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Structures of Zinc Ketone Enolates

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Solution- and solid-phase structural characterizations of a series of simple zinc ketone enolates are presented. The new enolate derivatives were prepared (isolated yields 38−69%) by the deprotonation of ketones by the bis(arylzinc) species ${}^{R}LZn_2Ph_2$ (**1**) (where ${}^{R}L^{2-}$ are bis(amidoamine) ligands). Ketones used include 2′,3′,4′,5′,6′-pentamethylacetophenone, cyclohexanone, 2,2-dimethylcyclopentanone, 2,4-dimethyl-3-pentanone, and isobutyrophenone. These ketones were chosen because they have varying degrees of substitution at the acidic carbon (i.e., α to the carbonyl group). Thus, the effect of sterics on the structural preferences of zinc enolates was examined. In all cases, both solid- and solution-phase structural data indicate that the anionic enolate ligands have isolated (and uncoordinated) carbon−carbon double bonds. The enolate anions bind to the Zn centers with O-bridged structures. Single-crystal X-ray diffraction data are reported for ${}^{Me}LZn_2[OC({=}CMe_2){}^{i}Pr]_2$ (**2a**), ${}^{iPr}LZn_2[OC({=}CMe_2){}^{i}Pr]_2$ (**2b**), and ${}^{iPr}LZn_2[OC({=}CH_2)C_6Me_5]_2$ (**4b**). The Zn_2O_2 core of **2a** is symmetrical with the four Zn−O bond lengths, varying only slightly ($Zn{-}O_{enolate} = 1.975(2){-}1.982(2)$ Å). In contrast, the structures of **2b** and **4b**, which are supported by the more sterically hindered ligand ${}^{iPr}L^{2-}$, display parallelogram-shaped Zn_2O_2 cores and longer intermetal distances. These structural distortions are accompanied with changes in the degree of polarization of the carbon−carbon double bonds of the enolate ligands. This is observed by considering the shift difference between the two ${}^{13}C$ resonances arising from the carbons of the enolate C−C double bond. The general trend is that the more hindered supporting ligand, ${}^{iPr}L^{2-}$, forms enolate derivatives with less polarized carbon−carbon double bonds. As expected, the Zn enolates also display carbon−carbon double-bond polarizations that are intermediate to those of closely related Li and Si enolates.

Introduction

Main-group and transition-metal enolates are carbon nucleophiles of importance in both organic syntheses[1] and metal-mediated polymerizations of polar monomers.[2] In this context, alkali and alkaline-earth enolates are most frequently used, but there is growing interest in the use of zinc enolates due to their ideal combination of good reactivity and tolerance of many functional groups.[3] To date, zinc enolates have been used in aldol additions to carbonyls,[4] additions to activated and simple alkenes,[5] and a variety of transmetalation reactions.[6] Surprisingly, despite the importance of these reagents there is very little structural information available that can be used to shed insight into their reactivity patterns and properties. This is because prior attempts to isolate and structurally characterize these species have been hindered by their tendencies toward aggregation, disproportionation, and rapid self-condensation processes.[7]

Metal enolates are known to adopt a variety of structural motifs (Chart 1), which are dependent on the choice of metal, solvent, and steric bulk of the ligands.[8] Generally, enolates of electropositive metals prefer O-bound structures. For example, the structurally characterized ketone enolate derivatives of the

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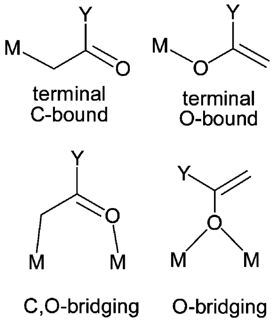
Chart 1



group 1−4 metals[9] and Ln[10] (Ln = lanthanides) nearly always feature terminal or bridging O-bound structures. In contrast, the related derivatives of soft metals, such as Hg,[11] Au,[12] Tl,[13] and Pb,[14] strongly prefer terminal C-bound (2-oxoalkyl) structures. A few C,O-bridging structures have also been observed for derivatives of Mg,[15] Ru(II),[16] and Pd(II).[17] Importantly, these structural preferences are generally thought to correlate with reactivity. Thus metal enolates with O-bound ground states are usually more reactive in nucleophilic additions with carbonyls and nitriles. Mechanistically these species are thought to bind the substrates to the metal center so that the C−C bond forming step occurs via a cyclic, chairlike transition state. Empirical observations and calculations also suggest that metal enolates with C-bound ground states rearrange to O-bound structures prior to undergoing addition reactions.[18]

The structural preferences of zinc enolates remain uncertain. We recently reported that Zn amide enolates adopt C,O-bridging structures with extensive delocalization of the anionic charge.[19] These results were similar to those reported earlier by Boersma and co-workers for ester enolates. These species were shown by X-ray diffraction to adopt C,O-bridging structures that are maintained in common solvents.[20−22] Following those studies Boersma proposed that Zn ketone enolates adopt analogous C,O-bridging structures.[7a] Others, however, have proposed that Zn ketone enolates are O-bound on the basis of IR absorption data.[23] To resolve this issue, additional solution- and solid-phase structural information is needed. Currently, such data are limited to one Na zincate species[24] and two chelate-stabilized Zn enolates (β-amino-substituted enolates).[25] Here we describe the preparation and first structural characterizations of a series of simple Zn ketone enolates supported by binucleating bis(amidoamine) ligands.[26] These studies indicate a preference for O-zincation without any Zn−C interactions.

Experimental Section

General Considerations. Standard Schlenk-line and glovebox techniques were used unless stated otherwise. $ZnPh_2$,[27] $^{Me}LH_2$,[26b] $^{iPr}LH_2$,[26b] and $^{Me}LZn_2Ph_2$[26b] (**1a**) were prepared as described in published procedures. 2,4-Dimethyl-3-pentanone, cyclohexanone, and isobutyrophenone were Kugelrohr distilled from CaH_2 prior to use. 2,2-Dimethylcyclopentanone and 2′,3′,4′,5′,6′-pentamethylacetophenone 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 Na-benzophenone ketyl. CD_2Cl_2 and $CDCl_3$ were vacuum transferred from CaH_2. Elemental analyses were determined by Desert Analytics.

$^{Me}LZn_2[OC({=}CMe_2)^iPr]_2$ (2a). Toluene (20 mL) was added to $ZnPh_2$ (0.273 g, 1.24 mmol) and $^{Me}LH_2$ (0.212 g, 0.622 mmol) in a 100 mL round-bottomed flask. The clear, colorless solution was stirred for 2 h, during which time a white precipitate formed. 2,4-Dimethyl-3-pentanone (0.88 mL, 6.2 mmol) was added, and the mixture was heated to 75 °C. After 3 days, the clear solution was concentrated to 10 mL under reduced pressure. Cooling to −40 °C yielded **2a** as colorless crystals (0.265 g, 61.2%). ^1H NMR (CD_2Cl_2): δ 7.05 (t, J = 7.6 Hz, 2H), 6.86 (dd, J = 1.2, 7.6 Hz, 2H), 6.34 (dd, J = 1.2, 7.6 Hz, 2H), 3.30 (t, J = 5.6 Hz, 4H), 2.76 (t, J = 5.6 Hz, 4H), 2.74 (sept, J = 6.8 Hz, 2H), 2.47 (s, 12H, N*Me*$_2$), 1.94 (s, 6H), 1.59 (s, 6H), 0.64 (d, J = 6.8 Hz, 12H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 157.2 ($OC({=}CMe_2)^iPr$), 145.3, 143.8, 124.7, 124.2, 105.8, 102.9, 102.1 ($OC({=}CMe_2)^iPr$), 62.5, 45.9, 43.3, 30.3, 20.2, 20.0, 18.8. IR: 2954 (s), 2923 (s), 2854 (s), 1654 (w), 1620 (m), 1597 (w), 1577 (m), 1490 (m), 1465 (s), 1420 (m), 1377 (m), 1363 (s), 1339 (m), 1259 (w), 1203 (w), 1174 (w), 1149 (m), 1102 (w), 1087 (w), 1055 (m), 1038 (w), 1024 (m), 952 (w), 934 (w), 833 (w), 787 (w), 758 (w), 752 (m), 722 (m). Anal. Calcd (found) for **2a**, $C_{34}H_{52}N_4O_3Zn_2$: C, 58.71 (58.63); H, 7.54 (7.37); N, 8.05 (8.21).

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$^{Me}LZn_2[O({=}CMe_2)Ph]_2$ (3). Isobutyrophenone (15.6 μL, 0.103 mmol), **1a** (32.2 mg, 0.0516 mmol), and C_6D_6 (0.5 mL) were combined in a NMR tube. The clear, colorless solution was heated to 75 °C for 2 days. Analysis by ^1H NMR spectroscopy indicated >95% conversion to **3**. ^1H NMR (C_6D_6): δ 7.46 (t, 7.6 Hz, 2H), 7.43 (m, 4H, OC(=CMe$_2$)*Ph*), 7.35 (dd, $J = 1.2$, 7.6 Hz, 2H), 6.96 (m, 4H, OC(=CMe$_2$)*Ph*), 6.87 (m, 2H, OC(=CMe$_2$)*Ph*), 6.62 (dd, $J = 1.2$, 7.6 Hz, 2H), 3.11 (t, $J = 5.6$ Hz, 4H), 2.12 (t, 5.6 Hz, 4H), 1.76 (s, 12H, N*Me*$_2$), 1.74 (s, 6H, OC(=C*Me*(Me))Ph), 1.59 (s, 6H, OC(=CMe(*Me*))Ph). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 150.9 (O*C*(=CMe$_2$)Ph), 146.2, 143.6, 142.2, 129.4, 128.9, 127.0, 125.6, 124.6, 107.8 (OC(=*C*Me$_2$)Ph), 106.8, 104.7, 62.1, 45.2, 43.4, 21.2, 19.0.

$^{Me}LZn_2[OC({=}CH_2)Ar]_2$ (Ar = C_6Me_5) (4a). Toluene (25 mL) was added to $ZnPh_2$ (0.464 g, 2.11 mmol) and $^{Me}LH_2$ (0.360 g, 1.06 mmol) in a 100 mL round-bottomed flask. The clear, colorless solution was stirred for 2 h, during which time a white precipitate formed. 2′,3′,4′,5′,6′-Pentamethylacetophenone (0.503 g, 2.64 mmol) in toluene (15 mL) was added, and the mixture was heated to 75 °C for 40 h. Colorless crystals of the product formed as the solution slowly cooled to room temperature. Further cooling to −15 °C yielded additional **4a** (0.663 g, 69.4% yield). ^1H NMR (CD_2Cl_2): δ 7.11 (t, $J = 7.6$ Hz, 2H), 6.89 (dd, $J = 1.0$, 7.6 Hz, 2H), 6.35 (dd, $J = 1.0$, 7.6 Hz, 2H), 4.46 (d, $^2J_{HH} = 0.5$ Hz, $^1J_{CH} = 153$ Hz, 2H, OC(=C*H*H)Ar), 3.57 (d, $^2J_{HH} = 0.5$ Hz, $^1J_{CH} = 159$ Hz, 2H, OC(=CH*H*)Ar), 3.17 (t, $J = 5.6$ Hz, 4H), 2.19 (s, 6H), 2.1 (br, 28H), 2.01 (s, 12H, N*Me*$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 162.8 (O*C*(=CH$_2$)Ar), 146.6, 143.9, 139.7, 134.5, 132.6, 132.4, 124.7, 124.3, 105.8, 103.0, 90.8 (OC(=*C*H$_2$)Ar), 61.2, 45.7, 43.4, 18.3, 16.9, 16.7. IR: 2954 (s), 2923 (s), 2853 (s), 1637 (w), 1619 (m), 1598 (m), 1580 (m), 1491 (m), 1463 (s), 1423 (m), 1378 (m), 1366 (m), 1338 (m), 1307 (w), 1274 (w), 1198 (w), 1171 (w), 1145 (w), 1096 (w), 1058 (w), 1022 (w), 975 (w), 956 (w), 934 (w), 832 (w), 804 (w), 759 (w), 751 (w), 721 (m). Anal. Calcd (found) for **4a**·(toluene)$_{1.2}$, $C_{54.4}H_{69.6}N_4O_3Zn_2$: C, 68.18 (68.15); H, 7.32 (7.24); N, 5.85 (5.69).

$^{iPr}LZn_2[OC({=}CH_2)Ar]_2$ (Ar = C_6Me_5) (4b). The compound was prepared using a method analogous to that used to prepare **2b** except that 2.5 equiv of 2′,3′,4′,5′,6′-pentamethylacetophenone was used in place of 5 equiv of 2,4-dimethyl-3-pentanone. The product was isolated as colorless crystals from the toluene solution at ambient temperature. Additional crystalline product formed as the mother liquor cooled to −15 °C (total yield: 56.7%). ^1H NMR (CD_2Cl_2, −20 °C): δ 7.08 (t, $J = 7.6$ Hz, 2H), 6.88 (d, $J = 7.6$ Hz, 2H), 6.30 (d, $J = 7.6$ Hz, 2H), 4.46 (s, $^1J_{CH} = 154$ Hz, 2H), 3.63 (s, $^1J_{CH} = 159$ Hz, 2H), 3.29 (br, 4H), 2.94 (br, 4H), 2.25 (s, 6H), 2.19 (s, 6H), 2.14 (s, 6H), 2.08 (s, 6H), 1.7 (s, 6H), 1.35 (br, 4H), 1.30 (d, $J = 6.8$ Hz, 6H), 1.26 (d, $J = 6.4$ Hz, 6H), 1.21 (d, $J = 6.4$ Hz, 6H), 0.72 (d, $J = 6.8$ Hz, 6H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −20 °C): δ 160.4 (O*C*(=CH$_2$)Ar), 145.8, 143.8, 138.6, 134.5, 133.3, 132.8, 132.6, 132.0, 124.2, 123.8, 105.9, 102.6, 95.4 (OC(=*C*H$_2$)Ar), 57.4, 51.8, 48.0, 46.2, 24.9, 24.5, 21.0, 18.6, 17.8, 17.0, 16.8, 16.5 (One expected resonance is not observed, presumably due to overlap). IR: 2954 (s), 2923 (s), 2854 (s), 1620 (m), 1609 (w), 1579 (m), 1491 (w), 1462 (s), 1422 (m), 1376 (m), 1364 (m), 1340 (m), 1303 (w), 1271 (w), 1192 (w), 1177 (w) 1149 (w), 1025 (w), 949 (w), 818 (w), 752 (w), 724 (w). Anal. Calcd (found) for **4b**, $C_{54}H_{76}N_4O_3Zn_2$: C, 67.56 (67.35); H, 7.98 (7.71); N, 5.84 (5.86).

$^{Me}LZn_2(OC_7H_{11})_2$ (5). Toluene (10 mL) was added to $ZnPh_2$ (0.211 g, 0.961 mmol) and $^{Me}LH_2$ (0.164 g, 0.480 mmol) in a 100 mL round-bottomed flask. The clear, colorless solution was stirred for 2 h, during which time a white precipitate formed. 2,2-Dimethylcyclopentanone (0.18 mL, 1.44 mmol) was added, and the mixture was heated to 55 °C. After 2 days, the clear solution was concentrated to 5 mL under reduced pressure. Cooling to −40 °C yielded **5** as colorless crystals in 37.8% yield. ^1H NMR (CD_2Cl_2): δ 7.06 (t, 7.6 Hz, 2H), 7.86 (dd, $J = 1.2$, 7.6 Hz, 2H), 6.36 (dd, $J = 1.2$, 7.6 Hz, 2H), 4.44 (t, $J = 2.5$ Hz, 2H, OC(=C*H*)), 3.33 (t, $J = 5.6$ Hz, 4H), 2.83 (t, $J = 5.6$ Hz, 4H), 2.58 (s, 12H, N*Me*$_2$), 1.99 (dt, $J = 2.5$, 6.0 Hz, 4H), 1.59 (t, $J = 6.0$ Hz, 4H), 0.83 (s, 12 H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 169.4 (O*C*(=CH)), 145.7, 143.7, 124.7, 124.2, 105.8, 103.1, 99.2 (OC(=*C*H)), 62.1, 46.5, 43.3, 43.2, 39.8, 26.3, 24.5. IR: 2953 (s), 2924 (s), 2854 (s), 1619 (m), 1603 (w), 1580 (m), 1491 (m), 1465 (s), 1420 (m), 1377 (m), 1363 (s), 1337 (m), 1294 (w), 1283 (w), 1234 (m), 1205 (w), 1171 (w), 1146 (m), 1135 (w), 1096 (w), 1057 (w), 1022 (w), 955 (w), 931 (w), 832 (w), 786 (w), 751 (m), 721 (m). Anal. Calcd (found) for **5**, $C_{54}H_{76}N_4O_3Zn_2$: C, 59.05 (59.26); H, 7.00 (7.18); N, 8.10 (8.35).

$^{Me}LZn_2(OC_6H_9)_2$ (6). Cyclohexanone (35.3 μL, 0.340 mmol), **1a** (106 mg, 0.170 mmol), and CH_2Cl_2 (5 mL) were combined in a 25 mL round-bottomed flask. The clear, colorless solution was stirred overnight. Removal of the volatiles under reduced pressure yielded **6** as a colorless solid (0.11 g, 90% yield). Attempts to crystallize this product failed. ^1H NMR analysis of the crude solid indicated approximately 90% purity. ^1H NMR (C_6D_6): δ 7.46 (t, 7.6 Hz, 2H), 7.36 (dd, $J = 1.2$, 7.6 Hz, 2H), 6.71 (dd, $J = 1.2$, 7.6 Hz, 2H), 4.94 (t, $J = 4.0$ Hz, 2H, OC(=C*H*)), 3.22 (t, $J = 5.6$ Hz, 4H), 2.29 (t, $J = 5.6$ Hz, 4H), 2.09 (s, 12H, N*Me*$_2$), 1.98 (t, $J = 6.8$ Hz, 4H), 1.87 (m, 4H), 1.33 (m, 4H), 1.24 (m, 2H), 1.13 (m, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 157.1 (O*C*(=CH)), 146.7, 143.8, 125.7, 124.8, 107.0, 105.0, 99.6 (OC(=*C*H)), 62.2, 45.7, 43.6, 32.0, 24.9, 24.2, 23.4.

NMR Spectroscopy. NMR spectra were measured on a Varian Inova-400 NMR spectrometer, at a ^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.

X-ray Crystallography. Table 1 lists a summary of crystal data and collection parameters for all crystallographically characterized compounds. 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 approximately −127 °C by a nitrogen low-temperature apparatus. Preliminary orientation matrix and cell constants were determined by the 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 refined using SAINT. Data analysis was performed using XPREP. Absorption correction was

Table 1. Crystallographic Data and Collection Parameters

	2a	**2b**	**4b·**(toluene)$_{0.5}$
formula	$C_{34}H_{52}N_4O_3Zn_2$	$C_{42}H_{68}N_4O_3Zn_2$	$C_{57.5}H_{80}N_4O_3Zn_2$
fw (g·mol^{-1})	695.54	807.74	1005.99
space group	*P*2(1)/*c* (#14)	*Pna*2(1) (#33)	*C*2/*c* (#15)
temp (K)	147	147	145
a (Å)	10.2301(4)	18.6748(5)	32.949(1)
b (Å)	19.8950(7)	13.3529(4)	19.2436(7)
c (Å)	17.3484(6)	16.9723(4)	19.7699(7)
α (deg)	90	90	90
β (deg)	94.168(1)	90	121.5010(10)
γ (deg)	90	90	90
Z	4	4	8
V (Å^3)	3521.5(2)	4232.3(2)	10687.9(7)
d_{calc} (g·cm^{-3})	1.312	1.268	1.250
θ range (deg)	1.56−27.88	1.87−27.88	2.01−27.88
μ (mm^{-1})	1.399	1.174	0.944
cryst size (mm)	0.45 × 0.35 × 0.08	0.25 × 0.20 × 0.20	0.50 × 0.30 × 0.25
no. of reflns collected	28 239	33 162	40 653
no. of data/restraints/params	8407/0/400	10 087/1/464	12 741/30/615
R1 (for $F_o > 4\sigma F_o$)	0.0515	0.0527	0.0564
R1, wR2 (all data)	0.0932, 0.1238	0.0837, 0.1187	0.0874, 0.1619
GOF	1.005	1.007	1.030
largest peak, hole (e·Å^{-3})	0.546, −0.494	0.557, −0.567	1.088, −0.533

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.[28] Notable details of each data collection and refinement are described below.

Structure of ^{Me}LZn$_2$[OC(=CMe$_2$)^{i}Pr]$_2$ (2a). Crystals that were suitable for X-ray diffraction studies were grown at ambient temperature by the vapor diffusion of hexanes into a C_6D_6 solution. Preliminary data indicated a primitive monoclinic cell. Systematic absences indicated space group *P*2(1)/*c* (#14). This choice of space group was confirmed by the successful solution and refinement of the structure. The asymmetric unit contains a single molecule of **2a**. 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$_2$[OC(=CMe$_2$)^{i}Pr]$_2$ (2b). Crystals that were suitable for X-ray diffraction studies were grown at ambient temperature from a toluene solution. Preliminary data indicated a primitive orthorhombic cell. Systematic absences were consistent with space groups *Pna*2(1) (#33) and *Pnam* (#62). The choice of *Pna*2(1) was confirmed by the successful solution and refinement of the structure. *Pnam* failed to yield a successful solution. The asymmetric unit contains a single molecule of **2b**. 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 refined to 0.05(1), indicating that the correct absolute structure was refined. Inversion of the structure led to an increase in R1 (all data) to 0.0953 and a Flack parameter of 0.88(2).

Structure of ^{iPr}LZn$_2$[OC(=CH$_2$)Ar]$_2$·(toluene)$_{0.5}$ (4b). Crystals that were suitable for X-ray diffraction studies were grown at −5 °C from a toluene solution. Preliminary data indicated a C-centered monoclinic cell. Systematic absences were consistent with space groups *C*2/*c* (#15) and *Cc* (#9). The choice of *C*2/*c* was confirmed by the successful solution and refinement of the structure. *Cc* failed to yield a successful solution. The asymmetric unit contains a molecule of **3b** and a half-occupancy cocrystallized toluene that is located on a crystallographic inversion center. All non-H atoms not associated with the disordered toluene molecule were refined anisotropically. Hydrogens were placed in idealized positions and were included in structure factor calculations but were not refined. The carbons of the cocrystallized toluene were modeled isotropically. The six 1,2 carbon−carbon distances were restrained to be equal within a standard deviation of 0.02. The six 1,3 carbon−carbon distances were restrained to be equal within a standard deviation of 0.04. The largest peak in the difference Fourier was located near the disordered toluene molecule (1.8 Å from H55a).

Results and Discussion

Synthesis. Zinc ketone enolates are commonly prepared in situ by reaction of simple ketones with Zn alkyls or amidos. Typically these generated enolates are then rapidly quenched by reaction with an electrophilic carbonyl or other substrate. In our initial attempts to prepare Zn enolate species, the dinuclear organozincs **1a** and **1b** (Scheme 1) were reacted with acetone in CD_2Cl_2 solution. After 12 h at 20 °C a mixture of products was observed (^{1}H NMR), likely due to self-condensation of the acetone. The use of acetophenone in place of acetone gave similar results.

The use of more sterically hindered ketones, however, led to the successful formation of isolable Zn ketone enolates. For example, heating a C_6D_6 solution of **1a** with excess 2,4-dimethyl-3-pentanone at 75 °C for 3 days cleanly formed (by ^{1}H NMR) the enolate derivative **2a**. Conveniently, it was found that **1a** could be formed in situ and reacted with ketones without significant reduction in isolated yields. Thus, a suspension of **1a** in toluene was generated by reaction of ^{Me}LH$_2$ with 2 equiv of ZnPh$_2$ for 2 h. The addition of 10 equiv of 2,4-dimethyl-3-pentanone to the solution followed by heating to 75 °C for 3 days formed a clear, colorless solution, from which **2a** was crystallized in 61% yield. Repeating the synthesis using the more hindered ligand ^{iPr}LH$_2$ in place of ^{Me}LH$_2$ formed **2b**, which was isolated in 62% yield. In an analogous fashion a C_6D_6 solution of **1a** reacted with 2 equiv of isobutyrophenone at 75 °C over 2 days to form the enolate product **3** in over 95% yield, as determined by ^{1}H NMR spectroscopy relative to an internal standard.

The aforementioned Zn enolates were each formed by the deprotonation of a tertiary carbon located α to the carbonyl functionality. In the interest of increasing the scope of this study, we have also explored enolates formed by the deprotonation of primary and secondary ketones. For example, heating a toluene solution of in situ formed **1a** with 2.5 equiv of 2′,3′,4′,5′,6′-pentamethylacetophenone to 75 °C for approximately 2 days formed a clear, colorless solution, from which **4a** crystallized upon cooling. The product was isolated in 69% yield. Using

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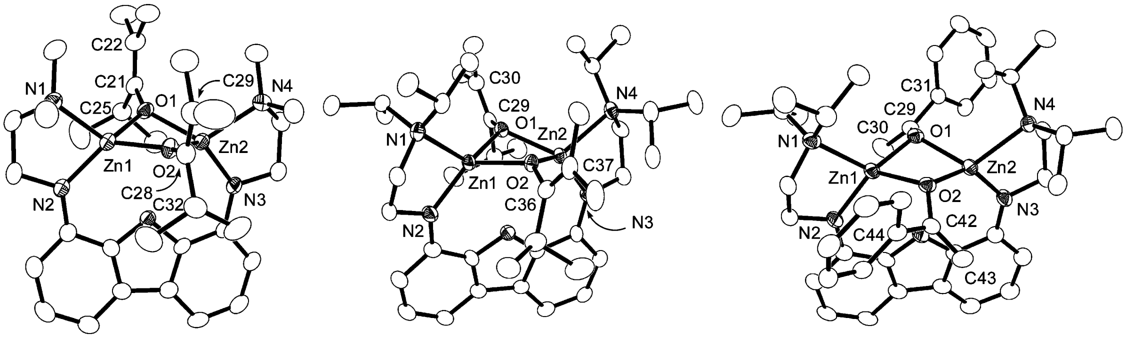
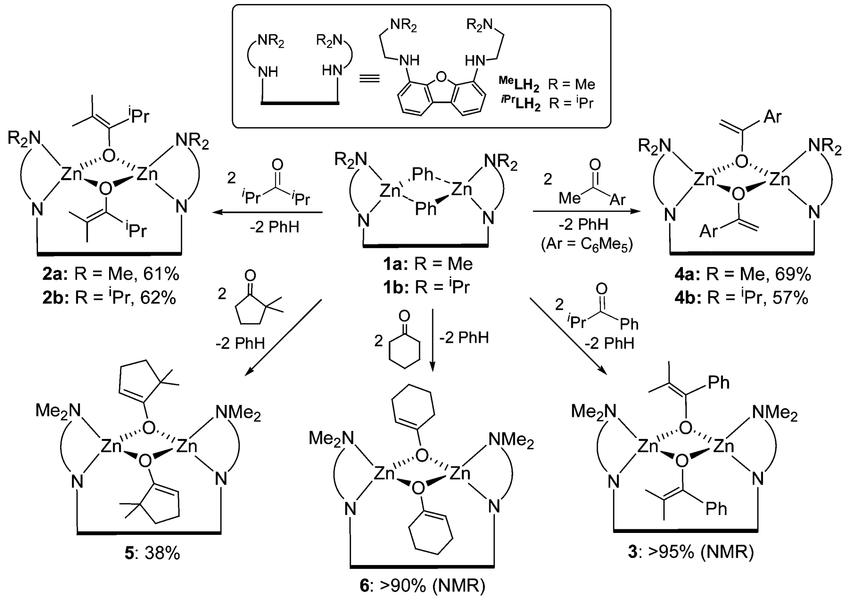
[28] Sheldrick, G. M. *SHELXTL-Plus, A Program for Crystal Structure Determination*, Version 5.1; Bruker AXS: Madison WI, 1998.



2a **2b** **4b**

Figure 1. Molecular structures of **2a**, **2b**, and **4b** drawn with 50% thermal ellipsoids. Hydrogens are omitted in all structures. Cocrystallized toluene and the methyls of the enolate ligands are omitted in **4b**.

Scheme 1



analogous reaction conditions, the related enolate product **4b** was prepared in 56% yield from the ketone and **1b**. Access to enolates of secondary ketones was achieved by the use of cyclic ketones to prevent the formation of mixtures of *E* and *Z* isomers. Heating a toluene solution of in situ formed **1a** with 3 equiv of 2,2-dimethylcyclopentanone to 55 °C for 2 days formed **5**, which was isolated as colorless crystals in 38% yield following cooling to −40 °C. In a similar fashion **6** was formed in 90% yield (by ^{1}H NMR) by reaction of **1a** with cyclohexanone in CH_2Cl_2 at ambient temperature.

Structures. The solid-state structures of **2a**, **2b**, and **4b** were determined by single-crystal X-ray diffraction. These are shown in Figure 1 as 50% thermal ellipsoid plots. Selected bond lengths and angles are included in Table 2.

Compound **2a** features a pair of four-coordinate Zn centers, each bound to a chelating amidoamine donor and two O-bridging enolates. Each amidoamine ligand is coordinated in an unsymmetrical fashion to a Zn center, with the $Zn-N_{amido}$ bonds being, on average, 0.18 Å shorter than the dative $Zn-N_{amine}$ bonds. This is typical for this type of ligand. Interestingly, the enolate oxygens adopt nearly planar geometries.[29] The sum of the angles around O1 and O2 are 358.9° and 359.9°, respectively. The Zn_2O_2 core is symmetrical with the four Zn−O bonds varying only slightly ($Zn-O_{enolate}$ = 1.975(2)−1.982(2) Å). Bond lengths and angles indicate the enolate ligands have isolated carbon−carbon double bonds with an average bond length of 1.36 Å. The enolate ligands are oriented approximately perpendicular to the Zn−Zn axis. This geometry appears to minimize the steric repulsions between the hindered enolates and the bis(amidoamine) ligand. Overall the structure of **2b** is similar to that of **2a** with a few exceptions. Most notable, the Zn_2O_2 core of **2b** is parallelogram shaped with alternating short and long Zn−O bonds that differ by an average of 0.04 Å. Accompanying this distortion is a lengthening of the Zn−Zn distance by 0.05 Å relative to **2a**. This modest expansion of the core likely arises due to increased steric pressures. Geometry at the enolate oxygens is slightly pyramidalized, with the sum of the angles at O1 and O2 being 347.7° and 348.7°, respectively.

The solid-state structure of **4b** differs significantly from those of **2a** and **2b**. Most notably, the enolates of **4b** are not oriented perpendicular to the Zn−Zn axis. This reflects the less hindered profile of the enolate. The Zn_2O_2 core is parallelogram shaped with alternating short and long Zn−O bonds that differ by an average of 0.07 Å. This expansion of the core results in a relatively long intermetal separation of 2.9610(5) Å. Metrical parameters of the enolate ligands again indicate the presence of localized carbon−carbon double bonds (C29−C30, 1.330(4) Å; C42−C43, 1.331(4) Å).

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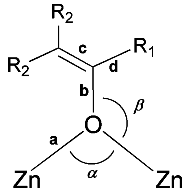
[29] Solid-state structures of related Zn alkoxide derivatives of $^{Me}L^{2-}$ and $^{iPr}L^{2-}$ all feature pyramidalized μ-alkoxide ligands. See ref 26c.

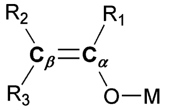
Table 2. Core Bond Lengths and Angles of Structurally Characterized Zn Enolates



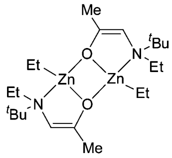
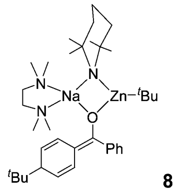
metrical parameter	**2a** (R_1 = ^{i}Pr, R_2 = Me)		**2b** (R_1 = ^{i}Pr, R_2 = Me)		**4b** (R_1 = C_6Me_5, R_2 = H)	
a (Å)	1.980(2)	Zn1−O1[a]	1.986(3)	Zn1−O1	1.973(2)	Zn1−O1
	1.982(2)	Zn1−O2	2.017(3)	Zn1−O2	2.045(2)	Zn1−O2
	1.975(2)	Zn2−O1	2.014(3)	Zn2−O1	2.047(2)	Zn2−O1
	1.980(2)	Zn2−O2	1.983(3)	Zn2−O2	1.980(2)	Zn2−O2
b (Å)	1.384(4)	O1−C21	1.387(5)	O1−C29	1.380(4)	O1−C29
	1.379(4)	O2−C28	1.399(5)	O2−C36	1.391(3)	O2−C42
c (Å)	1.341(5)	C21−C22	1.336(6)	C29−C30	1.330(4)	C29−C30
	1.334(5)	C28−C29	1.338(6)	C36−C37	1.331(4)	C42−C43
d (Å)	1.517(5)	C21−C25	1.523(6)	C29−C33	1.489(4)	C29−C31
	1.512(5)	C28−C32	1.523(6)	C36−C40	1.506(4)	C42−C44
α (deg)	92.77(9)	Zn1−O1−Zn2	93.7(1)	Zn1−O1−Zn2	94.86(8)	Zn1−O1−Zn2
	92.69(9)	Zn1−O2−Zn2	93.7(1)	Zn1−O2−Zn2	94.71(8)	Zn1−O2−Zn2
β (deg)	132.7(2)	Zn1−O1−C21	130.5(2)	Zn1−O1−C29	122.2(2)	Zn1−O1−C29
	133.4(2)	Zn2−O1−C21	123.5(2)	Zn2−O1−C29	123.3(2)	Zn2−O1−C29
	134.2(2)	Zn1−O2−C28	125.8(2)	Zn1−O2−C36	122.0(2)	Zn1−O2−C42
	133.0(2)	Zn2−O2−C28	129.2(2)	Zn2−O2−C36	123.0(2)	Zn2−O2−C42
Zn−Zn (Å)	2.8649(5)	Zn1−Zn2	2.9183(7)	Zn1−Zn2	2.9610(5)	Zn1−Zn2

[a] Atom numbers correspond to the those shown in Figure 1.

Table 3. ^{13}C NMR Spectroscopic Data for Ketone Enolates



(M = Li, Zn, Si)

Compound	δ($C_α$) (ppm)	δ($C_β$) (ppm)	Δδ(α-β) (ppm)	Solvent	Ref.
2a	157.2	102.1	55.1	CD_2Cl_2	b
2b	157.5	105.9	51.6	CD_2Cl_2	b
3	150.9	107.8	43.1	C_6D_6	b
4a	162.8	90.8	72.0	CD_2Cl_2	b
4b	160.4	95.4	65.0	CD_2Cl_2[a]	b
5	169.4	99.2	70.2	CD_2Cl_2	b
6	157.1	99.6	57.4	C_6D_6	b
{Li[OC(=CMe$_2$)Ph]}$_n$	155.6	95.6	60.0	D_8-THF	c
$Me_3SiOC(=CMe_2)Ph$	143.6	112.8	30.8	$CDCl_3$	d
 **7**	160.0	104.6	55.4	CD_2Cl_2	e
 **8**	146.6	106.8	39.8	C_6D_{12}	f

[a] *T* = 253K. [b] This work. [c] Reference 31. [d] Reference 35. [e] Reference 25a. [f] Reference 24.

NMR Spectroscopy. ^{1}H and ^{13}C NMR spectroscopic data for the Zn enolate complexes **2**−**6** are consistent with the structures shown in Scheme 1. Thus, they each have O-bridging enolate anions and overall C_{2v} symmetry in solution. Due to the similarity of these complexes, only selected NMR data will be discussed. ^{13}C NMR spectroscopic data for all new Zn enolates and some related compounds are shown in Table 3.

The ^{1}H NMR spectrum of **2a** (in CD_2Cl_2) is consistent with overall C_{2v} symmetry. Thus, one sharp singlet was observed at δ 2.47 ppm (12H) for the four Me groups of the two $-NMe_2$

donors.[30] Also, only three resonances, with integrated intensities of 2H each, were observed in the aromatic region for the dibenzofuran backbone. In addition to the aforementioned resonances attributable to the $^{Me}L^{2-}$ ligand, a pair of singlets were also found at δ 1.94 and 1.59 ppm (6H each), indicating that the two Me groups of the enolate ligand were inequivalent. Collectively these data suggest that **2a** has an O-zincated structure, almost certainly with the O atoms bridging the two Zn centers, as was observed in the solid-state structure. Additional confirmation of O-zincation can be found from the $^{13}C\{^1H\}$ NMR spectrum of **2a**, which features two downfield resonances at δ 157.2 (C_α) and 102.1 (C_β) ppm arising from the alkene carbons of the enolate ligand (Table 3). These resonances are comparable to those reported for other O-bound metal enolates, including the chelate-stabilized zinc enolate **7**[25a] (160.0, 104.6 ppm) and the sodium zincate species **8**[24] (146.6, 106.8 ppm). Likewise, the ^{13}C NMR spectrum of the lithium enolate $\{Li[OC({=}CMe_2)Ph]\}_n$ (in D_8-THF)[31] features olefinic resonances at δ 155.6 (C_α) and 95.6 (C_β) ppm.

The ^1H NMR spectrum of **4a** in CD_2Cl_2 solution is consistent with overall C_{2v} symmetry for the molecule. The spectrum features two doublets ($^2J = 0.5$ Hz) at δ 4.46 and 3.57 ppm (2H each), which are assigned to the two inequivalent vinylic hydrogens of each enolate. ^{13}C satellites for these two resonances indicate $^1J_{CH}$ values of 153 and 159 Hz for the resonances at 4.46 and 3.57 ppm, respectively. These values are consistent with sp^2-hybridized vinylic C$-$H bonds.[32] The ^1H NMR spectrum of **4b** (CD_2Cl_2) at ambient temperature displays broad resonances for the bis(amidoamine) ligand. This is a result of the $-N^iPr_2$ donors undergoing reversible dissociation at a rate that is similar to that of the NMR data acquisition.[33] Cooling the solution to -20 °C sharpens the spectrum. At this temperature four distinct doublets (6H each) are observed for the four inequivalent methyl groups of the coordinated $-N^iPr_2$ groups. In addition, the vinylic hydrogens are observed as singlets at δ 4.46 and 3.63 ppm.

Comparison of the ^{13}C NMR resonances arising from the enolate ligands can provide some insight into bonding and reactivity. Most notably, the difference in shift between the two ^{13}C resonances arising from the carbon$-$carbon double bond, $\Delta\delta(\alpha - \beta)$, can be used to describe the degree of polarization of the C$-$C bond.[34] This value should correlate with the nucleophilicity of the enolate. However, since $\Delta\delta(\alpha - \beta)$ is also dependent on the degree and type of substitution of the alkene functionality, meaningful comparisons can only be drawn from closely related species. The $^{13}C\{^1H\}$ NMR spectrum of **3** features resonances at δ 150.9 and 107.8 ppm for the alkene carbons C_α and C_β, respectively. The chemical shift difference between these resonances is 43.1 ppm (Table 3). This value is significantly less than that reported for the analogous Li enolate $\{Li[OC({=}CMe_2)Ph]\}_n$,[31] which has $\Delta\delta(\alpha - \beta) = 60.0$ ppm. This is consistent with the Zn enolate being less polarized and less nucleophilic. Consistent with this general trend, the analogous Si enolate $Me_3SiOC({=}CMe_2)Ph$,[35] which is only weakly nucleophilic, has an even smaller $\Delta\delta(\alpha - \beta)$ of 30.8 ppm.

The composition of Zn enolate **2b** is identical to that of **2a** except that it is supported by the more sterically hindered ligand $^{iPr}L^{2-}$ (instead of $^{Me}L^{2-}$). The same relationship exists between **4b** and **4a**. Thus, comparison of the ^{13}C NMR data for these pairs of molecules allows us to observe the effect of ligand sterics on enolate polarization. For **2b** $\Delta\delta(\alpha - \beta) = 51.6$ ppm, while the less hindered **2a** has $\Delta\delta(\alpha - \beta) = 55.1$ ppm. A similar trend is observed for **4b** and **4a**. Thus, the more hindered supporting ligands appear to form enolates with decreased polarization of the carbon$-$carbon bonds. This observation can be rationalized by considering solid-state structural data. The $Zn-N_{amine}$ bonds of **2b** are on average 0.06 Å longer than those of **2a**. Thus, the Zn centers of **2b** are expected to form stronger bonds to the enolate donors, which results in less charge localization at oxygen. In turn this should yield less polarization of the carbon$-$carbon double bond.

In conclusion, we have isolated and fully characterized the first series of zinc enolates derived from simple ketones. In all cases, O-bridging structures were observed in the crystalline state. NMR data suggest that these structures are maintained in solutions of noncoordinating solvents. Chemical shift differences observed for the enolate ligands indicate that Zn enolates have C$-$C bond polarizations that are intermediate to those of related Li and Si enolates. This polarization is also dependent on the degree of steric bulk on the supporting ligands. The use of these and related functionalized organozincs in a variety of bond-forming processes, including polymerizations, is currently being explored.

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[30] In contrast, the related Zn amide enolate $^{Me}LZn_2[OC(CH_2)NEt_2]_2$ has overall C_2 symmetry due to the presence of C,O-bridging $[OC(CH_2)NEt_2]^-$ groups. This is observed as two inequivalent Me groups in the $-NMe_2$ donors. See ref 19.

[31] Jackson, L. M.; Szeverenyi, N. M. *J. Am. Chem. Soc.* **1977**, *99*, 4954−4962.

[32] *Carbon-13 NMR Spectroscopy*, 3rd ed.; Breitmaier, E., Voelter, W., Eds.; Wiley-VCH: Weinheim, Germany, 1989; Table 3.6, p 137.

[33] The related dizinc alkoxide derivative $^iPrLZn_2[OCHPh_2]_2$ was similarly found to undergo this type of reversible amine dissociation. See ref 26c.

[34] Similar analysis of ^{13}C NMR spectroscopic data has been performed for Li aluminate ester enolates. See: Rodriguez-Delgado, A.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2005**, *127*, 961−974.

[35] Eames, J.; Coumbarides, G. S.; Suggate, M. J.; Weerasooriya, N. *Eur. J. Org. Chem.* **2003**, *4*, 634−641.