Evidence of Reversible N−H Exchange in a Three-Coordinate Amidozinc Complex. Syntheses and Structures of 1-Methyl-2-((*N*-*tert*-butylamino)methyl)benzimidazole Complexes of Zinc

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1-Methyl-2-((*N*-*tert*-butylamino)methyl)benzimidazole **1** reacts with 1 equiv of $Zn[N(SiMe_3)_2]_2$ in nonpolar solvents (benzene, toluene) yielding the monomeric, 3-coordinate, planar amidozinc complex **3** and $HN(SiMe_3)_2$. Compound **3** has been characterized by ^1H and ^{13}C NMR spectroscopy, elemental analysis, and X-ray crystallography. The crystal structure of this complex at −100 °C (monoclinic, $P2_1/n$, $a = 8.468(2)$ Å, $b = 18.700(4)$ Å, $c = 15.551(2)$ Å, $\beta = 98.10(2)°$, $Z = 4$, $R = 4.43\%$, $R_w = 5.35\%$) shows two short, equivalent amidozinc bonds of 1.874(4) Å and 1.887(4) Å and a longer Zn−N coordinate covalent bond of 2.067(4) Å to the benzimidazole N atom. No evidence of $Zn^-{=}N^+$ double bond character is found even though a N lone pair and an "empty", p-like Zn orbital are geometrically arranged for favorable overlap. Magnetization transfer studies show reversible, degenerate exchange between **3** and **1** at 40 °C. Compound **3** undergoes rapid, irreversible protonolysis with $HNMe_2$ to produce **1**, $HN(SiMe_3)_2$, and a white precipitate. Addition of **1** to a Et_2O solution of $ZnCl_2$ immediately forms a white precipitate of **2**. Single crystals of **2** were grown from CH_2Cl_2 solutions. The molecular structure of **2**, determined by X-ray crystallography at −100 °C (monoclinic, $P2_1/n$, $a = 7.622(2)$ Å, $b = 14.378$ (3) Å, $c = 14.476(3)$ Å, $\beta = 104.91(2)°$, $Z = 4$, $R = 3.14\%$, $R_w = 3.61\%$), shows the Zn atom in a distorted tetrahedral environment. Bonding between Zn and N atoms in four-coordinate **2** and three-coordinate **3** is compared.

Introduction

Coordinative and electronically unsaturated Zn(II) centers are interesting because of their proposed participation in important processes such as catalytic methanol synthesis,[1−5] biologically relevant CO_2 fixation and metabolism,[6−9] applications in new material synthesis,[10−13] and asymmetric organic synthesis.[14−17] In contrast to "open-shell" transition metal centers, novel coordination geometries of unsaturated group 12 metals (Zn, Cd, Hg) and their corresponding reactivities are less well known. Although dimeric three-coordinate Zn structures are well-established,[18] Parkin and co-workers first reported the X-ray characterization and reactivity of a monomeric, three-coordinate (bis(pyrazolyl)hydroborato)alkylzinc molecule,[19] and since then several other examples of monomeric, planar Zn(II) and Cd(II) have been reported.[20−24] Van Koten and co-workers have noted interesting reactivity associated with an unsaturated organozinc radical formed upon combining diimines or iminopyridines with dialkylzinc.[25−27] In spite of numerous reports of main group and transition metal amido complexes, little is known about the reactivity of amido Zn−N bonds[28−34] or planar Zn molecules having only N atoms in the first coordination sphere. We became interested in substituted aminobenzimidazoles as bi-

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dentate ligands that could chelate to $Zn-NR_2$ and $Cd-NR_2$ fragments based on the known coordinating ability of the benzimidazole functional group,[35] thermodynamic stability provided by bidentate chelation, and the flexibility and ease of synthesis. Herein we report the synthesis of 1-methyl-2-((*N*-*tert*-butylamino)methyl)benzimidazole (**1**), the structure of its $ZnCl_2$ complex (**2**), and the reaction between **1** and a diamidozinc compound resulting in a monomeric, three-coordinate, planar zinc species (**3**) which exhibits reversible exchange with N−H bonds.

Experimental Section

General Considerations. All air-sensitive manipulations were performed under an inert atmosphere of dry nitrogen. Tetrahydrofuran (THF) and hexane were distilled from potassium/benzophenone under nitrogen. Diethyl ether was distilled from Na/K (1:3) alloy under nitrogen. Dichloromethane was distilled from dri-Na (J. T. Baker) under nitrogen. ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker ARX-400, Varian XL-300, or JEOL GSX-270 spectrometer at the respective fields. ^{1}H and ^{13}C NMR chemical shifts are reported in units of parts per million (ppm, δ) relative to either residual protiated solvent (^{1}H) or deuterated solvent (^{13}C): $CDCl_3$, δ 7.24 [^{1}H], δ 77.0 [^{13}C]; C_6D_6, δ 7.15 [^{1}H], δ 128.0 [^{13}C]; DMSO-d_6, δ 2.49 [^{1}H], δ 39.5 [^{13}C]. Melting points were measured with a Mel-Temp apparatus and are reported uncorrected. Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA, and Schwarzkopf Microanalytical Laboratory, Inc., Woodside, NY. Anhydrous $ZnCl_2$ and Zn[N(SiMe)$_3$]$_2$ were prepared according to the literature.[36,37]

Synthesis of 1-Methyl-2-formylbenzimidazole.[38,39] This was prepared from 1-methylbenzimidazole[40] (10 g, 76 mmol) by adapting the procedure used to synthesize 1-methyl-2-formylimidazole.[41,42] The resulting yellow-white solid was purified by sublimation on to a cold finger (60 °C, 5 mTorr) to yield 4.3 g (36%) of white product. ^{1}H NMR ($CDCl_3$): δ 10.11 (s, $-CHO$), 7.91 (d, J = 8.1 Hz), 7.47 (m), 7.39 (m), 4.15 (s, $N-CH_3$); mp 114−118 °C (122.5 °C lit.).[38]

Synthesis of 1-Methyl-2-((*N*-*tert*-butylimino)methyl)benzimidazole. To a solution containing 1.4 g (8.8 mmol) of 1-methyl-2-formylbenzimidazole in 50 mL THF was added 1.8 g (27 mmol) of distilled *tert*-butylamine and 10 mg of pyridinium tosylate catalyst. This solution was heated at reflux for 3 h and cooled, and the solvent was removed by rotary evaporation. The remaining yellowish residue was purified by sublimation on to a cold finger (60 °C, 5 mTorr) to yield 1.4 g (74%) of white product. ^{1}H NMR ($CDCl_3$): δ 8.50 (s, $-N{=}CH-$), 7.78 (d, J = 7.9 Hz), 7.41−7.22 (m), 4.18 (s, $N-CH_3$), 1.32 (s, $N-Bu^t$); mp 57−65 °C.

Synthesis of 1-Methyl-2-((*N*-*tert*-butylamino)methyl)benzimidazole (1). A 1.9 g (8.8 mmol) sample of 1-methyl-2-((*N*-*tert*-butylimino)methyl)benzimidazole was dissolved in 20 mL of a 1:3 H_2O/EtOH mixture. $NaBH_4$ (0.97 g, 26 mmol) was added and the solution was maintained at 40 °C for 16 h. The solution was cooled, and the remaining $NaBH_4$ was removed by suction filtration and washed with 3 × 10 mL Et_2O. The filtrate was evaporated to dryness, redissolved in 50 mL of H_2O and extracted with 3 × 50 mL of Et_2O. The organic extracts were separated, combined, and dried over anhydrous Na_2SO_4. The solution was filtered, and the solvent was removed by rotary evaporation to give a white solid. This material was purified by sublimation onto a cold finger (55 °C, 10 mTorr) to yield 1.6 g (7.5 mmol, 86%) of a white product. ^{1}H NMR ($CDCl_3$): δ 7.73−7.68 (m), 7.35−7.15 (m), 4.00 (s, $-CH_2-$), 3.81 (s, $N-CH_3$), 1.20 (s, $N-Bu^t$). ^{13}C {^{1}H}NMR ($CDCl_3$): δ 153.77, 142.32, 136.15, 122.28, 121.76, 119.36, 108.96, 50.70, 40.09, 29.84, 28.83. Anal. Calcd for ($C_{13}H_{19}N_3$): C, 71.89; H, 8.76; N, 19.35. Found: C, 71.77; H, 8.75; N, 19.25. Mp: 79−83 °C.

Synthesis of Dichloro(1-methyl-2-((*N*-*tert*-butylamino)methyl)benzimidazole)zinc (II) (2). Anhydrous $ZnCl_2$ (80 mg, 0.59 mmol) was dissolved in 10 mL of freshly distilled Et_2O under a dry N_2 atmosphere. Dropwise addition of compound **1** (90 mg, 0.41 mmol) in 5 mL of anhydrous Et_2O to the room temperature $ZnCl_2$ solution resulted in the immediate formation of a white precipitate. The reaction mixture was stirred for an additional 15 min, and the white precipitate was isolated by suction filtration and washed with 3 × 5 mL Et_2O. Compound **2** (120 mg, 0.34 mmol) was isolated for an 83% yield. ^{1}H NMR (DMSO-d_6): δ 7.71 (d, J = 7.3 Hz), 7.56 (d, J = 8.4 Hz), 7.40−7.34 (m), 4.19 (d, J = 7.3 Hz, $-CH_2-$), 3.86 (s, $N-CH_3$), 1.28 (s, $N-Bu^t$). ^{13}C {^{1}H}NMR (DMSO-d_6): δ 155.38, 136.84, 135.59, 123.72, 123.57, 116.74, 111.23, 54.05, 38.66, 30.09, 27.53. Anal. Calcd for ($C_{13}H_{19}Cl_2N_3Zn$): C, 44.19; H, 5.38; N, 11.90. Found: C, 44.08; H, 5.34; N, 11.84. Mp: 275−280 °C dec. X-ray quality crystals of **2** were obtained by slow cooling of a concentrated CH_2Cl_2 solution at 5 °C.

Synthesis of 3. A Schlenk flask was charged with 10 mL of hexanes, 220 mg (1.0 mmol) of sublimed ligand **1**, and 410 mg (1.1 mmol) of $Zn[N(SiMe_3)_2]_2$. The flask was evacuated and stirred for 18 h. After this period a yellowish precipitate had formed, leaving a yellow supernatant. The solvent was removed *in vacuo*, and the reaction solids were dissolved in hot cyclohexane. Addition of an equal volume of hexanes and cooling to −20 °C overnight produced an orangeish-yellow solid. The remaining solvent was removed by filtration, leaving 290 mg (0.65 mmol, 65%) of yellow solid **3**. ^{1}H NMR (C_6D_6): δ 8.03 (d, J = 7.9 Hz, 1H), 7.16 (obscured by solvent), 7.06 (t, J = 7.3 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 3.90 (s, 2H, $-CH_2-$), 2.27 (s, 3H, $N-CH_3$), 1.48 (s, 9H, $N-Bu^t$), 0.48 (s, 18 H, $N(SiMe_3)_2$). ^{13}C {^{1}H} NMR (C_6D_6): δ 162.36, 138.98, 136.34, 123.69, 123.41, 118.11, 109.74, 52.67, 44.87, 32.46, 28.10, 6.06. Anal. Calcd for ($C_{19}H_{36}N_4Si_2Zn$): C, 51.61; H, 8.22; N, 12.68. Found: C, 50.64; H, 8.23; N, 12.60.

Magnetization Transfer Experiments. Compound **3** was generated *in situ* by combining 11.3 mg (0.052 mmol) of **1** and 12.0 mg (0.031 mmol) of $Zn[N(SiMe_3)_2]_2$ in 0.4 mL of C_6D_6 in an NMR tube. The tube was subjected to three freeze/pump/thaw cycles, and sealed under 550 Torr of N_2. The ^{1}H NMR spectrum obtained after standing at RT for 16 h showed resonances corresponding to **1**, **3**, and $HN(SiMe_3)_2$. The singlet for $Zn[N(SiMe_3)_2]_2$ had disappeared. T_1 values for peaks corresponding to *N*-methyl, methylene, and *N*-*tert*-butyl resonances for **1** and **3** were determined using the inversion−recovery sequence at 40 °C. Values for T_1 were obtained from exponential fitting of 10 τ values ranging from 100 ms to 15 s. Magnetization transfer was accomplished by irradiating the peak of interest for at least 3 T_1 before signal acquisition. Spectra acquired using off- and on-resonance irradiation were subtracted to give the difference spectrum. The integrals of exchanging resonances were normalized, measured and used in calculating the rate constant for two-site exchange.

Crystal Structure Determination of 2 and 3. Crystal structure determination was carried out on a Siemens P4/Series II diffractometer employing Mo Kα radiation (λ = 0.710 73 Å) and equipped with a LT-2a low temperature device. For compound **2**, a colorless block measuring 0.40 × 0.40 × 0.20 mm was mounted into the end of a glass capillary with the aid of PARATONE oil and the goniometer head secured into the N_2 cold stream (−100 °C). In a similar fashion a pale orange block of **3** measuring 0.4 × 0.6 × 0.3 mm was also mounted in a glass capillary and secured into the N_2 cold stream (−100 °C).

Crystals of either **2** or **3** were centered optically followed by the collection and autocentering of 24 or 26 random reflections which indicated a primitive monoclinic cell in both cases. Analysis of systematic absences in the complete data set of **2** or **3** both indicated

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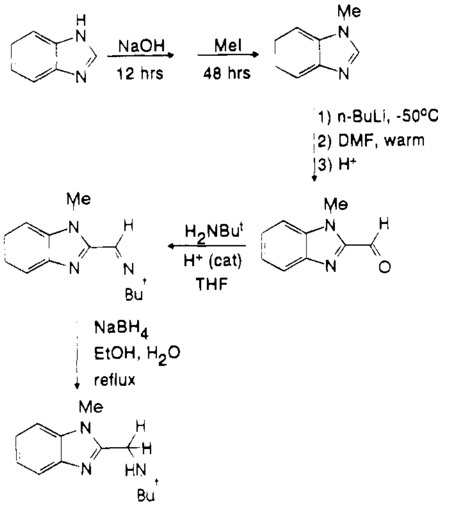
Table 1. Crystallographic Data for **2** and **3**

	2	**3**
empirical formula	$C_{13}H_{19}Cl_2N_3Zn$	$C_{19}H_{36}N_4Si_2Zn$
cell const		
a (Å)	7.622(2)	8.486(2)
b (Å)	14.378(3)	18.700(4)
c (Å)	14.476(3)	15.551(2)
β (deg)	104.91(2)	98.10(2)
volume (Å^3)	1532.9(7)	2443.0(8)
Z	4	4
fw	353.6	442.1
space group	$P2_1/n$	$P2_1/n$
temp (°C)	−100	−100
radiation	Mo Kα (*λ* = 0.710 73 Å)	
density (calcd) (g cc^{-1})	1.532	1.204
abs coeff (mm^{-1})	1.940	1.113
R (%)	*R* = 3.14	*R* = 4.43
	R_w = 3.61	R_w = 5.35

Scheme 1



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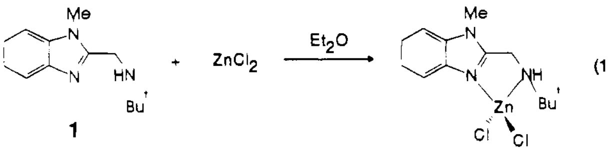
the space group $P2_1/n$, and both structures were solved using direct methods. Location and refinement of all heavy atoms in **2** and **3** were accomplished using SHELXTL PLUS software running on a VAX 3100 workstation. Hydrogen atom positions were generated using a riding model with C−H distances fixed at 0.96 Å and N−H distances of 0.80 Å. Table 1 provides a summary of data collection and refinement parameters for **2** and **3**.

Results

Synthesis of ligand **1** proceeded according to Scheme 1. 1-Methylbenzimidazole was metalated at low temperature with 1 equiv of *n*-butyllithium[43] and formylated with the addition of DMF.[41] The Schiff's base of 1-methyl-2-formylbenzimidazole was readily formed using *tert*-butylamine. Reduction with $NaBH_4$ gave aminobenzimidazole **1**. All intermediates and product **1** are conveniently purified by sublimation.

Complex **2** is readily synthesized upon combining ethereal solutions of **1** and $ZnCl_2$ (eq 1).



1 **2** (1)

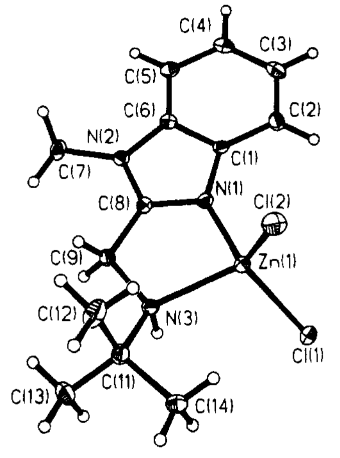


Figure 1. Molecular structure of **2** as determined by X-ray diffraction at −100 °C. Thermal ellipsoids are drawn at the 30% probability level.

Table 2. Selected Bond Lengths and Angles for **2**

	Bond Lengths (Å)		
Zn(1)−Cl(1)	2.233(1)	C(8)−C(9)	1.490(5)
Zn(1)−Cl(2)	2.213(1)	N(3)−C(9)	1.480(5)
Zn(1)−N(1)	2.024(3)	N(2)−C(8)	1.351(5)
Zn(1)−N(3)	2.115(3)	N(3)−C(11)	1.520(5)
N(1)−C(8)	1.325(5)		
	Bond Angles (deg)		
Cl(1)−Zn(1)−Cl(2)	115.6(1)	N(3)−C(9)−C(8)	109.1(3)
N(1)−Zn(1)−N(3)	81.6(1)	Zn(1)−N(3)−C(9)	110.1(2)
Zn(1)−N(1)−C(8)	112.2(2)	Zn(1)−N(3)−C(11)	119.8(2)
N(1)−C(8)−C(9)	122.6(3)		

Description of the Crystal Structure of 2. Figure 1 shows the molecular structure of **2** determined by X-ray diffraction at −100 °C. Selected bond distances and angles are listed in Table 2. The geometry about the Zn atom is distorted tetrahedral, with a Cl(1)−Zn(1)−Cl(2) bond angle of 115.6(1)°, and a N(1)−Zn(1)−N(3) angle (i.e. the ligand bite angle) of 81.6(1)°. This acute angle is consistent with bite angles found in other bidentate complexes that form 5-membered rings such as Cl_2Zn(tmeda) (87.9(4)°),[44] Cl_2Zn(phen) (80.4(3)°),[45] and Cl_2Zn[2-*tert*-butoxy-6-((*N*-*tert*-butylamino)methyl)pyridine] (81.3(3)°).[46] The zinc−imidazole (Zn(1)−N(1)) = 2.024(3) Å) and zinc−amine (Zn(1)−N(3)) = 2.115(3) Å) bond lengths are unexceptional.[47,48]

The diazametallacyclopentene ring in **2** composed of atoms Zn(1), N(1), C(8), C(9), and N(3) adopts a puckered or domed structure. The plane containing the benzimidazole ring and defined by atoms N(1), C(8), and N(2) forms an angle of 15.7° with the plane containing atoms Zn(1), N(3), and C(9). Other distances and angles within the 5-membered diazametallacyclopentene ring are unexceptional. The N(3)−C(9)−C(8) angle of 109.1° suggests little strain in the methylene tether of this bidentate ligand. The imidazole ring bond distances and angles all appear normal.

Synthesis of the Three-Coordinate Zn Complex 3. We chose to investigate the protonolysis of basic Zn−N bonds as a general method to generate unsaturated Zn species.[49] Combining 1 equiv of $Zn[N(SiMe_3)_2]_2$ with weakly acidic **1** in C_6D_6

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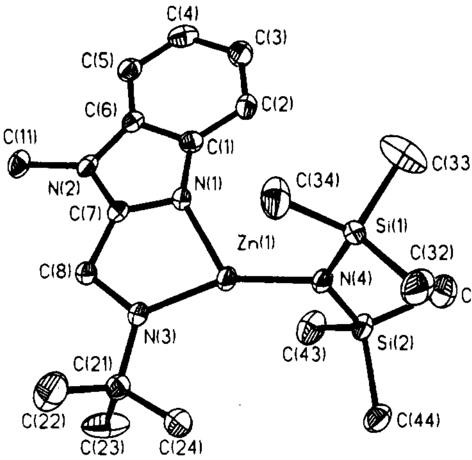
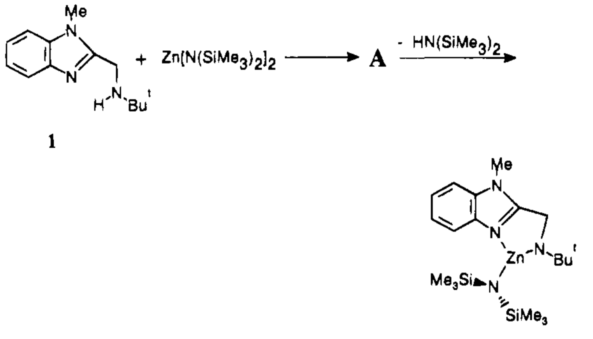


Figure 2. Molecular structure of **3** as determined by X-ray diffraction at −100 °C. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

affords new ^{1}H NMR resonances upon standing at room temperature for 2 h (eq 2). When excess $Zn[N(SiMe_3)_2]_2$ is



1

(2)

3

present, no free **1** is observed in the ^{1}H NMR spectrum but resonances corresponding to intermediate **A** are found shifted downfield relative to **1**.[50] Over time resonances attributed to **A** disappear and signals corresponding to complex **3** and free $HN(SiMe_3)_2$ are seen. The upfield trimethylsilyl region is especially informative here since formation of both free $HN(SiMe_3)_2$ (s, 0.089 ppm) and $Zn-N(SiMe_3)_2$ of **3** (s, 0.48 ppm) are observed along with concomitant loss of the trimethylsilyl singlet of **A** (0.34 ppm). Intermediate **A** displays a doublet pattern corresponding to tether $-CH_2-$ protons (^3J = 10 Hz) presumably due to coupling with the unobserved $N-H$ proton, whereas the methylene resonance of **3** appears as a singlet at 3.90 ppm consistent with amine deprotonation and an equivalent chemical environment for both methylene protons.

Magnetization transfer experiments at 40 °C were performed on similarly prepared samples using an excess of **1**. Irradiation of the $-CH_2-$ (3.90 ppm), $N-CH_3$ (2.27 ppm), and N-*tert*-butyl (1.48 ppm) singlet resonances in **3** led to quantifiable signal intensity in the corresponding resonances of **1**. When the $-Si(CH_3)_3$ singlet of **3** is irradiated, no measureable intensity in the $HN(SiCH_3)_3$ singlet is observed in the difference spectrum, in spite of the higher concentration of $HN(SiCH_3)_3$ compared to **1**.

X-ray quality crystals of **3** were grown from hexanes by slow cooling of a reaction mixture at −20 °C. The solid state structure of **3** was determined at −100 °C and is shown in Figure 2. Important bond distances and angles are collected in Table 3. The coordination geometry about Zn(1) is best described as a distorted tee-shape having two short amido Zn−N bonds and a longer benzimidazole Zn−N bond within the first coordination sphere. The diazametallacyclopentene ring, adjoining benzimidazole ring, and ancillary atoms N(4) and C(21) are all coplanar with the ZnN_3 coordination plane, which is nearly perpendicular with the plane defined by atoms Si(1), N(4), and Si(2) (N(3)−Zn(1)−N(4)−Si(1) torsional angle = 95°). Planar geometry about Zn(1) is realized as the sum of the bond angles around Zn(1) is 360.0(3)°. Amido atom N(3) is also nearly planar, having bond angles that sum to 358.2(6)°. The N(1)−Zn(1)−N(3) angle of 85.6(2)° is similar to that found in **2** (81.6(1)°), a consequence of diazametallacyclopentene ring formation. The Zn(1)−N(1) benzimidazole bond distance of 2.067(4) Å is slightly but significantly elongated compared to **2** (Zn(1)−N(1) = 2.024(3) Å), whereas the Zn(1)−N(3) amido bond has shortened dramatically to 1.874(4) Å (2.115(3) Å in **2**). Similar Zn−N amido bond distances are found for Zn(1)−N(3) and Zn(1)−N(4) (1.887(4) Å).

Table 3. Selected Bond Lengths and Angles for (**3**)

	Bond Lengths (Å)		
Zn(1)−N(1)	2.067(4)	C(7)−C(8)	1.494(8)
Zn(1)−N(3)	1.874(4)	N(3)−C(8)	1.447(7)
Zn(1)−N(4)	1.887(4)	N(3)−C(21)	1.465(7)
N(1)−C(7)	1.323(7)		
	Bond Angles (deg)		
N(1)−Zn(1)−N(3)	85.6(2)	N(1)−C(7)−C(8)	122.1(5)
N(1)−Zn(1)−N(4)	120.8(2)	N(3)−C(8)−C(7)	109.1(4)
N(3)−Zn(1)−N(4)	153.6(2)	Zn(1)−N(3)−C(8)	115.8(4)
Zn(1)−N(1)−C(7)	107.3(4)		

Another curious feature of **3** shows that methyl groups C(34) and C(43) are positioned over Zn(1) on both sides of the ZnN_3 coordination plane with a Si(1)−N(1)−Si(2) angle of 130.4(3)° while the Zn(1)−N(4)−Si(1) angle is 112.9(2)° and Zn(1)−N(4)−Si(2) angle is 116.6(2)°. This arrangement of atoms allows for a closest contact distance between Zn(1) and the H atom riding on C(34) of ca. 2.4 Å, a distance within the sum of Zn and H van der Waals radii (2.7 Å).

Discussion

Bonding Description of the ZnN_3 Core. Comparing structures **2** and **3**, notable bonding differences are evident as the coordination environment about Zn is varied from distorted tetrahedral in **2** to a distorted tee-shape in **3**. Furthermore, ligand **1** functions as a neutral bidentate donor in **2** forming two coordinate covalent bonds to Zn whereas in **3**, the conjugate base of **1** forms both a coordinate covalent bond and a polar covalent amido Zn−N bond. Thus the Zn(1)−N(1) bond length in **3** has a comparable distance to the Zn(1)−N(1) distance in **2** (2.067(4) and 2.024(3) Å, respectively), since both distances represent coordinate covalent bonds from the imidazole N atom to Zn. These Zn−N distances are representative of a strong Lewis base → Lewis acid interaction that results between an sp^2-hybridized N atom and Zn(II). Similar ligand bite angles observed in **2** and **3** are consistant with bidentate chelation. However, dramatic shortening of the Zn(1)−N(3) bond in **3** has occurred relative to the Zn(1)−N(3) bond in **2** (1.874(4) and 2.115(3) Å, respectively). This is consistent with a stronger polar covalent amido N−Zn bond resulting from deprotonation of a secondary amine compared to a coordinate covalent amine Zn−N interaction in **2**. In fact, this newly formed Zn−N(3) amido bond length is nearly identicle to the established Zn−N(4) amido bond measuring 1.887(4) Å in compound **3**. Thus the geometry of **3** can be described as a three-coordinate, distorted tee-shaped structure that results from a diamidozinc

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(50) ^{1}H NMR of A (C_6D_6): δ 8.21 (d, J = 8.9 Hz), 7.19 (t, J = 8.9 Hz), 7.10 (t, J = 8.9 Hz), 6.83 (d, J = 8.9 Hz), 3.99 (d, J = 10.0 Hz, $-CH_2-$), 3.05 (s, $N-CH_3$), 1.01 (s, $N-Bu^t$), 0.34 (s, $N(SiMe_3)_2$).

strongly coordinated to a benzimidazole N atom. Another example of tee-shaped Zn has been reported for a zinc dithiolate coordinated to ether.[22]

Equivalent Zn(1)−N(3) and Zn(1)−N(4) distances suggest negligible Zn(1)−N(3) π(p→p) interaction in spite of good orbital alignment that results from the planar environments around Zn(1) and N(3). Overlap between an empty p-like orbital on Zn(1) and a localized electron pair on N(3) would formally result in $Zn^{-}{=}N^{+}$ double bond character reducing the Zn(1)−N(3) bond distance. However, the Zn(1)−N(4) bond provides a convenient intramolecular check of a Zn−N single bond distance because both the remaining lone pair electron density on N(4) is attenuated through backbonding into empty Si d-orbitals[51] and this orbital is nearly orthogonal to the Zn-centered p-like orbital (N(3)−Zn(1)−N(4)−Si(1) torsional angle = 95°). Apparently the energy difference between these two orbitals is too large for a significant π-type interaction. The electronegativity difference between Zn and N would undoubtedly impart a significant ionic component to Zn−N bonding ($\Delta\chi = 1.41$) but it is interesting that the observed Zn−N amido bond distances agree well with the sum of Zn and N covalent radii (1.93 Å). The Zn(1)−N(4) amide bond distance of 1.887(4) Å is consistent with other reported terminal amido Zn−N bonds in linear compounds that range from 1.812−1.850Å.[32−34] Thus we conclude that π(p→p) bonding does not play a significant role in determining the Zn(1)−N(3) bond length in **3**.[52,53]

Evidence for an electron deficient Zn center in **3** was initially sought by studying intramolecular interactions between Zn(1) and the $-SiMe_3$ groups since short Zn•••H contact distances of ca. 2.4 Å were observed in the solid state. X-ray diffraction studies of trigonal planar $M\{[N(SiMe_3)_2]_2\}_3$ (M = Al[54] , Fe[55]) show more acute Si−N−Si angles (Al = 118°, Fe = 121.2°) and more obtuse M−N−Si angles (Al = 121°, Fe = 119.4°) compared to **3** (Si(1)−N(4)−Si(2) = 130.4(3)°, Zn(1)−N(4)−Si(1) = 112.9(2)°, Zn(1)−N(4)−Si(2) = 116.6(2)°). The relatively short N−Si bond lengths observed in **3** (N(4)−Si(1) = 1.716(4) Å, N(4)−Si(2) = 1.691(4) Å) are consistent with significant $p_{\pi}-d_{\pi}$ bonding between N and Si atoms enhanced by the polar character of the Zn(1)−N(4) bond.[56] Based on this data it appeared that the pendant methyl groups in **3** are drawn toward an electron deficient Zn center. However, structural studies of *linear* diamidozinc molecules suggest no unusual interactions as N−Zn−N bond angles of 126.9−130.4° and Zn−N−Si bond angles of 112.9−117.3° have been reported.[32−34]

The solution structure of **3** appears consistent with its solid state structure as neither cooling this reaction mixture to 183 K nor heating it to 313 K results in any excessive broadening of resonances attributable to **3**. One plausible explanation based on the singlet resonance observed for the trimethylsilyl groups of **3** over this temperature range is that the bis(trimethylsilyl)-amide ligand remains confined to a rotationally restricted conformation similar to that observed in the solid state and that rotation about the Zn(1)−N(4) bond is slow compared to the NMR time scale. However, we cannot exclude the alternate explanation of rapid Zn−N bond rotation based on this data.

Magnetization transfer experiments confirm that a reversible, degenerate, ligand exchange reaction occurs (eq 3). In the

$$1 + 3^{*} \rightleftharpoons 1^{*} + 3 \qquad (3)$$

absence of $Zn[N(SiMe_3)_2]_2$, irradiation of either the methylene, *N*-methyl, or the *N-tert*-butyl resonance of **3** at 40 °C in C_6D_6 resulted in observable signal intensity in the corresponding resonance of **1** as shown in the difference spectrum. A rate constant, $k_2 = 0.04\ M^{-1}\ s^{-1}$, was derived at 40 °C. However, similar degenerate exchange of free $HN[(SiMe_3)_2]_2$ with the more downfield trimethylsilyl resonance of **3** is not discernable under these conditions. Thus the dynamics of selective ligand substitution corresponding to reversible N−H exchange can be probed for this system. The poorer coordinating ability and weaker acid strength of $HN(SiMe_3)_2$ likely prevents observation of its exchange by magnetization transfer techniques. When an excess of $HNMe_2$ is introduced into a C_6D_6 solution of **3** at room temperature, complete protonolysis of **3** occurs within 20 min yielding **1**, $HN(SiMe_3)_2$, and an uncharacterized white precipitate. Apparently the smaller, more nucleophilic and acidic $HNMe_2$ is more reactive here.

We are currently investigating the reactivity of these three-coordinate Zn complexes with H_2 and CO_2 as homogeneous models for methanol synthesis.

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Supporting Information Available: Tables giving the details of crystallographic data collection and listings of final positional and equivalent isotropic displacement coefficients, bond lengths, bond angles, anisotropic displacement coefficients, and H atom coordinates (13 pages). Ordering information is given on any current masthead page.

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(52) A less plausible arguement would maintain that the diazametallacyclopentene ring is too strained to allow the Zn−N bond to shorten to lengths < 1.9 Å. However, competition experiments between aminopyridine ligands that would form 5- and 6-membered diazametallacyclic rings with $ZnCl_2$ show only a 2 kcal mol^{-1} energy difference favoring formation of the 6-membered ring.[46] For more extensive studies on the stability of metallacyclic ring systems, see: Hancock, R. D.; Martell, A. E. *Chem. Rev.* **1989**, *89*, 1875−1914.

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