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# Synthesis, Characterization, and Reactivity of Multinuclear Zinc(II) Alkyl Derivatives of Linked Phenoxides

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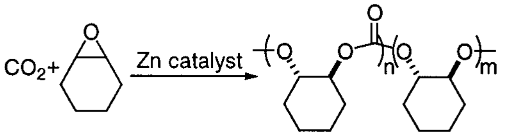
Alkyl zinc derivatives of tris(3,5-dialkyl-2-hydroxyphenyl)methanes (alkyl = *tert*-butyl **1a**, methyl **1b**, *tert*-pentyl **1c**) have been prepared by reaction with dimethyl or diethylzinc, and characterized. Whereas dimethylzinc with **1a** or diethylzinc with **1b** give $S_6$ symmetric, hexanuclear aggregates with the general formula $\mathbf{1}_2(\mathrm{ZnR})_6$ (R = Me **2a**, Et **2b**), when **1a** reacts with diethylzinc, solvent dependent reactions take place. If dichloromethane is used for the reaction solvent, a dimeric, $C_2$ symmetric, tetranuclear product with the formula $\mathbf{1a}_2\mathrm{Zn}_2(\mathrm{ZnEt})_2$ (**3**) is isolated while in diethyl ether, a $C_2$ symmetric, pentanuclear aggregate $\mathbf{1a}_2\mathrm{Zn}(\mathrm{ZnEt})_4$ (**4**) forms, and in tetrahydrofuran a $C_3$ symmetric trinuclear compound $\mathbf{1a}[\mathrm{ZnEt(THF)}]_3$ (**5a**) is produced. Each example is represented by a single-crystal X-ray structure determination. Preliminary studies regarding their activity toward the copolymerization of cyclohexene oxide and carbon dioxide are also reported.

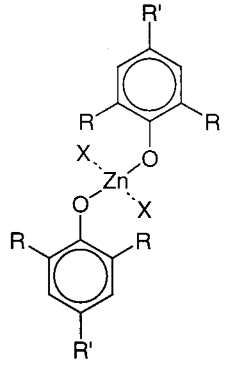
## Introduction

The utility of organozinc reagents for a wide range of organic transformations involving carbon−carbon bond forming reactions is well-known.[1] More recently, zinc(II) alkoxide or phenoxide derivatives have garnered interest for their ability to catalyze various reactions. Examples include the enantioselective alkylation of aldehydes,[2] asymmetric epoxidation of α,*β*-unsaturated ketones,[3] the decarboxylation of carboxylic acids,[4] phosphate diester transesterification,[5] and the ring-opening polymerization of *rac*-lactide.[6] Moreover, various zinc reagents, including aryl- and alkoxides, have thus far proved to be valuable catalysts for the copolymerization of carbon dioxide with epoxides (Scheme 1); this reaction is particularly noteworthy since it produces a useful polymer from a material which is generally viewed as a hazardous industrial waste gas, $CO_2$.

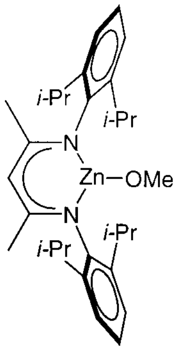
**Scheme 1**



A variety of zinc reagents are capable promoting the copolymerization process, and the simplest of these reagents, a catalyst derived from $Et_2Zn$ and $H_2O$, was first reported in 1969.[7] Since then, a number of alternate systems have been published, including soluble reagents derived from zinc aryl- and alkoxides. Coates has recently reported a highly active *β*-diimine based zinc methoxide compound[8] and Darensbourg has developed systems derived from bulky phenoxides,[9] both showing considerable activity for the copolymerization of cyclohexene oxide and $CO_2$. Furthermore, it was demonstrated by addition of various phosphine ligands that the steric bulk of the active zinc centers is of considerable importance for successful copolymerization with high incorporation of $CO_2$.[10]



Darensbourg Catalyst



Coates Catalyst

We have been systematically investigating the chemistry of the $C_3$ symmetric linked phenols, tris(3,5-dialkyl-2-hydroxyphenyl)methanes (**1**),[11] and have found these compounds to

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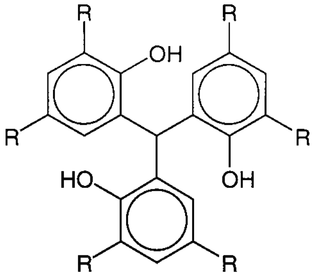
10.1021/ic000682r CCC: $20.00

exhibit quite diverse chemistry.[12] When alkali metal atoms are incorporated into the ligand framework, Lewis acidic aggregates can be prepared and often these clusters are capable of recognizing substrates possessing suitable size and shape to fit into pockets created by the aryl rings.[13] While these materials were interesting, they proved to be poor Lewis acid catalysts, so we turned our attention to the incorporation of other Lewis acidic metals. Since the metal centers in these aggregates are typically in a sterically congested environment and often have open coordination sites accessible to properly sized substrates, we reasoned zinc complexes of **1** may have interesting catalytic properties in reactions with small molecules such as $CO_2$, and an investigation into the synthesis of zinc clusters was undertaken. Noting that calix[4]arene reacts with diethylzinc to form a cluster complex featuring four zinc atoms ligated by two calix[4]arene units,[14] the chemistry of **1** with zinc alkyls was studied. The results of this work, together with data concerning the catalytic activity toward the copolymerization of carbon dioxide with cyclohexene oxide, are reported herein.



**1a** R = *tert*-butyl
**1b** R = methyl
**1c** R = *tert*-pentyl (*tert*-amyl)

## Experimental Section

All manipulations were carried out in a VAC Nexus drybox. Solvents were dried and distilled prior to use. Dimethylzinc (2 M in toluene) and diethylzinc (1 M in hexanes) were purchased from Aldrich and used as received. NMR spectra were recorded on a Varian VXR 300 MHz spectrometer at 299.95 and 75.43 MHz for the proton and carbon channels, respectively, using $C_6D_6$ solvent, unless otherwise stated. Elemental analyses were performed at Atlantic Microlab Inc., Norcross, Georgia. The tris(3,5-dialkyl-2-hydroxyphenyl)methane precursors, **1a**−**1c**, were prepared following reported procedures.[11] All reactions were carried out without agitation to allow the formation of crystalline materials, facilitating product isolation. If the mixtures were stirred, identical products were obtained almost immediately, but they tended to form as exceedingly fine, white powders, which were difficult to manipulate.

**Synthesis of 2a.** Dimethylzinc (0.6 mL, 2 M in toluene, 1.20 mmol) was added to a benzene solution (10 mL) of tris(3,5-di-*tert*-butyl-2-hydroxyphenyl)methane (0.250 g, 0.397 mmol), and the resulting mixture was allowed to stand undisturbed. Over several hours large colorless crystals formed, which were thoroughly washed with ether to give $2a{\cdot}3C_6H_6$ (0.333 g, 85%). Found: C, 67.36; H, 7.94%. Required for $C_{92}H_{140}O_6Zn_6{\cdot}3C_6H_6$: C, 67.11; H, 8.09%. $^1H$ NMR ($d_8$-toluene) $\delta$ 7.77 (s, 2H, C*H*), 7.68 (d, 6H, $^4J_{H,H} = 2.4$ Hz, Ar−*H*), 5.94 (d, 6H, $^4J_{H,H} = 2.4$ Hz, Ar−*H*), 1.51 (s, 54H, *t*Bu), 1.20 (s, 54H, *t*Bu), −0.95 (s, 18H, $ZnCH_3$); $^{13}C$ NMR ($d_8$-toluene) $\delta$ 157.3 ($C_{Ar}$−OZn), 144.2, 143.4, 131.6, 131.2, 130.1, ($C_{Ar}$), 37.3, 34.8 ($C(CH_3)_3$), 33.8, 31.9 ($C(CH_3)_3$), −8.2 ($ZnCH_3$), the *C*H resonance was not resolved.

**Synthesis of 2b.** Diethylzinc (4 mL, 1 M in hexanes, 4.00 mmol) was added to an ether solution (50 mL) of tris(3,5-dimethyl-2-hydroxyphenyl)methane (0.501 g, 1.33 mmol), and the resulting mixture was allowed to stand undisturbed. Over several hours colorless crystals formed, which were thoroughly washed with ether to give **2b** (0.856 g, 98%). The compound showed only very low solubility in organic solvents, precluding acquisition of $^{13}C$ NMR data. Found: C, 57.04; H, 6.35%. Required for $C_{62}H_{80}O_6Zn_6$: C, 56.69; H, 6.14%. $^1H$ NMR ($d_8$-toluene) $\delta$ 7.59 (s, 2H, C*H*), 6.84 (d, 6H, $^4J_{H,H} = 2.4$ Hz, Ar−*H*), 6.34 (d, 6H, $^4J_{H,H} = 2.4$ Hz, Ar−*H*), 2.29 (s, 18H, Ar−$CH_3$), 2.04 (s, 18H, Ar−$CH_3$), 1.09 (q, 18H, $^3J_{H,H} = 7.95$ Hz, $ZnCH_2CH_3$), 0.86 (m, 12H, $ZnCH_2CH_3$).

**Synthesis of 3.** Diethylzinc (1.1 mL, 1.0 M in toluene, 1.1 mmol) was added to a dichloromethane solution (10 mL) of tris(3,5-di-*tert*-butyl-2-hydroxyphenyl)methane (0.232 g, 0.369 mmol), and the resulting mixture was allowed to react undisturbed. Over several hours colorless crystals formed, which were thoroughly washed with dichloromethane and briefly dried under vacuum to give **3** (0.320 g, 97%) as a white powder. The material was found to be sensitive, even in the solid state, and decomposed slowly over the course of several weeks, evidenced by pale blue coloration. The compound showed only very low solubility in organic solvents, precluding acquisition of $^{13}C$ NMR data. Although the X-ray data identified 5 solvate molecules in the crystal lattice, integration of the $^1H$ NMR spectrum indicated only $2^1/_2$ remained after extensive drying of the solid material. Found: C, 62.25; H, 7.77%. Required for $C_{90}H_{132}O_6Zn_4{\cdot}2^1/_2CH_2Cl_2$: C, 62.28; H, 7.74%. $^1H$ NMR. $\delta$ 8.22 (d, 2H, $^4J_{H,H} = 2.4$ Hz, Ar−*H*), 8.06 (d, 2H, $^4J_{H,H} = 2.4$ Hz, Ar−*H*), 7.88 (d, 2H, $^4J_{H,H} = 2.4$ Hz, Ar−*H*), 7.63 (d, 2H, $^4J_{H,H} = 2.4$ Hz, Ar−*H*), 7.50 (d, 2H, $^4J_{H,H} = 2.4$ Hz, Ar−*H*), 7.29 (s, 2H, C*H*), 7.26 (d, 2H, $^4J_{H,H} = 2.4$ Hz, Ar−*H*), 1.71 (s, 18H, *t*Bu), 1.65 (s, 18H, *t*Bu), 1.51 (s, 18H, *t*Bu), 1.37 (s, 18H, *t*Bu), 1.29 (s, 18H, *t*Bu), 1.10 (t, 6H, $^3J_{H,H} = 8.0$ Hz, $ZnCH_2CH_3$), 0.17 (q, 4H, $^3J_{H,H} = 7.8$ Hz, $ZnCH_2CH_3$).

**Synthesis of 4.** Diethylzinc (1.2 mL, 1.0 M in toluene, 1.2 mmol) was added to an ether solution (10 mL) of tris(3,5-di-*tert*-butyl-2-hydroxyphenyl)methane (0.299 g, 0.475 mmol), and the resulting mixture was allowed to react undisturbed. Over several hours colorless crystals formed, which were thoroughly washed with ether to give $\mathbf{4}{\cdot}1^1/_3Et_2O$ (0.295 g, 73%). Like complex **3**, **4** was found to slowly decompose on prolonged storage at room temperature. Found: C, 66.29; H, 8.79%. Required for $C_{94}H_{142}O_6Zn_5{\cdot}1^1/_3Et_2O$: C, 66.51; H, 8.73%. $^1H$ NMR $\delta$ 8.04 (d, 2H, $^4J_{H,H} = 2.4$ Hz, Ar−*H*), 7.99 (d, 2H, $^4J_{H,H} = 2.4$ Hz, Ar−*H*), 7.92 (s, 2H, C*H*), 7.83 (d, 2H, $^4J_{H,H} = 2.4$ Hz, Ar−*H*), 7.57 (d, 2H, $^4J_{H,H} = 2.4$ Hz, Ar−*H*), 7.45 (d, 2H, $^4J_{H,H} = 2.4$ Hz, Ar−*H*), 7.40 (d, 2H, $^4J_{H,H} = 2.4$ Hz, Ar−*H*), 1.69 (s, 18H, *t*Bu), 1.623 (s, 18H, *t*Bu), 1.617 (s, 18H, *t*Bu), 1.31 (s, 18H, *t*Bu), 1.15 (s, 18H, *t*Bu), 1.08 (s, 18H, *t*Bu), 0.89 (m, 12H, $ZnCH_2CH_3$), 0.21−0.02 (m, 8H, $ZnCH_2CH_3$); $^{13}C$ NMR $\delta$ 159.6, 157.0, 154.2 ($C_{Ar}$-OZn), 145.6, 143.5, 143.3, 139.9, 139.8, 139.1, 137.9, 135.1, 131.1, 126.5, 126.1, 124.2, 123.2, 123.1 ($C_{Ar}$), 36.6 (*C*H), 36.0, 35.9, 35.7, 34.9, 34.8, 34.6 ($C(CH_3)_3$), 32.3, 31.90, 31.86, 31.2, 31.0 ($C(CH_3)_3$), 12.3, 11.0 ($ZnCH_2CH_3$), 5.2, 2.6 ($ZnCH_2CH_3$).

**Synthesis of 5a.** Diethylzinc (2.5 mL, 1.0 M in toluene, 2.5 mmol) was added to a vial containing THF (2 mL). In a separate vessel, tris(3,5-di-*tert*-butyl-2-hydroxyphenyl)methane (0.508 g, 0.807 mmol) was dissolved in THF (5 mL). Without stirring, the solutions were combined, and the resulting mixture was allowed to stand undisturbed. Over several hours colorless crystals formed, which were washed with THF and dried under vacuum to give **5a** (0.756 g, 78%). Found: C, 65.09; H, 9.10%. Required for $C_{61}H_{100}O_6Zn_3(THF)_3{\cdot}THF$: C, 65.18; H, 9.09%; $^1H$ NMR ($d_8$-toluene) $\delta$ 9.44 (s, 1H, C*H*), 8.21 (d, 3H, $^4J_{H,H} = 2.4$ Hz, Ar−*H*), 7.18 (d, 3H, $^4J_{H,H} = 2.4$ Hz, Ar−*H*), 3.10 (broad, 12H, THF), 1.78 (t, 9H, $^3J_{H,H} = 8.1$ Hz, $ZnCH_2CH_3$), 1.54 (s, 27H, *t*Bu), 1.41 (s, 27H, *t*Bu), 1.18 (broad, 12H, THF), 1.00 (q, 6H, $^3J_{H,H} = 8.10$ Hz, $ZnCH_2CH_3$); $^{13}C$ NMR ($d_8$-toluene) $\delta$ 159.2 ($C_{Ar}$-OZn), 141.7, 138.8, 138.1, 123.9, 121.1 ($C_{Ar}$), 69.2 (THF), 36.3, 34.9 ($C(CH_3)_3$), 32.8 (*C*H), 32.4, 31.5 ($C(CH_3)_3$), 25.8 (THF), 14.5 ($ZnCH_2CH_3$), 1.6 ($ZnCH_2CH_3$).

**Synthesis of 5.** In a fashion analogous to that described for **5a**, diethylzinc (2.1 mL, 1.0 M in toluene, 2.1 mmol) in THF (1 mL) was reacted with tris(3,5-di-*tert*-pentyl-2-hydroxyphenyl)methane (0.501 g, 0.703 mmol) in THF (5 mL), and the resulting solution allowed to

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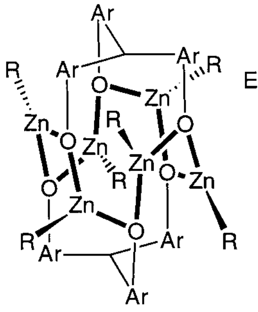
**Table 1.** X-ray Data[a] for the Crystal Structures of the Tris(3,5-dialkyl-2-hydroxyphenyl)methane Alkyl Zinc Derivatives **2a**, **2b**, **3**, **4**, **5a**

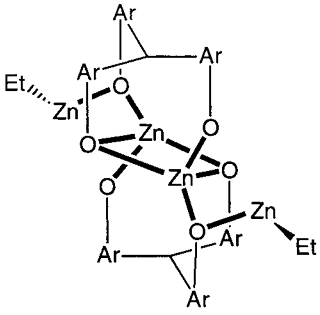
| | **2a**·3C$_6$H$_6$ | **2b** | **3**·5CH$_2$Cl$_2$ | **4**·1$^1/_3$Et$_2$O | **5a**·THF |
|---|---|---|---|---|---|
| empirical formula | $C_{110}H_{158}O_6Zn_6$ | $C_{62}H_{80}O_6Zn_6$ | $C_{95}H_{142}O_6Cl_{10}Zn_4$ | $C_{99.33}H_{155.33}O_{7.33}Zn_5$ | $C_{65}H_{108}O_7Zn_3$ |
| fw | 1968.58 | 1313.48 | 1996.07 | 1793.76 | 1197.62 |
| space group | $Pa\bar{3}$ | $R\bar{3}$ | $C2/c$ | $Pbcn$ | $Pa\bar{3}$ |
| $a$ (Å) | 21.8012(9) | 20.559(2) | 25.163(3) | 24.167(1) | 23.6040(6) |
| $b$ (Å) | | | 12.717(2) | 25.941(1) | |
| $c$ (Å) | | 11.878(1) | 32.909(4) | 32.738(2) | |
| $\beta$ (deg) | | | 106.23(1) | | |
| $V_c$ (Å$^3$) | 10361.9(7) | 4347.9(6) | 10111(2) | 20523(2) | 13150.9(6) |
| $D_c$ (g cm$^{-3}$) | 1.262 | 1.505 | 1.311 | 1.161 | 1.210 |
| Z | 4 | 3 | 4 | 8 | 8 |
| $\mu$(Mo K$\alpha$) (mm$^{-1}$) | 1.417 | 2.492 | 1.250 | 1.200 | 1.133 |
| R1[b] | 0.0288 | 0.0233 | 0.0554 | 0.0395 | 0.0462 |
| wR2[c](all data) | 0.0775 | 0.0652 | 0.1516 | 0.117 | 0.1091 |

[a] Obtained with monochromatic Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å). [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (XP)^2 + YP]$ where $P = (F_o^2 + 2F_c^2)/3\}$.

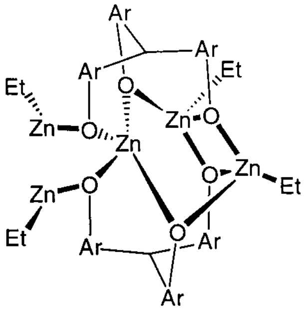
react undisturbed. A clump of colorless crystals formed over several hours, which were washed with pentane and dried to give **5c** (0.548 g, 65%). Found: C, 65.70; H, 9.35%. Required for $C_{67}H_{112}O_6Zn_3(THF)_3$: C, 66.52; H, 9.33%. $^1$H NMR $\delta$ 9.47 (s, 1H, C*H*), 8.12 (d, 3H, $^4J_{H,H}$ = 2.4 Hz, Ar−*H*), 7.09 (d, 3H, $^4J_{H,H}$ = 2.4 Hz, Ar−*H*), 3.14 (broad, 12H, THF), 1.91 (q, 6H, $^3J_{H,H}$ = 7.5 Hz, CC*H*$_2$CH$_3$), 1.85 (t, 9H, $^3J_{H,H}$ = 8.0 Hz, ZnCH$_2$C*H*$_3$), 1.76 (q, 6H, $^3J_{H,H}$ = 7.20 Hz, CC*H*$_2$CH$_3$), 1.53 (s, 18H, C(C*H*$_3$)$_2$), 1.40 (s, 18H, C(C*H*$_3$)$_2$), 1.18 (broad, 12H, THF), 1.07 (q, 6H, $^3J_{H,H}$ = 8.1 Hz, ZnC*H*$_2$CH$_3$), 0.95 (t, 9H, $^3J_{H,H}$ = 7.5 Hz, CCH$_2$C*H*$_3$), 0.69 (t, 9H, $^3J_{H,H}$ = 7.50 Hz, CCH$_2$C*H*$_3$); $^{13}$C NMR $\delta$ 158.5 (*C*$_{Ar}$-OZn), 138.6, 138.0, 137.8, 124.1, 122.6 (C$_{Ar}$), 68.8 (THF), 38.9, 37.7 (*C*CH$_2$CH$_3$), 37.4, 34.7 (*C*(CH$_3$)$_2$), 29.4, 28.0 (C(*C*H$_3$)$_2$), 25.4 (THF), 13.9 (ZnCH$_2$*C*H$_3$), 9.9, 9.3 (CCH$_2$CH$_3$), 1.3 (Zn*C*H$_2$CH$_3$), *C*H not resolved.

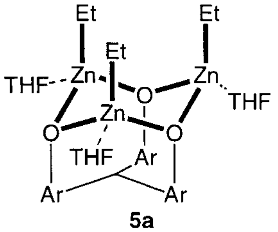


**2a**; R = Me
Ar = 3,5-di-*t*-butylphenyl
**2b**; R = Et
Ar = 3,5-dimethylphenyl



**3**
Ar = 3,5-di-*t*-butylphenyl





**5a**
Ar = 3,5-di-*t*-butylphenyl

**4**
Ar = 3,5-di-*t*-butylphenyl

**5c**
Ar = 3,5-di-*t*-pentylphenyl

**Copolymerizations of Epoxides and Carbon Dioxide.** In a drybox, the appropriate epoxide (30 mL) was poured into a high-pressure bomb and a sample of the zinc compound, typically 0.125 g, which had previously been sealed under vacuum in a glass ampule, was added. The bomb was sealed, removed from the drybox, and charged with 600 psi of carbon dioxide. Stirring by means of an internal propeller was initiated, shattering the ampule. The bomb was then warmed to 100 °C and the mixture allowed to react for 18 h. After allowing the apparatus to cool, the excess CO$_2$ was vented off, the bomb opened, and the mixture poured into a flask. Methanol was added, immediately precipitating any polymer formed. The polymer was subsequently characterized by NMR spectroscopy as described by Darensbourg.[9]

**X-ray Crystallography.** Unit cell dimensions and intensity data for all the structures were obtained on a Siemens CCD SMART diffractometer at −100 °C. The data collections nominally covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different $\phi$ angle for the crystal and each exposure covered 0.3° in $\omega$. The crystal to detector distance was 5.0 cm. The data sets were corrected empirically for absorption using SADABS.[15] All the structures were solved using the Bruker SHELXTL software package for the PC, using the direct methods option of SHELXS. The space groups for all of the structures were determined from an examination of the systematic absences in the data, and the successful solution and refinement of the structures confirmed these assignments. All hydrogen atoms were assigned idealized locations and were given a thermal parameter equivalent to 1.2 or 1.5 times the thermal parameter of the carbon atom to which it was attached. For the methyl groups, where the location of the hydrogen atoms was uncertain, the AFIX 137 card was used to allow the hydrogen atoms to rotate to the maximum area of residual density, while fixing their geometry.

For the structure **3**·5CH$_2$Cl$_2$, which resides on an inversion center, three dichloromethane solvates were located in the residual electron density in the asymmetric unit. One was disordered over two positions, with occupancy factors of 0.6 and 0.4, while a second was severely disordered over an inversion center. This latter solvate was subsequently removed ("squeezed") from the data by use of the Platon for Windows software program,[16] while the remaining, ordered CH$_2$Cl$_2$ was modeled with full occupancy. Structural and refinement data for the complexes are presented in Table 1. All ORTEP diagrams were drawn using the ORTEP-3 for Windows package,[17] and the space-filling representations were rendered using MolPOV 2 for Windows.[18]

## Results and Discussion

When an excess of dimethylzinc is reacted with tris(3,5-di-*tert*-butyl-2-hydroxyphenyl)methane **1a** dissolved in benzene and allowed to stand undisturbed, large colorless blocks form over several hours. The product is virtually insoluble in most common organic solvents, such as benzene, ether, and dichloromethane, but shows limited solubility in THF and, surprisingly, toluene. Proton NMR spectra could be obtained in the latter

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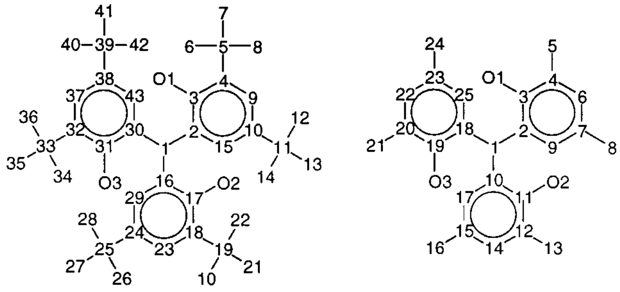

**Figure 1.** Atom numbering schemes employed in the X-ray structural determinations.

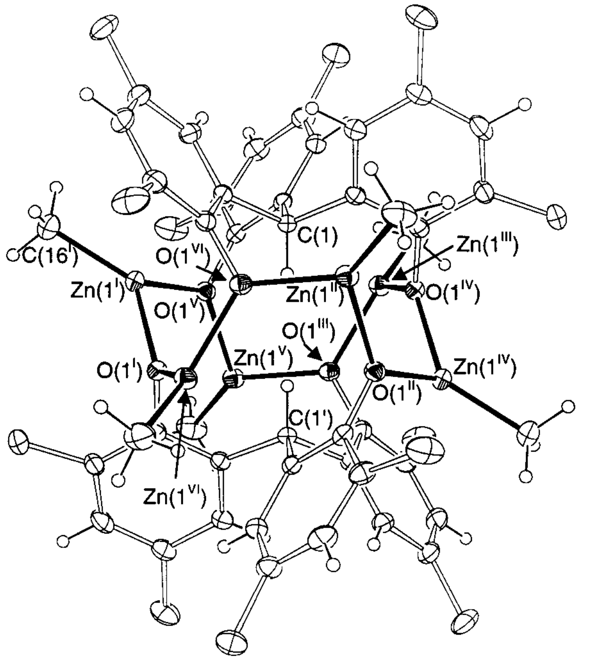

**Figure 2.** ORTEP representation (thermal ellipsoids shown at the 30% probability level) of **2a**·3$C_6H_6$. Bonds to zinc atoms have been drawn with solid lines. The solvent molecules and *tert*-butyl methyl groups have been omitted, for clarity. The molecule resides on an $\bar{3}$-symmetry position. The complete numbering scheme is depicted in Figure 1. Selected bond lengths (Å) and angles (deg): Zn(1$^{I}$)−C(16$^{I}$) 1.951(3); Zn(1$^{I}$)−O(1$^{I}$) 2.001(2); Zn(1$^{I}$)−O(1$^{V}$) 1.985(2). O(1$^{I}$)−Zn(1$^{I}$)−C(16$^{I}$) 129.7(1); O(1$^{V}$)−Zn(1$^{I}$)−C(16$^{I}$) 129.2(1); O(1$^{I}$)−Zn(1$^{I}$)−O(1$^{V}$) 96.52(7).

solvent, although the low solubility precluded acquisition of $^{13}$C NMR data. The $^{1}$H NMR spectrum was consistent with a $C_3$ symmetric compound, with three ZnMe units per ligand. Other reaction solvents were also tested, including diethyl ether, dichloromethane, and THF, and NMR studies indicated the identical product was formed in each case. The absolute connectivity was not obvious from the NMR data, so the material was subjected to full characterization by a single-crystal X-ray analysis. Figure 1 outlines the atom numbering scheme for the ligand system while an ORTEP representation of the structure is depicted in Figure 2.

The compound crystallizes in a cubic space group ($Pa\bar{3}$) on a $\bar{3}$-symmetry position; accordingly only one aromatic ring and associated zinc alkyl are crystallographically unique. The compound is an aggregate of two triphenoxymethane units incorporating six zinc centers. The overall conformation of the molecule bears a close resemblance to that previously observed for the lithium salt of tris(3,5-di-*tert*-butyl-2-hydroxyphenyl)methane, which was also found to be a hexanuclear dimer with each metal bound to two oxygens.[13] The zinc atoms adopt a distorted trignonal planar coordination geometry, with the zinc puckered 0.327 Å out from its coordination plane and showing a O−Zn−O bite angle of 96.52(7)°. The puckering is apparently induced to maintain a weak interaction with an adjacent aryl ring, with distances of 2.674(5) and 3.060(5) Å for Zn(1$^{I}$)···C(2$^{VI}$) and Zn(1$^{I}$)···C(3$^{VI}$), respectively. As normally seen in hexanuclear aggregates of **1**, the aromatic rings are not perpendicular to the core but rather canted, in this case by 57.6(1) °. This angle is comparable to those found in the free ligand **1a**, for which values of 43.5(1), 49.87(9), and 42.20(6)° were measured for the three rings, indicating only minimal rearrangement is required for aggregate formation.

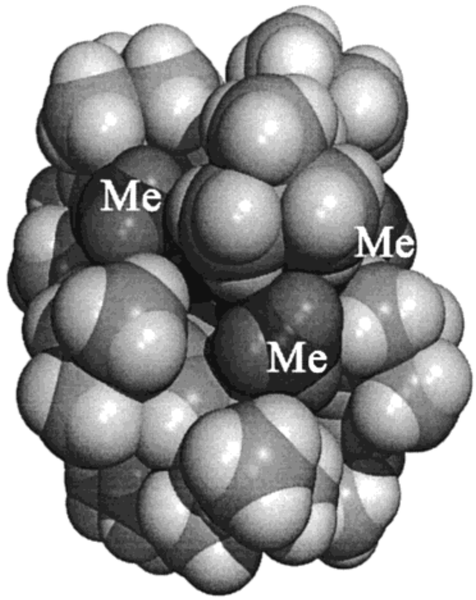

**Figure 3.** CPK representation of **2a**. For clarity, the Zn−Me groups have been rendered darker than the surrounding organic fragments.

Surprisingly few methylzinc alkoxides have been structurally characterized, and **2a** represents the first example of a methylzinc aryloxide. Comparing the Zn−Me bond length with those of methylzinc alkoxides reveals it to be typical, at 1.951(3) Å, and it is indistinguishable from the bonds in tetrameric methylzinc methoxide[19] and *tert*-butoxide.[20] The two Zn−O lengths in **2a** are essentially identical [2.001(2) and 1.985(2) Å], and these are also comparable to those measured for the dimeric structure of ethyl(2,6-di-*tert*-butylphenoxy)zinc.[21]

From the CPK representation of **2a** (Figure 3), the steric congestion about the metal center is clearly evident, and the metal would, in all likelihood, be unable to accommodate larger alkyl substituents. In agreement with this observation, reactions of diethylzinc with **1a** do not give structures analogous to **2a** (vide infra), but with the less bulky ligand tris(3,5-dimethyl-2-hydroxyphenyl)methane, **1b**, aggregates akin to **2a** will form from diethylzinc, as confirmed by a single-crystal X-ray analysis. Figure 4 depicts the structure of **2b** from above, drawn with a view 90° away from that of **2a**.

Because the structure of **2b** bears a very close resemblance to that of **2a**, most of the parameters are analogous, and have been highlighted above. Indeed, the majority of the corresponding bond lengths are statistically identical to those found for **2a**. The bond angles associated with the zinc atoms are only

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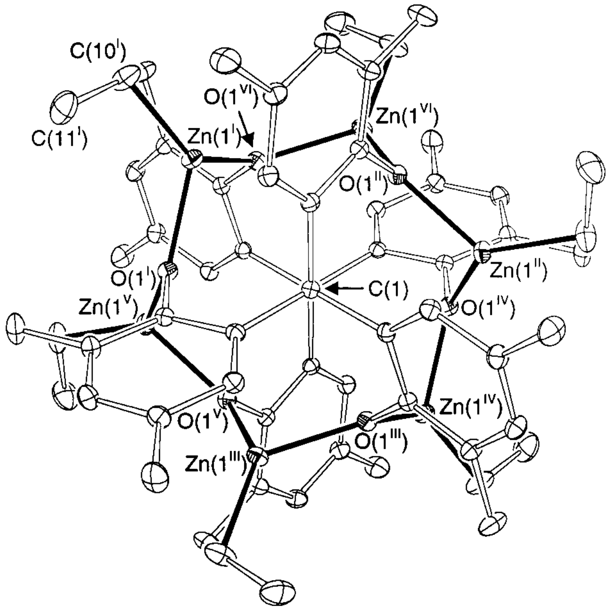

**Figure 4.** ORTEP representation (thermal ellipsoids shown at the 30% probability level) of **2b**. Bonds to zinc atoms have been drawn with solid lines. All hydrogen atoms have been omitted, for clarity. The molecule resides on a 3-symmetry position. The compound is depicted looking from the top relative to the analogous system shown in Figure 2, with C(1′) directly beneath C(1). The complete numbering scheme is depicted in Figure 1. Selected bond lengths (Å) and angles (deg): Zn(1$^{I}$)−C(10$^{I}$) 1.961(2); Zn(1$^{I}$)−O(1$^{I}$) 2.005(1); Zn(1$^{I}$)−O(1$^{VI}$) 1.991(1). O(1$^{I}$)−Zn(1$^{I}$)−C(10$^{I}$) 125.56(7); O(1$^{VI}$)−Zn(1$^{I}$)−C(16$^{I}$) 134.12(6); O(1$^{I}$)−Zn(1$^{I}$)−O(1$^{VI}$) 93.78(5).

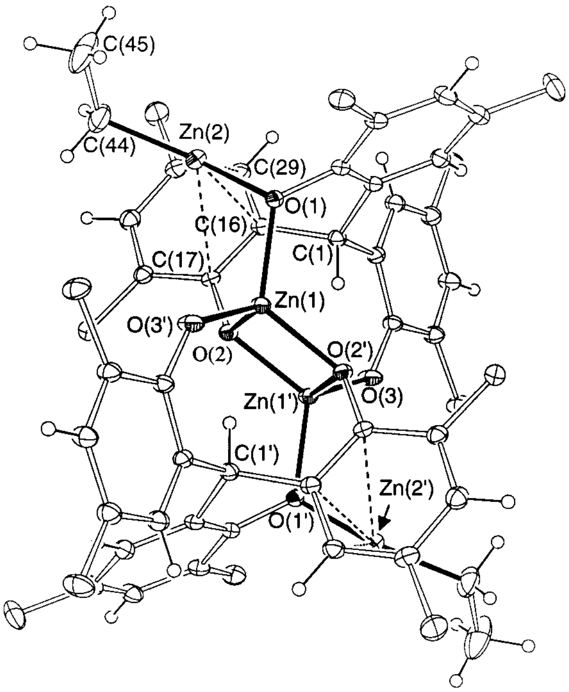

**Figure 5.** ORTEP representation (thermal ellipsoids shown at the 30% probability level) of $\mathbf{3}\cdot 5CH_2Cl_2$. All bonds to the zinc atoms have been drawn with solid lines. The solvent molecules and *tert*-butyl methyl groups have been omitted, for clarity. The molecule resides on an inversion center. The complete numbering scheme is depicted in Figure 1. Selected bond lengths (Å) and angles (deg): Zn(1)−O(1) 1.969(2); Zn(1)−O(2) 2.075(2); Zn(1)−O(2′) 1.977(2); Zn(1)−O(3′) 1.852(2); Zn(2)−C(44) 1.944(4); Zn(2)−O(1) 1.940(2); Zn(2)···C(16) 2.474(3); Zn(2)···C(17) 2.662(3); O(1)−Zn(1)−O(3′) 110.52(9); O(1)−Zn(1)−O(2) 99.25(8); O(1)−Zn(1)−O(2′) 119.03(9); O(2)−Zn(1)−O(2′) 84.84(9); O(2)−Zn(1)−O(3′) 115.3(1); O(2′)−Zn(1)−O(3′) 122.22(9); Zn(1)−O(2)−Zn(1′) 95.16(9); Zn(1)−O(1)−Zn(2) 111.2(1).

marginally different, and the canting of aryl rings, at 56.01(4)°, are almost identical to that of **2a**.

The $^1$H NMR spectra of both compounds were collected and, as discussed above, THF and toluene were the only suitable solvents for the compounds. The spectra are fully consistent with the structural data, indicating retention of $C_3$ symmetry in solution, and exhibit a number of noteworthy features. The diagnostic central methine resonance appears at 7.77 and 7.59 ppm for **2a** and **2b**, respectively. These positions are indicative of salt formation and a comparable chemical shift value was measured for sodium salt of **1a** (8.15 ppm), also a hexanuclear dimer.[13] The metal-alkyl protons resonate at −0.95 for **2a** ($CH_3$) and 0.89 for **2b** ($CH_2CH_3$), typical chemical shift values for methyl[20] and ethyl[21] zincalkoxides.

Like **2a**, **2b** exhibits poor solubility in most organic solvents, and can be isolated in 98% yield directly out of the reaction solvent (diethyl ether). The insolubility of the compounds severely limits their utility for further reactions, so the syntheses of compounds derived from **1a** and diethylzinc were investigated.

When three equivalents of diethylzinc were added to a dichloromethane solution of **1a**, colorless blocks formed at the solvent surface upon standing. Analysis of the NMR spectrum of the product suggested the molecule possessed a lower symmetry structure than **2a**, with three inequivalent aromatic rings. The connectivity of the material was not certain from these data, and the structure was determined by X-ray crystallography. An ORTEP representation of **3** is depicted in Figure 5.

Like **2a** and **2b**, the material is dimeric, with an inversion center, but despite the presence of sufficient zinc reagent, a hexanuclear material did not form in this case. Rather, a tetranuclear zinc species results, with two four-coordinate zinc atoms ligated exclusively by oxygen donors and a pair of two-coordinate zinc atoms each with a single ethyl substituent. The angles around Zn(1) are distorted significantly from tetrahedral geometry, with O−Zn−O angles ranging from 84.84(9) to 122.22(9)°. Additionally, some of the zinc−oxygen bond lengths are significantly longer than those seen in **2a** and **2b**, the longest being that of Zn(1)−O(2) at 2.075(2) Å. Structures incorporating zinc alkoxides arranged in a tetrahedral fashion are quite rare, with only a handful of additional examples, and as in **3**, the metals atoms in these compounds adopt distorted tetrahedral arrangements with long and short Zn−O bond distances.[14,22] The remaining two zinc atoms, Zn(2) and Zn(2′), each have a single ethyl group and are, atypically, only two-coordinate, although some interaction with the aryl $\pi$-electrons is evident. To the best of our knowledge, this represents the first example of a two-coordinate O−Zn−C moiety. At 141.9(2)°, the O(1)−Zn(2)-C(44) angle is nonlinear, puckering toward the aromatic ring; Zn(2) interacts with the bond formed by C(16) [from which it is 2.474(3) Å distant] and C(17) [2.662(3) Å] and possibly with C(29) [2.728(3) Å]. Since each aromatic ring is substituted at the oxygen in discrete ways, the rings are canted at very different angles relative to the plane formed by O(1), O(2), and O(3). The rings beginning C(2), C(16), and C(30) are thus inclined at angles of 25.1(1), 77.95(9), and 55.3(1) °, respectively. Finally, there may exist an interaction of the central methine hydrogens with Zn(1), since the two atoms are only

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(22) (a) Purdy, A. P.; George, C. F. *Polyhedron* **1994**, *13*, 709. (b) Olmstead, M. M.; Power, P. P.; Shoner, S. C. *J. Am. Chem. Soc.* **1991**, *113*, 3379. (c) Atwood, J. L.; Junk, P. C.; Lawrence, S. M.; Raston, C. L. *Supramol. Chem.* **1996**, *7*, 15.

2.224(2) Å apart, within their van der Waal radii. Given the unique geometry of the two-coordinate metal, Zn(2) would be expected to be a highly reactive center, and indeed, the material **3** is sensitive in the solid-state, slowly turning pale blue over the period of several weeks at room temperature in a pure nitrogen environment.

In agreement with the solid-state structure, three inequivalent aromatic rings, and a single Zn-Et environment that integrates to one group per each triarylmethane unit can be identified in the NMR spectrum of **3**. Additionally, the spectrum of **3** does not noticeably change over a few days, indicating the product is somewhat stable in solution. The central methine resonance appears at 7.29 ppm, slightly upfield from those measured in **2a** (7.77 ppm) and **2b** (7.59 ppm). The ZnC$H_2$ chemical shift value, however, at 0.17 is significantly upfield relative to that seen for **2b**, where this signal is found at 0.86 ppm. Clearly, significant shielding of these protons is in effect, and they are in a markedly dissimilar environment to those in **2a**. Unfortunately, the poor solubility of **3** in noncoordinating solvents precluded acquisition of $^{13}$C data.

We wondered if the compound **3**, or a derivative thereof, could form if coordinating solvents were used. Hence, analogous syntheses were carried out both in diethyl ether and THF solvents, resulting in startlingly different reaction outcomes. When ether is used as a solvent, large colorless rods of **4** formed in the reaction mixture over the course of several hours. In comparison to **3**, the crystals exhibited much higher solubility, suggesting a different compound was produced, and the $^1$H NMR spectrum of the material, although intimating a low symmetry complex, clearly was not the same as that of **3**. A single X-ray diffraction study was therefore undertaken to determine the connectivity of this compound. Figure 6 shows an ORTEP representation.

Ether was consistently detected in the $^1$H NMR spectrum of single crystals of **4**, and several noninteracting ether molecules were identified in the lattice. As before, the product contains two triarylmethane units, but now the aggregate incorporates five zinc atoms rather than four. Although the asymmetric unit contains the single cluster, the compound appears to have a pseudo inversion center, with Zn(2) and Zn(5) being equivalent, together with Zn(3) and Zn(4). As opposed to the structure of **3**, only a single tetrahedral zinc [Zn(1)] resides in **4**, and this metal is ligated to two oxygens from each triphenoxymethane unit. In a manner similar to **3**, Zn(1) adopts a distorted tetrahedral arrangement, although in this species the geometry is much closer to ideal, with O−Zn−O angles ranging from 101.77(7)−124.66(7)°. The Zn−O bond distances are inequivalent, with the oxygen atoms forming bonds to adjacent two-coordinate ZnEt groups being ~0.035 Å longer than those bridging to the tetrahedrally bound ZnEt moieties.

The remaining four zinc atoms are each bound to a terminal ethyl group. The Zn(3)/Zn(4) metals are only two-coordinate, analogous to Zn(2)/Zn(2′) in the structure of **3**, while Zn(2)/Zn(5) exhibit extremely distorted tetrahedral geometries. For the latter, angles were measured ranging from 83.59(7)° to 146.3(1)° for the O(2)−Zn(2)−O(5) and O(2)−Zn(2)−C(87) angles, respectively. Additionally, the Zn−O distances around Zn(2) and Zn(5) vary greatly, with the Zn(2)−O(2) bond length being typically 1.961(2) Å, while the remaining two are significantly longer, at 2.079(2) and 2.301(2) Å, for Zn(2)−O(5) and Zn(2)−O(6), respectively. Like those in the structure of **3**, the two-coordinate zincs are not linear and show significant interactions with an adjacent aromatic ring and Zn(4) forms close contacts to C(73) [2.413(3) Å] and C(74) [2.503(2) Å], while Zn(3) is slightly more distant, 2.482(2) and 2.600(2) Å, from C(2) and C(3), respectively. The orientation of the aromatic rings in **4** are extremely similar to those in **3**, with a wide variation of twists relative to the plane defined by O(1), O(2), and O(3) of 76.97(7)°, 64.26(9)°, and 27.50(9)° for the respective rings beginning with C(2), C(16), and C(30). The three remaining, independent corresponding rings, starting with C(73), C(59), and C(45), form, as expected, similar angles of 80.72(7)°, 64.89(9)°, and 24.87(9)°. Much like **3**, there apparently exist interactions of the central methine hydrogen atoms with Zn(1), with a C(1)H···Zn(1) distance of 2.248(2) Å and a C(44)H··· Zn(1) length of 2.339(2) Å. The remaining structural parameters are typical.

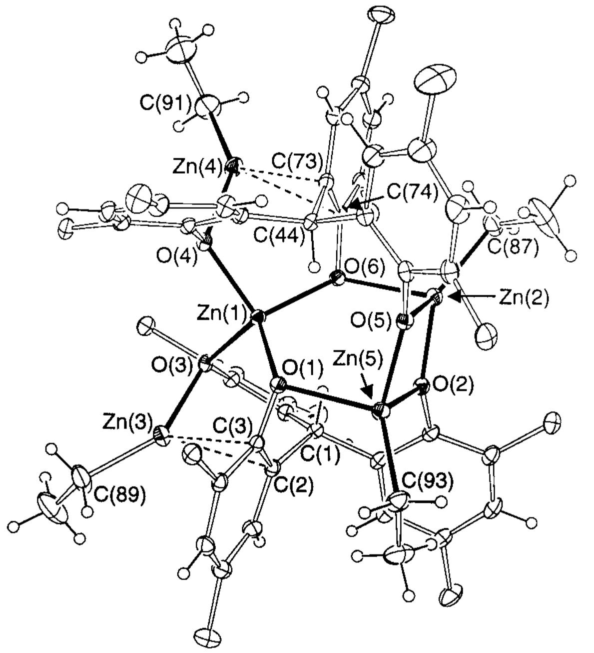

**Figure 6.** ORTEP representation (thermal ellipsoids shown at the 30% probability level) of **4**·1$^1/_3$Et$_2$O. Bonds to zinc atoms have been drawn with solid lines. The solvent molecules and *tert*-butyl methyl groups have been omitted, for clarity. The complete numbering scheme is depicted in Figure 1. Selected bond lengths (Å) and angles (deg): Zn(1)−O(1) 1.970(2); Zn(1)−O(3) 2.009(2); Zn(1)−O(4) 1.996(2); Zn(1)−O(6) 1.963(2); Zn(2)−C(87) 1.970(3); Zn(2)−O(2) 1.961(2); Zn(2)−O(5) 2.079(2); Zn(2)−O(6) 2.301(2); Zn(3)−C(89) 1.941(3); Zn(3)−O(3) 1.941(2); Zn(3)···C(2) 2.482(2); Zn(3)···C(3) 2.600(2); Zn(4)···C(73) 2.413(3); Zn(4)···C(74) 2.503(2); O(1)−Zn(1)−O(3) 101.77(7); O(1)−Zn(1)−O(4) 124.66(7); O(1)−Zn(1)−O(6) 106.51(7); O(3)−Zn(1)−O(4) 102.12(7); O(3)−Zn(1)−O(6) 123.65(7); O(4)−Zn(1)−O(6) 100.19(7); O(2)−Zn(2)−O(6) 88.85(7); O(2)−Zn(2)−C(87) 146.3(1); O(2)−Zn(2)−O(5) 83.59(7); C(87)−Zn(2)−O(5) 116.0(1); C(87)−Zn(2)−O(6) 112.9(1); O(5)−Zn(2)−O(6) 99.13(6); O(3)−Zn(3)−C(89) 148.2(1).

The $^1$H NMR spectrum of **4** closely resembles that of **3**, with both halves of the dimer being magnetically equivalent and the majority of the resonances appearing in very similar positions, with the exception of the diagnostic central methine carbon which, at 7.92, is significantly further downfield. The Zn−Et groups resonate at similar positions and were not resolved, with multiplets at 0.89 and 0.10 ppm for the C$H_2$ and C$H_3$ protons, respectively. Compound **4** shows significantly higher solubility than **3**, and $^{13}$C NMR data could be obtained. The central carbon resonance appears at 36.6 ppm, which compares with a value of 42.5 for the starting material **1a**. A similar upfield shift of this resonance was observed for the sodium salt derivatives of **1a**.[13] The two unique Zn$CH_2$ resonances are present at slightly different shift values of 5.2 and 2.6 ppm, and these compare

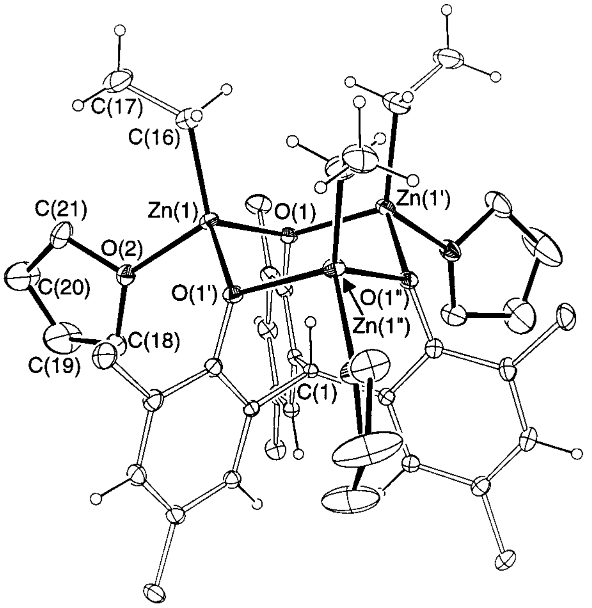

**Figure 7.** ORTEP representation (thermal ellipsoids shown at the 20% probability level) of **5a**·THF. Bonds to zinc atoms and the THF molecules have been drawn with solid lines. The noncoordinating THF molecule, all THF hydrogens, and *tert*-butyl methyl groups have been omitted, for clarity. The molecule resides on a 3-fold symmetry position. The complete numbering scheme is depicted in Figure 1. Selected bond lengths (Å) and angles (deg): Zn(1)−C(16) 1.983(3); Zn(1)−O(1) 2.052(2); Zn(1)−O(1′) 2.048(2); Zn(1)−O(2) 2.130(2); O(1)−Zn(1)−O(1′) 104.94(9); O(1)−Zn(1)−C(16) 114.3(1); O(1)−Zn(1)−O(2) 101.31(8); O(2)−Zn(1)−C(16) 117.3(1); O(1′)−Zn(1)−C(16) 117.3(1); O(1′)−Zn(1)−O(2) 99.37(8).

with a value of 2.1 ppm measured for dimeric ethyl(2,6-di-*tert*-butylphenoxy)zinc.[21] The diagnostic resonances for the central methine proton in the $^1$H NMR spectrum of **3** (7.29 ppm) and **4** (7.92 ppm) do not change even after prolonged periods of time in solution, indicating the interconversion between the two compounds does not occur at room temperature. Moreover, addition of excess diethylzinc to solutions of **3** does not induce the formation of **4**.

The final solvent tested for the reaction of **1a** with diethylzinc was THF. Once again, colorless blocks formed in the reaction mixture upon standing, and contrary to the reactions performed in dichloromethane or ether, the $^1$H NMR spectrum of the isolated material suggested a $C_3$ symmetric compound had formed in this case. A structural analysis of the crude crystalline material was undertaken to determine if monomeric, dimeric, or larger constructs had formed. Figure 7 depicts an ORTEP representation of the structure of **5a**.

Distinct from when **1a** is reacted with *dimethyl*zinc in THF, the introduction of a coordinating solvent precludes aggregate formation between adjacent molecules with the bulky ligand and the more sterically demanding *diethyl*zinc reagent. In the present case, THF occupies the fourth coordination site in a monomeric trinuclear system. The compound exhibits a high degree of symmetry, and crystallizes in $Pa\bar{3}$, with only one aromatic ring and one THF molecule in the asymmetric unit. As is typical for most derivatives of **1**[11,13] and all current examples, the oxygen atoms point "up" with respect to the central methine. The three ethyl groups are oriented in the same direction pointing away from the aryl rings, while the THF molecules are canted down, presumably due to steric restraints imposed by the *ortho tert*-butyl moieties. The zinc atoms thus adopt distorted tetrahedral geometries, with O−Zn−O/C angles ranging from 99.37(8)° to 117.3(1)°. The two Zn−O$_{\text{phenoxide}}$ distances of 2.052(2) and 2.048(2) Å are on average significantly longer than the other zinc derivatives. At 1.983(3) Å, the Zn−C bond is somewhat longer than those seen in **2b** [1.961(2) Å] and **3** [1.944(4) Å], although comparable to the tetrahedrally coordinated zincs seen in **4** [1.970(3) Å]. In order for each zinc to bridge an adjacent oxygen atom, the rings are canted almost perpendicular to the core, at 79.67(6)°. Large twist angles (80.6−82.2°) were also observed for the sodium and potassium aggregates derived from **1a**, which likewise feature atoms bridging adjacent atoms to give $C_3$ symmetric compounds.[13]

Although the solubility of **5a** in THF, benzene, dichloromethane, and ether is marginal, the compound exhibits surprisingly high solubility in toluene. The $^1$H NMR spectrum is consistent with the X-ray data, exhibiting $C_3$ symmetry. The central methine resonance appears at 9.44 ppm, and this value is ~1.5−2 ppm higher than previously seen in the other zinc derivatives. The methine carbon in $^{13}$C NMR spectrum of **5** falls at 32.8 ppm, close to the value of 36.6 ppm measured for **4**. The ZnC$H_2$ resonance appears at 1.00 ppm, a very different value to that measured for **3** and **4**, but similar to that measured for **2b**.

With the desire to increase the solubility of the trinuclear species, the 3,5-*tert*-pentyl triarylmethane, **1c**, was reacted with diethylzinc. While the product was not characterized crystallographically, $^1$H and $^{13}$C NMR data confirmed the formation of **5c**, by analogy with the spectra of **5a**. In most instances, we have found the reactivity of **1c** to mimic **1a**, but the solubility of the products invariably tends to be significantly greater in non-polar organic solvents. Accordingly, compound **5c** even has limited solubility in pentane.

**Copolymerization Reactions.** Since alkylzinc reagents are rarely used as copolymerization catalysts for carbon dioxide and epoxides, the substitution of the alkyl substituents with alkoxy groups was attempted for complexes **2**−**5** by reaction with dry methanol or ethanol as described by Coates.[8] These reactions, however, led only to extensive decomposition of the materials and alkoxy derivatives of **2**−**5** thus far remain elusive. Similar difficulties were encountered with phenoxide substitution. Nevertheless, in view of the unusual low coordination number of the metal centers in the complexes and the fact that the first polymerization catalysts were simply derived from the partial hydrolysis of diethylzinc, we attempted several preliminary investigations regarding the catalytic activity, if any, of the prepared alkyl zinc materials. Both complexes **3** and **4** contain two-coordinate zinc centers, which, although somewhat sterically hindered, should be sufficiently accessible to substrates for catalytic activity (Figure 8). Moreover, complexes **5a** and **5b** feature THF ligands, which, like the Darensbourg materials,[9] could be adequately labile for catalysis. The products formed were characterized by NMR spectroscopy, but a detailed analysis of the polymer products was not carried out. A summary of the results of the studies is tabulated in Table 2.

Relative to the mononuclear materials reported previously,[8,9] the zinc reagents **2**−**5** were poor catalysts. In line with research reported by Darensbourg,[9] none of the materials catalyzed the copolymerization of CO$_2$ and propylene oxide. When cyclohexene oxide was used as the epoxide source, however, complexes **2a**, **2b**, and **5a** showed limited activity and produced modest numbers of carbonate linkages, 60, 84, and 81%, respectively. The very low turnover numbers displayed by these compounds may be in part a result of their very poor solubility in cyclohexene oxide, as opposed to particularly low activity. Compound **3**, being somewhat more soluble and less stable than **2** and **5**, gave considerable quantities of polymer, although in

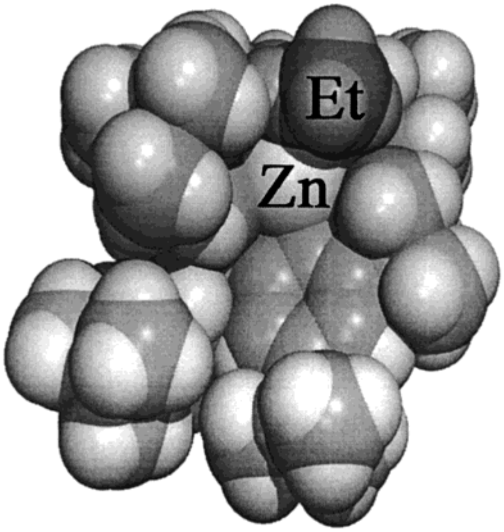

**Figure 8.** CPK representation of **3** highlighting the accessibility of the two-coordinate zinc centers. For clarity, the Zn−Et groups have been rendered darker than the surrounding organic fragments.

**Table 2.** Results of Cyclohexene Oxide/$CO_2$ Polmerization Reactions for Compounds **2**−**5**[a]

| catalyst | % carbonate linkages[b] | ∼syn to iso/others[c] | TON[d] |
|---|---|---|---|
| **2a** | 60 | 1.4 | 21 |
| **2b** | 84 | 1.6 | 11 |
| **3** | 0 | | 331 |
| **4** | | | 0 |
| **5a** | 81 | 1.1 | 24 |

[a] Reactions carried out in neat cyclohexene oxide at 800 psi at 100 °C for 18 h. [b] Determined by integration of $^1$H NMR signals at 4.6 and 3.4 ppm for carbonate and ether linkages, respectively. [c] Syndiotactic:isotactic/others linkage ratio determined by integration of $^{13}$C NMR resonances at 154 and ∼153 ppm, respectively. [d] Moles of cyclohexene oxide consumed per mole of active zinc sites.

this case only homopolymerization of the epoxide occurred giving solely the polyether product. The very reactive and more accessible active zinc centers in **3** possibly allow homopolymerization to occur at a faster rate than the copolymerization reaction. Although compound **4** structurally shares a number of features with that of **3**, **4** failed to catalyze the polymerization reaction, perhaps due to the thermal instability of **4**. Under the reaction conditions the complexes may undergo significant structural rearrangement but, given the poor results obtained in the polymerization reactions, no attempt was made to identify the reactive species at 100 °C in cyclohexene oxide.

**Conclusions.** A number of alkyl zinc derivatives of bulky linked phenols have been prepared and fully characterized. Examples of hexa-, penta-, tetra- and trinuclear compounds were isolated, and the formation of these products was found to be unpredictable but reproducible (each reaction was undertaken multiple times). In each case, the identity of the product was highly dependent on both the steric requirements of the dialkylzinc reagent/tris-phenol precursors and on the solvent used. Since in many cases the complexes contained two- and three-coordinate zinc centers, the catalytic activity toward polycarbonate formation from cyclohexene oxide and $CO_2$ was examined. In most instances, however, the compounds were found to be only relatively poor catalysts for the copolymerization reaction. Presumably, the instability of the reactive metal centers in the zinc aggregates under the polymerization conditions hindered the formation of polycarbonate polymer, and efforts are underway to enhance the reactivity of these novel zinc clusters.

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**Supporting Information Available:** X-ray crystallographic files in CIF format for the structure determinations of complexes **2a**, **2b**, **3**, **4**, and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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