

Oxygenation of Simple Zinc Alkyls: Surprising Dependence of Product Distributions on the Alkyl Substituents and the Presence of Water

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Oxygenation reactions of dialkylzinc solutions have been investigated. Me_2Zn reacts with oxygen in the absence of water to give the bis(heterocubane) $[(\text{MeZn})_6\text{Zn}(\text{OMe})_8]$, whereas Et_2Zn and ${}^i\text{Pr}_2\text{Zn}$ afford the mono-(heterocubanes) $[(\text{RZn})_4(\text{OR})_4]$. In the presence of small amounts of water (added during or after the oxygenation) the product types are reversed for Me_2Zn and Et_2Zn giving $[(\text{MeZn})_4(\text{OMe})_4]$ and $[(\text{EtZn})_6\text{Zn}(\text{OEt})_8]$, while being retained for ${}^i\text{Pr}_2\text{Zn}$ (giving $[({}^i\text{PrZn})_4(\text{O}^i\text{Pr})_4]$). Full characterization of all products by NMR spectroscopy, mass spectrometry, and elemental analyses is provided, and crystal structures of $[(\text{EtZn})_6\text{Zn}(\text{OEt})_8]$ and $[({}^i\text{PrZn})_4(\text{O}^i\text{Pr})_4]$ are reported. A rationalization of the different reactivities is attempted on the basis of DFT-calculated energies of some key reactants.

Introduction

Although the discovery of zinc alkyls reaches back to 1849, when Frankland prepared zinc diethyl from metallic zinc and ethyl iodide in the search for the ethyl radical,¹ oxygenation of these simple representatives of organometallic compounds is still not well understood. In his pioneering studies, Frankland contended in 1849 that the controlled oxygenation of Et_2Zn affords $\text{Zn}(\text{OEt})_2$,^{1a} and in 1864 Butlerov² and Lissenko³ independently argued for the formation of a partly oxygenated species $\text{Zn}(\text{Et})\text{OOEt}$. In 1890, Demuth and Meyer postulated the insertion of an O_2 molecule into the $\text{Zn}-\text{C}$ bond of Et_2Zn to result in the formation of the alkylperoxide $\text{Zn}(\text{Et})\text{OOEt}$,⁴ which was later classified as an oxenoid.⁵ Since this time, it is widely believed that oxygenation reactions of homoleptic zinc alkyls are

almost uncontrollably fast. The kinetics of the oxygenation of Me_2Zn and Et_2Zn have been investigated in the gas phase, and the formation of alkylzinc alkoxides was found to take place under these conditions.⁶ However, most of the later studies considered the oxygenation reaction to proceed via oxygen insertion into both $\text{Zn}-\text{C}$ bonds and the formation of compounds formulated as $\text{Zn}(\text{OOR})_2$, $\text{Zn}(\text{OR})\text{OOR}$, and $\text{Zn}(\text{OR})_2$.⁷

Only very recently, Lewiński et al. have demonstrated convincingly that a controlled oxygenation of Me_2Zn and ${}^t\text{Bu}_2\text{Zn}$ in solution affords partially oxygenated species in high yields. In this way first examples of zinc alkylperoxides derived from the reaction of O_2 with monoalkylzinc chelate complexes or with dialkylzinc, e.g., $[\text{EtOOZn}(\text{BDI})_2]$ (BDI = β -diketiminate ligand),⁸ $\{[\text{Zn}^i\text{Bu}(\mu\text{-OO}^i\text{Bu})(\text{py-Me})]_2\}$ could be structurally characterized.⁹

Apart from a fundamental interest in the interaction of zinc alkyls with dioxygen, many practical applications of such oxygenation processes have been found in both organic and materials chemistry.^{10,11} Furthermore, zinc alkoxides have attracted much attention due to their rich structural diversity

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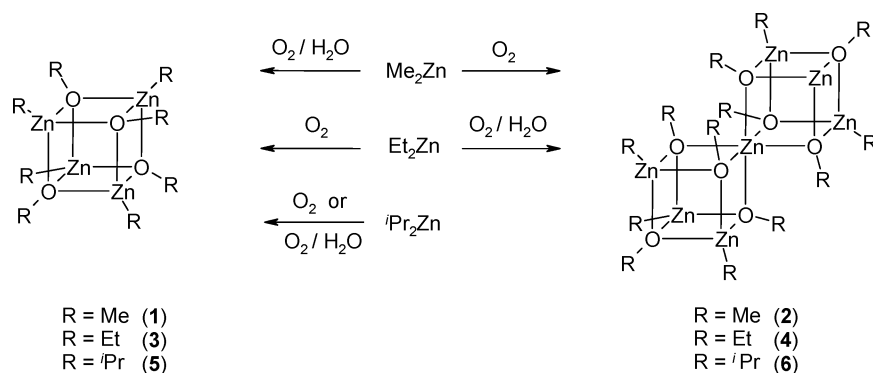
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Scheme 1



and bonding features. Consequently, a large number of zinc alkoxides have been obtained from reactions between alcohols and zinc alkyls and have been structurally characterized.¹² The most common structural motif for such zinc alkoxides is the heterocubane type.

Lewiński and co-workers recently reported the reaction of dimethylzinc with molecular oxygen to result in the direct formation of $[(\text{MeZn})_6\text{Zn}(\text{OMe})_8]$ (**2**),⁸ a bis(heterocubane). This seemed to be in contrast to our serendipitous observation that Et_2Zn was oxygenated to give the mono(heterocubane) $[(\text{EtZn})_4(\text{OEt})_4]$ (**3**). To address the fundamental question whether a further so far neglected factor (most likely moisture) led to these different types of products, we decided to carry out oxygenation reactions of the three simple zinc alkyls Me_2Zn , Et_2Zn , and $\textit{iPr}_2\text{Zn}$ under rigorous anhydrous conditions and in the presence of defined amounts of water.

Results and Discussion

Oxidation of Me_2Zn . First we repeated Lewiński's experiments⁸ and carried out the oxygenation of dimethylzinc with molecular oxygen with various periods of time of oxygen application. In all experiments solely the formation of $[(\text{MeZn})_6\text{Zn}(\text{OMe})_8]$ (**2**) was observed and, thus, confirmed the observations of Lewiński's group.

However, **2** consists formally of 6 equiv of MeZnOMe and 1 equiv of the doubly oxidized $\text{Zn}(\text{OMe})_2$, which points to the question whether this double oxygenation can be avoided if the reaction is carried out with substoichiometric amounts of O_2 . Notwithstanding, these experiments also resulted in the formation of the bis(cubane) **2** but with reduced yields. This shows that the formation of **2** is not a

simple follow-up process of an oxygenation of an intermediate like the tetrameric $[(\text{MeZn})_4(\text{OMe})_4]$, but **2** itself seems to be a thermodynamically favored product.

The next question to be addressed was that of the role of water. By contrast to the above results, the reaction of Me_2Zn and O_2 , followed by addition of a small amount of water, afforded solely the mono(heterocubane) $[(\text{MeZn})_4(\text{OMe})_4]$ (**1**) (Scheme 1). This compound and its structure were already described, prepared by methanolysis of Me_2Zn .¹³ Compound **1** was identified by NMR spectroscopy, mass spectrometry, and a redetermination of its crystal structure (see the Supporting Information).

To investigate whether there is a difference if the water is present during the oxygenation or whether product **2** is transformed into **1** after completed oxygenation, both types of reactions were carried out. We found that it makes no difference if the addition of water is during the application of the O_2 flow or added after the O_2 flow was stopped: in both cases **1** was the obtained product. To check the possibility of a transformation of **2** into **1** by water, we treated isolated and redissolved **2** with H_2O , which again led to the formation of **1**. Depending upon the amount of water added, sometimes both compounds **2** and **1** are observed in the reaction mixtures (i.e., incomplete reaction). During the reactions in the presence of water, some turbidity is observed, which is typical for the formation of zinc oxide or hydroxide.

Oxygenation of Et_2Zn and $\textit{iPr}_2\text{Zn}$. We experienced a solid surprise when carrying out the above experiments analogously with diethylzinc and diisopropylzinc instead of dimethylzinc. For this a solution of R_2Zn ($\text{R} = \text{Et}, \textit{iPr}$) in *n*-hexane (the reaction was also conducted in toluene and Et_2O leading to the same results) at 0°C was treated with an excess of molecular O_2 diluted with N_2 ($\text{O}_2:\text{N}_2 = 1:10$) for approximately 5 min and then stirred for another 1 h at ambient temperature. In clear contrast to the reactions with Me_2Zn resulting in the bis(heterocubane) **2**, these reactions led solely to the mono(heterocubanes) $[(\text{EtZn})_4(\text{OEt})_4]$ (**3**) and $[(\textit{iPrZn})_4(\text{O}^i\text{Pr})_4]$ (**5**), which were isolated in high yields (Scheme 1). Compound **3** is a sticky grayish solid and was characterized by NMR spectroscopy

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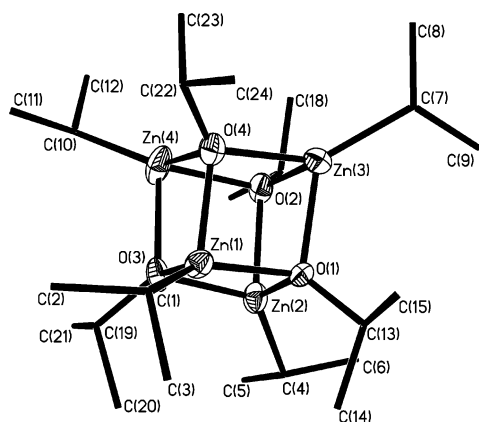


Figure 1. Molecular structure of $[(i\text{PrZn})_4(\text{O}^i\text{Pr})_4]$ (**5**) (50% probability ellipsoids). Carbon atoms are drawn without ellipsoids and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn(1)–C(1) 1.982(5), Zn(1)–O(1) 2.037(3), Zn(1)–O(4) 2.081(8), Zn(1)–O(3) 2.081(8), O(1)–C(13) 1.447(5); O(1)–Zn(1)–O(3) 82.4(3), O(1)–Zn(1)–O(3) 83.5(1), Zn(1)–O(1)–Zn(3) 95.6(3), Zn(4)–O(2)–Zn(3) 96.2(3).

and mass spectrometry. Compound **5** was isolated as platelike crystalline solid and was characterized by NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray structure determination.

Compounds **3** and **5** are soluble in hydrocarbons and ethereal solvents. Both compounds decompose before reaching their melting points lying beyond 300 °C. The ^1H NMR spectra of these compounds show only one set of peaks for each of the distinguishable protons of the alkyl groups at zinc and the alkoxide units. The stoichiometric ratio of alkylzinc units to alkoxide groups is 1:1 according to the integrals. The highest peaks in the mass spectra for **3** and **5** correspond to the masses of the cations $[(\text{RZn})_4(\text{OR})_4]^+$ (R = Et, $i\text{Pr}$) diminished by the mass of one of the respective alkyl groups at the Zn atoms.

Single crystals of **5** (monoclinic system, $P2_1$) were obtained by keeping n -hexane solutions for a few days at -26 °C. In the heterocubane structure of **5** (Figure 1) the shortest Zn–O bond Zn(1)–O(1) is found at 2.037(3) Å and the longest Zn(3)–O(1) at 2.119(9) Å. The narrowest Zn–O–Zn bond angle Zn(1)–O(1)–Zn(3) measures $95.6(3)^\circ$, and the widest O(2)–Zn(3)–O(1) is $81.3(4)^\circ$. The structure is similar to that of **1** (Supporting Information and literature¹³).

To study the effect of water on the formation of aggregates, we conducted the oxygenations under the same conditions, but a small amount of water was added to the reaction mixture during the application of O_2 . Again unexpectedly, in the case of Et_2Zn the isolatable product was no longer $[(\text{EtZn})_4(\text{OEt})_4]$ (**3**) but the bis(heterocubane) $[(\text{EtZn})_6\text{Zn}(\text{OEt})_8]$ (**4**), whereas, for the oxygenation of $i\text{Pr}_2\text{Zn}$, the product was the same with and without the presence of water: $[(i\text{PrZn})_4(\text{O}^i\text{Pr})_4]$ (**5**). Bis(heterocubane) type structures of heteroleptic zinc alkoxides have earlier been prepared by the reaction of zinc dialkyls with alcohols.^{12a,b}

It should be mentioned that in none of the observed zinc dialkyl oxygenation products any traces of peroxides could be detected in standard peroxide tests.

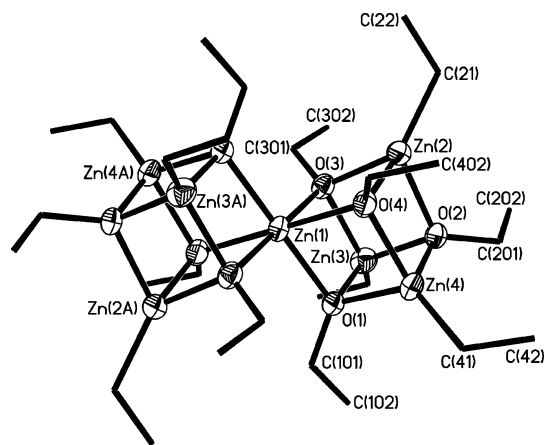
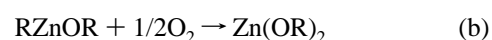
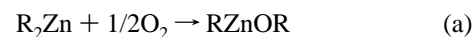


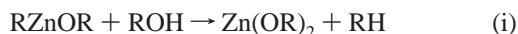
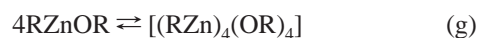
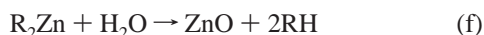
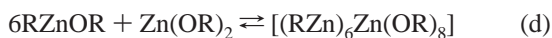
Figure 2. Molecular structure of $[(\text{EtZn})_6\text{Zn}(\text{OEt})_8]$ (**4**) (30% probability ellipsoids). Carbon atoms are drawn without ellipsoids and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn(1)–O(1) 2.127(3), Zn(1)–O(3) 2.118(3), Zn(1)–O(4) 2.105(3), Zn(2)–O(4) 2.056(4), Zn(2)–O(3) 2.061(3), Zn(2)–O(2) 2.066(4), Zn(3)–O(2) 2.067(4), Zn(4)–O(2) 2.053(4), O(1)–C(101) 1.430(7); O(4)–Zn(1)–O(3) 81.0(1), O(4)–Zn(1)–O(1) 82.1(1), O(3)–Zn(1)–O(1) 81.0(1), O(4)–Zn(1)–O(1A) 97.9(2), O(3)–Zn(1)–O(1A) 99.0(2), O(1)–Zn(1)–O(1A) 180.0(1), C(21)–Zn(2)–O(2) 127.2(2), O(4)–Zn(2)–O(3) 83.6(2), Zn(4)–O(2)–Zn(2) 96.3(2). Symmetry transformation to generate equivalent atoms marked with “A”: $-x + 1, -y, -z$.

Compound **4** melts at 217–218 °C. Two types of ethoxy-proton peaks in a ratio of 3:1 are found in the ^1H NMR and ^{13}C NMR spectra of **4**. These NMR data are consistent with time averaged D_3 symmetry and confirm the formation of bis(heterocubane) structures with the cubes sharing one Zn vertex. The compound is less soluble in hydrocarbons although single crystals were obtained from n -hexane solutions upon keeping them a few days at -10 °C. The heaviest ion in the mass spectra for **4** corresponds to the molecular ion minus one complete heterocubane framework (i.e., $\text{Et}_3\text{Zn}_3\text{OEt}_4$).

Compound **4** crystallizes in monoclinic system, space group $P2_1/n$. There are two heterocubane units sharing one vertex (Zn(1)). In this molecule, two types of Zn–O bond lengths are observed (Figure 2). The Zn–O bonds to the central Zn(1) atom are approximately 0.06 Å longer than those to the other Zn atoms. The Zn–O–Zn angles are generally larger ($95.5(1)$ – $97.6(1)^\circ$) than the O–Zn–O angles within one cube.

Possible Reaction Pathways and Energetical Aspects. The following equilibrium reactions can be assumed to play a role during the oxygenation of zinc alkyls, whereby the plethora of possible aggregation types are neglected apart from the tetramerization and bis(heterocubane) formation. In particular there is no information about the aggregation or adduct formation of the R_2Zn and $\text{Zn}(\text{OR})_2$ units. This might play an important role in the energetics involved in the key steps. On the basis of the present information only some statements of speculative nature on the ongoing processes can be made:



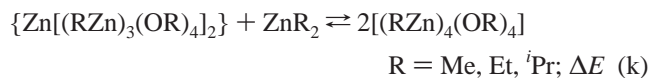


For Me_2Zn the fast oxygenation leads to the preferred product $[(\text{MeZn})_6\text{Zn}(\text{OMe})_8]$ (**2**), which subsequently reacts under the presence of water to give **1**, regardless at which time the water is applied. The following hypothetical and simplified tree of reactions and equilibria (ignoring most of the unknown intermediate aggregation chemistry and peroxide formation) may illustrate the likely processes in solution. Step c seems to lie on the right-hand side in the case of Me_2Zn in the absence of water. Otherwise the equivalent of $\text{Zn}(\text{OMe})_2$ required for the formation of **1** (step d) would not be formed. For Et_2Zn and ${}^i\text{Pr}_2\text{Zn}$ equilibrium c seems to lie preferably on the left-hand side, and therefore, no dealkylated zinc species is formed. Since formation and decomposition of peroxides are expected to happen very fast (at least at room temperature), these reactions were ignored. Consequently, these reactions should not influence the product concentrations.

The mechanisms involving the action of water remain unclear, as none of the isolated products contains OH or Zn–O–Zn functions, which is to be expected to result from the hydrolysis of zinc alkyls or alkoxides (liberation of alkanes or alcohols). However, if water has an influence on equilibrium c, by removing $\text{Zn}(\text{OR})_2$ or R_2Zn by a reaction of type e or f, this could explain the formation of **1** from **2** in the presence of water, if reaction e is quicker than reaction f. The reverse would follow for $\text{R} = \text{Et}$, with (f) being faster than (e), thus explaining the formation of the bis(heterocubane) from the mono(heterocubane) upon addition of water.

The observation that in case of ${}^i\text{Pr}_2\text{Zn}$ the formation of the bis(heterocubane) $[({}^i\text{PrZn})_6\text{Zn}(\text{O}{}^i\text{Pr})_8]$ is not occurring under any of the tested conditions points to steric reasons, as the ${}^i\text{Pr}$ groups in the bis(heterocubane) could come close and therefore disfavor this product.

This argument could be confirmed by investigating the energetic differences between the mono- and bis(heterocubane) species and their dependence on the nature of the alkyl substituents. For this purpose the energy release of reaction k, already investigated in 1968 by van Wazer and Eisenhut¹⁴ with ${}^1\text{H}$ NMR, was calculated with DFT methods (see computational details):



The resulting energy differences ΔE of -42 , -52 , and -242 kJ mol^{-1} for $\text{R} = \text{Me}, \text{Et}$, and ${}^i\text{Pr}$, respectively, show that the mono(heterocubane) forms are favored in all three cases (for $\text{R} = \text{Me}$, the energy release of this reaction was also calculated by Steudel and Steudel with DFT methods (B3LYP/6-31+G*/B3LYP/6-31G*) resulting in -39 kJ mol^{-1}).¹⁵

The reaction energy for methyl- and ethyl-substituted species is only moderate and of comparable magnitude for both cases. This shows that this and comparable equilibria may be easily influenced by other parameters and thus the conversion between mono- and bis(heterocubanes) as described above for $\text{R} = \text{Me}$ and Et is not unexpected in terms of energetics. In contrast, the formation of the bis(heterocubane) in the isopropyl case is consuming a comparatively large amount of energy and its products are therefore expected to be inaccessible. This is in agreement with Steudel's consideration of shortest interligand distances, which led to the same conclusion that the bis(heterocubane) with $\text{R} = {}^i\text{Pr}$ will not be stable.¹⁵ Drastically elongated Zn–O distances in the bis(heterocubane) with $\text{R} = {}^i\text{Pr}$ (average Zn–O: 2.273 Å) as compared to the methyl (average Zn–O: 2.148 Å) and ethyl (average Zn–O: 2.162 Å) analogues are underlining the inherent instability of this species.

Conclusion. The different behaviors of the three zinc alkyls Me_2Zn , Et_2Zn , and ${}^i\text{Pr}_2\text{Zn}$ under oxygenation conditions with or without the presence of water are summarized in Table 1. In the case of ${}^i\text{Pr}_2\text{Zn}$ as well in the presence as in the absence of water, the oxygenated product is the mono-(cubane) type compound. In the case of Et_2Zn and Me_2Zn nonuniformly either mono- or bis(cubanes) depending on the presence of water are formed.

In summary, the described observations are an instructive textbook-suitable example of the sensitivity of product distributions in simple organometallic reactions. Reproducibility of results is strongly dependent on reaction conditions such as the rigorous exclusion of moist and air.

Experimental Section

General Methods. All manipulations of air-sensitive compounds were carried out under a purified nitrogen atmosphere with standard Schlenk and high-vacuum techniques using double manifolds or in a glovebox under argon. Solvents were purified and dried by standard methods immediately prior to use. Diethylzinc was purchased from Crompton Inc. Dimethylzinc and diisopropylzinc were prepared by slightly modified procedures according to the literature.¹⁶ ${}^1\text{H}$ and ${}^{13}\text{C}$ assignments spectra were recorded on Bruker AC 200 and Varian Inova-300 spectrometers in dried solvents. All spectra were referenced internally to residual protiosolvent (${}^1\text{H}$) or solvent (${}^{13}\text{C}$) resonances. Chemical shifts are quoted in ppm and coupling constants in Hz.

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Table 1. Summary of the Products Isolated from Oxygenation Reactions of Dialkylzinc Solutions with O₂ in Presence or Absence of H₂O

dialkylzinc	O ₂ reactn	O ₂ + H ₂ O reactn
Me ₂ Zn	bis(cubane), [(MeZn) ₆ Zn(OMe) ₈]	mono(cubane), [(MeZn) ₄ (OMe) ₄]
Et ₂ Zn	mono(cubane), [(EtZn) ₄ (OEt) ₄]	bis(cubane), [(EtZn) ₆ Zn(OEt) ₈]
ⁱ Pr ₂ Zn	mono(cubane), [(ⁱ PrZn) ₄ (O ⁱ Pr) ₄]	mono(cubane), [(ⁱ PrZn) ₄ (O ⁱ Pr) ₄]

General Procedure for Preparation of 2, 3, and 5. All procedures with air- and moisture-sensitive compounds were carried out by using a Schlenk line operated under nitrogen. R₂Zn (R = Me, Et, ⁱPr) (4.00 mL of a 2.0 M solution in *n*-hexane; 8.0 mmol) was added via syringe to 20 mL of *n*-hexane in a three-necked round-bottom flask (RB). The reaction was also carried out in toluene and diethyl ether leading to the same results. Oxygen mixed with nitrogen (N₂:O₂ = 10:1, measured by counting bubbles) was passed through the RB with a mild speed for 5 min at 0 °C while stirring the reaction mixture. After stoppage of the O₂ flow, the mixture was stirred for another 1 h and allowed to warm to ambient temperature. The solvents were removed under reduced pressure; the resulting residue was dissolved in *n*-hexane and filtered. The clear, colorless filtrate was stored at -26 °C to afford colorless crystals of **5**. Compound **3** was obtained as a sticky solid.

Data for 2: yield 65% (1.03 g, 1.29 mmol); mp >300 °C (dec); ¹H NMR (200.1 MHz, C₆D₆) δ = -0.41 (s, 18 H; ZnCH₃), 3.37 (s, 18 H; OCH₃), 3.40 ppm (s, 6H; OCH₃); ¹³C{¹H} NMR (50.3 MHz, C₆D₆) δ = -20.47 (ZnCH₃), 54.29, 55.02 ppm (OCH₃); IR (Nujol, ν, cm⁻¹) 2953 (vs), 1375 (s), 1093 (br), 1022 (vs), 802 (s), 546 (w). Anal. Calcd for C₁₄H₄₂O₈Zn₇: C, 21.12; H, 5.32. Found: C, 20.92; H, 5.15. EI-MS [*m/z* (%): 685 (100) [M⁺ - CH₃-ZnOCH₃].

Data for 3: yield 74% (660 mg, 1.48 mmol); mp >300 °C (dec); ¹H NMR (200.1 MHz, C₆D₆) δ = 0.56 (q, *J* = 8.2 Hz, 8 H; ZnCH₂), 1.16 (t, *J* = 7.0 Hz, 12 H; OCH₂CH₃), 1.50 (t, *J* = 8.1 Hz, 12 H; ZnCH₂CH₃), 3.69 ppm (q, *J* = 6.9 Hz, 8 H; OCH₂CH₃); ¹³C{¹H} NMR (50.3 MHz, C₆D₆) δ = -1.70 (ZnCH₂), 12.75 (ZnCH₂CH₃), 20.79 (OCH₂CH₃), 63.15 ppm (OCH₂CH₃); IR (Nujol, ν, cm⁻¹) 2952 (s), 1132 (w), 1036 (br), 962 (w), 490 (br); EI-MS [*m/z* (%) 529 (55) [M⁺ - C₂H₅].

Data for 5: yield 70% (940 mg, 1.40 mmol); mp >300 °C (dec); ¹H NMR (200.1 MHz, C₆D₆) δ = 0.97 (sep, *J* = 7.6 Hz, 4 H; ZnCH), 1.16 (d, *J* = 5.9 Hz, 24 H; OCH(CH₃)₂), 1.54 (d, *J* = 7.6 Hz, 24 H; ZnCH(CH₃)₂), 4.07 (sep, *J* = 5.9 Hz, 4 H; OCH(CH₃)₂); ¹³C{¹H} NMR (50.3 MHz, C₆D₆) δ = 13.62 (ZnCH), 24.02 (ZnCH-(CH₃)₂), 27.52 (OCH(CH₃)₂), 68.69 ppm (OCH(CH₃)₂); IR (Nujol, ν, cm⁻¹) 2922 (vs), 2723 (s), 1340 (w), 1302 (w), 1151 (w), 1024 (w), 800 (w), 721 (s); EI-MS [*m/z* (%) 685 (51) [M⁺ - C₃H₇].

General Procedures for the Preparation of 1 and 4. R₂Zn (R = Me, Et) (4.00 mL of a 2.0 M solution in *n*-hexane; 8.0 mmol) was added to 20 mL of *n*-hexane in a RB. Oxygen mixed with nitrogen (N₂:O₂ = 10:1) was passed through the RB with a mild speed for 1 min at 0 °C followed by the addition of water (0.33 g, 1.82 mmol) and continuing the flow of oxygen for another 4 min. The mixture was stirred for another 1 h and allowed to warm to ambient temperature. The solvents were removed under reduced pressure; the resulting residue was dissolved in *n*-hexane and filtered. The clear, colorless filtrate was stored at -10 °C to afford colorless crystals of **1** and **4** (crystallization also take place at -26 °C with same cell data but with worse crystal quality).

Data for 1: yield 35% (496 mg, 0.70 mmol); mp >300 °C (dec); ¹H NMR (200.1 MHz, CDCl₃) δ = -0.74 (s, 6 H; ZnCH₃), 3.63

ppm (s, 6 H; OCH₃); ¹³C{¹H} NMR (50.3 MHz, CDCl₃) δ = -21.21 (ZnCH₃), 54.34 ppm (OCH₃); IR (Nujol, ν, cm⁻¹) 2953 (vs), 2722 (s), 1458 (s), 1306 (w), 1259 (w), 1020 (br). Anal. Calcd for C₈H₂₄O₄Zn₄: C, 21.55; H, 5.42. Found: C, 21.43; H, 5.41. EI-MS [*m/z* (%): 445 (3) [M⁺], 431(8) [M⁺ - CH₃].

Data for 4: yield 49% (0.950 g, 0.98 mmol); mp 217–218 °C; ¹H NMR (300.1 MHz, CDCl₃) δ = 0.26 (q, *J* = 8.2 Hz, 12 H; ZnCH₂), 1.18 (t, *J* = 8.2 Hz, 18 H; ZnCH₂CH₃), 1.27 (t, *J* = 6.9 Hz, 6 H; OCH₂CH₃), 1.31 (t, *J* = 6.9 Hz, 18 H; OCH₂CH₃), 3.81 (q, *J* = 6.9 Hz, 12 H; OCH₂CH₃), 3.82 ppm (q, *J* = 6.9 Hz, 4 H; OCH₂CH₃); ¹³C{¹H} NMR (75.5 MHz, CDCl₃) δ = -0.45 (ZnCH₂), 12.56 (ZnCH₂CH₃), 20.69, 21.12 (OCH₂CH₃), 62.16, 62.90 ppm (OCH₂CH₃); EI-MS [*m/z* (%) 529 (100) [M⁺ - Zn₃O₄-(C₂H₅)₇]; IR (KBr film, ν, cm⁻¹) 2964 (s), 2861 (s), 1583 (br), 1445 (w), 1384 (s), 1095 (s), 1048 (vs), 883 (vs), 614 (s). Anal. Calcd for C₂₈H₇₀O₈Zn₇: C, 33.88; H, 7.11. Found: C, 33.29; H, 6.60.

X-ray Structural Analyses. Single crystals of **4** and **5** were grown from the appropriate solution.

Crystal data for 4: C₂₈H₇₀O₈Zn₇, *M* = 992.43; monoclinic, space group *P*2₁/*n*; *a* = 11.362(1), *b* = 15.621(1), *c* = 11.831(1) Å; β = 95.35(1)°; *V* = 2090.7(3) Å³; *D*_c (*Z* = 2) = 1.576 g cm⁻³; 12 702 reflections collected on a Nonius Kappa CCD four circle diffractometer [*ω*-scan, 2θ_{max} = 53°, Mo Kα radiation, λ = 0.710 73 Å, *T* = 198(2) K] merged to 4244 unique (*R*_{int} = 0.060) refining to *R*₁ = 0.048 for 4244 data [*F*_o > 4σ(*F*_o)] and *wR*₂ = 0.115 for all 4244 data. All thermal displacement parameters were refined anisotropically for non-H atoms and isotropically for H atoms.

Crystal data for 5: C₂₄H₅₆O₄Zn₄, *M* = 670.17; monoclinic, space group *P*2₁; *a* = 9.526(2), *b* = 14.747(3), *c* = 11.963(2) Å; β = 107.7(3)°; *V* = 1601.0(6) Å³; *D*_c = 1.390 g cm⁻³ (*Z* = 2); 18 588 reflections collected on a Bruker AXS CCD diffractometer [*ω*-scan, 2θ_{max} = 60°, Mo Kα radiation, λ = 0.710 73 Å, *T* = 153(2) K] merged to 9273 unique (*R*_{int} = 0.055) refining to *R*₁ = 0.055 for 5552 data [*F*_o > 4σ(*F*_o)] and *wR*₂ = 0.115 for all 9273 data. The thermal displacement parameters for non-H atoms were refined anisotropically except those of C17, C18, C21, and C23, which were refined isotropically due to instabilities otherwise occurring in the refinement (this is due to the limited crystal quality).

The refinements were carried out using SHELXTL 6.10^{17a} and SHELXL-93.^{17b}

The crystal data and refined parameters have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC-621750 (**4**) and CCDC-621748 (**5**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K (fax (+44)-1223-336-033 or deposit@ccdc.cam.ac.uk)).

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Supporting Information Available: Information on the crystal structure redetermination of compound **2**, NMR spectra of the products, computational details, and coordinates of the quantum-chemically calculated structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(17) (a) SHELXTL 6.10; Bruker-AXS X-Ray Instrumentation Inc.: Madison, WI, 2000. (b) Sheldrick, G. M. SHELXL-93, Program for Crystal Structure Refinement; Universität Göttingen: Göttingen, Germany, 1993.