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Solid- and Solution-Phase Structures of Zinc Enolates of Amides and Ketones

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Solid-phase structural data for five Zn enolate derivatives are presented. Included are the amide enolates BrZn[CH$_2$C(O)NEt$_2$](thf) (**1a**), BrZn[CH$_2$C(O)NEt$_2$](dmso) (**1b**), and BrZn[CH$_2$C(O)NEt$_2$](^{t}Bu-py) (**1c**), which are all dimeric in the solid phase with each of the enolate ligands binding in a C,O-bridging fashion. Solution molecular weight data for **1a**, determined using diffusion-order NMR spectroscopy, indicate a degree of association of 3.8 in C$_6$D$_6$ solution. In the presence of added Lewis base, however, dimeric (in 1:9 D$_8$-thf/C$_6$D$_6$) and monomeric (in D$_6$-dmso) species are formed. Similar solution behavior is observed for the Reformatsky ester BrZn[CH$_2$C(O)O^{t}Bu](thf). Structural data are also presented for the Zn ketone enolates BrZn[OC(=CMe$_2$)^{i}Pr](dmf) (**2b**) and BrZn[OC(=CH$_2$)Mes](dmf) (**3b**). These are dimeric in the solid phase, with O-bridging enolate ligands. This nuclearlity is maintained for **2b** in noncoordinating solvents and in the presence of 10% thf. Dissolution of **2b** in D$_6$-dmso, however, appears to form a mononuclear species.

Introduction

Zinc enolates are frequently used as nucleophilic reagents[1] in organic synthesis for both addition reactions[2] and metal-catalyzed couplings.[3] Recently cationic Zn ketone enolates have also been shown to be effective catalysts for the polymerization of alkylacrylates.[4] Despite the importance of this class of compounds, there is relatively little solution- and solid-phase structural information available that can be used to shed insight into their reactivity patterns and properties. Notably, Boersma and co-workers reported the solid-state structure of the Reformatsky ester BrZn[CH$_2$C(O)O^{t}Bu](thf),[5] which was found to be dimeric with C,O-bridged enolate ligands. Molecular weight determinations indicated that this nuclearity was maintained in common solvents, but in strongly coordinating solvents monomeric species formed. Other structurally characterized Zn enolates include mixed-metal species[6] and chelation-stabilized β-substituted enolates.[7] Also, we recently reported a series of well-defined bimetallic Zn enolate derivatives of ketones,[4,8a] amides,[8b] and phosphine oxides[8b] that were supported by chelating bis(amidoamine) ligands. Here we report structural studies of Zn enolate derivatives of ketones and amides in the presence of various monodentate Lewis bases.

Experimental Section

General Considerations. Standard Schlenk-line and glovebox techniques were used unless stated otherwise. Tetrahydrofuran (thf), toluene, hexanes, and benzene were passed through columns of activated alumina and sparged with N$_2$ prior to use. C$_6$D$_6$ was vacuum transferred from Na-benzophenone ketyl. CD$_2$Cl$_2$ was vacuum transferred from CaH$_2$. Dimethyl sulfoxide-D$_6$ (D$_6$-dmso) and D$_8$-thf were passed through activated alumina and degassed using three freeze–pump–thaw cycles. BrZn[CH$_2$C(O)O^{t}Bu](thf) and BrZn[CH$_2$C(O)NEt$_2$](thf)[9] (**1a**) were prepared as described by Hartwig and co-workers.[3b] Dimethyl sulfoxide (dmso), 4-*tert*-butylpyridine (^{t}Bu-py), and *N*,*N*-dimethylformamide (dmf) were distilled from CaH$_2$ under N$_2$. Both 2-bromo-2,4-dimethyl-3-pentanone and 2-bromo-1-(2,4,6-trimethylphenyl)ethanone were prepared by the procedure reported by Keinan and co-workers.[10] Chemical shifts (δ) for ^{1}H NMR spectra are given relative to residual protium in the deuterated solvent at δ 7.16, 5.32, 7.27, and 2.50 ppm for C$_6$D$_6$, CD$_2$Cl$_2$, CDCl$_3$, and D$_6$-dmso, respectively. Elemental analyses were determined by Desert Analytics and the University of Michigan elemental analysis laboratory.

BrZn[CH$_2$C(O)NEt$_2$](dmso) (1b). Solid **1a** (0.0805 g, 0.242 mmol Zn) was dissolved in benzene (3 mL). The solution was filtered, and dmso (0.017 mL, 0.24 mmol) was added. The mixture was then vigorously shaken. After 1 h, hexanes was added to the clear, colorless solution by vapor diffusion. After a few days the

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Table 1. Crystallographic Data and Collection Parameters

	1a	**1b**	**1c**	**2b**·(benzene)$_2$	**3b**
formula	$C_{20}H_{40}Br_2N_2O_4Zn_2$	$C_{16}H_{36}Br_2N_2O_4S_2Zn_2$	$C_{30}H_{50}Br_2N_4O_2Zn_2$	$C_{32}H_{52}Br_2N_2O_4Zn_2$	$C_{28}H_{40}Br_2N_2O_4Zn_2$
fw (g·mol^{-1})	663.10	675.15	789.30	819.32	759.18
space group	$P2_1/n$ (#14)	$P\bar{1}$ (#2)	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P2_1/c$ (#14)
temp (K)	151(2)	147(2)	149(2)	147(2)	147(2)
a (Å)	10.6870(5)	8.0442(4)	7.8297(7)	11.7235(11)	8.123(4)
b (Å)	8.8254(4)	9.6895(5)	10.2172(9)	9.2870(8)	12.489(6)
c (Å)	14.8247(7)	9.9379(5)	21.834(2)	17.3462(15)	16.180(7)
α (deg)	90	103.446(1)	90	90	90
β (deg)	99.5370(10)	99.177(1)	95.325(2)	96.592(2)	101.26(1)
γ (deg)	90	106.337(1)	90	90	90
Z	2	1	2	2	2
V (Å^3)	1378.90(11)	701.65(6)	1739.1(3)	1876.1(3)	1610(1)
d_{calc} (g·cm^{-3})	1.597	1.598	1.507	1.450	1.566
θ range (deg)	2.19–27.88	2.17–27.88	1.87–27.48	1.75–27.87	2.08–27.48
μ (mm^{-1})	4.662	4.726	3.708	3.442	4.005
cryst size (mm)	0.20 × 0.15 × 0.10	0.50 × 0.40 × 0.30	0.26 × 0.23 × 0.12	0.50 × 0.25 × 0.05	0.25 × 0.23 × 0.21
no. of reflns collected	10 751	5389	13 232	7696	12 226
no. of data/restraints/params	2383/0/136	2787/0/131	3988/0/186	2150/0/196	3695/0/172
R1 (for $F_o > 4\sigma F_o$)	0.0476	0.0512	0.0511	0.0800	0.0749
R1, wR2 (all data)	0.0741, 0.1162	0.0570, 0.1395	0.0812, 0.1220	0.1715, 0.2144	0.1470, 0.2140
GOF	0.994	1.036	0.982	0.951	0.945
largest peak, hole (e·Å^{-3})	0.989, −0.695	1.119, −1.026	0.951, −0.735	0.823, −0.813	1.501, −1.210

product was isolated as clear, colorless crystals (0.059 g, 72%). ^{1}H NMR (CD_2Cl_2): δ 3.32 (q, 8H, J = 7.2 Hz, $-NCH_2CH_3$), 2.77 (s, 12H, dmso), 1.81 (s, 4H, $-ZnCH_2-$), 1.22 (t, 6H, J = 7.2 Hz, $-NCH_2CH_3$), 1.11 (t, 6H, J = 7.2 Hz, $-NCH_2CH_3$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 182.7, 44.2, 41.4, 39.9 (dmso), 22.5, 13.9, 13.7 ppm. IR: 2918 (s), 2853 (s), 1540 (s), 1494 (s), 1457 (s), 1419 (m), 1377 (s), 1362 (m), 1316 (m), 1291 (m), 1077 (w), 1066 (m), 1034 (m), 998 (s), 943 (s), 671 (w), 635 (w) cm^{-1}. Anal. Calcd (Found) for BrZn[$CH_2C(O)NEt_2$](dmso), $C_8H_{18}BrNO_2SZn$: C, 28.46 (28.33); H, 5.37 (5.13); N, 4.15 (3.96).

BrZn[$CH_2C(O)NEt_2$](^{t}Bu-py) (1c). Benzene (3 mL) and **1a** (0.104 g, 0.312 mmol Zn) were combined in a vial. Then 4-*tert*-butylpyridine (0.091 mL, 0.62 mmol) was added, and the mixture was shaken. After 1 h, hexanes was added by vapor diffusion to afford the product as clear, colorless crystals over several days (0.094 g, 76%). ^{1}H NMR (CD_2Cl_2): δ 8.64 (d, 4H, J = 6.8 Hz, ^{t}Bu-*py*), 7.52 (d, 4H, J = 6.8 Hz, ^{t}Bu-*py*), 3.35 (br, 4H, $-NCH_2CH_3$), 3.23 (br, 4H, $-NCH_2CH_3$), 1.93 (br, 4H, $-ZnCH_2C(O)-$), 1.35 (s, 18H, ^{t}*Bu*-py), 1.11 (m, 12H, $-NCH_2CH_3$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 182.9, 166.0 (^{t}Bu-*py*), 149.0 (^{t}Bu-*py*), 121.9 (^{t}Bu-*py*), 43.8, 40.9, 35.1, 30.3, 28.4, 22.0, 13.6, 13.5 ppm. IR: 2955 (s), 2929 (s), 2855 (s), 1614 (m), 1536 (s), 1491 (s), 1458 (s), 1421 (s), 1377 (m), 1357 (m), 1308 (w), 1289 (m), 1228 (w), 1073 (m), 1037 (w), 1023 (m), 973 (m), 844 (w), 835 (m), 759 (w), 727 (w), 637 (m), 572 (s) cm^{-1}. Anal. Calcd (Found) for BrZn[$CH_2C(O)NEt_2$](^{t}Bu-py), $C_{15}H_{25}BrN_2OZn$: C, 45.65 (45.46); H, 6.38 (6.38); N, 7.10 (6.75).

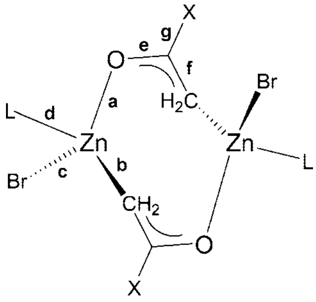
BrZn[OC(=CMe_2)^{i}Pr](dmf) (2b). The Zn enolate BrZn[OC(=CMe_2)^{i}Pr](thf) (**2a**) was prepared from activated Zn and 2-bromo-2,4-dimethyl-3-pentanone using a procedure analogous to that reported for the synthesis of **1a**. The product was isolated as a colorless solid. NMR spectra acquired for solutions of this enolate were extremely broad. Toluene (10 mL) and **2a** (0.064 g, 0.19 mmol Zn) were combined in a vial to form a clear, colorless solution. Then dmf (0.046 mL, 0.59 mmol) was added, and the mixture was shaken. The solution was then cooled –40 °C. The product was isolated as colorless crystals (0.058 g, 90%). ^{1}H NMR (CD_2Cl_2): δ 8.07 (s, 2H, $Me_2NC(O)H$), 3.06 (s, 6H, $-N(Me)Me$), 2.97 (s, 6H, $-N(Me)Me$), 2.80 (sept, 2H, J = 7 Hz, $-CHMe_2$), 1.73 (s, 6H, $-C{=}C(Me)Me$), 1.59 (s, 6H, $-C{=}C(Me)Me$), 1.03 (d, 12H, J = 7 Hz, $-CHMe_2$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 166.5 (dmf), 121.6, 104.1, 38.6 (dmf), 33.3 (dmf), 30.0, 21.1, 19.4, 19.1 ppm. IR: 2952 (s), 2928 (s), 2856 (s), 1658 (s) (νCO), 1457 (s), 1437 (s), 1369 (s), 1258 (s), 1191 (s), 1157 (s), 1116 (s), 1088 (m), 1049 (s), 931 (w), 724 (m), 698 (s) cm^{-1}. Anal. Calcd (Found) for BrZn[OC(^{i}Pr)=CMe_2](dmf), $C_{10}H_{20}BrNO_2Zn$: C, 36.22 (36.06); H, 6.08 (6.09); N, 4.22 (4.18).

BrZn[OC(=CH_2)Mes](dmf) (3b). The Zn enolate BrZn[OC(=CH_2)Mes](thf) (**3a**) was prepared from activated Zn and 2-bromo-1-(2,4,6-trimethylphenyl)ethanone using a procedure analogous to that reported for the synthesis of **1a**. The product was isolated as a colorless solid. NMR spectra acquired for solutions of this enolate were extremely broad. CH_2Cl_2 (10 mL) and **3a** (0.214 g, 0.566 mmol Zn) were combined in a vial to form a colorless slurry. Then dmf (0.088 mL, 1.1 mmol) was added, and the resulting solution was filtered. The solution was cooled to –15 °C overnight. The product was obtained as colorless crystals (0.086 g, 40%), which were isolated and dried under reduced pressure. ^{1}H NMR (CD_2Cl_2): δ 7.58 (s, 2H, dmf), 6.74 (s, 4H, Ar), 4.45 (s, 2H, $-C{=}C(H)H$), 3.75 (s, 2H, $-C{=}C(H)H$), 2.94 (s, 6H, dmf), 2.91 (s, 6H, dmf), 2.28 (s, 12H), 2.21 (s, 6H) ppm. $^{13}C\{^1H\}$ (CD_2Cl_2): δ 166.4 (dmf), 150.1, 138.2, 137.1, 136.9, 128.1, 89.1, 38.7, 33.2, 21.4 (dmf), 20.6 (dmf) ppm. IR: 2853 (s), 2361 (m), 2337(m), 1653 (s), 1458 (s), 1376 (s), 1281 (m), 1169 (w), 1082 (w), 983 (w), 721 (w), 696 (w), 668 (w) cm^{-1}. Anal. Calcd (Found) for BrZn[OC(=CH_2)Mes](dmf), $C_{14}H_{20}BrNO_2Zn$: C, 44.29 (43.98); H 5.31 (5.04); N 3.69 (3.45).

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; λ = 0.71073 Å; graphite monochromator), and cooled to approximately −125(5) °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 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-squared.[11] Notable details of each data collection and refinement are described below.

Table 2. Core Metrical Parameters of BrZn[$CH_2C(O)O^tBu$](thf),[a] 1a, 1b, and 1c



metrical parameter	BrZn[$CH_2C(O)O^tBu$](thf) (X = O^tBu, L = thf)	**1a** (X = NEt_2, L = thf)	**1b** (X = NEt_2, L = dmso)	**1c** (X = NEt_2, L = ^{t}Bu-py)
a (Å)	2.02(1)	1.991(3)	1.985(2)	1.981(3)
b (Å)	1.98(2)	2.034(4)	2.028(3)	2.040(4)
c (Å)	2.346(3)	2.3678(6)	2.4030(5)	2.4100(6)
d (Å)	2.05(1)	2.077(3)	2.022(3)	2.074(4)
e (Å)	1.31(2)	1.266(5)	1.276(4)	1.292(5)
f (Å)	1.41(2)	1.451(5)	1.461(4)	1.456(6)
g (Å)	1.32(2)	1.349(5)	1.346(4)	1.339(5)

[a] Reference 5.

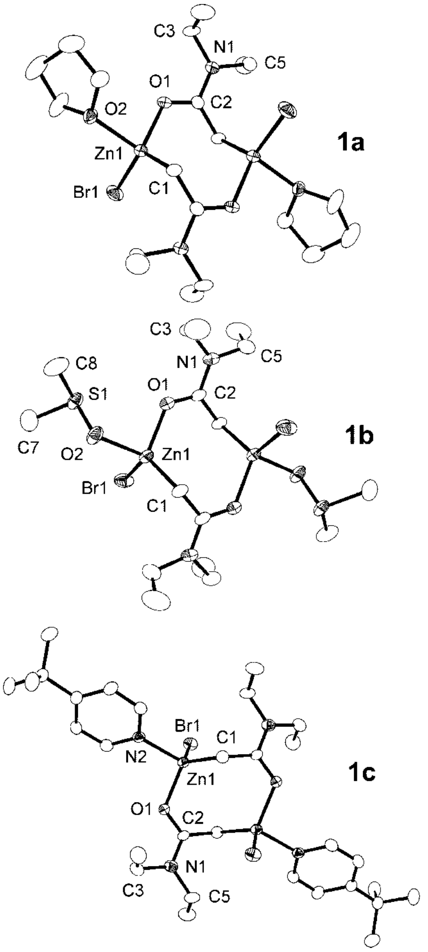


Figure 1. Solid-phase structures of {BrZn[$CH_2C(O)NEt_2$](thf)}$_2$ (**1a**), {BrZn[$CH_2C(O)NEt_2$](dmso)}$_2$ (**1b**), and {BrZn[$CH_2C(O)NEt_2$](^{t}Bu-py)}$_2$ (**1c**) drawn with 50% thermal ellipsoids. Hydrogens are omitted.

Structure of 1a. Crystals of **1a** formed in a thf solution at –40 °C. Preliminary data indicated a primitive monoclinic cell. Analysis of the systematic absences of the full data set indicated the space group *P*2$_1$/*n* (#14). This choice was confirmed by the successful solution and refinement of the structure. The molecule rests 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.

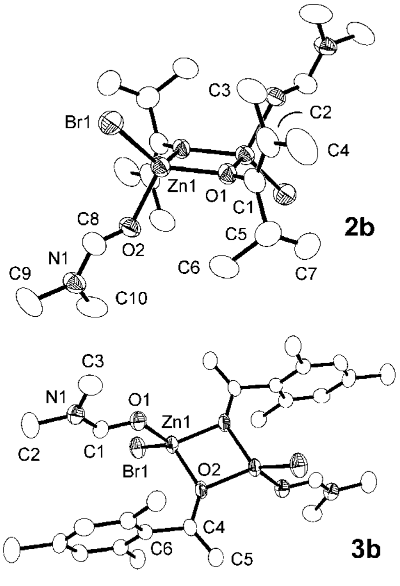


Figure 2. Solid-phase structures of {BrZn[OC(=CMe_2)^{i}Pr](dmf)}$_2$·(benzene)$_2$ (**2b**) and {BrZn[OC(=CH_2)Mes](dmf)}$_2$ (**3b**) drawn with 50% thermal ellipsoids. Hydrogens and cocrystallized solvent are omitted.

Structure of 1b. Crystals of **1b** formed in a toluene solution at ambient temperature. 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 molecule rests 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 1c. Crystals of **1c** were grown by vapor diffusion of hexanes into a benzene solution at ambient temperature. Preliminary data indicated a primitive monoclinic cell. Analysis of the systematic absences of the full data set indicated space group *P*2$_1$/*c* (#14). This choice was confirmed by the successful solution

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

and refinement of the structure. The molecule rests upon 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 2b·(benzene)$_2$. Crystals of **2b** were grown by vapor diffusion of hexanes into a benzene solution at ambient temperature. Preliminary data indicated a primitive monoclinic cell. Analysis of the systematic absences of the full data set indicated space group $P2_1/c$ (#14). This choice was confirmed by the successful solution and refinement of the structure. The molecule rests on a crystallographic inversion center. There is also one cocrystallized molecule of benzene in the asymmetric unit. 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 3b. Crystals of **3b** were grown by diffusion of hexanes into a benzene solution at room temperature. Preliminary data indicated a primitive monoclinic cell. Analysis of the systematic absences of the full data set indicated space group $P2_1/c$ (#14). This choice was confirmed by the successful solution and refinement of the structure. All non-H atoms were refined anisotropically. The vinylidene hydrogens (H1 and H2) were located in the difference Fourier map and were refined isotropically. All other hydrogens were placed in idealized positions and were included in structure factor calculations but were not refined.

Diffusion Ordered Spectroscopy (DOSY). DOSY experiments were performed on a Varian Inova-500 NMR spectrometer operating at 500.372 MHz for ^{1}H observation. The instrument was equipped with a Nalorac PFG triple-resonance, indirect detection probe. This probe, combined with the Varian Performa-II PFG gradient amplifier, delivered a maximum PFG strength of 68 gauss/cm. The diffusion dimension was resolved using the standard bipolar pulsed pair stimulated echo (Dbppste) sequence provided by Varian, Inc., and the 2D-DOSY calculation was performed according to the equations of Stejskal and Tanner,[12] using the DOSY analysis tools in the VNMR 6.1C software package. Experiments were performed at ambient temperature using adequate air flow around the sample to minimize thermal gradients and corresponding convection currents. Proton 90° pulses of 9.6 μs were used, and for each experiment the diffusion delay time (del) was calibrated such that a maximum PFG strength of 58 gauss/cm caused the gradient echo to decay nearly to zero. Each experiment was performed using an array of 22 pulsed field gradient (PFG) strengths, to give high-quality statistical fits in the diffusion calculation. The diffusion constant (D) of a particular molecule can be related to its molecular weight through its hydrodynamic radius, as shown by the Stokes–Einstein equation.[13] Assuming similar molecular geometries, the ratio of diffusion constants of two different molecular species should be inversely proportional to the square root of the molecular weights of those molecules in the equation $(D_1/D_R) = ((M_R/M_1))^{1/2}$, where D_1 and M_1 are the diffusion constant and molecular weight of the metal complex, and D_R and M_R are the diffusion constant and molecular weight of the reference respectively.[14] Using this relationship, sample molecular weights were estimated from their diffusion constants and that of a suitable reference sample (1,3,5-triphenylbenzene). It is also worth noting that measuring the ratio of D versus an internal standard also removes the need to consider parameters such as the viscosity of the solution.

Results and Discussion

Preparation of Zn Enolates. The amide enolate derivative $BrZn[CH_2C(O)NEt_2](thf)$ (**1a**) was conveniently prepared by the reaction of activated Zn with $BrCH_2C(O)NEt_2$ in thf solution as described by Hartwig and co-workers.[3b] The crude product was isolated as a colorless solid by evaporation of the reaction solution. Dissolution of the product in thf followed by filtration and cooling to −40 °C afforded purified product as nice colorless crystals. Both ^{1}H NMR spectroscopy and combustion analysis confirmed the formulation of a single thf per $[CH_2C(O)NEt_2]$ group. Reaction of a benzene solution of **1a** with 1.0 equiv (per Zn) of dmso gave no observable change. However, the dmso adduct $BrZn[CH_2C(O)NEt_2](dmso)$ (**1b**) crystallized over a few days upon the slow addition of hexanes by vapor diffusion. The product was isolated in 72% yield as colorless crystals. In an analogous manner the related 4-*tert*-butylpyridine adduct $Zn[CH_2C(O)NEt_2](^t\text{Bu-py})$ (**1c**) was prepared and isolated in 76% yield. The empirical formulations of both **1b** and **1c** were determined using NMR spectroscopy and combustion analysis.

Activated Zn and 2-bromo-2,4-dimethyl-3-pentanone were reacted in thf solution to form the Zn ketone enolate $BrZn[OC({=}CMe_2)^i\text{Pr}](thf)$ (**2a**), which was isolated as a solid by evaporation of the reaction solution. Characterization of this product by NMR spectroscopy in noncoordinating solvents was not useful due to the broadness of the spectra. A toluene solution of **2a** was then combined with a modest excess of dmf to form a clear, colorless solution. Cooling of this solution to –40 °C overnight afforded colorless crystals of the dmf adduct $BrZn[OC({=}CMe_2)^i\text{Pr}](dmf)$ (**2b**) in 90% yield. Repeating the above two-step process using 2-bromo-1-(2,4,6-trimethylphenyl)ethanone in place of 2-bromo-2,4-dimethyl-3-pentanone formed the Zn ketone enolate $BrZn[OC({=}CH_2)Mes](dmf)$ (**3b**), which was isolated as colorless crystals in 40% yield. The empirical formulations of both **2b** and **3b** were determined by ^{1}H NMR spectroscopy and combustion analysis.

Structural Studies. The X-ray crystal structure of the Zn ester enolate $BrZn[CH_2C(O)O^t\text{Bu}](thf)$ has been reported by Boersma and co-workers.[5] This revealed that the complex was dinuclear, with the enolates acting as C,O-bridging ligands to form a central eight-membered $(ZnCCO)_2$ ring that was located on a crystallographic inversion center. The Zn−C and Zn−O bond lengths (Table 2) involving the enolate ligand were fairly short and consistent with single bonds. This finding was consistent with their solution molecular weight determinations that showed a dimeric structure persisting when $BrZn[CH_2C(O)O^t\text{Bu}](thf)$ was dissolved in thf, pyridine, or dioxane. Dissolution in dmso, however, formed a mononuclear C-metalated species.

The solid-state structures of the Zn amide enolates **1a**, **1b**, and **1c** were determined by single-crystal X-ray diffraction (Figure 1). Core bond lengths and angles are shown in Table 2. The general features of each of the three structures are similar to those of $BrZn[CH_2C(O)O^t\text{Bu}](thf)$. All are dinuclear and located on crystallographic inversion centers. Also, the enolates all bind as C,O-bridging ligands to form centrosymmetric eight-membered $(ZnCCO)_2$ rings. Due to their similarities, only the structure of **1a** will be described in detail.

For complex **1a** the geometric arrangement of donors at Zn is typical pseudo-tetrahedral with bond angles ranging from 91.0(1)° (O1−Zn−O2) to 124.7(1)° (C1−Zn−Br). The three smallest angles all involve the thf donor ligand. This arrangement allows the three stronger, and more substantially polarized, donors to be farther apart than in a true tetrahedral geometric

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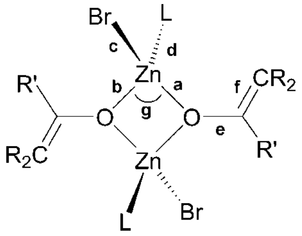
Table 3. Core Metrical Parameters of Zn Ketone Enolates 2b and 3b[a]



metrical parameter	**2b** (R = Me, R′ = ^{i}Pr)		**3b** (R = H, R′ = Mes)	
a (Å)	1.952(5)	Zn1−O1	1.955(5)	Zn1−O2
b (Å)	1.973(5)	Zn1−O1A	1.954(5)	Zn1−O2A
c (Å)	2.336(1)	Zn1−Br1	2.315(2)	Zn1−Br1
d (Å)	1.983(5)	Zn1−O2	1.984(5)	Zn1−O1
e (Å)	1.384(9)	O1−C1	1.370(8)	O2−C4
f (Å)	1.35(1)	C1−C2	1.30(1)	C4−C5
g (deg)	82.2(2)	O1−Zn1−O1A	80.7(2)	O2−Zn1−O2A
Zn−Zn (Å)	2.957(2)	Zn1−Zn1A	2.978(2)	Zn1−Zn1A
torsion (deg)	81.0(9)	Zn1−O1−C1−C2	166.3(6)	Zn1−O2−C4−C5
	−82.3(9)	Zn1A−O1−C1−C2	−18(1)	Zn1A−O2−C4−C5

[a] Atom numbers correspond to those in Figure 2.

arrangement. The $Zn-O_{enolate}$ (1.991(3) Å) and Zn−C (2.034(4) Å) bond lengths are both fairly short and indicate strong interactions. The $-NEt_2$ group is acting as a π-donor to the enolate ligand. This is apparent from the planar geometry at N1 (sum of angles = 359.7°) and the orientation of the $-NEt_2$ group being such that the donating $N(p_z)$ orbital is aligned with the enolate π-orbitals (torsion angle (O1−C2−N1−C3) = 2.9(5)°).

The solid-state structures of the Zn ketone enolates **2b** and **3b** were also determined (Figure 2). Both were found to be dinuclear and located on crystallographic inversion centers. Unlike the amide enolates, the ketone enolates are coordinated to the Zn centers as O-bridging ligands. Thus, both compounds feature flat, essentially diamond-shaped Zn_2O_2 cores. This O-bridging motif was also observed for related Zn ketone enolates supported by binucleating bis(amidoamine) ligands.[8a]

For **2b**, the geometry at the bridging oxygen (O1) is nearly planar, with the sum of angles being 358.6°. The enolate double bond is oriented nearly perpendicular to the Zn_2O_2 plane, as is shown by the Zn1−O1−C1−C2 torsion angle of 81.0(9)°. Lastly, the C−C bond length of 1.35(1) Å is consistent with a bond order of two. Compound **3b** is overall quite similar, with one notable exception. Thus, while geometry at the enolate oxygen (O2) is once again planar (sum of angles = 359.9°), the orientation of the enolate double bond is nearly coplanar to the Zn_2O_2 core. This is indicated by the Zn1−O2−C4−C5 torsion angle of 166.3(6)°. Evaluating the two distinct enolate orientations, it appears likely that the perpendicular orientation of **2b** is caused by unfavorable steric interactions between the very hindered $[OC(=CMe_2)^iPr]$ groups and the other ligands coordinated to Zn.

Solution-phase molecular weights for **1a** and **2b** were obtained by diffusion-ordered NMR spectroscopy (DOSY). For comparison, data were also collected for the ester enolate $BrZn[CH_2C(O)O^tBu](thf)$. The calculated solution molecular weights (MW) for the three species dissolved in various solvents are presented in Table 4. The structural similarity of the ester and amide enolate derivatives in the solid state is mirrored in solution. Both **1a** and $BrZn[CH_2C(O)O^tBu](thf)$ appear to be approximately tetranuclear in C_6D_6 solution. The solution MW of 1370 $g \cdot mol^{-1}$ for $BrZn[CH_2C(O)O^tBu](thf)$ in C_6D_6 is consistent with a degree of association (DA) of 4.1. Similarly the value of 1250 $g \cdot mol^{-1}$ for **1a** is consistent with a DA of 3.8. The addition D_8-thf (10% by volume) to the enolates drops the measured MW values to 570 and 600 $g \cdot mol^{-1}$ for $BrZn[CH_2C(O)O^tBu](thf)$ and **1a**, respectively. This suggests the formation of dinuclear species ($DA(BrZn[CH_2C(O)O^tBu](thf)) = 1.7$, DA(**1a**) = 1.8).[15] Dissolution of the same two enolates in D_6-dmso resulted in the formation of even lower MW species. The value of 420 $g \cdot mol^{-1}$ for $BrZn[CH_2C(O)O^tBu](thf)$ is consistent with the formation of mononuclear $[BrZn[CH_2C(O)O^tBu](D_6\text{-dmso})_2]$, which has a calculated MW of 428.8 $g \cdot mol^{-1}$. Similarly the solution MW of 430 $g \cdot mol^{-1}$ for **1a** suggests the formation of the analogous mononuclear species. We note that the solution MW results that we obtained for $BrZn[CH_2C(O)O^tBu](thf)$ agree with the values obtained previously (for thf and dmso solutions) using ebulliometric and cryoscopic methods.[5a]

Table 4. Solution Molecular Weights of Zn Enolates as Determined by DOSY Experiments

complex	solvent	MW (g/mol)[a]
$BrZn[CH_2C(O)O^tBu]$ (thf)	C_6D_6	1370 ± 20
	1:9 D_8-thf/C_6D_6	570 ± 10
	D_6-dmso	420 ± 20
$BrZn[CH_2C(O)NEt_2]$ (thf) (**1a**)	C_6D_6	1250 ± 30
	1:9 D_8-thf/C_6D_6	600 ± 30
	D_6-dmso	430 ± 20
$BrZn[OC(=CMe_2)^iPr]$ (dmf) (**2b**)	3:1 C_6D_6/CD_2Cl_2	510 ± 60
	0.44:3:1 D_8-thf/C_6D_6/CD_2Cl_2	510 ± 20
	D_6-dmso	400 ± 20

[a] Values are the average of data acquired from two independently prepared samples. Errors are estimated from the maximum variance in the positions of diffusion signals in the DOSY spectra.

The ketone enolate **2b** dissolved in 3:1 C_6D_6/CD_2Cl_2 was found to have a solution MW of 510 $g \cdot mol^{-1}$. An identical MW value was obtained for the sample in the presence of 10% (volume) D_8-thf. Thus, **2b** appears to be dimeric in both of those

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(15) We have not observed data suggesting Schlenk-type disproportionations for the systems reported here. Nonetheless we note that disproportionations would affect the *interpretation* of the solution MW data.

solutions. However, the MW value of 510 g·mol^{-1} is somewhat lower than expected. This may suggest the formation of a Lewis base-free dimer in solution by the dissociation of dmf. This scenario gives a calculated DA of 2.0. The solution MW of **2b** in D_6-dmso was found to be 400 g·mol^{-1}. This is most consistent with the formation of the mononuclear species [BrZn(enolate)(D_6-dmso)$_2$], which has a calculated MW of 426.8 g·mol^{-1}.

Conclusion

Here we have presented structural studies for a series of simple Zn ketone and amide enolates. Our studies indicate that as solids Zn ketone enolates adopt O-bridging structures, while the amide enolates prefer C,O-bridging motifs; the latter are analogous to those previously reported for Zn ester enolates. Thus for Zn complexes the C,O-bridging motif is found only for those enolate ligands with a π-donating heteroatom (N or O). Solution molecular weight studies performed in a variety of solvents indicate that Zn amide and ester enolates adopt monomeric, dimeric, and tetrameric structures. As expected, the degree of association tracks inversely with the donor strength of the Lewis base present. Similarly solution molecular weight studies of Zn ketone enolates indicate the presence of both monomeric and dimeric species, which are base dependent.

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Supporting Information Available: Crystallographic information files (CIF) for all structurally characterized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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