Phenylation of Benzaldehyde by Dizinc Organometallics Supported by Binucleating Bis(amidoamine) Ligands

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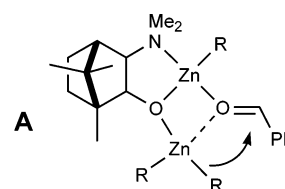
Several new dizinc organometallics that are supported by dianionic bis(amidoamine) ligands are reported. The reaction of N,N'-bis(2-(diisopropylamino)ethyl)dibenzofuran-4,6-diamine ($^{iPr}LH_2$) with excess ZnR_2 (R = Et, Me) in toluene solution forms the dizinc derivatives $^{iPr}LZn_2Et_2$ (**1**) and $^{iPr}LZn_2Me_2$ (**2**), which were isolated in 69% and 72% yields, respectively. Both **1** and **2** feature three-coordinate zinc centers in the solid state. Reaction of 2 equiv of $ZnPh_2$ with N,N'-bis(2-(dimethylamino)ethyl)dibenzofuran-4,6-diamine ($^{Me}LH_2$) forms $^{Me}LZn_2Ph_2$ (**3**), which was isolated in 73% yield. The analogous reaction using $^{iPr}LH_2$ instead of $^{Me}LH_2$ forms $^{iPr}LZn_2Ph_2$ (**4**), which was isolated in 56% yield. The solid-state structure of **3** (two independent molecules) reveals a parallelogram-shaped $[Zn_2(\mu\text{-Ph})_2]^{2+}$ core, with the overall molecule having approximate (noncrystallographic) C_2 symmetry and a short intermetal separation (2.7279(6) and 2.7809(6) Å). In contrast, the ^1H NMR spectrum of **3** (CD_2Cl_2) indicates overall C_{2v} symmetry; this is likely due to cleavage of the phenyl bridges in solution. The solid-state structure of **4**, which features the bulkier ^iPr-substituted ligand, reveals the absence of Ph bridges. Instead, each molecule of **4** has a pair of essentially noninteracting three-coordinate Zn centers. Benzene solutions of **3** react with 1 equiv of benzaldehyde to form the addition product $^{Me}LZn_2(Ph)(OCHPh_2)$ (**5**) in 87% isolated yield. The solid-state structure of **5** reveals a symmetric and puckered $[Zn_2(\mu\text{-Ph})(\mu\text{-OCHPh}_2)]^{2+}$ core with a short Zn−Zn separation of 2.6977(13) Å. In CD_2Cl_2 solution, the Ph bridge of **5** undergoes reversible cleavage. This process followed by rotation about the Zn−Ph bond leads to exchange of the inequivalent ortho (and meta) protons of the μ-Ph ligand. Variable-temperature ^1H NMR spectroscopic data indicates that this exchange occurs with $\Delta G^\ddagger = 11.5(1)$ kcal mol^{-1} (-50 °C). At 70 °C, benzene solutions of **5** react with 1 equiv of benzaldehyde to form the double-addition product $^{Me}LZn_2(OCHPh_2)_2$ (**6**) in 67% isolated yield. The related species $^{iPr}LZn_2(OCHPh_2)_2$ (**7**) was formed in good yield by the reaction of 2 equiv of benzaldehyde with **4** at 70 °C for 24 h.

Introduction

The activation of organic carbonyls by Zn-based Lewis acids is a topic of relevance to several C−C bond-forming processes, including aldol reactions[1] and asymmetric additions to aldehydes[2] and ketones.[3] Many of these reactions are believed to proceed via dizinc reaction intermediates that use novel ambifunctional mechanisms,[4] with one Zn center acting as a Lewis acid and the other Zn providing the nucleophile. One of the best defined examples of an ambifunctional mechanism is Noyori's (−)-DAIB-catalyzed (DAIB = 3-*exo*-(dimethylamino)isoborneol) addition of dialkylzincs to benzalde-

(1) (a) Trost, B. M.; Ito, H. *J. Am. Chem. Soc.* **2000**, *122*, 12003−12004. (b) Trost, B. M.; Ito, H.; Silcoff, E. R. *J. Am. Chem. Soc.* **2001**, *123*, 3367−3368. (c) Trost, B. M.; Yeh, V. S. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 861−863.

(2) (a) Soai, K.; Niwa, S. *Chem. Rev.* **1992**, *92*, 833−856. (b) Pu, L.; Yu, H. *Chem. Rev.* **2001**, *101*, 757−824.

(3) (a) Dosa, P.; Fu, G. *J. Am. Chem. Soc.* **1998**, *120*, 445−446. (b) Ramon, D.; Yus, M. *Tetrahedron* **1998**, *54*, 5651−5666. (c) Garcia, C.; LaRochelle, L.; Walsh, P. *J. Am. Chem. Soc.* **2002**, *124*, 10970−10971. (d) Jeon, S.; Walsh, P. *J. Am. Chem. Soc.* **2003**, *125*, 9544.

(4) (a) Rowlands, G. *Tetrahedron* **2001**, *57*, 1865−1882. (b) Williams, N.; Takasaki, B.; Wall, M.; Chin, J. *Acc. Chem. Res.* **1999**, *32*, 485−493.

Chart 1

hyde.[5] In the first step of this reaction, the dialkylzinc (R_2Zn) reacts with the alcohol group of (−)-DAIB to form the Zn alkoxide species [(−)-DAIB]ZnR. Interestingly, this complex does not react with benzaldehyde to give the addition product unless a second equivalent of R_2-Zn is added. These data and subsequent calculations and structural studies[6] provide strong evidence that the key intermediate is the dizinc species **A** (Chart 1), which efficiently activates the aldehyde toward nucleophilic attack while increasing the nucleophilicity of the R_2Zn reagent.

(5) Kitamura, M.; Suga, S.; Kawai, K.; Noyori, R. *J. Am. Chem. Soc.* **1986**, *108*, 6071−6072.

(6) (a) Yamakama, M.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 6327−6335. (b) Yamakuma, M.; Noyori, R. *Organometallics* **1999**, *18*, 128−133.

Chart 2
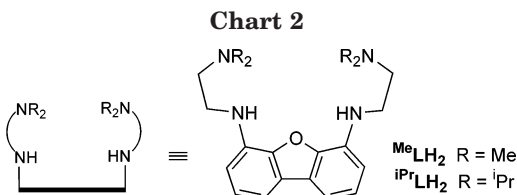
Largely because of the success of Noyori's system, the design and development of ambifunctional catalysts continues to be a topic of great interest. In this context, we have been developing preorganized binucleating ligands that are suitable for the preparation of discrete main-group bimetallic complexes.[7] These ligands include a series of bis(diaminoethanes) that feature a dibenzofuran "backbone" (Chart 2). This relatively rigid ligand system was chosen because it provides some control over key structural features, such as intermetal separation and sterics. In this paper we describe the use of these ligands for the preparation of several new dizinc organometallics. These discrete, structurally characterized complexes provide an unusual opportunity to study the addition of organozincs to benzaldehyde with well-defined reactants. Solid-state structures are reported for **1**, **2**, **4**, and **5**. The structure of **3** was recently communicated.[8]

Experimental Section

General Considerations. Standard Schlenk-line and glovebox techniques were used unless stated otherwise. 4,6-Diiododibenzofuran[9] and $ZnPh_2$[10] were prepared by following literature procedures. Benzaldehyde was distilled from CaH_2 under N_2 prior to use. *N,N*-Dimethylethylenediamine, *N,N*-diisopropylethylenediamine, $ZnEt_2$, $ZnMe_2$, and $OPMe_3$ were purchased from commercial sources (Sigma-Aldrich, Alfa, Lancaster, TCI) 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 Na–benzophenone ketyl. CD_2Cl_2 and $CDCl_3$ were vacuum-transferred from CaH_2. Chemical shifts (δ) for ^{1}H 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. Elemental analyses were determined 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.

N,N′-Bis(2-(dimethylamino)ethyl)dibenzofuran-4,6-diamine (MeLH2). 4,6-Diiododibenzofuran (20.0 g, 47.7 mmol), K_3PO_4 (40.5 g, 191 mmol), and CuI (0.908 g, 4.77 mmol) were combined in a 500 mL round-bottomed flask. 2-Propanol (250 mL) was added to the solids to form a white suspension. Next, ethylene glycol (10.6 mL, 191 mmol) and *N,N*-dimethylethylenediamine (10.7 mL, 97.8 mmol) were added by syringe. The flask was then equipped with a condenser, and the reaction mixture was heated to reflux. After 2 days, ^{1}H NMR spectroscopic analysis of the crude reaction mixture indicated that the 4,6-diiododibenzofuran was completely consumed. The reaction mixture was cooled to room temperature and filtered

(7) (a) Hlavinka, M. L.; Hagadorn, J. R. *Chem. Commun.* **2003**, 2686–2687. (b) Clare, B. C.; Sarker, N.; Shoemaker, R.; Hagadorn, J. R. *Inorg. Chem.* **2004**, *43*, 1159–1166.

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(9) Tsang, K.; Diaz, H.; Gracin, N.; Kelly, J. *J. Am. Chem. Soc.* **1994**, *116*, 3988–4005.

(10) Ashby, E.; Willard, G.; Goel, A. *J. Org. Chem.* **1979**, *44*, 1221–1232.

through a fritted disk to afford a brown solution. Evaporation of the solvent left a brown semisolid, which was taken up in H_2O (200 mL) and Et_2O (250 mL). The organics were separated and washed with H_2O (3 × 150 mL) and brine (100 mL). The solution was dried over $MgSO_4$ and filtered through a pad of Florisil. The yellow solution was concentrated to 75 mL and cooled to −40 °C to afford the product as pale yellow crystals (8.25 g, 51.4%). ^{1}H NMR ($CDCl_3$): δ 7.26 (dd, $J = 1.0$, 7.6 Hz, 2H), 7.18 (t, $J = 7.6$ Hz, 2H), 6.69 (dd, $J = 1.0$, 7.6 Hz, 2H), 4.77 (t, $J = 5.0$ Hz, 2H, −NH), 3.36 (q, $J = 5.9$ Hz, 4H, −NHCH_2), 2.66 (t, $J = 6.2$ Hz, 4H, −CH_2NMe2), 2.30 (s, 12H, −NMe_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 144.5, 134.6, 124.7, 123.5, 109.1, 107.9, 58.2, 45.4 (−NMe2), 41.3. Anal. Calcd (found) for $C_{20}H_{28}N_4O$: C, 70.56 (70.82); H, 8.29 (8.33); N, 16.46 (16.08).

N,N′-Bis(2-(diisopropylamino)ethyl)dibenzofuran-4,6-diamine (iPrLH2). This compound was made analogously to MeLH2, except that *N,N*-diisopropylethylenediamine was used instead of *N,N*-dimethylethylenediamine. The product was isolated as colorless crystals in 38.0% yield. ^{1}H NMR ($CDCl_3$): δ 7.27 (dd, $J = 0.8$, 7.5 Hz, 2H), 7.19 (t, $J = 7.5$ Hz, 2H), 6.71 (dd, $J = 0.8$, 7.5 Hz, 2H), 4.97 (t, $J = 5$ Hz, 2H, −NH), 3.28 (q, $J = 6$ Hz, 4H, −NHCH_2), 3.11 (sept, $J = 6.5$ Hz, 4H, −CHMe2), 2.85 (t, $J = 6$ Hz, 4H, −CH_2N^{i}Pr2), 1.08 (d, $J = 6.5$ Hz, 24H, −CHMe_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 144.8, 135.1, 124.9, 123.6, 108.9, 108.4, 44.7 (−NHCH_2), 43.0 (−CHMe2), 42.3 (−CH2-N^{i}Pr2), 22.0 (−CHMe_2).

iPrLZn2Et2 (1). To a toluene (75 mL) solution of iPrLH2 (1.00 g, 2.21 mmol) was added $ZnEt_2$ (0.905 mL, 8.84 mmol), forming a colorless solution. The reaction mixture was stirred for 24 h at 60 °C. The solution was cooled to 5 °C to yield the product as colorless crystals, which were isolated and dried under reduced pressure (0.978 g, 69.2%). ^{1}H NMR (CD_2Cl_2): δ 7.04 (t, $J = 7.6$ Hz, 2H), 6.97 (dd, $J = 1.5$, 7.6 Hz, 2H), 6.55 (dd, $J = 1.5$, 7.6 Hz, 2H), 3.47 (t, $J = 5.6$ Hz, 4H, −NCH_2), 3.37 (sept, $J = 6.4$ Hz, 4H, −CHMe2), 3.07 (t, $J = 5.6$ Hz, 4H, −CH_2-N^{i}Pr2), 1.27 (d, $J = 6.4$ Hz, 24H, −CHMe_2), 1.09 (t, $J = 8$ Hz, 6H, −ZnCH2CH_3), 0.56 (q, $J = 8$ Hz, 4H, −ZnCH_2CH3). ^{13}C-{^{1}H} NMR (CD_2Cl_2): δ 146.8, 144.8, 125.1, 123.9, 108.1, 104.7, 50.3 (−NCH_2), 46.5 (−CHMe2), 46.3, (−CH2N^{i}Pr2), 20.7 (−CHMe_2), 12.1 (−ZnCH2CH3), 6.23 (−ZnCH2CH3). Anal. Calcd (found) for **1**·(toluene), $C_{39}H_{60}N_4OZn_2$: C, 64.02 (64.47); H, 8.27 (8.42); N, 7.66 (7.65).

iPrLZn2Me2 (2). The synthesis was carried out analogously to that of **1**, except $ZnMe_2$ was used instead of $ZnEt_2$. The product crystallized from toluene, yielding colorless crystals in 72.3% yield. ^{1}H NMR (CD_2Cl_2): δ 7.09 (t, $J = 7.6$ Hz, 2H), 7.00 (dd, $J = 1.0$, 7.6 Hz, 2H), 6.54 (dd, $J = 1.0$, 7.6 Hz, 2H), 3.45 (t, $J = 5.6$ Hz, 4H, −NCH_2), 3.37 (sept, $J = 6.4$ Hz, 4H, −CHMe2), 3.09 (t, $J = 5.6$ Hz, 4H, −CH_2N^{i}Pr2), 1.26 (d, $J = 6.4$ Hz, 24H, −CHMe_2), −0.30 (s, 6H, −ZnCH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 146.6, 144.6, 124.9, 124.0, 107.5, 104.7, 49.6 (−NCH_2), 46.1 (−CHMe2), 45.9, (−CH2N^{i}Pr2), 20.4 (−CHMe_2), −6.23 (−ZnCH3). Anal. Calcd (found) for **2**·1.5(toluene), $C_{40.5}H_{60}N_4OZn_2$: C, 64.88 (64.79); H, 8.07 (8.08); N, 7.47 (7.58).

MeLZn2Ph2 (3). $ZnPh_2$ (3.24 g, 14.7 mmol) and MeLH2 (2.50 g, 7.35 mmol) were combined in toluene (200 mL) to form a clear colorless solution. The reaction mixture was heated to 75 °C for 1 h. The hot solution was filtered into a warm 250 mL Schlenk tube. Colorless crystals of the product formed as the solution was slowly cooled to room temperature. The solution was cooled to −15 °C overnight. The product was isolated by filtration and dried under reduced pressure (3.37 g, 73.3%). ^{1}H NMR (CD_2Cl_2): δ 7.76 (dd, $J = 2.0$, 5.6 Hz, 4H), 7.28 (m, 6H), 7.11 (t, $J = 7.6$ Hz, 2H), 6.96 (d, $J = 7.6$ Hz, 2H), 6.36 (d, $J = 7.6$ Hz, 2H), 3.09 (t, $J = 6.0$ Hz, 4H, −NCH_2), 2.12 (t, $J = 5.6$ Hz, 4H, −CH_2NMe2), 2.10 (s, 12H, −NMe_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 148.5 (ipso-Zn−Ph), 146.2, 143.9, 142.4, 128.8, 128.5, 127.9, 124.2, 105.9, 103.2, 60.1, 43.2 (−NMe_2), 43.7. ^{1}H NMR (CD_2Cl_2, −90 °C): δ 7.67 (d, $J = 6.4$ Hz, 4H), 7.26 (m, 6H), 7.06 (t, $J = 7.6$ Hz, 2H), 6.89 (d, $J = 7.6$ Hz, 2H), 6.29 (d, $J = 7.6$ Hz, 2H), 3.0 (br, 4H, −NCH_2), 2.0

Table 1. Crystallographic Data and Collection Parameters

	1·(toluene)	**2·1.5(toluene)**	**4**	**5**
formula	$C_{39}H_{60}N_4OZn_2$	$C_{40.5}H_{60}N_4OZn_2$	$C_{40}H_{52}N_4OZn_2$	$C_{39}H_{42}N_4O_2Zn_2$
formula wt	731.65	749.66	735.60	729.51
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	Cc (No. 9)
temp (°C)	−130	−129	−117	−122
a (Å)	10.4858(4)	10.2478(3)	22.577(1)	19.0274(9)
b (Å)	31.631(1)	12.9348(4)	15.4249(8)	12.0167(6)
c (Å)	11.3696(4)	15.8925(5)	20.916(1)	17.0229(8)
α (deg)	90	67.037(1)	90	90
β (deg)	99.613(1)	81.799(1)	97.819(1)	118.837(1)
γ (deg)	90	89.405(1)	90	90
Z	4	2	8	4
V (Å^3)	3718.1(2)	1917.5(1)	7216.1(7)	3409.6(3)
d_{calcd} (g/cm^3)	1.307	1.298	1.354	1.421
μ (mm^{-1})	1.325	1.287	1.366	1.447
cryst size (mm)	0.45 × 0.2 × 0.2	0.4 × 0.2 × 0.1	0.4 × 0.31 × 0.11	0.4 × 0.2 × 0.06
θ range (deg)	1.93−27.88	1.74−27.88	1.60−27.48	2.09−27.88
no. of data/restraints/params	8837/13/426	9060/13/437	16 553/0/863	7141/2/428
R1 (for $F_o > 4\sigma F_o$)	0.0537	0.0579	0.0776	0.0777
R1, wR2 (all data)	0.0675, 0.1436	0.0757, 0.1587	0.1965, 0.2038	0.1145, 0.1983
GOF	1.040	1.026	0.940	0.991
largest peak, hole (e/Å^3)	1.09, −0.52	1.17, −0.79	1.29, −0.98	0.87, −0.66

(br, 16H, −CH_2NMe$_2$, −NMe$_2$). Anal. Calcd (found) for **3**, $C_{32}H_{36}N_4OZn_2$: C, 61.65 (61.30); H, 5.82 (5.64); N, 8.99 (9.19).

^{iPr}LZn$_2$Ph$_2$ (4). The synthesis was carried out analogously to that of **3**, except that ^{iPr}LH$_2$ was used instead of ^{Me}LH$_2$ and the reaction mixture was heated for 12 h. The product was isolated as colorless crystals in 56% yield. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.54 (m, J = 1.6, 6.4 Hz, 4H), 7.1 (m, 10H), 6.67 (dd, J = 1.2, 7.6 Hz, 2H), 3.46 (t, J = 5.6 Hz, 4H, −NCH_2), 3.34 (sept, J = 6.8 Hz, 4H, −NCHMe_2), 2.71 (t, J = 5.6 Hz, 4H, −CH_2-N^{i}Pr$_2$), 1.06 (d, J = 6.8 Hz, 24H, −CHMe_2). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 150.4, 146.8, 140.8, 127.4, 127.2, 125.5, 124.1, 109.3, 109.3, 105.0, 50.5, 46.0, 44.8, 20.6 (−CHMe_2).

^{Me}LZn$_2$(Ph)(OCHPh$_2$) (5). Benzaldehyde (19.3 μL, 0.190 mmol) and **3** (0.118 g, 0.190 mmol) were combined in C$_6$H$_6$ (10 mL) to form a pale yellow solution. The mixture was stirred for 24 h, during which time a white precipitate of the product formed. This crude product was recrystallized by the vapor diffusion of hexanes into a CH$_2$Cl$_2$ solution of **5** (0.120 g, 86.7%). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.73 (br, 2H, ortho ZnPh), 7.27−7.40 (m, 7H, Ar H), 7.08−7.18 (m, 8H, Ar H), 6.92 (dd, J = 0.8, 7.6 Hz, 2H), 6.24 (dd, J = 0.8, 7.6 Hz, 2H), 6.11 (s, 1H, −OCHPh$_2$), 2.93 (m, 2H), 2.77 (m, 2H), 2.30 (s, 6H), 1.94 (m, 2H), 1.52 (m, 2H), 1.34 (s, 6H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 147.8, 146.3, 144.5, 136.2 (ipso-Zn−Ph), 133.2, 128.8, 128.7, 128.4, 128.3, 127.4, 124.7, 124.5, 105.3, 102.5, 80.7, 60.2, 47.1, 43.5, 42.1. Anal. Calcd (found) for **5**, $C_{39}H_{42}N_4O_2Zn_2$: C, 64.21 (64.05); H, 5.80 (5.81); N, 7.68 (7.64).

^{Me}LZn$_2$(OCHPh$_2$)$_2$ (6). Benzaldehyde (41.3 μL, 0.406 mmol) and **3** (0.126 g, 0.203 mmol) were combined in C$_6$H$_6$ (5 mL) in a 25 mL round-bottomed flask. The solution was heated to 70 °C for 24 h. The yellow solution was cooled to ambient temperature. The slow addition of hexanes by vapor diffusion yielded the product as colorless crystals, which were isolated and dried under reduced pressure (0.113 g, 66.6%). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.20−7.05 (m, 22H, Ar H), 7.01 (dd, J = 1.2, 7.6 Hz, 2H), 6.30 (d, J = 7.6 Hz, 2H), 5.99 (s, 2H, −OCHPh$_2$), 2.77 (t, J = 5.6 Hz, 4H), 1.81 (s, 12H), 1.64 (t, J = 5.6 Hz, 4H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 147.2, 145.9, 144.5, 128.5, 128.2, 127.5, 125.1, 124.6, 105.8, 102.5, 80.5, 60.8, 45.6, 43.1. Anal. Calcd (found) for **6**, $C_{46}H_{48}N_4O_3Zn_2$: C, 66.11 (66.40); H, 5.79 (5.88); N, 6.70 (6.66).

^{iPr}LZn$_2$(OCHPh$_2$)$_2$ (7). The synthesis was carried out analogously to that of **6**, except that **4** was used instead of **3**. The product was isolated as colorless crystals in 69.1% yield. ^{1}H NMR (C$_6$D$_6$): δ 7.63 (t, J = 7.6 Hz, 2H), 7.55 (dd, J = 0.8 Hz, 7.6 Hz, 2H), 7.11−7.16 (m, 8H, Ar H), 6.88−6.93 (m, 12H, Ar H), 6.64 (dd, J = 0.8, 7.6 Hz, 2H), 6.20 (s, 2H, −OCHPh$_2$), 2.79 (t, J = 5.6 Hz, 4H), 2.69 (sept, J = 6.8 Hz, 4H), 1.77 (t, J

= 5.6 Hz, 4H), 0.9 (br, 24H). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 147.0, 146.3, 144.5, 129.4, 127.9, 127.3, 126.0, 125.4, 107.2, 104.3, 81.9, 53.5, 52.2, 45.6, 21.8.

X-ray Crystallography. Table 1 lists a summary of crystal data and collection parameters for all crystallographically characterized compounds. Table 2 lists selected bond lengths and angles.

(a) General Procedure. A crystal of appropriate size was mounted on a glass fiber using Paratone-N oil, transferred to a Siemens SMART diffractometer/CCD area detector, centered in the beam (Mo Kα; λ = 0.710 73 Å; graphite monochromator), and cooled to ca. −123 °C by a nitrogen low-temperature apparatus. The preliminary orientation matrix and cell constants were determined by collection of 60 10 s 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 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 V5.0) on F^2.[11]

(b) Structure of ^{iPr}LZn$_2$Et$_2$·toluene (1·(toluene)). Needle-shaped crystals that were suitable for X-ray diffraction studies were grown from toluene at 20 °C. Preliminary data indicated a primitive monoclinic cell. Systematic absences indicated space group $P2_1/n$ (No. 14), which was confirmed by the successful solution and refinement of the structure. All non-H atoms were refined anisotropically. Hydrogens were placed in idealized positions and were included in structure factor calculations but were not refined. It was necessary to constrain the 1,2- and 1,3-bond distances of the cocrystallized toluene to obtain acceptable metrical parameters.

(c) Structure of ^{iPr}LZn$_2$Me$_2$·1.5(toluene) (2·1.5(toluene)). Needle-shaped crystals that were suitable for X-ray diffraction studies were grown from a toluene at 20 °C. Preliminary data indicated a triclinic cell. The choice of the centric space group was confirmed by the successful solution and refinement of the structure. The structure of **2** contains 1.5 molecules of cocrystallized toluene in the asymmetric unit. The half-occupancy toluene is disordered and resides on a crystallographic inversion center. The 1,2- and 1,3-bond distances were constrained for the disordered molecule, and it was refined with isotropic thermal parameters. All other

(11) Sheldrick, G. M. SHELXTL-Plus, a Program for Crystal Structure Determination, Version 5.1; Bruker AXS, Madison, WI, 1998.

Table 2. Selected Bond Distances and Angles

Compound 1

Zn1–N1	2.218(2)	Zn1–Zn2	4.0997(5)	Zn2–N4	2.215(2)	Zn2–C31	1.952(3)
Zn2–N3	1.897(2)	Zn1–N2	1.909(2)	Zn1–C29	1.955(3)		
N2–Zn1–C29	146.9(1)	N1–Zn1–N2	85.74(9)	N1–Zn1–C29	126.1(1)	N3–Zn2–C31	153.0(1)
N4–Zn2–C31	120.9(1)	N3–Zn2–N4	85.6(1)				

Compound 2

Zn1–N1	2.209(3)	Zn1–Zn2	3.9645(5)	Zn2–N4	2.218(2)	Zn2–C30	1.951(3)
Zn2–N3	1.903(2)	Zn1–N2	1.905(2)	Zn1–C29	1.944(3)		
N2–Zn1–C29	152.4(1)	N1–Zn1–N2	85.8(1)	N1–Zn1–C29	120.8(1)	N3–Zn2–C30	151.0(1)
N4–Zn2–C30	122.2(1)	N3–Zn2–N4	85.7(1)				

Compound 3

Zn1–N1	2.149(3)	Zn1–N2	1.922(3)	Zn2–C21	2.546(3)	Zn2–N4	2.139(3)
Zn1–C27	2.618(3)	Zn2–N3	1.940(3)	Zn1–C21	2.013(4)	Zn1–Zn2	2.7279(6)
Zn2–C27	2.008(3)						
N1–Zn1–N2	85.8(1)	N1–Zn1–C21	115.2(1)	N2–Zn1–C21	136.9(1)	N4–Zn2–C27	114.9(1)
N3–Zn2–N4	84.8(1)	N3–Zn2–C27	137.4(1)				

Compound 4

Zn1–N1	1.899(5)	Zn1–Zn2	4.020(1)	Zn2–N4	2.225(5)	Zn2–C35	1.945(7)
Zn2–N3	1.901(5)	Zn1–N2	2.234(5)	Zn1–C29	1.954(6)		
N2–Zn1–C29	121.9(2)	N1–Zn1–N2	85.7(2)	N1–Zn1–C29	150.9(2)	N3–Zn2–C35	156.7(2)
N4–Zn2–C35	118.3(2)	N3–Zn2–N4	84.2(2)				

Compound 5

|							
Zn1–O2	2.029(6)	Zn1–N1	2.131(7)	Zn2–C21	2.183(9)	Zn2–N3	1.948(7)
Zn1–C21	2.086(8)	Zn2–O2	1.961(5)	Zn1–N2	1.934(7)	Zn1–Zn2	2.698(1)
Zn2–N4	2.118(7)						
O2–Zn1–N1	115.1(3)	N3–Zn2–N4	85.8(3)	O2–Zn2–N4	117.5(3)	N2–Zn1–C21	135.4(3)
N1–Zn1–N2	84.5(3)	O2–Zn1–N2	119.5(3)	N3–Zn2–C21	127.8(3)	O2–Zn2–C21	91.7(3)
O2–Zn2–N3	126.9(3)	N1–Zn1–C21	110.4(3)	O2–Zn1–C21	92.7(3)	N4–Zn2–C21	107.8(3)

non-H atoms were refined anisotropically. Hydrogens were placed in idealized positions and were included in structure factor calculations but were not refined.

(d) Structure of $^{iPr}LZn_2Ph_2$ (4). Crystals that were suitable for X-ray diffraction studies were grown from toluene at 20 °C. Preliminary data indicated a primitive monoclinic cell. Systematic absences indicated space group $P2_1/c$ (No. 14), which was confirmed by the successful solution and refinement of the structure. There are two independent molecules in the asymmetric unit. Analysis using Platon did not reveal any additional 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.

(e) Structure of $^{Me}LZn_2(Ph)(OCHPh_2)$ (5). Crystals that were suitable for X-ray diffraction studies were grown from a hexanes–CD_2Cl_2 mixture at ambient temperature. Preliminary data indicated a C-centered monoclinic cell. Systematic absences were consistent with space groups Cc and $C2/c$. The choice of Cc (No. 9) was confirmed by the successful solution and refinement of the structure. All non-H atoms were refined anisotropically. Hydrogens were placed in idealized positions and were included in structure factor calculations but were not refined. The Flack parameter was refined to 0.03(2), indicating that the correct absolute structure was refined.

Results and Discussion

The bis(diaminoethane) ligands shown in Chart 2 readily undergo protonolysis with common organozinc reagents to form isolable bis(amidoamine) derivatives of the general formula LZn_2R_2 (R = alkyl, aryl). For example, the reaction of $^{iPr}LH_2$ with excess $ZnEt_2$ in toluene solution at 60 °C formed $^{iPr}LZn_2Et_2$ (1), which was isolated as colorless crystals in 69% yield following cooling to 5 °C (Scheme 1). The related reaction using $ZnMe_2$ formed $^{iPr}LZn_2Me_2$ (2), which was isolated in 72% yield. The ^1H NMR spectrum of 1 in CD_2Cl_2 solution

Scheme 1

1 R = Et, 69%
2 R = Me, 72%
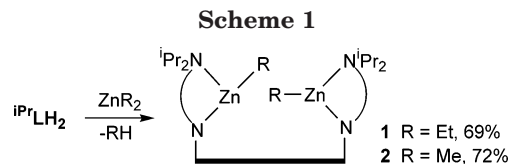
features an upfield quartet at δ 0.56 ppm for the α-methylene protons of each Zn–Et group. The resonances assigned to the bis(amidoamine) ligand reveal that the complex has overall C_{2v} symmetry in solution. ^1H NMR spectroscopic data for 2 (CD_2Cl_2) are similar and feature a sharp upfield singlet at δ −0.03 ppm for the two equivalent Zn–Me groups. The solid-state structures of 1 and 2 (Figure 1) were determined by single-crystal X-ray diffraction. The overall features of the two molecules are very similar; therefore, only the structure of 1 will be described. It features a pair of essentially independent three-coordinate Zn centers, each of which is coordinated by an Et anion and a chelating amidoamine donor. The geometry at Zn is best described as between trigonal planar and T-shaped. The sums of the angles for the three ligands bound to Zn1 and Zn2 are 358.7 and 359.5°, respectively. As expected, the amidoamine ligands are coordinated unsymmetrically, with the Zn–N_{amido} bonds being, on average, 0.31 Å shorter than the dative Zn–N_{amine} bonds. The Zn–Et bonds of 1.955(3) and 1.952(3) Å are similar to other reported Zn–C(sp^3) bond lengths.[12] The Zn–Zn distance is 4.0997(5) Å. Compounds 1 and 2 are rare examples of isolable three-coordinate organozincs.[12] Closely related syntheses using simple chelating amidoamine ligands have yielded only dimeric or oligomeric products with four-coordinate Zn centers.[13] For example, *N,N,N′*-trimethylethylenediamine has been reported to undergo
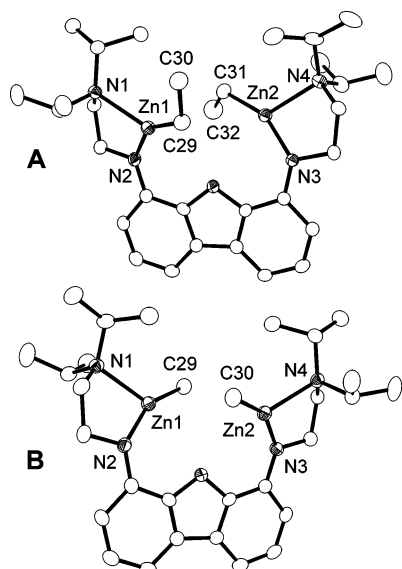
Figure 1. (A) Structure of **1**·(toluene) drawn with 50% thermal ellipsoids. Hydrogen atoms and cocrystallized toluene are omitted. (B) Structure of **2**·1.5(toluene) drawn with 50% thermal ellipsoids. Hydrogen atoms and cocrystallized toluene are omitted.

protonolysis with ZnR$_2$ (R = Me, Et) to form dimeric [ZnR(μ-NMeCH$_2$CH$_2$NMe$_2$)]$_2$, which feature strong amido bridges between the two Zn centers. Apparently the steric bulk and rigidity of the ^{iPr}L^{2-} ligand prevents dimerization in **1** and **2** and allows for the isolation of these relatively Lewis acidic Zn species. Attempts to prepare analogues of **1** and **2** using the less bulky ^{Me}L^{2-} ligand afforded only insoluble products.

To study the reactivity and structural differences between alkyl and arylzinc species, we have also prepared a series of bimetallic arylzinc derivatives. The reaction of ^{iPr}LH$_2$ with 2 equiv of ZnPh$_2$ at 75 °C led to the elimination of benzene and the formation of ^{iPr}LZn$_2$-Ph$_2$ (**4**) in 56% isolated yield (Scheme 2). ^{Me}LZn$_2$Ph$_2$ (**3**) was prepared in good yield in a similar fashion. The solid-state structure of **4** (Figure 2A) is very similar to those of **1** and **2**. Thus, **4** features a pair of essentially independent three-coordinate Zn centers with geometries that are between trigonal planar and T-shaped. The T-shaped distortion can be attributed to the small bite angle of the chelating amidoamine ligands (ca. 85°), which is incompatible with trigonal-planar geometry. With the T-shaped distortion, the two stronger donors (N$_{amido}$, Ph) occupy positions opposite to each other. This is seen in the Ph−Zn−N$_{amido}$ angles of 150.9(2) and 156.7(2)° for Zn1 and Zn2, respectively. The Zn−Ph bond lengths (Zn1−C29, 1.936(5); Zn2−C35, 1.947(6) Å) are in the range expected for Zn−C(sp^2) single bonds.^{12e} The Zn1−Zn2 distance of 4.022(1) Å is similar to that of compounds **1** and **2**.

(12) (a) Hannat, M.; Schormann, M.; Bochmann, M. *Dalton Trans.* **2002**, 4071−4073. (b) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 8738−8749. (c) Liang, L.; Lee, W.; Hung, C. *Inorg. Chem.* **2003**, *42*, 5471−5473. (d) Looney, A.; Han, R.; Gorrell, I.; Cornebise, M.; Yoon, K.; Parkin, G. *Organometallics* **1995**, *14*, 274−288. (e) Prust, J.; Stasch, A.; Zheng, W.; Roesky, H.; Alexopoulos, E.; Uson, I.; Bohler, D.; Schuchardt, T. *Organometallics* **2001**, *20*, 3825−3828.
(13) Malik, M. A.; O'Brien, P.; Motevalli, M.; Jones, A. C. *Inorg. Chem.* **1997**, *36*, 5076−5081.

Scheme 2
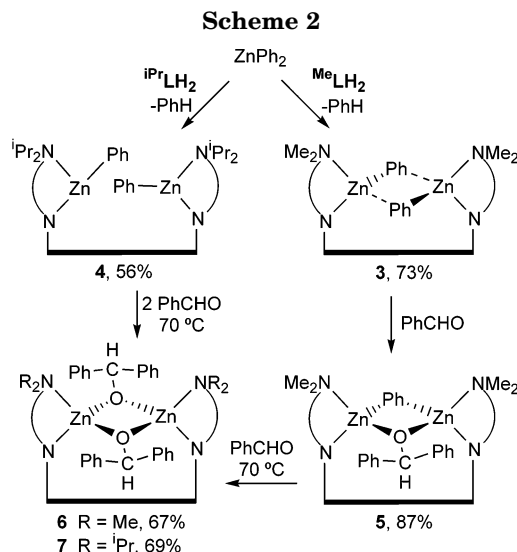
The composition of **3** is identical with that of **4**, except that it is supported by the Me-substituted amidoamine ligand (^{Me}L^{2-}) instead of the ^{i}Pr-substituted one. The use of this less bulky ligand results in a significant structural change. The solid-state structure of **3**^{8} is shown in Figure 2B. There are two molecules in the asymmetric unit. Both feature a parallelogram-shaped [Zn$_2$(μ-Ph)$_2$]$^{2+}$ core with two strong Zn−C σ bonds (average 1.99−2.01 Å) and two weak bridging interactions (average 2.55−2.64 Å).^{14} The Zn−Ph σ bonds of **3** are longer than those of **4** by approximately 0.06 Å. Thus, it appears that the additional bridging interactions are achieved with some expense to the Zn−Ph σ bonds. The two independent molecules have similar Zn−Zn distances of 2.7279(6) and 2.7809(6) Å. In contrast to the solid-state structure, which has approximate C_2 symmetry, the ^{1}H NMR spectrum of **3** (CD$_2$Cl$_2$) indicates
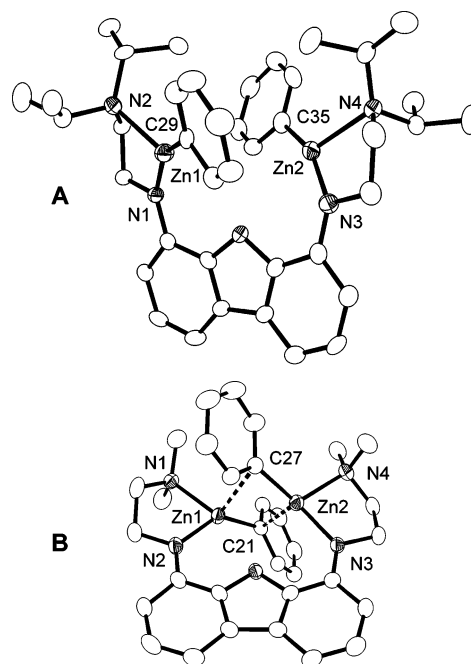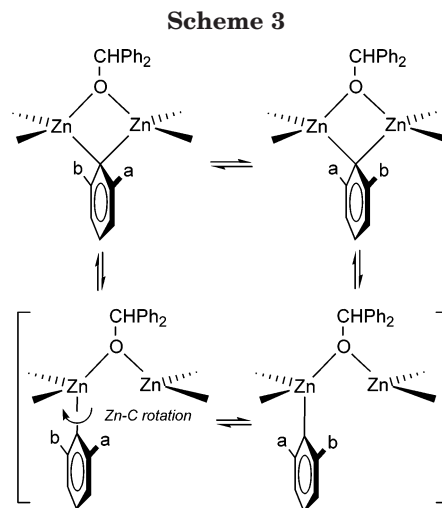

Figure 2. (A) Structure of **4** drawn with 50% thermal ellipsoids. One of two molecules in the asymmetric unit and hydrogens are omitted. (B) Structure of **3** drawn with 50% thermal ellipsoids. One of two molecules in the asymmetric unit and hydrogens are omitted.

overall C_{2v} symmetry. Accordingly, the four Me groups of the bis(amidoamine) ligand are equivalent and are observed as a singlet at δ 2.10 ppm. The higher symmetry of the solution structure may result from cleavage of the weak Ph bridges and rotation about the dibenzofuran–N bonds in solution. Alternatively, rapid Ph group transfer between the Zn centers may occur to give time-averaged C_{2v} symmetry. However, at −90 °C the ^{1}H NMR spectrum did not indicate lower symmetry; therefore, the simple cleavage of the Ph bridges probably best explains the symmetric solution structure.
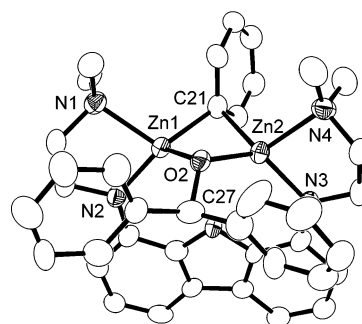
Organozinc reagents are commonly used as nucleophiles in addition reactions with unsaturated organics, such as aldehydes,[2] ketones,[3] and olefins.[15] Consistent with this, we have found that the arylzinc species **3** and **4** readily react with electrophilic organics. For example, the addition of 1 equiv of benzaldehyde to a C_6H_6 solution of **3** at ambient temperature formed the addition product $^{Me}LZn_2(Ph)(OCHPh_2)$ (**5**), which was isolated in 87% yield as colorless crystals from CH_2Cl_2/hexanes. The 400 MHz ^{1}H NMR spectrum of **5** dissolved in CD_2Cl_2 indicates overall C_s symmetry, which is consistent with a structure featuring both bridging Ph and alkoxide ligands. The Me groups of the dimethylamino donors are observed as two sharp singlets at δ 2.30 and 1.34 ppm. There is also a distinct singlet at δ 6.11 ppm, which is assigned to the nonaromatic proton of the diphenylmethoxide ligand. Resonances assigned to the μ-Ph ligand are broad at room temperature. At −70 °C, however, the ortho protons are observed as a pair of distinct doublets at δ 7.96 and 7.27 ppm with integrated intensities of one proton each. Thus at low temperatures rotation about the Zn–Ph bond is slow. Since this phenomenon was not observed for the related arylzinc derivatives **3** and **4**, this suggests that **5** has a more robust Ph bridge. At higher temperatures, the inequivalent ortho (and meta) protons of the Ph group undergo dynamic exchange, with an observed coalescence temperature of −8 °C. At −50 °C, the rate constant for the exchange was determined to be 25(1) s^{-1} and $\Delta G^{\ddagger}$ was calculated to be 11.5(1) kcal mol^{-1}. These values are not affected by the addition of 1 equiv of benzaldehyde. The ^{1}H NMR spectroscopic data are consistent with **5** having a permanent μ-diphenylmethoxide ligand and a Ph ligand that undergoes reversible cleavage of its bridging interaction (Scheme 3). This cleavage then allows for free rotation about the Zn–Ph bond and scrambling of the inequivalent ortho (and meta) protons. To our knowledge, the low-temperature NMR study of **5** has provided the first observation of a Ph bridge between Zn centers in the solution state.

The solid-state structure of **5** is shown in Figure 3. The molecule features a $[Zn_2(\mu\text{-Ph})(\mu\text{-OCHPh}_2)]^{2+}$ core that is significantly puckered. The plane defined by Zn1–Zn2–C21 intersects that defined by Zn1–Zn2–O2 at an angle of 35.5(2)°. The bond lengths of the core reveal a significant amount of asymmetry in the bonds between Zn and the bridging ligands. The Zn1–O2 bond

(14) Other structurally characterized complexes with $[Zn_2(\mu\text{-Ph})_2]^{2+}$ cores: (a) Markles, P. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1990**, *9*, 2243–2247. (b) Dickson, R. S.; Fallon, G. D.; Zhang, Q.-Q. *Dalton Trans.* **2000**, 1973–1974.
(15) (a) Alexakis, A.; Polet, D.; Rosset, S.; March, S. *J. Org. Chem.* **2004**, *69*, 5660–5667. (b) Choi, H.; Hua, Z.; Ojima, I. *Org. Lett.* **2004**, *6*, 2689–2691.

Scheme 3

(2.029(6) Å) is nearly 0.07 Å longer than the Zn2–O2 bond. The μ-Ph group, however, has a bond to Zn1 (2.086(8) Å) that is 0.1 Å shorter than the bond to Zn2. Thus, the Ph ligand is more strongly bound to Zn1 and the alkoxide is more strongly bound to Zn2. As expected for a bimetallic complex with two single-atom bridges, the Zn–Zn distance is quite short (2.698(1) Å).

The synthesis of **5** involved the room-temperature addition of one of the two Zn–Ph groups of **3** to benzaldehyde. The remaining Ph group can also undergo addition to benzaldehyde, but at a much slower rate. Heating a C_6H_6 solution of **3** with 2 equiv of benzaldehyde to 70 °C for 24 h formed the double-addition product $^{Me}LZn_2(OCHPh_2)_2$ (**6**), which was isolated as colorless crystals in 67% yield following the addition of hexanes. The related $^{iPr}LZn_2(OCHPh_2)_2$ (**7**) was formed in good yield by the reaction of 2 equiv of benzaldehyde with **4** under similar conditions. The composition of **6** is supported by NMR spectroscopic data and combustion analysis. The ^{1}H NMR spectrum of **6** (CD_2Cl_2) indicates overall C_{2v} symmetry. The nonaromatic protons of the diphenylmethoxide ligands are observed as a sharp singlet at δ 5.99 ppm. For comparison, the related proton of **5** was observed at δ 6.11 ppm. The methyls of the dimethylamino groups are all equivalent (in **6**) and are observed as a singlet at δ 1.81 ppm. These data and intuition suggest that **6** features two bridging alkoxide ligands in solution. The characterization of **6** by single-crystal X-ray diffraction confirmed this structural motif in the solid state, but the data are not presented here due to difficulties in the refinement of the data set.

Figure 3. Structure of **5** drawn with 50% thermal ellipsoids. Hydrogens are omitted.

The addition of the Zn–Ph group of **5** to benzaldehyde may occur by an ambifunctional mechanism similar to that proposed for DAIB-catalyzed additions (Scheme 1). Thus, cleavage of the Ph bridge of **5** would be followed by binding of benzaldehyde to the three-coordinate Zn center. This forms an intermediate in which the nucleophilic Ph group could attack the electrophilic carbonyl with the formation of a cyclic six-membered transition state.

In conclusion, we have used sterically hindered bis-(amidoamine) ligands to prepare a new class of coordinatively unsaturated dizinc organometallics. Members of this class of complexes readily undergo addition to benzaldehyde to form dizinc alkoxide products. These reactions may be of relevance to asymmetric additions of dialkylzincs to aldehydes and ketones that are effectively catalyzed by DAIB and other related ligands.

Supporting Information Available: Crystallographic information files (CIF) are provided for compounds **1**, **2**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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