5586 *Organometallics* **1996,** *15,* 5586−5590

Conformationally Rigid Diamide Complexes of Zirconium: Electron Deficient Analogues of Cp_2Zr

Frédéric Guérin,† David H. McConville,*,† and Jagadese J. Vittal

Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7

Received May 31, 1996⊗

Zirconium complexes bearing a pyridine−diamide ligand $[2,6\text{-}(RNCH_2)_2NC_5H_3]^{2-}$ (R = 2,6-diisopropylphenyl, 2,6-diethylphenyl (BDEP), 2,6-dimethylphenyl) have been synthesized. The mixed amide complexes $[2,6\text{-}(RNCH_2)_2NC_5H_3]Zr(NMe_2)_2$ are prepared in high yield from $[2,6\text{-}(RHNCH_2)_2NC_5H_3]$ and $Zr(NMe_2)_4$. The mixed amides react with excess $ClSiMe_3$ to afford the dichlorides $[2,6\text{-}(RNCH_2)_2NC_5H_3]ZrCl_2$ in nearly quantitative yield. Dimethyl complexes are prepared from $[2,6\text{-}(RNCH_2)_2NC_5H_3]ZrCl_2$ and 2 equiv of MeMgBr. A single-crystal X-ray diffraction study of $(BDEP)ZrMe_2$ revealed a distorted trigonal bipyramid structure with the amides occupying the axial positions. The frontier orbitals of a model of the fragment (BDEP)Zr are very similar the those of Cp_2Zr, suggesting that complexes bearing the pyridine−diamide ligand may behave as sources of Cp_2Zr.

Introduction

The chemistry of group 4 olefin polymerization catalyst precursors such as Cp_2MX_2,[1,2] $CpMX_3$,[3−11] and linked Cp−amide derivatives,[12−18] have been studied extensively. Much of the work in this area has been concerned with the way in which the catalytic activity, comonomer incorporation, and stereoregularity can be altered with changes to the Cp ligand(s). There is, however, a growing interest in new non-Cp ligand environments as possible alternatives for olefin polymerization catalysts.[19−26] Previously we have investigated the α-olefin polymerization chemistry of chelating diamide ancillaries that incorporate bulky aryl substituents at nitrogen.[27] Complexes of the type, $[RN(CH_2)_3NR]TiMe_2$ (R = 2,6-$^iPr_2C_6H_3$, 2,6-$Me_2C_6H_3$), when activated with methyl alumoxane, are highly active catalysts for the polymerization of 1-hexene. In contrast, the analogous zirconium complexes show little or no activity for the polymerization of α-olefins under the same conditions.[28] Strong binding of the cocatalyst to the electrophilic, low-coordinate zirconium metal center may preclude formation of a cationic alkyl complex, as has been observed for other chelating diamides of Ti and Zr.[26]

We have since turned our attention to a tridentate diamide ligand system which incorporates a neutral pyridine donor between the amides.[29] This dinegative ligand has been shown to stabilize five-coordinate complexes of tantalum[30] and titanium[31] and appears to coordinate exclusively in a meridional fashion. In this paper, we describe the synthesis and structure of tridentate diamide complexes of zirconium. The similarities between this new ligand system and the typical coordination geometry of metallocenes[32] are presented.

Results

The reaction of 2 equiv of LiNHR (R = 2,6-diisopropylphenyl (BDPP), 2,6-diethylphenyl (BDEP), 2,6-dim-

---

† Current address: Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Z1.

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1996.

(1) Mohring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1.

(2) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

(3) Bochmann, M.; Karger, G.; Jaggar, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1038.

(4) Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455.

(5) Pellecchia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 4473.

(6) Gómez, R.; Green, M. L. H.; Haggitt, J. L. *J. Chem. Soc., Chem. Commun.* **1993**, 1415.

(7) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1994**, *13*, 4142.

(8) Quan, R. W.; Bazan, G. C.; Kiely, A. F.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4489.

(9) Quyoum, R.; Wang, Q.; Tudoret, M.-J.; Baird, M. C. *J. Am. Chem. Soc.* **1994**, *116*, 6435.

(10) Bazan, G. C.; Rodriguez, G.; Cleary, B. P. *J. Am. Chem. Soc.* **1994**, *116*, 2177.

(11) Fryzuk, M. D.; Mao, S. S. H.; Duval, P. D.; Rettig, S. J. *Polyhedron* **1995**, *14*, 11.

(12) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867.

(13) Okuda, J. *Chem. Ber.* **1990**, *123*, 1649.

(14) Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. Y. (Dow) Eur. Pat. Appl. EP-416-815-A2, March 13, 1991.

(15) Canich, J. A. (Exxon) Eur. Pat. Appl. EP-420-436-A1, April 4, 1991.

(16) Hughes, A. K.; Meetsma, A.; Teuben, J. A. *Organometallics* **1993**, *12*, 1936.

(17) Devore, D. D.; Timmers, F. J.; Hasha, D. L.; Rosen, R. K.; Marks, T. J.; Deck, P. A.; Stern, C. L. *Organometallics* **1995**, *14*, 3132.

(18) Mu, Y.; Piers, W. E.; MacGillivray, L. R.; Zaworotko, M. J. *Polyhedron* **1995**, *14*, 1.

(19) Miyatake, T.; Mizunuma, K.; Seki, Y.; Kakugo, M. *Makromol. Chem., Rapid Commun.* **1989**, *10*, 349.

(20) Canich, J. A.; Turner, H. W. (Exxon) W. PCT Int. Appl. WO 92/12162, December 26, 1991.

(21) Uhrhammer, R.; Black, D. G.; Gardner, T. G.; Olsen, J. D.; Jordan, R. F. *J. Am. Chem. Soc.* **1993**, *115*, 8493.

(22) Brand, H.; Capriotti, J. A.; Arnold, J. *Organometallics* **1994**, *13*, 4469.

(23) van der Linden, A.; Schaverien, C. J.; Meijboom, N.; Ganter, C.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008.

(24) Cozzi, P. G.; Gallo, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1995**, *14*, 4994.

(25) Herskovics-Korine, D.; Eisen, M. S. *J. Organomet. Chem.* **1995**, *503*, 307.

(26) Warren, T. H.; Schrock, R. R.; Davis, W. M. *Organometallics* **1996**, *15*, 562.

(27) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Macromolecules* **1996**, *29*, 5241.

(28) Scollard, J. D.; McConville, D. H. Unpublished results.

(29) Cai, S.; Schrock, R. R. *Inorg. Chem.* **1991**, *30*, 4105.

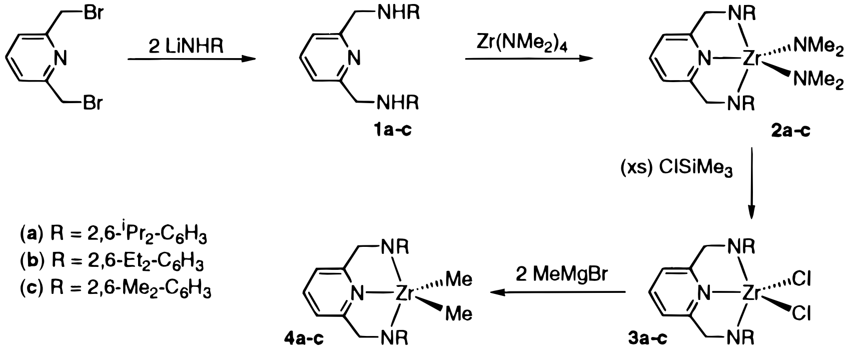
(30) Guérin, F.; McConville, D. H.; Vittal, J. J. *Organometallics* **1995**, *14*, 3154.

(31) Guérin, F.; McConville, D. H.; Payne, N. C. *Organometallics*, in press.

(32) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

S0276-7333(96)00427-X CCC: $12.00 © 1996 American Chemical Society

Scheme 1



ethylphenyl (BDMP)) with 2,6-bis(bromomethyl)pyridine[33] yields the diamine ligands (BDPP)H_2 (**1a**), (BDEP)H_2 (**1b**), and (BDMP)H_2 (**1c**), as shown in Scheme 1. (BDPP)H_2 is a white crystalline solid, while (BDEP)H_2 and (BDMP)H_2 are viscous oils. All three diamines can be prepared in 50−80% yield on a scale of 5−10 g. The aminolysis reaction between the diamines **1a**−**c** and $Zr(NMe_2)_4$[34] provides 2 equiv of $HNMe_2$ and the yellow crystalline mixed amide complexes (BDPP)$Zr(NMe_2)_2$ (**2a**), (BDEP)$Zr(NMe_2)_2$ (**2b**), and (BDMP)$Zr(NMe_2)_2$ (**2c**) in greater than 90% yield (Scheme 1).

Room temperature proton NMR spectra of complexes **2a**−**c** exhibit a single sharp resonance for the methylene protons (CH_2N) of the ligand consistent with a meridional coordination mode and local C_{2v} symmetry of the compounds. The isopropylmethyl groups of complex **2a** and the ethylmethylene protons of compound **2b** are diastereotopic, which we interpret as a consequence of restricted rotation[30] about the $N-C_{ipso}$ bond (no evidence of $N-C_{ipso}$ bond rotation is observed for compound **2a** to 80 °C). We have no direct spectroscopic means of determining whether the same restricted rotation exists in the 2,6-dimethylphenyl substituted derivative **2c**; however, modeling studies[35] and other structurally characterized BDMP complexes[31] indicate that the barrier to rotation is high.

Chloride derivatives were desired as precursors to alkyl derivatives. We have previously shown that $[Me_2NH_2]Cl$ reacts preferentially with the dimethylamido ligands in the mixed amide complex $[RN(CH_2)_3NR]Zr(NMe_2)_2$ (R = 2,6-$^iPr_2C_6H_3$).[36] Presumably, the substituents in the 2,6-position kinetically protect the ligand amides from proton attack. In contrast, we observe protonolysis of the BDPP ligand in complex **2a**, as has been noted for other chelating amide derivatives of zirconium.[18] However, a remarkably selective reaction between compounds **2a**−**c** and excess $ClSiMe_3$ yields the white crystalline dichloride derivatives in nearly quantitative yield (Scheme 1). The chloride complexes **3a**−**c** are very soluble in THF, soluble in aromatic solvents, and insoluble in aliphatic solvents. Again, spectral data for complexes **3a**−**c** are consistent with meridional coordination of the pyridine−diamide ligand and restricted rotation about the $N-C_{ipso}$ bond.

Table 1. Summary of Crystallographic Data, Collection Parameters, and Refinement Parameters for Compound 4b[a]

empirical formula	$C_{29}H_{39}N_3Zr$
formula weight	520.85
crystal color, habit	light orange, triclinic
crystal dimensions (mm)	0.54 × 0.26 × 0.23
crystal system	monoclinic
reflections used for unit cell determination (2θ range (deg))	26 (24.12−25.02)
a (Å)	12.355(2)
b (Å)	15.761(2)
c (Å)	15.701(3)
β (deg)	111.71(1)
V (Å^3)	2840.5(8)
space group	$P2_1/c$
Z	4
ρ (calc) (g/mol)	1.218
collection temp (°C)	25
F_{000}	1096
Mo Kα	graphite (monochromated)
scan mode	ω (variable 2−30 deg/min)
total no. of unique reflections	4950
no. of observations with $F_o \geq 4\sigma(F_o)$	3011
no. of variable parameters	244
$R1$	0.0592
w$R2$	0.1335
goodness of fit (GooF)	1.038

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; w$R2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$; GooF = $[\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (where n is the number of reflections and p is the number of parameters refined).

The readily available dichlorides are excellent precursors for the preparation of a number of alkyl derivatives.[37] In particular, reaction of the dichlorides **3a**−**c** with 2 equiv of MeMgBr affords the white crystalline dimethyl complexes in 80−90% yield (Scheme 1). The C_{2v} symmetry of complexes **4a**−**c** is evidenced by a single sharp resonance (^1H NMR) for the ligand methylene protons (NCH_2). The ^1H and $^{13}C\{^1H\}$ NMR spectra of complex **4a** display a $Zr-CH_3$ resonance at 0.45 ppm and a $Zr-CH_3$ signal at 44.71 ppm. These data are comparable to the closely related complex $[RN(CH_2)_3NR]ZrMe_2$ (R = 2,6-$^iPr_2C_6H_3$; $Zr-CH_3$ δ = 0.42 ppm; $Zr-CH_3$ δ = 39.9 ppm)[36] and other complexes.[26,38−41]

The solid state structure of **4b** was determined by X-ray crystallography (Table 1). The molecular structure of complex **4b** can be found in Figure 1, and

---

(33) Haeg, M. E.; Whitlock, B. J.; Whitlock, H. W., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 692.

(34) Bradley, D. C.; Thomas, I. M. *Proc. Chem. Soc., London* **1959**, 225.

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

(36) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1995**, *14*, 5478.

(37) Guérin, F.; McConville, D. H. Unpublished results.

(38) Anderson, R. A. *Inorg. Chem.* **1979**, *18*, 2928.

(39) Anderson, R. A. *Inorg. Chem.* **1979**, *18*, 1724.

(40) Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718.

(41) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731.

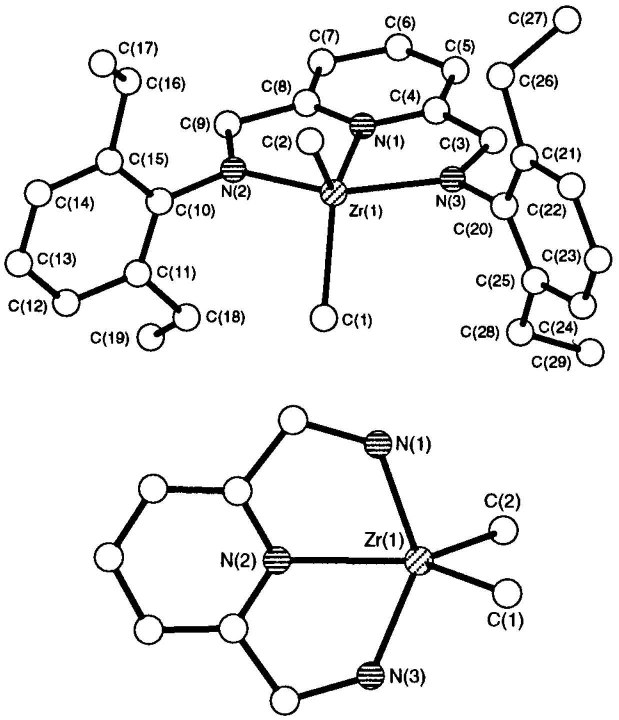


Figure 1. Chem 3D drawing of the molecular structure of **4b** (top). Chem 3D drawing of the core of **4b** (bottom).

relevant bond distances and angles can be found in Table 2. The structure is best described as a distorted trigonal bipyramid with the amide nitrogens (N(2) and N(3)) occupying the axial positions (Figure 1). The zirconium atom lies 2.4° out of the plane of the three nitrogens. The Zr−amide distances (2.104(5) and 2.101(4) Å) are comparable to other zirconium−amido complexes.[16,36,42−47] Each amide is sp^2-hybridized as evidenced by the sum of the angles about each nitrogen (N(2) = 359.9° and N(3) = 359.9°). The aryl rings lie perpendicular to the plane of the ligand with dihedral angles of 89.8° and 89.6°. The rigid coordination of the ligand and enforced location of the aryl ethyl groups necessarily protects the metal above and below the N$_3$ plane.

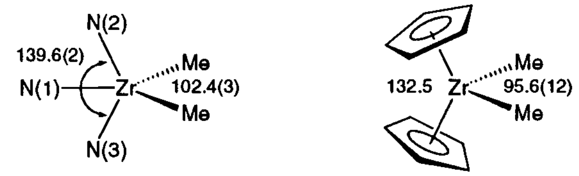


Figure 2.

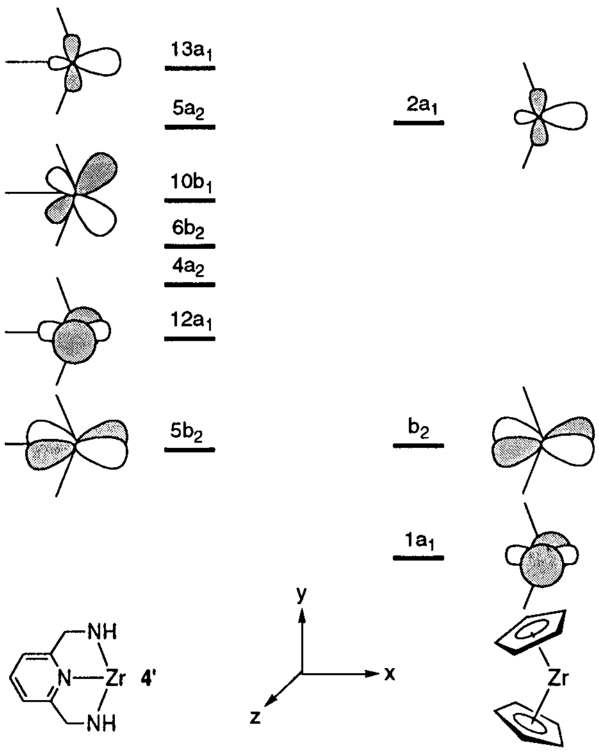


Figure 3. Frontier orbitals of **4′** and Cp$_2$Zr.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 4b

Bond Distances			
Zr(1)−C(1)	2.248(7)	Zr(1)−C(2)	2.243(6)
Zr(1)−N(1)	2.325(4)	Zr(1)−N(2)	2.101(4)
Zr(1)−N(3)	2.104(5)		
Bond Angles			
N(2)−Zr(1)−N(3)	139.6(2)	C(1)−Zr(1)−C(2)	102.4(3)
N(2)−Zr(1)−N(1)	70.0(2)	N(3)−Zr(1)−N(1)	69.7(2)
Zr(1)−N(3)−C(3)	126.4(3)	Zr(1)−N(3)−C(20)	121.5(3)
C(3)−N(3)−C(20)	112.0(4)	Zr(1)−N(2)−C(9)	126.2(3)
Zr(1)−N(2)−C(10)	122.7(4)	C(9)−N(2)−C(10)	111.0(4)

Calculations

The coordination sphere of compound **4b** closely resembles that of Cp$_2$ZrMe$_2$[48] (Figure 2). The amide−Zr−amide and Me−Zr−Me angles in **4b** are about 7° larger than the Cent−Zr−Cent (Cent = Cp centroid) and Me−Zr−Me angles in Cp$_2$ZrMe$_2$, as expected for a distorted trigonal bipyramid versus a distorted tetrahedron. In addition, the associated bond lengths (amide−Zr, Cent−Zr, and Me−Zr) of **4b** and Cp$_2$ZrMe$_2$ are comparable, and hence the pyridine−diamide ligand system can be viewed as a Cp$_2$ equivalent.

Extended Hückel MO calculations[35] were performed on an idealized (C_{2v} symmetry) model of compound **4b** (**4′**) and compared to the frontier orbitals of Cp$_2$Zr[32] (Figure 3). The b$_2$ orbital of Cp$_2$Zr and the 5b$_2$ orbital of **4′** (d$_{xz}$ orbital) have very similar energies as a consequence of the limited π-donation from the pyridine to the zirconium. In contrast, the 12a$_1$ orbital (d$_{z^2}$) of **4′** is raised in energy relative to the 1a$_1$ orbital of Cp$_2$Zr due to the significant σ-donation from the pyridine. This also raises the energy of the 13a$_1$ orbital (d$_{x^2-y^2}$) of **4′**, albeit to a lesser extent. Other orbitals of interest include the 10b$_1$ orbital (d$_{xy}$) of **4′**, which appears at low energy compared to Cp$_2$Zr, due to the absence of a second π-bond in the amides.

It was noted that the reaction of (BDPP)Zr(NMe$_2$)$_2$ with [Me$_2$NH$_2$]Cl resulted in protonolysis of the appar-

---

(42) Alcock, N. M.; Pierce-Butler, M.; Willey, G. R. *J. Chem. Soc., Chem. Commun.* **1974**, 627.

(43) Airoldi, C.; Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Malik, K. M. A.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1980**, 2010.

(44) Planalp, R. P.; Andersen, R. A.; Zalkin, A. *Organometallics* **1983**, *2*, 16.

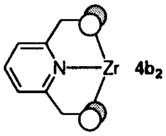
(45) Cummins, C. C.; Duyne, G. D. V.; Schaller, C. P.; Wolczanski, P. T. *Organometallics* **1991**, *10*, 164.

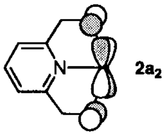
(46) Bai, Y.; Roesky, H. W.; Noltemeyer, M.; Witt, M. *Chem. Ber.* **1992**, *125*, 825.

(47) Okuda, J.; Schattenmann, F. J.; Wocadlo, S.; Massa, W. *Organometallics* **1995**, *14*, 789.

(48) Hunter, W. E.; Hrncir, D. C.; Bynum, V.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750.

ently more basic amides of the BDPP ligand. This is supported by the observation of a ligand centered nonbonding orbital on the amides (4b$_2$, HOMO-3). The dimethylamido groups in (BDPP)Zr(NMe$_2$)$_2$ can utilize a combination of the 5b$_2$ and 10b$_1$ orbitals for π-bond formation. The 5b$_2$ orbital mentioned above is of the correct symmetry to interact with the symmetrical combination of the p-orbitals on the amides; however, the amide−Zr−amide angle of 139.6(2)° precludes efficient overlap (a small contribution from the p$_z$ (0.2%) and the d$_{xz}$ (0.5%) orbitals of Zr is present). Consequently, the pyridine−diamide ligand is formally an eight-electron donor, four electrons less than the combination of two cyclopentadienyl ligands. The zirconium metal center in these new complexes is likely to be very electrophilic which may, in part, explain the statistically shorter Zr−Me bonds in compound **4b** (2.243(6) and 2.248(7) Å) versus Cp$_2$ZrMe$_2$ (2.273(5) and 2.280(5) Å). The 2a$_2$ orbital (HOMO-5) represents the π-overlap of the amide p-orbitals with the metal d$_{yz}$ orbital. The antibonding combination of this orbital is the 4a$_2$ orbital (Figure 3).





Conclusion

In summary, a high-yield route into pyridine−diamide complexes of zirconium has been demonstrated. The restricted rotation about the N−C$_{ipso}$ bond of the ligand and the availability of substituted anilines provide an opportunity to vary the sterics with little change to the electronic environment about the metal. In addition, the pyridine−diamide ligand system exhibits coordination behavior at zirconium which is very similar to a metallocene (Cp$_2$ZrX$_2$). The three frontier orbitals of a metallocene (1a$_1$, b$_2$, 2a$_1$) are present in these new fragments, albeit at slightly different energies. The ligand-centered nonbonding orbital based on the amide nitrogens gives rise to an unusually low electron count at zirconium; for example, (BDEP)ZrMe$_2$ is formally a 12-electron complex. Finally, the molecular structure of (BDEP)ZrMe$_2$ has revealed a coordination geometry which is expected to direct an incoming olefin cis to the Zr−Me bond in a putative cationic alkyl complex (e.g., (BDEP)ZrMe$^+$). Work is in progress to isolate an authentic cationic alkyl complex. Successful polymerization of olefins[49] and further ligand variations will be reported shortly.

Experimental Section

General Details. All experiments were performed under a dry dinitrogen atmosphere using standard Schlenk techniques 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. 2,6-Dimethylaniline, 2,6-diethylaniline, and 2,6-diisopropylaniline were purchased from Aldrich and distilled under reduced pressure before use. Methylmagnesium bromide was purchased from Aldrich and used as received. Zr(NMe$_2$)$_4$[34] was synthesized as reported in the literature. Unless otherwise specified, proton (300 MHz) and carbon (75.46 MHz) NMR spectra were recorded in C$_6$D$_6$ at approximately 22 °C on a Varian Gemini-300 spectrometer. The proton chemical shifts were referenced to internal C$_6$D$_5$*H* (δ = 7.15 ppm) and the carbon resonances to *C*$_6$D$_6$ (δ = 128.0 ppm). Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, NY.

2,6-[RHNCH$_2$]$_2$NC$_5$H$_3$ (R = 2,6-Diisopropylphenyl), (BDPP)H$_2$ (1a). A THF (150 mL) solution of LiNHR (12.226 g, 66.77 mmol) was added slowly to a stirring THF (100 mL) solution of 2,6-bis(bromomethyl)pyridine (8.842 g, 33.37 mmol) at −78 °C. The mixture was warmed to room temperature and stirred for 12 h. The solution was quenched with a saturated NaHCO$_3$ solution (100 mL) and extracted with ether. The solvent was removed *in vacuo*, and the resulting solid was dissolved in a minimum amount of hexanes and cooled to −30 °C for 12 h. A white crystalline **1a** was isolated by filtration and dried under vacuum (7.792 g, 17.02 mmol, 51%). ^{1}H NMR: δ 7.10−7.20 (m, 6H, Ar), 7.12 (t, 1H, py), 6.84 (d, 2H, py), 4.24 (s, 4H, NC*H*$_2$), 3.53 (sept, 4H, C*H*Me$_2$), 1.24 (d, 24H, CH*Me*$_2$). ^{13}C{^{1}H} NMR: δ 158.21, 154.18, 143.27, 137.25, 125.12, 124.17, 121.16, 57.02, 28.24, 24.62. MS (EI): *m/z* 457.346 (M$^+$). Calcd for C$_{31}$H$_{43}$N$_3$: 457.346.

2,6-[RHNCH$_2$]$_2$NC$_5$H$_3$ (R = 2,6-Diethylphenyl), (BDEP)H$_2$ (1b). The preparation of compound **1b** is identical to that for **1a**. LiNHR (10.40 g, 67.02 mmol) and 2,6-bis(bromomethyl)pyridine (8.876 g, 33.50 mmol) gave a yellow-brown liquid **1b** (9.753 g, 24.29 mmol, 73%). ^{1}H NMR: δ 6.90−7.10 (m, 6H, Ar and py), 6.80 (d, 2H, py), 4.35 (broad, 2H, N*H*), 4.19 (s, 4H, NC*H*$_2$), 2.72 (q, 8H, C*H*$_2$CH$_3$), 1.21 (t, 12H, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR: δ 128.93, 145.77, 136.86, 136.36, 127.17, 123.20, 120.27, 56.44, 25.10, 15.17. MS (EI): *m/z* 401.284 (M$^+$). Calcd for C$_{27}$H$_{35}$N$_3$: 401.283.

2,6-[RHNCH$_2$]$_2$NC$_5$H$_3$ (R = 2,6-Dimethylphenyl), (BDMP)H$_2$ (1a). The preparation of compound **1c** is identical to that for **1a**. LiNHR (2.879 g, 22.65 mmol) and 2,6-bis(bromomethyl)pyridine (3.000 g, 11.32 mmol) gave a yellow-brown liquid **1c** (3.105 g, 8.987 mmol, 79%). ^{1}H NMR: δ 6.95−7.05 (m, 5H, Ar and py), 6.86 (m, 2H, Ar), 6.67 (d, 2H, py), 4.21 (broad, 2H, N*H*), 4.15 (s, 4H, NC*H*$_2$), 2.25 (s, 12H, Me). ^{13}C{^{1}H} NMR: δ 159.04, 146.88, 136.72, 18.50, 129.24, 122.18, 120.24, 53.93, 18.87. MS (EI): *m/z* 345.220 (M$^+$). Calcd for C$_{23}$H$_{27}$N$_3$: 345.220.

(BDPP)Zr(NMe$_2$)$_2$ (2a). A toluene solution of Zr(NMe$_2$)$_4$ (1.748 g, 6.534 mmol) was added to a toluene solution (50 mL) of **1a** (2.990 g, 6.532 mmol) at room temperature. The solution was refluxed for 12 h. The solvent was removed *in vacuo*, and the resulting solid was extracted with hexanes (3 × 50 mL) and filtered through Celite. The volume of the filtrate was reduced to 50 mL and cooled to −30 °C for 12 h. Yellow crystalline **2a** was isolated by filtration and dried under vacuum (1.791 g, 3.425 mmol, 92%). ^{1}H NMR: δ 7.05−7.20 (m, 6H, Ar), 6.87 (t, 1H, py), 6.47 (d, 2H, py), 4.81 (s, 4H, NC*H*$_2$), 3.69 (sept, 4H, C*H*Me$_2$), 2.53 (s, 12H, N*Me*$_2$), 1.31 (d, 12H, CH*Me*$_2$), 1.29 (d, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR: δ 163.26, 150.89, 146.28, 137.56, 124.59, 123.73, 117.18, 60.62, 41.51, 28.06, 26.44, 24.69. Anal. Calcd for C$_{35}$H$_{53}$N$_5$Zr: C, 66.20; H, 8.41; N, 11.03. Found: C, 66.69; H, 8.39; N, 10.77.

(BDEP)Zr(NMe$_2$)$_2$ (2b). The preparation of compound **2b** is identical to that for complex **2a**. Zr(NMe$_2$)$_4$ (1.000 g, 3.738 mmol) and compound **1b** (1.500 g, 3.735 mmol) gave yellow crystalline **2b** (1.950 g, 3.368 mmol, 90%). ^{1}H NMR: δ 7.21 (d, 6H, Ar), 7.05 (m, 2H, Ar), 6.88 (t, 1H, py), 6.47 (d, 2H, py), 4.69 (s, 4H, NC*H*$_2$), 2.86 (m, 8H, C*H*$_2$CH$_3$), 2.58 (s, 12H, N*Me*$_2$), 1.29 (t, 12H, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR: δ 164.07, 152.54, 141.22, 138.63, 126.03, 123.83, 117.30, 62.27, 41.44, 24.39, 15.85.

---

(49) Compound **3a** (10 μmol), activated with MAO (Al:Zr = 500:1), in 50 mL toluene under 4 atm ethylene for 5 min: activity, 6000 g of poly(ethylene)/mmol of catalyst·h.

(BDMP)Zr(NMe$_2$)$_2$ (2c). The preparation of compound **2c** is identical to that for complex **2a**. Zr(NMe$_2$)$_4$ (1.000 g, 3.738 mmol) and compound **1c** (1.300 g, 3.763 mmol) gave yellow crystalline **2c** (1.950 g, 3.368 mmol, 90%). ^{1}H NMR: δ 7.16 (d, 4H, Ar), 6.97 (m, 2H, Ar), 6.90 (t, 1H, py), 6.46 (d, 2H, py), 4.63 (s, 4H, NC*H*$_2$), 2.58 (s, 12H, N*Me*$_2$), 2.37 (s, 12H, Me). ^{13}C{^{1}H} NMR: δ 164.45, 153.25, 137.54, 135.67, 128.58, 123.34, 117.34, 63.70, 41.32, 18.86.

(BDPP)ZrCl$_2$ (3a). ClSiMe$_3$ (5.200 g, 47.86 mmol) was added to a toluene solution (50 mL) of **2a** (3.000 g, 4.724 mmol) at room temperature. The solution was stirred for 12 hours, and a white precipitate gradually formed. The solution was cooled to −30 °C. White crystalline **3a** was isolated by filtration and dried under vacuum (2.862 g, 4.632 mmol, 98%). ^{1}H NMR: δ 7.10−7.20 (m, 6H, Ar), 6.76 (t, 1H, py), 6.27 (d, 2H, py), 4.81 (s, 4H, NC*H*$_2$), 3.74 (sept, 4H, C*H*Me$_2$), 1.54 (d, 12H, CH*Me*$_2$), 1.20 (d, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR: δ 162.94, 146.03, 138.86, 127.40, 124.72, 117.74, 68.19, 28.59, 27.03, 24.78.

(BDEP)ZrCl$_2$ (3b). The preparation of compound **3b** is identical to that for complex **3a**. ClSiMe$_3$ (2.705 g, 24.90 mmol) and compound **2b** (1.434 g, 2.477 mmol) gave light orange crystalline **3b** (1.378 g, 2.453 mmol, 99%). ^{1}H NMR: δ 7.10−7.20 (m, 6H, Ar), 6.86 (t, 1H, py), 6.37 (d, 2H, py), 4.63 (s, 4H, NC*H*$_2$), 2.98 (m, 8H, C*H*$_2$CH$_3$), 1.29 (t, 12H, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR: δ 163.93, 154.80, 141.74, 138.68, 127.12, 126.72, 117.81, 67.20, 24.60, 15.58.

(BDMP)ZrCl$_2$ (3c). The preparation of compound **3c** is identical to that for complex **3a**. ClSiMe$_3$ (9.430 g, 86.80 mmol) and compound **2c** (4.538 g, 8.679 mmol) gave white crystalline **3c** (4.021 g, 7.953 mmol, 92%). ^{1}H NMR: δ 7.09 (m, 4H, Ar), 7.03 (m, 2H, Ar), 6.84 (t, 1H, py), 6.36 (d, 2H, py), 4.44 (s, 4H, NC*H*$_2$), 2.46 (s, 12H, Me). ^{13}C{^{1}H} NMR: δ 163.01, 153.03, 138.46, 136.24, 129.31, 127.37, 117.70, 65.60, 19.30.

(BDPP)ZrMe$_2$ (4a). To a suspension of compound **3a** (0.250 g, 0.405 mmol) in diethyl ether (25 mL) was added 2.2 equiv of MeMgBr (0.49 mL, 1.80 M, 0.88 mmol) at room temperature. The mixture 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 light 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. White crystalline **4a** was isolated by filtration and dried under vacuum (0.207 g, 0.359 mmol, 89%). ^{1}H NMR: δ 7.20−7.30 (m, 6H, Ar), 6.88 (t, 1H, py), 6.40 (d, 2H, py), 4.95 (s, 4H, NC*H*$_2$), 3.84 (sept, 4H, C*H*Me$_2$), 1.41 (d, 12H, CH*Me*$_2$), 1.21 (d, 12H, CH*Me*$_2$), 0.45 (s, 6H, Zr*Me*$_2$). ^{13}C{^{1}H} NMR: d 163.94, 147.12, 137.98, 126.38, 124.44, 117.36, 67.48, 44.71 (ZrMe2), 28.32, 28.17, 24.18. Anal. Calcd for $C_{33}H_{47}N_3Zr$: C, 68.70; H, 8.21; N, 7.28. Found: C, 69.50; H, 8.57; N, 7.49.

(BDEP)ZrMe$_2$ (4b). The preparation of compound **4b** is identical to that for complex **4a**. Compound **3b** (0.400 g, 0.712 mmol) and 2.2 equiv of MeMgBr (0.87 mL, 1.80 M, 1.57 mmol) gave white crystalline **4b** (0.307 g, 0.589 mmol, 83%). ^{1}H NMR: δ 7.30−7.20 (m, 6H, Ar), 6.87 (t, 1H, py), 6.45 (d, 2H, py), 4.77 (s, 4H, NC*H*$_2$), 2.94 (m, 8H, C*H*$_2$CH$_3$), 1.27 (t, 12H, CH$_2$C*H*$_3$), 0.29 (s, 6H, Zr*Me*$_2$). ^{13}C{^{1}H} NMR: δ 164.34, 146.73, 142.63, 137.83, 126.60, 126.08, 117.60, 66.41, 42.83 (Zr*Me*$_2$), 24.14, 16.17. Anal. Calcd for $C_{29}H_{39}N_3Zr$: C, 66.87; H, 7.55; N, 8.07. Found: C, 66.37; H, 7.71; N, 7.83.

(BDMP)ZrMe$_2$ (4c). The preparation of compound **4c** is identical to that for complex **4a**. Compound **3c** (0.100 g, 0.198 mmol) and 2.2 equiv of MeMgBr (0.24 mL, 1.80 M, 0.432 mmol) gave white crystalline **4c** (0.074 g, 0.159 mmol, 80%). ^{1}H NMR: δ 7.16 (m, 4H, Ar), 7.06 (m, 2H, Ar), 6.88 (t, 1H, py), 6.44 (d, 2H, py), 4.58 (s, 4H, NC*H*$_2$), 2.40 (s, 12H, Me), 0.34 (s, 6H, Zr*Me*$_2$). ^{13}C{^{1}H} NMR: δ 164.34, 142.83, 137.56, 136.81, 128.87, 125.47, 117.42, 64.60, 47.88 (Zr*Me*$_2$), 18.54.

Molecular Orbital Calculations. All molecular orbital calculations were performed on a CAChe Worksystem, a product developed by Tektronix. The parameters used for the extended Hückel calculations of the model **4′** (restricted to C_{2v} symmetry) were taken from the literature[50] and are listed in the Supporting Information. The bond lengths and angles for **4′** were taken from the X-ray crystal structure analysis of (BDEP)ZrMe$_2$ (*vide supra*). The Cartesian coordinates and a full list of the eigenvalues and symmetry labels for the model can be found in the Supporting Information. For the model, the following standard bond lengths were used: C−H, 1.090 Å; N−H, 1.070 Å.

X-ray Crystallographic Analysis. A suitable crystal of **4b** was grown from a saturated ether solution at −30 °C. Crystal data may be found in Table 1. Data were collected on a Siemans P4 diffractometer with the XSCANS software package.[51] The Laue symmetry $2/m$ was determined by merging symmetry equivalent positions. A total of 5706 data were collected in the range of $\theta = 1.77-25.0°$ ($-1 \le h \le 14$, $-1 \le k \le 18$, $-18 \le l \le 17$). Three standard reflections monitored at the end of every 297 reflections collected showed no decay of the crystal. The data processing, solution, and refinement were done using SHELXTL-PC programs.[52] The faces of the crystal were indexed, and the distance between them was measured for a Gaussian absorption correction on the data. During the least-squares cycles, the isotropic temperature factor for methyl groups C(19) and C(29) were relatively high, 0.15 and 0.13, respectively. Attempts to model the disorder did not yield satisfactory results. Anisotropic thermal parameters were refined for all non-hydrogen atoms except the carbons in the two phenyl rings. The phenyl and pyridine were restrained to have 2-fold symmetry. The C−Me distances were restrained to be equal using the option SADI. Some hydrogens were observed in the least-squares cycles; however, no attempt was made to locate them. All hydrogens were placed in calculated positions. In the final difference Fourier synthesis, the electron density fluctuates in the range from 0.891 to −0.421 e Å^3.

Acknowledgment. Funding from the NSERC (Canada), in the form of a Research Grant to D.H.M., and Union Carbide Canada is gratefully acknowledged.

Supporting Information Available: Listings of the extended Hückel parameters, Cartesian coordinates for **4′**, labeled model of **4′**, eigenvalue and symmetry labels for **4′**, X-ray crystallographic details, crystal data and experimental details, final crystallographic atomic coordinates and equivalent isotropic thermal parameters, complete tables of bond lengths and angles, anisotropic thermal parameters, hydrogen atom parameters, torsional angles, least-squares planes for **4b**, and crystal structure for **4b** (14 pages). Ordering information can be found on any current masthead page.

OM9604278

---

(50) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

(51) XSCANS: Siemans Analytical X-ray Instruments Inc., Madison WI, 1990.

(52) SHELXTL, Version 5: Siemans Analytical X-ray Instruments Inc., Madison WI, 1994.