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Arylzinc Alkoxides: $[ArZnOCHPr^i_2]_2$ and $Ar_2Zn_3(OCHPr^i_2)_4$ When Ar = C_6H_5, *p*-$CF_3C_6H_4$, 2,4,6-$Me_3C_6H_2$, and C_6F_5

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From the reactions between diarylzinc compounds (Ar_2Zn) and the alcohol (Pr^i_2CHOH) in toluene, the compounds $[ArZn(OCHPr^i_2)]_2$ (Ar = C_6H_5, C_6F_5, *p*-$CF_3C_6H_4$, and 2,4,6-$Me_3C_6H_2$) have been isolated and shown to exist in equilibra with the trinuclear complexes $Ar_2Zn_3(OCHPr^i_2)_4$ and Ar_2Zn when Ar = C_6H_5, C_6F_5, and *p*-$CF_3C_6H_4$. The trinuclear complexes have also been prepared from reactions of the Ar_2Zn compounds with the alcohol, which reveals that the ease of Zn–C(aryl) bond cleavage is sensitive to the nature of the Ar group: C_6H_5 > 4-$CF_3C_6H_4$ > C_6F_5. The molecular structures of $Ar_2Zn_3(OCHPr^i_2)_4$ where Ar = *p*-$CF_3C_6H_4$ and C_6F_5 and $[ArZn(OCHPr^i_2)]_2$ where Ar = C_6F_5, *p*-$CF_3C_6H_4$, and 2,4,6-$Me_3C_6H_2$ are reported based on single-crystal X-ray diffraction studies. The X-ray structure of Zn(*p*-$CF_3C_6H_4)_2$ is also reported. The reactivity of these new compounds toward the polymerization of propylene oxide (PO) and the copolymerization of PO and CO_2 have been investigated along with related reactions involving the partial hydrolysis of the Ar_2Zn and R_2Zn compounds, where R = *t*-Bu, *n*-Bu, and *n*-Oct. These results are compared with the previous studies employing Et_2Zn as an organozinc precursor.

Introduction

Diethylzinc is commonly employed as a starting material in the synthesis of alkeneoxide polymers. Most typically, the diethylzinc is allowed to react with water or an alcohol to form the active catalyst precursor system. The first report of the formation of polypropylenecarbonate (PPC), which is the regular alternating copolymer derived from propylene oxide (PO) and carbon dioxide, appeared in 1969.[1] This was derived from the reaction between PO and CO_2 on a $ZnEt_2/H_2O$ catalyst system. Discrete ethylzinc alkoxide clusters were reported by Tsuruta and co-workers to be involved in the polymerization of *rac*-PO to give isotactic polypropyleneoxide, poly *R*- and poly *S*-PO.[2] In all of the polymerizations, the zinc−carbon bond is a spectator. This led us to question whether related diarylzinc complexes might prove useful as catalyst precursors since both steric and electronic factors could now be brought to bear influence on the nature of the active zinc site. In this paper, we describe our studies of the reactions of diarylzinc compounds (Ar_2Zn) with the sterically demanding alcohol Pr^i_2CHOH, which has led to the formation of mixed aryl zinc alkoxides,$((Ar)_aZn_b(OR)_c)$ where Ar = C_6H_5, *p*-$CF_3C_6H_4$, 2,4,6-$Me_3C_6H_2$, and C_6F_5. Also described are the reactions of these compounds toward PO polymerization and copolymerization with CO_2. Pertinent to the present study is the recent pioneering work of Darensbourg with zinc aryloxides and Coates' studies of β-diketonate zinc alkoxides in the copolymerization of epoxides and carbon dioxide.[3]

Experimental Section

General. All reactions were carried out under an atmosphere of N_2 purified over 4 Å molecular sieves. Standard vacuum line, Schlenk flasks, and N_2-atmosphere drybox techniques were employed. Toluene, diethyl ether (Et_2O), and tetrahydrofuran (THF) were distilled from purple solutions of sodium/benzophenone. 2-Bromomesitylene ($C_9H_{11}Br$), 4-bromobenzotrifluoride ($CF_3C_6H_4$-Br), bromopentafluorobenzene (C_6F_5Br), 1,4-dioxane ($C_4H_8O_2$), 2,4-dimethyl-3-pentanol [$HOCHPr^i_2$], and propylene oxide (C_3H_6O) were bought from Aldrich and dried by 4 Å molecular sieves. Mg

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pellets, $ZnCl_2$, 1.9 M PhLi solution in cyclohexane, 1.0 M Et_2Zn solution in hexane, and 2.5 M *n*-BuLi solution in hexane were purchased from Aldrich and used as received. $Zn(2,4,6\text{-}Me_3C_6H_2)_2$, $Zn(C_6F_5)_2$, $Zn(C_6H_5)_2$, $Zn[N(SiMe_3)_2]_2$, $(n\text{-}Bu)_2Zn$, $(t\text{-}Bu)_2Zn$, and $(n\text{-}Oct)_2Zn$ were prepared according to literature procedures.[4−9]

Elemental analyses were performed by Atlantic Microlab Inc. ^1H and ^{13}C {H} NMR experiments were carried out with a Bruker DPX-400 spectrometer equipped with a 5 mm broad-band probe. The sample concentration for polymers were 50 mg/mL in $CDCl_3$, and the parameters used were as follows: number of scans, NS = 2000, number of data point, TD = 65536. Gel permeation chromatography measurements were carried out on a Waters 1525 binary HPLC pump and Waters 410 differential refractometer equipped with styragel HR 2, HR 4, and HR 6 columns (100 and 10000 Å). The GPC was eluted with THF at 35 °C running at 1 mL/min and was calibrated using polystyrene standard. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF) was performed on a Bruker Reflex III mass spectrometer operated in linear, positive ion mode with a N_2 laser. 2,5-Dihydroxybenzoic acid (DHBA) was used as matrix.

Synthesis. (a) $(p\text{-}CF_3C_6H_4)_2Zn$. 5.0 g (22 mmol) of $CF_3C_6H_4$-Br in diethyl ether (Et_2O, 40 mL) at −78 °C was slowly added into 8.8 mL (2.5 M in hexane, 22 mmol) of *n*-BuLi dissolved in 40 mL of Et_2O. The mixture was stirred for 1 h under −78 °C before 1.5 g of $ZnCl_2$ (11 mmol) in Et_2O (100 mL) was added. The orange solution was warmed slowly to room temperature, stirred overnight, and then filtered to remove LiBr. Volatile solvent was removed under a dynamic vacuum, and the solid was purified by vacuum sublimation (110 °C/10^{-2} mbar), yielding a white solid, 2.6 g, 67%.

A single crystal was obtained by sublimation in a sealed glass tube (60−80 °C, 10^{-2} mbar). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.63 (d, $J = 7.6$, 4H, C_6H_4), 7.80 (d, $J = 7.6$, 4H, C_6H_4). $^{13}C\{H\}$ ($CDCl_3$, 100 MHz): δ 124.18, 124.31, 130.56, 137.76, 151.33. Anal. Calcd for $C_{14}H_8F_6Zn$: C, 47.29; H, 2.27. Found: C, 45.53; H, 2.19. EI−HRMS (*m*/*z*) calcd for $C_{14}H_8F_6Zn$: 353.9822. Found: 353.9841 (5.4 ppm).

(b) $(p\text{-}CF_3C_6H_4)_2Zn_2(OCHPr^i_2)_2$. To a solution of 1.06 g (3.0 mmol) of $(p\text{-}CF_3C_6H_4)_2Zn$ in toluene (20 mL) was slowly added 0.32 g (2.8 mmol) of $HOCHPr^i_2$ dissolved in toluene (30 mL). The solution was stirred for 1 h, and volatile components were removed under vacuum, yielding a white powder. The reaction was complete according to NMR spectroscopy. ^1H NMR (benzene-d_6, 400 MHz): δ 0.80 (d, $J = 6.7$, 12H, $CH(CH_3)_2$), 0.89 (d, $J = 6.7$, 12H, $CH(CH_3)_2$), 1.61 (m, 4H, $CH(CH_3)_2$), 3.22 (t, $J = 5.8$, 2H, CH), 7.50 (d, $J = 7.8$, 4H, CH), 7.58 (d, $J = 7.6$, 4H, CH). $^{13}C\{H\}$ (benzene-d_6, 100 MHz): δ 17.49, 20.31, 32.07, 85.98, 123.98, 124.37, 126.68, 129.38, 129.63, 129.95, 130.27, 130.58, 138.69, 150.47. Anal. Calcd for $C_{28}H_{38}O_2F_6Zn_2$: C, 51.63; H, 5.88. Found: C, 50.21; H, 5.79. EI−HRMS (*m*/*z*) calcd for $C_{28}H_{38}O_2F_5Zn_2$: 631.1344. Found: 631.1352 (1.3 ppm).

(c) $(p\text{-}CF_3C_6H_4)_2Zn_3(OCHPr^i_2)_4$. To a solution of 2.6 g (7.3 mmol) of $(p\text{-}CF_3C_6H_4)_2Zn$ dissolved in toluene (20 mL) was added 0.93 g (8.1 mmol) of $HOCHPr^i_2$ in 30 mL of toluene. The mixture was stirred for 1 day, and volatile components were removed under vacuum. The residue was re-dissolved by 20 mL of toluene and 0.5 g (4.3 mmol) of $HOCHPr^i_2$ in 10 mL of toluene was added. The solution was concentrated to saturation status and put in a refrigerator at −15 °C. Fine crystals were obtained. Yield: 1.0 g, 43%. ^1H NMR (benzene-d_6, 400 MHz): δ 0.95 (d, $J = 6.8$, 24H, $CH(CH_3)_2$), 1.05 (d, $J = 6.8$, 24H, $CH(CH_3)_2$), 1.80 (m, 8H, $CH(CH_3)_2$), 3.43 (t, $J = 5.6$, 4H, CH), 7.53 (d, $J = 7.5$, 4H, CH), 7.66 (d, $J = 7.5$, 4H, CH). $^{13}C\{H\}$ (benzene-d_6, 100 MHz): δ 18.91, 20.19, 33.05, 85.11, 124.26, 137.8, 154.23. Anal. Calcd for $C_{42}H_{68}O_4F_6Zn_2$: C, 53.26; H, 7.24. Found: C, 52.33; H, 7.04.

(d) $[2,4,6\text{-}(CH_3)_3C_6H_2]_2Zn_2(OCHPr^i_2)_2$. In a solution of 1.26 g (4.1 mmol) of $[2,4,6\text{-}(CH_3)_3C_6H_2]_2Zn$ in 50 mL of toluene was added 0.44 g (3.8 mmol) of $HOCHPr^i_2$ in 50 mL of toluene slowly. The mixture was stirred overnight and filtered, and the filtrate was evaporated under vacuum. Yield: 1.0 g, 80%. ^1H NMR (benzene-d_6, 400 MHz): δ 0.78 (d, $J = 6.7$, 12H, $CH(CH_3)_2$), 0.99 (d, $J = 6.7$, 12H, $CH(CH_3)_2$), 1.57 (m, 4H, $CH(CH_3)_2$), 2.23 (s, 6H, CH_3), 2.55 (s, 12H, CH_3), 3.16 (t, $J = 5.9$, 2H, CH), 6.92 (s, 4H, CH). $^{13}C\{H\}$ (benzene-d_6, 100 MHz): δ 18.08, 20.30, 21.28, 28.45, 32.15, 84.80, 126.37, 137.13, 144.32, 146.42. Anal. Calcd for $C_{32}H_{52}O_2Zn_2$: C, 64.11; H, 8.74. Found: C, 61.85; H, 8.64. EI−HRMS(*m*/*z*) calcd for $C_{32}H_{52}O_2Zn_2$: 598.2519; found: 598.2538 (3.2 ppm).

(e) $(C_6F_5)_2Zn_2(OCHPr^i_2)_2$. To the solution of 0.5 g (1.2 mmol) of $(C_6F_5)_2Zn$ in 20 mL of toluene was added 0.13 g (1.1 mmol) of $HOCHPr^i_2$ in 20 mL of toluene. Mixture was stirred for 1 h, and the volatile components were removed under vacuum. As deduced by NMR spectroscopy, the reaction was complete. ^1H NMR (benzene-d_6, 400 MHz): δ 0.74 (d, $J = 6.7$, 12H, $CH(CH_3)_2$), 0.91 (d, $J = 6.7$, 12H, $CH(CH_3)_2$), 1.56 (m, 4H, $CH(CH_3)_2$), 3.27 (t, $J = 5.8$, 2H, CH). $^{13}C\{H\}$ (benzene-d_6, 100 MHz): δ 17.24, 20.04, 31.72, 86.08, 136, 138.5, 147.59, 150.07. Anal. Calcd for $C_{26}H_{30}O_2F_{10}Zn_2$: C, 44.92; H, 4.35; F, 27.33. Found: C, 44.05; H, 4.28; F, 26.58.

(f) $(C_6F_5)_2Zn_3(OCHPr^i_2)_4$. To the solution of 0.44 g (1.2 mmol) of $(C_6F_5)_2Zn$ in 10 mL of toluene was added 0.26 g (2.2 mmol) of $HOCHPr^i_2$ directly. The mixture was heated to 85 °C and kept for 20 h. The volatile components were removed under vacuum. NMR spectroscopy showed that 95% of $(C_6F_5)_2Zn_2(OCHPr^i_2)_2$ was converted to $(C_6F_5)_2Zn_3(OCHPr^i_2)_4$. ^1H NMR (benzene-d_6, 400 MHz): δ 0.94 (d, $J = 6.8$, 24H, $CH(CH_3)_2$), 1.04 (d, $J = 6.8$, 24H, $CH(CH_3)_2$), 1.74 (m, 8H, $CH(CH_3)_2$), 3.43 (t, $J = 5.6$, 4H, CH). $^{13}C\{H\}$ (benzen-d_6, 100 MHz): δ 18.58, 19.93, 33.12, 85.44. Anal. Calcd for $C_{40}H_{60}O_4F_{10}Zn_3$: C, 48.48; H, 6.10; F, 19.17. Found: C, 45.63; H, 5.77; F, 19.18.

(g) $(C_6H_5)_2Zn_2(OCHPr^i_2)_2$. To a solution of 1.05 g (4.5 mmol) of $(C_6H_5)_2Zn$ in toluene (20 mL) was slowly added 0.50 g (4.3 mmol) of $HOCHPr^i_2$ dissolved in toluene (30 mL). The solution was stirred for 1 h, and volatile components were removed under vacuum, yielding a white powder. The reaction was complete according to NMR spectroscopy. ^1H NMR (benzene-d_6, 400 MHz): δ 0.84 (d, $J = 6.7$, 12H, $CH(CH_3)_2$), 0.96 (d, $J = 6.7$, 12H, $CH(CH_3)_2$), 1.70 (m, 4H, $CH(CH_3)_2$), 3.34 (t, $J = 5.8$, 2H, CH), 7.26 (m, 2H, C_6H_5), 7.34 (m, 4H, C_6H_5), 7.74 (m, 4H, C_6H_5). $^{13}C\{H\}$ (benzene-d_6, 100 MHz): δ 17.74, 20.48, 32.29, 85.93, 128.12, 128.36, 138.98, 145.69. Anal. Calcd for $C_{26}H_{40}O_2Zn_2$: C, 60.59; H, 7.82. Found: C, 57.45; H, 7.41. EI−HRMS(*m*/*z*) calcd for $C_{26}H_{40}O_2Zn_2$: 514.1580; found: 514.1628 (9.3 ppm).

(h) $(C_6H_5)_2Zn_3(OCHPr^i_2)_4$. To a solution of 0.53 g (2.4 mmol) of $(C_6H_5)_2Zn$ in toluene (20 mL) was added 0.56 g (4.8 mmol) of $HOCHPr^i_2$ dissolved in toluene (30 mL). The mixture was stirred

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for 1 day, and volatile components were removed under vacuum, yielding a white powder. NMR indicated 97% conversion. By recrystallization 0.30 g of crystalline sample was obtained, 61%.

^{1}H NMR (benzene-d_6, 400 MHz): δ 0.97 (d, $J = 6.8$, 24H, CH(CH$_3$)$_2$), 1.11 (d, $J = 9.4$, 24H, CH(CH$_3$)$_2$), 1.90 (m, 8H, CH(CH$_3$)$_2$), 3.48 (t, $J = 5.6$, 4H, CH), 7.22 (m, 2H, C$_6$H$_5$), 7.34 (t, $J = 7.5$, 4H, C$_6$H$_5$). 7.77 (m, 4H, C$_6$H$_5$). ^{13}C{H} (benzen-d_6, 100 MHz): δ 19.10, 20.22, 33.14, 85.07, 127.57, 128.19, 137.92, 148.99. Anal. Calcd for $C_{40}H_{70}O_4Zn_3$: C, 59.23; H, 8.70. Found: C, 56.23; H, 8.49. EI−HRMS(*m*/*z*) calcd for $C_{33}H_{55}O_3Zn_3$: 693.1994; found: 693.2002 (1.2 ppm).

Attempted Preparation of $[Zn(OR)_2]_a$. To pure 1.0 g (2.6 mmol) of $Zn[N(SiMe_3)_2]_2$ was added 1.5 g (12.9 mmol) of $HOCHPr^{i}_{2}$ (no solvent was used). The resulting mixture was stirred for 3 days, and the volatile components were removed under vacuum, yielding a white solid, 0.6 g. ^{1}H NMR (benzene-d_6, 400 MHz): δ 1.05 (m, CH(C*H*$_3$)$_2$), 1.16 (m, CH(C*H*$_3$)$_2$), 1.89 (m, C*H*(CH$_3$)$_2$), 1.98 (m, C*H*(CH$_3$)$_2$), 3.28 (t, 1H, OCH), 3.37 (t, 1H, OCH), 3.42 (t, 1H, OCH), 3.50 (t, 1H, OCH). ^{13}C{H} (benzen-d_6, 100 MHz): 17.99, 19.10, 19.12, 19.27, 19.95, 20.73, 20.88, 21.92, 32.84, 33.55, 34.65, 35.11, 84.43, 84.74, 84.87. Anal. Calcd for $C_{14}H_{30}O_2Zn$: C, 56.85; H, 10.22. Found: C, 51.77; H, 9.50.

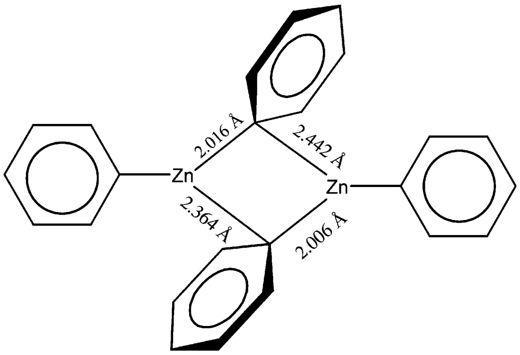
Copolymerization Studies. The compounds prepared above were all evaluated for the copolymerization of propylene oxide and carbon dioxide. As a comparison, the compounds (p-CF$_3$C$_6$H$_4$)$_2$Zn, Zn(2,4,6-Me$_3$C$_6$H$_2$)$_2$, Zn(C$_6$F$_5$)$_2$, Zn(C$_6$H$_5$)$_2$, (n-Bu)$_2$Zn, (t-Bu)$_2$Zn, (n-Oct)$_2$Zn, and Et$_2$Zn were also each allowed to react with H$_2$O in the ratio of 1:1 in three different solvents: 1,4-dioxane, diethyl ether, and tetrahydrofuran. The volatile components in those reaction mixtures were removed under vacuum, and the residues were then used as polymerization reagents. All the copolymerization reactions were carried out by employing 50 mg of the solid catalysts with 2 mL of propylene oxide under a pressure of carbon dioxide (60 bar) at 60 °C in a 45-mL autoclave fitted with a magnetic stirrer for 20 h. Yields of products were determined by ^{1}H NMR spectroscopy; the results are listed in Table 4.

Homopolymerization Studies. 50 mg of each complex $[ArZn(OCHPr^{i}_{2})]_2$ and $Ar_2Zn_3(OCHPr^{i}_{2})_4$ was added to 2 mL of propylene oxide at 60 °C in a 45-mL autoclave fitted with a magnetic stirrer for 20 h. 50 mg of corresponding hydrolyzed Ar$_2$Zn (with ratio Ar$_2$Zn: H$_2$O = 1:1) described previously were also prepared in THF and used as heterogeneous catalysts with 2 mL of propylene oxide in Schlenk flasks, stirring for 20 h. Yield of products were estimated by ^{1}H NMR spectroscopy.

X-ray Crystallography. All the crystals are clear and colorless. All work was done on a Nonius Kappa CCD diffractometer with Mo Kα radiation at either 150 or 200 K using an Oxford Cryosystems Cryostream Cooler. A combination of ϕ and ω scans with a frame width of 1.0 was used, and highly redundant data sets were measured. Data integration was done with Denzo.[10] Scaling and merging of the data were done with Scalepack.[10] The structures were solved by the Patterson method or by direct methods in SHELXS-86.[10] The rest of the non-hydrogen atoms were located by standard Fourier methods. Full-matrix least-squares refinements based on F2 were performed in SHELXL-93.[10] Neutral atom scattering factors were used and include terms for anomalous dispersion.

Results and Discussion

Synthesis. The diarylzinc precursors Ar$_2$Zn, where Ar = C$_6$H$_5$, C$_6$F$_5$, and 2,4,6-Me$_3$C$_6$H$_2$, were known compounds and the new compound (p-CF$_3$C$_6$H$_4$)$_2$Zn was prepared similarly. This series was selected from considerations of their electron-releasing properties and also the steric hindrance around the zinc center. Most organozinc compounds of the form ZnR$_2$ are linear including (C$_6$F$_5$)$_2$Zn and (2,4,6-Me$_3$C$_6$H$_2$)$_2$Zn.[4] However, diphenylzinc has a dimeric structure in the solid-state as a result of weak Zn···C(ipso) bonds of the type schematically represented by **1**.[5] It was, therefore, of interest to us to determine the influence of the p-CF$_3$ group on the solid-state molecular structure of (p-CF$_3$C$_6$H$_4$)$_2$Zn and that is reported later in this work.



A

$[ArZn(OCHPr^{i}_{2})]_2$. The reactions between Ar$_2$Zn and 1 equiv of the alcohol in toluene at room temperature in all cases yielded $[ArZn(OCHPr^{i}_{2})]_2$ compounds as white air-sensitive, crystalline solids that were readily soluble in benzene and toluene. The compound where Ar = p-CF$_3$C$_6$H$_4$ was unstable in solution and existed in equilibrium with Ar$_2$Zn and Ar$_2$Zn$_3$(OR)$_4$ (eq 1):

$$Ar_2Zn + Ar_2Zn_3(\mu\text{-}OR)_4 = 2[Ar_2Zn_2(\mu\text{-}OR)_2] \qquad (1)$$

For Ar = CF$_3$C$_6$H$_4$, the trinuclear compound was notably less soluble in toluene which impedes the crystallization of the dimeric compound Ar$_2$Zn$_2$(OR)$_2$. Mixing pure Ar$_2$Zn and Ar$_2$Zn$_3$(OR)$_4$ yields the dimeric compounds Ar$_2$Zn$_2$(OR)$_2$, as judged by ^{1}H NMR spectroscopy, when Ar = p-CF$_3$C$_6$H$_4$.

$Ar_2Zn_3(OCHPr^{i}_{2})_4$. The compounds $Ar_2Zn_2(OCHPr^{i})_2$ react further with the diisopropylmethanol in toluene in a manner that reflects upon the electronic and steric properties of the aryl group. For Ar = C$_6$H$_5$, C$_6$F$_5$, and p-CF$_3$C$_6$H$_4$, the trinuclear complex is the kinetic product; its rate of formation follows the order C$_6$H$_5$ > p-CF$_3$C$_6$H$_4$ > C$_6$F$_5$. Indeed, whereas the compound $(C_6H_5)_2Zn_3(OCHPr^{i}_{2})_4$ is formed in toluene at room temperature within 1 day (>90% conversion), the related pentafluorophenyl derivative requires heating to 90 °C for an equivalent period. In the case of Ar = 2,4,6-Me$_3$C$_6$H$_2$, a trinuclear complex could not be isolated because further alcoholysis occurred to give what we

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Table 1. Summary of Crystallographic Data

	1	2	3	4	5	6
formula	$C_{14}H_8F_6Zn$	$C_{28}H_{38}F_6O_2Zn_2$	$C_{32}H_{52}O_2Zn_2$	$C_{26}H_{30}F_{10}O_2Zn_2$	$C_{42}H_{68}F_6O_4Zn_3$	$C_{40}H_{60}F_{10}O_4Zn_3$
fw	355.57	651.32	599.48	695.24	947.07	990.99
temp (K)	200	15	150	200	150	200
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	9.9007(1)	11.8764(1)	8.1374(1)	7.8035(1)	12.4100(1)	19.3632(1)
b (Å)	14.1319(2)	21.9804(3)	22.4401(3)	9.7433(1)	14.2090(1)	15.4720(1)
c (Å)	9.9475(2)	12.3577(2)	8.8604(1)	11.0728(1)	14.7423(1)	16.4475(1)
α (deg)				114.135(1)	75.629(1)	
β (deg)	106.245(1)	109.728(1)	92.628(1)	95.441(1)	69.088(1)	110.604(1)
γ (deg)				104.636(1)	76.624(1)	
V (Å^3)	1336.24(4)	3036.61(7)	1616.24(3)	724.403(14)	2322.89(3)	4612.28(5)
Z	4	4	2	1	2	4
d (calcd) (g/cm^3)	1.767	1.425	1.232	1.594	1.354	1.427
abs coeff (mm^{-1})	1.896	1.639	1.508	1.742	1.597	1.624
crystal Size (mm^3)	0.12 × 0.12 × 0.23	0.35 × 0.38 × 0.38	0.04 × 0.19 × 0.27	0.15 × 0.23 × 0.31	0.08 × 0.27 × 0.35	0.19 × 0.35 × 0.38
θ range	2.57−27.43	2.04−27.48	2.47−27.49	2.42−27.50	2.08−27.51	2.25−27.49
reflns collected	25180	58774	32103	18855	59944	91848
independent reflns	3052	6948	3705	3322	10640	10580
GOF on F^2	1.038	1.041	1.042	1.044	1.031	1.048
R1(F)^a (all data)	0.0589	0.0485	0.0357	0.0292	0.0642	0.0467
wR2(F^2)^a (all data)	0.1165	0.0736	0.0664	0.0627	0.1141	0.0877

[a] $R1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2(F^2) = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$. [b] For data collection.

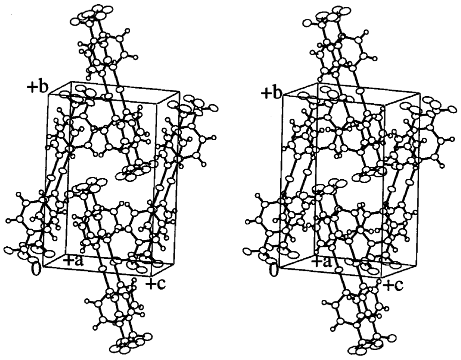

Figure 1. Arrangement of $Zn(p\text{-}CF_3C_6H_4)_2$ in unit cell.

presume to be the ultimate thermodynamic product $[Zn(OR)_2]_n$. Further alcoholysis employing Pr^i_2CHOH and the other trinuclear arylalkoxides is much slower.

The $Ar_2Zn_3(\mu\text{-}OCHPr^i_2)_4$ compounds are white air-sensitive crystalline solids and must be handled in dry solvents. All of the compounds react with their respective Ar_2Zn compounds to produce the dimeric compounds $Ar_2Zn_2(OR)_2$, as predicted by eq 1.

$[Zn(OR)_2]_a$ Where R = Pr^i_2CH. The ultimate product of alcoholysis would be a compound of formula $Zn(OR)_2$, few of which are known and none has been structurally characterized.[12] Because of the ambiguity in the ultimate product in the reaction between dimesitylzinc and diisopropylmethanol, we examined the reaction between solid $Zn(NSi_2Me_6)_2$ and the neat alcohol Pr^i_2CHOH. This gave a white solid that we formulate as $[Zn(OR)_2]_{2.8}$ ZnO based on elemental analysis, infrared, and ^1H NMR spectroscopy. In the ^1H NMR, there are at least three types of OR groups. We can say little more about the nature of this compound beyond that it is nonvolatile but soluble in benzene. Because of the low carbon elemental composition, we propose it is an oxo alkoxide and exists as an aggregate.

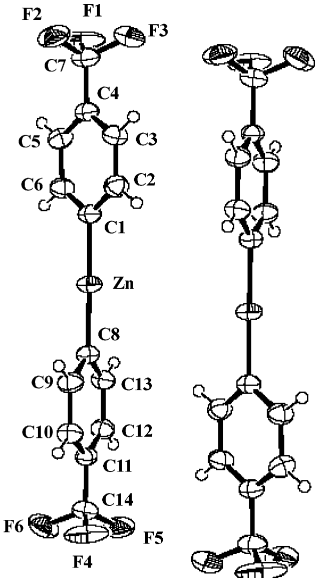

Figure 2. Intermolecular interactions of $Zn(p\text{-}CF_3C_6H_4)_2$.

Spectroscopic Characterization Data. The ^1H and ^{13}C NMR and mass spectral data for the new compounds are given in the Experimental Section. We note that none of the new compounds give satisfactory carbon elemental analysis. This is quite puzzling as in all other respects the samples prepared by crystallization appear quite pure and even the proton and fluorine EA data are acceptable. The carbon analyses are 1−3% low. Yet the compounds show molecular ions in the mass spectrometer.

Solid-State and Molecular Structures. A summary of crystallographic data is given in Table 1.

$Zn(p\text{-}CF_3C_6H_4)_2$. The molecule contains a near linear C−Zn−C central moiety, 178.50(9)°, with Zn−C = 1.939(2) Å. The molecules are arranged in rows in the solid-state as shown in the stereo unit cell drawing in Figure 1. Within each row, the intermolecular interactions involve aryl CH···aryl π bonding as shown in Figure 2. Thus, in contrast

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(11) Chisholm, M. H.; Gallucci, J.; Phomphrai, K. *Inorg. Chem.* **2002**, *41* (10), 2785−2794.

(12) Su, K.; Tilley, T. D.; Sailor, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 3459−3468.

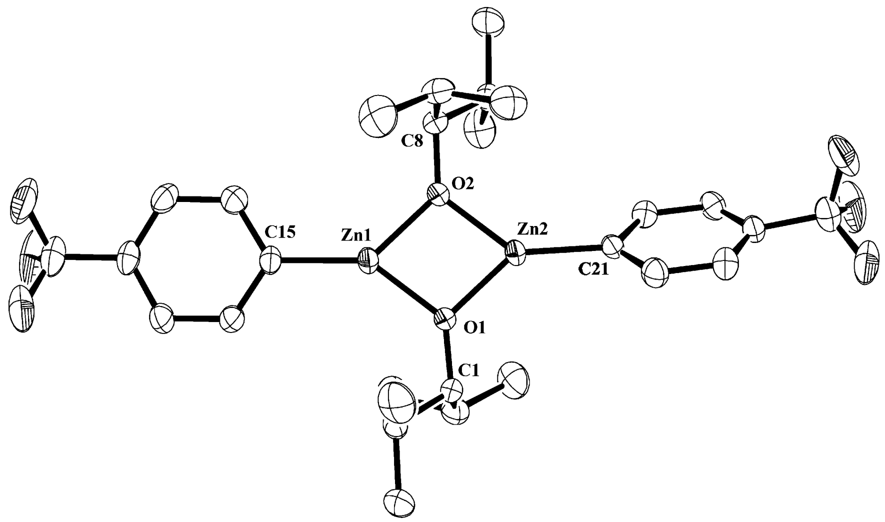

Figure 3. ORTEP drawing of complex $[CF_3C_6H_4Zn(OCHPr^i_2)]_2$ with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

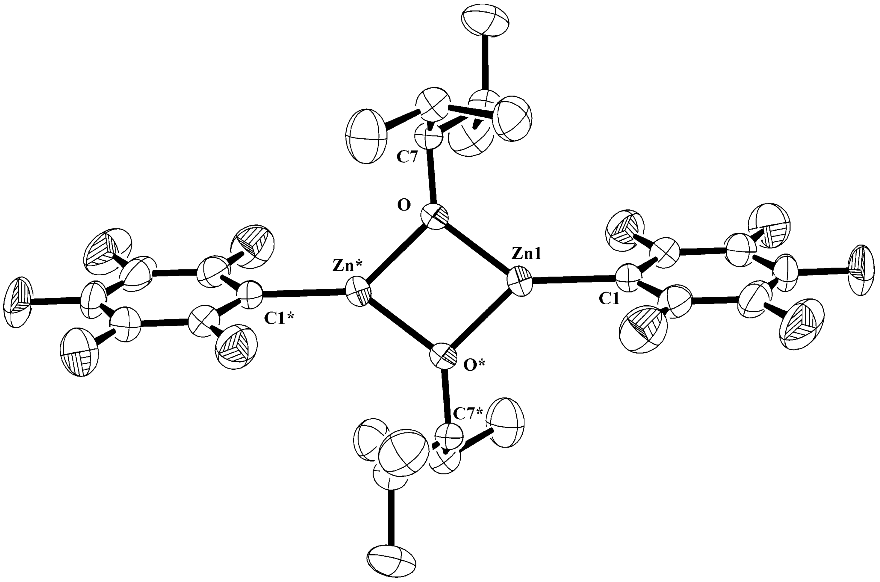

Figure 4. ORTEP drawing of complex $(C_6F_5)_2Zn_2(OCHPr^i_2)_2$ with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

to $Zn(C_6H_5)_2$, there are no short intermolecular Zn···C interactions of the type shown in **1**.[5]

$[ArZn(OCHPr^i_2)]_2$ Where Ar = *p*-$CF_3C_6H_4$, C_6F_5, and 2,4,6-$Me_3C_6H_2$. These three compounds share a common structure involving two three-coordinate zinc atoms united by a pair of alkoxide bridges. In the solid-state when Ar = C_6F_5 and 2,4,6-$Me_3C_6H_2$, there is a crystallographically imposed center of inversion. This is not the case for Ar = *p*-$CF_3C_6H_4$ whose molecular structure is shown in Figure 3. Selected bond distances and angles for these related compounds are given in Table 2. The Zn−C distances are all very similar, 1.942(3) Å (avg) and are mostly slightly longer than the Zn−O distances that fall in the range of 1.91−1.95 Å. These Zn−μ-O distances are notably longer than the Zn−O (terminal) distance of 1.800(5) Å in the three coordinate complex CH(CMeN−2,6-$Pr^i_2C_6H_3)_2Zn(O^tBu)$.[11] The O−Zn−O angles ca. 81° are notably smaller than the O−Zn−C angles, which range from 132 to 148°. Those structures resemble the architecture of the dimer zinc and cadmium bis-aryloxides reported by Darensbourg for Ar = 2,6-$^tBuC_6H_3$.[13]

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[ArZn(OCHPr^i_2)]_2$

Complex $[CF_3C_6H_4\,Zn(OCHPr^i_2)]_2$			
Zn(1)−O(1)	1.923(1)	Zn(1)−O(2)	1.926(1)
Zn(1)−C(15)	1.944(2)		
O(1)−Zn(1)−O(2)	80.77(5)	O(1)−Zn(1)−C(15)	142.92(7)
O(2)−Zn(1)−C(15)	136.30(7)	C(15)−Zn(1)−Zn(2)	176.74(6)
C(1)−O(1)−Zn(1)	132.13(10)	Zn(1)−O(1)−Zn(2)	99.49(5)
Complex $[C_6F_5Zn(OCHPr^i_2)]_2$			
Zn−O*	1.911(1)	Zn−O	1.913(1)
Zn−C(1)	1.940(2)		
O*−Zn−O	81.65(4)	O*−Zn−C(1)	137.37(5)
O−Zn−C(1)	140.98(5)	C(1)−Zn−Zn*	178.14(5)
C(7)−O−Zn	131.19(9)	Zn−O−Zn*	98.36(4)
Complex $[2,4,6\text{-}Me_3C_6H_2(OCHPr^i_2)]_2$			
Zn−O	1.916(1)	Zn−C(1)	1.945(2)
Zn−O*	1.955(1)		
O*−Zn−O	80.07(5)	O−Zn−C(1)	147.62(6)
O*−Zn−C(1)	131.97(6)	C(1)−Zn−Zn*	170.78(5)
C(10)−O−Zn	132.6(1)	Zn−O−Zn*	99.93(5)

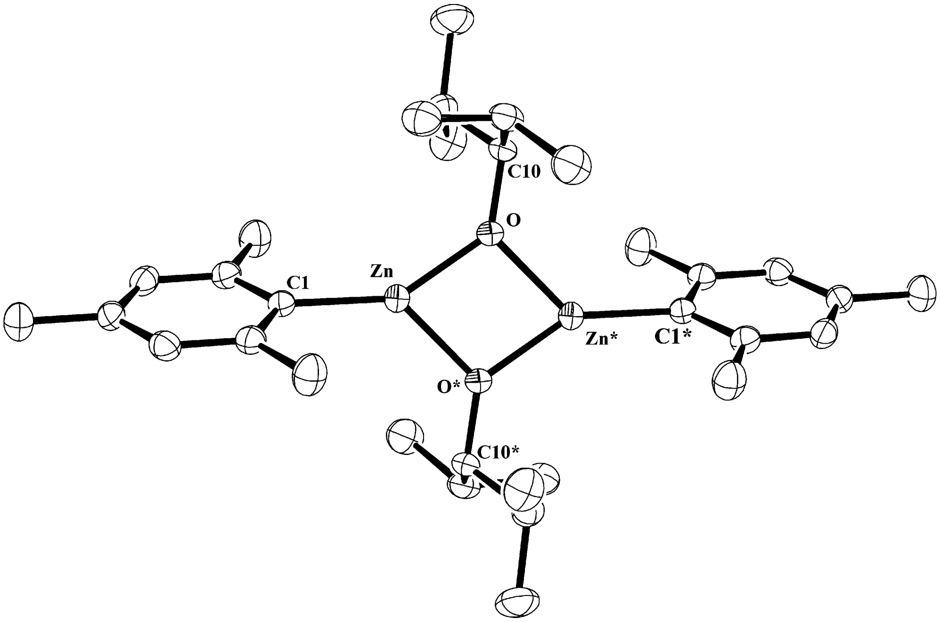

Figure 5. ORTEP drawing of complex $[2,4,6\text{-}(CH_3)_3C_6H_2]_2Zn_2(OCHPr^i_2)_2$ with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

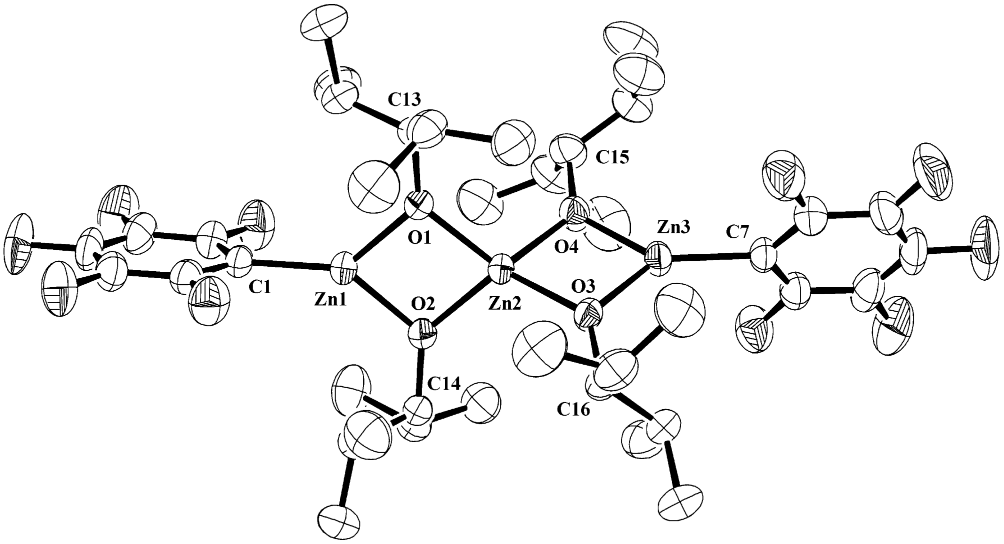

Figure 6. ORTEP drawing of complex $(C_6F_5)_2Zn_3(OCHPr^i_2)_4$ with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

$Ar_2Zn_3(OCHPr^i_2)_4$, Where Ar = p-$CF_3C_6H_4$ and C_6F_5. These two structures are very similar, and that of the pentafluorophenyl complex is given in Figure 6. The central zinc(2+) ion is four-coordinate in a pseudo-tetrahedral environment, while the outer zinc ions are three-coordinate and closely resemble those seen in the molecular structures of the $[ArZn(OR)]_2$ compounds just described. A summary of bond distances and bond angles is given in Table 3.

Copolymerization of Propylene Oxide and Carbon Dioxide. The arylzinc alkoxides are inactive in the copolymerization of PO and CO_2 at 60 °C and 20 h. For $(CF_3C_6H_4)_2Zn_2(OR)_2$, $(C_6F_5)_2Zn_2(OR)_2$, and $(C_6F_5)_2Zn_3(OR)_4$ no polypropylenecarbonate (PPC) was obtained; for $(CF_3C_6H_4)_2Zn_3(OR)_4$, $(C_9H_{11})_2Zn_2(OR)_2$, $Ph_2Zn_2(OR)_2$, and $Ph_2Zn_3(OR)_4$, the yield of PPC was barely detectable (<1%). Each reaction produced cyclic propylene carbonate (PC) with yields varying from a trace amount for $(C_6F_5)_2Zn_2(OR)_2$ to 12% for $Ph_2Zn_2(OR)_4$. Thus $Ar_2Zn_x(OR)_y$ are not comparable to Darensbourg's $Zn(OAr)_2(THF)_2$ catalysts, which gave 1441 g of polymer/g of Zn in copolymerization of cyclohexene oxide (CHO) and CO_2, and 100% PC for PO and CO_2 reactions.[3f,13]

As a comparison, corresponding partially hydrolyzed Ar_2Zn (Ar_2Zn:H_2O = 1:1) in three different solvents were studied as catalyst precursors under similar reaction conditions. Results are listed in Table 4. Hydrolyzed Ph_2Zn, which was prepared in THF, resulted in the highest PPC yield of 33% with 4% cyclic carbonate and 10% polyether linkage. A similar catalyst precursor prepared in dioxane gave the second highest PPC yield of 24%. Other hydrolyzed aryl

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(13) Darensbourg, D. J.; Wildeson, J. R.; Lewis, S. J.; Yarbrough, J. C. *J. Am. Chem. Soc.* **2002**, *124* (24), 7075−7083.

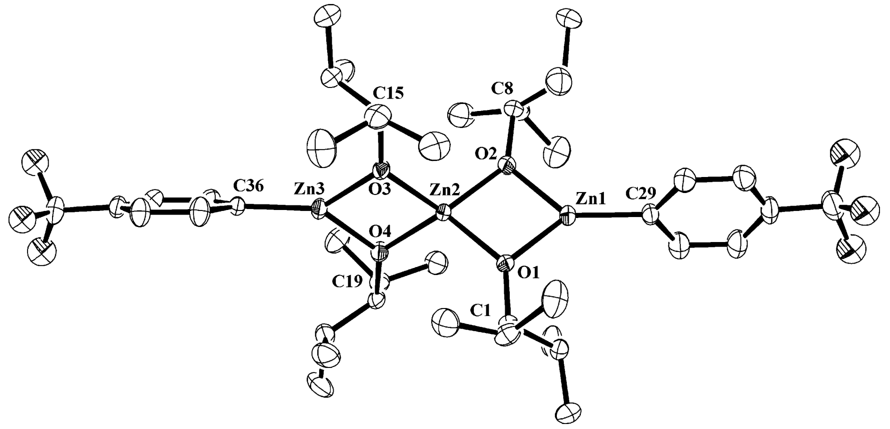

Figure 7. ORTEP drawing of complex $(p\text{-}CF_3C_6H_4)_2Zn_3(OCHPr^i_2)_4$ with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

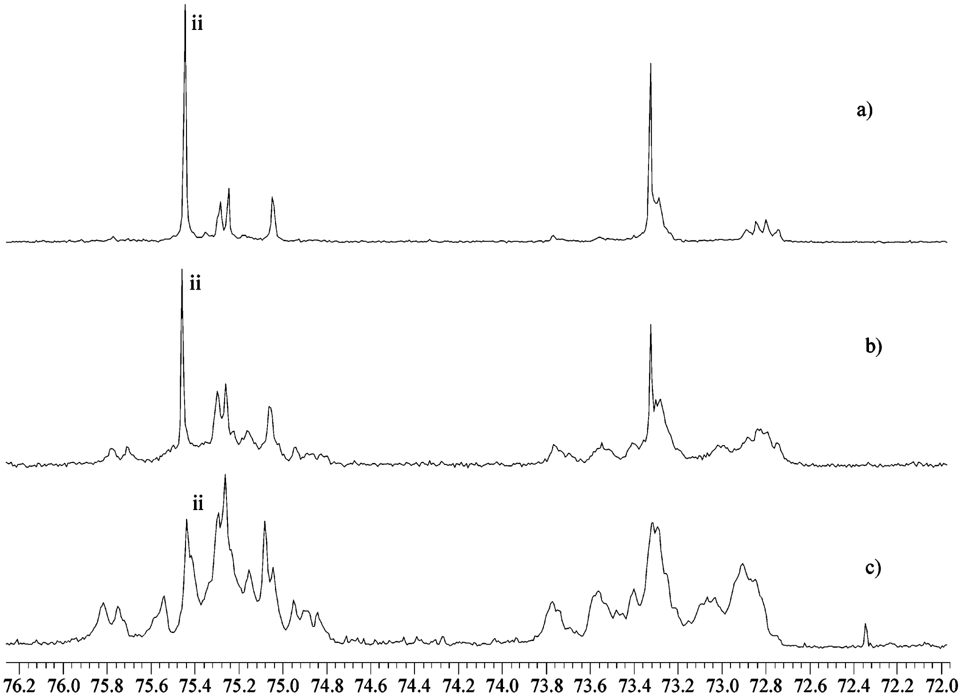

Figure 8. $^{13}C\ \{^1H\}$ NMR of PPO prepared with $Ar_2Zn + H_2O$ (1:1) at CH and CH_2 region. (a) By $(C_6H_6)_2Zn + H_2O$. (b) By $(p\text{-}CF_3C_6H_4)_2Zn + H_2O$. (c) By $(C_6F_5)_2Zn + H_2O$.

zinc compounds resulted in PPC in yields that ranged from 0% for $(C_6F_5)_2Zn + H_2O$ prepared in THF to 16% for $(CF_3C_6H_4)_2Zn + H_2O$ prepared in Et_2O. By looking at the reactions with the highest PPC yield for each Ar_2Zn, it can be concluded from the ratio of polyether versus polycarbonate linkages that electron-donating aryl groups favor incorporation of CO_2 and copolymer formation. There is, however, no obvious relationship between solvents and the yields of PPC. Results of copolymerization reactions catalyzed by $R_2Zn + H_2O$ (R= Et, n-Bu, t-Bu, *n*-Oct) in three solvents, THF, Et_2O, dioxane, are also listed in Table 4.

The long-chain catalyst precursor, $(n\text{-}Oct)_2Zn + H_2O$, resulted in the highest PPC yield of 11% when THF was used, and the yield decreased with the solvent sequence THF > Et_2O > dioxane. In contrast $(n\text{-}Bu)_2Zn + H_2O$ yielded 19% PPC in dioxane and only a trace in THF. $(t\text{-}Bu)_2Zn + H_2O$ and $Et_2Zn + H_2O$ each gave similar PPC yields for all three solvents.

The regiosequence of the PPC prepared by partially hydrolyzed Ar_2Zn or R_2Zn precursors was determined by looking at the $^{13}C\ \{^1H\}$ NMR spectra of the carbonate carbon signals.[14] It is surprising to see that the ratio of the TT:HT:HH junction for all PPC samples are close to 1:5:1, and thus ring-opening probability at the β-position, the methylene carbon of PO during PPC formation, is calculated to be 0.8. This fact suggests that for copolymerization, the active zinc centers have similar steric and electronic structures when they activate and ring open PO. In other words, for hydrolyzed aryl or alkyl zinc systems, only certain sites are active, and these are not significantly influenced by the initial R or Ar group.

Homopolymerization of Propylene Oxide. Unlike the copolymerization reactions noted above, the homopolymer-

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[14] (a) Chisholm, M. H.; Navarro-Llobet, D.; Zhou, Z. *Macromolecules* **2002**, *35* (17), 6494−6504. (b) Lednor, P. W.; Rol, N. C. *J. Chem. Soc., Chem. Commun.* **1985**, *9*, 598−599.

Table 3. Selected Bond Distances and Angles for $Ar_2Zn_3(OCHPr^i_2)_4$

Complex $(CF_3C_6H_4)_2Zn_3[(OCHPr^i_2)]_4$			
Zn(1)−O(1)	1.923(2)	Zn(1)−O(2)	1.937(2)
Zn(1)−C(29)	1.946(3)	Zn(2)−O(1)	1.952(2)
Zn(2)−O(4)	1.955(2)	Zn(2)−O(2)	1.956(2)
Zn(2)−O(3)	1.962(2)	Zn(3)−O(3)	1.928(2)
Zn(3)−O(4)	1.928(2)	Zn(3)−C(36)	1.940(2)
O(1)−Zn(1)−O(2)	82.55(7)	O(1)−Zn(1)−C(29)	140.84(9)
O(2)−Zn(1)−C(29)	136.6(1)	O(1)−Zn(2)−O(2)	81.33(7)
O(1)−Zn(2)−O(4)	113.09(7)	O(4)−Zn(2)−O(2)	139.89(8)
O(1)−Zn(2)−O(3)	137.55(8)	O(2)−Zn(2)−O(3)	113.75(8)
O(3)−Zn(2)−O(4)	83.05(7)	Zn(1)−O(1)−Zn(2)	98.36(8)
Zn(1)−O(2)−Zn(2)	97.75(8)	Zn(3)−O(3)−Zn(2)	97.58(8)
Zn(3)−O(4)−Zn(2)	97.81(8)	Zn(3)−Zn(2)−Zn(1)	178.77(1)
Complex $(C_6F_5)_2Zn_3[(OCHPr^i_2)]_4$			
Zn(1)−O(1)	1.916(1)	Zn(1)−O(2)	1.913(1)
Zn(1)−C(1)	1.950(2)	Zn(2)−O(1)	1.957(1)
Zn(2)−O(4)	1.956(1)	Zn(2)−O(2)	1.954(1)
Zn(2)−O(3)	1.954(1)	Zn(3)−O(3)	1.919(1)
Zn(3)−O(4)	1.903(1)	Zn(3)−C(7)	1.950(2)
O(1)−Zn(1)−O(2)	84.12(6)	O(2)−Zn(1)−C(1)	135.61(7)
O(1)−Zn(1)−C(1)	140.22(7)	O(1)−Zn(2)−O(2)	81.99(6)
O(1)−Zn(2)−O(4)	135.54(7)	O(4)−Zn(2)−O(2)	109.57(6)
O(1)−Zn(2)−O(3)	116.94(6)	O(4)−Zn(2)−O(3)	81.98(6)
O(2)−Zn(2)−O(3)	140.22(6)	Zn(1)−O(1)−Zn(2)	96.78(6)
Zn(1)−O(2)−Zn(2)	96.98(6)	Zn(3)−O(3)−Zn(2)	96.63(6)
Zn(3)−O(4)−Zn(2)	97.09(6)	Zn(3)−Zn(2)−Zn(1)	172.88(1)

Table 4. Copolymerization of Carbon Dioxide with Propylene Oxide[a]

catalyst	solvent[b]	PPC (%)	PC (%)	PPO (%)	Mn ($\times 10^{-3}$)	PDI
$(CF_3C_6H_4)_2Zn_2(OR)_2$	toluene	0	trace	trace		
$(CF_3C_6H_4)_2Zn_3(OR)_4$	toluene	1	3	trace		
$(C_9H_{11})_2Zn_2(OR)_2$	toluene	trace	4	5		
$(C_6F_5)_2Zn_2(OR)_2$	toluene	0	trace	12		
$(C_6F_5)_2Zn_3(OR)_4$	toluene	0	1	8		
$Ph_2Zn_2(OR)_2$	toluene	trace	2	trace		
$Ph_2Zn_3(OR)_4$	toluene	1	12	2		
$(CF_3C_6H_4)_2Zn + H_2O$	THF	10	2	8	44.8	3.92
	Et_2O	16	1	11	69.9	4.97
	dioxane	1	1	trace		
$(C_9H_{11})_2Zn + H_2O$	THF	9	2	2	65.0	3.03
	Et_2O	4	2	2	39.8	3.50
	dioxane	4	1	1	86.9	3.97
$(C_6F_5)_2Zn + H_2O$	THF	0	0	9		
	Et_2O	10	5	7	27.2	3.57
	dioxane	2	1	1	16.0	1.49
$Ph_2Zn + H_2O$	THF	33	4	10	66.5	4.19
	Et_2O	1	trace		trace	
	dioxane	24	5	6	75.0	3.44
$(n\text{-}Bu)_2Zn + H_2O$	THF	trace	trace	trace		
	Et_2O	2	trace	2	68.2	4.24
	dioxane	19	6	4	123	2.86
$(t\text{-}Bu)_2Zn + H_2O$	THF	5	2	1	28.7	3.45
	Et_2O	9	3	3	45.6	5.05
	dioxane	3	2	trace	46.7	4.87
$(Oct)_2Zn + H_2O$	THF	11	4	4	77.4	2.96
	Et_2O	3	2	3	312	1.41
	dioxane	2	trace	trace		
$Et_2Zn + H_2O$	THF	12	4	4	127	3.32
	Et_2O	9	2	2	135	2.17
	dioxane	11	4	4	73.5	3.86

[a] All reactions were carried under similar conditions: catalyst, 50 mg; PO, 2 mL (1.2 g); temperature, 60 °C; P_{CO_2}, 60 bar; reaction time, 20 h; no solvent applied. Yield estimated from ^1H NMR spectrum of product mixture, $CDCl_3$ as solvent. [b] Solvent applied in preparation of catalysts.

ization of PO by $Ar_2Zn_x(OR)_y$ resulted in 10−48% conversion to PPO at 60 °C in 20 h. However, only -OH-ended chains were observed by MALDI-TOF mass spectroscopy, which suggests that it is Zn−OH, not Zn−OR that functions as the active initiator during the homopolymerization of PO.

Table 5. Homopolymerization of Propylene Oxide by $Ar_2Zn_x(OR)_y$ and Partially Hydrolyzed Ar_2Zn Compounds

catalyst	PPO (%)	Mn ($\times 10^{-3}$)	PDI
$Ph_2Zn_2(OR)_2$[a]	39	10.9	1.85
$Ph_2Zn_3(OR)_4$[a]	39	16.4	1.89
$(CF_3C_6H_4)_2Zn_2(OR)_2$[a]	23	10.5	1.72
$(CF_3C_6H_4)_2Zn_3(OR)_4$[a]	20	20.4	1.72
$(C_6F_5)_2Zn_2(OR)_2$[a]	48	8.80	1.62
$(C_6F_5)_2Zn_3(OR)_4$[a]	41	8.03	1.56
$(C_9H_{11})_2Zn_2(OR)_2$[a]	10	1.17	3.00
$Ph_2Zn + H_2O$ (1:1)[b]	>95	12.5	1.53
$(p\text{-}CF_3C_6H_4)_2Zn + H_2O$ (1:1)[b]	25	28.1	1.79
$(C_6F_5)_2Zn + H_2O$ (1:1)[b]	23	11.8	1.51
$(C_9H_{11})_2Zn + H_2O$ (1:1)[b]	0	na[c]	na[c]

[a] Reactions were carried out under similar conditions: catalyst, 50 mg; PO, 2 mL (1.2 g); temperature, 60 °C; reaction time, 20 h. Yield estimated from ^1H NMR spectrum of product mixture, $CDCl_3$ as solvent. [b] Catalysts prepared in THF. Polymerization reaction parameters are the same in *a* except that reaction temperature is 25 °C. [c] na, not applicable.

Further support for this proposal is seen in the following. The complex $(C_6H_6)_2Zn_2(OR)_2$ was mixed with 10 equiv of PO in a sealed J-Young tube and heated at 60 °C for 40 h, 30% of PO was converted into PPO, and there was no observable change in chemical shifts for complex $(C_6H_6)_2Zn_2(OR)_2$. The $^{13}C\ \{^1H\}$ NMR revealed that the stereosequence of PPO that was catalyzed by $Ar_2Zn_x(OR)_y$ have identical patterns at CH and CH_2 region as those catalyzed by partially hydrolyzed Ar_2Zn catalysts. So it is quite reasonable to propose that the active Zn−OH center comes from the hydrolysis of $(C_6H_6)_2Zn_2(OR)_2$. The regioregularity of PPO followed the order of C_6H_6 > p-$CF_3C_6H_4$ > C_6F_5. As shown in Figure 5, hydrolyzed $(C_6H_5)_2Zn$ opens PO to give over 90% regioregular PPO (HTHTHT), with enriched ii tetrads being seen in the CH region.[15] However, the hydrolyzed $(C_6F_5)_2Zn$ catalyst system ring opens PO almost randomly to give regioirregular PPO (see Figure 5). This is evidence of the influence of the aryl group on the active zinc center.

The regiosequence difference in the PPO can be explained in terms of the activation of PO upon complexation to the metal as originally proposed by Kuran.[16] Electron-withdrawing groups such as C_6F_5 generate Lewis acidic metal centers and promote the ring-opening of PO by an S_N1 mechanism. This leads to regioirregular PPO as the PO undergoes C−O bond rupture and formation at both the methine and methylene carbon atoms. With less electrophilic metal centers as with phenyl or ethyl zinc + H_2O, the ring-opening is regioselective by attack at the methylene carbon, and the mechanism can by described as metal-promoted base catalysis.

Concluding Remarks. It seems that none of the discrete zinc alkoxides reported here is active in either the homopolymerization of PO or in its copolymerization with CO_2. This lends credence to the view that, in the Coates and Darensbourg catalyst systems, it is the terminal OR or OAr ligands that initiate and sustain polymerization. Bridging OR groups are inactive.

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Supporting Information Available: Crystallographic information on $(p\text{-}CF_3C_6H_4)_2Zn_3(OCHPr^i_2)_4$, CCDC 203296; $(C_6F_5)_2Zn_3(OCHPr^i_2)_4$, CCDC 203297; $[2,4,6\text{-}(CH_3)_3C_6H_2]_2Zn_2(OCHPr^i_2)_2$, CCDC 203298; $(p\text{-}CF_3C_6H_4)_2Zn$, CCDC 203299; $(p\text{-}CF_3C_6H_4)_2Zn_2(OCHPr^i_2)_2$, CCDC 203300; $(C_6F_5)_2Zn_2(OCHPr^i_2)_2$, CCDC 203301. This material is available free of charge via the Internet at http://pubs.acs.org.

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