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Defect-Induced Acceleration of a Solid-State Chemical Reaction in Zinc Alkoxide Single Crystals

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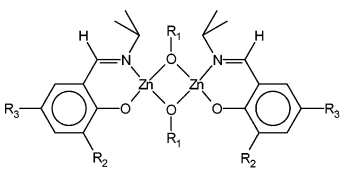
A family of dinuclear (salicylaldimato)zinc(μ_2-alkoxide) complexes show unusual behavior, decomposing to olefins and the corresponding μ_2-hydroxide complexes under very mild conditions in the solid state. The reaction in homogeneous solution is, on the other hand, not observable, even at elevated temperatures over extended periods of time. The reaction in the solid state occurs preferentially on one crystallographic face and displays kinetics characteristic of polymorphic transformations in single crystals.

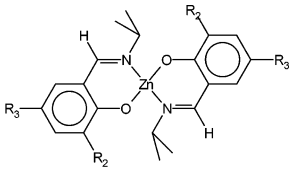
Introduction

Thermal decomposition of transition metal alkoxides is widely used to prepare metal oxide films and materials.[1] The alkoxides are used because they are cost-effective and have, in the best cases, a well-defined stoichiometry. Nevertheless, their thermal decomposition—a reaction in which an olefin is eliminated—normally requires high temperatures. We report a novel acceleration of the olefin elimination reaction in the solid state for a particular family of zinc alkoxide complexes **1** which, depending on the polymorph, is triggered by either mechanical damage to the surface of X-ray quality single crystals or loss of an ordered solvent molecule.



1 "1:1 complex"

(a) R_1 = *t*-Bu, R_2 = CH_3, R_3 = H
(b) R_1 = *t*-Bu, R_2 = H, R_3 = CH_3
(c) R_1 = *t*-Bu, R_2 = Ph, R_3 = H
(d) R_1 = *t*-Bu, R_2 = *i*-Pr, R_3 = H
(e) R_1 = *t*-Bu, R_2 = H, R_3 = NO_2
(f) R_1 = H, R_2 = CH_3, R_3 = H
(g) R_1 = H, R_2 = H, R_3 = CH_3
(h) R_1 = H, R_2 = *i*-Pr, R_3 = H
(i) R_1 = H, R_2 = H, R_3 = NO_2



2 "2:1 complex"

(a) R_2 = CH_3, R_3 = H
(b) R_2 = H, R_3 = CH_3

Surprisingly, the solid-state reaction can proceed considerably faster than the corresponding reaction in homogeneous solution, occurring visibly on the time scale of minutes even at room temperature, as opposed to months at elevated temperatures for the same complexes in solution. Moreover, as can be observed macroscopically, in at least one polymorphic form of the crystal, the elimination occurs preferentially on one crystallographic face. The combination of unusual features makes this reaction a model by which the general elimination reaction, and possible means by which it may be manipulated to promote reaction under milder conditions, can be studied.

Experimental Section

Methods and Materials. Unless otherwise specified, all syntheses and manipulations of Zn(II) complexes were carried out under an argon atmosphere using standard Schlenk techniques or in an argon filled glovebox. THF, benzene-d_6, and toluene were distilled from sodium prior to being used. The solvents for ligand syntheses were purchased in p.A. quality from Fluka. Infrared spectra were recorded on a Paragon1000 FT-IR spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Gemini 300 and Varian Mercury 300 instruments. Chemical shifts (δ) are given in ppm relative to tetramethylsilane with residual solvent proton resonance as internal standard and coupling constants in (J) in hertz. Elemental analyses were carried out by the Mikrolabor of the Laboratorium für Organische Chemie der ETH Zürich.

General Procedure for the Preparation of the *N*-Isopropylsalicylaldimine Ligands. To a 1.1 M solution of *N*-isopropylamine in dichloromethane was added the salicylaldehyde in an equimolar ratio. After 1 h of stirring at room temperature the yellow reaction mixture was dried with anhydrous $MgSO_4$ and filtered. Evaporation of the solvent gave the desired imine in excellent yield, which was used without further purification.

General Procedure for [SalZnO^{t}Bu] 1a−e. To a solution of zinc bis(trimethylsilyl)amide (0.76 mL, 1.909 mmol) in THF (8 mL) was added a solution of the 3-methylsalicylaldimine (338 mg,

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(1) Mehrotra, R. C.; Singh, A. *Prog. Inorg. Chem.* **1997**, *46*, 239. Mehrotra, R. C. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 269.

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1.909 mmol) in THF (2 mL). After 5 min of stirring, 172 of μL *t*-BuOH (1.909 mmol) was added via a syringe to the yellow solution. The resulting pale yellow-green solution was stirred for an extra 90 min and then concentrated down to 1−2 mL.

[(3Me-sal)Zn(μ-O^{t}Bu)]$_2$ (1a). The resulting pale yellow-green solution was stirred for an additional 90 min and then concentrated down to 1−2 mL. Approximately 2 mL of hexane was added, and the solution was then placed at −20 °C. Pale yellow crystals formed after 2 days. The supernatant liquor was removed, and the crystals were dried under vacuum and collected to yield 405 mg (68%). Anal. Calcd for $(C_{15}H_{23}NO_2Zn)_2$: C, 57.24; H, 7.37; N, 4.45. Found: C, 56.98; H, 7.23; N, 4.73. ^{1}H NMR (C_6D_6, 300 MHz): δ 1.26 (d, J = 6.54 Hz, 12H, CH(CH_3)$_2$), 1.41 (s, 18H, C(CH_3)$_3$), 2.50 (s, 6H, 3-CH_3), 3.08 (sept, 2H, J = 6.54 Hz, CH(CH$_3$)$_2$), 6.5−6.65 (m, 2H, aryl-H), 6.8−6.9 (m, 2H, aryl-H), 7.2−7.3 (m, 2H, aryl-H), 7.78 (s, 2H, aldimine-H). ^{13}C NMR (C_6D_6, 75.45 MHz): δ 17.18, 24.70, 33.50, 63.04, 71.50, 113.84, 116.74, 132.01, 133.82, 135.24, 169.27. X-ray analysis of the crystals revealed that the complex exists as a μ-*t*-butoxide-bridged dimer in the solid state.

(3Me-sal)Zn(μ-O^{t}Bu)]$_2$·2Toluene (1a·2Toluene). To a solution of zinc bis(trimethylsilyl)amide (0.90 mL, 2.23 mmol) in toluene (8 mL) was added a solution of the 3-methylsalicylaldimine **1** (395 mg, 2.23 mmol) in toluene (2 mL). After 5 min of stirring, 213 μL of *t*-BuOH (2.32 mmol) was added via a syringe to the yellow solution. The resulting pale yellow-green solution was stirred for an additional 90 min and then concentrated down to 1−2 mL. The solution was then placed at −20 °C. Colorless block-shaped crystals formed after several days. The supernatant liquid was removed, and the crystals were dried under an argon flow at −30 °C for 60 min (59%). Anal. Calcd for $(C_{22}H_{31}NO_2Zn)_2$: C, 64.94; H, 7.68; N, 3.44. Found: C, 60.97; H, 6.99; N, 3.92. ^{1}H NMR (C_6D_6, 200 MHz): δ 1.25 (d, J = 6.64 Hz, 12H, CH(CH_3)$_2$), 1.40 (s, 18H, C(CH_3)$_3$), 2.11 (s, 3H, CH_3-toluene), 2.50 (s, 6H, 3-CH_3), 3.08 (sept, J = 6.64 Hz, 2H, CH(CH$_3$)$_2$), 6.58 ("t", J = 7.85 Hz, 2H, aryl-H), 6.86 (dd, J = 7.85, 1.66 Hz, 2H, aryl-H), 6.95−7.2 (m, 5H, aryl-H), 7.2−7.3 (m, 2H, aryl-H), 7.76 (s, 2H, aldimine-H). ^{13}C NMR (C_6D_6, 50.3 MHz): δ 17.40, 21.38, 24.84, 33.64, 63.17, 71.58, 113.84, 116.73, 125.68, 129.33, 132.00, 133.81, 135.20, 169.18, 170.48. IR (KBr, disk): $\tilde{\nu}$ = 3422 (w) [v(H−O−H)], 2966, 2896 (m), 2366, 1846, 1812, 1736 (w), 1614, 1550, 1465, 1415 (s), 1350, 1342 (w), 1326 (m), 1242, 1219, 1182, 1144, 1089 (m), 1040, 992, 971 (w), 936 (s), 870 (w), 752 (s), 723, 628 (w), 594 (s) cm^{-1}. X-ray analysis of the crystals revealed that the complex exits as a μ-*t*-butoxide-bridged dimer with two toluene molecules per dimer unit (one per metal atom) in the solid state.

[(5Me-sal)Zn(μ-O^{t}Bu)]$_2$·thf (1b·thf). The complex **1b·thf** was prepared according to the general procedure (75%). Anal. Calcd for $(C_{15}H_{23}NO_2Zn)_2$: C, 57.24; H, 7.37; N, 4.45. Found: C, 56.77; H, 7.00; N, 5.05. ^{1}H NMR (C_6D_6, 300 MHz): δ 1.28 (d, J = 6.64 Hz, 12H, CH(CH_3)$_2$), 1.41 (s, 18H, C(CH_3)$_3$), 2.14 (s, 6H, 5-CH_3), 3.17 (sept, J = 6.64 Hz, 2H, CH(CH$_3$)$_2$), 3.57 (traces THF), 6.65 (d, J = 2.49 Hz, 2H, Aryl-3H), 7.01 (dd, J = 8.72, 2.49 Hz, 2H, Aryl-4H), 7.23 (d, J = 8.72 Hz, 2H, Aryl-6H), 7.72 (s, 2H, aldimine-H). ^{13}C NMR (C_6D_6, 75.45 MHz): δ 20.24, 24.90, 25.83 (THF), 33.90, 62.97, 67.83 (THF), 71.53, 110.02, 117.30, 122.22, 124.19, 135.28, 136.83, 169.01, 170.45. IR (CH_2CL_2): $\tilde{\nu}$ = 3055 (s), 2975, 2360, 2305, 1758 (w), 1621 (s), 1534, 1458, 1474, 1421 (m), 1398, 1369, 1316, 1211, 1154, 1134, 1104 (m), 1063 (w), 896 (s), 831, 806 (w) cm^{-1}. Block-shaped, slightly yellow crystals suitable for X-ray analysis were obtained at −20 °C from THF/hexane after 2 days. The X-ray analysis revealed that the complex exists as a μ-*t*-butoxide-bridged dimer with one molecule of THF in the solid state.

[(3Ph-sal)Zn(μ-O^{t}Bu)]$_2$ (1c). The complex **1c** was prepared according to the general procedure (77%). Anal. Calcd for $(C_{20}H_{25}NO_2Zn)_2$: C, 63.75; H, 6.69; N, 3.72. Found: C, 63.78; H, 6.64; N, 3.91. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 1.09 (s, 18H, C(CH_3)$_3$), 1.49 (d, J = 6.54 Hz, 12H, CH(CH_3)$_2$), 3.72 (sept, J = 6.54 Hz, 2H, CH(CH$_3$)$_2$), 6.64 ("t", J = 7.5 Hz, 2H, aryl-H), 7.12 (dd, J = 7.78, 1.87 Hz, 2H, aryl-H), 7.29−7.35 (m, 6H, Ph-H), 7.47 (dd, J = 7.47, 1.87 Hz, 2H, aryl-H), 7.7−7.8 (m, 4H, Ph-H), 8.29 (s, 2H, aldimine-H). ^{13}C NMR (CD_2Cl_2, 75.45 MHz): δ 24.95, 33.41, 63.60, 71.42, 114.22, 118.95, 126.50, 127.86, 127.93, 130.05, 134.24, 135.37, 135.99, 140.09, 168.86, 169.52.

[(3^{i}Pr-sal)Zn(μ-O^{t}Bu)]$_2$·thf (1d·thf). The complex **1d·thf** was prepared according to the general procedure (50%). Anal. Calcd for $(C_{34}H_{54}NO_2Zn)_2$: C, 59.57; H, 7.94; N, 4.09. Found: C, 59.51; H, 7.99; N, 4.01. ^{1}H NMR (C_6D_6, 300 MHz): δ 1.25 (d, J = 6.53 Hz, 12H, CH(CH_3)$_2$), 1.37 (d, J = 6.84 Hz, 12H, NCH(CH_3)$_2$), 1.42 (s, 18H, C(CH_3)$_3$), 3.10 (sept, J = 6.53 Hz, 2H, CH(CH$_3$)$_2$), 3.98 (sept, J = 6.84 Hz, 2H, NCH(CH$_3$)$_2$), 6.67 ("t", J = 7.47 Hz, 2H, aryl-5H), 6.87 (dd, J = 8.09, 1.87 Hz, 2H, aryl-4H), 7.34 (dd, 2H, J = 7.16, 1.87 Hz, aryl-6H), 7.77 (s, 2H, aldimine-H). ^{13}C NMR (C_6D_6, 75.45 MHz): δ 23.06, 24.86, 27.07, 33.79, 63.05, 71.52, 114.17, 117.22, 131.18, 133.74, 142.39, 169.31. IR (KBr): $\tilde{\nu}$ = 3425 (w), 2972, 1621, 1547, 1458, 1410 (s), 1368, 1326, 1288, 1259, 1231 (w), 1208, 1146 (m), 1104, 1052, 1019, 986 (w), 934 (m), 892, 854, 835, 807 (w), 750 (s), 712, 627, 590, 566, 529 (w) cm^{-1}. Block-shaped, slightly yellow crystals suitable for X-ray analysis were obtained at −20 °C from THF/hexane after 2 days. The X-ray analysis revealed that the complex exists as a μ-*t*-butoxide-bridged dimer with one molecule of THF in the solid state.

[(5Nitrosal)Zn(μ-O^{t}Bu)]$_2$·Toluene (1e·Toluene). The complex **1e·**toluene was prepared in toluene according to the general procedure (77%). Anal. Calcd for $(C_{14}H_{20}N_2O_4Zn)_2$·(C_7H_8): C, 53.65; H, 6.17; N, 7.15. Found: C, 53.37; H, 6.18; N, 7.23. ^{1}H NMR (C_6D_6, 200 MHz): δ 1.14 (d, J = 6.53 Hz, 12H, CH(CH_3)$_2$), 1.24 (s, 18H, C(CH_3)$_3$), 2.11 (s, 3H, CH_3-toluene), 3.02 (sept, J = 6.54 Hz, 2H, CH(CH$_3$)$_2$), 6.74 (d, J = 9.65 Hz, 2H, Aryl-3H,), 7.0−7.2 (m, 5H, toluene-H), 7.26 (s, 2H, aldimine-H), 7.86 (d, J = 3.11 Hz, 2H, aryl-6H), 7.98 (dd, J = 9.65, 3.11 Hz, 2H, aryl-4H). ^{13}C NMR (C_6D_6, 50.28 MHz): δ 21.25, 24.36, 33.57, 62.99, 71.75, 116.15, 124.00, 125.71, 128.54, 129.33, 130.00, 136.69, 168.59, 175.74. IR (KBr): $\tilde{\nu}$ = 2968 (m), 2359 (w), 1625, 1604 (s), 1550 (m), 1508 (w), 1490 (m), 1438 (w), 1417, 1358 (m), 1317 (s), 1247, 1194, 1144, 1130, 1105 (m), 1033, 1000 (w), 948, 930 (m), 842, 788, 762, 742, 690, 652, 590, 512 cm^{-1}.

(3Mesal)$_2$Zn·Toluene (2a·Toluene). Zinc acetate dihydrate (436 mg, 2 mmol) was added to a solution of 3-methylsalicylaldimine (709 mg, 4 mmol) in 20 mL of methanol and refluxed for 16 h. The resulting yellow solution was cooled to 5 °C. The precipitate formed was filtered and dried in a vacuum to give 660 mg (79%) of yellow block-shaped crystals of the desired bis-salicylaldiminato complex of zinc. Anal. Calcd for $C_{22}H_{28}N_2O_2Zn$: C, 63.24; H, 6.75; N, 6.70. Found: C, 63.20; H, 6.94; N, 6.63. ^{1}H NMR (C_6D_6, 200 MHz): δ 0.82, 1.10 (2d, J = 6.23 Hz, 12H, CH(CH_3)$_2$), 2.47 (s, 6H, 3-CH_3), 2.91 (sept, J = 6.23 Hz, 2H, CH(CH$_3$)$_2$), 6.58 ("t", 2H, Aryl-H), 6.84 (dd, 2H, aryl-H), 7.26 (dd, 2H, aryl-H), 7.66 (s, 2H, aldimine-H). ^{13}C NMR (C_6D_6, 75.45 MHz): δ 17.38, 23.38, 24.56, 62.87, 113.96, 117.34, 131.80, 133.99, 135.28, 169.26, 170.13. IR (KBr, disk): $\tilde{\nu}$ = 2962, 2915, 2359 (m), 1613, 1547, 1458, 1425, 1406 (s), 1368, 1316 (w), 1264, 1217, 11421, 1090 (m), 1033, 962 (w), 863 (w), 797, 750 (s), 722 (w) cm^{-1}. X-ray analysis of the crystals from toluene revealed that the complex exists as a four coordinate monomer with distorted tetrahedral geometry and one molecule of toluene in the solid state.

(5Mesal)$_2$Zn (2b). Zinc acetate dihydrate (280.97 mg, 1.28 mmol) was added to a solution of 5-methylsalicylaldimine (453 mg, 2.55 mmol) in 20 mL of methanol and refluxed for 16 h. The resulting yellow solution was cooled to 5 °C. The precipitate formed was filtered and dried in a vacuum to give 252 mg (77%) of yellow crystals of the desired bis-salicylaldiminato complex of zinc. Anal. Calcd for $C_{22}H_{28}N_2O_2Zn$: C, 63.24; H, 6.75; N, 6.70. Found: C, 63.17; H, 6.68; N, 6.60. ^{1}H NMR (C_6D_6, 200 MHz): δ 0.89, 1.15 (b, 12H, CH(CH_3)$_2$), 2.15 (s, 6H, 3-CH_3), 2.96 (sept, 2H, CH(CH$_3$)$_2$), 6.63 (dd, 2H, aryl-*H*), 7.03 (dd, 2H, aryl-*H*), 7.21 (d, 2H, aryl-*H*), 7.61 (s, 2H, aldimine-*H*).

Thermolysis of (1a·2Toluene) to [(3Me-sal)Zn(OH)]$_2$ (1f). The thermolysis of *t*-butoxide (**1a·2toluene)** was carried out without additional solvent in a sidearm flask with Young valve connected with another sidearm flask. The zinc complex (75 mg) was held for 16 h at room temperature in the closed flask, the valve was then opened, and the volatile products were distilled for 6 h into the connected cooled flask (−40 °C) filled with 1 mL of $CDCl_3$. The only detectable products were toluene and traces of condensed water. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.55 (H_2O), 2.36 (s, 3H, CH_3), 7.17 (m, 4H, aryl-CH(*o*/*p*)), 7.25 (m, 2H, aryl-CH(*m*)). The solid, powdered residue could be identified as the 1:1 Zn complex without toluene as solvent molecule. ^{1}H NMR (C_6D_6, 300 MHz): δ 1.26 (d, 6H, J_{HH} = 6.64 Hz, CH(CH_3)$_2$), 2.50 (s, 3H, 3-CH_3), 3.08 (sept, 1H, J = 6.64 Hz, CH(CH$_3$)$_2$), 6.58 (t, 1H, aryl-*H*), 6.86 (dd, 1H, J = 7.89 Hz, 2.03 Hz), 7.26 (m, 1H, aryl-*H*), 7.76 (s, 1H, aldimine-*H*). The solid residue (60 mg) was held for an extra 24 h at ambient temperature, and the volatile products were distilled into the connected, opened cooling trap (−40 °C) filled with 1.5 mL of $CDCl_3$ under an argon atmosphere. The detected, volatile products were isobutene and traces of water. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.53 (H_2O), 1.73 (t, 6H, J = 1.25 Hz), 4.66 (sept, 2H, J = 1.25 Hz). The powdered, slightly yellow product could by identified as the hydroxide [(3Mesal)Zn(OH)]$_2$, **1f**, by elemental analysis and IR. The NMR of the hydroxide **1f** upon dissolution of the powder in C_6D_6 showed the same signals as the bis-salicylaldiminato complex of zinc **2a**. Anal. Calcd for $C_{22}H_{30}N_2O_4Zn_2$: C, 51.08; H, 5.85; N, 5.42. Found: C, 50.82; H, 5.95; N, 5.35. ^{1}H NMR (C_6D_6, 300 MHz): δ 0.82 (d, 3H, J = 6.54 Hz, CH(CH_3)$_2$), 1.10 (d, 3H, J = 6.54 Hz, CH(CH_3)$_2$), 2.47 (s, 3H, 3-CH_3), 2.90 (sept, 1H, J = 6.54 Hz, CH(CH$_3$)$_2$), 6.59 (t, 1H, aryl-*H*), 6.83 (dd, 1H, J = 7.89 Hz, 2.03 Hz), (m, 1H, aryl-*H*), 7.65 (s, 1H, aldimine-*H*). IR (KBr, disk): $\tilde{\nu}$ = 3386 (s) [ν(O−H)], 2968, 2896 (m), 1622, 1551, 1457, 1429, 1409 (s), 1375 (w), 1317 (s), 1240 (w), 1217, 1141 (s), 1090, 1034, 984, 968, 869, 856 (m), 752 (s), 721, 628 (w), 544 (m) cm^{-1}. The transformation of a single crystal of **(1a·2toluene)** to the hydroxide at three different times is shown in Figure 3.

Attempted Thermolysis of Crystals of [(3Mesal)Zn(μ-O^{t}Bu)]$_2$ (1a) to the Hydroxide [(3Mesal)Zn(OH)]$_2$ (1f). X-ray Structural Study. Single crystals suitable for X-ray analysis of **1a** (without ordered solvent) were obtained after 7 days from a concentrated THF solution of the complex layered with hexane and maintained at −20 °C. The colorless, block-shaped single crystal employed in this experiment was picked out directly from the pale yellow mother liquor. The temperature dependence of the thermolysis of **1a** should be determined in principle by heating gradually the single crystal of **1a** and solving the structure at different temperature. A phase transformation of **1a** could be monitored between 251 and 266 K, but even after several days at 343 K no crystalline state transformation to the hydroxide or any other product proceeded. This result was confirmed by NMR: three crystals of the dimeric zinc complex **1a** from THF (15 mg) were dried for 30 min under an argon flow at −20 °C and heated for 24 h at 50 °C. No conversion proceeded to the hydroxide; the NMR signals at the initial and at the final stage were exactly the same.

Thermolysis of [(3Mesal)Zn(μ-O^{t}Bu)]$_2$ (1a) to [(3Mesal)Zn-(OH)]$_2$ (1f). The crystals of the same batch used for X-ray analysis were powdered for 1 min. The NMR of the obtained powder, taken immediately, still showed the signals of the μ-bridged *t*-butoxide **1a**; 10 mg of the powder was heated for 16 h (50 °C) to afford a product that could be identified as the hydroxide by elemental analysis and IR. Anal. Calcd for $C_{22}H_{30}N_2O_4Zn_2$: C, 51.08; H, 5.85; N, 5.42. Found: C, 51.34; H, 6.14; N, 5.24. ^{1}H NMR (C_6D_6, 300 MHz): δ 0.81 (d, 3H, J = 6.54 Hz, CH(CH_3)$_2$), 1.10 (d, 3H, J = 6.54 Hz, CH(CH_3)$_2$), 2.48 (s, 3H, 3-CH_3), 2.90 (sept, 1H, J = 6.54 Hz, CH(CH$_3$)$_2$), 6.59 (t, 1H, aryl-*H*), 6.83 (dd, 1H, J = 7.89 Hz, 2.03 Hz), 7.27 (m, 1H, aryl-*H*), 7.64 (s, 1H, aldimine-*H*). IR (KBr, disk): $\tilde{\nu}$ = 3396 (m, b) [ν(O−H)], 2967, 2896 (m), 1618, 1550, 1455, 1429, 1409 (s), 1375 (w), 1317 (s), 1264 (w), 1216, 1145, 1090 (s), 1031 (m), 984, 968 (w), 869, 856 (m), 752 (s), 721, 626. 606 (m), 544 (w) cm^{-1}.

Thermolysis of [(3Mesal)Zn(μ-O^{t}Bu)]$_2$ (1a) to the 2:1 Complex (3Mesal)$_2$Zn (2a). Kinetic Study in Solution. In a drybox, 0.7 mL of toluene-d_8, distilled trap-to-trap from molecular sieves and then degassed by three freeze−pump−thaw cycles, and 80 mg of the Zn complex **1a** were placed in a NMR tube equipped with a Young valve, the tube was closed, and the starting complex was characterized by ^{1}H NMR spectroscopy. The slightly yellow solution was heated to 80 °C. The conversion was calculated by the averaged ratio of intensities of the following signals of the 1:1 complex (δ 1.25 (d, 12H, CH(CH_3)$_2$), 2.38 (s, 6H, 3-CH_3), 3.07 (sept, 2H, CH(CH$_3$)$_2$), 7.67 (s, 2H, aldimine-*H*)) to the corresponding signals of the 2:1 complex (δ 0.80, 1.07 (2d, 12H, CH(CH_3)$_2$), 2.34 (s, 6H, 3-CH_3), 2.89 (sept, 2H, CH(CH$_3$)$_2$), 7.68 (s, 2H, aldimine-*H*)). After an initial immediate conversion of some **1a** to **2a** by traces of residual water, no further conversion could be seen at 5, 13, and 81 days reaction time in the homogeneous solution. A similar experiment with benzene-d_6 at 50 °C gave the same results.

Thermolysis of Crystals of [(3Mesal)Zn(μ-O^{t}Bu)]$_2$·2Toluene (1a·2Toluene) to the Hydroxide [(3Mesal)Zn(OH)]$_2$ (1f). Kinetic Study in the Solid State. Eight single crystals of **1a**·2toluene, all of a similar size, were chosen directly from the toluene mother liquor and placed in an empty Schlenk tube through which dry argon was slowly flowed. Periodically, a crystal was removed and dissolved in dry benzene-d_6 (dried over molecular sieves, distilled, and then filtered through activated Al_2O_3) and checked by ^{1}H NMR. This drying procedure works better than the sieves alone, and leaves no significant trace water. The extent of conversion of **1a** to **1f** (and subsequently to **2a** in solution) was determined by comparing the relative intensities of the peaks assigned to both the isopropyl and methyl groups on the ligand. Moreover, the amount of toluene remaining in the crystal could be determined by integration of peak from its methyl protons. The results are displayed in Figure 4.

Thermolysis of [(5Mesal)Zn(μ-O^{t}Bu)]$_2$·thf (1b·thf) to [(5Me-sal)Zn(OH)]$_2$ (1g). The crystals of the *t*-butoxide (**1b**·thf) were heated for 16 h at ambient temperature under an argon atmosphere to to afford a yellow powder object shaped as the initial crystal. The product could be identified as the hydroxide **1g** (100%) by elemental analysis. The NMR of the hydroxide **1g** after dissolution of the powder in C_6D_6 showed the same signals as the bis-salicylaldiminato complex of zinc **2b**. Anal. Calcd for $C_{22}H_{30}N_2O_4Zn_2$: C, 51.08; H, 5.85; N, 5.42. Found: C, 51.15; H, 6.00; N, 5.34. ^{1}H NMR (C_6D_6, 200 MHz): δ 0.88, 1.15 (2d, 12H, CH(CH_3)$_2$), 2.15 (s, 6H, 5-CH_3), 2.96 (sept, 2H, CH(CH$_3$)$_2$), 6.62 (d,

2H, aryl-3*H*), 7.03 (dd, 2H, aryl-4*H*), 7.21 (d, 2H, aryl-6*H*), 7.61 (s, 2H, aldimine-*H*).

Thermolysis of [(3^{i}Prsal)Zn(μ-O^{t}Bu)]$_2$·thf (1d·thf) to [(3^{i} Prsal)Zn(OH)]$_2$ (1h). The procedure is analogous to the one used for hydroxide **1g**. The obtained, slightly yellow powder could be identified as [(3^{i} Prsal)Zn(OH)]$_2$ (**1h**) (100%) by elemental analysis and IR. Anal. Calcd for $C_{26}H_{38}N_2O_4Zn_2$: C, 54.46; H, 6.68; N, 4.89. Found: C, 54.54; H, 6.65; N, 4.74. ^{1}H NMR (C_6D_6, 200 MHz): δ 0.84 (d, 3H, CH(C*H*$_3$)$_2$) 1.00 (d, 2H, CH(C*H*$_3$)$_2$) 1.10 (d, 4H, CH(C*H*$_3$)$_2$) 1.19 (d, 3H, CH(C*H*$_3$)$_2$), 1.37 (m, 12H, CH(C*H*$_3$)$_2$), 2.15 (s, 6H, 5-C*H*$_3$), 2.92 (sept, 2H, C*H*(CH$_3$)$_2$), 3.95 (sept, 2H, C*H*(CH$_3$)$_2$), 6.66 (m, 2H, aryl-*H*), 6.82 (m, 2H, aryl-*H*), 7.34 (dd, 2H, aryl-*H*), 7.68 (s, 2H, aldimine-*H*). IR (KBr, disk): $\tilde{\nu}$ = 3422 (m, b), 2966, 1624, 1547, 1460, 1429, 1409 (s), 1366, 1324, 1287, 1231 (w), 1208, 1146 (m), 1108, 1052, 1019 (w), 934, 893, 857, 837, 807 (w), 750 (s), 708, 669, 628, 606, 568, 521 (w) cm^{-1}.

Thermolysis of [(5Nitro)Zn(μ-O^{t}Bu)]$_2$·Toluene (1e·Toluene) to [(5Nitro)Zn(OH)]$_2$ (1i). The procedure is analogous to the one used for hydroxide **1g**. The obtained, slightly yellow powder could be identified as [(5Nitro)Zn(OH)]$_2$ (**1i**) (100%) by elemental analysis and IR. Anal. Calcd for $C_{20}H_{24}N_4O_8Zn_2$: C, 41.47; H, 4.18; N, 9.67. Found: C, 41.73; H, 4.32; N, 9.35. IR (KBr, disk): $\tilde{\nu}$ = 3425 (m,b), 2963, 2925, 2868 (m), 2368 (w), 1736, 1686, 1654, 1637, 1604 (s), 1560, 1474, 1408 (m), 1319 (s), 1102 (m), 948, 906 (m), 835, 788, 755, 731, 688, 656 (w), 590.

Results

While previous studies of salicylaldimato zinc complexes[2] found only the 2:1 complexes **2**, careful crystallization of solutions containing zinc salts and salicylaldimines in the proper stoichiometry produces the novel μ-alkoxy-bridged 1:1 complexes **1**, the structures of which were confirmed by single-crystal X-ray diffraction. The overall structural pattern, with the doubly bridged dinuclear core, is a common motif in zinc alkoxide complexes.[3] In the present case, X-ray-quality crystals of either **1** or (**1**·solvent) can be reproducibly prepared, depending on the crystallization solvent and conditions. While the structure of **1a** differs only slightly in the crystals with or without toluene, Figure 1, the crystals grown from toluene contain ordered solvent molecules, as can be seen in the depictions of the unit cells in Figure 2.

As expected, the 1:1 complex **1** showed a single, clean, quantitative thermal decomposition reaction: loss of isobutene, converting the μ-alkoxy-bridged 1:1 complex into the μ-hydroxy-bridged analogue. The isobutene elimination reaction was identified as the decomposition pathway in the solid state by condensation of the released isobutene in a cold trap and elemental analysis, as well as IR spectroscopy, of the powdery material left by decomposition of the crystal. In solution, the reaction can be followed by ^{1}H NMR, by which one sees conversion of the μ-alkoxy-bridged 1:1 complexes, **1a** or **1b**, into the corresponding 2:1 complexes **2a** or **2b**,

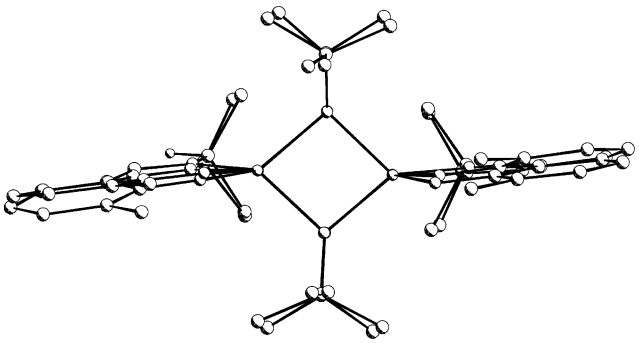

Figure 1. Superposition of the molecular structures of **1a** as found by X-ray analysis. Crystals of (**1a·2toluene)** grown from toluene and **1a** in solvent-free crystals grown from THF/hexane show similar structures.

with presumed coformation of $Zn(OH)_2$ which would be expected to be colloidal and hence difficult to see. One assumes that **1f** or **1g** is the first-formed product in the solid state or in solution, the subsequent ligand rearrangement to form **2** in solution would be driven by the insolubility of $Zn(OH)_2$.

While the elimination of isobutene is the expected reaction, the observed rate of the reaction was initially extremely confusing. Dissolved in solution, **1a** was found to be stable for up to nearly 12 weeks in both benzene and toluene at 50 °C and 80 °C, respectively. The time scale for decomposition, at room temperature, of different X-ray-quality crystals of **1a** and **1b** depended on the origin of the particular crystal and its handling, ranging from minutes to months. A striking example of the intrinsic thermal stability of **1a** is given by a temperature-dependent X-ray structure study. A single crystal of **1a**, grown from THF/hexane, was selected and carefully mounted (without cutting) under exclusion of oxygen and moisture on the diffractometer. Starting at 191 K, the temperature was stepped up by increments of 5, 10, or 20 K up to a final temperature of 343 K. The crystal was held at each temperature for approximately 2 days, during which a dataset was collected. Between 251 and 266 K, a change in the cell dimensions of the unit cell was observed (see Supporting Information), presumably corresponding to phase transitions in the crystal, but the conformation of the molecule structure, the basic composition, structure, and visible appearance of the crystal remained unchanged throughout the entire measurement period of eight weeks. On the other hand, other identically grown crystals of **1a** could also be observed to react in the solid state within minutes at room temperature with different handling.

With careful experimentation, reproducible conditions were found by which the accelerated reaction could be induced or inhibited in the solid state. These were tested repeatedly with crystals from the same batch, as well as from different batches. Crystals of **1a** grown from THF/alkane and containing no solvent in the unit cell are extremely thermally stable until their surface is damaged, for example, by cutting or scratching, upon which the crystal immediately begins to decompose. The visible alteration of the crystal starts at the site of damage and propagates rapidly throughout the entire bulk, leaving a fragile, opaque object in the shape of the original crystal. Crystals of **1a** grown from toluene and

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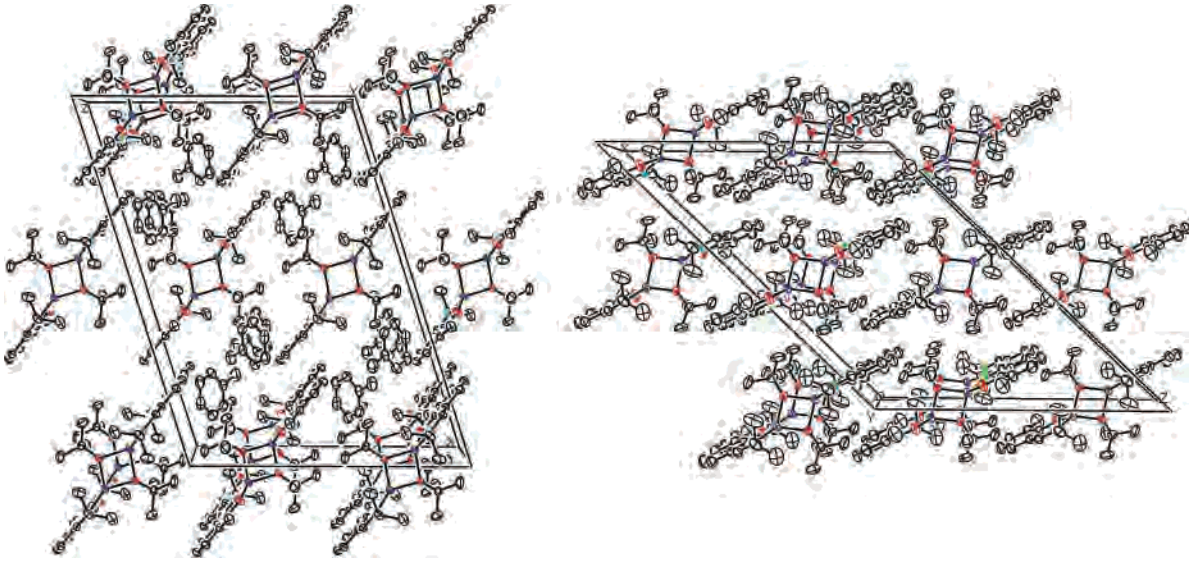

Figure 2. Unit cells of crystals of **1a** for crystals grown from toluene (left panel) versus those grown from THF/hexane (right panel). The former crystals contain one ordered toluene molecule per zinc atom, while the latter are solvent-free.

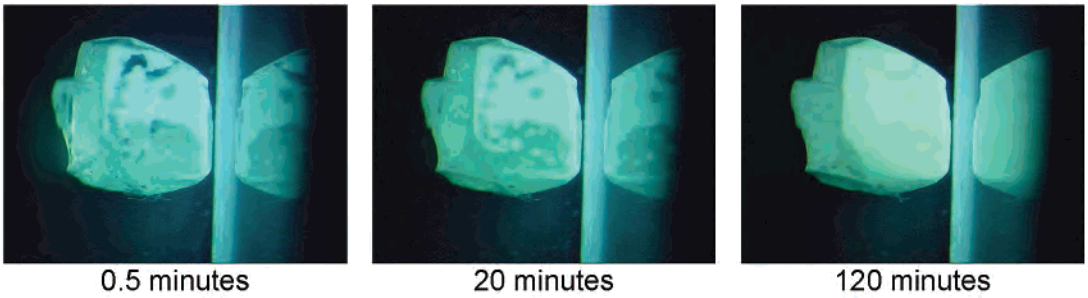

Figure 3. Changes in a single crystal of **(1a·2toluene)** as dry nitrogen is slowly flowed over it at 20 °C. The visible change corresponding to the conversion of the single crystal into a powder aggregate in the shape of the original crystal proceeds selectively from the [100] face of the crystal.

containing one ordered molecule of toluene per metal atom are stable at room temperature as long as they remain in the mother liquor from which they were grown. If they are removed from the mother liquor, they remain stable in a closed Schlenk tube. If they are mechanically damaged, they react quickly. If they are subjected to vacuum, or if a slow stream of dry inert gas is blown over the crystals, they react as well. The reaction of a single, well-faceted crystal of **1a·**2toluene as dry nitrogen was gently blown over the crystal at 20 °C was followed photographically over time. The crystal at three different times is shown in Figure 3. The reaction clearly occurs preferentially from one face of the crystal, identified as the [100] face. A more quantitative examination of the solid-state decomposition of single crystals of **(1a·2toluene)** is shown in Figure 4, where eight comparable single crystals were chosen, placed in a dry Schlenk under flowing argon at room temperature, and then one-by-one removed and analyzed for extent of conversion. As is evident from Figure 4, approximately half of the toluene escapes from the crystal rapidly, which triggers a somewhat slower decomposition of **1a** which is complete in a few hours at room temperature.

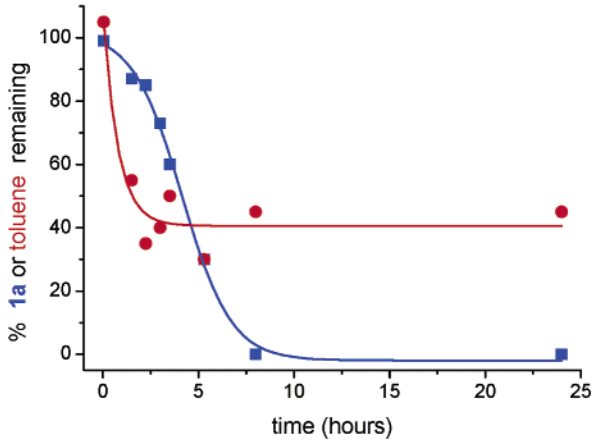

Figure 4. Percentage of either **1a** (blue) or toluene (red) remaining in each one of eight single crystals of **(1a·2toluene)** at the specified time as dry argon is blown over the crystals at room temperature. The fit to the toluene data is a single exponential; that for **1a** is sigmoidal.

Discussion

The preparation of high-performance metal oxide materials, thin films in particular, for mechanical, optical, and electronic applications by thermolysis of metal alkoxides of known structure and stoichiometry has led to a reexamination of this long-known class of compounds. Particularly interesting are metal alkoxides of low nuclearity because their improved solubility properties[4] make deposition of thin layers more convenient. The vast majority of these alkoxides require, however, high temperatures, typically >200°C, to

eliminate an olefinic fragment[5] and thus begin transformation to an oxide material.

The specialized zinc alkoxide complexes **1a**−**e** exhibit the same basic chemistry in that they undergo a clean, quantitative elimination of isobutene upon thermolysis. The unsurprising reaction displays, however, surprising characteristics. Whereas the solution-phase thermolysis indicates that the temperature needed for a practical conversion is as high as would be expected from the vast majority of analogous complexes, the solid-state reaction can be much faster. Moreover, the accelerated solid-state reaction requires some kind of physical damage to the crystal surface for initiation. Whether the physical damage is induced mechanically or by evaporative loss of ordered solvent molecules from the crystal, the reaction, once initiated, propagates rapidly through the entire bulk of the crystal.

The observed phenomena are strongly reminiscent of polymorphic transformations[6] in organic crystals. Several substances have well-documented solid-state transformations corresponding to conformational changes in the molecule, but which from the point-of-view of the crystal may be treated as phase transitions.[7,8] Most notable is the mechanochromic behavior of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate,[9] for which a phase transition in the solid state may be induced by scratching the surface of the yellow polymorph; the transformation to the white polymorph propagates from the scratch along the [100] direction until the entire crystal is transformed. Furthermore, the rate of the solid-state transformation in the present work, depicted in Figure 4, displays sigmoidal kinetics which is typical for polymorphic transformations.[10] The putative role of physical damage in initiating the present reaction finds precedent in the theory put forth by Mnyukh,[11] who proposed that phase transitions in crystals initiate exclusively at defect sites. The present solid-state reaction differs, however, from most polymorphic transformations in that the specific process, elimination of isobutene in this case, does not occur at a perceptible rate in homogeneous solution even at temperatures well in excess of those used in the solid-state reaction. Nevertheless, the shape of the curve in Figure 4, as well as the gross chemical behavior of crystals of **1**, underlines the fundamental similarity of the chemical process to those generally regarded as polymorphic transformations.

Conclusion

We have synthesized and characterized a new family of zinc alkoxide complexes in which the stoichiometry of the salicylaldimine ligand and the zinc is 1:1. The μ-bridging alkoxide serves as a model for the investigation of the olefin elimination from the more general metal alkoxide complex. As we see for **1a** and **1b**, it is possible to induce a gigantic rate acceleration, which potentially is of considerable practical value. While the experiment was performed on X-ray-quality single crystals, mechanistic understanding could lead to the same acceleration becoming available for films, amorphous solids, or the polycrystalline materal. The mechanistic studies are underway.

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Supporting Information Available: Seven X-ray crystallographic files, in CIF format. Details of X-ray crystallography, table of X-ray crystallographic data, and figures depicting X-ray crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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