMR: δ 163.49, 150.53, 138.32, 135.85, 129.34, 125.39, 117.53, 64.94, 58.43, 19.54, 3.00.

(BDPP)ZrCpCl (4a). To a diethyl ether (25 mL) suspension of compound **1a** (0.100 g, 0.162 mmol) was added 1.3 equiv of NaCp·DME (0.038, 0.213 mmol) at −20 °C. The suspension was stirred for 12 h. The solvent was removed in vacuo. The resulting solid was extracted with toluene (3 × 10 mL) and filtered through Celite to give a colorless solution. The solvent was removed in vacuo, and the solid was dissolved in a minimum amount of diethyl ether and cooled to −30 °C for 12 h. White crystalline **4a** was isolated by filtration and dried under vacuum (0.093 g, 0.144 mmol, 89%). ^1H NMR: δ 7.10−7.25 (m, 6H, Ar), 6.75 (t, 1H, py), 6.33 (d, 2H, py), 6.04 (s, 5H, Cp), 4.78 (AB quartet, $^2J_{HH} = 20.2$ Hz, 4H, NCH_2), 3.90 and 3.23 (sept, 2H each, $CHMe_2$), 1.53, 1.35, 1.32 and 0.92 (d, 6H each, $CHMe_2$). $^{13}C\{^1H\}$ NMR: δ 161.50, 157.38, 145.12, 142.52, 137.61, 125.24, 124.77, 123.81, 116.56, 116.26 (C_5H_5), 68.30, 28.70, 27.82, 27.67, 26.68, 24.04, 23.54. Anal. Calcd for $C_{36}H_{46}ClN_3Zr$: C, 66.78; H, 7.16; N, 6.49. Found: C, 66.98; H, 7.24; N, 6.35.

(BDEP)ZrCpCl (4b). The preparation of compound **4b** is identical to that for complex **4a**. Compound **1b** (0.100 g, 0.178 mmol) and NaCp·DME (0.040 g, 0.224 mmol) gave white crystalline **4b** (0.091 g, 0.154 mmol, 87%). ^1H NMR: δ 7.00−7.25 (m, 6H, Ar), 6.79 (t, 1H, py), 6.37 (d, 2H, py), 5.89 (s, 5H, Cp), 4.51 (AB quartet, $^2J_{HH} = 20.6$ Hz, 4H, NCH_2), 3.05 and 2.49 (m, 4H each, CH_2Me), 1.39 and 1.08 (t, 6H each, CH_2Me). $^{13}C\{^1H\}$ NMR: δ 161.48, 159.444, 140.21, 137.62, 137.50, 126.88, 126.11, 124.74, 116.85, 116.38 (C_5H_5), 67.14, 24.59, 24.05, 15.88, 14.84.

(BDMP)ZrCpCl (4c). The preparation of compound **4c** is identical to that for complex **4a**. Compound **1c** (0.100 g, 0.98 mmol) and NaCp·DME (0.045 g, 0.253 mmol) gave white crystalline **4c** (0.093 g, 0.174 mmol, 88%). ^1H NMR: δ 6.98−7.15 (m, 6H, Ar), 6.83 (t, 1H, py), 6.38 (d, 2H, py), 5.88 (s, 5H, Cp), 4.45 (AB quartet, $^2J_{HH} = 20.9$ Hz, 4H, NCH_2), 2.55 and 1.98 (s, 6H each, Me). $^{13}C\{^1H\}$ NMR: δ 161.75, 159.36, 137.38, 134.89, 132.19, 129.33, 128.76, 124.35, 116.90, 116.43 (C_5H_5), 65.39, 19.00, 18.75.

(BDPP)Zr(C_4H_6) (5a). To a diethyl ether (25 mL) suspension of compound **1a** (0.100 g, 0.162 mmol) was added 1.3 equiv of Mg(C_4H_6)·2THF (0.044 g, 0.198 mmol) at −20 °C. The suspension was stirred for 12 h. The solvent was removed in vacuo. The resulting solid was extracted with toluene (3 × 10 mL) and filtered through Celite to give a bright-yellow solution. The solvent was removed in vacuo, and the solid was dissolved in a minimum amount of diethyl ether and cooled to −30 °C for 12 h. Yellow crystalline **5a** was isolated by filtration and dried under vacuum (0.093 g, 0.155 mmol, 96%). ^{1}H NMR: δ 7.0−7.15 (m, 2H, Ar), 6.98 (t, 1H, py), 6.57 (d, 1H, py), 6.49 (d, 1H, py), 5.07 (s, 2H, NC*H*$_2$), 5.03 (m, 2H, ZrCH$_2$C*H*, H$_m$), 4.72 (s, 2H, NC*H*$_2$), 4.00 (sept, 2H, C*H*Me$_2$), 3.56 (m, 2H, ZrC*H*$_2$CH, H$_a$), 3.08 (sept, 2H, C*H*Me$_2$), 2.38 (sept, 6H each, C*H*Me$_2$), 1.33, 1.23, 1.16 and 1.01 (d, 6H each, CH*Me*$_2$), 0.28 (m, 2H, ZrC*H*$_2$CH, H$_s$). ^{13}C{^{1}H} NMR: δ 165.52, 164.58, 150.75, 149.92, 146.10, 143.78, 137.69, 125.21, 124.89, 124.31, 123.46, 119.35, 117.65, 117.20, 67.99, 67.73, 58.20, 28.48, 27.98, 27.78, 27.48, 24.33, 23.27. Satisfactory elemental analysis was not obtained due to incomplete combustion. Different combustion additives were used without success.

(BDEP)Zr(C_4H_6) (5b). The preparation of compound **5b** is identical to that for complex **5a**. Compound **1b** (0.100 g, 0.178 mmol) and $C_4H_6Mg{\cdot}2THF$ (0.044 g, 0.198 mmol) gave yellow crystalline **5b** (0.083 g, 0.152 mmol, 85%). ^{1}H NMR: δ 7.0−7.15 (m, 2H, Ar), 6.97 (t, 1H, py), 6.59 (d, 1H, py), 6.51 (d, 1H, py), 4.92 (m, 2H, ZrCH$_2$C*H*, H$_m$), 4.83 (s, 2H, NC*H*$_2$), 4.47 (s, 2H, NC*H*$_2$), 3.41 (m, 2H, ZrC*H*$_2$CH, H$_a$), 2.97 (m, 4H, C*H*$_2$Me), 2.38 (m, 4H, C*H*$_2$Me), 1.24 and 1.11 (t, 6H each, CH$_2$*Me*), 0.16 (m, 2H, ZrC*H*$_2$CH, H$_s$). ^{13}C{^{1}H} NMR: δ 165.64, 164.75, 140.95, 138.82, 137.58, 129.35, 126.39, 125.46, 124.72, 124.36, 119.64, 117.79, 117.34, 67.06, 66.57, 58.50, 23.66, 23.36, 15.73, 15.29.

(BDMP)Zr(C_4H_6) (5c). The preparation of compound **5c** is identical to that for complex **5a**. Compound **1a** (0.100 g, 0.198 mmol) and $C_4H_6Mg{\cdot}2THF$ (0.049 g, 0.249 mmol) gave yellow crystalline **5c** (0.093 g, 0.190 mmol, 96%). ^{1}H NMR: δ 6.8−7.15 (m, 2H, Ar), 6.91 (t, 1H, py), 6.62 (d, 1H, py), 6.52 (d, 1H, py), 4.98 (m, 2H, ZrCH$_2$C*H*, H$_m$), 4.47 (s, 2H, NC*H*$_2$), 4.36 (s, 2H, NC*H*$_2$), 3.42 (m, 2H, ZrC*H*$_2$CH, H$_s$), 2.39 and 1.95 (s, 6H each, Me), 0.17 (m, 2H, ZrC*H*$_2$CH, H$_a$). ^{13}C{^{1}H} NMR: δ 165.69, 164.80, 153.40, 151.57, 137.47, 135.49, 133.38, 129.23, 128.24, 124.28, 123.94, 119.59, 117.76, 117.31, 65.31, 64.73, 58.54, 18.36. Anal. Calcd for $C_{27}H_{31}N_3Zr$: C, 66.35; H, 8.60; N, 6.39. Found: C, 66.71; H, 8.44; N, 6.42.

(BDPP)Zr($C_6H_6Pr_2$) (6a). A benzene (10 mL) solution of compound **5a** (0.100 g, 0.17 mmol) and an excess of 4-octyne (0.050 g, 0.45 mmol) were heated in a glass pressure vessel to 90 °C for 12 h. The solution changed from yellow to orange. The solvent was removed in vacuo, and the resulting solid was recrystallize from a toluene/pentane mixture (10/50) at −30 °C. White crystalline **6a** was isolated by filtration and dried under vacuum (0.098 g, 0.014 mmol, 84%). ^{1}H NMR: δ 7.25−7.10 (m, 6H, Ar), 7.00 (t, 1H, py), 6.55 (br d, 2H, py), 5.35 (m, 1H, ZrCH$_2$C*H*═CHCH$_2$), 5.01 (AB quartet, $^2J_{HH} = 20.6$ Hz, 2H, NC*H*$_2$), 4.94 (AB quartet, $^2J_{HH} = 20.6$ Hz, 2H, NC*H*$_2$), 4.42 (m, 1H, ZrCH$_2$CH═C*H*CH$_2$), 4.05 (sept, 1H, C*H*Me$_2$), 3.66 (sept, 1H, C*H*Me$_2$), 3.61 (sept, 1H, C*H*Me$_2$), 3.55 (sept, 1H, C*H*Me$_2$), 3.12 (d, 2H, ZrCH$_2$CH═CHC*H*$_2$), 2.45 (dd, 1H, ZrC*H*$_2$-CH═CHCH$_2$), 2.25 (m, 2H, C*H*$_2$CH$_2$CH$_3$), 2.1 (m, 2H, C*H*$_2$CH$_2$-CH$_3$), 1.60 (m, 1H, ZrC*H*$_2$CH═CHCH$_2$), 1.60 (m, 2H, CH$_2$C*H*$_2$-CH$_3$), 1.50−1.10 (8 doublets, 3H each, CH*Me*$_2$), 1.50−1.10 (buried, 2H, CH$_2$C*H*$_2$CH$_3$), 0.88 (t, 3H, CH$_2$CH$_2$C*H*$_3$), 0.60 (t, 3H, CH$_2$CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR: δ 187.97, 168.97, 163.87, 163.51, 148.38, 147.04, 146.43, 145.84, 145.72, 138.82, 137.91, 129.29, 126.28, 125.45, 124.62, 124.52, 124.38, 123.27, 119.23, 117.38, 117.31, 68.06, 67.66, 67.27, 42.23, 38.91, 34.83, 28.52, 28.44, 28.27, 28.20, 28.07, 27.87, 27.64, 27.35, 24.92, 24.27, 24.07, 23.96, 23.45, 23.25, 15.52, 15.40.

(BDPP)Zr($C_6H_7SiMe_3$) (7a). The preparation of compound **7a** is identical to that of complex **6a**. Compound **5a** (0.050 g, 0.09 mmol) and trimethylsilylacetylene (0.020 g, 0.20 mmol) gave white crystalline **7a** (0.046 g, 0.07 mmol, 79%). ^{1}H NMR: δ 8.02 (t, $^3J_{HH} = 2.7$ Hz 1H, (SiMe$_3$)C═C*H*), 7.10−7.25 (m, 6H, Ar), 6.98 (d, 1H, py), 6.58 (d, 1H, py), 6.55 (d, 1H, py), 5.38 (m, 1H, ZrCH$_2$C*H*═CHCH$_2$), 5.03 (AB quartet, $^2J_{HH} = 20.6$ Hz, 2H, NC*H*$_2$), 4.99 (AB quartet, $^2J_{HH} = 20.3$ Hz, 2H, NC*H*$_2$), 4.78 (m, 1H, ZrCH$_2$CH═C*H*CH$_2$), 3.98 (sept, 1H, C*H*Me$_2$), 3.59 (sept, 1H, C*H*Me$_2$), 3.48 (m, 2H, C*H*Me$_2$), 3.02 (m, 2H, ZrCH$_2$-CH═CHC*H*$_2$), 2.43 (dd, 1H, ZrC*H*$_2$CH═CHCH$_2$), 1.70 (dd, 1H, ZrC*H*$_2$CH═CHCH$_2$), 1.20−1.40 (6 doublets, 18H, CH*Me*$_2$), 1.09 (d, 3H, CH*Me*$_2$), 1.07 (d, 3H, CH*Me*$_2$), −0.03 (s, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR: δ 193.83, 172.22, 164.53, 164.04, 147.97, 147.35, 147.06, 146.67, 145.75, 145.55, 141.35, 138.22, 126.52, 125.73, 124.72, 124.58, 124.48, 123.94, 123.34, 117.61, 68.11, 67.52, 67.27, 42.84, 28.74, 28.61, 28.31, 28.25, 28.07, 27.22, 27.09, 23.88, 23.80, 23.21, 22.73, 1.42.

(BDPP)Zr(C_6H_9Bu) (8a). The preparation of compound **8a** is identical to that of complex **6a**. Compound **5a** (0.250 g, 0.43 mmol) and 1-hexene (0.100 g, 1.19 mmol) gave white crystalline **8a** (0.213 g, 0.31 mmol, 73%). ^{1}H NMR: δ 7.05−7.20 (m, 6H, Ar), 6.87 (t, 1H, py), 6.45 (d, 1H, py), 6.44 (d, 1H, py), 5.41 (m, 1H, ZrCH$_2$C*H*═CHCH$_2$), 4.80 (AB quartet, $^2J_{HH} = 19.8$ Hz, 2H, NC*H*$_2$), 4.69 (AB quartet, $^2J_{HH} = 19.8$ Hz, 2H, NC*H*$_2$), 3.80 (m, 3H, C*H*Me$_2$), 3.80 (m, 1H, ZrCH$_2$CH═C*H*CH$_2$), 3.38 (sept, 1H, C*H*Me$_2$), 3.17 (m, 1H, ZrCH$_2$C*H*Bu), 2.93 (broad d, 1H, ZrCH$_2$CH═CHC*H*$_2$), 2.51 (dd, 1H, ZrC*H*$_2$CH═CHCH$_2$) 2.17 (m, 1H, ZrCH$_2$CH═CHC*H*$_2$), 1.72 (m, 1H, ZrC*H*$_2$CHBu), 1.46 (m, 1H, ZrC*H*$_2$CH═CHCH$_2$), 1.28−1.43 (5 doublets, 15H, CH*Me*$_2$), 1.28−1.43 (buried, 6H, C*H*$_2$C*H*$_2$C*H*$_2$), 1.22 (d, 3H, CH*Me*$_2$), 1.08 (d, 3H, CH*Me*$_2$), 1.05 (d, 3H, CH*Me*$_2$), 0.92 (t, 3H, CH$_2$C*H*$_3$), 0.12 (t, 1H, ZrC*H*$_2$CHBu). ^{13}C{^{1}H} NMR: δ 163.03, 162.82, 149.55, 148.22, 146.27, 145.90, 145.51, 137.76, 135.93, 125.79, 125.08, 124.45, 124.23, 123.86, 123.63, 120.48, 117.18, 67.19, 67.01, 66.51, 56.95, 54.10, 42.49 (Zr*C*HBuCH$_2$), 41.37, 31.11, 29.50, 29.39, 28.03, 27.67, 27.54, 27.46, 26.96, 26.53, 24.80, 24.47, 24.04, 23.47, 14.51. Anal. Calcd for $C_{41}H_{59}N_3Zr$: C, 71.87; H, 8.68; N, 6.13. Found: C, 72.00; H, 8.80; N, 6.12.

X-ray Crystallographic Analysis. A suitable crystal of **5a** was grown from a saturated ether solution at −30 °C. Crystal data may be found in Table 1. Data were collected on a Siemens Smart system CCD diffractometer. The data were collected in the range of $\theta = 1.47{-}21.49°$ ($-20 = h = 21$, $-21 = k = 15$, $-32 = l = 35$). Unit-cell parameters were calculated from reflections obtained from 60 data frames collected at different sections of the Ewald sphere. No absorption corrections were necessary ($\mu = 3.36$ cm^{-1}). The molecule is located on a 2-fold axis with the diene disordered with a 50/50 site occupation. The diene was refined as a flat, rigid body with chemically equivalent bonds restrained to be equal. A cocrystallized, partially occupied ether solvent molecule was located severely disordered at a 4-fold rotoinversion axis with a net occupancy of 0.35. The Flack parameter refined to 0.0(2), indicating that the true hand of the data was correctly determined. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. The structure was solved by direct methods, completed by subsequent Fourier syntheses, and refined with full-matrix least-squares methods. All scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library.[26] In the final difference Fourier synthesis the electron density fluctuates in the range 0.551−−0.489 e Å^{-3}.

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Supporting Information Available: The final crystallographic atomic coordinates, equivalent isotropic thermal parameters, hydrogen atom parameters, anisotropic thermal parameters, complete tables of bond lengths and angles, and ORTEPs for **2a** and **5a** (19 pages). Ordering information can be found on any current masthead page.

OM980146V

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[26] *SHELXTL Version 5*; Siemans Analytical X-ray Instruments Inc.: Madison WI, 1994.