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The Ethylsulfinate Ligand: A Highly Efficient Initiating Group for the Zinc β-Diiminate Catalyzed Copolymerization Reaction of CO_2 and Epoxides

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*Summary: The quantitative synthesis of a series of new zinc(II) sulfinate complexes (**4a**−**e**) by insertion of SO_2 into zinc−ethyl bonds of β-diiminate complexes ((ArN═C(CH_3)CH═(CH_3)CNAr)Zn(O(S═O)Et); Ar = 2,6-diisopropylphenyl (**4a**), 2,6-diethylphenyl (**4b**), 2-ethyl-6-isopropylphenyl (**4c**), 2,6-diphenylphenyl (**4d**), 2,6-bis(4-tert-butylphenyl)phenyl (**4e**)) is described. X-ray structure analysis reveals a dinuclear, μ-ethylsulfinate-bridged structure for **4a** in the solid state, which in solution exists in an equilibrium with the mononuclear species. The easily accessible complexes **4a**−**c** are highly active catalysts for the alternating copolymerization of CO_2 and cyclohexene oxide, leading to products with narrow molecular weight distributions.*

Introduction

Aliphatic polycarbonates are materials with interesting properties, which are accessible by a metal-catalyzed copolymerization reaction of CO_2 and epoxides. The combination of exergonic epoxide ring opening with endergonic carbonate formation is presumably one of the most important examples for CO_2 activation, since valuable materials are obtained. Furthermore, CO_2 and epoxides are cheap building blocks and especially CO_2 is readily available. Early attempts to catalyze this copolymerization reaction were hardly efficient. Usually undefined zinc alkyl/alcohol mixtures or simple metal salts have been applied.[2]

One of the first well-defined catalysts (zinc(II) bis(phenoxide)) was developed by Darensbourg in the 1990s.[3] Coates et al. reported in 1998 on β-diimine Zn(II) complexes ((BDI)ZnX) as excellent catalysts for the copolymerization reaction of CO_2 and cyclohexene oxide (CHO).[4] These complexes of the general type (BDI)ZnX (X = alcoholate, acetate, bis(trimethylsilyl)amide) bear X as the initiating group and are already active under mild conditions. Chiral, 2-methyloxazoline-substituted catalysts even afforded stereoregular polycarbonates.[5]

Diethylzinc reacts easily with ligands bearing an acidic proton (e.g. BDI-H) to form 1 equiv of ethane. Unfortunately, the resulting (BDI)ZnEt complexes are not able to initiate the copolymerization reaction. A known route for activation is their conversion to alcoholates (Scheme 1b).[4] This, however, results only in moderate catalyst yield through protonolysis of the BDI complexes with alcohols.

We report here on a new and simple strategy to yield active single-component catalysts (**4a**−**e**) in quantitative yield (Scheme 1b).[6] The essential feature of the structures **4a**−**e** is the ethylsulfinate ligand [(BDI)Zn*OS(O)-Et*] that results from a quantitative insertion of dry SO_2 into the Zn−carbon bond of **3a**−**e**.[7] In addition to the behavior of this initiating group, also the influence of BDI-H ligands of variable steric demand on the copolymerization reaction is discussed.

Results and Discussion

Synthesis and Structure of Zinc Sulfinate Complexes. The β-diimine ligands **2a**−**d** were prepared by refluxing 2 equiv of the desired aniline with 1 equiv of 2,4-pentanedione in acidified ethanol, yielding the corresponding hydrochlorides or hydrobromides (Scheme 1a).[8] Neutralization with aqueous carbonate solution gives **2a**−**d** in yields up to 80% after recrystallization. Preparation of **2e** works best in a two-step process. Excess 2,4-pentanedione is condensed with aniline in benzene. The isolated monoimine is heated under reflux after addition of 1.1 equiv of aniline hydrobromide in ethanol, resulting in a mixture of the β-diimine **2e** and

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[6] Another one-step route to BDI−zinc complexes starts from commercially available Zn[N($SiMe_3$)$_2$]$_2$, which yields (BDI)ZnN($SiMe_3$)$_2$ catalysts after several days in quantitative yield.[4b]

[7] (a) Hobson, J. T. *Justus Liebigs Ann. Chem.* **1857**, *102*, 73−85. (b) Wischin, G. *Justus Liebigs Ann. Chem.* **1866**, *139*, 364−372. (c) Carey, N. A. D.; Clark, H. C. *Can. J. Chem.* **1968**, *46*, 649−651.

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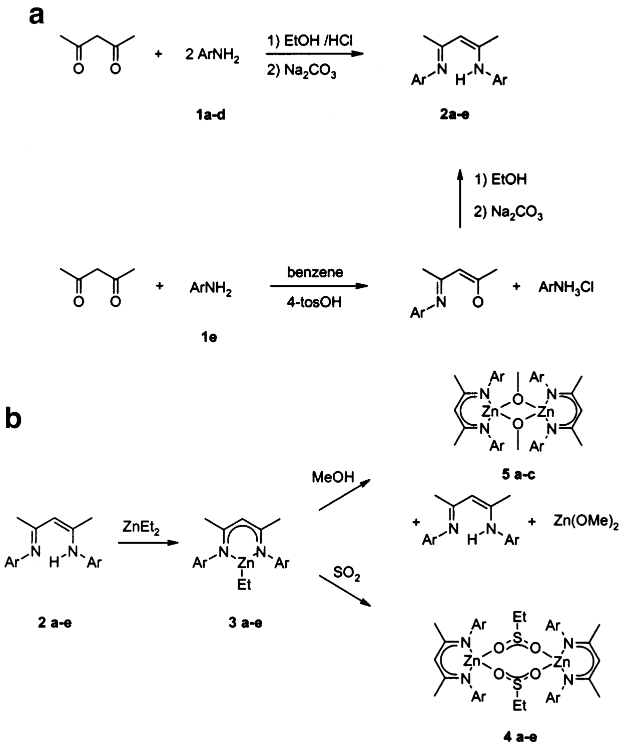
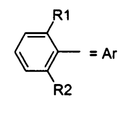
Scheme 1





1-5	R1	R2
a	*i*-Pr	*i*-Pr
b	Et	Et
c	*i*-Pr	Me
d	Ph	Ph
e	4-*t*-Bu-Ph	4-*t*-Bu-Ph

the aniline **1e**. Separation can be accomplished by conversion of the product mixture into hydroperchlorates and subsequent crystallization.

The conversion of dialkylzinc reagents with SO_2 to produce O-bound zinc(II) bis(alkyl) sulfinates, which after acidic workup yield sulfinic acids, is a known reaction.[7] We investigated the synthesis of (BDI)ZnO(SO)Et complexes (**4a**–**e**), due to the structural similarity of these alkyl sulfinates to carboxylates and carbonates, that allow a CO_2/epoxide copolymerization reaction to occur. Reaction of (BDI)H with $ZnEt_2$ gives (BDI)ZnEt in quantitative yield.[4] Treatment with excess SO_2 in toluene at −10 °C leads to an orange solution. After the temperature is raised and SO_2 is removed, the (BDI)ZnO(SO)Et complexes were isolated quantitatively as white (**4a**–**c**) or pale yellow (**4d**,**e**) solids. The complex **4a** exists as a μ-sulfinate-bridged dimer in the solid state (X-ray structure analysis; see Figure 1).[9] The eight-membered jagged metallacycle shows a torsion angle of about 96° at each zinc sulfinate moiety (O(2,2′)–S(S′)–O(1,1′)–Zn(Zn′)). The Zn–Zn′ separation is 4.98 Å, and the six-membered chelate ring is slightly puckered (torsion angle C(2,2′)–C(1,1′)–N(1,1′)–Zn,Zn′ = 7.2°). However, the dimeric **4a** exists in solution in an equilibrium with its mononuclear analogue. Variable-temperature ^{1}H NMR investigations in toluene revealed two sets of resonances whose intensities vary with temperature. The set that becomes more intense with higher temperatures is assigned to the monomeric complex. The calculated equilibrium constants $K_{eq}([Zn_2] \rightleftharpoons 2[Zn])$ for the monomer and dimer of **4a** (toluene-d_8; at 60 °C, $K_{eq} = 2.2 \times 10^{-4}$ M, and at 80 °C, $K_{eq} = 2.6 \times 10^{-3}$ M) show that the equilibrium favors the dimeric species more than in the case of the analogous acetate complexes (C_6D_6, 20 °C, 2.9×10^{-2} M).[4a] The ^{1}H NMR spectra of **4b**–**e** show only one set of signals. These are attributed to the sulfinate-bridged species for the less crowded complexes **4b**,**c** and to the monomeric forms of **4d**,**e**, which carry bulky terphenylaniline and (substituted terphenyl)aniline moieties.

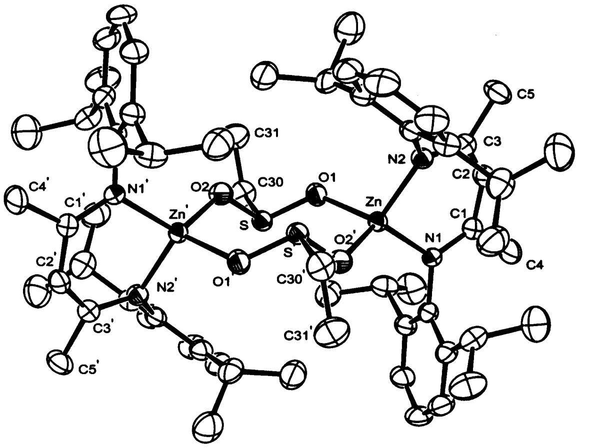


Figure 1. ORTEP plot of **4a** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Atoms labeled with a slanted prime (′) were generated by symmetry operations.

Table 1. Summary of Crystallographic Data for 4a

empirical formula	$C_{64}H_{96}Cl_4N_4O_4S_2Zn_2$
fw	1322.11
temp (K)	220(2)
wavelength (Å)	0.710 73
cryst syst	monoclinic
space group	*C*2/*c*
unit cell dimens	
a (Å)	20.752(4)
b (Å)	12.4136(16)
c (Å)	27.113(5)
β (deg)	101.19(2)
V (Å^3)	6852(2)
Z	4
D_c (Mg/m^3)	1.282
abs coeff, μ (mm^{-1})	0.963
F(000)	2800
cryst size (mm^3)	0.62 × 0.42 × 0.38
θ range for data collecn (deg)	1.92–24.12
index ranges	$-23 \le h \le 23$ $-14 \le k \le 14$ $-31 \le l \le 31$
no. of rflns collected	21 700
no. of indep rflns	5417 (R(int) = 0.0449)
no. of obsd rflns ($I > 2\sigma(I)$)	4087
goodness of fit on F^2	1.007
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0384, wR2 = 0.0914
R indices (all data)	R1 = 0.0562, wR2 = 0.0979
extinction coeff	0.00050(11)
largest diff peak and hole (e Å^{-3})	0.723 and −0.612

Copolymerization of Cyclohexene Oxide and Carbon Dioxide. Polymerization experiments with the single-component catalysts **4a**–**e** were performed in neat CHO at 10 bar of CO_2 pressure (Table 2). All polycarbonates produced are atactic, with chains com-

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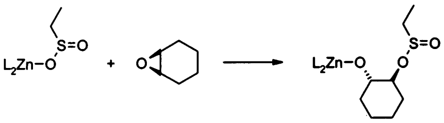
[9] A similar structure was also found for sulfinate complexes of Pd: Gates, D. P.; White, P. S.; Brookhart, M. *Chem. Commun.* **2000**, 47–48.

Table 2. CHO/CO_2 Copolymerization Results Obtained with Catalysts 4a−e[a]

entry	cat.	temp (°C)	time (h)	$10^{-3}M_n$[b]	M_w/M_n[b]	carbonate linkages[c] (%)	TON[d]	TOF (h^{-1})[e]
1	**4a**	40	2	25.9	4.29	90	128	64
2	**4a**	50	2	38.7	1.11	98	284	142
3	**4a**	60	2	39.8	1.11	97	312	156
4	**4a**	70	2	34.0	1.50	94	336	168
5	**4a**	80	2	32.0	1.40	93	330	165
6	**4a**	25−60[f]	0.5	7.6	5.57	87		
7	**4b**	60	2	31.8	1.13	97	328	164
8	**4b**[g]	60	3	49.6	1.30	96	651	217
9	**4c**	60	2	20.8	1.30	95	270	135
10	**4d**[h]	90	4	29.3	3.20	38	16	4
11	**4e**	60	3			16	9	3

[a] All reactions were performed in 50 mL steel autoclaves at 10 bar of CO_2 pressure in neat cyclohexene oxide with [Zn]:[epoxide] = 1:1000. [b] Determined by gel-permeation chromatography in THF, calibrated with narrow polystyrene standards. [c] Calculated by ^1H NMR in $CDCl_3$. [d] In units of (mol of CHO converted to poly(cyclohexene carbonate))/(mol of zinc). [e] In units of (mol of CHO converted to poly(cyclohexene carbonate))/((mol of zinc) h). [f] The temperature was raised from 25 to 60 °C within 30 min. [g] The reaction was carried out in a 250 mL Büchi reactor equipped with an online ATR-IR system. [h] Because of poor catalyst solubility, the reaction was carried out in 2000 equiv of CHO at 90 °C.

Scheme 2



prising only *trans*-cyclohexane linkages.[10] The carbonate content of the obtained polymers was higher than 87%, except of those produced with **4d**,**e**, which show predominantly polyether sequences. Experiments in an autoclave equipped with online ATR-IR monitoring (Table 2, entry 8) indicated an immediate initiation after addition of CO_2 and a nearly linear increase of polycarbonate concentration.[11]

Quenching of the polymerization experiments after 20 min resulted in the formation of low-molecular-weight poly(cyclohexene carbonate) that enabled us to analyze endgroups. The ^1H NMR spectrum ($CDCl_3$) shows two sextets at δ 2.35 and 2.46 ($J = 7.5$ Hz), which are attributed to diastereotopic protons of the methylene groups in ethylsulfinic acid esters which result from epoxide insertion into a zinc−ethylsulfinate bond (Scheme 2).[12]

4a shows nearly constant polymerization activity at reaction temperatures between 60 and 80 °C and produces polymers with predominantly carbonate linkages.[13] The activities are similar to those reached with corresponding (BDI)ZnX complexes bearing other initiating groups. Polymerization experiments at $T_p = 40$ °C (Table 2, entry 1) lead to medium-molecular-weight products, however, of broad molecular weight distribution ($M_w/M_n = 4.3$). Further increase of T_p affords higher activities, and the molecular weights reach a maximum at $T_p = 60$ °C ($M_n = 40\,000$).[13] The molecular weight distributions at elevated temperatures ($T_p = 50−60$ °C) are narrow and—most interestingly—show a shoulder at higher molecular weights. This prompted us to investigate a possible correlation of these bimodal distributions with the observed temperature-dependent monomer/dimer equilibrium of the organometallic species. Therefore, we performed one experiment using a temperature gradient (25 → 60 °C) which was shown by means of variable-temperature NMR to be the decisive temperature range for the equilibrium (Table 2, entry 6). Indeed, the resulting polymer material gave a clearly bimodal distribution with two maximums at $M_n = 4800$ and $M_n = 56\,000$. This observation led us to the assumption that monomer and dimer of **4a** are active catalysts, affording lower and higher molecular weight products, respectively.[14] The dimeric **4a** decays slowly into the monomeric species, which might give an explanation for the observed broader molecular weight distribution at 40 °C. In addition, the difference in polymerization performance between 40 and 50 °C suggests also a slow initiation of the polymerization reaction at lower temperature.[15]

Polymers produced with **4b**,**c** show similar activity and molecular weights and also give a shoulder at higher M_n, indicating a behavior comparable to that of **4a**. The sterically more crowded complexes **4d**,**e** produce only traces of polymers with a surprisingly high ether content.[16]

Experimental Section

General Comments. Unless otherwise specified, all syntheses and manipulations were carried out under a dry argon atmosphere using conventional Schlenk techniques. Toluene and THF were dried by distillation from $LiAlH_4$. Dichloromethane and cyclohexene oxide were distilled from CaH_2. Diethylzinc (solution in toluene 15%), epoxides, and sulfur dioxide were purchased from Fluka and Aldrich. Dry carbon dioxide was purchased from BASF Aktiengesellschaft, Ludwigshafen, Germany. β-Diiminate ligands **2a**−**c** and 2,6-diarylanilines **1d**,**e** were prepared according to literature procedures.[8,17] Diffraction data were recorded on an IPDS instrument from STOE. Crystal data and structure refinement details are presented in Table 1. Absorption corrections were not applied. The structure was solved by direct methods (SHELXS-86). Refinement was performed with the SHELXL-97 program.

2d. To a mixture of 2,4-pentanedione (1.85 mL, 18 mmol) and 2,6-diphenylaniline (**1d**; 9.8 g, 40 mmol) in 120 mL of ethanol was added concentrated HCl (1.5 mL, 18 mmol). After the mixture was stirred for 72 h under reflux, ethanol was removed in vacuo. The residue was suspended in 50 mL of dichloromethane and vigorously mixed with a sodium carbonate solution (2 M). The organic layer was separated and washed with 20 mL of water and dried over sodium sulfate. Solvent was removed under vacuum, and the remaining yellow

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(10) Determined by ^{13}C NMR spectroscopy.

(11) The linear increase of the carbonate band was observed only over the first 1 h, which might be due to the high viscosity of the reaction media.

(12) Norton, R. V.; Douglass, I. B. *Org. Magn. Reson.* **1974**, *6*, 89−91.

(13) Visible amounts of cyclic carbonate are formed at reaction temperatures above 60 °C, presumably due to a depolymerization reaction of previously formed polycarbonate. This additional process helps to explain the nearly constant polymerization activity (cyclic carbonate is not considered) over a broad temperature range and the lower molecular weights occurring at higher temperatures.

(14) For the low-molecular-weight fraction, molecular weights are comparable to results found by Coates et al. with acetate and alcoholate complexes.[4a,b]

(15) In contrast to similar complexes from Coates et al., **4a** shows no activity at 20 °C, which is presumably due to a hindered initiation at low temperature.

(16) Similar behavior (no activity) was also found for complexes bearing 2,6-di-*n*-propyl substitution.[4b]

(17) Schmid, M.; Eberhardt, R.; Klinga, M.; Leskelä, M.; Rieger, B. *Organometallics* **2001**, *20*, 2321−2330.

oil was mixed with ethanol and refluxed for a few minutes, yielding a slightly yellow powder, which was isolated. To a solution of the powder in a minimum amount of dichloromethane was added methanol. Overnight at 4 °C a yellow powder precipitated, which was isolated and dried under vacuum, to give 5.4 g of clean product **2d** (54%). Anal. Calcd for $\mathrm{C_{41}H_{34}N_2}$: C, 88.77; H, 6.18; N, 5.05. Found: C, 88.64; H, 6.24; N, 5.04. ^{1}H NMR (400 MHz, $\mathrm{C_2D_2Cl_4}$): δ 1.17 (s, 6H), 4.07 (s, 1H), 7.06 (d, 8H), 7.15 (d, 8H), 7.25 (t, 2H), 7.32 (d, 4H), 12.02 (s, 1H). ^{13}C NMR (100 MHz, $\mathrm{C_2D_2Cl_4}$): δ 20.78, 96.28, 123.88, 126.30, 127.79, 129.08, 129.54, 131.95, 136.58, 140.57, 159.48.

2-Hydroxy-4-(2,6-bis(4-*tert*-butylphenyl)phenyl)imino-2-pentene. 2,6-Bis(4-*tert*-butylphenyl)phenylamine (**1e**; 1.6 g, 4.5 mmol), 2,4-pentanedione (0.91 mL, 6.3 mmol), and toluene-4-sulfonic acid (10 mg) was dissolved in 60 mL of benzene and refluxed for 18 h using a Dean-Stark condenser. Benzene was removed completely, and the remaining sticky solid was dissolved in 3 mL of dichloromethane. After addition of 15 mL of methanol, dichloromethane was partially removed under vacuum, yielding a white precipitate, which was isolated (1.78 g, 90%). Anal. Calcd for $\mathrm{C_{31}H_{37}NO}$: C, 84.69; H, 8.48; N, 3.19. Found: C, 84.88; H, 8.42; N, 3.10. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 1.28 (s, 3H), 1.33 (s, 18H), 1.92 (s, 3H), 4.76 (s, 1H), 7.32−7.40 (m, 11H), 12.13 (s, 1H). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 19.50, 28.91, 31.44, 34.52, 96.42, 125.22, 125.48, 127.71, 128.96, 129.91, 133.72, 136.08, 140.40, 150.10, 162.22, 195.22.

2e. 2-Hydroxy-4-((2,6-bis(4-*tert*-butylphenyl)phenyl)imino)-2-pentene (1.23 g, 2.8 mmol) and (2,6-bis(4-*tert*-butylphenyl)-phenyl)ammonium bromide (1.36 g, 3.1 mmol) were dissolved in 15 mL of ethanol and refluxed for 65 h. All volatiles were removed under vacuum, and the remaining solid was suspended in dichloromethane and treated with aqueous sodium carbonate solution until all solid was dissolved. The organic layer was separated and the volume reduced to about 5 mL. The ligand was precipitated with 25 mL of methanol, filtered, washed with methanol, and dried under vacuum to yield 1.2 g of **2e** (54%). Anal. Calcd for $\mathrm{C_{57}H_{66}N_2}$: C, 87.87; H, 8.54; N, 3.60. Found: C, 87.48; H, 8.48; N, 3.49. ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 1.13 (s, 6H), 1.18 (s, 36H), 4.05 (s, 1H), 7.13−7.27 (m, 22H), 12.27 (s, 1H). ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 20.81, 31.22, 34.28, 96.97, 123.80, 124.76, 128.89, 129.62, 137.69, 140.90, 148.76, 159.70.

General Synthesis of 3a−e (Modified from Ref 4a). To a solution of **2a**−**e** (4 mmol) in 40 mL of toluene at 0 °C was added a solution of $\mathrm{ZnEt_2}$ (16 mmol) in 14.5 mL of toluene. The mixture was stirred for 18 h at 80 °C, and the clear solution was dried under vacuum, giving a quantitative yield of the desired compound as a light yellow oil or solid.

3a. ^{1}H NMR (500 MHz, toluene-d_8): δ 0.36 (q, 2H), 1.02 (t, 3H), 1.38 (d, 12H), 1.45 (d, 12H), 1.90 (s, 6H), 3.36 (m, 4H), 5.17 (s, 1H), 7.29 (m, 6H). ^{13}C NMR (125 MHz, toluene-d_8): δ −1.30, 12.04, 23.23, 23.47, 24.20, 28.51, 95.41, 123.73, 125.95, 141.48, 145.02, 167.32.

3b. ^{1}H NMR (500 MHz, benzene-d_6): δ 0.22 (q, 2H), 0.92 (t, 3H), 1.16 (t, 12H), 1.63 (s, 6H), 2.45 (m, 4H), 2.61 (m, 4H), 4.93 (s, 1H), 7.04 (m, 6H). ^{13}C NMR (500 MHz, benzene-d_6): δ −2.01, 12.09, 14.56, 22.99, 25.18, 95.42, 125.37, 126.74, 136.92, 146.83, 167.00.

3c. ^{1}H NMR spectroscopic analysis revealed a 1:1 mixture of the cis and trans isomers. ^{1}H NMR (500 MHz, benzene-d_6): δ 0.25 (q, 4H), 0.92 (t, 3H), 0.95 (t, 3H), 1.15 (d, 12H), 1.21 (d, 12H), 1.63 (s, 12H), 2.14 (s, 12H), 3.16 (m, 4H), 4.95 (s, 1H), 4.96 (s, 1H), 7.01 (m, 4H), 7.11 (m, 2H).

3d. ^{1}H NMR (500 MHz, benzene-d_6): δ 0.13 (q, 2H), 0.97 (t, 3H), 1.39 (s, 6H), 4.20 (s, 1H), 6.99 (t, 2H), 7.11 (m, 4H), 7.18 (d, 4H), 7.21 (m, 16 H).

3e. ^{1}H NMR (500 MHz, benzene-d_6): δ 0.04 (q, 2H), 0.78 (t, 3H), 1.27 (s, 36H), 1.48 (s, 6H), 4.34 (s, 1H), 7.035 (t, 2H), 7.31 (d, 4H), 7.38 (d, 8H), 7.53 (d, 8H). ^{13}C NMR (benzene-d_6): δ 11.33, 24.09, 31.47, 34.55, 97.42, 125.28, 125.33, 130.11, 131.03, 137.09, 138.57, 145.30,149.37, 167.09.

General Synthesis of Ethylsulfinate Complexes 4a−e. A solution of **3a**−**e** (2 mmol) in 40 mL of toluene was cooled to −10°C. An excess of dry $\mathrm{SO_2}$ was added with rapid stirring. The solution turned immediately to red-orange and was stirred for 15 min at −10 °C. The mixture was warmed to room temperature and stirred another 15 min at 50 °C. Solvent and excess $\mathrm{SO_2}$ were removed in vacuo while the solution discolored. The solid product could be isolated in quantitative yield. In some cases small amounts of hydrolyzed products were found. Purification was achieved by dissolving the complex in toluene, dichloromethane, or THF, filtering the insoluble residues, and crystallizing in a minimum amount of the desired solvent.

4a. This compound is a white solid and can be crystallized from toluene or dichloromethane at −30 °C. X-ray analysis of the crystals revealed that the complex exists as μ,η^2-sulfinato dimer in the solid state. Anal. Calcd for $\mathrm{C_{62}H_{92}N_4O_4S_2Zn_2}$: C, 64.63; H, 8.05, N, 4.86. Found: C, 64.42, H, 7.97, N, 4.84. ^{1}H NMR (500 MHz, 80 °C, toluene-d_8, "M" denotes monomer, "D" denotes dimer): δ 0.53 (t, 6H, $\mathrm{O(SO)CH_2C}\mathit{H}_3$, M), 0.91 (t, 6H, $\mathrm{O(SO)CH_2C}\mathit{H}_3$, D), 1.05 (d, 12H, CH*Me*Me, M), 1.17 (d, 48H, CH*MeMe*, D), 1.40 (d, 12H, CHMe*Me*, M), 1.59 (s, 12H, α-Me, D), 1.73 (s, 6H, α-Me, M), 2.13 (m, 6H, $\mathrm{O(SO)C}\mathit{H}_2\mathrm{CH_3}$, M + D), 3.28 (m, 12H, C*H*$\mathrm{Me_2}$, M + D), 4.63 (s, 2H, β-CH, D), 4.89 (s, 1H, β-CH, M), 7.11 (m, 18H, Ar H, M + D).

4b. This compound is a white solid and can be crystallized from toluene at −30 °C. Anal. Calcd for $\mathrm{C_{54}H_{76}N_4O_4S_2Zn_2}$: C, 62.36; H, 7.37, N, 5.39. Found: C, 61.95, H, 7.43, N, 5.29. ^{1}H NMR (500 MHz, 60 °C, benzene-d_6): δ 0.79 (t, 6H, $\mathrm{O(SO)CH_2C}\mathit{H}_3$), 1.10 (t, 24H, $\mathrm{CH_2}$*Me*), 1.51 (s, 12H, α-Me), 1.82 (q, 4H, $\mathrm{O(SO)C}\mathit{H}_2\mathrm{CH_3}$), 2.59 (m, 16H, C$\mathit{H}_2$Me), 4.63 (s, 2H, β-CH), 7.04 (m, 12H, Ar H).

4c. This compound is a white solid and can be crystallized from toluene at −30 °C. Anal. Calcd for $\mathrm{C_{54}H_{76}N_4O_4S_2Zn_2}$: C, 62.36; H, 7.37, N, 5.39. Found: C, 62.18, H, 7.45, N, 5.33. ^{1}H NMR spectroscopic analysis shows multiple signal sets suggesting a mixture of isomers (combination of cis and trans configuration in dimers). ^{1}H NMR (500 MHz, 70 °C, toluene-d_8): δ 0.92 (m, 6H, $\mathrm{O(SO)CH_2C}\mathit{H}_3$), 1.11 (m, 24H, CH*MeMe*), 1.58 (m, 12H, α-Me), 2.06 (m, 12H, *o*-Me), 2.21 (m, 4H, $\mathrm{O(SO)C}\mathit{H}_2\mathrm{CH_3}$), 3.36 (m, 2H, C*H*$\mathrm{Me_2}$), 4.67 (m, 2H, β-CH), 6.92 (m, 4H, Ar H), 7.04 (m, 8H, Ar H).

4d. This compound is a slightly yellow solid and can be crystallized from THF at −30 °C. Anal. Calcd for $\mathrm{C_{43}H_{38}N_2O_2SZn}$: C, 72.52; H, 5.38, N, 3.93. Found: C, 71.89, H, 5.44, N, 3.78. ^{1}H NMR (500 MHz, 70 °C, $\mathrm{C_2D_2Cl_4}$): δ 0.26 (t, 3H, $\mathrm{O(SO)CH_2C}\mathit{H}_3$), 1.28 (q, 2H, $\mathrm{O(SO)C}\mathit{H}_2\mathrm{CH_3}$), 1.38 (s, 6H, α-Me), 4.05 (s, 1H, β-CH), 7.23 (m, 20H, Ar H), 7.36 (m, 6H, Ar H).

4e. This compound is a slightly yellow solid and can be crystallized from THF at −30 °C. Anal. Calcd for $\mathrm{C_{59}H_{70}N_2O_2SZn}$: C, 75.66; H, 7.53, N, 2.99. Found: C, 74.95, H, 7.53, N, 2.92. ^{1}H NMR (500 MHz, 70 °C, toluene-d_8): δ 0.55 (t, 3H, $\mathrm{O(SO)CH_2C}\mathit{H}_3$), 1.16 (q, 2H, $\mathrm{O(SO)C}\mathit{H}_2\mathrm{CH_3}$), 1.31 (s, 6H, α-Me), 1.33 (s, 18H, C*Me*$_3$), 1.47 (s, 18H, C*Me*$_3$), 3.98 (s, 1H, β-CH), 7.38 (m, 22H, Ar H).

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Supporting Information Available: Tables of crystallographic data, bond distances, bond angles, anisotropic displacement parameters, all atom coordinates, and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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