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Bimetallic Fluorine-Substituted Anilido–Aldimine Zinc Complexes for CO_2/(Cyclohexene Oxide) Copolymerization

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Regioselective nucleophilic aromatic substitution of an *o*-fluorine occurs to afford fluorine-substituted *o*-phenylene-bridged bis(anilido–aldimine) compounds $o\text{-}C_6H_4\{(C_6H_2R_2)N{=}CH{-}C_6F_4{-}(H)N(C_6H_3R'_2)\}_2$ when $Li(H)N{-}C_6H_3R'_2$ (R′ = *i*Pr, Et, Me) is reacted with $o\text{-}C_6H_4\{(C_6H_2R_2)N{=}CH{-}C_6F_5\}_2$ (R = *i*Pr, Et, Me) in a nonpolar solvent such as diethyl ether or toluene. Successive additions of Me_2Zn and SO_2 gas to the bis(anilido–aldimine) compounds afford quantitatively dinuclear μ-methylsulfinato zinc complexes $o\text{-}C_6H_4\{[(C_6H_2R_2)N{=}CH{-}C_6F_4{-}N(C_6H_3R'_2)\text{-}\kappa 2N,N]\text{-}Zn(\mu\text{-}OS(O)Me)\}_2$ (R = *i*Pr, R′ = *i*Pr, **3a**; R = *i*Pr, R′ = Me, **3c**; R = Et, R′ = ^{i}Pr, **3d**; R = Et, R′ = Et, **3e**; R = Et, R′ = Me, **3f**; R = Me, R′ = *i*Pr, **3g**; R = Me, R′ = Et, **3h**; R = Me, R′ = Me, **3i**). The molecular structure of **3c** was confirmed by X-ray crystallography. Fluorine-substituted complexes **3a**–**i** show significantly higher TOF (turnover frequencies) than the unfluorinated analogues for CO_2/(cyclohexene oxide) copolymerization. The TOF is highly sensitive to the substituents R and R′, and the highest TOF (2480 h^{-1}) is obtained with **3g** (R = Me, R′ = *i*Pr). Complex **3g** is less sensitive to the residual protic impurities present in the monomers and shows activity at such a low catalyst concentration as [Zn]:[cyclohexene oxide] = 1:50 000, at which the unfluorinated analogue is completely inactive. By realizing the activity at such an extremely low [Zn]:[cyclohexene oxide] ratio, we achieve a high TON (turnover number) up to 10 100. High-molecular-weight polymers (M_n, 100 000–200 000) are obtained with a rather broad molecular-weight distribution (M_w/M_n, 1.3–2.5). The obtained polymers are not perfectly alternating, and variable carbonate linkages (65–85%) are observed depending on the *N*-aryl ortho substituents R and R′ and the polymerization conditions.

Introduction

Recently, chemistry utilizing CO_2 as a feedstock has drawn considerable attention because CO_2 is abundant, inexpensive, and nontoxic.[1] Environmental and economical benefits would be great if the polymers derived from CO_2 could replace totally petroleum-derived polymers. Carbon dioxide by itself cannot be transformed to a polymer, but its copolymerization with epoxide was reported in 1969 by Inoue et al.[2] The copolymerization requires a metal-containing catalyst, and in recent decades numerous catalytic systems have been developed.[3] Landmarks in recent developments are the β-diketiminato−Zn system[4] introduced by Coates and the salen-based chromium[5] and cobalt systems[6] introduced by Darensbourg and Coates. Even though the turnover number (TON) and the turnover frequency (TOF) have been dramatically improved by the advent of the two catalytic systems, the TON and TOF should be further improved to reach commercial viability.

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(1) (a) Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; Dubois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W. *Chem. Rev.* **2001**, *101*, 953. (b) Santamaria, D.; Cano, J.; Royo, P.; Mosquera, M. E. G.; Cuenca, T.; Frutos, L. M.; Castano, O. *Angew. Chem., Int. Ed.* **2005**, *44*, 5828. (c) Kong, L.-Y.; Zhang, Z.-H.; Zhu, H.-F.; Kawaguchi, H.; Okamura, T.-a.; Doi, M.; Chu, Q.; Sun, W.-Y.; Ueyama, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 4352. (d) Mori, K.; Mitani, Y.; Hara, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Chem. Commun.* **2005**, 3331. (e) Jiang, J.-L.; Gao, F.; Hua, R.; Qiu, X. *J. Org. Chem.* **2005**, *70*, 381. (f) Garcıa-Espanna, E.; Gavina, P.; LaTorre, J.; Soriano, C.; Verdejo, B. *J. Am. Chem. Soc.* **2004**, *126*, 5082. (g) Castro-Rodriguez, I.; Nakai, H.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. *Science* **2004**, *305*, 1757.

(2) (a) Inoue, S.; Koinuma, H.; Tsuruta, T. *J. Polym. Sci., Part B* **1969**, *7*, 287. (b) Inoue, S.; Koinuma, H.; Tsuruta, T. *Makromol. Chem.* **1969**, *130*, 210.

(3) Review: Coates, G. W.; Moore, D. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6618.

(4) (a) Allen, S. D.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 14284. (b) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 8738. (c) Byrne, C. M.; Allen, S. D.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2004**, *126*, 11404.

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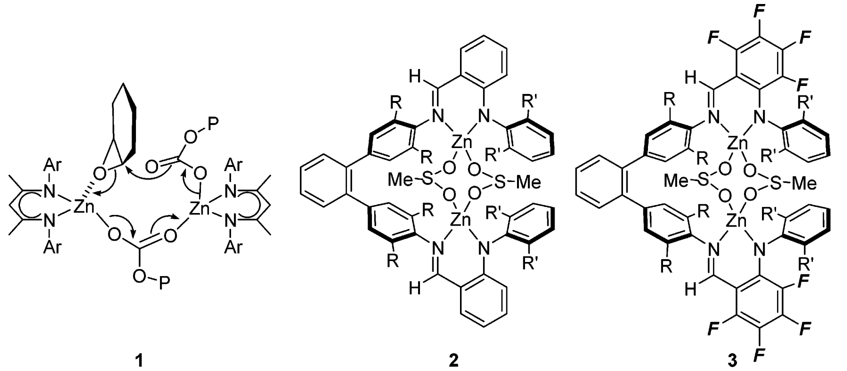
Chart 1



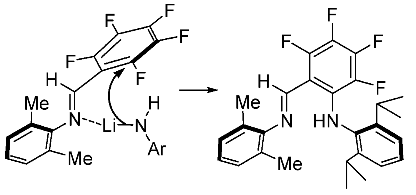
1 2 3

We recently reported bimetallic anilido−aldimine-based zinc catalysts (see Chart 1, compound **2**) with which the TON and the molecular weight of the polymer could be significantly improved.[7] The advantage of the bimetallic system over the mononuclear analogue results from the fact that two metal centers are involved in the chain propagation reaction, as shown below (Chart 1, compound **1**).[8] To achieve a high TON, we need the catalyst to be active even at a condition of very low catalyst concentration. The mononuclear complex, which is highly active at a condition of [Zn]:[cyclohexene oxide (CHO)] = 1:1000, shows negligible activity when the [Zn]:[CHO] ratio is reduced to 1:5600.[7,9] Because the bimetallic system is active even at such a low catalyst concentration as [Zn]:[CHO] = 1:16 800, the TON could be increased up to 3000. When the [Zn]:[CHO] ratio is further reduced to 1:22 500 to increase the TON, it does not show any activity because of the catalyst decomposition by the residual protic impurities (presumably water) in the monomers. That is, the catalyst should be less sensitive to the protic impurities in order to increase TON further above 3000.

In the Coates' β-diketiminato−Zn system, the introduction of electron-withdrawing substituent(s) in the ligand backbone results in dramatic increases in the TOF.[10] From the Coates' report, it is well expected that the bimetallic fluorine-substituted anilido−aldimine system (see Chart 1, compound **3**) would give a higher TOF. An increase in TON can also be expected because the fluorinated system might be less sensitive to the protic impurities. The sensitivity of the anilido−aldimine Zn system to the protic impurities may come from the basicity of the deprotonated anilido nitrogen atom. By the presence of the electron-withdrawing group on the anilido ring, the basicity must be reduced, possibly relieving the sensitivity of the complex toward the protic impurities. Fluorinated phenoxyzinc complexes have been shown to resist hydrolysis.[11]

Results and Discussion

Synthesis and Characterization. The anilido−aldimine ligand system was first prepared by Piers by a nucleophilic attack of LiN(H)Ar on a Schiff's base constructed from 2-fluorobenzaldehyde and aniline,[12] and the ligand system used for the construction of **2** was prepared by the same strategy. We guessed that the nitrogen donor on the Schiff's base facilitated the nucleophilic displacement of the fluoride by coordinating to the lithium ion on LiN(H)Ar. If the guess is correct, it is well-expected that the LiN(H)Ar can regioselectively displace an *o*-fluorine atom on a Schiff's base constructed from pentafluorobenzaldehyde (eq 1). As expected, the desired ortho-attacked product is obtained as a major product in 60% yield when the Schiff's base is reacted with 4 equiv of LiN(H)(2,6-iPr$_2$C$_6$H$_3$) in THF for 3 days at room temperature (eq 1). The observation of 4 signals and the splitting pattern for each signal (−82.7 (td), −68.1, −58.3 (t), −54.6 (d) ppm in C_6D_6) in the ^{19}F NMR spectrum strongly support the ortho-attacked structure drawn in eq 1. The ^{1}H NMR and ^{13}C spectra are also in agreement with the structure.



(1)

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(5) (a) Darensbourg, D. J.; Phelps, A. L.; Gall, N. L.; Jia, L. *Acc. Chem. Res.* **2004**, 37, 836 and references therein. (b) Chisholm, M. H.; Zhou, Z. *J. Am. Chem. Soc.* **2004**, *126*, 11036. (c) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Phelps, A. L. *Inorg. Chem.* **2004**, *43*, 1831. (d) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Fang, C. C.; Billodeaux, D. R.; Reibenspies, J. H. *Inorg. Chem.* **2004**, *43*, 6024. (e) Darensbourg, D. J.; Mackiewicz, R. M.; Billodeaux, D. R. *Organometallics* **2005**, *24*, 144. (f) Darensbourg, D. J.; Phelps, A. L. *Inorg. Chem.* **2005**, *44*, 4622. (g) Darensbourg, D. J.; Mackiewicz, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 14026.

(6) (a) Lu, X.-B.; Wang, Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 3574. (b) Qin, Z.; Thomas, C. M.; Lee, S.; Coates, G. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 5484. (c) Paddock, R. L.; Nguyen, S. T. *Macromolecules* **2005**, *38*, 6251. (d) Cohen, C. T.; Chu, T.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 10869.

(7) (a) Lee, B. Y.; Kwon, H. Y.; Lee, S. Y.; Na, S. J.; Han, S.-i.; Yun, H.; Lee, H.; Park, Y.-W. *J. Am. Chem. Soc.* **2005**, *127*, 3031. (b) Xiao, Y.; Wang, Z.; Ding, K. *Macromolecules* **2006**, *39*, 128. (c) Xiao, Y.; Wang, Z.; Ding, K. *Chem.*−*Eur. J.* **2005**, *11*, 3668.

(8) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2003**, *125*, 11911.

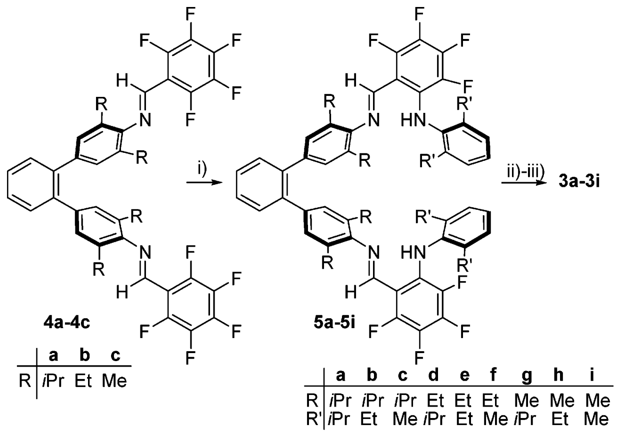
(9) van Meerendonk, W. J.; Duchateau, R.; Koning, C. E.; Gruter, G.-J. M. *Macromol. Rapid Commun.* **2004**, *25*, 382.

(10) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *Angew. Chem., Int. Ed.* **2002**, *41*, 2599.

(11) Darensbourg, D. J.; Wildeson, J. R.; Yarbrough, J. C.; Reibenspies, J. H. *J. Am. Chem. Soc.* **2000**, *122*, 12487.

(12) Hayes, P. G.; Welch, G. C.; Emslie, D. J. H.; Noack, C. L.; Piers, W. E.; Parvez, M. *Organometallics* **2003**, *22*, 1577.

Scheme 1 [a]



	a	b	c
R	*i*Pr	Et	Me

	a	b	c	d	e	f	g	h	i
R	*i*Pr	*i*Pr	*i*Pr	Et	Et	Et	Me	Me	Me
R'	*i*Pr	Et	Me	*i*Pr	Et	Me	*i*Pr	Et	Me

[a] Legend: (i) $C_6H_3R'_2NHLi$; (ii) $ZnMe_2$; (iii) SO_2

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Schiff's bases **4a**−**c** are prepared in excellent yields by conventional methods from the 4,4″-diamino-*o*-terphenyl derivatives bearing alkyl substituents at the 3, 5, 3″, and 5″ positions.[7] In contrast with the success on the construction of the mononuclear ligand system shown in eq 1, the construction of the dinuclear ligand system (**5** in Scheme 1) is unsuccessful under the same conditions. However, when less-polar diethyl ether was employed as a solvent instead of THF, desired compounds **5** are obtained as major products. In the case of **5d**, **5g**, and **5i**, the product is deposited as a solid during the reaction to block further attacks of the LiN(H)Ar; consequently, this gives satisfactory yields (50−67%), but in the preparations of the other derivatives, yields are rather low (30−40%). The yield can be significantly improved by employing nonpolar toluene as a solvent (60−80%). Four signals are observed as two triplets, a doublet, and a broad singlet in the ^{19}F NMR spectra. The splitting pattern supports the ortho-attacked products, as shown in Scheme 1. In the ^{1}H NMR spectra, the N−H signals are observed at 10.80−11.14 ppm (C_6D_6), slightly downfield shifted from the chemical shifts observed for the unfluorinated compounds (10.50−10.80 ppm in C_6D_6).

The addition of Me_2Zn to the ligands cleanly affords the desired bimetallic Zn−CH_3 complexes. In the ^{1}H spectra, the N−H signals disappear and new Zn−CH_3 signals appear at −0.61 to −0.85 ppm as singlets. The Zn−CH_3 carbon signals are observed at −17.4 to −16.9 ppm in the ^{13}C NMR spectra. In the ^{19}F NMR spectra, four well-split signals are observed (Figure 1). The splitting pattern is unambiguously assignable to a 1,2-disubstituted tetrafluorobenzene on the basis of coupling constants of $^3J_{FF} = 22$ and 16 Hz, $^4J_{FF} =$ 6 and 8 Hz, and $^5J_{FF} = 8$ Hz, which are in agreement with the tabulated coupling constants.[13]

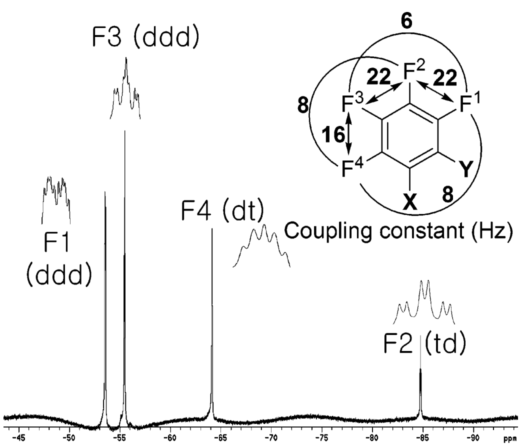
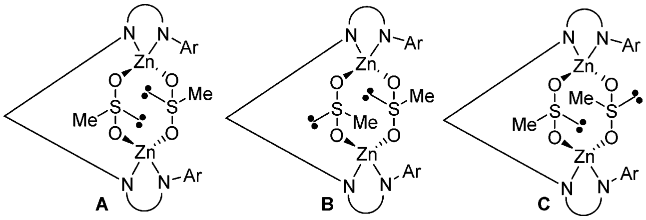


Figure 1. ^{19}F NMR spectrum of a methyl zinc complex of **5**.

Chart 2



The addition of SO_2 gas to the methyl zinc complexes results in disappearance of the Zn−CH_3 signals in the ^{1}H NMR spectra.[14] New signals are observed at 1.3−1.8 ppm (C_6D_6), which can be assigned to Zn−OS(CH_3), but four signals, instead of one, are observed as singlets, two of which show the same intensity. Four singlet signals with the same intensity ratio as that observed for the Zn−OS(CH_3) signals are also observed for the $C_6R_2H_2$ hydrogens at 6.6−6.9 ppm. This observation of several sets of signals instead of one set of signals in the ^{1}H NMR spectra arises from the isomerism due to the tetrahedral nature of the sulfur atom shown below. We can expect formation of three isomers **A**, **B**, and **C** by the direction of the two methyl groups attached on the sulfur atoms. For isomer **A**, the two Zn−OS(CH_3) methyls are magnetically inequivalent and hence two methyl signals should be observed in a 1:1 intensity ratio. The two hydrogens on a $C_6R_2H_2$ ring also become inequivalent by the situation of the methyls, and two signals should be observed in a 1:1 ratio as well. For isomers **B** and **C**, the two Zn−OS(CH_3) methyls and the two hydrogens on a $C_6R_2H_2$ ring are, respectively, equivalent, and one singlet signal should be observed for each hydrogen. Mostly three signals are observed for the N═CH hydrogen at 8.12−8.46 ppm as singlets; but in some cases, two signals are observed, presumably due to the collapse of the two signals. From the intensity values for the singlet signals of Zn−OS(CH_3), $C_6R_2H_2$, or N═CH hydrogens, we can calculate the ratios of the three isomers **A**:**B**:**C** or **A**:**C**:**B** (see Chart 2). For **3a** and **3d**−**f**, the ratios are (0.41−0.43):(0.41−0.44):(0.12−0.18), but for **3g**−**4i**, the ratios are (0.50−0.57):(0.25−0.39):(0.11−0.21). Interestingly, only two isomers are observed in a 0.25:0.75 ratio for complex **3c**, from which single crystals suitable for X-ray crystallography can be obtained by the slow evaporation of solvent from a diethyl ether solution.

X-ray Crystallographic Studies. The structure of **3c** was confirmed by X-ray crystallographic studies (Figure 2). The structure is not deviated severely from that observed for the unfluorinated analogue.[7] By the presence of the fluorine

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(13) Becker, E. D. *High-Resolution NMR: Theory and Chemical Application*, 2nd ed.; Academic Press: London, 1980; p 101.

(14) Eberhardt, R.; Allmendinger, M.; Luinstra, G. A.; Rieger, B. *Organometallics* **2003**, *22*, 211.

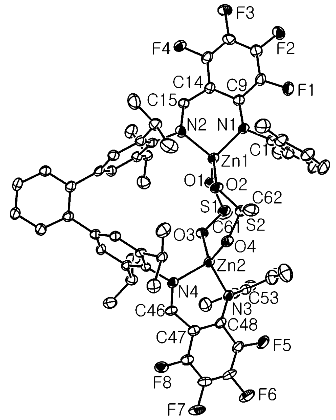

Figure 2. Thermal ellipsoid plot (30% probability level) of **3c**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): N(1)−Zn(1), 1.959(6); N(2)−Zn(1), 1.979(6); N(3)−Zn(2), 1.960(6); N(4)−Zn(2), 1.997(5); O(1)−Zn(1), 1.973(6); O(2)−Zn(1), 1.966(5); O(3)−Zn(2), 1.951(5); O(4)−Zn(2), 1.962(6); N(2)−C(15), 1.307(8); N(4)−C(46), 1.291(8); N(1)−C(9), 1.340(8); N(3)−C(48), 1.348(8); Zn(1)−Zn(2), 4.821; N(2)−N(4), 6.991; N(1)−N(3), 7.866; C(9)−N(1)−C(1), 121.9(6); C(9)−N(1)−Zn(1), 124.7(4); C(1)−N(1)−Zn(1), 112.5(4); N(1)−Zn(1)−N(2), 96.3(2); N(3)−Zn(2)−N(4), 95.4(2); O(2)−Zn(1)−O(1), 102.2(2); O(3)−Zn(2)−O(4), 105.8(2); O(3)−S(1)−O(1), 108.7(3).

atoms, the N(anilido)−Zn distances are increased to 1.959(6) and 1.960(6) Å from those observed for the unfluorinated analogue (1.938(4) and 1.938(4) Å, respectively). Some electron density on the anilido nitrogen atom is surely withdrawn by the fluorinated benzene ring, and hence the coordinating ability of the nitrogen atom is reduced; this consequently leads to an increase in the N−Zn distance. Because of more electron donation from the nitrogen atom to the fluorinated benzene ring, the N(1)−C(9) and N(3)−C(48) distances (1.340(8) and 1.348(8) Å, respectively) become shorter than those observed for the unfluorinated analogue (1.358(6) and 1.360(5) Å, respectively). The anilido N atoms (N(1) and N(3)) show trigonal structure (sum bond angles around the N atom of 359.1 and 359.9°), but the C(1) and the C(53) atoms are not situated on the C_6F_4 plane (dihedral angles of C(14)−C(9)−N(1)−C(1) and C(47)−C(48)−N(3)−C(53) are 21.3 and 30.6°, respectively). The corresponding carbon atoms are situated almost on the C_6H_4 plane in case of the unfluorinated analogue (the corresponding dihedral angles are 13.9 and 11.4°). The Zn−Zn separation is 4.821 Å, which is slightly shorter than those observed for the unfluorinated analogue (4.867 Å).

Polymerization Studies. The newly prepared fluorine-substituted bimetallic complexes **3** are tested as catalysts for CO_2/[cyclohexene oxide (CHO)] copolymerization at a condition of [Zn]:[CHO] = 1:5600, at which the unfluorinated complexes **2** were studied. As previously reported, the mononuclear β-diketiminato zinc complex shows negligible activity at such a low catalyst concentration (entry 10 in Table 1), which can be attributed to dissociation of the active associated dimeric species **1** from the less-active monomeric species at the low catalyst concentration. The TOF can be roughly estimated by reading the rate of CO_2 pressure drop. Because some fluorine-substituted complexes show significantly rapid CO_2 pressure drop compared with that of the unfluorinated system **2**, the standard reaction time is reduced to 2 from 5 h. As shown in Table 1, the activity is highly sensitive to the *N*-aryl ortho substituents. When both substituents on the imine moiety (R) and the anilido moiety (R′) are too large (**3a**, R = R′ = *i*Pr), the activity is very low (TOF = 130 h^{-1}), presumably because of the steric congestion at the reaction site. Interestingly, all complexes bearing the small methyl substituents on the anilido moiety (**3c**, **3f**, and **3i**) show low activity (entries 2, 5, and 8), whereas high activities are obtained with the complexes bearing large substitutes on the anilido moiety (R′ = *i*Pr, Et) and small substituents on the imine moiety (R = Me or Et) (**3d**, **e**, **g**, and **h**). A similar activity dependency on the *N*-aryl ortho substituents was also observed for both the unfluorinated complexes **2** and the mononuclear β-diketiminato zinc complexes.[7,10] The highest TOF is obtained with **3g** (R= Me, R′ = *i*Pr), with which the maximum conversion attainable in this bulk polymerization (30%) is observed when the reaction is quenched in 2 h (TON, 1570; TOF, 785 h^{-1}). With the unfluorinated analogue of **3g**, almost the same conversion was achieved in 5 h (TON, 1560; TOF 312 h^{-1}).

In this kind of polymerization, the molecular weight increases by the increase in TON if the chain-transfer reactions can be excluded. Actually, by increasing the TON with bimetallic system **2**, we were able to increase the molecular weight (M_n) up to 284 000. The reported molecular weights (M_n) of the polymers obtained by the mononuclear β-diketiminato zinc complexes have not exceeded 50 000. As expected, the high-molecular-weight polymers are obtained when the TONs are high (entries 3, 4, 6, and 7). The

Table 1. CO_2/(Cyclohexene Oxide) Copolymerization Results[a]

entry	catalyst	TON[b]	TOF[c]	% carbonate[d]	M_n[e]	M_w/M_n[e]
1	**3a**	260	130	25	75 000	4.7
2	**3c**	320	160	44	25 000	1.7
3	**3d**	1420	710	72	120 000	1.7
4	**3e**	1080	540	86	91 000	1.3
5	**3f**	550	275	84	43 000	1.8
6	**3g**	1570	785	65	118 000	2.1
7	**3h**	1200	600	86	122 000	1.4
8	**3i**	490	245	75	38 000	1.4
9	unfluorinated **3g**[f]	1560	312	94	225 000	1.7
10	[(bdi)Zn(μ-OS(O)Me)]$_2$[g]	56	5.6	74	27 000	1.8

[a] Polymerization conditions: neat CHO (8.0 mL, 79 mmol), [Zn]:[CHO] = 1:5600, 80 °C, 14 bar CO_2 (initial pressure), 2 h. [b] Turnover number in moles of CHO consumed per mole of Zn. [c] Turnover frequency in moles of CHO consumed per mole of Zn per hour. [d] Estimated by ^{1}H NMR spectroscopy. [e] Determined by GPC, calibrated with polystyrene standard in $CDCl_3$. [f] Data from ref 7. [g] Polymerization data of mononuclear complex bdi = $(C_6H_3Et_2)N{=}C(Me)CH{=}C(Me)N(C_6H_3Et_2)$; data from ref 7.

Table 2. CO_2/(Cyclohexene Oxide) Copolymerization Results in Reduced [Zn]:[CHO] Ratios[a]

entry	catalyst	[Zn]:[CHO]	time	TON	TOF	% carbonate	M_n	M_w/M_n
1	**3g**	1:5600	2	1570	785	65 (80)[g]	118 000	2.1
2	**3g**	1:5600	1	1170	1170	75	147 000	1.8
3	**3g**	1:22 400	3	4860	1620	69	179 000	1.7
4	**3g**	1:33 600	4.5	7760	1720	70	214 000	1.7
5	**3g**	1:50 000	6.7	10 100	1510	72	118 000	2.5
6[b]	**3g**	1:50 000	3.3	9440	2860	79 (88)[g]	245 000	1.2
7[b,c]	**3g**	1:50 000	4	9930	2480	78	221 000	1.4
8	**3g**	1:67 200	9	1070	119	19	136 000	2.1
9	unfluorinated **3g**[d]	1:16 800	15	2980	200	91	284 000	1.7
10	CrCl(tfpp)/DMAP[e]	1:4275	18	3120	173	97	3900	1.2
11	[Zn(μ-OMe)(bdi)]$_2$[f]	1:1000	0.17	382	2290	90	23 000	1.1

[a] Polymerization conditions: neat CHO (8.0 mL and 79 mmol for entries 1−2; 16 mL and 158 mmol for entries 3−6), 80 °C, 14 bar CO_2 (initial pressure). [b] Contact time between the catalyst and CHO was eliminated and more-efficient stirring was exerted. [c] Polymerization temperature = 50 °C. [d] Data from ref 7. [e] tfpp = tetraperfluorphenylphorphyrin, DMAP = 4-(dimethylamino)pyridine; data from ref 15. [f] bdi = $(C_6H_3Me_2)N{=}C(Me)C(CN){=}C(Me)N(C_6H_3i\text{Pr}_2)$; data from ref 10. [g] The values in the parenthesis are the carbonate linkages after the polyether was removed by precipitation of the polymer in THF by the addition of petroleum ether.

number-average molecular weights (M_n) exceeding 100 000 are obtained with complexes **3d**, **g**, and **h**. The molecular weight distributions (M_w/M_n) are rather broad (1.3−2.1), which indicates that there are some kind of chain-transfer reactions. The presence of chain-transfer reactions is further supported by the fact that the observed molecular weights are lower than those calculated from the TONs.

Unfluorinated complexes **2** gave almost-alternating copolymers (the carbonate linkages, >90%) but fluorine-substituted complexes **3** do not give such highly alternating copolymers. The carbonated linkage, which can be calculated from the ^{1}H NMR spectra, varies by the *N*-aryl substituents. With **3e** (R = R′ = Et), **3f** (R = Et, R′ = Me), and **3h** (R = Me, R′ = Et), the carbonate linkages are high (84−86%), but highly active complexes **3d** (R = Et, R′ = *i*Pr) and **3g** (R = Me, R′= *i*Pr) give polymers of moderate carbonate linkage (72 and 65%, respectively).

To achieve high TON, we need the complex to be active at a low [Zn]:[CHO] ratio. The polymerizations were carried out with **3g** at reduced [Zn]:[CHO] ratios (Table 2). The final status of the polymer solution obtained with **3g** in the standard condition ([Zn]:[CHO] = 1:5600 and time = 2 h) is so viscous (conversion, 28%) that we suspect the catalyst might not work in the later stage of the polymerization time because of diffusion problems. When the polymerization time is cut to 1 h under the same condition, 20% conversion is obtained, which corresponds to a slight decrease in TON (1170) but a significant increase in TOF (1170 h^{-1}; entry 2). When the [Zn]:[CHO] ratio is reduced four times to 1:22 400 from 1:5600 and the reaction time is increased to 3 h, the complex is still active, giving 22% conversion, which corresponds to TON = 4860 and TOF = 1620 h^{-1} (entry 3). When the ratio is further reduced to 1:33 600 and 1:50 000 (2.0 mg of catalyst in a neat 16 mL of CHO), most of the catalyst is still alive and almost the same TOF values are obtained (entries 4 and 5). Because the reaction time is increased to 4.5 and 6.7 h inversely to the [Zn]:[CHO] ratios, the TONs are increased to 7760 and 10 100, respectively. When the ratio is further decreased to 1:67 200, a dramatic decrease in TOF is observed, surely due to the catalyst decomposition by the residual protic impurities present in the monomers (entry 8). The highest TON, 10 100, attained by **3g** corresponds to 20 kg of polymer/g of Zn; this number is astonishing when considering the highest TONs reported with the unfluorinated analogue and the mononuclear β-diketiminato Zn complexes are, respectively, 3000 (6.5 kg of polymer/g of Zn) and 651 (1.4 kg of polymer/g of Zn).[7,14] As previously discussed, a high TON can be obtained only when the catalyst is active at a low [Zn]:[CHO] ratio. The mononuclear β-diketiminato Zn complexes cannot show activity at low [Zn]:[CHO] by dissociation to the less-active monomeric species. Most of polymerization studies have been carried out at a condition of [Zn]:[CHO] = 1:1000. The unfluorinated analogue of **3g** showed activity only at a [Zn]:[CHO] ratio up to 1:16 800. When the ratio is decreased further to 1:22 400, unfluorinated complex **2** shows negligible activity due to catalyst decomposition. Reduced basicity of the anilido nitrogen because of the presence of the electron-withdrawing fluorine atoms might relieve the sensitivity toward the protic impurities, consequently preventing catalyst decomposition at such a low catalyst concentration as [Zn]:[CHO] = 1:50 000. The highest TON reported in this polymerization up to now is 3120, which was realized with the porphyrin chromium complex CrCl(tfpp) (tfpp = tetraperfluorphenylporphyrin) activated with DMAP (4-(dimethylamino)pyridine).[15] It was attained with a long reaction time of 18 h (TOF = 173 h^{-1}), and a very low molecular-weight polymer (M_n = 3900) was obtained (entry 10).

A demerit of the fluorinated system compared with the unfluorinated analogue is relatively low carbonate linkage in the obtained polymer, and the percent carbonate linkages is not improved significantly by reducing the [Zn]:[CHO] ratio (~70%). The low carbonate linkage is possibly ascribed either to contacting the catalyst with CHO in the absence of CO_2[16] or to a diffusion problem of the CO_2 gas caused by inefficient stirring. The carbonate linkage is actually improved from 72 to 79% by eliminating the contacting time between the catalyst and CHO in the absence of CO_2 and exerting more-efficient stirring (entry 6). When the polymerization temperature is lowered, the CO_2 concentration in

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(15) Mang, S.; Cooper, A. I.; Colclough, M. E.; Chauhan, N.; Holmes, A. B. *Macromolecules* **2000**, *33*, 303.

(16) Koning, C.; Wildeson, J.; Parton, R.; Plum, B.; Steeman, P.; Darensbourg, D. J. *Polymer* **2001**, *42*, 3995.

the solution increases and hence more carbonate linkage can be expected; however, it is not improved by lowering the polymerization temperature from 80 to 50 °C (entry 7). To see whether the low carbonate linkage arises from contamination of the polymer with polyether that can be generated during the polymerization reaction by some other species, we fractionated the polymer by dissolving it in THF and precipitated it by adding petroleum ether. The polyether is soluble in petroleum ether and hence it can be removed by the procedure. After the fractionation, the carbonate linkage is improved further from 79 to 88% (entry 6), which is close to that observed for the polymer obtained by the unfluorinated complex (91%). It is guessed that some anionic species, which is active for the ring-opening polymerization of CHO, is generated by the complex decomposition. Actually, the polymer obtained at extremely a low [Zn]:[CHO] ratio, where most of catalyst is decomposed, shows very low carbonate linkage (19%, entry 8).

By exerting more efficient stirring, we increased the TOF almost doubly, and the highest TOF obtained by **3g** is 2860 h^{-1} (entry 6), which corresponds to one CHO consumption in every 1.3 s. The TOF is 9 times higher than that obtained by the unfluorinated complex (312 h^{-1}). The TOF is also higher than that obtained by the highly efficient mononuclear β-diketiminato Zn complexes $\{[(C_6H_3Me_2)N{=}C(Me)C(CN){=}C(Me)N(C_6H_3i\mathrm{Pr}_2)]Zn(\mu\text{-}OMe)\}_2$ (2290 h^{-1}, entry 11).

The molecular weight (M_n) increases from 147 000 to 179 000 and finally 214 000 by an increase in the TON from 1170 to 4870 and 7760, respectively (entries 2−4), but the molecular weight is decreased to 118 000 by the further increase in the TON to 10 100. This unexpected decrease in the molecular weight indicates that some chain-transfer reactions occur by reducing the [Zn]:[CHO] ratio severely.[17]

Summary. $Li(H)N{-}C_6H_3R'_2$ (R′ = *i*Pr, Et, Me) regioselectively attacks, in nonpolar solvent such as diethyl ether or toluene, an *o*-fluorine atom on the Schiff's base constructed from pentafluorobenzaldehyde, $o\text{-}C_6H_4\{(C_6H_2R_2)N{=}CH{-}C_6F_5\}_2$ (R = *i*Pr, Et, Me), to afford fluorine-substituted *o*-phenylene-bridged bis(anilido−aldimine) compounds $o\text{-}C_6H_4\text{-}\{(C_6H_2R_2)N{=}CH{-}C_6F_4{-}(H)N(C_6H_3R'_2)\}_2$, from which dinuclear *μ*-methylsulfinato zinc complexes $o\text{-}C_6H_4\text{-}\{[(C_6H_2R_2)N{=}CH{-}C_6F_4{-}N(C_6H_3R'_2)\text{-}\kappa^2N,N]Zn(\mu\text{-}OS(O)\text{-}Me)\}_2$ (**3a**−**i**) are prepared quantitatively by the successive addition of Me_2Zn and SO_2 gas. The structure of a complex is confirmed by the X-ray crystallographic studies. Complexes **3** show higher TOF (turnover frequency) for CO_2/(cyclohexene oxide) copolymerization than the unfluorinated analogues. The activity is very sensitive to substituents R and R′, and the highest TOF (2860 h^{-1}) is obtained with the complex of R = Me and R′ = *i*Pr (**3g**). Complex **3g** shows activity at such a low catalyst concentration as [Zn]:[cyclohexene oxide] = 1:50 000 that a TON up to 10 100 is attained. High-molecular-weight polymers (M_n, 100 000−200 000) are obtained with rather broad molecular-weight distributions (M_w/M_n, 1.3−2.5). The obtained polymers are not perfectly alternating, and variable carbonate linkages (65−85%) are observed depending on the *N*-aryl ortho substituents, R and R′, and the polymerization conditions.

Experimental Section

General Remarks. All manipulations were performed under an inert atmosphere using standard glovebox and Schlenk techniques. Toluene, diethyl ether, and C_6D_6 were distilled from benzophenone ketyl. The CO_2 gas (99.99%) was purified by storing it overnight in a bomb-reactor (500 mL) containing P_2O_5 at 17 bar pressure. Cyclohexene oxide (CHO) was purified by stirring over KH for several days and it was transferred under vacuum to a reservoir. ^1H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{19}F NMR (376 MHz) spectra were recorded on a Varian Mercury plus 400. ^{19}F NMR spectra were calibrated and reported downfield from external α,α,α-trifluorotoluene. Elemental analyses were carried out at the Inter-University Center Natural Science Facilities, Seoul National University. Gel permeation chromatograms (GPC) were obtained at room temperature in $CDCl_3$ using Waters Millennium.

Compound 4a. $o\text{-}C_6H_4(C_6H_2i\mathrm{Pr}_2{-}NH_2)_2$ (1.50 g, 3.50 mmol), pentafluorobenzaldehyde (2.74 g, 14.0 mmol), molecular sieves (4 Å, 500 mg), and toluene (30 mL) were added to a flask. After the solution was refluxed overnight with a Dean−Stark apparatus, it was filtered to remove the molecular sieves. The solvent was removed by a rotary evaporator, and the residue was triturated with hexane to give a yellow solid (2.69 g, 98%). Mp = 207 °C. IR (NaCl): 1634 (C=N) cm^{-1}. ^1H NMR (C_6D_6): δ 1.18 (d, J = 7.2 Hz, 12H, CH_3), 3.13 (septet, J = 7.2 Hz, 2H, CH), 7.14 (s, 2H, C_6H_2), 7.34 (AA′BB′, 1H, C_6H_4), 7.63 (AA′BB′, 1H, C_6H_4), 8.11 (s, 1H, N=CH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 23.88, 28.57, 111.3 (m), 125.66, 130.46, 136.88, 137.8 (dm, $^2J_{CF}$ = 260 Hz), 139.10, 141.93, 142.3 (dm, $^2J_{CF}$ = 260 Hz), 145.0 (dm, $^2J_{CF}$ = 250 Hz), 147.95, 150.93. $^{19}F\{^1H\}$ NMR (C_6D_6): δ −69.21 (td, $^3J_{FF}$ = 21 Hz, $^4J_{FF}$ = 7.4 Hz, meta), −58.29 (t, $^3J_{FF}$ = 21 Hz, para), −50.64 (dm, $^3J_{FF}$ = 21 Hz, ortho). Anal. Calcd. for ($C_{44}H_{38}F_{10}N_2$): C, 67.34; H, 4.88; N, 3.57. Found: C, 67.60; H, 4.67; N, 3.34.

Compound 4b. The compound was synthesized by the same conditions and procedures as those used for **4a** using $o\text{-}C_6H_4(C_6H_2\text{-}Et_2{-}NH_2)_2$. A yellow solid was obtained in 92% yield. Mp = 207 °C. IR (NaCl): 1643 (C=N) cm^{-1}. ^1H NMR (C_6D_6): δ 1.13 (t, J = 7.6 Hz, 6H, CH_3), 2.50 (q, J = 7.6 Hz, 4H, CH_2), 7.07 (s, 2H, C_6H_2), 7.35 (AA′BB′, 1H, C_6H_4), 7.60 (AA′BB′, 1H, C_6H_4), 8.01 (s, 1H, N=CH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 15.36, 25.32, 111.2 (m), 128.86, 130.68, 132.50, 137.7 (dm, $^2J_{CF}$ = 250 Hz), 138.93, 141.28, 142.2 (dm, $^2J_{CF}$ = 250 Hz), 145.9 (dm, $^2J_{CF}$ = 260 Hz), 149.04, 150.92. $^{19}F\{^1H\}$ NMR (C_6D_6): δ −69.36 (td, $^3J_{FF}$ = 21 Hz, $^4J_{FF}$ = 6.7 Hz, meta), −58.46 (t, $^3J_{FF}$ = 21 Hz, para), −50.62 (dm, $^3J_{FF}$ = 21 Hz, ortho). Anal. Calcd. for ($C_{40}H_{30}F_{10}N_2$): C, 65.93; H, 4.15; N, 3.84. Found: C, 65.60; H, 4.37; N, 3.54.

Compound 4c. The compound was synthesized by the same conditions and procedures as those used for **4a** using $o\text{-}C_6H_4(C_6H_2\text{-}Me_2{-}NH_2)_2$. A yellow solid was obtained in 94% yield. Mp = 202 °C. IR (NaCl): 1634 (C=N) cm^{-1}. ^1H NMR (C_6D_6): δ 2.07 (s, 6H, CH_3), 7.14 (s, 2H, C_6H_2), 7.34 (AA′BB′, 1H, C_6H_4), 7.55 (AA′BB′, 1H, C_6H_4), 7.74 (s, 1H, N=CH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 18.63, 111.2 (m), 126.41, 130.31, 131.26, 137.6 (dm, $^2J_{CF}$ = 260 Hz), 138.92, 140.87, 142.1 (dm, $^2J_{CF}$ = 250 Hz), 145.9 (dm, $^2J_{CF}$ = 260 Hz), 149.88, 151.15. $^{19}F\{^1H\}$ NMR (C_6D_6): δ −69.59 (td, $^3J_{FF}$ = 20 Hz, $^4J_{FF}$ = 7.1 Hz, meta), −58.68 (t, $^3J_{FF}$ = 20 Hz, para), −50.24 (dm, $^3J_{FF}$ = 20 Hz, ortho). Anal. Calcd. for ($C_{36}H_{22}F_{10}N_2$): C, 64.29; H, 3.30; N, 4.17. Found: C, 64.38; H, 3.22; N, 4.34.

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(17) van Meerendonk, W. J.; Duchateau, R.; Koning, C. E.; Gruter, G.-J. M. *Macromolecules* **2005**, *38*, 7306.

Compound 5a. Compound **4a** (0.282 g, 0.360 mmol), 2,6-$i\mathrm{Pr_2C_6H_3N(Li)H}$ (0.460 g, 1.80 mmol), and toluene (4 mL) were added to a vial inside a glovebox. The resulting slurry was stirred for 2 days. After a saturated aqueous $\mathrm{NaHCO_3}$ solution (20 mL) was added, the organic compound was extracted with ethyl acetate (20 mL × 3). After the organic phase was dried with anhydrous $\mathrm{MgSO_4}$, the solvent was removed by a rotary evaporator to give an oily residue, which was purified by column chromatography on silica gel eluting with hexane and toluene (v/v, 30:1). A yellow solid was obtained in 62% yield (0.225 g). Mp = 230 °C. IR (NaCl): 3158 (N−H), 1656 (C=N) cm^{-1}. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.05 (d, J = 7.2 Hz, 12H, $\mathrm{CH_3}$), 1.14 (d, J = 7.2 Hz, 6H, $\mathrm{CH_3}$), 1.23 (d, J = 7.2 Hz, 6H, $\mathrm{CH_3}$), 3.04 (septet, J = 7.2 Hz, 2H, CH), 3.35 (septet, J = 7.2 Hz, 2H, CH), 7.05 (s, 2H, $\mathrm{C_6H_2}$), 7.09 (d, J = 7.6 Hz, 2H, $\mathrm{C_6H_3}$), 7.20 (t, J = 7.6 Hz, 1H, $\mathrm{C_6H_3}$), 7.34 (AA′BB′, 1H, $\mathrm{C_6H_4}$), 7.61 (AA′BB′, 1H, $\mathrm{C_6H_4}$), 8.58 (s, 1H, N=CH), 11.14 (s, 1H, NH). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 23.26, 24.00, 24.90, 28.62, 29.47, 102.2 (m), 123.58, 125.75, 127.88, 128.15, 130.35, 131.0 (dm, $^{2}J_{\mathrm{CF}}$ = 240 Hz), 135.50, 136.41, 136.9 (dm, $^{2}J_{\mathrm{CF}}$ = 260 Hz), 137.97, 139.23, 141.83, 144.3 (dm, $^{2}J_{\mathrm{CF}}$ = 260 Hz), 146.26, 146.54, 148.7 (dm, $^{2}J_{\mathrm{CF}}$ = 240 Hz), 158.03. ^{19}F{^{1}H} NMR ($\mathrm{C_6D_6}$): δ −82.36 (br t, $^{3}J_{\mathrm{FF}}$ = 18 Hz), −67.92 (s), −57.89 (br t, $^{3}J_{\mathrm{FF}}$ = 18 Hz), −55.72 (br d, $^{3}J_{\mathrm{FF}}$ = 17 Hz). Anal. Calcd. for ($\mathrm{C_{68}H_{74}F_8N_4}$): C, 74.29; H, 6.78; N, 5.10. Found: C, 74.50; H, 6.47; N, 5.26.

Compound 5b. The compound was synthesized by the same conditions and procedures as those used for **5a** using **4a** and 2,6-$\mathrm{Et_2C_6H_3N(Li)H}$. A yellow solid was obtained in 82% yield. Mp = 212 °C. IR (NaCl): 3157 (N−H), 1656 (C=N) cm^{-1}. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.03 (d, J = 7.2 Hz, 12H, $\mathrm{CH_3}$), 1.14 (t, J = 7.2 Hz, 6H, $\mathrm{CH_3}$), 2.58 (dq, J = 21 and 7.2 Hz, 2H, $\mathrm{CH_2}$), 2.68 (dq, J = 21 and 7.2 Hz, 2H, $\mathrm{CH_2}$), 3.02 (septet, J = 7.2 Hz, 2H, CH), 7.02 (d, J = 7.2 Hz, 2H, $\mathrm{C_6H_3}$), 7.03 (s, 2H, $\mathrm{C_6H_2}$), 7.10 (t, J = 7.2 Hz, 1H, $\mathrm{C_6H_3}$), 7.34 (AA′BB′, 1H, $\mathrm{C_6H_4}$), 7.59 (AA′BB′, 1H, $\mathrm{C_6H_4}$), 8.56 (s, 1H, N=CH), 11.13 (s, 1H, NH). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 15.39, 23.96, 25.80, 28.64, 102.5 (m), 125.75, 126.70, 127.56, 127.85, 130.34, 131.1 (dm, $^{2}J_{\mathrm{CF}}$ = 240 Hz), 135.87, 136.6 (dm, $^{2}J_{\mathrm{CF}}$ = 250 Hz), 137.00, 137.93, 139.26, 141.62, 141.64, 141.89, 144.2 (dm, $^{2}J_{\mathrm{CF}}$ = 250 Hz),146.51, 148.7 (dm, $^{2}J_{\mathrm{CF}}$ = 250 Hz), 157.84. ^{19}F{^{1}H} NMR ($\mathrm{C_6D_6}$): δ −82.27 (td, $^{3}J_{\mathrm{FF}}$ = 22 Hz, $^{3}J_{\mathrm{FF}}$ = 6.7 Hz), −67.59 (m), −57.92 (t, $^{3}J_{\mathrm{FF}}$ = 19 Hz), −55.85 (dm, $^{3}J_{\mathrm{FF}}$ = 20 Hz). Anal. Calcd. for ($\mathrm{C_{64}H_{66}F_8N_4}$): C, 73.68; H, 6.38; N, 5.37. Found: C, 73.53; H, 6.53; N, 5.45.

Compound 5c. The compound was synthesized by the same conditions and procedures as those used for **5a** using **4a** and 2,6-$\mathrm{Me_2C_6H_3N(Li)H}$. A yellow solid was obtained in 75% yield. Mp = 225 °C. IR (NaCl): 3158 (N−H), 1652 (C=N) cm^{-1}. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.02 (d, J = 7.2 Hz, 12H, $\mathrm{CH_3}$), 2.20 (s, 6H, $\mathrm{CH_3}$), 2.99 (septet, J = 7.2 Hz, 2H, CH), 6.80−7.00 (m, 3H, $\mathrm{C_6H_3}$), 7.02 (s, 2H, $\mathrm{C_6H_2}$), 7.34 (AA′BB′, 1H, $\mathrm{C_6H_4}$), 7.60 (AA′BB′, 1H, $\mathrm{C_6H_4}$), 8.55 (s, 1H, N=CH), 11.13 (s, 1H, NH). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 18.68, 23.73, 28.69, 102.7 (m), 125.71, 126.85, 127.85, 128.24, 130.27, 131.2 (dm, $^{2}J_{\mathrm{CF}}$ = 240 Hz), 135.22, 135.25, 136.5 (dm, $^{2}J_{\mathrm{CF}}$ = 240 Hz), 137.59, 137.65, 138.30, 139.17, 141.89, 144.0 (dm, $^{2}J_{\mathrm{CF}}$ = 250 Hz), 146.41, 148.7 (dm, $^{2}J_{\mathrm{CF}}$ = 240 Hz), 157.62. ^{19}F-{^{1}H} NMR ($\mathrm{C_6D_6}$): δ −82.50 (td, $^{3}J_{\mathrm{FF}}$ = 22 Hz, $^{3}J_{\mathrm{FF}}$ = 6.3 Hz), −68.33 (m), −58.02 (t, $^{3}J_{\mathrm{FF}}$ = 23 Hz), −55.80 (dm, $^{3}J_{\mathrm{FF}}$ = 19 Hz). Anal. Calcd. for ($\mathrm{C_{60}H_{58}F_8N_4}$): C, 73.00; H, 5.92; N, 5.68. Found: C, 73.32; H, 5.73; N, 5.46.

Compound 5d. The compound was synthesized by conditions and procedures similar to those used for **5a** using **4b** and 2,6-$i\mathrm{Pr_2C_6H_3N(Li)H}$. Diethyl ether was used as a solvent. A yellow solid was obtained in 47% yield. Mp = 216 °C. IR (NaCl): 3162 (N−H), 1656 (C=N) cm^{-1}. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.99 (t, J = 7.6 Hz, 6H, $\mathrm{CH_3}$), 1.12 (d, J = 7.2 Hz, 6H, $\mathrm{CH_3}$), 1.22 (d, J = 7.2 Hz, 6H, $\mathrm{CH_3}$), 2.41 (q, J = 7.6 Hz, 4H, $\mathrm{CH_2}$), 3.33 (septet, J = 7.2 Hz, 2H, CH), 7.02 (s, 2H, $\mathrm{C_6H_2}$), 7.09 (d, J = 7.6 Hz, 2H, $\mathrm{C_6H_3}$), 7.21 (t, J = 7.6 Hz, 1H, $\mathrm{C_6H_3}$), 7.34 (AA′BB′, 1H, $\mathrm{C_6H_4}$), 7.59 (AA′BB′, 1H, $\mathrm{C_6H_4}$), 8.51 (s, 1H, N=CH), 11.10 (s, 1H, NH). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 15.36, 23.45, 24.81, 25.28, 29.41, 102.3 (m), 123.62, 127.83, 128.12, 128.85, 130.65, 131.0 (dm, $^{2}J_{\mathrm{CF}}$ = 240 Hz), 133.51, 136.47, 136.8 (dm, $^{2}J_{\mathrm{CF}}$ = 240 Hz), 139.10, 141.20, 144.3 (dm, $^{2}J_{\mathrm{CF}}$ = 250 Hz), 146.30, 147.86, 148.7 (dm, $^{2}J_{\mathrm{CF}}$ = 250 Hz), 158.04. ^{19}F{^{1}H} NMR ($\mathrm{C_6D_6}$): δ −82.46 (td, $^{3}J_{\mathrm{FF}}$ = 22 Hz, $^{4}J_{\mathrm{FF}}$ = 7.4 Hz), −67.75 (m), −58.03 (ddd, $^{3}J_{\mathrm{FF}}$ = 21 Hz), −55.34 (ddd, $^{3}J_{\mathrm{FF}}$ = 18 Hz). Anal. Calcd. for ($\mathrm{C_{64}H_{66}F_8N_4}$): C, 73.68; H, 6.38; N, 5.37. Found: C, 73.60; H, 6.50; N, 5.24.

Compound 5e. The compound was synthesized by the same conditions and procedures as those used for **5a** using **4b** and 2,6-$\mathrm{Et_2C_6H_3N(Li)H}$. A yellow solid was obtained in 54% yield. Mp = 214−215 °C. IR (NaCl): 3158 (N−H), 1652 (C=N) cm^{-1}. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.97 (t, J = 7.6 Hz, 6H, $\mathrm{CH_3}$), 1.12 (t, J = 7.6 Hz, 6H, $\mathrm{CH_3}$), 2.38 (q, J = 7.6 Hz, 4H, $\mathrm{CH_2}$), 2.52−2.70 (m, 4H, $\mathrm{CH_2}$), 6.99 (s, 2H, $\mathrm{C_6H_2}$), 7.01 (d, J = 7.6 Hz, 2H, $\mathrm{C_6H_3}$), 7.11 (t, J = 7.6 Hz, 1H, $\mathrm{C_6H_3}$), 7.34 (AA′BB′, 1H, $\mathrm{C_6H_4}$), 7.57 (AA′BB′, 1H, $\mathrm{C_6H_4}$), 8.50 (s, 1H, N=CH), 11.06 (s, 1H, NH). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 15.29, 15.43, 25.33, 25.68, 102.4 (m), 126.60, 127.51, 128.88, 130.58, 131.0 (dm, $^{2}J_{\mathrm{CF}}$ = 250 Hz), 133.49, 135.92, 136.7 (dm, $^{2}J_{\mathrm{CF}}$ = 240 Hz), 137.08, 139.07, 141.24, 141.58, 144.1 (dm, $^{2}J_{\mathrm{CF}}$ = 250 Hz), 147.84, 148.7 (dm, $^{2}J_{\mathrm{CF}}$ = 240 Hz), 157.97. ^{19}F-{^{1}H} NMR ($\mathrm{C_6D_6}$): δ −82.29 (td, $^{3}J_{\mathrm{FF}}$ = 22 Hz, $^{4}J_{\mathrm{FF}}$ = 6.3 Hz), −67.53 (m), −58.00 (t, $^{3}J_{\mathrm{FF}}$ = 20 Hz), −55.50 (dm, $^{3}J_{\mathrm{FF}}$ = 19 Hz). Anal. Calcd. for ($\mathrm{C_{60}H_{58}F_8N_4}$): C, 73.00; H, 5.92; N, 5.68. Found: C, 73.28; H, 5.73; N, 5.43.

Compound 5f. The compound was synthesized by the same conditions and procedures as those used for **5a** using **4b** and 2,6-$\mathrm{Me_2C_6H_3N(Li)H}$. A yellow solid was obtained in 63% yield. Mp = 215−216 °C. IR (NaCl): 3153 (N−H), 1652 (C=N) cm^{-1}. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.96 (t, J = 7.6 Hz, 6H, $\mathrm{CH_3}$), 2.16 (s, 6H, $\mathrm{CH_3}$), 2.35 (q, J = 7.6 Hz, 4H, $\mathrm{CH_2}$), 6.92−6.98 (m, 3H, $\mathrm{C_6H_3}$), 6.99 (s, 2H, $\mathrm{C_6H_2}$), 7.34 (AA′BB′, 1H, $\mathrm{C_6H_4}$), 7.57 (AA′BB′, 1H, $\mathrm{C_6H_4}$), 8.47 (s, 1H, N=CH), 10.99 (s, 1H, NH). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 15.35, 18.71, 25.44, 102.8 (m), 126.85, 128.89, 130.60, 131.1 (dm, $^{2}J_{\mathrm{CF}}$ = 250 Hz), 133.41, 135.42, 136.6 (dm, $^{2}J_{\mathrm{CF}}$ = 250 Hz), 138.40, 139.10, 141.25, 144.2 (dm, $^{2}J_{\mathrm{CF}}$ = 250 Hz), 147.79, 148.7 (dm, $^{2}J_{\mathrm{CF}}$ = 250 Hz), 157.64. ^{19}F{^{1}H} NMR ($\mathrm{C_6D_6}$): δ −82.16 (td, $^{3}J_{\mathrm{FF}}$ = 22 Hz, $^{4}J_{\mathrm{FF}}$ = 6.3 Hz), −68.45 (m), −58.16 (t, $^{3}J_{\mathrm{FF}}$ = 21 Hz), −55.58 (dm, $^{3}J_{\mathrm{FF}}$ = 20 Hz). Anal. Calcd. ($\mathrm{C_{56}H_{50}F_8N_4}$): C, 72.24; H, 5.41; N, 6.02. Found: C, 72.40; H, 5.37; N, 6.34.

Compound 5g. The compound was synthesized by conditions and procedures similar to those used for **5a** using **4c** and 2,6-$i\mathrm{Pr_2C_6H_3N(Li)H}$. Diethyl ether was used as a solvent. A yellow solid was obtained in 67% yield. Mp = 213−214 °C. IR (NaCl): 3162 (N−H), 1656 (C=N) cm^{-1}. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.07 (d, J = 7.2 Hz, 6H, $\mathrm{CH_3}$), 1.19 (d, J = 7.2 Hz, 6H, $\mathrm{CH_3}$), 1.95 (s, 6H, $\mathrm{CH_3}$), 3.28 (septet, J = 7.2 Hz, 2H, CH), 7.08 (d, J = 7.6 Hz, 2H, $\mathrm{C_6H_3}$), 7.16 (s, 2H, $\mathrm{C_6H_2}$), 7.21 (t, J = 7.6 Hz, 1H, $\mathrm{C_6H_3}$), 7.31 (AA′BB′, 1H, $\mathrm{C_6H_4}$), 7.53 (AA′BB′, 1H, $\mathrm{C_6H_4}$), 8.28 (s, 1H, N=CH), 11.10 (s, 1H, NH). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 18.70, 23.32, 24.75, 29.39, 102.3 (m), 123.60, 127.42, 130.35, 130.9 (dm, $^{2}J_{\mathrm{CF}}$ = 240 Hz), 131.23, 135.77, 136.2 (dm, $^{2}J_{\mathrm{CF}}$ = 250 Hz), 136.42, 138.99, 140.75, 144.5 (dm, $^{2}J_{\mathrm{CF}}$ = 250 Hz), 146.28, 148.7 (dm, $^{2}J_{\mathrm{CF}}$ = 250 Hz), 148.77, 158.05. ^{19}F{^{1}H} NMR ($\mathrm{C_6D_6}$): δ −82.73 (td, $^{3}J_{\mathrm{FF}}$ = 22 Hz, $^{4}J_{\mathrm{FF}}$ = 6.7 Hz), −68.01 (m), −58.23 (t, $^{3}J_{\mathrm{FF}}$ = 20 Hz), −54.75 (dm, $^{3}J_{\mathrm{FF}}$ = 18 Hz). Anal. Calcd. for ($\mathrm{C_{60}H_{58}F_8N_4}$): C, 73.00; H, 5.92; N, 5.68. Found: C, 73.24; H, 5.72; N, 5.40.

Compound 5h. The compound was synthesized by the same conditions and procedures as those used for **5a** using **4c** and 2,6-$Et_2C_6H_3N(Li)H$. A yellow solid was obtained in 67% yield. It was obtained in 35% yield when diethyl ether was used as a solvent. Mp = 199 °C. IR (NaCl): 3158 (N−H), 1656 ($C{=}N$) cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.07 (t, J = 7.6 Hz, 6H, CH_3), 1.93 (s, 6H, CH_3), 2.46−2.62 (m, 4H, CH_2), 7.00 (d, J = 7.6 Hz, 2H, C_6H_3), 7.07 (s, 2H, C_6H_2), 7.12 (t, J = 7.6 Hz, 1H, C_6H_3), 7.32 (AA′BB′, 1H, C_6H_4), 7.52 (AA′BB′, 1H, C_6H_4), 8.28 (s, 1H, $N{=}CH$), 10.95 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 15.26, 18.76, 25.71, 102.4 (m), 126.60, 127.45, 130.31, 131.9 (dm, $^2J_{CF}$ = 240 Hz), 135.85, 136.6 (dm, $^2J_{CF}$ = 260 Hz), 137.25, 139.02, 140.83, 141.63, 143.9 (dm, $^2J_{CF}$ = 250 Hz), 148.6 (dm, $^2J_{CF}$ = 240 Hz), 148.84, 157.96. $^{19}F\{^1H\}$ NMR (C_6D_6): δ −82.61 (td, $^3J_{FF}$ = 22 Hz, $^4J_{FF}$ = 6.7 Hz), −67.65 (m), −58.25 (t, $^3J_{FF}$ = 20 Hz), −54.90 (dm, $^3J_{FF}$ = 19 Hz). Anal. Calcd. for ($C_{56}H_{50}F_8N_4$): C, 72.24; H, 5.41; N, 6.02. Found: C, 72.57; H, 5.37; N, 6.30.

Compound 5i. The compound was synthesized by conditions and procedures similar to those used for **5a** using **4c** and 2,6-$Me_2C_6H_3N(Li)H$. Diethyl ether was used as a solvent. A yellow solid was obtained in 50% yield. Mp = 124 °C. IR (NaCl): 3153 (N−H), 1656 ($C{=}N$) cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.91 (s, 6H, CH_3), 2.09 (s, 6H, CH_3), 6.93 (d, J = 7.6 Hz, 2H, C_6H_3), 7.00 (t, J = 7.6 Hz, 1H, C_6H_3), 7.09 (s, 2H, C_6H_2), 7.33 (AA′BB′, 1H, C_6H_4), 7.53 (AA′BB′, 1H, C_6H_4), 8.24 (s, 1H, $N{=}CH$), 10.80 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 18.73, 18.84, 102.7 (m), 126.83, 127.50, 127.63, 130.27, 131.1 (dm, $^2J_{CF}$ = 240 Hz), 131.31, 135.40, 135.59, 135.62, 136.6 (dm, $^2J_{CF}$ = 250 Hz), 138.57, 139.12, 140.88, 143.8 (dm, $^2J_{CF}$ = 250 Hz), 148.6 (dm, $^2J_{CF}$ = 240 Hz), 148.92, 157.81. $^{19}F\{^1H\}$ NMR (C_6D_6): δ −82.48 (td, $^3J_{FF}$ = 22 Hz, $^4J_{FF}$ = 7.1 Hz), −68.51 (m), −58.46 (t, $^3J_{FF}$ = 18 Hz), −55.08 (dm, $^3J_{FF}$ = 20 Hz). Anal. Calcd. for ($C_{52}H_{42}F_8N_4$): C, 71.39; H, 4.84; N, 6.40. Found: C, 71.48; H, 4.51; N, 6.72.

Compound 3a. Compound **5a** (0.200 g, 0.182 mmol) was dissolved in toluene (2 mL), and Me_2Zn (0.847 g, 2.0 M toluene solution, 1.82 mmol) was added. The solution was stirred for 2 days at room temperature. The solvent was removed by vacuum to give an orange solid, which is pure according to the analysis of the NMR spectra. The yield was quantitative. ^{1}H NMR (C_6D_6): δ −0.61 (s, 3H, $ZnCH_3$), 1.06 (d, J = 7.2 Hz, 6H, CH_3), 1.13 (d, J = 7.2 Hz, 6H, CH_3), 1.26 (d, J = 7.2 Hz, 6H, CH_3), 1.29 (d, J = 7.2 Hz, 6H, CH_3), 3.02 (septet, J = 7.2 Hz, 2H, CH), 3.37 (septet, J = 7.2 Hz, 2H, CH), 7.05 (t, J = 7.6 Hz, 1H, C_6H_3), 7.10 (s, 2H, C_6H_2), 7.17 (d, J = 7.6 Hz, 2H, C_6H_3), 7.28 (AA′BB′, 1H, C_6H_4), 7.45 (AA′BB′, 1H, C_6H_4), 8.55 (s, 1H, $N{=}CH$). $^{13}C\{^1H\}$ NMR(C_6D_6): δ −16.92 (ZnC), 23.64, 24.31, 24.36, 29.25, 101.1 (m), 123.58, 125.93, 126.04, 128.52, 129.28, 130.79, 140.44, 140.97, 141.01, 141.68, 141.73, 144.53, 144.82, 145.18, 161.4 (m). $^{19}F\{^1H\}$ NMR (C_6D_6): δ −84.23 (td, $^3J_{FF}$ = 22 Hz, $^4J_{FF}$ = 8 Hz), −61.91 (dt, $^3J_{FF}$ = 16 Hz, $^4J_{FF}$ and $^5J_{FF}$ = 8 Hz), −55.02 (ddd, $^3J_{FF}$ = 22 and 16 Hz, $^4J_{FF}$ = 6 Hz), −54.07 (ddd, $^3J_{FF}$ = 22 Hz, $^5J_{FF}$ = 8 Hz, $^4J_{FF}$ = 6 Hz). The freshly prepared methyl zinc compound was dissolved in toluene (4 mL), and the flask containing it was connected to a Schlenk line by a glass joint. The solution was cooled to −10 °C and evacuated briefly. The SO_2 gas, dried in a flask (1 L) containing P_2O_5 overnight, was introduced through the Schlenk line. The solution was stirred for 30 min at room temperature. The solution was evacuated briefly to remove the remaining SO_2 gas, and the flask was brought into a glovebox. The solution was filtered over Celite to remove small amounts of insoluble impurities. Removal of the solvent gave a yellow solid. The yield was quantitative. Analysis of the ^{1}H NMR spectrum indicated the presence of three isomers **A**, **B** (or **C**), and **C** (or **B**) in a 0.43:0.43:0.14 ratio. Unambiguous signals for **A**, **B** (or **C**), and **C** (or **B**) isomers are marked in bold, italic, and underlined, respectively. ^{1}H NMR (C_6D_6): δ 0.98−1.38 (m, 24H, CH_3), *1.38*, **1.54**, *1.70*, and **1.90** (s, 3H, SCH_3), 2.21−2.60 and 3.20−3.55 (m, 4H, CH), **6.76**, *6.82*, *6.83*, and **6.86** (s, 2H, C_6H_2), 6.98−7.14 (m, 3H, C_6H_3), 7.32 (AA′BB′, 1H, C_6H_4), 7.53 (AA′BB′, 1H, C_6H_4), *8.16*, *8.27*, and **8.23** (s, 1H, $N{=}CH$).

Compound 3b. The compound was synthesized by the same conditions and procedures as those used for **3a** using **5b**. ^{1}H NMR (C_6D_6) for the methyl zinc complex: δ −0.71 (s, 3H, $ZnCH_3$), 1.04 (d, J = 7.2 Hz, 6H, CH_3), 1.10 (d, J = 7.2 Hz, 6H, CH_3), 1.19 (t, 7.2 Hz, 6H, CH_3), 2.53−2.70 (m, 4H, CH_2), 2.95 (septet, J = 7.2 Hz, 2H, CH), 7.02 (t, J = 7.2 Hz, 1H, C_6H_3), 7.08 (d, J = 7.2 Hz, 2H, C_6H_3), 7.09 (s, 2H, C_6H_2), 7.25 (AA′BB′, 1H, C_6H_4), 7.42 (AA′BB′, 1H, C_6H_4), 8.51 (s, 1H, $N{=}CH$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ −17.18 (ZnC), 15.00, 23.67, 24.40, 25.71, 29.19, 101.1 (m), 125.36, 126.04, 126.44, 128.08, 130.77, 126.86, 136.91, 140.49, 140.97, 141.02, 144.24, 144.82, 146.87, 146.91, 161.3 (m). $^{19}F\{^1H\}$ NMR (C_6D_6): δ −84.38 (td, $^3J_{FF}$ = 22 Hz, $^4J_{FF}$ = 8 Hz), −62.45 (dt, $^3J_{FF}$ = 16 Hz, $^4J_{FF}$ and $^5J_{FF}$ = 8 Hz), −54.94 (ddd, $^3J_{FF}$ = 22 and 16 Hz, $^4J_{FF}$ = 6 Hz), −54.39 (ddd, $^3J_{FF}$ = 22 Hz, $^5J_{FF}$ = 8 Hz, $^4J_{FF}$ = 6 Hz). The addition of SO_2 gas gave an intractable yellow solid.

Compound 3c. The compound was synthesized using the same conditions and procedures as those used for **3a** using **5c**. ^{1}H NMR (C_6D_6) for the methyl zinc complex: δ −0.61 (s, 3H, $ZnCH_3$), 1.02 (d, J = 7.2 Hz, 6H, CH_3), 1.08 (d, J = 7.2 Hz, 6H, CH_3), 2.22 (s, 6H, CH_3), 2.97 (septet, J = 7.2 Hz, 2H, CH), 6.98 (t, J = 7.2 Hz, 1H, C_6H_3), 7.03 (d, J = 7.2 Hz, 2H, C_6H_3), 7.06 (s, 2H, C_6H_2), 7.25 (AA′BB′, 1H, C_6H_4), 7.41 (AA′BB′, 1H, C_6H_4), 8.48 (s, 1H, $N{=}CH$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ −17.40 (ZnC), 19.12, 23.66, 24.33, 29.20, 30.43, 101.4 (m), 124.81, 126.01, 128.08, 128.45, 129.27, 130.77, 131.14, 131.18, 140.38, 140.95, 141.00, 143.71, 144.82, 148.17, 161.3 (m). $^{19}F\{^1H\}$ NMR (C_6D_6): δ −84.25 (td, $^3J_{FF}$ = 22 Hz, $^4J_{FF}$ = 8 Hz), −64.18 (dt, $^3J_{FF}$ = 16 Hz, $^4J_{FF}$ and $^5J_{FF}$ = 8 Hz), −54.96 (ddd, $^3J_{FF}$ = 22 and 16 Hz, $^4J_{FF}$ = 6 Hz), −54.36 (ddd, $^3J_{FF}$ = 22 Hz, $^5J_{FF}$ = 8 Hz, $^4J_{FF}$ = 6 Hz). ^{1}H NMR (C_6D_6) for **3c** (**A**:(*B* or *C*) = 0.25:0.75): δ **1.03** and *1.01* (d, J = 7.2 Hz, 6H, CH_3), *1.18* and **1.21** (d, J = 7.2 Hz, 6H, CH_3), **1.52**, **1.67**, and *1.71* (s, 3H, SCH_3), **2.16**, *2.23*, and **2.32** (s, 6H, CH_3), **3.02** and *3.11* (septet, J = 7.2 Hz, 2H, CH), 6.90−7.08 (m, 5H, C_6H_3 and C_6H_2), 7.33 (AA′BB′, 1H, C_6H_4), 7.57 (AA′BB′, 1H, C_6H_4), *8.42* and **8.46** (s, 1H, $N{=}CH$).

Compound 3d. The compound was synthesized by the same conditions and procedures as those used for **3a** using **5d**. ^{1}H NMR (C_6D_6) for the methyl zinc complex: δ −0.67 (s, 3H, $ZnCH_3$), 1.01 (t, J = 7.6 Hz, 6H, CH_3), 1.26 (d, J = 7.2 Hz, 6H, CH_3), 1.28 (d, J = 7.2 Hz, 6H, CH_3), 2.33−2.52 (m, 4H, CH_2), 3.34 (septet, J = 7.2 Hz, 2H, CH), 7.00 (s, 2H, C_6H_2), 7.06 (t, J = 7.6 Hz, 1H, C_6H_3), 7.18 (d, J = 7.6 Hz, 2H, C_6H_3), 7.34 (AA′BB′, 1H, C_6H_4), 7.50 (AA′BB′, 1H, C_6H_4), 8.47 (s, 1H, $N{=}CH$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ −16.98 (ZnC), 15.10, 24.35, 25.41, 29.22, 101.2 (m), 123.55, 125.88, 128.93, 130.70, 135.45, 140.58, 140.63, 141.66, 141.71, 144.50, 145.22, 146.23, 161.4 (m). $^{19}F\{^1H\}$ NMR (C_6D_6): δ −84.57 (td, $^3J_{FF}$ = 22 Hz, $^4J_{FF}$ = 8 Hz), −61.87 (dt, $^3J_{FF}$ = 16 Hz, $^4J_{FF}$ and $^5J_{FF}$ = 8 Hz), −55.28 (t, $^3J_{FF}$ = 16 Hz), −53.70 (m). ^{1}H NMR (C_6D_6) for **3d** (**A**:(*B* or *C*):(*C* or *B*) = 0.41:0.41:0.18): δ 0.98−1.45 (m, 18H, CH_3), **1.55**, *1.65*, *1.72*, and **1.93** (s, 3H, SCH_3), 2.36−2.62 (m, 4H, CH_2), 3.22−3.60 (m, 2H, CH), **6.79**, *6.83*, *6.84*, and **6.89** (s, 2H, C_6H_2), 7.01−7.22 (m, 3H, C_6H_3), 7.35 (AA′BB′, 1H, C_6H_4), 7.54 (AA′BB′, 1H, C_6H_4), *8.20*, **8.26**, and **8.30** (s, 1H, $N{=}CH$).

Compound 3e. The compound was synthesized by the same conditions and procedures as those used for **3a** using **5e**. ^{1}H NMR (C_6D_6) for the methyl zinc complex: δ −0.69 (s, 3H, $ZnCH_3$), 0.97 (t, $J = 7.6$ Hz, 6H, CH_3), 1.18 (t, $J = 7.6$ Hz, 6H, CH_3), 2.37−2.54 (m, 4H, CH_2), 2.62−2.78 (m, 4H, CH_2), 6.96 (s, 2H, C_6H_2), 7.03 (t, $J = 7.6$ Hz, 1H, C_6H_3), 7.09 (d, 2H, C_6H_3), 7.30 (AA′BB′, 1H, C_6H_4), 7.47 (AA′BB′, 1H, C_6H_4), 8.44 (s, 1H, N═CH). ^{13}C{^{1}H} NMR (C_6D_6): δ −17.23 (ZnC), 15.01, 15.19, 25.42, 25.69, 101.2 (m), 125.31, 126.40, 128.06, 128.95, 130.63, 165.48, 136.83, 136.88, 140.57, 140.65, 144.17, 146.22, 146.94, 161.4 (m). ^{19}F{^{1}H} NMR (C_6D_6): δ −84.69 (td, $^3J_{FF} = 22$ Hz, $^4J_{FF} = 8$ Hz), −62.44 (dt, $^3J_{FF} = 16$ Hz, $^4J_{FF}$ and $^5J_{FF} = 8$ Hz), −55.18 (ddd, $^3J_{FF} = 22$ and 16 Hz, $^4J_{FF} = 6$ Hz), −54.08 (ddd, $^3J_{FF} = 22$ Hz, $^5J_{FF} = 8$ Hz, $^4J_{FF} = 6$ Hz). ^{1}H NMR (C_6D_6) for **3e** (**A**:(*B* or *C*):(*C* or *B*) = 0.41:0.41:0.18): δ 0.85−1.40 (m, 12H, CH_3), **1.48**, *1.65*, and **1.71** (s, 3H, SCH_3), 2.24−2.90 (m, 8H, CH_2), **6.78**, *6.83*, *6.82*, and **6.86** (s, 2H, C_6H_2), 6.96−7.16 (m, 3H, C_6H_3), 7.32 (AA′BB′, 1H, C_6H_4), 7.54 (AA′BB′, 1H, C_6H_4), ***8.20***, ***8.25***, and *8.28* (s, 1H, N═CH).

Compound 3f. The compound was synthesized by the same conditions and procedures as those used for **3a** using **5f**. ^{1}H NMR (C_6D_6) for the methyl zinc complex: δ −0.67 (s, 3H, $ZnCH_3$), δ 0.95 (t, $J = 7.6$ Hz, 6H, CH_3), 2.19 (s, 6H, CH_3), 2.27−2.44 (m, 4H, CH_2), 6.95 (s, 2H, C_6H_2), 6.98 (t, $J = 7.6$ Hz, 1H, C_6H_3), 7.03 (d, $J = 7.6$ Hz, 2H, C_6H_3), 7.29 (AA′BB′, 1H, C_6H_4), 7.45 (AA′BB′, 1H, C_6H_4), 8.41 (s, 1H, N═CH). ^{13}C{^{1}H} NMR (C_6D_6): δ −17.41 (ZnC), 15.22, 19.15, 25.44, 101.4 (m), 124.77, 128.42, 128.95, 130.65, 131.10, 131.14, 135.42, 140.57, 140.61, 143.64, 146.20, 148.22, 161.3 (m). ^{19}F{^{1}H} NMR (C_6D_6): δ −84.54 (td, $^3J_{FF} = 22$ Hz, $^4J_{FF} = 8$ Hz), −64.15 (dt, $^3J_{FF} = 16$ Hz, $^4J_{FF}$ and $^5J_{FF} = 8$ Hz), −55.20 (ddd, $^3J_{FF} = 22$ and 16 Hz, $^4J_{FF} = 6$ Hz), −54.14 (ddd, $^3J_{FF} = 22$ Hz, $^5J_{FF} = 8$ Hz, $^4J_{FF} = 6$ Hz). ^{1}H NMR (C_6D_6) for **6f** (**A**:(*B* or *C*):(*C* or *B*) = 0.44:0.44:0.12): δ 0.86−1.17 (m, 6H, CH_3), *1.38*, **1.54**, *1.69*, and **1.74** (s, 3H, SCH_3), **2.13**, *2.24*, *2.34*, and **2.41** (s, 6H, CH_3), 2.36−2.61 (m, 4H, CH_2), **6.63**, *6.73*, **6.77**, and *6.84* (s, 2H, C_6H_2), 6.98−7.14 (m, 3H, C_6H_3), 7.33 (AA′BB′, 1H, C_6H_4), 7.53 (AA′BB′, 1H, C_6H_4), ***8.19***, ***8.25***, and *8.29* (s, 1H, N═CH).

Compound 3g. The compound was synthesized by the same conditions and procedures as those used for **3a** using **5g**. ^{1}H NMR (C_6D_6) for the methyl zinc complex: δ −0.70 (s, 3H, $ZnCH_3$), 1.24 (d, $J = 7.2$ Hz, 12H, CH_3), 1.95 (s, 6H, CH_3), 3.30 (septet, $J = 7.2$ Hz, 2H, CH), 6.96 (s, 2H, C_6H_2), 7.06 (t, $J = 7.6$ Hz, 1H, C_6H_3), 7.16 (s, $J = 7.6$ Hz, 2H, C_6H_3), 7.34 (AA′BB′, 1H, C_6H_4), 7.50 (AA′BB′, 1H, C_6H_4), 8.31 (s, 1H, N═CH). ^{13}C{^{1}H} NMR (C_6D_6): δ −17.26 (ZnC), 18.78, 24.25, 24.45, 29.16, 101.4 (m), 123.55, 125.87, 128.07, 128.67, 129.30, 130.68, 140.11, 140.32, 141.65, 141.70, 144.36, 145.24, 145.28, 147.06, 161.0 (m). ^{19}F{^{1}H} NMR (C_6D_6): δ −84.78 (td, $^3J_{FF} = 22$ Hz, $^4J_{FF} = 8$ Hz), −61.83 (dt, $^3J_{FF} = 16$ Hz, $^4J_{FF}$ and $^5J_{FF} = 8$ Hz), −55.49 (ddd, $^3J_{FF} = 22$ and 16 Hz, $^4J_{FF} = 6$ Hz), −53.18 (ddd, $^3J_{FF} = 22$ Hz, $^5J_{FF} = 8$ Hz, $^4J_{FF} = 6$ Hz). ^{1}H NMR (C_6D_6) for **3g** (**A**:(*B* or *C*):(*C* or *B*) = 0.50:0.39:0.11): δ 0.90−1.20 (m, 12H, CH_2CH_3), *1.31*, **1.54**, *1.62*, and **1.84** (s, 3H, SCH_3), **1.87**, *1.99*, *2.09*, and **2.20** (s, 6H, CH_3), **3.26**, *3.42*, and **3.49** (septet, $J = 7.2$ Hz, 2H, CH), **6.63**, *6.73*, *6.77*, and **6.84** (s, 2H, C_6H_2), 6.98−7.15 (m, 3H, C_6H_3), 7.30 (AA′BB′, 1H, C_6H_4), 7.47 (AA′BB′, 1H, C_6H_4), *8.12*, **8.15**, and *8.16* (s, 1H, N═CH).

Compound 3h. The compound was synthesized by the same conditions and procedures as those used for **3a** using **5g**. ^{1}H NMR (C_6D_6) for the methyl zinc complex: δ −0.85 (s, 3H, $ZnCH_3$), 1.15 (t, $J = 7.6$ Hz, 6H, CH_3), 1.91 (s, 6H, CH_3), 2.47−2.63 (m, 4H, CH_2), 6.90 (s, 2H, C_6H_2), 7.02 (t, $J = 7.6$ Hz, 1H, C_6H_3), 7.09 (d, $J = 7.6$ Hz, 2H, C_6H_3), 7.26 (AA′BB′, 1H, C_6H_4), 7.46 (AA′BB′, 1H, C_6H_4), 8.28 (s, 1H, N═CH). ^{13}C{^{1}H} NMR (C_6D_6): δ −17.39 (ZnC), 15.10, 18.80, 25.70, 101.3 (m), 125.30, 126.41, 127.50, 129.28, 129.30, 130.60, 130.68, 136.83, 136.89, 140.14, 140.41, 144.06, 147.03, 161.0 (m). ^{19}F{^{1}H} NMR (C_6D_6): δ −84.95 (td, $^3J_{FF} = 22$ Hz, $^4J_{FF} = 8$ Hz), −62.46 (dt, $^3J_{FF} = 16$ Hz, $^4J_{FF}$ and $^5J_{FF} = 8$ Hz), −55.43 (ddd, $^3J_{FF} = 22$ and 16 Hz, $^4J_{FF} = 6$ Hz), −53.54 (ddd, $^3J_{FF} = 22$ Hz, $^5J_{FF} = 8$ Hz, $^4J_{FF} = 6$ Hz). ^{1}H NMR (C_6D_6) for **3h** (**A**:(*B* or *C*):(*C* or *B*) = 0.53:0.26:0.21): δ 1.10−1.34 (m, 6H, CH_2CH_3), **1.42**, *1.64*, and **1.72** (s, 3H, SCH_3), **1.89**, *2.00*, *2.09*, and **2.18** (s, 6H, CH_3), 2.50−2.92 (m, 4H, CH_2), **6.64**, *6.73*, *6.78*, and **6.82** (s, 2H, C_6H_2), 6.98−7.15 (m, 3H, C_6H_3), 7.30 (AA′BB′, 1H, C_6H_4), 7.47 (AA′BB′, 1H, C_6H_4), *8.14* and ***8.17*** (s, 1H, N═CH).

Table 3. Crystallographic Parameters of **3c**

	3c
formula	$C_{62}H_{62}F_8N_4O_4S_2Zn_2 \cdot (C_4H_{10}O)$
fw	1348.14
color	yellow
size (mm^3)	0.60 × 0.55 × 0.45
a (Å)	10.983(4)
b (Å)	21.099(6)
c, Å	28.304(10)
β, deg	100.955(12)°
V (Å^3)	6439(4)
cryst syst	monoclinic
space group	*P*21/*n*
D_{calcd} (g cm^{-1})	1.391
Z	4
μ (mm^{-1})	0.885
no. of data collected	50 137
no. of unique data	13 769
no. of variables	784
R^a (%)	0.1041
$R_w{}^a$ (%)	0.2742
GOF	1.004

[a] Data collected with Mo Kα radiation (λ(Kα) = 0.7107 Å), $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ with $F_o > 2.0\sigma(I)$; $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o)^2]^2]^{1/2}$ with $F_o > 2.0\sigma(I)$.

Compound 3i. The compound was synthesized by the same conditions and procedures as those used for **3a** using **5i**. ^{1}H NMR (C_6D_6) for the methyl zinc complex: δ −0.72 (s, 3H, $ZnCH_3$), 1.90 (s, 6H, CH_3), 2.16 (s, 6H, CH_3), 6.90 (s, 2H, C_6H_2), 6.98 (t, $J = 7.6$ Hz, 1H, C_6H_3), 7.03 (d, $J = 7.6$ Hz, 2H, C_6H_3), 7.30 (AA′BB′, 1H, C_6H_4), 7.45 (AA′BB′, 1H, C_6H_4), 8.25 (s, 1H, N═CH). ^{13}C{^{1}H} NMR (C_6D_6): δ −17.40 (ZnC), 18.81, 19.17, 101.61 (m), 124.71, 128.40, 129.23, 129.27, 130.61, 130.68, 131.07, 131.12, 140.13, 140.38, 143.52, 147.03, 148.25, 148.29, 161.0 (m). ^{19}F{^{1}H} NMR (C_6D_6): δ −84.78 (td, $^3J_{FF} = 22$ Hz, $^4J_{FF} = 8$ Hz), −64.14 (dt, $^3J_{FF} = 16$ Hz, $^4J_{FF}$ and $^5J_{FF} = 8$ Hz), −55.49 (ddd, $^3J_{FF} = 22$ and 16 Hz, $^4J_{FF} = 6$ Hz), −53.56 (ddd, $^3J_{FF} = 22$ Hz, $^5J_{FF} = 8$ Hz, $^4J_{FF} = 6$ Hz). ^{1}H NMR (C_6D_6) for **3i** (**A**:(*B* or *C*):(*C* or *B*) = 0.57:0.25:0.18): δ *1.33*, **1.51**, *1.69*, and **1.74** (s, 3H, SCH_3), **1.89**, *2.00*, *2.08*, *2.10*, **2.17**, **2.22**, *2.26*, and **2.41** (s, 12H, CH_3), **6.64**, *6.74*, *6.78*, and **6.85** (s, 2H, C_6H_2), 6.98−7.15 (m, 3H, C_6H_3), 7.31 (AA′BB′, 1H, C_6H_4), 7.47 (AA′BB′, 1H, C_6H_4), *8.14* and ***8.16*** (s, 1H, N═CH).

CO_2/(Cyclohexene Oxide) Copolymerization. Into glassware that fits into a bomb reactor (50 mL) were added, inside a glovebox, the Zn complex (14 μmol of Zn) and cyclohexene oxide (8.0 mL, 79 mmol). After the glassware was placed in the bomb unit, the reactor was assembled and brought out from the glovebox. The reactor was immersed in an oil bath whose temperature had been set to 80 °C. The CO_2 gas was charged into the reactor to 14 bar. After the solution was stirred for 2 h with a magnetic stirring bar at 80 °C, the CO_2 gas was released and the reactor was disassembled. When the pressure dropped below 11 bar, additional CO_2 gas was charged. The viscous solution was poured into a flask containing methanol, giving a white lump. After the lump was broken, it was stirred over methanol overnight. The solid was collected by decantation and dried under vacuum.

Crystallographic Studies. Crystals of **3c** coated with grease (Apiezon N) were mounted onto a thin glass fiber with epoxy glue and placed in a cold nitrogen stream at 150(2) K on a Rigaku single-crystal X-ray diffractometer. The structures were solved by direct methods (SHELXL-97)[18] and refined against all F^2 data (SHELXL-97). All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were treated as idealized contributions. The crystal data and refinement results for **3c** are summarized in Table 3.

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Supporting Information Available: Crystallographic data for **3c** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.