Inorg. Chem. **2006**, *45*, 1815–1822

Inorganic Chemistry
Article

Dizinc Alkoxides and Amides Supported by Binucleating Bis(amidoamine) Ligands

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Received September 28, 2005

Several new dizinc complexes that are supported by dianionic bis(amidoamine) ligands are reported. Reaction of *N*,*N*′-bis(2-dimethylaminoethyl)dibenzofuran-4,6-diamine ($^{Me}LH_2$) with 2 equiv of $EtZn(O^iPr)$ forms the dizinc bis(alkoxide) $^{Me}LZn_2(O^iPr)_2$ (1), which was isolated in 76% yield. Similarly, $^{Me}LH_2$ reacts cleanly with EtZn(OPh) and $EtZn(OCHPh_2)$ to form $^{Me}LZn_2(OPh)_2$ (**2**) and $^{Me}LZn_2(OCHPh_2)_2$ (**3**), respectively. The solid-state structures of **1** and **2** feature puckered $[Zn_2(\mu\text{-}OR)_2]^{2+}$ cores, with short intermetal separations (2.81–2.88 Å). Overall, the molecules have approximate (noncrystallographic) C_{2v} symmetry. The use of the more-hindered ^{i}Pr-substituted ligand *N*,*N*′-bis(2-diisopropylaminoethyl)dibenzofuran-4,6-diamine ($^{iPr}LH_2$) to prepare zinc alkoxides gave similar results. Thus, reaction of $^{iPr}LH_2$ with 2 equiv of EtZn(OPh), EtZn(OMe), $EtZn(OCHPh_2)$, and $EtZn(OCH_2Ph)$ forms $^{iPr}LZn_2(OPh)_2$ (**4**), $^{iPr}LZn_2(OMe)_2$ (**5**), $^{iPr}LZn_2(OCHPh_2)_2$ (**6**), and $^{iPr}LZn_2(OCH_2Ph)_2$ (**7**), respectively (isolated yields 48–63%). At 70 °C, C_6D_6 solutions of **6** undergo β-hydride transfer with 2 equiv of benzaldehyde to form **7** and benzophenone in quantitative yield (according to ^{1}H NMR spectroscopy). Benzene solutions of **1** react with 1 equiv of trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf) to form $^{Me}LZn_2(O^iPr)(OTf)$ (**8**) in 70% isolated yield. In the solid state, **8** features a bridging alkoxide donor as well as a 1,3-bridging triflate group. The previously reported dinuclear organozinc species $^{Me}LZn_2Ph_2$ (**9**) reacts with 1 equiv of *tert*-butylamine to form the protonolysis product $^{Me}LZn_2(Ph)(NH^tBu)$ (**10**) in 66% isolated yield. The solid-state structure of **10** (two independent molecules) reveals a somewhat asymmetric $[Zn_2(\mu\text{-}Ph)(\mu\text{-}NH^tBu)]^{2+}$ core with short Zn–Zn separations [2.6761(5) and 2.6518(5) Å]. In CD_2Cl_2 solution, the Ph bridge of **10** undergoes rapid reversible cleavage. Cleavage of this bridging interaction followed by rotation about the Zn–Ph bond and re-formation of the bridging interaction results in exchange of the inequivalent ortho (and meta) protons of the phenyl ligand. Variable-temperature ^{1}H NMR spectroscopic data indicate that this exchange occurs with $\Delta G^\ddagger = 12.7(1)$ kcal·mol^{-1} (–27 °C). At 75 °C, toluene solutions of $^{Me}LH_2$ react with 2 equiv of $EtZnNH^tBu$ to form the dizinc bis(amido) product $^{Me}LZn_2(NH^tBu)_2$ (**11**) in 46% isolated yield. The solid-state structure of **11** (two independent molecules) features a puckered and fairly symmetric $[Zn_2(\mu\text{-}NH^tBu)_2]^{2+}$ core with short intermetal separations [2.775(1), 2.760(1) Å].

Introduction

Bimetallic complexes play important roles in numerous areas of chemistry, including metalloprotein modeling, supramolecular chemistry, and catalysis.[1] To control the physical properties and chemical reactivities of this class of compounds, it is necessary that a broad range of well-defined binucleating ligands be developed.[2] Generally, these ligands feature multiple donor groups that are linked together with some sort of unreactive spacer. When properly designed, these ligands can prevent unwanted processes such as fragmentation and oligomerization. Their design can also useful for tailoring reactivity. In this context, we have been developing new preorganized binucleating ligands that are suitable for the preparation of main-group-metal bimetallics, including a range of dialuminum and dizinc complexes

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10.1021/ic051669f CCC: $33.50

supported by bis(amidinate)[3,4] and bis(amidoamine)[5] ligands. Here, we present the preparation and characterization of a series of dizinc alkoxide and amido derivatives supported by bis(amidoamine) ligands. These results contribute to the growing number of well-defined zinc alkoxides of low nuclearity that have attracted significant interest as catalysts for lactide polymerization[6] and epoxide/CO_2 copolymerization reactions.[7]

Experimental Section

General Considerations. Standard Schlenk-line and glovebox techniques were used unless stated otherwise. $^{Me}LH_2$,[5a,8] $^{iPr}LH_2$,[8] and $^{Me}LZn_2Ph_2$ [5a,8b] (**9**) were prepared as previously described. 2-Propanol, *tert*-butylamine, benzaldehyde, and methanol were distilled from CaH_2 under N_2 prior to use. Phenol, benzhydrol, benzyl alcohol, trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf), and $ZnEt_2$ were purchased from Sigma-Aldrich and were used as received. Hexanes, Et_2O, toluene, tetrahydrofuran (THF), and CH_2Cl_2 were passed through columns of activated alumina and sparged with N_2 prior to use. C_6D_6 and C_7D_8 were vacuum-transferred from sodium benzophenone ketyl. CD_2Cl_2 and $CDCl_3$ were vacuum-transferred from CaH_2. Elemental analyses were performed by Desert Analytics and the University of Michigan elemental analysis laboratory. Analytical data are provided for at least one representative of each type of compound reported.

$^{Me}LZn_2(O^iPr)_2$ (1). Toluene (10 mL) and $ZnEt_2$ (1.19 mL, 11.6 mmol) were combined in a 100-mL round-bottomed flask. The mixture was cooled to 0 °C, and 2-propanol (0.890 mL, 11.6 mmol) was added. Gas evolution was observed. The colorless solution was stirred for 30 min during which time it reached ambient temperature. To the mixture was added $^{Me}LH_2$ (1.98 g, 5.80 mmol) in toluene (15 mL) to form a colorless solution. The mixture was heated to 75 °C for 2 days. The removal of the volatiles under reduced pressure afforded the crude product as a colorless solid. This was purified by crystallization from Et_2O at −40 °C (2.56 g, 75.6%). ^1H NMR (C_6D_6): δ 7.51 (t, J = 7.8 Hz, 2H), 7.39 (dd, J = 1.0, 7.8 Hz, 2H), 6.76 (dd, J = 1.0, 7.8 Hz, 2H), 4.06 (sept, J = 6.0 Hz, 2H), 3.26 (t, J = 5.5 Hz, 4H), 2.26 (t, J = 5.5 Hz, 4H), 1.99 (s, 12H, NMe_2) 0.98 (d, J = 6.0 Hz, 12H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 146.3, 144.2, 125.9, 125.0, 106.7, 104.6, 67.4, 62.1, 45.9, 43.8, 29.0. Anal. Calcd (found) for $C_{26}H_{40}N_4O_3Zn_2$: C, 53.16 (53.56); H, 6.86 (6.60); N, 9.54 (9.38).

$^{Me}LZn_2(OPh)_2$ (2). The compound was prepared using a method analogous to that described for **1** with the following differences: Phenol was used in place of 2-propanol. The reaction mixture was heated to 75 °C for 3 days and then filtered while hot into a warm Schlenk tube. Colorless crystals of the product formed as the solution slowly cooled to room temperature. Further cooling to 5 °C yielded additional $^{Me}LZn_2(OPh)_2$ (58% yield). ^1H NMR (CD_2Cl_2): δ 7.07 (t, J = 1.0, 7.8 Hz, 2H), 7.01 (t, J = 7.6 Hz, 4H), 6.88 (d, J = 7.6 Hz, 2H), 6.77 (d, J = 8.0 Hz, 4H), 6.68 (t, J = 7.6 Hz, 2H), 6.41 (d, J = 8.0 Hz, 2H), 3.39 (t, J = 5.6 Hz, 4H), 2.88 (t, J = 5.6 Hz, 4H), 2.55 (s, 12H, NMe_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 162.8, 145.9, 143.5, 130.1, 124.8, 124.5, 119.7, 119.6, 106.4, 103.8, 62.6, 46.3, 43.3. Anal. Calcd (found) for $C_{32}H_{36}N_4O_3Zn_2$: C, 58.64 (58.35); H, 5.54 (5.34); N, 8.55 (8.30).

$^{Me}LZn_2(OCHPh_2)_2$ (3). The compound was prepared using a method analogous to that described for **1** with the following differences: Benzhydrol was used in place of 2-propanol. Colorless crystals of the product formed in the reaction mixture at 75 °C. After being cooled to ambient temperature, they were isolated and dried under reduced pressure to give $^{Me}LZn_2(OCHPh_2)_2$ in 68% yield. ^1H NMR (CD_2Cl_2): δ 7.20−7.05 (m, 22H, ArH), 7.01 (dd, J = 1.2, 7.6 Hz, 2H), 6.30 (d, J = 7.6 Hz, 2H), 5.99 (s, 2H, OC*H*Ph$_2$), 2.77 (t, J = 5.6 Hz, 4H), 1.81 (s, 12H), 1.64 (t, J = 5.6 Hz, 4H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 147.2, 145.9, 144.5, 128.5, 128.2, 127.5, 125.1, 124.6, 105.8, 102.5, 80.5 (O*C*HPh$_2$), 60.8, 45.6, 43.1. Anal. Calcd (found) for $C_{46}H_{48}N_4O_3Zn_2$: C, 66.11 (66.40); H, 5.79 (5.88); N, 6.70 (6.66).

$^{iPr}LZn_2(OPh)_2$ (4). The compound was prepared using a method analogous to that described for **1** with the following differences: Benzene, phenol, and $^{iPr}LH_2$ were used in place of toluene, 2-propanol, and $^{Me}LH_2$, respectively. The reaction mixture was heated to 75 °C for 3 days. Colorless crystals of the product formed upon cooling of the reaction solution to ambient temperature. The solution was then cooled to 5 °C overnight, and the product was isolated and dried under reduced pressure (56% yield). ^1H NMR (CD_2Cl_2): δ 7.08 (t, J = 7.8 Hz, 2H), 6.91−6.96 (m, 6H), 6.63−6.70 (m, 6H), 6.33 (dd, J = 1.0, 7.8 Hz, 2H), 3.39 (sept, J = 6.8 Hz, 4H), 3.27 (t, J = 5.8 Hz, 4H), 3.02 (t, J = 5.8 Hz, 4H), 1.37 (d, J = 6.4 Hz, 12H), 1.09 (d, 6.8 Hz, 12H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 162.2, 145.5, 143.6, 129.7, 124.9, 124.4, 121.2, 120.0, 106.2, 103.5, 53.3, 52.2, 45.9, 21.5, 21.2.

$^{iPr}LZn_2(OMe)_2$ (5). The compound was prepared using a method analogous to that described for **1** with the following differences: Methanol and $^{iPr}LH_2$ were used in place of 2-propanol and $^{Me}LH_2$, respectively. The reaction mixture was heated to 100 °C for 3 days. Colorless crystals of the product formed as the solution was cooled to ambient temperature. The solution was then cooled to 5 °C overnight, and the product was isolated and dried under reduced pressure (63% yield). ^1H NMR (C_6D_6): δ 7.55 (t, J = 7.8 Hz, 2H), 7.43 (dd, J = 1.0, 7.6 Hz, 2H), 6.81 (dd, J = 1.0, 7.8 Hz, 2H), 3.44 (s, 6H, OMe), 3.33 (t, J = 5.8 Hz, 4H), 3.06 (sept, J = 6.6 Hz, 4H), 3.60 (t, J = 5.8 Hz, 4H), 0.98 (d, J = 6.8 Hz, 12H), 0.96 (d, J = 6.4 Hz, 12H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 146.9, 144.8, 125.6, 124.9, 106.5, 104.5, 55.1, 51.1, 49.2, 45.0, 20.5, 20.3.

$^{iPr}LZn_2(OCHPh_2)_2$ (6). The compound was prepared using a method analogous to that described for **1** with the following

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differences: Benzhydrol and $^{iPr}LH_2$ were used in place of 2-propanol and $^{Me}LH_2$, respectively. Colorless crystals of the product formed upon cooling of the reaction solution to ambient temperature. Vapor diffusion of hexanes into the mixture afforded additional product (48%). ^1H NMR (C_6D_6): δ 7.63 (t, $J = 7.6$ Hz, 2H), 7.55 (dd, $J = 0.8, 7.6$ Hz, 2H), 7.11−7.16 (m, 8H, ArH), 6.88−6.93 (m, 12H, ArH), 6.64 (dd, $J = 0.8, 7.6$ Hz, 2H), 6.20 (s, 2H, OC*H*Ph$_2$), 2.79 (t, $J = 5.6$ Hz, 4H), 2.69 (sept, $J = 6.8$ Hz, 4H), 1.77 (t, $J = 5.6$ Hz, 4H), 0.90 (br, 24H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 147.0, 146.3, 144.5, 129.4, 127.9, 127.3, 126.0, 125.4, 107.2, 104.3, 81.9 (O*C*HPh$_2$), 53.5, 52.2, 45.6, 21.8.

$^{iPr}LZn_2(OCH_2Ph)_2$ (7). The compound was prepared using a method analogous to that described for **1** with the following differences: Benzyl alcohol and $^{iPr}LH_2$ were used in place of 2-propanol and $^{Me}LH_2$, respectively. The product was isolated as colorless crystals following the cooling of the reaction solution to −40 °C (63%). ^1H NMR (C_6D_6): δ 7.60 (t, $J = 7.6$ Hz, 2H), 7.48 (dd, $J = 1.0, 7.6$ Hz, 2H), 7.06−7.30 (m, 10H), 6.82 (dd, $J = 1.0, 7.6$ Hz, 2H), 4.70 (s, 4H, OC*H*$_2$Ph), 3.21 (t, $J = 6.0$ Hz, 4H), 2.86 (sept, $J = 6.8$ Hz, 4H), 2.20 (t, $J = 6.0$ Hz, 4H), 0.95 (d, $J = 6.8$ Hz, 12H), 0.80 (d, $J = 7.8$ Hz, 12H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 146.8, 144.9, 144.7, 129.6, 128.3, 127.3, 125.8, 125.2, 106.7, 104.5, 70.0 (O*C*H$_2$Ph), 51.4, 50.0, 45.2, 21.2, 20.6.

Reduction of PhCHO with 6. Benzaldehyde (10.0 μL, 98.2 μmol) was added to a C_6D_6 solution (0.5 mL) of **6** (46.5 mg, 49.1 μmol) in the presence of an internal standard (1,3,5-trimethoxybenzene). The clear colorless solution was allowed to stand at ambient temperature for 6 d. Analysis by ^1H NMR spectroscopy indicated 80% conversion to **7** and benzophenone. The solution was heated to 70 °C for 12 h, after which NMR spectroscopy indicated complete conversion to the aforementioned products.

$^{Me}LZn_2(O^iPr)(OTf)$ (8). Me_3SiOTf (0.188 mL, 1.04 mmol) was added to a benzene solution (100 mL) of **1** (0.608 g, 1.04 mmol) to form a clear, colorless solution. The solution was allowed to stand for 30 h during which time colorless crystals of product formed (0.490 g, 69.6%). ^1H NMR (CD_2Cl_2): δ 7.11 (t, $J = 7.6$ Hz, 2H), 6.93 (dd, $J = 1.2, 7.6$ Hz, 2H), 6.45 (dd, $J = 1.2, 7.6$ Hz, 2H), 4.27 (sept, $J = 6.0$ Hz, 2H, ZnOC*H*Me$_2$), 3.39 (m, 4H), 3.04 (m, 2H), 2.84 (m, 2H), 2.60 (s, 6H), 2.57 (s, 6H), 1.24 (d, $J = 6.0$ Hz, 6H, ZnOCH*Me*$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 145.7, 143.5, 125.1, 124.5, 106.8, 103.8, 71.0, 61.8, 46.5, 46.1, 44.2, 28.2. ^{19}F NMR (CD_2Cl_2) δ −78.2 (s). Anal. Calcd (found) for $C_{25.5}H_{34.5}F_3N_4O_5SZn_2$ [**8**·(benzene)$_{0.25}$]: C, 43.93 (43.63); H, 4.99 (5.17); N, 8.04 (7.66).

$^{Me}LZn_2(Ph)(NHtBu)$ (10). Toluene (20 mL) was added to $^{Me}LZn_2Ph_2$ (**9**) (0.362 g, 0.581 mmol). To the colorless suspension was added *tert*-butylamine (61.0 μL, 0.581 mmol). The solution was stirred for 24 h at ambient temperature. Cooling the solution to 5 °C yielded the product as colorless crystals (0.212 g, 66.2%). ^1H NMR (CD_2Cl_2): δ 7.1−7.7 (br, 5H, ZnPh), 7.06 (t, $J = 7.8$ Hz, 2H), 6.48 (dd, $J = 1.0, 7.6$ Hz, 2H), 6.29 (dd, $J = 1.0, 7.6$ Hz, 2H), 3.30 (m, 2H), 3.11 (m, 4H), 2.56 (s, 6H), 2.43 (m, 2H), 1.40 (s, 6H), 1.38 (s, 1H, NH), 1.20 (s, 9H, N^{t}Bu). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 145.6, 144.5, 144.3 (ipso Zn−Ph), 131.4, 128.1 (br), 124.6, 124.4, 105.2, 102.4, 61.3, 51.5, 47.4, 44.1, 42.1, 35.2. Anal. Calcd (found) for $C_{30}H_{41}N_5OZn_2$: C, 58.26 (58.23); H, 6.68 (6.43); N, 11.32 (11.32).

$^{Me}LZn_2(NHtBu)_2$ (11). $ZnEt_2$ (0.302 mL, 2.94 mmol), *tert*-butylamine (0.307 mL, 2.94 mmol), and toluene (125 mL) were combined in a 250-mL round-bottomed flask. The colorless solution was heated to 75 °C for 24 h. At ambient temperature, $^{Me}LH_2$ (0.501 g, 1.47 mmol) was added, and the resulting colorless solution was heated to 75 °C for 24 h. The hot solution was filtered into a warm Schlenk tube, which was slowly cooled to 5 °C. The product was isolated as colorless crystals (0.418 g, 46.4%). ^1H NMR ($CDCl_3$): δ 7.12 (t, $J = 7.6$ Hz, 2H), 6.86 (dd, $J = 1.2, 7.6$ Hz, 2H), 6.37 (dd, $J = 1.2, 7.6$ Hz, 2H), 3.41 (t, $J = 5.6$ Hz, 4H), 2.88 (t, $J = 5.6$ Hz, 4H), 2.54 (s, 12H, NMe$_2$), 0.97 (s, 18H, N^{t}Bu), 0.22 (s, 2H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 144.5, 144.1, 125.0, 123.9, 104.7, 102.2, 61.7, 51.0, 47.0, 44.0, 35.8. Anal. Calcd (found) for $C_{30.3}H_{48.7}N_6OZn_2$ [**11**·(toluene)$_{0.33}$]: C, 56.56 (56.31); H, 7.61 (7.38); N, 13.04 (12.87).

NMR Spectroscopy. NMR spectra were measured on a Varian Inova-400 NMR spectrometer, at an ^1H observation frequency of 400.16 MHz. Chemical shifts (δ) for ^1H NMR (400 MHz) spectra are given relative to residual protium in the deuterated solvent at 7.16, 5.32, 7.27, and 2.09 ppm for C_6D_6, CD_2Cl_2, $CDCl_3$, and C_7D_8, respectively. Sample temperatures for variable-temperature NMR experiments were calibrated using 100% methanol by measuring the chemical shift between the OH resonance and the CH_3 resonance and using the temperature calibration utility in the VNMR 6.1C software. Variable-temperature NMR spectra were simulated, and exchange rate constants were determined using the DNMR3 utilities within the SpinWorks 2.4 software.[9]

X-ray Crystallography. Table 1 summarizes crystal data and collection parameters for all crystallographically characterized compounds. Table 2 lists selected bond lengths and angles for the core atoms. Additional data are presented as Supporting Information.

General Procedure. A crystal of appropriate size was mounted on a glass fiber using hydrocarbon oil (Paratone-N), transferred to a Siemens SMART diffractometer/CCD area detector, centered in the beam (Mo Kα, $\lambda = 0.71073$ Å, graphite monochromator), and cooled to −125 ± 10 °C by a nitrogen low-temperature apparatus. Preliminary orientation matrix and cell constants were determined by collection of 60 frames, followed by spot integration and least-squares refinement. A minimum of a hemisphere of data was collected using 0.3° ω scans. The raw data were integrated, and the unit cell parameters were refined using SAINT. Data analysis was performed using XPREP. Absorption correction was applied using SADABS. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. Structure solutions and refinements were performed (SHELXTL-Plus V5.1) on F^2.[10] Notable details of each data collection and refinement are described below.

Structure of $^{Me}LZn_2(O^iPr)_2$·Et_2O (1·Et_2O). Crystals suitable for X-ray diffraction studies were grown from Et_2O at −40 °C. Preliminary data indicated a triclinic cell. Choice of the centric space group was confirmed by the successful solution and refinement of the structure. The asymmetric unit contains two independent molecules of **1** and two cocrystallized Et_2O. Analysis using PLATON did not reveal any missed symmetry, and an attempt to solve the structure in space group *C*2/*m* failed. One of the μ-O^{i}Pr groups is disordered over two positions (C47−C49, C47A−C49A) with 67% and 33% occupancies. These atoms were refined isotropically. All other non-H atoms were refined anisotropically. Hydrogens were placed in idealized positions and were included in structure factor calculations but were not refined.

Structure of $^{Me}LZn_2(OPh)_2$·(Toluene)$_{0.5}$ [2·(Toluene)$_{0.5}$]. Crystals suitable for X-ray diffraction studies were grown from toluene at ambient temperature. Preliminary data indicated a primitive monoclinic cell. Systematic absences indicated space group $P2_1/n$ (No. 14). This choice was confirmed by the successful solution

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(9) Software by Kirk Marat at the University of Manitoba. For more information, see http://www.umanitoba.ca/chemistry/nmr/spinworks.

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Table 1. Crystallographic Data and Collection Parameters

	1·Et$_2$O	**2·(toluene)$_{0.5}$**	**4**
formula	$C_{30}H_{50}N_4O_4Zn_2$	$C_{35.5}H_{40}N_4O_3Zn_2$	$C_{40}H_{52}N_4O_3Zn_2$
formula wt (g·mol^{-1})	661.48	701.46	767.60
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
temp (K)	140(2)	142(2)	150(2)
a (Å)	10.1422(4)	10.2097(4)	12.2365(4)
b (Å)	16.8789(8)	12.0692(5)	19.4966(6)
c (Å)	19.4637(9)	26.8683(10)	15.2313(5)
α (deg)	82.1670(10)	90	90
β (deg)	75.3130(10)	90.7290	92.6670(10)
γ (deg)	89.6530(10)	90	90
Z	4	4	4
V (Å^3)	3191.6(2)	3310.5(2)	3629.8(2)
d_{calc} (g·cm^{-3})	1.377	1.407	1.405
θ range (deg)	2.35−29.23	2.27−31.47	2.34−31.22
μ (mm^{-1})	1.542	1.490	1.365
crystal size (mm)	0.40 × 0.15 × 0.15	0.36 × 0.34 × 0.30	0.40 × 0.30 × 0.20
reflections collected	21682	25413	23855
data/restraints/parameters	15019/0/741	7594/13/438	10103/0/450
R1 (for $F_o > 4sF_o$)	0.0649	0.0700	0.0548
R1, wR2 (all data)	0.1250, 0.1811	0.1330, 0.1470	0.0865, 0.1428
GOF	0.958	1.009	1.016
largest peak, hole (e·Å^{-3})	0.71, −1.00	0.69, −0.76	0.70, −0.82

	8·benzene	**10**	**11·(toluene)$_{0.25}$**
formula	$C_{30}H_{39}F_3N_4O_5SZn_2$	$C_{30}H_{41}N_5OZn_2$	$C_{28}H_{46}N_6OZn_2$
formula wt (g·mol^{-1})	755.45	618.42	613.45
space group	$P\bar{1}$ (No. 2)	$Pbca$ (No. 61)	$P2_1/n$ (No. 14)
temp (K)	156(2)	154(2)	152(2)
a (Å)	9.5997(10)	18.5586(5)	20.4807(9)
b (Å)	15.5502(10)	18.7571(6)	15.6023(7)
c (Å)	22.370(2)	33.5543(9)	20.6304(9)
α (deg)	89.489(2)	90	90
β (deg)	79.351(2)	90	109.5000(10)
γ (deg)	87.199(3)	90	90
Z	4	16	8
V (Å^3)	3278.0(6)	11680.4(6)	6214.2(5)
d_{calc} (g·cm^{-3})	1.531	1.407	1.311
θ range (deg)	2.19−26.42	2.39−27.46	2.39−18.96
μ (mm-1)	1.588	1.674	1.573
crystal size (mm)	0.35 × 0.20 × 0.10	0.50 × 0.20 × 0.15	0.20 × 0.10 × 0.10
reflections collected	26694	89337	50031
data/restraints/parameters	15613/0/823	13932/0/707	14810/0/667
R1 (for $F_o > 4sF_o$)	0.0969	0.0466	0.0866
R1, wR2 (all data)	0.1899, 0.2607	0.0978, 0.1125	0.2267, 0.2046
GOF	0.970	0.999	0.886
largest peak, hole (e·Å^{-3})	2.64, −2.05	0.46, −0.43	0.69, −0.62

and refinement of the structure. The asymmetric unit contains one molecule of **2** and a disordered, half-occupancy toluene located on a crystallographic inversion center. All non-H atoms were refined anisotropically. Hydrogens were placed in idealized positions and were included in structure factor calculations but were not refined.

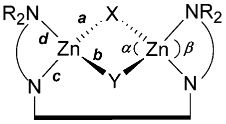
Structure of ^{iPr}LZn$_2$(OPh)$_2$ (4). Crystals suitable for X-ray diffraction studies were grown from C_6D_6 at ambient temperature. Preliminary data indicated a primitive monoclinic cell. Systematic absences indicated space group $P2_1/n$ (No. 14). This choice was confirmed by the successful solution and refinement of the structure. The asymmetric unit contains only one molecule of **4**. All non-H atoms were refined anisotropically. Hydrogens were placed in idealized positions and were included in structure factor calculations but were not refined.

Structure of ^{Me}LZn$_2$(O^{i}Pr)(OTf)·Benzene (8·Benzene). Needle-shaped crystals suitable for X-ray diffraction studies were grown from benzene at ambient temperature. Preliminary data indicated a triclinic cell. Choice of the centric space group was confirmed by the successful solution and refinement of the structure. The asymmetric unit contains two independent molecules of **8** and two cocrystallized benzene molecules. Analysis using PLATON did not reveal any missed symmetry. All non-H atoms were refined anisotropically. Hydrogens were placed in idealized positions and were included in structure factor calculations but were not refined.

Structure of ^{Me}LZn$_2$(Ph)(NHtBu) (10). Crystals suitable for X-ray diffraction studies were grown from toluene at 5 °C. Preliminary data indicated a primitive orthorhombic cell. Systematic absences indicated space group $Pbca$ (No. 61). This choice was confirmed by the successful solution and refinement of the structure. The asymmetric unit contains two independent molecules of **10**. Analysis using PLATON did not reveal any missed symmetry. All non-H atoms were refined anisotropically. Hydrogens were placed in idealized positions and were included in structure factor calculations but were not refined.

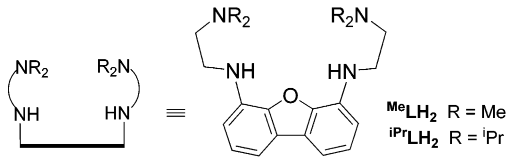
Structure of ^{Me}LZn$_2$(NHtBu)$_2$·(Toluene)$_{0.25}$ [11·(Toluene)$_{0.25}$]. Crystals suitable for X-ray diffraction studies were grown from hot toluene. Preliminary data indicated a primitive monoclinic cell. Systematic absences indicated space group $P2_1/n$ (No. 14). This choice was confirmed by the successful solution and refinement of the structure. The asymmetric unit contains two independent molecules of **11** and a cocrystallized toluene molecule located on a crystallographic inversion center. Analysis using PLATON did not reveal any missed symmetry. Attempts to model the disordered toluene molecule gave unacceptable metrical parameters. The data

Table 2. Core Bond Lengths and Angles for Dizinc Species

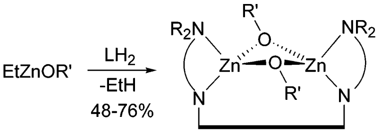


compound (X, Y)	(*a*) Zn−X (Å)	(*b*) Zn−Y (Å)	(*c*) Zn−N_{amido} (Å)	(*d*) Zn−N_{amine} (Å)	(a) X−Zn−Y (deg)	(b) N−Zn−N (deg)	Zn···Zn (Å)
$^{Me}LZn_2(O^iPr)_2$ (**1**)	1.982(3)	1.957(3)	1.941(4)	2.116(4)	83.3(1)	86.3(2)	2.8185(7)
(O^iPr, O^iPr)	1.971(3)	1.970(3)	1.939(4)	2.129(4)	83.2(1)	85.5(2)	
two molecules	1.986(3)	1.956(3)	1.942(4)	2.123(4)	83.3(1)	86.1(2)	2.8048(7)
	1.960(3)	1.973(3)	1.932(4)	2.134(4)	83.6(1)	85.5(2)	
$^{Me}LZn_2(OPh)_2$ (**2**)	1.972(3)	1.996(3)	1.917(4)	2.087(3)	80.5(1)	87.3(1)	2.8771(6)
(Oph, OPh)	2.001(3)	1.955(3)	1.925(3)	2.090(3)	80.8(1)	87.2(1)	
$i^{Pr}LZn_2(OPh)_2$ (**4**)	1.995(2)	1.993(2)	1.926(2)	2.143(3)	79.69(8)	87.1(1)	2.9435(5)
(Oph, OPh)	2.005(2)	1.988(2)	1.914(2)	2.131(2)	79.57(8)	88.2(1)	
$^{Me}LZn_2(O^iPr)(OTf)$ (**8**)	1.891(5)	2.082(5)	1.895(7)	2.107(7)	97.8(2)	87.8(3)	3.270(1)
(O^iPr, OTf)	1.906(5)	2.122(6)	1.889(6)	2.104(7)	97.4(2)	88.5(3)	
two molecules	1.921(5)	2.112(5)	1.908(6)	2.128(7)	94.5(2)	87.2(3)	3.274(1)
	1.910(6)	2.082(6)	1.893(7)	2.121(6)	100.4(2)	88.7(3)	
$^{Me}LZn_2(Ph)(NH^tBu)$ (**10**)	2.212(4)	2.003(3)	1.944(3)	2.153(3)	91.4(1)	84.5(1)	2.6761(5)
(Ph, NH^tBu)	2.130(4)	2.032(3)	1.962(3)	2.184(3)	93.0(1)	83.3(1)	
two molecules	2.211(4)	2.003(3)	1.950(3)	2.139(3)	92.5(1)	83.9(1)	2.6518(5)
	2.135(4)	2.031(3)	1.960(3)	2.151(3)	94.0(1)	84.2(1)	
$^{Me}LZn_2(NH^tBu)_2$ (**11**)	2.041(6)	2.066(6)	1.914(7)	2.198(6)	86.4(3)	83.5(3)	2.775(1)
(NH^tBu, NH^tBu)	2.017(6)	2.030(6)	1.939(6)	2.161(7)	88.0(2)	85.7(3)	
two molecules	2.024(6)	2.038(6)	1.938(6)	2.167(6)	88.7(2)	84.2(3)	2.760(1)
	2.055(6)	2.025(6)	1.938(6)	2.158(6)	88.2(2)	85.3(2)	

Chart 1



Scheme 1



	R	R'		R	R'
1	Me	^iPr	**4**	^iPr	Ph
2	Me	Ph	**5**	^iPr	Me
3	Me	$CHPh_2$	**6**	^iPr	$CHPh_2$
			7	^iPr	CH_2Ph

were corrected for the disordered solvent using PLATON/SQUEEZE. This gave a calculated potential solvent area of 360.0 Å (5.8% total volume) containing 108 electrons, which is consistent with ca. 2.2 molecules of toluene in the unit cell. The R1 value improved from 0.0985 to 0.0866 after the correction, and refinement of the model gave acceptable convergence. All non-H atoms were refined anisotropically. Hydrogens were placed in idealized positions and were included in structure factor calculations but were not refined.

Results and Discussion

The bis(diaminoethane) ligands $^{Me}LH_2$ and $^{iPr}LH_2$, shown in Chart 1, readily undergo protonolysis with zinc(alkoxy)-alkyl reagents. The products of these reactions are zinc alkoxide derivatives of the general formula $LZn_2(OR')_2$ (R′ = alkyl, aryl). For example, a toluene solution of $^{Me}LH_2$ reacted with 2 equiv of $EtZnO^iPr$, generated in situ from $ZnEt_2$ and 2-propanol, over 2 days at 75 °C to form $^{Me}LZn_2(O^iPr)_2$ (**1**) (Scheme 1). The product was isolated in 76% yield as colorless crystals following Et_2O workup. Repeating the reaction using phenol and benzhydrol in place of 2-propanol formed the closely related species $^{Me}LZn_2(OPh)_2$ (**2**) and $^{Me}LZn_2(OCHPh_2)_2$ (**3**), respectively. Complexes **2** and **3** were isolated as colorless crystals in moderate to good yields from toluene solutions. The ^1H NMR spectrum of **1** (in C_6D_6) indicates that the molecule has overall C_{2v} symmetry in solution. Thus, the four Me groups of the $^{Me}L^{2-}$ ligand are equivalent and appear as a singlet at δ 1.99 ppm. Also, the two isopropoxide ligands are equivalent, with the methine protons being observed as a septet at δ 4.06 ppm and the methyls as a doublet at δ 0.98 ppm. These data are consistent with **1** having a pair of bridging isopropoxide ligands. Alternatively, C_{2v} symmetry could also be observed for a structure without any bridging alkoxides, but this is quite unlikely given the general preference of Zn^{2+} for a coordination number of four instead of three. ^1H NMR spectroscopic data for both **2** and **3** (in CD_2Cl_2) similarly reveal C_{2v}-symmetric solution structures.

The solid-phase structures of 1 and **2** were determined by single-crystal X-ray diffraction. Thermal ellipsoid drawings are shown in Figure 1. Compound 1 crystallizes with two independent molecules in the asymmetric unit. The two molecules feature similar coordination geometries. Each distorted tetrahedral Zn center is coordinated to one bidentate bis(amidoamine) and two bridging isopropoxide ligands. The puckered $Zn_2(\mu\text{-}O^iPr)_2^{2+}$ cores feature Zn−O bonds that vary between 1.956 and 1.986 Å, which are comparable to reported values.[11] The alkoxide oxygens are significantly pyramidalized [$\sum$(angles at O)$_{avg}$ = 338°] consistent with

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(11) Melnik, M.; Györyová, K.; Skorsepa, J.; Holloway, C. E. *J. Coord. Chem.* **1995**, *35*, 179.

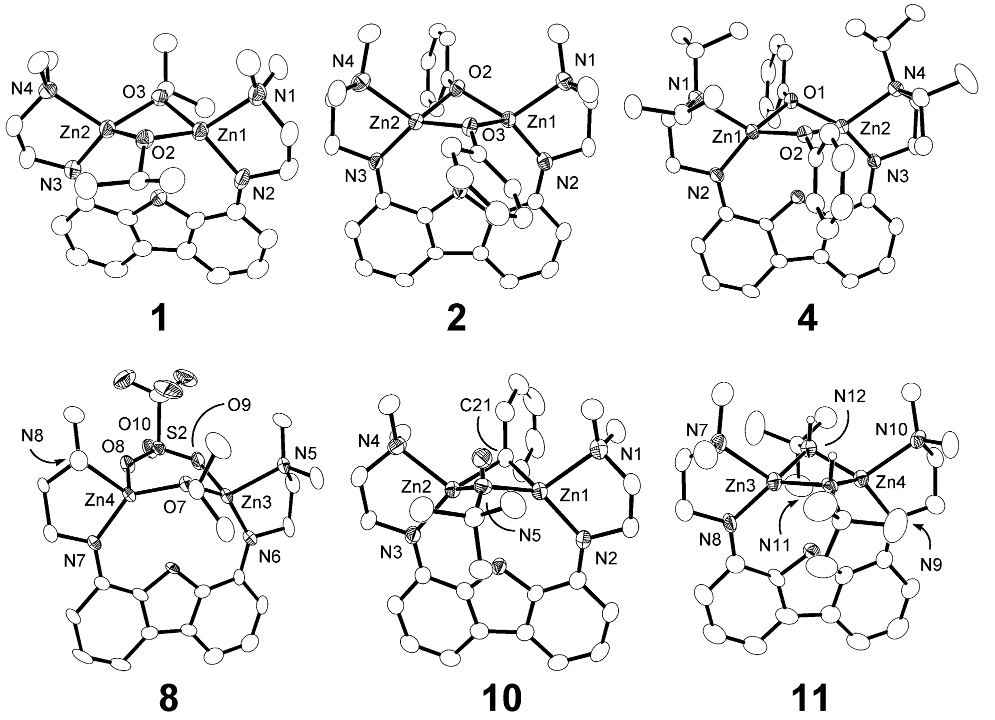

Figure 1. Molecular structures of all crystallographically characterized complexes drawn with 50% thermal ellipsoids. Hydrogens are omitted except for the N−H groups of the *tert*-butyl amido ligands of 11. Only one of two molecules in the asymmetric unit is shown for structures **1**, **8**, **10**, and **11**. Cocrystallized solvent molecules are omitted for **1**, **2**, **8**, and **11**.

the expected lack of π bonding with the d^{10} metal centers. The structural features of **2** are very similar to those of **1**, although the phenolate oxygens are less pyramidalized [Σ(angles at O) = 343.7, 349.5°] and the Zn−N bonds are slightly shorter.

A series of dizinc alkoxides supported by the isopropyl-substituted ligand $^{iPr}LH_2$ were studied to evaluate the effect of increased steric bulk on both structure and reactivity. Complexes **4**−**7** (Scheme 1) were prepared in a fashion similar to that used for the preparation of **1**−**3**. The complexes were all isolated in moderate to good yields as colorless crystals from benzene or toluene solutions and were characterized by a combination of NMR spectroscopy, combustion analysis, and single-crystal X-ray diffraction. The ^{1}H NMR spectra of **4**, **5**, and **7** are all fundamentally similar, so only that of **5** will be discussed. Analogous to what was observed for compounds **1**−**3**, compound **5** features C_{2v} symmetry in C_6D_6 solution. The bridging methoxides are observed as a singlet at δ 3.44 ppm, and the methine protons of the isopropyl groups are equivalent and appear as a septet at δ 3.06 ppm. The two methyls of each isopropyl group are inequivalent and are observed as doublets at δ 0.98 and 0.96 ppm. $^{13}C\{^1H\}$ NMR spectroscopic data confirm the inequivalence of the methyls (δ 20.5 and 20.3 ppm). These data indicate that the two methyls of each isopropyl group do not exchange on the NMR spectroscopic time scale. This suggests that the diisopropylamine donors remain coordinated to the Zn centers. In contrast, NMR spectroscopic data for **6** reveals some distinct behavior, which is a consequence of the bulky diphenylmethoxy ligands. The ^{1}H NMR spectrum of **6** (C_6D_6) features a single broad resonance at δ 0.90 ppm with an integrated intensity of 24 hydrogens for the methyls of the isopropyl groups. This suggests that the coordinated diisopropylamine donors undergo reversible dissociation followed by inversion at nitrogen to exchange the methyls of each isopropyl group. It is likely that this process is observed for only **6** because this molecule features a combination of the most hindered ligands used in this study.

The solid-state structures of **4** and **6** were determined by single-crystal X-ray diffraction. The structure of **6** is not included here because of the low quality of the data, but its overall structural features are related to those of **4**. Compound **4** features a symmetric and puckered $[Zn_2(\mu\text{-}OPh)_2]^{2+}$ core that is similar to that of **2**, which is supported by the less-hindered $^{Me}L^{2-}$ ligand. The effect of the isopropyl substitution of the bis(amidoamine) ligand is evident in several structural perturbations relative to compound **2**. First, for **4**, the Zn−Zn distance [2.9435(5) Å] is 0.066 Å longer and its O−Zn−O angles [79.57(8), 79.69(8)°] are about 1° smaller than the related parameters of **2**. Steric repulsions between the isopropyl groups and the metal center also result in an average 0.05 Å increase in the $Zn-N_{amine}$ distances relative to those of **2**.

Zinc alkoxides have been shown to catalyze the oxidation of alcohols to aldehydes and ketones[12] in a fashion similar to that of the Zn-containing enzyme liver alcohol dehydrogenase (LADH).[13] We examined whether $^{iPr}LZn_2(OCHPh_2)_2$

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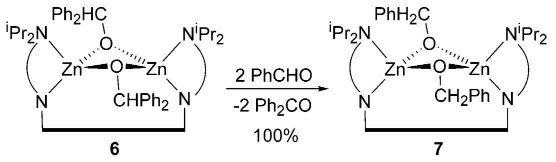
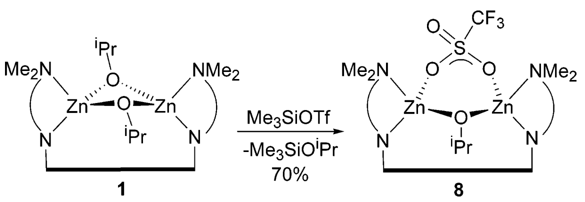
(12) (a) Bergquist, C.; Parkin, G. *Inorg. Chem.* **1999**, *38*, 422. (b) Walz, R.; Vahrenkamp, H. *Inorg. Chim. Acta* **2001**, *314*, 58.

(13) (a) Holm, R. H.; Kennepohl, P.; Solomon, E. I. *Chem. Rev.* **1996**, *96*, 2239. (b) Lipscomb, W. N.; Strater, N. *Chem. Rev.* **1996**, *96*, 2239. (c) Berreau, L. M.; Makowska-Grzyska, M. M.; Arif, A. M. *Inorg. Chem.* **2001**, *40*, 2212. (d) Kimura, E.; Shionoya, M.; Hoshino, A.; Ikeda, T.; Yamada, Y. *J. Am. Chem. Soc.* **1992**, *114*, 10134. (e) Cronin, L.; Walton, P. H. *Chem. Commun.* **2003**, 1572.

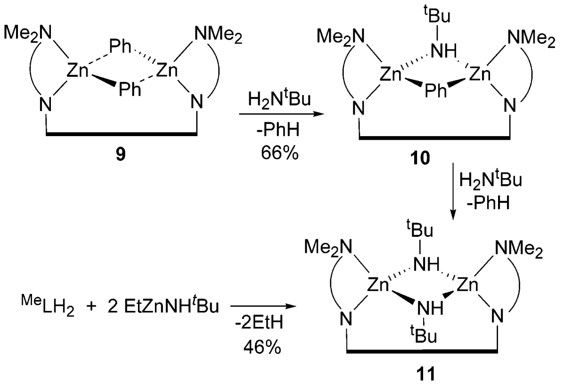
Scheme 2



Scheme 3



Scheme 4



was compatible with the reduction of organic carbonyls. As shown in Scheme 2, a C_6D_6 solution of 6 and 2 equiv of benzaldehyde showed 80% conversion (^{1}H NMR spectroscopy) to **7** and benzophenone over 6 days. Heating of the solution to 70 °C overnight gave quantitative conversion to the products. The reaction occurs by the formal hydride transfer from the diphenylmethoxy ligand to benzaldehyde.

A single isopropoxide ligand of **1** can be selectively substituted using Si-based reagents. Thus, the addition of 1 equiv of Me_3SiOTf (OTf = O_3SCF_3) to a benzene solution of **1** formed the mixed-ligand complex $^{Me}LZn_2(O^iPr)(OTf)$ (**8**; Scheme 3), which crystallized from the reaction solution in 70% yield. The ^{1}H NMR spectrum of 8 dissolved in CD_2Cl_2 indicates overall C_s symmetry, with the mirror plane of symmetry oriented perpendicular to the intermetal axis and passing through the bridging triflate and alkoxide ligands. Thus, the two methyls of each dimethylamino donor are inequivalent, and they are observed as two sharp singlets at δ 2.60 and 2.57 ppm. There is also a distinct septet at δ 4.27 ppm (1H) that is assigned to the methine of the isopropoxide ligand. The presence of the triflate ligand was confirmed by a single fluorine resonance in the ^{19}F NMR spectrum (δ −78.2 ppm). The molecular structure of **8** was determined by single-crystal X-ray diffraction. There are two independent molecules in the asymmetric unit. They are essentially identical with the exception of some minor variations ($\lesssim$1%) in metrical parameters. Each complex features a $[Zn_2(1,3\text{-}\mu\text{-OTf})(\mu\text{-O}^iPr)]^{2+}$ core with bridging isopropoxide and triflate ligands. The triflate anion forms a three-atom bridge between the two Zn centers with Zn−O bonds formed to two of the three sulfonate oxygens. As expected, the Zn−alkoxide bonds (avg 1.907 Å) are much shorter than the Zn−OTf bonds (avg 2.100 Å). It is also notable that the Zn−O^{i}Pr bonds of **8** are, on average, 0.07 Å shorter than the related bonds of the bis(isopropoxide) derivative **1**. This is expected because the triflate ligand is a much poorer donor than the alkoxide. It is likely that the weakly basic triflate ligand is susceptible to displacement by added Lewis bases, but we have not yet explored these reactions.

In addition to the aforementioned zinc alkoxide derivatives, we have also prepared some related zinc amido derivatives. The first of these complexes, $^{Me}LZn_2(Ph)(NH^tBu)$ (10), was prepared in the interest of comparing its properties to those of $^{Me}LZn_2(Ph)(OCHPh_2)$, which was recently shown to feature a bridging phenyl group that undergoes reversible cleavage in solution with $\Delta G^\ddagger = 11.5(1)$ kcal·mol^{-1} (−50 °C).[8b] Compound **10** was formed by reaction of 1 equiv of *tert*-butylamine with $^{Me}LZn_2Ph_2$ (**9**) in toluene solution (Scheme 4). Cooling the solution to 5 °C afforded the product as colorless crystals in 66% yield. The structure of 10 was determined. One of the two independent molecules in the asymmetric unit is shown in Figure 1. Overall, the structure of **10** is quite similar to that of $^{Me}LZn_2(Ph)(OCHPh_2)$. It features a dizinc core with bridging amido and phenyl groups. Each phenyl group bridges two Zn centers in an unsymmetrical fashion, with one short [Zn2−C21, 2.130(4) Å; Zn4−C51, 2.135(4) Å] and one long [Zn1−C21, 2.212(4) Å; Zn3−C51, 2.211(4) Å] Zn−Ph interaction. The zinc centers (e.g., Zn2) that form the shorter bonds to the phenyl donors are, on average, 1.04 Å out of the calculated phenyl group planes. In contrast, the zincs involved in the longer Zn−Ph bonds are, on average, 1.60 Å out of the calculated phenyl planes. These latter Zn centers are expected to have less overlap with the in-plane donor orbital.

The ^{1}H NMR spectrum of **10** in CD_2Cl_2 indicates overall C_s symmetry, with the mirror plane of symmetry oriented perpendicular to the Zn···Zn internuclear axis. The Me groups of the dimethylamino donors are observed as two sharp singlets at δ 2.56 and 1.40 ppm. Resonances at δ 1.38 (1H) and 1.20 (9H) ppm were assigned to the NH and ^{t}Bu groups of the bridging amido ligand, respectively. The ortho and meta hydrogens of the Zn−Ph group were observed as two very broad overlapping resonances between δ 7.1 and 7.7 ppm. These sharpen into two distinct resonances at elevated temperatures. The equivalence of the ortho protons at elevated temperatures is consistent with a dynamic process in which the bridging Ph group is cleaved to form a species with a terminal Zn−Ph group.[8b] Rotation about the Zn−Ph bond prior to reformation of the Ph bridge would lead to exchange of the two ortho (and meta) protons. Consistent with this mechanism, ^{1}H NMR spectroscopic data acquired at −70 °C reveal five distinct resonances for the Zn−Ph group (ortho, δ 7.67 and 7.14 ppm; meta, δ 7.35 and 7.03 ppm; para, δ 7.25 ppm), consistent with an intact Ph bridge under these conditions. Analysis of the temperature dependence of these data indicates that the exchange occurs with

$\Delta G^{\ddagger} = 12.7(1)$ kcal·mol^{-1} (-27 °C). These data show that the phenyl bridge in complex **10** is slightly more robust than that of $^{Me}LZn_2(Ph)(OCHPh_2)$.

Dizinc bis(amido) derivatives can be prepared analogously to the bis(alkoxides)described earlier. For example, a toluene solution of $EtZn(NH^tBu)$, prepared in situ from $ZnEt_2$ and *tert*-butylamine, reacted with $^{Me}LH_2$ at 75 °C to form $^{Me}LZn_2(NH^tBu)_2$ (11). Cooling the solution to 5 °C afforded the product as colorless crystals in 46% yield. The same product can be formed in high yield by reaction of **10** with 1 equiv of *tert*-butylamine in toluene at 70 °C. The ^{1}H NMR spectrum of **11** ($CDCl_3$) indicates a highly symmetric (C_{2v}) structure. The solid-state structure of **11** was determined by single-crystal X-ray diffraction. Two independent molecules are present in the asymmetric unit. Each molecule features a pair of pseudo-tetrahedral Zn centers coordinated to the bis(amidoamine) ligand and two bridging amido ligands. The $[Zn_2(\mu\text{-}NH^tBu)_2]^{2+}$ cores are moderately puckered. The core atoms of each molecule form a slightly asymmetric Zn_2N_2 four-membered ring. The Zn−N bond lengths average 2.04 Å, but the individual bonds vary from 2.017(6) to 2.066(6) Å.

In conclusion, we have reported a new series of dizinc alkoxide and amido derivatives supported by preorganized bis(amidoamine) ligands. Reactivity studies of these and related derivatives are currently being pursued.

Acknowledgment. We thank the Petroleum Research Fund (38046-G3), administered by the ACS, for funding. NMR instrumentation used in this work was supported in part by the National Science Foundation CRIF program, Award CHE-0131003.

Supporting Information Available: Crystallographic information files (CIF) are provided for compounds **1**, **2**, **4**, **8**, **10**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC051669F