Cone vs an Alternate Structure in the Synthesis of Organometallic Calixarene Inclusion Complexes

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Reaction of 1,3-di-*O*-methylcalix[4]arene ligands with 2 equiv of R_2Zn results in the mixture of the two bimetallic products: an organometallic alkylzinc inclusion complex with the ligand in the conic conformation and an isomeric complex, where the calixarene scaffold affords the flattened cone structure. This reaction has been systematically studied with regard to a variety of factors, such as temperature, concentration, and steric bulk. All were found to influence the ratio between the products, with the low temperature, high R_2Zn concentration, and low steric hindrance favoring the formation of inclusion complexes with the calixarene ligand in the conic conformation. An excess of the dialkylzinc reagent also facilitates the exchange with the alkylzinc coordinated to the calixarene ligand. However, only the external alkylzinc fragment is capable of participating in this Schlenk-type equilibrium process.

Introduction

As a result of the relatively low inversion energy barrier of aromatic rings, the conformational flexibility of the calixarene scaffold provides a variety of three-dimensional structures that differ in their ability to complex various guest molecules inside the hydrophobic cavity.[1−3] Attaching a transition-metal center to the lower (phenolic) rim of the calixarene ligand enables the formation of compounds in the cone conformation, often capable of complexing an additional molecule or ion inside the calixarene cavity.[4] Although several approaches toward metal-capped calixarene inclusion complexes have been described,[5−7] no systematic analysis of various factors, which influence their formation, has been reported. An understanding of these factors is essential in the design of calixarene organometallic inclusion complexes, which remain scarce relative to similar complexes containing organic molecules and ions.[8]

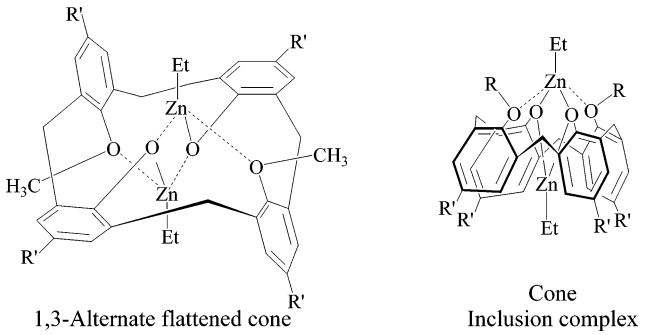

Figure 1.

While the reaction of the dimethyl calixarene ether **1a** with 2 equiv of Et_2Zn gave the bimetallic zinc complex in the 1,3-alternate flattened cone conformation (Figure 1),[9] we recently showed that replacing the

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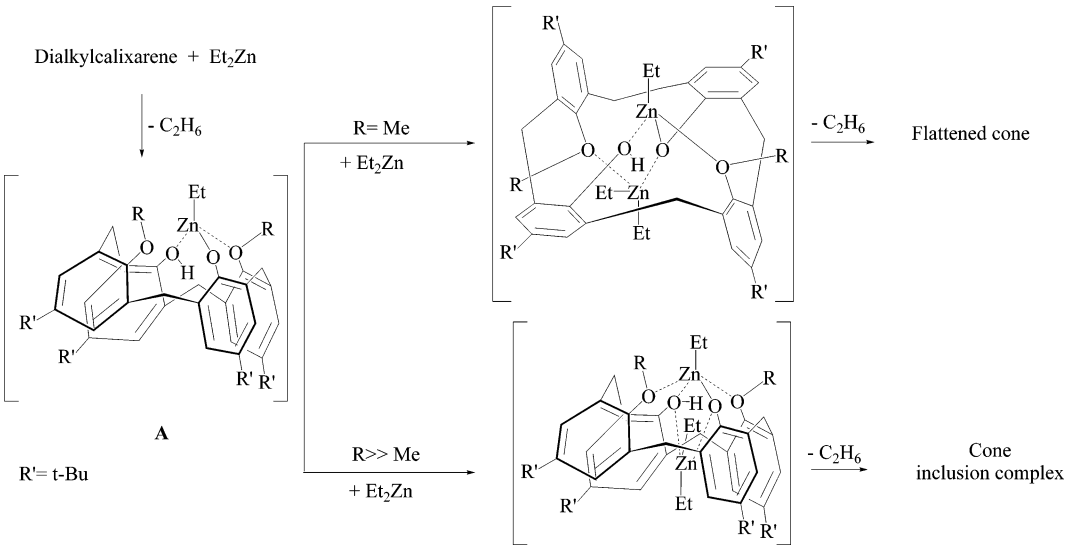
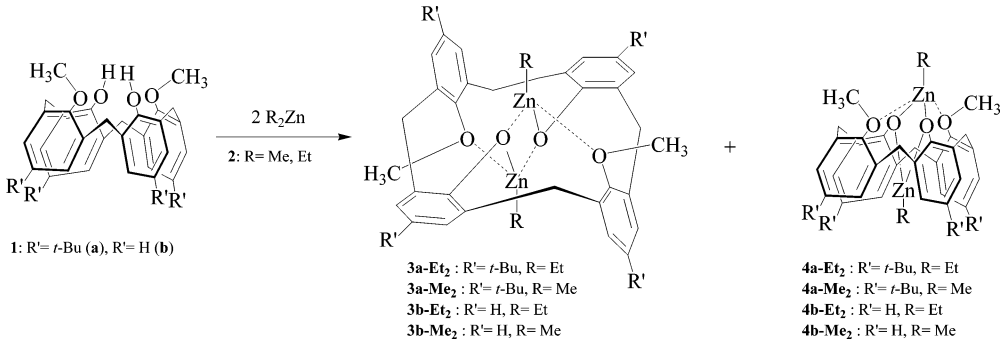
Scheme 1



Scheme 2



methyl groups with bulkier ones (propyl or larger) provides the conic inclusion complexes (Figure 1) exclusively, independent of the substituent electronic properties.[10] This difference in reactivity was attributed to the inability of the phenolic ring possessing a bulky substituent at the oxygen atom to undergo ring flipping in the proposed common intermediate **A** for the two products. Penetration of the hydrophobic calixarene cavity by the organometallic reagent locks the final product in the pinched conic conformation (Scheme 1). While repeating the reaction between **1a** and Et_2Zn, we discovered the formation of small amounts of the conic inclusion product **4a-Et2** in the crude material. This observation suggested that the ring-inversion process, leading to **3a-Et2** (Scheme 2), occurs in the same time frame as that of the formation of the inclusion complex. Thus, we decided to investigate various factors that may influence both processes and control isomer formation. Herein we present systematic mechanistic studies, which demonstrate that the formation of the inclusion complexes can be effected by *any* of the following parameters: temperature, concentration, and substituent at the upper rim.

Results and Discussion

As the inclusion of diethylzinc into the calixarene cavity can be sterically hindered, we were interested in studying the reactivity of a smaller dimethylzinc. We found that, similar to Et_2Zn, the smaller Me_2Zn gave the pinched conic complexes exclusively upon reacting at room temperature for 5−8 h in toluene or C_6D_6 with ligands possessing bulky substituents at the lower rim. Interestingly, mixing the dimethyl calixarene ligand **1a** with Me_2Zn afforded a 3:7 mixture of the bimetallic complexes **3a-Me2** (1,3-alternate flattened cone) and **4a-Me2** (pinched cone), respectively, as determined by ^1H NMR spectroscopy (Scheme 2). Both complexes could be crystallized from cold pentane, and their structures (both containing a pentane molecule) are shown in Figures 2 and 3, respectively. The structure of complex **3a-Me2** demonstrates that the two four-coordinate zinc centers are in the symmetrical environment, with a distance of 3.1256(5) Å between the metal atoms.[11] In contrast with **3a-Me2**, in **4a-Me2** the zinc atoms are located in a different ligand configuration, with one of the methylzinc fragments being of the three-coordinate type and immersed in the calixarene cavity. The other is coordinated to five ligands (four oxygen donors and the methyl group) at the calixarene's lower rim. The distance between the metal centers (3.0667(6) Å) is nearly identical with that in the previously reported bimetallic alkylzinc inclusion complex.[10] The bond lengths between the aryloxide ligands with the internal zinc atom (1.961(2) and 1.982(2) Å) are slightly shorter than their bonds with the external zinc atom (1.990(2) and 1.999(2) Å), to compensate for the coordinative unsaturation. Similarly, the distance between the ether

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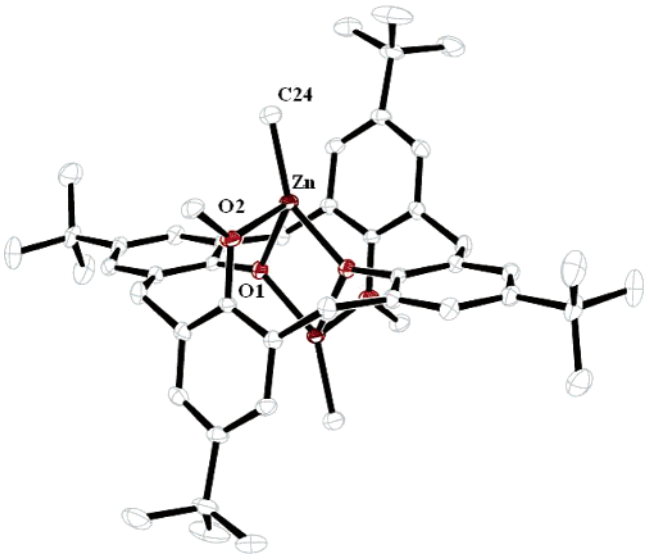

Figure 2. ORTEP view of a molecule of **3a-Me2** with thermal ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Zn−C24 = 1.950(2), Zn−O1 = 1.9595(15), Zn−O1 = 1.9972(16), Zn−O2 = 2.1944(16), Zn- - -Zn = 3.1256(5).

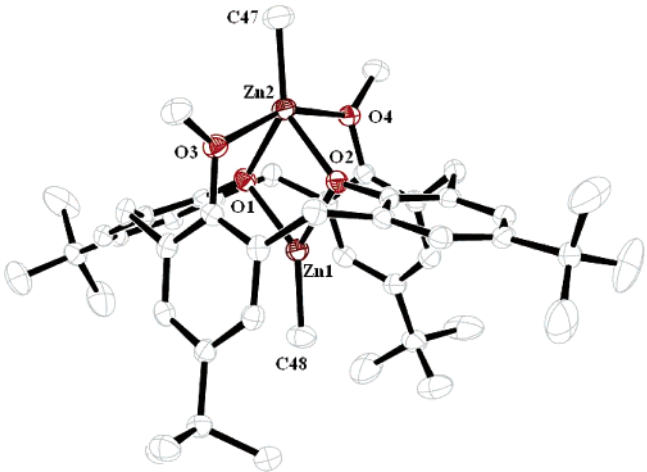

Figure 3. ORTEP view of a molecule of **4a-Me2** with thermal ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Zn1−C48 = 1.928(4), Zn1−O2 = 1.961(2), Zn1−O1 = 1.982(2), Zn2−C47 = 1.954(4), Zn2−O1 = 1.990(2), Zn2−O2 = 1.999(2), Zn2−O4 = 2.391(2), Zn2−O3 = 2.406(2), Zn1- - -Zn2 = 3.0667(6).

oxygen atoms and the four-coordinate zinc centers in **3a-Me2** (2.1944(16) Å) is shorter than the corresponding distances with the pentacoordinate external zinc atom in **4a-Me2** (2.391(2) and 2.406(2) Å).

The obtained results suggest that, in the case of the smaller Me_2Zn guest molecule, the guest inclusion rate can compete favorably with that of the ring inversion. As the ring inversion reaction should be slowed at lower temperature, we also studied the temperature effect on the product distribution. We found that, in agreement with this assertion, performing the reaction at 0 °C gave a **4a-Me2**:**3a-Me2** ratio of about 9:1.[12] Similarly, an excess of the dialkylzinc reagent should increase the rate of formation of the inclusion product. Here too we observed that increasing the concentration of Me_2Zn from 2 to 6 equiv gave a **4a-Me2**:**3a-Me2** ratio of 9:1 at room temperature. A combination of these two factors, temperature and concentration, was therefore sought to increase the formation of the inclusion complex **4a-Me2**. Indeed, **4a-Me2** was formed almost exclusively (about 97% vs 3% of **3a-Me2**) when the reaction was performed at 0 °C and with 6 equiv of Me_2Zn. Conversely, dilution of the reaction mixture considerably increased the yield of **3a-Me2** (from 30% to 45% upon 5× dilution at room temperature), indicating that the formation of both isomers can easily be manipulated.

These observations demonstrate that the product distribution is only dependent on the ratio between the energy barriers of the calixarene conformational inversion and organometallic guest complexation in the postulated intermediate monometalated complex **A**.[10,13] Thus, any system modification that favors the latter should also favor the formation of the cone structure. Removal of the bulky t-Bu groups from the ligand's upper rim in **1b** serves this purpose and, indeed, significantly increases the amount of the inclusion complex **4b-Me2** relative to its 1,3-alternate isomer **3b-Me2**, giving a 9:1 product ratio at room temperature (Scheme 2). With these results in mind, we performed the reaction of ligand **1b** with Et_2Zn. To our delight, the formation of the inclusion complex **4b-Et2** as a major product was also observed in this case with the 1,3-alternate flattened cone bimetallic compound **3b-Et2** being the minor product (9:1 ratio).

It is important to note that although a high concentration of the dialkylzinc reagent favors the formation of the pinched conic product, it might also lead to the concurrent Schlenk-type equilibrium between the free zinc reagent and the calixarene-bound zinc atoms.[14] Such an equilibrium, common for the Grignard reagents, would result in an exchange of the accessible alkylzinc groups. While this would not change our rationale on the competing ring-inversion/inclusion complex formation processes, we investigated this effect in the calixarene system. Addition of a 10-fold excess of Et_2Zn to a solution of **3b-Me2** and **4b-Me2** in benzene gave the new complex **4b-Et,Me** (alone with **3b-Et2**) within 16 h at room temperature (Scheme 3). The ^1H NMR spectrum of **4b-Et,Me** showed ethylzinc group signals very similar to those of the external zinc fragment in **4b-Et2** at 0.82 ppm (q) and 1.64 ppm (t) and a singlet at −2.21 ppm, which corresponds to the

(11) The calixarene molecule is located at the center of inversion in the centrosymmetric form (Supporting Information). Selected X-ray structure data for **3a-Me2**: $C_{29}H_{44}O_2Zn$, colorless prisms, $M_r = 490.01$, 0.25 × 0.20 × 0.15 mm^3, monoclinic, space group $P2_1/n$, $a = 15.7763(2)$ Å, $b = 9.9339(1)$ Å, $c = 17.0127(3)$ Å, $\beta = 95.9790(6)°$, $V = 2651.73(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.227$ g cm^{-3}, Nonius KappaCCD, Mo Kα radiation ($\lambda = 0.710\ 73$ Å), graphite monochromator, $T = 110(2)$ K, 6246 collected reflections, 5449 unique reflections. The structure was refined by full-matrix least squares on F^2 data (SHELXL-97, 283 parameters with no restraints), with R1 = 0.0452 and wR2 = 0.1232 (all data). Selected X-ray structure data for **4a-Me2**: $C_{48}H_{64}O_4Zn_2 \cdot C_5H_{12}$, colorless plates, $M_r = 907.88$, 0.25 × 0.25 × 0.15 mm^3, monoclinic, space group $P2_1/c$, $a = 12.5318(3)$ Å, $b = 19.7643(8)$ Å, $c = 20.0664(8)$ Å, $\beta = 96.235(2)°$, $V = 4940.7(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.221$ g cm^{-3}, Nonius KappaCCD, Mo Kα radiation ($\lambda = 0.710\ 73$ Å), graphite monochromator, $T = 110(2)$ K, 11 726 collected reflections, 7609 unique reflections. The structure was refined by full-matrix least squares on F^2 data (SHELXL-97, 550 parameters with no restraints), with R1 = 0.0586 and wR2 = 0.1185 (all data).

(12) The reactions slowed at lower temperatures.

(13) The ^1H NMR spectrum of the free ligand at −60 °C shows only signals of the cone conformer. See also ref 2.

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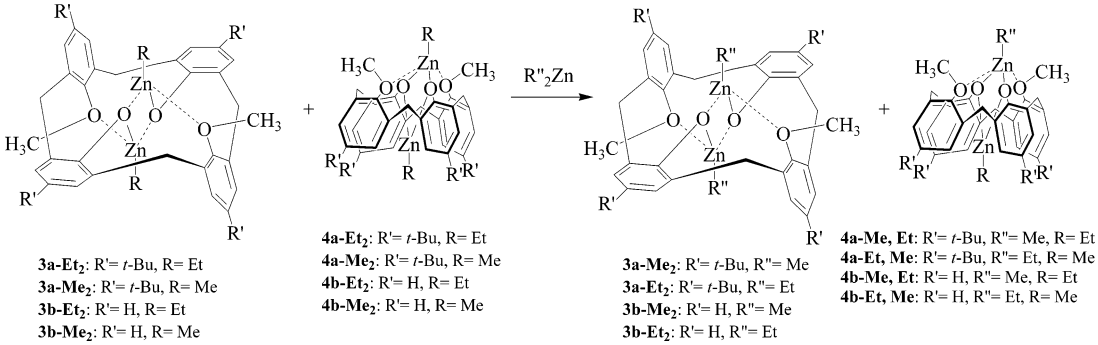
Scheme 3



internal methylzinc fragment. Similarly, addition of 10 equiv of Me_2Zn to a mixture of **3b-Et2** and **4b-Et2** in benzene led to the formation of **3b-Me2** and **4b-Me,Et**, which is isomeric with **4b-Et,Me** (Scheme 3). Importantly, no change in the ratio between the 1,3-alternate flattened cone and pinched cone products was observed, indicating that the observed Schlenk-type equilibrium does not influence the product distribution when an excess of the dialkylzinc reagent is used. The ^{1}H NMR spectra of complexes **4b-Me,Et** and **4b-Et,Me** and their corresponding precursors are shown in Figure 4. Similarly, the complex **4a-Me2** was converted into **4a-Et,-Me** upon reaction with an excess of Et_2Zn. Clearly, the internal organometallic fragment does not undergo an exchange reaction with an excess of the dialkylzinc.

Overall, we demonstrated that the formation of metal−calixarene inclusion complexes can be strongly influenced by the reaction conditions. As the guest incorporation into the calixarene cavity depends on a variety of factors, careful tuning of some or all of these factors—concentration, temperature, steric hindrance—may dramatically alter the product distribution. These

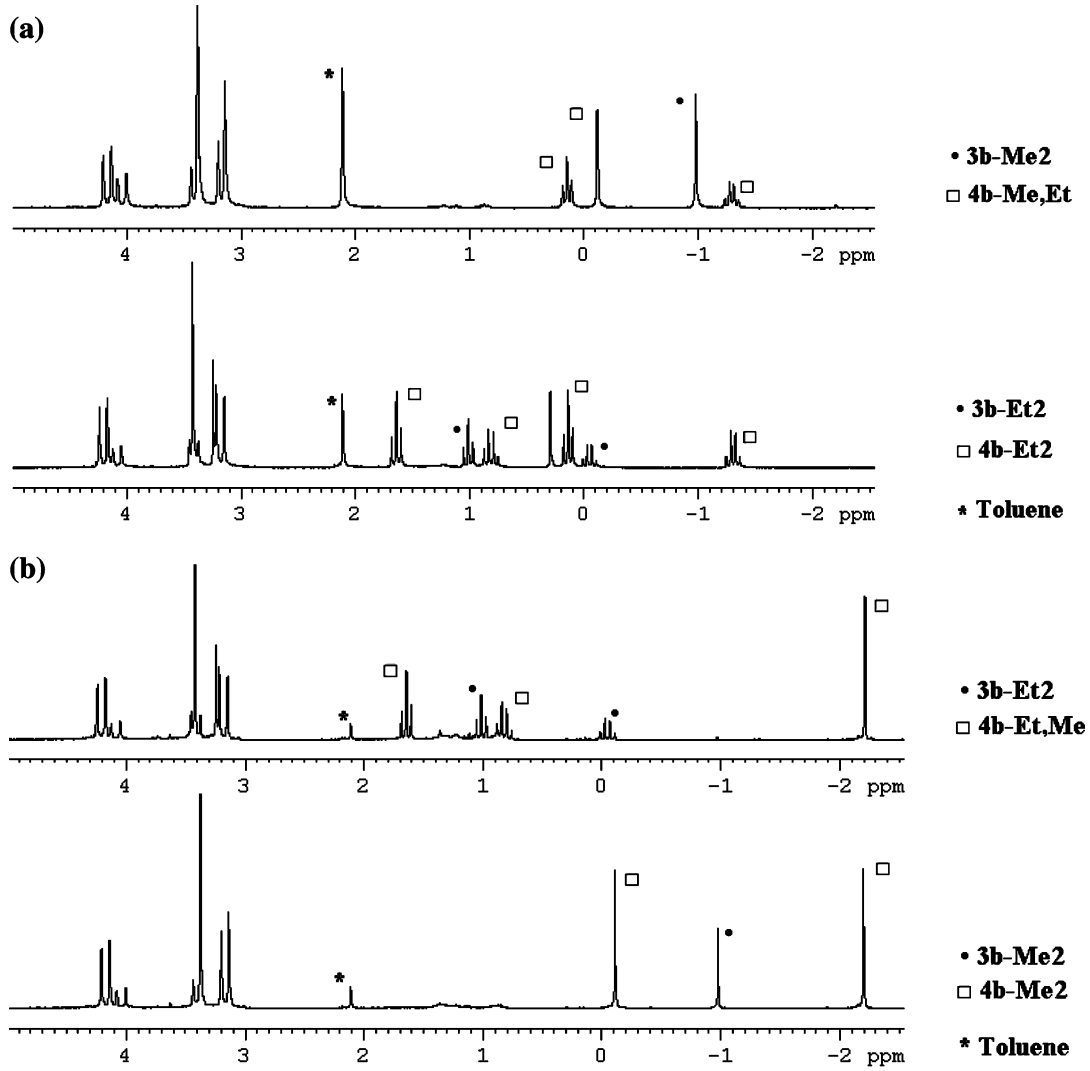


Figure 4. (a) Aliphatic region of the ^{1}H NMR spectrum of a mixture of **3b-Et2** and **4b-ET2** before (bottom) and after (top) the reaction with an excess of Me_2Zn. (b) Aliphatic region of the ^{1}H NMR spectrum of a mixture of **3b-Me2** and **4b-Me2** before (bottom) and after (top) the reaction with an excess of Et_2Zn.

Table 1

entry[a]	calix-arene ligand, **1**	R_2Zn, **2**	amt of R_2Zn, equiv	temp, °C	product ratio (**3**:**4**)
1	**1a**	Me_2Zn	2	23	3:7 (**3a-Me2**:**4a-Me2**)
2[b]	**1a**	Me_2Zn	2	23	4.5:5.5 (**3a-Me2**:**4a-Me2**)
3	**1a**	Me_2Zn	2	0	1:9 (**3a-Me2**:**4a-Me2**)
4	**1a**	Me_2Zn	6	23	1:9 (**3a-Me2**:**4a-Me2**)
5	**1a**	Me_2Zn	6	0	0.3:9.7 (**3a-Me2**:**4a-Me2**)
6	**1a**	Et_2Zn	2	23	8.5:1.5 (**3a-Et2**:**4a-Et2**)
7	**1b**	Et_2Zn	2	23	1:9 (**3b-Et2**:**4b-Et2**)
8	**1b**	Me_2Zn	2	23	1:9 (**3b-Me2**:**4b-Me2**)

[a] The reactions were performed under standard reaction conditions (see Experimental Section). [b] The reaction was performed in 10 mL of toluene (5× dilution).

factors must be considered in the preparation of calixarene inclusion complexes.

Experimental Section

All reactions were carried out under an inert atmosphere of purified nitrogen in an Innovative Technology glovebox. The solvents were dried prior to use. The NMR spectra were recorded in C_6D_6 at 25 °C using 200 or 400 MHz Avance Bruker spectrometers. **1a** was prepared according to a literature procedure.[15] One hundred percent conversion was achieved in all described syntheses. The conversion was monitored by ^{1}H NMR spectroscopy, with the ratio between the isomers determined by integration of the alkylzinc signals. In cases where signals of both isomers overlap, selected (unequivocally assigned) NMR data were given for the minor one. Table 1 contains the reaction conditions and product ratios. Elemental analyses were performed in the laboratory for microanalysis at the Hebrew University of Jerusalem.

General Procedure for the Synthesis of Complexes 3 and 4. To a solution of **1a** (5.0 mg, 0.0073 mmol) in 2 mL of toluene was added a solution of $ZnMe_2$ (9 μL, 0.018 mmol, 2 M in toluene), and the mixture was stirred overnight at room temperature. The solvent was evaporated under vacuum to give 6.1 mg (100%) of a 3:7 mixture of **3a-Me2** and **4a-Me2** (white solid). FAB-MS (*m/z*): found (calcd) for $C_{48}H_{64}O_4Zn_2$ 836 (836). Anal. Found (calcd) for $C_{48}H_{64}O_4Zn_2 \cdot C_5H_{12}$: C, 70.08 (70.11); H, 8.43 (8.44).

3a-Me2. Selected data are as follows. ^{1}H NMR (δ, ppm): −1.13 (6H, s, ZnCH_3), 1.25 (18H, s, ^{t}Bu), 1.40 (18H, s, ^{t}Bu), 3.19 (6H, s, OCH_3), 3.61 (4H, d, $^2J_{HH}$ = 15.4 Hz, CH_2), 4.22 (4H, d, $^2J_{HH}$ = 15.4 Hz, CH_2). ^{13}C NMR (δ, ppm): −16.03 (ZnCH$_3$), 59.40 (OCH$_3$).

4a-Me2. ^{1}H NMR (δ, ppm): −2.34 (3H, s, ZnCH_3), −0.05 (3H, s, ZnCH_3), 1.06 (18H, s, ^{t}Bu), 1.37 (18H, s, ^{t}Bu), 3.37 (4H, d, $^2J_{HH}$ = 13.7 Hz, CH_2), 3.46 (6H, s, OCH_3), 4.32 (4H, d, $^2J_{HH}$ = 13.7 Hz, CH_2), 7.21 (4H, m, Ar *H*), 7.28 (4H, s, Ar *H*). ^{13}C NMR (δ, ppm): −18.23 (ZnCH$_3$), −17.91 (ZnCH$_3$), 31.48, 32.09, (CMe_3), 34.29, 34.43 (CMe_3), 34.81 (CH_2), 60.84 (OCH$_3$); 126.45, 127.34, 130.66, 132.79, 141.96, 148.48, 153.80, 158.61 (all aromatic, s).

Complex **4a-Et2** was observed in ca. 15% yield in the crude form under the conditions reported in ref 9. ^{1}H NMR (δ, ppm): −1.48 (2H, q, $^2J_{HH}$ = 8.0 Hz, ZnCH_2CH$_3$), −0.05 (3H, t, $^3J_{HH}$ = 7.9 Hz, ZnCH$_2$CH_3), 0.87 (2H, q, $^2J_{HH}$ = 8.1 Hz, ZnCH_2CH$_3$), 1.13 (18H, s, ^{t}Bu), 1.37 (18H, s, ^{t}Bu), 1.70 (3H, t, $^3J_{HH}$ = 8.1 Hz, ZnCH$_2$CH_3), 3.37 (4H, d, $^2J_{HH}$ = 13.5 Hz, CH_2), 3.50 (6H, s, OCH_3), 4.36 (4H, d, $^2J_{HH}$ = 13.5 Hz, CH_2), 7.27−7.25 (4H, m, Ar *H*), 7.38 (4H, s, Ar *H*). ^{13}C NMR (δ, ppm): −5.31 (ZnCH$_2$-CH$_3$), −2.65 (ZnCH$_2$CH$_3$), 10.83 (ZnCH$_2$$CH_3$), 13.22 (ZnCH$_2$$CH_3$), 31.37, 32.15, (C$Me_3$), 34.73, 35.68 (C$Me_3$), 34.73 ($CH_2$), 61.38 (O$CH_3$); 126.44, 127.33, 130.30, 132.50, 141.10, 148.09, 153.89, 159.04 (all aromatic, s).

3b-Me2. Selected data are as follows. ^{1}H NMR (δ, ppm): −0.98 (6H, s, ZnCH_3), 3.14 (6H, s, OCH_3), 3.41 (4H, d (overlapped), CH_2), 4.04 (4H, d, $^2J_{HH}$ = 15.3 Hz, CH_2). ^{13}C NMR (δ, ppm): −15.14 (ZnCH$_3$), 34.53 (CH_2), 59.66 (OCH$_3$).

4b-Me2. ^{1}H NMR (δ, ppm): −2.20 (3H, s, ZnCH_3), −0.11 (3H, s, ZnCH_3), 3.17 (4H, d, $^2J_{HH}$ = 13.7 Hz, CH_2), 3.37 (6H, s, OCH_3), 4.17 (4H, d, $^2J_{HH}$ = 13.7 Hz, CH_2), 6.71−6.67 (4H, m, Ar *H*), 6.86−6.83 (4H, m, Ar *H*), 7.10−7.08 (4H, m, Ar *H*), 7.28 (4H, s, Ar *H*). ^{13}C NMR (δ, ppm): −18.06 (ZnCH$_3$), −17.00 (ZnCH$_3$), 33.71 (CH_2), 60.93 (OCH$_3$); 118.93, 126.77, 129.65, 129.98, 131.44, 133.43, 155.37, 160.75 (all aromatic, s). FAB-MS (*m/z*): found (calcd) for $C_{32}H_{32}O_4Zn_2$ 611 (611).

3b-Et2. Selected data are as follows. ^{1}H NMR (δ, ppm): −0.05 (4H, q, $^2J_{HH}$ = 8.1 Hz, ZnCH_2CH$_3$), 1.01 (6H, t, $^3J_{HH}$ = 8.1 Hz, ZnCH$_2$CH_3), 3.41 (4H, d, $^2J_{HH}$ = 15.5 Hz, CH_2), 3.24 (6H, s, OCH_3), 4.08 (4H, d, $^2J_{HH}$ = 15.5 Hz, CH_2). ^{13}C NMR (δ, ppm): 0.58 (ZnCH$_2$CH$_3$), 12.11 (ZnCH$_2$$CH_3$), 34.44 ($CH_2$), 60.12 (O$CH_3$).

4b-Et2. ^{1}H NMR (δ, ppm): −1.30 (2H, q, $^2J_{HH}$ = 7.9 Hz, ZnCH_2CH$_3$), 0.14 (3H, t, $^3J_{HH}$ = 7.9 Hz, ZnCH$_2$CH_3), 0.81 (2H, q, $^2J_{HH}$ = 8.1 Hz, ZnCH_2CH$_3$), 1.64 (3H, t, $^3J_{HH}$ = 8.1 Hz, ZnCH$_2$CH_3), 3.18 (4H, d, $^2J_{HH}$ = 13.6 Hz, CH_2), 3.42 (6H, s, OCH_3), 4.20 (4H, d, $^2J_{HH}$ = 13.6 Hz, CH_2), 6.74−6.83 (4H, m, Ar *H*), 6.94 (4H, d,$^2J_{HH}$ = 7.5 Hz, Ar *H*), 7.07 (4H, d,$^2J_{HH}$ = 7.5 Hz, Ar *H*). ^{13}C NMR (δ, ppm): −2.60 (ZnCH$_2$CH$_3$), 1.42 (ZnCH$_2$CH$_3$), 10.68 (ZnCH$_2$$CH_3$), 13.21 (ZnCH$_2$$CH_3$), 31.37, 32.15, (C$Me_3$), 33.67 ($CH_2$), 34.73, 35.68 (C$Me_3$), 61.41 (O$CH_3$); 118.90, 126.49, 129.65, 129.94, 131.17, 133.27, 155.54, 161.14 (all aromatic, s). FAB-MS (*m/z*): M − Et found (calcd) for $C_{34}H_{36}O_4Zn_2$ 611 (611). Anal. Found (calcd) for $C_{34}H_{36}O_4Zn_2$: C, 63.58 (63.87); H, 5.82 (5.67).

Complexes **4a-Et,Me**, **4b-Me,Et**, and **4b-Et,Me** were obtained by reacting a 10-fold excess of the dialkylzinc reagent at room temperature for 16 h with complexes **4a-Me2**, **4b-Et2**, and **4b-Me2**, respectively.

4b-Et,Me. ^{1}H NMR (δ, ppm): −2.21 (3H, s, ZnCH_3), 0.82 (2H, q, $^2J_{HH}$ = 8.1 Hz, ZnCH_2CH$_3$), 1.64 (3H, t, $^3J_{HH}$ = 8.1 Hz, ZnCH$_2$CH_3), 3.18 (4H, d, $^2J_{HH}$ = 13.7 Hz, CH_2), 3.42 (6H, s, OCH_3), 4.21 (4H, d, $^2J_{HH}$ = 13.7 Hz, CH_2), 6.65−7.11 (12H, m, Ar *H*). ^{13}C NMR (δ, ppm): −16.83 (ZnCH$_3$), −2.60 (ZnCH$_2$CH$_3$), 13.22 (ZnCH$_2$$CH_3$), 33.63 ($CH_2$), 61.40 (O$CH_3$); 118.91, 126.78, 129.65, 129.98, 131.33, 133.40, 155.48, 160.82 (all aromatic, s). FAB-MS (*m/z*): M − Et found (calcd) 597 (597); $C_{33}H_{34}O_4Zn_2$.

4b-Me,Et. ^{1}H NMR (δ, ppm): −1.29 (2H, q, $^2J_{HH}$ = 8.0 Hz ZnCH_2CH$_3$), −0.12 (3H, s, ZnCH_3), 0.15 (3H, t, $^3J_{HH}$ = 7.9 Hz ZnCH$_2$CH_3), 3.17 (4H, CH_2 overlapped with 6H, s, OCH$_3$ alternate cone), 3.38 (6H, s, OCH_3), 4.17 (4H, d, $^2J_{HH}$ = 13.6 Hz, CH_2), 6.72−7.10 (12H, m, Ar *H*). ^{13}C NMR (δ, ppm): −18.03 (ZnCH$_3$), −2.26 (ZnCH$_2$CH$_3$), 10.70 (ZnCH$_2$$CH_3$), 33.75 ($CH_2$), 60.94 (O$CH_3$); 118.93, 126.50, 129.66, 129.94, 131.28, 133.31, 155.42, 161.07 (all aromatic, s). FAB-MS (*m/z*): found (calcd) 625 (625); $C_{33}H_{34}O_4Zn_2$.

4a-Et,Me. ^{1}H NMR (δ, ppm): −2.37 (3H, s, ZnCH_3), 0.87 (2H, q, $^2J_{HH}$ = 8.1 Hz, ZnCH_2CH$_3$), 1.06 (18H, s, ^{t}Bu), 1.35 (18H, s, ^{t}Bu), 1.68 (3H, t, $^3J_{HH}$ = 8.1 Hz, ZnCH$_2$CH_3), 3.38 (4H, d, $^2J_{HH}$ = 13.7 Hz, CH_2), 3.50 (6H, s, OCH_3), 4.36 (4H, d, $^2J_{HH}$ = 13.6 Hz, CH_2), 7.20 (4H, s, Ar *H*), 7.28 (4H, s, Ar *H*). ^{13}C NMR (δ, ppm): −18.29 (ZnCH$_3$), −2.65 (ZnCH$_2$CH$_3$), 13.37 (ZnCH$_2$$CH_3$), 31.48, 32.08, (C$Me_3$), 34.22, 34.42 (C$Me_3$), 34.72 ($CH_2$), 61.34 (O$CH_3$); 126.40, 127.34, 130.53, 132.73, 140.91, 148.44, 153.92, 158.69 (all aromatic, s): FAB-MS (*m/z*): found (calcd) 850 (850); $C_{49}H_{66}O_4Zn_2$.

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Supporting Information Available: Crystallographic data for complexes **3a-Me2** and **4a-Me2** (CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

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