5 and **2** are described in the supplementary material. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions ($d_{C-H} = 0.96$ Å) and included in the final structure factor calculation by using a riding model.

Crystallographic Analysis of [Pb(μ,η¹-OCH₂CH₂OMe)₂]∞ (5). A colorless needle (0.10 × 0.23 × 1.00 mm) obtained from methoxyethanol solution was mounted in a capillary for diffraction analysis. All attempts to cleave such needles to provide a sample with the proper dimensions were destructive. Crystal data are listed in Table II. The structure was determined by direct methods in the space group Cc (No. 9) and subsequently transformed into space group $C2/c$ (No. 15). The reduction in the R index and some esd's for bond distances and angles confirmed the final choice of space group. Temperature factors (U) for hydrogen atoms were assigned a common value and refined to 0.08 (1) Å². The final residuals for 53 variables refined against the 1026 data for which $I > 3\sigma(I)$ were $R = 0.0258$ and $R_w = 0.0320$.

Crystallographic Analysis of [Pb₃(μ-O-t-Bu)₆] (2). A colorless prism (0.30 × 0.30 × 0.40 mm) was obtained from a synthetic reaction mixture and mounted in a glass capillary for diffraction analysis. Crystal data are listed in Table II. The hexagonal axial setting (R_{obv}) of the trigonal unit cell was chosen. Photographic evidence and systematic absences indicated the possible space groups were $R3$ (No. 146), $R\bar{3}$ (No. 148), $R32$ (No. 155), $R3m$ (No. 160), or $R\bar{3}m$ (No. 166). Successful refinement confirmed the space group to be $R\bar{3}$ (No. 148). Temperature factors (U) for hydrogen atoms were fixed at 0.21 Å². The final residuals for 52 variables refined against the 517 data for which $I > 3\sigma(I)$ were $R = 0.0504$ and $R_w = 0.0592$.

Attempted Crystallographic Analysis of [Pb(μ,η¹-O-i-Pr)₂]∞ (1). After the screening of more than 12 crystals, a marginally suitable sample was selected for diffraction studies. A monoclinic unit cell was determined: $a = 17.86$ (2) Å, $b = 7.77$ (1) Å, $c = 6.585$ (7) Å, $\beta = 99.60$ (1)°, and $V = 901$ (2) Å². Data collection and refinement in space group $P2_1/c$ by the general procedures described above ($T = 22$ °C, $Z = 4$, $D_c = 2.295$ g cm⁻³; of the 1854 intensities measured, 1063 unique reflections with $I > 3\sigma(I)$ were used) led directly to the structure represented in

Figure 3. However, the final difference map was not clean; several large residual peaks remained (largest difference peak 4.35 e Å³).

Attempted Crystallographic Analysis of Pb(OCMe₂Et)₂ (3). After the screening of more than 12 crystals from different synthetic runs, no ideal sample was found. A marginally suitable crystal was selected for preliminary studies. Broadening of the ω-scan peak profile was observed for several of the 24 reflections used in unit cell determination. A rhombohedral cell with a hexagonal axial setting similar to that for **2** was obtained: $a = b = 10.774$ (6) Å, $c = 30.38$ (2) Å, and $V = 3054$ (4) Å³. A hemisphere of data ($+h,\pm k,\pm l$) were collected in the $\theta/2\theta$ mode, 1.2° scan width and 3.66–9.77° min⁻¹. Space group $R3$ (No. 148) seemed to give the most convincing solution with lead atoms sitting on the origin, (0, 0, 0), and on the 3-fold axis, (0, 0, 0.1122), with a bridging oxygen atom in between. We were unable to locate the rest of the molecule, probably because of the severe disorder present and/or the questionable crystal quality.

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Preparation of Soluble and Volatile Zinc Dialkoxides. X-ray Crystal Structures of an (Amido)zinc Alkoxide and a Homoleptic Zinc Enolate: {Zn(μ-OCEt₃)[N(SiMe₃)₂]}₂ and Zn(1,4,7-η³-OCH=CHNMeCH₂CH₂NMe₂)₂

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Seven new zinc dialkoxides prepared by alcoholyses of Zn[N(SiMe₃)₂]₂ are reported: Zn(OCEt₃)₂ (**1**), Zn(OCEt₂Me)₂ (**2**), Zn(OCH₂CH₂OMe)₂ (**3**), Zn(OCH₂CH₂OCH₂CH₂OMe)₂ (**4**), Zn(OCH₂CH₂NMe₂)₂ (**5**), Zn(OCHMeCH₂NMe₂)₂ (**6**), and Zn(OCH₂CH₂NMeCH₂CH₂NMe₂)₂ (**7**). Each is soluble (**1**, **6**, and **7** in hydrocarbons), volatile (**1**, **6**, and **7** in hydrocarbons), or both. Sublimation of **7** gives enolate Zn(1,4,7-η³-OCH=CHNMeCH₂CH₂NMe₂)₂ (**8**) by thermal dehydrogenation. Two compounds are structurally characterized: mononuclear **8** and (amido)zinc alkoxide intermediate {Zn(μ-OCEt₃)[N(SiMe₃)₂]}₂ (**9**). Crystal data for **8**: monoclinic, $P2_1/n$, $a = 8.715$ (5) Å, $b = 16.525$ (5) Å, $c = 12.989$ (4) Å, $\beta = 106.95$ (4)°, $V = 1789.4$ (12) Å³, $T = 22$ °C, $Z = 4$, and $D_c = 1.306$ g cm⁻³. Of the 4562 intensities measured, 2304 unique reflections with $I > 3\sigma(I)$ yielded $R(F_o) = 0.0383$ and $R_w(F_o) = 0.0512$. Crystal data for **9**: triclinic, $P\bar{1}$, $a = 8.836$ (5) Å, $b = 10.611$ (7) Å, $c = 11.431$ (8) Å, $\alpha = 93.40$ (6)°, $\beta = 105.88$ (5)°, $\gamma = 104.29$ (5)°, $V = 989.6$ (11) Å³, $T = 22$ °C, $Z = 1$, and $D_c = 1.144$ g cm⁻³. Of the 3949 intensities measured, 2393 unique reflections with $I > 3\sigma(I)$ yielded $R(F_0) = 0.0375$ and $R_w(F_0) = 0.0443$.

Introduction

Zinc oxide materials are used in varistors,[1] electronic thin films,[2] and heterogeneous catalysts, particularly methanol-synthesis catalysts.[3] Solution-phase preparations of ZnO powders for varistors[4] and catalysts[5] and vapor-phase depositions of ZnO films[6]

for electronic and optical applications have been recently described. Homoleptic alkoxides, $M_x(OR)_y$, are often useful precursors in such oxide syntheses;[7] however, presently available Zn(OR)₂

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compounds have not been tested in routes to zinc oxide because of their insolubility and nonvolatility.

The alkoxides of divalent metals, such as zinc(II), copper(II), and magnesium(II), are typically insoluble and nonvolatile.[8] Twenty years ago, Mehrotra and Arora prepared the series Zn-(OR)$_2$, R = Me, Et, i-Pr, n-Bu, t-Bu, and n-octyl; none of the compounds were soluble or volatile.[9] More recently, Geerts, Huffman, and Caulton described the first soluble zinc *aryl*oxides, Zn(OAr)$_2$, using the very bulky ligands OAr = 2,6-di-*tert*-butylphenoxide and 2,4,6-tri-*tert*-butylphenoxide.[10] Many soluble, *heteroleptic* compounds [RZn(OR')]$_n$, R = H[11] or alkyl,[12] are available; one of these (R = Et, R' = t-Bu) was used in a solution-phase route to zinc oxide.[1b]

The goal of the present study was to prepare soluble and volatile zinc dialkoxides, which might be implemented in solution- or vapor-phase zinc oxide preparations. We now report seven soluble and/or volatile examples obtained by alcoholyses of Zn[N-(SiMe$_3$)$_2$]$_2$ according to Caulton et al.[10] The new zinc compounds contain the bulky or chelating alkoxide ligands that were effective for solubilizing and volatilizing the dialkoxides of copper(II)[13] and lead(II);[14] a comparison of the three families of divalent-metal dialkoxides is presented. We also report the thermal decomposition of one example, which gave a mononuclear, homoleptic, zinc enolate. Two compounds have been characterized crystallographically: {Zn(μ-OCEt$_3$)[N(SiMe$_3$)$_2$]}$_2$ and Zn(1,4,7-η^3-OCH=CHNMeCH$_2$CH$_2$NMe$_2$)$_2$. Applications of the new zinc alkoxide precursors to the preparation of ZnO and Cu/ZnO powders will be described separately.[15]

Experimental Section

General Methods. All ambient-pressure procedures were carried out under dry N$_2$ by using standard inert-atmosphere techniques. Zn[N-(SiMe$_3$)$_2$]$_2$ was prepared by a literature procedure.[16] The alcohol reagents were purchased from Aldrich and distilled or used as received. All were stored over type 4A molecular sieves before use. Hexane, benzene, and THF were distilled from sodium benzophenone ketyl. Pyridine was distilled from CaH$_2$. NMR solvents were sparged with N$_2$ and stored over type 4A sieves.

Melting points were measured under N$_2$. C, H, and N analyses were performed by Oneida Research Services, Whitesboro, NY. Zn was determined by EDTA titration.[17] Molecular weights were determined cryoscopically in benzene. NMR spectra were recorded at a field corresponding to 300 MHz for ^{1}H, except where noted. NMR probe temperatures were calibrated with methanol or ethylene glycol standards in variable-temperature experiments.

Preparation of Zn(OCEt$_3$)$_2$ (1). Et$_3$COH (2.06 g, 17.7 mmol) was added to a solution of Zn[N(SiMe$_3$)$_2$]$_2$ (2.00 g, 5.17 mmol) in benzene (20 mL), resulting in an exothermic reaction. The mixture was refluxed for 2 h, and then volatiles were removed in vacuo to give a viscous, semisolid residue. The residue aged (1 day) to give 1 (1.45 g, 4.90 mmol, 95%) as a white solid, which was ≥95% pure by ^{1}H NMR spectroscopy. Mp: 90–92 °C. Anal. Calcd for C$_{14}$H$_{30}$O$_2$Zn: Zn, 22.10. Found: Zn, 21.85. MW: calcd for [Zn(OCEt$_3$)$_2$]$_n$, n = 2.5, 738; found, 738 (62) (concentration 333 mg/20.0 mL).

Compound **1** was soluble in THF, benzene, and hexane; recrystallization attempts under a variety of conditions were unsuccessful. **1** (1.21 g, 4.1 mmol) distilled (10^{-4} Torr, 220–225 °C bath) on a short-path stillhead to yield a semisolid (0.72 g, 2.43 mmol, 60%), which did not resolidify upon standing. Anal. Calcd for **1**: C, 56.85; H, 10.22; Zn, 22.10. Found: C, 56.36; H, 10.16; Zn, 22.38. MW: calcd for [Zn-(OCEt$_3$)$_2$]$_4$, 1180; found, 1211 (88) (average of measurements on three solutions with concentrations of 220–251 mg/20.0 mL). IR (cm^{-1}, KBr): 2964 s, 2935 s, 2877 m, 1458 m, 1384 m, 1279 w, 1200 w, 1146 m, 1042 m, 1018 m, 992 m, 949 s, 925 m, 798 w, 702 w, 601 m, 572 m, 513 w. ^{1}H NMR (δ, toluene-d_8): 1.64 (d, ^3J = 7.5 Hz, 0.64 × 12 H), 1.56 (d, ^3J = 7.6 Hz, 0.36 × 12 H), 1.05 (t, ^3J = 7.5 Hz, 0.36 × 18 H), 0.95 (t, ^3J = 7.5 Hz, 0.64 × 18 H). ^{1}H NMR (δ, benzene-d_6, 500 MHz): 1.88–1.80 (m, 0.05 × 12 H), 1.80–1.71 (m, 0.10 × 12 H), 1.66 (q, ^3J = 7.5 Hz, 0.53 × 12 H), 1.59 (q, ^3J = 7.5 Hz, 0.32 × 12 H), 1.07 (t, ^3J = 7.5 Hz, 0.34 × 18 H), 1.01 (pseudo q, ^3J = 8.0 Hz, 0.16 × 18 H), 0.96 (t, ^3J = 7.5 Hz, 0.50 × 18 H). ^{13}C{^{1}H} NMR (ppm, benzene-d_6): 76.74 (s, O*C*Et$_3$ major), 74.40 (s, O*C*Et$_3$ minor), 34.30 (s, CH$_2$ minor), 32.99 (s, CH$_2$ major), 8.61 (s, CH$_3$ minor), 8.47 (s, CH$_3$ major).

Preparation of Zn(OCEt$_2$Me)$_2$ (2). A solution of Et$_2$MeCOH (5.0 mL, 4.1 g, 40 mmol) and Zn[N(SiMe$_3$)$_2$]$_2$ (2.50 g, 6.47 mmol) in benzene (25 mL) was refluxed for 10 h. **2** formed as a white precipitate and was collected by filtration, washed with benzene (2 × 10 mL), and dried (1.62 g, 6.05 mmol, 93%). Mp: >250 °C. Anal. Calcd for C$_{12}$H$_{26}$O$_2$Zn: C, 53.83; H, 9.78, Zn, 24.42. Found: C 53.91; H, 9.41; Zn, 24.15. IR (cm^{-1}, KBr): 2966 s, 2881 m, 1460 m, 1383 m, 1259 s, 1247 s, 1182 w, 1148 s, 1061 s, 1031 s, 976 s, 849 s, 800 s, 750 w, 714 w, 672 w, 590 m, 572 m, 532 m, 491 w, 451 w.

Compound **2** was insoluble in benzene, ether, THF, and Et$_2$MeCOH. **2** (1.0 g, 3.7 mmol) sublimed (10^{-4} Torr, 180–185 °C bath) in low yield (0.34 g, 1.3 mmol, 34%). Anal. Calcd for **2**: Zn, 24.42. Found: Zn, 24.10.

Preparation of Zn(OCH$_2$CH$_2$OMe)$_2$ (3). 2-Methoxyethanol (900 μL, 0.87 g, 11.4 mmol) was added dropwise to a hexane (15 mL) solution of Zn[N(SiMe$_3$)$_2$]$_2$ (2.00 g, 5.18 mmol), giving an exothermic reaction and the formation of **3** as a white precipitate. The mixture was stirred for 4 h, and then **3** was collected by filtration, washed with hexane (2 × 6 mL), and dried in vacuo (0.92 g, 4.3 mmol, 82%). Anal. Calcd for C$_6$H$_{14}$O$_4$Zn: C, 33.42; H, 6.54; Zn, 30.33. Found: C, 33.12; H, 6.54; Zn, 30.47. IR (cm^{-1}, KBr): 2975 m, 2919 s, 2872 s, 2711 w, 1453 m, 1384 m, 1364 m, 1332 w, 1289 w, 1243 w, 1199 s, 1124 s, 1085 s, 1026 s, 962 m, 897 m, 840 m, 548 m, 465 m.

Compound **3** was soluble in 2-methoxyethanol and pyridine and sparingly soluble in benzene and THF. Attempts to recrystallize **3** under a variety of conditions were unsuccessful. **3** gradually decomposed between 130–250 °C; attempted sublimation (10^{-4} Torr, 100–150 °C bath) resulted only in decomposition.

Preparation of Zn(OCH$_2$CH$_2$OCH$_2$CH$_2$OMe)$_2$ (4). 2-(2-Methoxyethoxy)ethanol (4.0 mL, 4.0 g, 33 mmol) was added to a solution of Zn[N(SiMe$_3$)$_2$]$_2$ (2.00 g, 5.17 mmol) in benzene (20 mL), resulting in a gelatinous precipitate, which partially dissolved when alcohol addition was complete. Stirring was continued for 7 h, and then volatiles were removed in vacuo to give **4** as a glassy solid (1.50 g, 4.93 mmol, 95%). Anal. Calcd for C$_{10}$H$_{22}$O$_6$Zn: C, 39.55; H, 7.30; Zn, 21.53. Found: C, 40.23; H, 7.41; Zn, 21.0. IR (cm^{-1}, KBr): 2877 s, 1454 m, 1352 m, 1247 m, 1200 m, 1103 s, 936 m, 896 m, 851 m, 513 m.

Compound **4** was soluble in 2-(2-methoxyethoxy)ethanol and pyridine and insoluble in benzene and THF. Attempted recrystallization from 2-(2-methoxyethoxy)ethanol/benzene was unsuccessful. **4** gradually decomposed between 125–240 °C; attempted sublimation (10^{-4} Torr, 140–200 °C bath) gave decomposition.

Preparation of Zn(OCH$_2$CH$_2$NMe$_2$)$_2$ (5). 2-(Dimethylamino)ethanol (1.06 g, 11.9 mmol) was added to a solution of Zn[N(SiMe$_3$)$_2$]$_2$ (2.00 g, 5.20 mmol) in hexane (20 mL), giving an exothermic reaction. The mixture was stirred for 2 h. **5** precipitated as a white solid and was collected by filtration, washed with hexane (2 × 5 mL) and dried (0.90 g, 3.97 mmol, 72%). Anal. Calcd for C$_8$H$_{20}$N$_2$O$_2$Zn: C, 39.76; H, 8.34; N, 11.59; Zn, 27.05. Found: C, 39.46; H, 7.83; N, 11.36; Zn, 27.24.

Compound **5** was soluble in 2-(dimethylamino)ethanol and insoluble in benzene, hexane, and THF. Recrystallization attempts under a variety of conditions were unsuccessful. **5** (0.32 g, 1.32 mmol) sublimed (10^{-4} Torr, 170 °C bath) in moderate yield (0.17 g, 0.70 mmol, 53%). Anal. Calcd for **5**: Zn, 27.05. Found: Zn, 27.14. IR (cm^{-1}, KBr): 2969 m, 2935 m, 2852 s, 2813 s, 2760 s, 1461 m, 1384 w, 1348 w, 1330 w, 1257 m, 1187 w, 1157 m, 1089 s, 1077 s, 1055 s, 1024 s, 956 m, 888 w, 864 w, 788 m, 621 w, 578 w, 518 w, 458 m.

Preparation of Zn(OCHMeCH$_2$NMe$_2$)$_2$ (6). 1-(Dimethylamino)-2-propanol (1.07 g, 10.36 mmol) was added to Zn[N(SiMe$_3$)$_2$]$_2$ (2.00 g, 5.18 mmol) in hexane (10 mL), resulting in an exothermic reaction and the formation of colorless crystals. The mixture was refluxed for 2 h,

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during which the crystals redissolved. Volatiles were then removed in vacuo to give crude **6** as a viscous liquid (1.36 g, 5.04 mmol, 97%), which gave an acceptable zinc analysis. Anal. Calcd for $C_{10}H_{24}N_2O_2Zn$: Zn, 24.24. Found, Zn, 24.00. **6** was soluble in hexane, benzene, and THF.

Crude **6** (1.13 g, 4.19 mmol) was purified further by distillation (10^{-4} Torr, 170 °C bath) on a short-path stillhead (0.90 g, 3.34 mmol, 80%). Anal. Calcd for $C_{10}H_{24}N_2O_2Zn$: C, 44.53; H, 8.96; N, 10.38, Zn, 24.24. Found: C, 44.17; H, 8.71; N, 10.14; Zn, 24.18. MW: calcd for [Zn-(OCHMeCH$_2$NMe$_2$)$_2$]$_3$, 809; found, 819 (79) (average of measurements on two solutions with concentrations of 164–278 mg/20.0 mL). IR (cm^{-1}, KBr): 2962 m, 2856 m, 2828 m, 2766 m, 1464 m, 1384 m, 1363 m, 1314 w, 1262 w, 1137 s, 1099 s, 1034 s, 1016 m, 949 s, 856 w, 836 m, 585 m, 511 w, 476 w, 422 w. ^{1}H NMR (δ, benzene-d_6): 4.07 (br s, 2 H), 2.29 (br s with high-field shoulder, 16 H), 1.36 (br s, 6 H). ^{1}H NMR (δ, toluene-d_8, 92 °C): 4.08–3.98 (m, 2 H), 2.34–2.30 (m, 2 H, partially obscured), 2.28 (s, 12 H), 2.05 (br dd, ^3J = 4.2 Hz, ^2J = 11.5 Hz, 2 H), 1.27 (d, ^3J = 5.9 Hz, 6 H).

Preparation of Zn(OCH$_2$CH$_2$NMeCH$_2$CH$_2$NMe$_2$)$_2$ (7) and Zn-(OCH=CHNMeCH$_2$CH$_2$NMe$_2$)$_2$ (8). Me$_2$NCH$_2$CH$_2$NMeCH$_2$CH$_2$OH (1.70 g, 11.62 mmol) was added to a solution of Zn[N(SiMe$_3$)$_2$]$_2$ (2.25 g, 5.82 mmol) in hexane (15 mL), resulting in an exothermic reaction. The mixture was stirred for 16 h, and then volatiles were removed in vacuo to give **7** as a viscous liquid, which solidified upon standing for 1–2 days (1.96 g, 5.50 mmol, 95%). Mp: 60–61 °C. Anal. Calcd for $C_{14}H_{34}N_4O_2Zn$: C, 47.25; H, 9.63; N, 15.73; Zn, 18.37. Found: C, 46.85; H, 9.61; N, 15.43; Zn, 17.52. MW: calcd for [Zn-(OCH$_2$CH$_2$NMeCH$_2$CH$_2$NMe$_2$)$_2$]$_n$, n = 2.4, 854; found, 845 (88) (average of measurements on two solutions with concentrations of 215–217 mg/20.0 mL). IR (cm^{-1}, KBr): 2943 s, 2813 s, 2769 s, 1462 s, 1384 w, 1292 m, 1263 w, 1164 w, 1141 w, 1122 m, 1097 s, 1075 s, 1040 s, 989 w, 956 w, 939 w, 885 w, 843 w, 787 w, 617 w, 574 w, 470 w. ^{1}H NMR (δ, benzene-d_6): 4.50 (br s, rel area 1), 3.88 (br s, rel area 1), 2.88 (br s, rel area 1), 2.78 (br s, rel area 1), 2.49 (br s, rel area 3), 2.31 (br s, rel area 5), 2.18 (br s, rel area 4), 1.99 (br s, rel area 1). ^{1}H NMR (δ, toluene-d_8, 110 °C): 3.98 (br t, ^3J = 5.5 Hz, 4 H), 2.54 (t, ^3J = 5.8 Hz, 4 H), 2.45 (br t, ^3J = 6.0 Hz, 4 H), 2.35 (s, 6 H), 2.31 (t, ^3J = 6.2 Hz, 4 H), 2.25 (s, 12 H).

Compound **7** was soluble in hexane, benzene, and THF; recrystallization attempts under a variety of conditions were unsuccessful. **7** (1.86 g, 5.23 mmol) sublimed (10^{-4} Torr, 170 °C bath) to give dehydrogenation product **8** as a crystalline solid (1.01 g, 2.87 mmol, 55%). Mp: 123–124 °C. Anal. Calcd for $C_{14}H_{30}N_4O_2Zn$: C, 47.06; H, 8.49; N, 15.56; Zn, 18.58. Found: C, 47.80; H, 8.59; N, 15.91; Zn, 18.05. MW: calcd for Zn(OCH=CHNMeCH$_2$CH$_2$NMe$_2$)$_2$ 352; found, 378 (29) (concentration 184 mg/20.0 mL). IR (cm^{-1}, KBr): 3002 m, 2964 m, 2856 m, 2814 m, 1618 m, 1605 s, 1595 s, 1466 m, 1454 m, 1378 m, 1347 w, 1295 m, 1276 s, 1269 s, 1227 w, 1185 w, 1172 m, 1118 m, 1102 m, 1067 m, 1038 m, 1016 m, 961 m, 940 m, 854 m, 783 m, 729 w, 697 m, 681 m, 610 w, 556 w, 461 w, 447 w, 427 m. ^{1}H NMR (δ, benzene-d_6): 7.50 (d, ^3J = 2.6 Hz, 2 H), 4.28 (d, 2.8 Hz, 2 H), 3.00 (br pseudo t, $^3J \approx {}^2J \approx$ 12.7 Hz, 2 H), 2.82 (br pseudo t, $^3J \approx {}^2J \approx$ 12.5 Hz, 2 H), 2.54 (s, 6 H), 2.19 (s, 12 H), 1.59 (br d, ^2J = 12.0 Hz, 2 H), 1.47 (br d, ^2J = 11.7 Hz, 2 H).

Compound **8** was soluble in hexane, benzene, and THF. **8** (0.40 g, 1.1 mmol) resublimed (10^{-4} Torr, 100 °C bath) at a lower temperature (0.29 g, 0.82 mmol, 72%) and was substantially decomposed after storage under N$_2$ at room temperature for 4 months.

Preparation of Zn(OCEt$_3$)[N(SiMe$_3$)$_2$] (9). A solution of Et$_3$COH (0.60 g, 5.2 mmol) and Zn[N(SiMe$_3$)$_2$]$_2$ (2.00 g, 5.18 mmol) in hexane (10 mL) was stirred for 16 h and then transferred to a 6 °C refrigerator, whereupon large crystals of **9** separated and were collected by filtration, washed with cold hexane (2 mL), and dried (0.70 g, 2.05 mmol, 40%). Mp: 136–137 °C. Anal. Calcd for $C_{13}H_{33}NOSi_2Zn$: C, 45.79; H, 9.75; N, 4.10; Zn, 19.19. Found: C, 46.05; H, 9.78; N, 3.80; Zn, 19.16. MW: calcd for {Zn(OCEt$_3$)[N(SiMe$_3$)$_2$]}$_3$, 1023; found, 957 (105) (average of measurements on two solutions with concentrations of 206–362 mg/20.0 mL). IR (cm^{-1}, KBr): 2964 m, 2950 m, 2879 m, 1459 m, 1377 w, 1247 m, 1146 m, 988 s, 947 m, 881 s, 849 m, 828 m, 750 w, 671 m, 601 m, 527 w. ^{1}H NMR (δ, benzene-d_6): 1.71–1.63 (m, very minor), 1.52 (q, ^3J = 7.5 Hz, 6 H), 0.99–0.91 (m, very minor), 0.83 (t, ^3J = 7.5 Hz, 9 H), 0.30 (s, 18 H).

Structure Determination of {Zn(μ-OCEt$_3$)[N(SiMe$_3$)$_2$]}$_2$ (9). Crystallographic data are given in Table I, and atomic positional parameters in Table II. Details of data collection and analysis are summarized in the supplementary material. A colorless platelike crystal (0.25 × 0.63 × 0.86 mm) was obtained from hexane and was sealed in a glass capillary. Ambient-temperature data collection was carried out with the ω scan mode by using monochromated MoKα radiation in a Nicolet P3 diffractometer. A triclinic unit cell and orientation matrix were determined on the basis of the setting angles of 15 carefully centered reflec-

Table I. Crystallographic Data for Zn(1,4,7-η^3-OCH=CHNMeCH$_2$CH$_2$NMe$_2$)$_2$ (8) and {Zn(μ-OCEt$_3$)[N(SiMe$_3$)$_2$]}$_2$ (9)

	8	9
chem formula	$C_{14}H_{30}N_4O_2Zn$	$C_{26}H_{66}N_2O_2Si_4Zn_2$
a, Å	8.715 (5)	8.836 (5)
b, Å	16.525 (5)	10.611 (7)
c, Å	12.989 (4)	11.431 (8)
α, deg	90	93.40 (6)
β, deg	106.95 (4)	105.88 (5)
γ, deg	90	104.29 (5)
V, Å^3	1789.4 (12)	989.6 (11)
Z	4	1
fw	351.8	681.9
space group	$P2_1/n$ (nonstd. No. 14)	$P\bar{1}$ (No. 2)
T, °C	22	22
λ, Å	0.710 73	0.710 73
D_c, g cm^{-3}	1.306	1.144
μ, cm^{-1}	14.14	13.82
transm coeff		0.421–0.557
$R(F_o)^a$	0.0383	0.0375
$R_w(f_o)^b$	0.0512^c	0.0443^d

$^a R(F_o) = \sum ||F_o| - |F_c||/\sum |F_o|$. $^b R_w(F_o) = (\sum w||F_o| - |F_c||^2/ \sum w|F_o|^2)^{1/2}$; $w = [\sigma^2(F_o) + g(F_o)^2]$. $^c g = 0.0007$. $^d g = 0.0014$.

Table II. Atomic Positional Parameters for {Zn(μ-OCEt$_3$)[N(SiMe$_3$)$_2$]}$_2$ (9)

	x	y	z
Zn	0.4325 (1)	0.9186 (1)	0.8798 (1)
Si(1)	0.4846 (2)	0.7442 (1)	0.6840 (1)
Si(2)	0.1457 (2)	0.7869 (1)	0.6509 (1)
O	0.4457 (3)	0.9025 (2)	1.0494 (2)
N	0.3492 (4)	0.8134 (3)	1.7273 (3)
C(1)	0.3880 (5)	0.7944 (3)	1.1117 (3)
C(2)	0.5364 (6)	0.7770 (4)	1.2100 (4)
C(3)	0.6672 (7)	0.7384 (5)	1.1648 (5)
C(4)	0.3071 (6)	0.6730 (3)	1.0133 (4)
C(5)	0.2414 (7)	0.5459 (4)	1.0622 (5)
C(6)	0.2680 (7)	0.8288 (5)	1.1729 (5)
C(7)	0.1130 (7)	0.8476 (6)	1.0887 (7)
C(11)	0.6729 (6)	0.7713 (5)	0.8165 (4)
C(12)	0.5538 (7)	0.8187 (6)	0.5571 (5)
C(13)	0.3968 (8)	0.5630 (5)	0.6351 (6)
C(21)	0.0690 (7)	0.9179 (6)	0.7103 (6)
C(22)	0.0152 (7)	0.6272 (5)	0.6710 (5)
C(23)	0.1085 (8)	0.7879 (7)	0.4835 (5)

tions (3.5° < 2θ < 19°). A fixed scan rate of 29.3°/min was used throughout the data set (3.5° < 2θ < 50°). Three check reflections were measured every 50 reflections, and no significant variation in intensities was found. A total of 3949 reflections ($+h$, $\pm k$, $\pm l$) were collected. Lorentz, polarization, and empirical absorption corrections were applied to the data set in which 2393 unique reflections (R_{av} = 0.0054) with $I > 3\sigma(I)$ were retained and used in the subsequent structure analysis with the Siemens SHELXTL PLUS program system.

The space group assignment, $P\bar{1}$ (No. 2), was based on the statistical data and was subsequently confirmed by successful refinement and convergence. The structure was solved by direct methods, which revealed all but one non-hydrogen position. The remaining atom (C7) was located in the first difference Fourier map. Hydrogens were placed in unrefined, calculated positions and assigned a common, refined, thermal parameter. All non-hydrogen atoms were refined anisotropically. Refinement was carried out by use of the full-matrix least-squares method, giving a final R value of 0.0375. In the last cycles, individual weights were given as $w = 1/[\sigma^2(F) + 0.0007(F^2)]$. The final difference electron density map was essentially flat (largest peak, 0.31 e/Å^3).

Structure Determination of Zn(1,4,7-η^3-OCH=CHNMeCH$_2$CH$_2$NMe$_2$)$_2$ (8). In general, the same techniques employed for **9** were employed for **8**. See Table I for crystallographic data and Table III for atomic positional parameters. Details of data collection and analysis are summarized in the supplementary material. A pale yellow triangular crystal was obtained by sublimation and was sealed in a glass capillary. Ambient-temperature data collection was carried out with the $\theta/2\theta$ scan mode. A monoclinic unit cell and orientation matrix were determined on the basis of the setting angles of 15 centered reflections (22.0° < 2θ < 35.0°). A variable scan rate (4.88–29.3°/min) was used throughout the data collection; two octants ($+h$, $+k$, $\pm l$) were collected.

Table III. Atomic Positional Parameters for
$Zn(1,4,7-\eta^3-OCH=CHNMeCH_2CH_2NMe_2)_2$ (8)

	x	y	z
Zn	0.9942 (1)	0.6597 (1)	0.3004 (1)
O(1)	1.1601 (3)	0.6060 (2)	0.4194 (2)
O(2)	0.8605 (3)	0.7173 (2)	0.1698 (2)
N(1)	1.1190 (5)	0.5821 (2)	0.1991 (3)
N(2)	0.8253 (5)	0.5458 (2)	0.2690 (3)
N(3)	1.1422 (4)	0.7770 (2)	0.3157 (3)
N(4)	0.8888 (4)	0.7296 (3)	0.4145 (3)
C(1)	1.2642 (6)	0.5651 (3)	0.3845 (4)
C(2)	1.2548 (6)	0.5513 (3)	0.2820 (4)
C(3)	1.1656 (7)	0.6203 (3)	0.1116 (4)
C(4)	1.0004 (7)	0.5185 (3)	0.1513 (4)
C(5)	0.9234 (7)	0.4856 (3)	0.2322 (4)
C(6)	0.6756 (6)	0.5616 (3)	0.1837 (4)
C(7)	0.7878 (7)	0.5128 (4)	0.3633 (4)
C(8)	0.9299 (5)	0.7849 (3)	0.1508 (3)
C(9)	1.0628 (6)	0.8160 (3)	0.2147 (3)
C(10)	1.3174 (5)	0.7706 (3)	0.3321 (4)
C(11)	1.1154 (6)	0.8200 (3)	0.4083 (3)
C(12)	0.9437 (6)	0.8144 (3)	0.4058 (4)
C(13)	0.9495 (6)	0.7001 (3)	0.5265 (3)
C(14)	0.7115 (6)	0.7310 (4)	0.3807 (4)

Three check reflections were measured every 50 reflections, and during the last part of the first shell of data collection ($3.5° < 2\theta < 45.0°$), a 23% drop in the intensity of the $34\bar{4}$ check reflection signaled a slight shift in the crystal position. The higher angle data ($45.0° < 2\theta < 55.0$) were collected with a new orientation matrix calculated from recentered reflections. The merging residual ($R_w = 0.019$) for equivalent reflections indicated no significant deviation resulting from the crystal shift. A total of 4562 reflections was collected, of which 2304 unique reflections with $I > 3\sigma(I)$ were retained. Lorentz and polarization corrections were applied to the data set, and the subsequent structure analysis was carried out with the Siemens SHELXTL PLUS program system.

Space group $P2_1/n$ (No. 14) was unambiguously determined from systematic absences and photographic evidence. The first-shell data ($3.5° < 2\theta < 45.0°$) were sufficient to reveal the whole structure. The Zn position was obtained by direct methods; the remaining non-hydrogen atoms were located in difference Fourier maps. Hydrogens were placed in unrefined, calculated positions and assigned a common, refined, thermal parameter. Refinement was carried out by use of the full-matrix least-squares method, giving a final R value of 0.0383. In the last cycles, individual weights were given as $w = 1/[\sigma^2(F) + 0.0014(F^2)]$. The final difference electron density map was essentially flat (largest peak, 0.49 $e/Å^3$).

Results

Synthesis and Properties. The new zinc dialkoxides were prepared according to eq 1, which we found to be a simple, general, synthetic method.[10] Compounds **1–5** and **7** were isolated as

$$Zn[N(SiMe_3)_2]_2 + 2 ROH \longrightarrow Zn(OR)_2 + 2 HN(SiMe_3)_2 \quad (1)$$
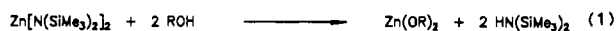
$$1-7$$

R = CEt₃ (1)

CEt₂Me (2)

CH₂CH₂OMe (3)

CH₂CH₂OCH₂CH₂OMe (4)

CH₂CH₂NMe₂ (5)

CHMeCH₂NMe₂ (6)

CH₂CH₂NMeCH₂CH₂NMe₂ (7)

powders or glassy solids; **6** was a viscous liquid. Satisfactory elemental analyses were obtained, and the compounds were characterized by standard spectroscopic methods.

Alkoxides **1–7** showed solubilities and volatilities considerably higher than those of previously reported zinc dialkoxides.[9] Compounds **1, 6,** and **7** were readily soluble in hexane, benzene, toluene, and THF. Although **3–5** were not soluble in these solvents, they could be dissolved in their respective parent alcohols. Of the new alkoxides, only **2** appeared to be insoluble. Except for **3** and **4** (which were nonvolatile), the new compounds distilled or sublimed in the range 170–225 °C at 10^{-4} Torr. The order of decreasing volatilities was **5** = **6** = **7** > **2** > **1**. Compound **6** distilled with the best recovery (80%); **2** sublimed with the poorest
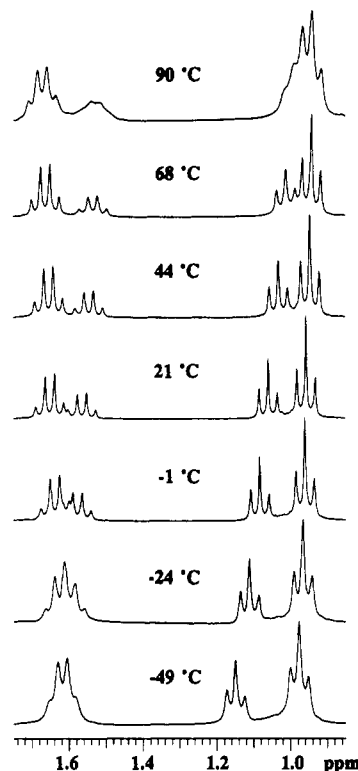

Figure 1. Variable-temperature ¹H NMR spectra of $[Zn(OCEt_3)_2]_n$ in toluene-d_8.

(34%). Compound **7** underwent a dehydrogenation reaction upon sublimation (see below).

In the preparations of **1** and **6**, intermediate products crystallized from solution during the course of eq 1. The intermediate formed in the synthesis of **1** was isolated and identified as the mono-substitution product $Zn(OCEt_3)[N(SiMe_3)_2]$ (**9**); see eq 2. The crystal structure of **9**, one of the few crystalline compounds encountered in the present study, is discussed below.

$$Zn[N(SiMe_3)_2]_2 + Et_3COH \longrightarrow Zn(OCEt_3)[N(SiMe_3)_2] + HN(SiMe_3)_2 \quad (2)$$

$$9$$
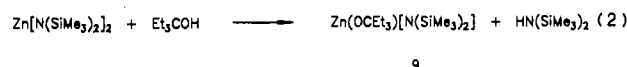
The solution–phase properties of the hydrocarbon-soluble compounds **1, 6,** and **7** were studied in the most detail. Each of **1, 6,** and **7** was initially obtained from solution as a viscous substance; **1** and **7** solidified after 1–2 days. Cryoscopic molecular weight measurements in benzene using aged (or distilled) samples indicated average molecular complexities of 4.1 (3) for **1**, 3.0 (3) for **6**, and 2.4 (3) for **7**. Thus, all three compounds were oligomeric in benzene solution. The average molecular complexity of a freshly prepared sample of **1** (less than 1-day old) was 2.5 (2), establishing that molecular complexity was age dependent. All of the cryoscopic measurements were carried out on solutions having approximately the same concentrations (see Experimental Section).

The ¹H NMR spectra of **1, 6,** and **7** showed complex behavior. The data for **1** were temperature, solvent, and age dependent. Variable-temperature ¹H NMR spectra of **1** in toluene-d_8 are presented in Figure 1. Two triplets and two quartets were present, corresponding to two types of ethyl groups in a ratio of ca. 2:1 (integrated intensities were in the range 1.8–2.0:1.0). A ¹³C NMR spectrum (see Experimental Section) contained two methyl, two methylene, and two quarternary (OCEt₃) signals with 2:1 ratios, which established the existence of two types of OCEt₃ ligands rather than two types of nonequivalent Et groups within a single OCEt₃. The smaller triplet and quartet in Figure 1 shifted progressively downfield with decreasing temperature; the shifts for the larger triplet and quartet were essentially temperature invariant. The temperature effects were reversible.

The ¹H NMR spectra of **1** in benzene-d_6 revealed additional complications. Temperature-dependent shifts analogous to Figure 1 were observed, but with temperature displacements of ca. 20

°C; thus, the room-temperature spectrum in benzene-d_6 resembled the −1 °C spectrum in Figure 1, etc. Furthermore, in benzene-d_6 the ratios of the sets of resonances were not 2:1 as in Figure 1 but were 1.5–1.8:1.0 (average 1.65:1.00). No concentration dependences of ratios or chemical shifts were observed in the range 0.04–0.28 M.

Additional minor resonances (see Experimental Section) were detected in benzene-d_6 in both the methyl and methylene regions that were not found in toluene-d_8, accounting for ca. 15% of the total integrated intensities. Presumably these were due to other isomers or oligomers of **1**. The minor resonances broadened or disappeared at higher temperatures.

Two structures are typical of $[M(OR)_2]_n$ complexes having bulky R substituents, **I** and **II**.[18,19] The molecular complexity and NMR data for **1** were consistent with neither **I** or **II**.

I   O = OR   **II**
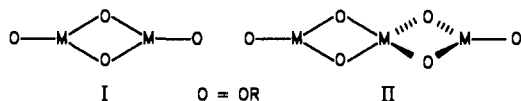
¹H NMR spectra of **1** also depended on the age of **1**. The spectrum of freshly prepared **1** (obtained by concentration of the reaction mixture; see Experimental Section) in benzene-d_6 resembled the 90 °C spectrum in Figure 1 with respect to chemical shifts, but the lines were sharper and the ligand ratio was 1.3:1.0. Samples prepared from **1** that had aged under dry N_2 for ≥1 month showed the room-temperature spectrum described above. Samples prepared from **1** that had aged for 15 h and 2 days, respectively, showed intermediate spectral properties. Distilled **1** produced spectra that were the same as fully aged samples.

A simple structural model that uniquely accounts for the above observations is not apparent. However, such temperature, solvent, and age dependences are typical aggregation-related phenomena and have been observed for other alkoxide compounds.[20] Obviously, the variability in the spectra of **1** complicates its routine characterization by ¹H NMR spectroscopy. We prefer zinc analysis for routine purity checks on **1**.

The ¹H NMR spectra of **6** and **7** were also very temperature dependent. Both gave a single set of sharp resonances at elevated temperatures. The spectra were considerably broadened at room temperature and became inextricably complex with the emergence of numerous additional-resonances at lower temperatures.

The sublimation of **7**, which was a viscous liquid or waxy solid, produced colorless, transparent, rectangular crystals. The ¹H NMR spectrum of the crystals differed considerably from **7** and contained olefinic resonances (see Experimental Section). The data were consistent with enolate **8**, formed by dehydrogenation (eq 3, 55%); no attempt was made to detect the evolved H_2. The
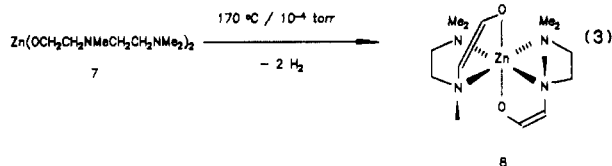
molecular structure of **8** was established crystallographically (see below). Cryoscopic measurements indicated a molecular complexity of 1.1 (1) in solution, consistent with the monomeric structure found in the solid state and depicted in eq 3. Additionally, **8** was the most volatile compound in the present study, subliming at 100 °C/10⁻⁴ Torr (72% recovery).

Solid-State Structures. Although cryoscopic measurements were consistent with solution-phase trimers of (amido)zinc alkoxide **9**, the NMR data did not support a static structure related to **II**, as established earlier for homoleptic and heteroleptic alkoxides of beryllium.[18] Consequently, we determined the solid-state structure of **9**, as described in Tables I, II, and IV.

(18) Andersen, R. A.; Coates, G. E. *J. Chem. Soc., Dalton Trans.* **1972**, 2153.
(19) Calabrese, J.; Cushing, M. A., Jr.; Ittel, S. D. *Inorg. Chem.* **1988**, *27*, 867.
(20) Reference 8, pp 122–134.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $\{Zn(\mu\text{-}OCEt_3)[N(SiMe_3)_2]\}_2$ (9)

Zn–O	1.930 (3)	Si(2)–C(22)	1.866 (6)
Zn–N	1.868 (3)	Si(2)–C(23)	1.852 (6)
Zn–Zn(a)	2.929 (2)	O–C(1)	1.446 (5)
Zn–O(a)	1.936 (3)	C(1)–C(2)	1.534 (6)
Si(1)–N	1.712 (4)	C(1)–C(4)	1.538 (5)
Si(1)–C(11)	1.865 (5)	C(1)–C(6)	1.521 (8)
Si(1)–C(12)	1.867 (6)	C(2)–C(3)	1.517 (9)
Si(1)–C(13)	1.874 (5)	C(4)–C(5)	1.532 (6)
Si(2)–N	1.714 (4)	C(6)–C(7)	1.509 (8)
Si(2)–C(21)	1.859 (7)		
O–Zn–N	138.9 (1)	Zn–O–C(1)	133.3 (2)
O–Zn–Zn(a)	40.8 (1)	Zn–O–Zn(a)	98.5 (1)
N–Zn–Zn(a)	179.1 (1)	C(1)–O–Zn(a)	128.1 (2)
O–Zn–O(a)	81.5 (1)	Zn–N–Si(1)	115.2 (2)
N–Zn–O(a)	139.6 (1)	Zn–N–Si(2)	117.8 (2)
Zn(a)–Zn–O(a)	40.7 (1)	Si(1)–N–Si(2)	126.9 (2)
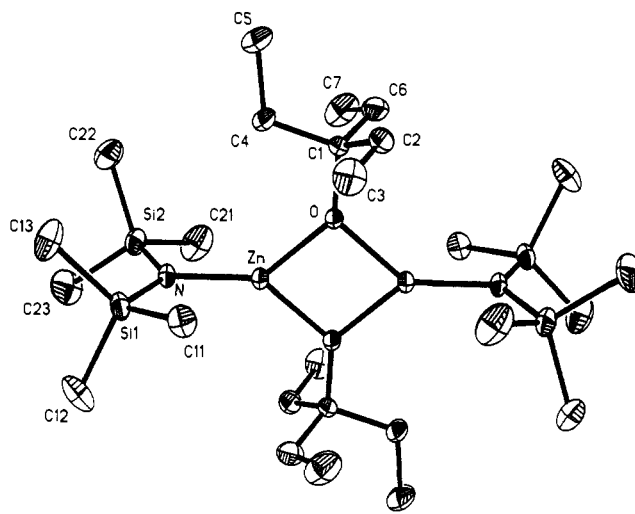
Figure 2. ORTEP view of the molecular structure of $\{Zn(\mu\text{-}OCEt_3)[N(SiMe_3)_2]\}_2$ (9). Hydrogen atoms were omitted for clarity.
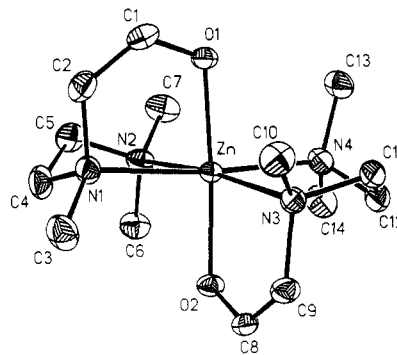
Figure 3. ORTEP view of the molecular structure of $Zn(1,4,5\text{-}\eta^3\text{-}OCH\text{=}CHNMeCH_2CH_2NMe_2)_2$ (8). Hydrogen atoms were omitted for clarity.

Compound **9** adopts a dimeric rather than a trimeric solid-state structure (see Figure 2), which conforms to type I, having $OCEt_3$ and $N(SiMe_3)_2$ ligands in bridging and terminal positions, respectively. The planarity of the $NZn(\mu\text{-}O)_2ZnN$ central unit is crystallographically imposed. The $OCEt_3$ ligands bridge symmetrically (within error), and the Zn–O distances of 1.93 (1) Å are similar to the Zn–O distances of 1.95 (1)–2.03 (1) Å found for the doubly bridging alkoxides in the structure of $[Zn_2Et(OCHMeCH_2OMe)_3]_2$.[21] The Zn–O distances of 1.89 (1) Å for the terminal aryloxide ligands in $Zn(OAr)_2(THF)_2$, OAr = 2,4,6-tri-*tert*-butylphenoxide, are perhaps slightly shorter.[10] The planar $N(SiMe_3)_2$ ligands in **9** adopt a conformation that mini-

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Table V. Selected Bond Distances (Å) and Angles (deg) for
$Zn(1,4,7-\eta^3-OCH=CHNMeCH_2CH_2NMe_2)_2$ (8)

Zn–O(1)	1.991 (3)	N(2)–C(6)	1.468 (5)
Zn–O(2)	1.997 (3)	N(2)–C(7)	1.462 (7)
Zn–N(1)	2.322 (4)	N(3)–C(9)	1.444 (5)
Zn–N(2)	2.350 (4)	N(3)–C(10)	1.483 (6)
Zn–N(3)	2.305 (4)	N(3)–C(11)	1.473 (6)
Zn–N(4)	2.273 (4)	N(4)–C(12)	1.496 (7)
O(1)–C(1)	1.313 (6)	N(4)–C(13)	1.478 (6)
O(2)–C(8)	1.327 (5)	N(4)–C(14)	1.478 (6)
N(1)–C(2)	1.441 (5)	C(1)–C(2)	1.329 (7)
N(1)–C(3)	1.457 (7)	C(4)–C(5)	1.503 (9)
N(1)–C(4)	1.479 (6)	C(8)–C(9)	1.317 (6)
N(2)–C(5)	1.479 (7)	C(11)–C(12)	1.491 (7)
O(1)–Zn–O(2)	169.6 (1)	N(1)–Zn–N(3)	99.8 (1)
O(1)–Zn–N(1)	80.8 (1)	N(2)–Zn–N(3)	174.2 (1)
O(2)–Zn–N(1)	92.0 (1)	O(1)–Zn–N(4)	93.5 (1)
O(1)–Zn–N(2)	93.1 (1)	O(2)–Zn–N(4)	93.7 (1)
O(2)–Zn–N(2)	93.1 (1)	N(1)–Zn–N(4)	174.2 (1)
N(1)–Zn–N(2)	80.4 (1)	N(2)–Zn–N(4)	99.7 (1)
O(1)–Zn–N(3)	92.7 (1)	N(3)–Zn–N(4)	80.7 (1)
O(2)–Zn–N(3)	81.1 (1)		

mizes steric interactions with the bulky alkoxide ligands, and the Zn–N distance of 1.87 (1) Å is longer than the Zn–N distance of 1.82 (1) Å determined for $Zn[N(SiMe_3)_2]_2$ in the gas phase.[22] The structure of **9** has no exceptional features.

The molecular structure of **8** is shown in Figure 3 and described in Tables I, III, and V. The enolate ligands are bound in a η^3 manner with oxygen atoms in trans positions, giving the molecule approximate C_2 symmetry. The zinc atom has distorted octahedral coordination, with the intraligand L–Zn–L angles compressed below the ideal of 90°. The Zn–O distances of 1.99 (1) Å are close to those cited above for **9**, but the Zn–N distances of 2.27 (1)–2.35 (1) Å are longer than the Zn–N distances in $ZnCl_2$-(tmeda) of 2.06 (1) and 2.11 (1) Å.[23] After correction for the differing coordination numbers of the zinc atoms in **8** and $ZnCl_2$(tmeda),[24] Zn–N distances of ca. 2.23 Å might be predicted for **8**; the slightly longer observed Zn–N interactions presumably relieve chelate-ring strain. Note the double-bond distances of 1.33 (1) and 1.32 (1) between C(1) and C(2), and C(8) and C(9), respectively.

The structures of two dinuclear zinc enolates were recently reported.[25,26] Of the two, structure III is most comparable to **8**.[25] The Zn–O distances in III are 2.02 (1) and 2.12 (1) Å, and the Zn–N distance is 2.21 (2) Å.

III
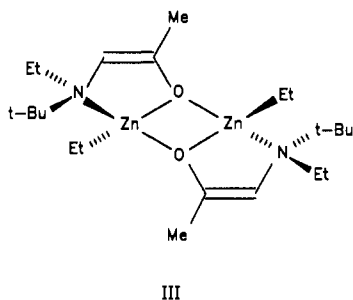
Discussion

The low solubilities and volatilities of conventional, divalent-metal alkoxides are attributed to extensive alkoxide bridging and the polymeric structures that result.[8] The number and/or strength of such bridges is large because of normal preferences for metal coordination numbers higher than 2. At least two features can generally diminish alkoxide bridging: (1) bulky alkoxide substituents or (2) chelating alkoxide substituents. In the present

study, we have made use of both strategies 1 and 2.

Our work shows that the reaction (eq 1) reported by Caulton et al.[10] is generally applicable to the synthesis of zinc dialkoxides. Although diethylzinc is a more readily available starting material than $Zn[N(SiMe_3)_2]_2$, which is used in eq 1, alcoholysis reactions of dialkylzincs generally lead to monosubstituted cubane-type $[RZn(OR')]_4$ compounds.[10,12] Complete replacement of R by OR' is difficult and not preparatively useful.[12,21,27] Equation 1 *does* proceed via related, monosubstituted intermediates, $[Zn(OR)-[N(SiMe_3)_2]_n$, one of which (**9**) was isolated and structurally characterized as described above (eq 2). However, all such intermediates were readily converted into the fully substituted $Zn(OR)_2$ products.

In contrast to the $[RZn(OR')]_4$ compounds, **9** is not a solid-state cubane but rather a dimer having trigonal-planar, 3-coordinate zinc atoms (see Figure 2). The recently reported $\{Sn(O-t-Bu)[N(SiMe_3)_2]\}_2$ is structurally similar to **9**, except the tin centers are pyramidal.[28] In both compounds the amido ligands occupy terminal positions and the alkoxide ligands occupy bridging positions. The ease with which our $\{Zn(OR)[N(SiMe_3)_2]\}_n$ intermediates undergo further alcoholysis likely reflects either a greater reactivity of terminal amido ligands relative to terminal alkyl ligands or a greater susceptibility of the 3-coordinate zinc centers to nucleophilic attack relative to the 4-coordinate zinc centers in the $[RZn(OR')]_4$ cubanes.

Although our efforts to diminish alkoxide bridging did produce soluble and volatile zinc dialkoxides, all of **1–7** remain oligomeric or polymeric. The chelating amino–alkoxide ligands more effectively reduce molecular complexities, and thus the extent of alkoxide bridging, than the bulky ligands do. Even so, the lowest molecularity achieved was 2.4 (3), for the diamino–alkoxide **7**. Apparently, intermolecular alkoxide bridges compete very effectively with intramolecular chelating groups for available coordination sites at Zn.

In contrast, the copper(II) analogues[13b] of **6** and **7** show quite different properties. Both $Cu(OCHMeCH_2NMe_2)_2$ and $Cu-(OCH_2CH_2NMeCH_2CH_2NMe_2)_2$ are mononuclear in solution and in the solid state and are considerably more volatile than the corresponding zinc(II) compounds.[13b] For comparison, $Cu-(OCHMeCH_2NMe_2)_2$ sublimes at 60 °C/10^{-4} Torr whereas $Zn(OCHMeCH_2NMe_2)_2$ (**6**) sublimes at 170 °C/10^{-4} Torr. In contrast to the case for zinc(II), intermolecular alkoxide bridges obviously *do not* compete effectively with intramolecular chelation by amine donors in the copper(II) alkoxides. This is consistent with the findings of the classic 1953 paper by Irving and Williams;[29] although nitrogen donors bind with higher stability constants than do oxygen donors to *both* zinc(II) and copper(II), the difference is significantly greater for copper(II) than for zinc(II) (see Figure 4 in ref 29).

We may also draw comparisons to the dialkoxides of lead(II).[14] $Pb(OCHMeCH_2NMe_2)_2$, which is mononuclear in solution, distills at 106 °C/10^{-4} Torr. Thus, its volatility is intermediate to that for $Cu(OCHMeCH_2NMe_2)_2$ and $Zn(OCHMeCH_2NMe_2)_2$. The lead(II) analogue to $Zn(OCEt_3)_2$ (**1**), $Pb(OCEt_3)_2$, is also more volatile: $Pb(OCEt_3)_2$ distills at 165–170 °C/10^{-4} Torr; **1** sublimes at 220 °C/10^{-4} Torr. We have not been able to prepare bulky dialkoxides of copper(II), such as $Cu(OCEt_3)_2$.

Small changes in ligand structure induce significant differences in physical properties. For example, whereas $Zn(OCEt_2Me)_2$ (**2**) is insoluble in all solvents studied, $Zn(OCEt_3)_2$ (**1**) possesses excellent solubility in common organic solvents and is the derivative of choice for solution-phase chemistry.[15] Furthermore, whereas **7** is oligomeric, the enolate **8**, which differs only in having an etheno bridge instead of an ethano bridge between O_α and N_δ (see eq 3), is a mononuclear, octahedral complex. Of course, the

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rigidity imposed by such etheno bridges is well-known to increase the chelating tendencies of multidentate ligands relative to their flexible, ethano-bridged analogues.[30] Complex **8** is to our knowledge the first homoleptic zinc enolate.

The thermal dehydrogenation of **7** to **8** is a novel (and unanticipated) metal enolate synthesis. In a possibly related observation, Mazdiyasni reported several years ago[31] that the synthesis of "Y(O-*i*-Pr)₃"[32] from yttrium metal and refluxing 2-propanol was under some conditions accompanied by the formation of Y[OC(=CH₂)Me]₃. However, it was not shown (or claimed) that the enolate was derived from the alkoxide. The driving force for the **7** to **8** conversion is unknown, but it may be the thermodynamic stability of the chelated, mononuclear structure as discussed above. The mechanisms by which alkoxides undergo thermal decomposition have not been widely studied, but a number of pathways are apparently operative, which depend on the metal and the nature of the alkoxide substituents.[7c,13b,31,33] The dehydrogenation identified here may depict an early stage in some alkoxide-decomposition processes.

Our soluble zinc(II) dialkoxides hydrolyze rapidly to afford amorphous, hydrated zinc oxide powders. However, compound **1** and acetone react to give transparent gels, which afford amorphous, hydrated zinc oxide upon drying.[15a] The cohydrolyses of zinc(II) and copper(II) or copper(I) alkoxides lead to Zn/Cu oxides that are catalytically active for carbon monoxide hydrogenation to methanol.[15b] The details of these studies will be described in future publications. In conclusion, the zinc(II) dialkoxides provided herein should be ideal precursors for a wide range of experiments aimed at ZnO fabrication.

Supplementary Material Available: Listings of crystallographic data collection parameters, equivalent isotropic thermal parameters, bond distances, bond angles, calculated hydrogen atom parameters, and anisotropic thermal parameters (11 pages); tables of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Physical Properties of (μ-Oxo)(μ-carboxylato)bis{(tris(2-pyridylmethyl)amine)chromium(III)} Complexes

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Three μ-oxo-μ-carboxylato-bridged complexes of the form [(tmpa)Cr(O)(RCO₂)Cr(tmpa)]³⁺ (R = H, CH₃, C₆H₅; tmpa = tris(2-pyridylmethyl)amine) have been prepared and characterized through measurements of electronic and infrared spectra, ionization constants of conjugate hydroxy-bridged acids, magnetic susceptibility temperature dependences, and cyclic voltammograms. A perchlorate salt of the methyl derivative, [(tmpa)Cr(O)(CH₃CO₂)Cr(tmpa)](ClO₄)₃ (Cr₂Cl₃O₁₅N₈C₃₈H₃₉·0.7H₂O), crystallizes in the monoclinic system (space group *P*2₁/*c* (No. 14)), with *a* = 10.509 (5) Å, *b* = 21.040 (16) Å, *c* = 20.724 (7) Å, β = 98.46 (4°), and *V* = 4532 (4) Å³; *Z* = 4. The Cr–O–Cr core is characterized by nonequivalent Cr–O bond distances of 1.789 (9) and 1.853 (9) Å, a bond angle of 131.9° and trans influences toward Cr–N bonds of 0.054 and 0.034 Å, respectively. Linear correlations of free carboxylic acid p*K*ₐ values with both the p*K*ₐ's of [(tmpa)Cr(OH)(RCO₂)Cr(tmpa)]⁴⁺ species and the antiferromagnetic coupling constants of [(tmpa)Cr(O)(RCO₂)Cr(tmpa)]³⁺ dimers demonstrate that enhanced Cr–O(carboxylate) bond strengths, linked to increasing RCO₂⁻ nucleophilicity, occur at the expense of π-bonding within the CrOCr bridging unit. Electronic spectra and one-electron oxidation waves of the μ-oxo-μ-carboxylato dimers are consistent with expectations when a linear (*D*₄ₕ) CrOCr complex is bent to pseudo-*C*₂ᵥ symmetry with some retention of π-bonding.

Introduction

The unusual lability of a bridging hydroxy group in [(tmpa)-Cr(OH)₂Cr(tmpa)]⁴⁺ (tmpa = tris(2-pyridylmethyl)amine)[1] and related dihydroxo-bridged chromium(III) dimers with aromatic amine ligands led to our recent synthesis of LN₄CrOCrN₄L²⁺ linear μ-oxo complexes,[2] where L⁻ = NCS⁻, NCO⁻, N₃⁻, CN⁻, and Cl⁻. An early attempt to extend this series with L⁻ = acetate showed that μ-OH⁻ displacement proceeds readily in the presence of a carboxylate incoming group, but the product contains only one CH₃CO₂⁻ ion per dinuclear Cr unit.[2] A very different syn-thetic route featuring carboxylate-induced aggregation of monomer units yields [L₂Cr₂(μ-OH)(μ-CH₃CO₂)₂]³⁺ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane), characterized by weak antiferromagnetic coupling between the triply-bridged Cr(III) centers (*J* = −15.5 cm⁻¹).[3,4] Reversible ionization of the μ-OH function accompanied by enhancement of Δ*E*(singlet–triplet) has recently been established for the [L₂M₂(μ-OH)(μ-CH₃CO₂)₂]³⁺ series of

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