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(Salen)Tin Complexes: Syntheses, Characterization, Crystal Structures, and Catalytic Activity in the Formation of Propylene Carbonate from CO_2 and Propylene Oxide

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A series of (salen)tin(II) and (salen)tin(IV) complexes was synthesized. The (salen)tin(IV) complexes, (salen)SnX_2 (X = Br and I), were prepared in good yields via the direct oxidation reaction of (salen)tin(II) complexes with Br_2 or I_2. (Salen)SnX_2 successfully underwent the anion-exchange reaction with AgOTf (OTf = trifluoromethanesulfonate) to form (salen)Sn(OTf)$_2$ and (salen)Sn(X)(OTf) (X = Br). The (salen)Sn(OTf)$_2$ complex was easily converted to any of the dihalide (salen)SnX_2 compounds using halide salts. All complexes were fully characterized by ^{1}H NMR spectroscopy, mass spectrometry, and elemental analysis, while some were characterized by ^{13}C, ^{19}F, and ^{119}Sn NMR spectroscopy. Several crystal structures of (salen)tin(II) and (salen)tin(IV) were also determined. Finally, both (salen)tin(II) and (salen)tin(IV) complexes were shown to efficiently catalyze the formation of propylene carbonate from propylene oxide and CO_2. Of the series, (3,3′,5,5′-Br_4-salen)$SnBr_2$, **3i**, was found to be the most effective catalyst (TOF = 524 h^{-1}).

Introduction

Salen ligands[1] have been used extensively in the preparation of various complexes of transition and main group metals.[2−6] In part, this is because salen ligands are easily accessible and can stabilize multiple oxidation states of a single metal.[3] Tin salen complexes are one such example where the salen ligand system can coordinate to both tin(II) and tin(IV) centers, allowing for a potential modulation of metal Lewis acidity within a single ligand framework. Although there have been several reports on the preparation of (salen)Sn(II)[7−11] and (salen)Sn(IV)[8,12] complexes, the generality of many of these syntheses has not been demonstrated for a wide range of salen ligand backbones, especially for those that are very soluble in organic solvents. In addition, for (salen)Sn(IV) complexes the choice of anionic ancillary ligands has often been limited to chloride and iodide.

We have been interested in exploring metal salen complexes as Lewis acid catalysts in the preparation of cyclic carbonates via the cycloaddition of CO_2 to epoxides.[13] With this goal in mind, (salen)Sn complexes of both II and IV oxidation states are worthy targets for investigation. Although Lewis acidic tin(II) and tin(IV) complexes have been shown to be quite useful in organic synthesis[14] and catalysis,[15−17]

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(1) The general term "salen-type" more correctly describes the class of [O$^-$,N,N,O$^-$] tetradentate bis(Schiff base) ligands. "Salen" itself is often used to indicate a member of this class that is derived from ethylenediamine. However, for ease of nomenclature in the remainder of this article the term salen will also be used to describe the general class of bis(salicylaldimine) ligands and their complexes.

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(salen)tin complexes have had only limited use as catalysts.[18−20] Specifically, (salen)tin complexes have not been examined for their catalytic activity in the formation of cyclic carbonates from epoxides.

In this paper, we report a convenient and general strategy for making (salen)Sn(IV) complexes with a wide range of anionic ligands. (Salen)$SnBr_2$ and (salen)SnI_2 can be readily prepared in high yields by directly oxidizing (salen)Sn(II) with iodine[8] and bromine. Anion-exchange reactions then allow ready access to (salen)$Sn(OTf)_2$, (salen)Sn(OTf)(Br), and (salen)$SnCl_2$. We have examined both (salen)Sn(II) and (salen)Sn(IV) complexes for their catalytic activity in the coupling of CO_2 and propylene oxide as a function of the ligand environment, oxidation state, and axial anions (in the case of Sn(IV)). Our results indicate that (salen)Sn compounds are a promising group of catalysts for the formation of cyclic carbonates.

Experimental Section

General Information. ^{1}H and ^{13}C NMR spectra were recorded on either a Varian Inova 500 (499.773 MHz for ^{1}H and 125.669 MHz for ^{13}C) or Varian Mercury 400 (400.178 MHz for ^{1}H and 100.576 MHz for ^{13}C) spectrometer. ^{19}F NMR spectra were recorded on a Varian Mercury 400 (376.503 MHz for ^{19}F) and ^{119}Sn NMR spectra were recorded on a Varian Inova 400 (149.141 MHz for ^{119}Sn) spectrometer, respectively. ^{1}H NMR data are reported as follows: chemical shift (multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and b = broad), and integration). ^{1}H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) with the solvent resonances as internal standards. ^{119}Sn chemical shifts are reported in ppm from an external $(CH_3)_4Sn$ standard, while ^{19}F chemical shifts are based on a $CFCl_3$ external standard. Mass spectra were obtained from the Mass Spectrometry Laboratory, University of Illinois (Urbana, IL), or from the Analytical Services Laboratory of the chemistry department of Northwestern University. Elemental analyses were provided by Atlantic Microlab, Inc. (Norcross, GA). All reactions were carried out under a dry nitrogen atmosphere either in an inert-atmosphere glovebox or by using standard Schlenk techniques, unless otherwise noted. Flash column chromatography was carried out with 230−400 mesh silica gel purchased from Merck.

GC analyses of the propylene carbonate reactions were carried out on a Hewlett-Packard 5890A gas chromatograph equipped with an FID detector and a 30-m HP-5 capillary column with a 0.32-mm inner diameter and a 0.25-mm film thickness. Method used: initial time = 0 min, initial temperature = 50 °C, rate = 15 °C/min, final time = 10 min, final temperature = 250 °C.

Materials. Schiff base ligands **a** (1,2-ethanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)), **b** (1-methyl-1,2-ethanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)), **c** (1,2-benzenediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)), **d** ((*R*,*R*)-(−)-1,2-cyclohexanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)), **f** (1,2-ethanediamino-*N*,*N*′-bis(5-bromosalicylidene)), **g** ((*S*,*S*)-(+)-1,2-cyclohexanediamino-*N*,*N*′-bis(3,5-dibromosalicylidene)), **h** (1,2-ethanediamino-*N*,*N*′-bis(3-methoxysalicylidene)), and **i** (1,2-ethanediamino-*N*,*N*′-bis(3,5-dibromosalicylidene)) were synthesized from the corresponding salicylaldehydes and diamines following literature procedures.[21,22] Dichloromethane was dried over calcium hydride, tetrahydrofuran (THF) and hexanes were dried over sodium/benzophenone, and ethanol was dried over $Mg(OEt)_2$. All solvents were distilled under nitrogen, collected in Strauss flasks, and degassed before use. Deuterated dichloromethane was purchased from Cambridge Isotope Laboratories and distilled over calcium hydride. Silica gel (Merck) was activated at 600 °C for 6 h to remove surface hydroxyl groups before being used in the chromatography of (salen)$SnCl_2$ complexes. Ligand **e** ((*S*,*S*)-(+)-1,2-cyclohexanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)) and all other chemicals were purchased from Aldrich and used without further purification.

General Procedure for the Synthesis of 1a−i. A mixture of the salenH_2 ligand (1 mmol), $SnCl_2$ (189 mg, 1 mmol), NEt_3 (0.28 mL, 2 mmol), and EtOH (5−10 mL) was heated at 85 °C for 10−24 h in a sealed 50-mL Schlenk tube equipped with a Kontes 8-mm PTFE valve. After cooling, the reaction mixture was transferred to a 50-mL Schlenk flask, taken out of the glovebox, and attached to a Schlenk line. It was then filtered via cannula, washed with ethanol (2 × 5 mL) and hexanes (2 × 5 mL), and dried in vacuo.

1,2-Ethanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) Tin(II) (1a). Orange solid, yield = 514 mg (84%). Anal. Calcd for $C_{32}H_{46}N_2O_2Sn$: C, 63.07; H, 7.61; N, 4.60. Found: C, 62.80; H, 7.69; N, 4.70. ^{1}H NMR (CD_2Cl_2): δ 8.67 (s, 2H), 7.44 (d, 2H, J = 2.4 Hz), 6.97 (d, 2H, J = 2.4 Hz), 3.92 (m, 2H), 3.72 (m, 2H), 1.47 (s, 18H), 1.30 (s, 18H). ^{13}C NMR (CD_2Cl_2): δ 167.8 (*C*H═N), 163.5, 142.2, 137.6, 129.8, 128.1, 120.1, 56.1, 35.9, 34.4, 31.9 (C(*C*H$_3$)$_3$), 30.2 (C(*C*H$_3$)$_3$). ^{119}Sn NMR (CD_2Cl_2): δ −516.7. EIMS: *m*/*z* 610.3 (M^+, 0.5), 595.2 (0.3), 492.4 (100), 259.2 (46), 231.2 (44). HREIMS Calcd for $[C_{32}H_{46}N_2O_2Sn]^+$: *m*/*z* 610.258. Found: *m*/*z* 610.2587.

1-Methyl-1,2-ethanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) Tin(II) (1b). Orange solid, yield = 491 mg (79%). Anal. Calcd for $C_{33}H_{48}N_2O_2Sn$: C, 63.58; H, 7.76; N, 4.49. Found: C, 63.39; H, 7.91; N, 4.59. ^{1}H NMR (CD_2Cl_2): δ 8.20−8.14 (m, 2H, C*H*═N), 7.43 (q, 2H, J = 2.8, 3.2 Hz), 6.98 (q, 2H, J = 2.8, 2.8 Hz), 4.05−3.75 (m, 2H), 3.63 and 3.39 (2 m, 1H), 1.47 (d, 3H, J = 6.0 Hz), 1.45 (s, 18H), 1.30 (s, 18H). ^{13}C NMR (CD_2Cl_2): δ 168.9 (*C*H═N), 168.2 (*C*H═N), 166.3, 164.0, 163.8, 163.1, 142.6, 142.4, 142.3, 137.9, 137.8, 137.7, 130.0, 129.8, 129.7, 128.5, 128.3, 128.2, 120.6, 120.4, 120.1, 120.0, 62.4, 62.1, 61.9, 58.2, 35.8, 34.3, 31.7 (C(*C*H$_3$)$_3$), 30.1 (C(*C*H$_3$)$_3$), 19.4 (*C*H$_3$), 19.2 (*C*H$_3$). ^{119}Sn NMR (CD_2Cl_2): δ −526.5. EIMS: *m*/*z* 624.3 (M^+, 0.6), 609.2 (0.3), 506.4 (100), 273.2 (62), 238.2 (41). HREIMS Calcd for $[SnC_{33}H_{48}N_2O_2]^+$: *m*/*z* 624.2738. Found: *m*/*z* 624.2746.

1,2-Benzenediamino-(*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)) Tin(II) (1c). Red solid, yield = 332 mg (50%). Anal. Calcd for $C_{36}H_{46}N_2O_2Sn \cdot {}^3/_4C_2H_5OH$: C, 65.09; H, 7.36; N, 4.05. Found: C, 64.96; H, 7.07; N, 4.24. ^{1}H NMR (CD_2Cl_2): δ 8.41 (s, 2H), 7.56 (m, 4H), 7.42 (m, 2H), 7.08 (d, 2H, J = 2.4 Hz), 1.53 (s, 18H), 1.36 (s, 18H). ^{13}C NMR (CD_2Cl_2): δ 164.4 (*C*H═N), 162.2, 142.3, 139.9, 138.2, 131.4, 129.2, 129.1, 120.3, 118.0, 35.9, 34.5, 31.7 (C(*C*H$_3$)$_3$), 30.2 (C(*C*H$_3$)$_3$). ^{119}Sn NMR (CD_2Cl_2): δ −501.4.

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EIMS: *m*/*z* 658.2 (M^+, 22), 643.2 (12), 540.4 (50), 446.1 (17), 323.2 (73), 119.1(100). HREIMS Calcd for $[C_{36}H_{46}N_2O_2Sn]^+$: *m*/*z* 658.2581. Found: *m*/*z* 658.2588.

(*R*,*R*)-(−)-1,2-Cyclohexanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) Tin(II) (1d). Orange crystalline solid.[8] NMR data match the literature report.

(*S*,*S*)-(+)-1,2-Cyclohexanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) Tin(II) (1e). Orange solid, yield = 620 mg (93%). Anal. Calcd for $C_{36}H_{52}N_2O_2Sn$: C, 65.17; H, 7.90; N, 4.22. Found: C, 65.09; H, 7.95; N, 4.25. ^{1}H NMR (CD_2Cl_2): δ 8.18 (s, 1H, J_{Sn-H} = 12 Hz), 8.11 (s, 1H, J_{Sn-H} = 13.6 Hz), 7.46 (d, 1H, J = 2.8 Hz), 7.43 (d, 2H, J = 2.4 Hz), 7.06 (d, 1H, J = 2.8 Hz), 6.96 (d, 1H, J = 2.4 Hz), ∼3.57 (m, 1H), ∼3.14 (b, 1H), ∼2.53 (b, 1H), ∼2.30 (m, 1H), ∼2.06 (m, 2H), ∼1.61 (m, 2H), 1.49 (s, 18H), 1.33 (s, 9H), 1.32(s, 9H). ^{13}C NMR (CD_2Cl_2): δ 167.1 (*C*H═N), 163.7, 163.2, 161.5 (*C*H═N), 142.2, 142.0, 137.5, 137.3, 129.8, 129.3, 128.6, 128.5, 120.2, 119.8, 66.4, 64.5, 36.0, 35.8, 34.4, 31.8 (C(*C*H$_3$)$_3$), 30.7 (C(*C*H$_3$)$_3$), 30.2, 27.6, 25.3, 24.8. ^{119}Sn NMR (CD_2Cl_2): δ −521.5. FABMS Calcd: *m*/*z* 663.5. Found: *m*/*z* 664.2 (M^+).

1,2-Ethanediamino-*N*,*N*′-bis(5-bromosalicylidene) Tin (II) (1f). Orange solid, yield = 498 mg (77%). Anal. Calcd for $C_{16}H_{12}Br_2N_2O_2Sn$: C, 35.41; H, 2.23; N, 5.16. Found: C, 35.48; H, 2.28; N, 5.31. ^{1}H NMR (CD_2Cl_2): δ 8.08 (s, 2H), 7.35 (dd, 2H, J_1 = 2.4 Hz, J_2 = 9.6 Hz), 7.23 (d, 2H, J_1 = 2.4 Hz), 6.76 (d, 2H, J_2 = 9.6 Hz), 4.06 (m, 2H), 3.67 (m, 2H). EIMS: *m*/*z* 542 (M^+, 100), 426 (20), 344 (58), 316 (46), 304 (44).

(*S*,*S*)-(+)-1,2-Cyclohexanediamino-*N*,*N*′-bis(3,5-dibromosalicylidene) Tin(II) (1g). Orange solid, yield = 863 mg (96%). Anal. Calcd for $C_{20}H_{16}Br_4N_2O_2Sn$: C, 31.83; H, 2.14; N, 3.71. Found: C, 32.05; H, 2.22; N, 3.68. ^{1}H NMR (CD_2Cl_2): δ 8.18 (s, 1H), 8.09 (s, 1H), 7.98 (s, 1H), 7.75 (s, 1H), 7.32 (d, 1H, J = 2.4 Hz), 7.20 (d, 1H, J = 2.4 Hz), 3.05 (m, 2H), 2.34−1.53 (m, 8H). EIMS: *m*/*z* 753.6 (M^+, 3), 637.8 (43), 358.9 (100), 279.9 (33), 183 (8).

1,2-Ethanediamino-*N*,*N*′-bis(3-methoxysalicylidene) Tin (II) (1h). Orange solid, yield = 509 mg (96%). Anal. Calcd for $C_{18}H_{18}N_2O_4Sn$: C, 48.58; H, 4.08; N, 6.29. Found: C, 48.16; H, 4. 32; N, 6.28. ^{1}H NMR (CD_2Cl_2): δ 8.16 (s, 2H), 6.90 (d, 2H, J = 7.6 Hz), 6.76 (d, 2H, J = 6.8 Hz), 6.60 (m, 2H, J = 7.6 Hz), 4.05 (m, 6H), 3.68 (m, 4H). EIMS: *m*/*z* 446.2 (M^+, 100), 417.2 (8), 268.1 (48), 225 (8), 162.2 (12).

1,2-Ethanediamino-*N*,*N*′-bis(3,5-dibromosalicylidene) Tin (II) (1i). Orange solid, yield = 286 mg (77%). Anal. Calcd for $C_{16}H_{10}Br_4N_2O_2Sn\cdot{}^1/_2C_2H_5OH$: C, 28.31; H, 1.82; N, 3.89. Found: C, 28.27; H, 1.69; N, 4.22. ^{1}H NMR (CD_2Cl_2): δ 8.28 (s, 1H), 8.10 (s, 1H), 7.76−7.25 (m, 4H), 3.04 (s, 4H). EIMS: *m*/*z* 699.6 (M^+, 98), 621.7 (18), 421.8 (100), 395.7 (82), 198.9 (98).

Isolation of the Bis Ligand Complex Bis[1,2-ethanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)] Tin(II) (1a′). Complex **1a** (200 mg) was dissolved in THF (5 mL) in a 50-mL Schlenk flask equipped with a septum that had been punctured with several holes. The reaction was allowed to stir for 5 days under a static atmosphere of nitrogen over which time the color of the solution changed from orange to yellow-green, and a white precipitate appeared in the reaction flask. The mixture was cannula-filtered into another Schlenk flask. The yellow-green filtrate was dried in vacuo, and the residue obtained was then recrystallized in benzene/hexanes to yield product as a pale yellow-green solid (92 mg, 51%). ^{1}H NMR (CD_2Cl_2): δ 13.69 (s, 2H, OH), 8.40 (s, 4H), 7.36 (d, 4H), 7.09 (d, 4H), 3.92 (s, 8H), 1.40 (s, 36H), 1.27 (s, 36H). ^{13}C NMR (CD_2Cl_2): δ 167.9 (*C*H═N), 158.2, 140.5, 136.7, 127.3, 126.4, 118.21, 60.1, 35.5, 34.6, 31.8 (C(*C*H$_3$)$_3$), 29.7 (C(*C*H$_3$)$_3$). FABMS Calcd: *m*/*z* 1101.2. Found: *m*/*z* 1101.6 $[M]^+$ with perfect isotopic pattern simulation for $C_{64}H_{93}N_4O_4Sn$ (see Supporting Information).

General Procedure for the Synthesis of 2a and 2e. $SnCl_4$ (0.26 g, 1 mmol) was added to a CH_2Cl_2 solution (10 mL) of salenH_2 **a** or **e** (1 mmol), and NEt_3 (0.202 g, 2 mmol), in a 50-mL Schlenk flask equipped with a magnetic stirbar under nitrogen. After stirring for 12 h, the reaction mixture was transferred to a silica gel column kept under nitrogen and eluted with CH_2Cl_2. Only the yellow fraction was collected and the solvent was removed in vacuo.

1,2-Ethanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) Tin-(IV) Dichloride (2a). Pale yellow solid, yield = 102 mg (15%). Anal. Calcd for $C_{32}H_{46}Cl_2N_2O_2Sn$: C, 56.45; H, 6.82; N, 4.12. Found: C, 56.61; H, 6.85; N, 4.17. ^{1}H NMR (CD_2Cl_2): δ 8.30 (s, 2H, J_{Sn-H} = 43.0 Hz), 7.67 (d, 2H), 7.14 (d, 2H, J = 2.4 Hz), 4.20 (s, 4H), 1.50 (s, 18H), 1.35 (s, 18H). ^{13}C NMR (CD_2Cl_2): δ 171.2 (*C*H═N), 163.9, 142.8, 140.6, 132.9, 130.3, 117.4, 52.3, 35.8, 34.3, 31.5 (C(*C*H$_3$)$_3$), 29.8 (C(*C*H$_3$)$_3$). ^{119}Sn NMR (CD_2Cl_2): δ. −595.5. FABMS Calcd: *m*/*z* 644.9. Found: *m*/*z* 645.1 ($[M - Cl]^+$).

(*S*,*S*)-(+)-1,2-Cyclohexanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) Tin(IV) Dichloride (2e). Yellow solid, yield = 106 mg (20%). Anal. Calcd for $C_{36}H_{52}Cl_2N_2O_2Sn\cdot{}^1/_2CH_2Cl_2$: C, 56.43; H, 6.88; N, 3.61. Found: C, 56.43; H, 6.85; N, 3.67. ^{1}H NMR ($CDCl_3$): δ 8.16 (s, 2H, J_{Sn-H} = 44.0 Hz), 7.61 (d, 2H, J = 3.6 Hz), 7.06 (s, 2H, J = 3.2 Hz), 4.02 (m, 2H), 2.56 (m, 2H), 2.12 (m, 2H), 1.53 (m, 4H), 1.49 (s, 18H), 1.32 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 167.9 (*C*H═N), 163.7, 142.7, 141.1, 132.8, 131.3, 117.9, 62.7, 54.6, 36.0, 34.6, 31.5 (C(*C*H$_3$)$_3$), 29.9 (C(*C*H$_3$)$_3$), 27.0, 24.0. ^{119}Sn NMR (CD_2Cl_2): δ −593.9. FABMS Calcd: *m*/*z* 699.0. Found: *m*/*z* 700 ($[M - Cl]^+$).

General Procedure for the Synthesis of 3a−i. Br_2 (26 μL, 0.5 mmol) was added to a CH_2Cl_2 solution (10 mL) of the corresponding (salen)Sn(II) complex, **1a**−**i** (0.5 mmol), in a 50-mL Schlenk flask equipped with a magnetic stirbar under nitrogen. After stirring for 12 h, the reaction mixture was concentrated to near dryness. Hexanes (10 mL) was added, and the resulting mixture was allowed to stir for an additional 2−4 h. The reaction mixture was filtered via cannula; the solid residue was washed with hexanes (2 × 10 mL) and dried under vacuum.

1,2-Ethanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) Tin-(IV) Dibromide (3a). Yellow solid, yield = 362 mg (94%). Anal. Calcd for $C_{32}H_{46}Br_2N_2O_2Sn\cdot CH_2Cl_2$: C, 49.51; H, 5.99; N, 3.60. Found: C, 49.55; H, 5.91; N, 3.66. ^{1}H NMR (CD_2Cl_2): δ 8.25 (s, 2H, J_{Sn-H} = 39.5 Hz), 7.67 (s, 2H), 7.13 (d, 2H, J = 2.4 Hz), 4.18 (s, 4H), 1.50 (s, 18H), 1.34 (s, 18H). ^{13}C NMR (CD_2Cl_2): δ 170.9 (*C*H═N), 162.9, 142.4, 140.9, 132.9, 130.5, 117.2, 51.8, 35.8, 34.4, 31.3 (C(*C*H$_3$)$_3$), 29.8 (C(*C*H$_3$)$_3$). ^{119}Sn NMR (CD_2Cl_2): δ −719.1. FABMS Calcd: *m*/*z* 689.3. Found: *m*/*z* 689.3 ($[M - Br]^+$).

1-Methyl-1,2/-ethanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) Tin(IV) Dibromide (3b). Yellow solid, yield = 352 mg (90%). Anal. Calcd for $C_{33}H_{48}Br_2N_2O_2Sn\cdot{}^1/_4CH_2Cl_2$: C, 49.68; H, 6.09; N, 3.49. Found: C, 49.66; H, 6.15; N, 3.55. ^{1}H NMR ($CDCl_3$): δ 8.20 (s, 2H, J_{Sn-H} = 40.0 Hz), 7.63 (s, 2H), 7.05 (d, 2H, J = 11.5 Hz), 4.53 (m, 1H), 4.03 (m, 2H), 1.67 (d, 3H, J = 6.5 Hz), 1.52 (s, 18H), 1.32 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 171.4 (*C*H═N), 169.5, 142.9, 142.8, 141.2, 133.3, 133.1, 131.3, 130.8, 117.6, 58.0, 56.0, 36.0, 34.6, 31.5 (C(*C*H$_3$)$_3$), 30.0 (C(*C*H$_3$)$_3$), 17.3 (*C*H$_3$). ^{119}Sn NMR (CD_2Cl_2): δ −714.6. APCIMS (MeCN) Calcd: *m*/*z* 703.2. Found: *m*/*z* 703 ($[M - Br]^+$).

1,2-Benzenediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) Tin(IV) Dibromide (3c). Orange-red solid, yield = 368 mg (90%). Anal. Calcd for $C_{36}H_{46}Br_2N_2O_2Sn\cdot 1{}^1/_2CH_2Cl_2$: C, 47.77; H, 5.24; N, 2.97. Found: C, 47.67; H, 5.24; N, 3.12. ^{1}H NMR (CD_2Cl_2): δ 8.78 (s, 2H, J_{Sn-H} = 39.2 Hz), 7.84 (q, 2H, J = 3.4, 3.2 Hz), 7.76

(d, 2H, J = 2.4 Hz), 7.60 (q, 2H, J = 3.4, 3.2 Hz), 7.29 (d, 2H, J = 2.4 Hz), 1.53 (s, 18H), 1.36 (s, 18H). ^{13}C NMR (CD_2Cl_2): δ 164.7 (*C*H═N), 163.8, 143.1, 141.9, 135.2, 133.0, 132.0, 130.2, 117.6, 117.3, 36.0, 34.7, 31.4 (C(*C*H$_3$)$_3$), 30.0 (C(*C*H$_3$)$_3$). ^{119}Sn NMR (CD_2Cl_2): δ −720.4. APCIMS (MeCN) Calcd: *m*/*z* 737.4. Found: 737 ([M − Br$^+$]).

(*R*,*R*)-(−)-1,2-Cyclohexanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) Tin(IV) Dibromide (3d). Yellow solid, yield = 91%. Anal. Calcd for $C_{36}H_{52}Br_2N_2O_2Sn\cdot CH_2Cl_2$: C, 52.06; H, 6.32; N, 3.36. Found: C, 51.97; H, 6.27; N, 3.40. ^{1}H NMR (CD_2Cl_2): δ 8.15 (s, 2H, J_{Sn-H} = 43.6 Hz), 7.64 (d, 2H, J = 2.8 Hz), 7.16 (d, 2H, J = 2.4 Hz), 4.09 (m, 2H), 2.54 (m 2H), 2.08 (m, 2H), 1.62 (b, 4H), 1.48 (s, 18H), 1.33 (s, 18H). ^{13}C NMR (CD_2Cl_2): δ 167.5 (*C*H═N), 163.0, 142.5, 140.9, 132.8, 131.2, 117.3, 61.9, 36.0, 34.7, 31.6 (C(*C*H$_3$)$_3$), 30.0 (C(*C*H$_3$)$_3$), 27.0, 24.1, 19.2. ^{119}Sn NMR (CD_2Cl_2): δ −711.8. APCIMS (MeCN) Calcd: *m*/*z* 743.4. Found: *m*/*z* 744 ([M-Br]$^+$).

(*S*,*S*)-(+)-1,2-Cyclohexanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) Tin(IV) Dibromide (3e). Yellow solid, yield = 375 mg (90%). Anal. Calcd for $C_{36}H_{52}Br_2N_2O_2Sn\cdot{}^1/_4CH_2Cl_2$: C, 51.47; H, 6.50; N, 3.31. Found: C, 51.46; H, 6.14; N, 3.25. ^{1}H NMR (CD_2Cl_2): δ 8.16 (s, 2H, J_{Sn-H} = 43.6 Hz), 7.65 (d, 2H, J = 2.0 Hz), 7.17 (d, 2H, J = 2.0 Hz), 4.09 (m, 2H), 2.54 (m 2H), 2.08 (m, 2H), 1.5−1.6 (b, 4H), 1.49 (s, 18H), 1.33 (s, 18H). ^{13}C NMR (CD_2Cl_2): δ 167.5 (*C*H═N), 163.0, 142.5, 140.9, 132.8, 131.2, 117.3, 61.9, 36.0, 34.7, 31.6 (C(*C*H$_3$)$_3$), 30.0 (C(*C*H$_3$)$_3$), 27.0, 24.1, 19.2. ^{119}Sn NMR (CD_2Cl_2): δ −709.7. FABMS Calcd: *m*/*z* 743.4. Found: *m*/*z* 744 ([M − Br]$^+$).

1,2-Ethanediamino-*N*,*N*′-bis(5-bromosalicylidene) Tin(IV) Dibromide (3f). Orange solid, yield = 255 mg (72%). Anal. Calcd for $C_{16}H_{12}Br_4N_2O_2Sn\cdot{}^1/_2CH_2Cl_2$: C, 26.70; H, 1.77; N, 3.78. Found: C, 26.37; H, 1.73; N, 3.75. ^{1}H NMR (DMSO-d_6): δ 8.11 (s, 1H), 7.91 (s, 1H), 7.03 (s, 2H), 6.91 (d, 1H, J = 8.0 Hz), 6.82 (d, 1H, J = 8.8 Hz), 6.20 (d, 1H, J = 8.8 Hz), 6.05 (d, 1H, J = 8.8 Hz), 3.34 (s, 4H). EIMS: *m*/*z* 622.7 ([M − Br]$^+$, 12), 541.7 (11), 358.6 (23), 198.8 (86), 131 (100).

(*S*,*S*)-(+)-1,2-Cyclohexanediamino-(*N*,*N*′-bis(3,5-dibromosalicylidene) Tin(IV) Dibromide (3g). Yellow solid, yield = 372 mg (81%). Anal. Calcd for $C_{20}H_{16}Br_6N_2O_2Sn\cdot CH_2Cl_2$: C, 25.37; H, 1.83; N, 2.82. Found: C, 25.09; H, 1.75; N, 2.93. ^{1}H NMR (CD_2Cl_2): δ 8.06 (s, 2H), 7.97 (d, 2H, J = 2.4 Hz), 7.49 (d, 2H, J = 2.4 Hz), 4.15 (m, 2H), 2.51 (m, 2H), 2.12 (m, 2H), 1.62 (m, 2H), 1.52 (m, 2H). APCIMS (CH_2Cl_2) Calcd: *m*/*z* 834.6. Found: *m*/*z* 834.8 ([M − Br]$^+$).

1,2-Ethanediamino-*N*,*N*′-bis(3-methoxysalicylidene) Tin(IV) Dibromide (3h). Yellow solid, yield = 270 mg (90%). Anal. Calcd for $C_{18}H_{18}Br_2N_2O_4Sn\cdot{}^1/_2CH_2Cl_2$: C, 34.37; H, 2.96; N, 4.34. Found: C, 34.58; H, 2.84; N, 4.46. ^{1}H NMR (CD_2Cl_2): δ 8.26 (s, 1H), 8.24 (s, 1H), 7.13 (m, 1H), 6.92 (m, 4H), 4.19 (s, 4H), 3.94 (s, 6H). EIMS: *m*/*z* 524.9 ([M − Br]$^+$, 15), 444 (0.3), 268.9 (11), 240.9 (13), 162 (23).

1,2-Ethanediamino-*N*,*N*′-bis(3,5-dibromosalicylidene) Tin(IV) Dibromide (3i). Orange solid, yield = 286 mg (77%). Anal. Calcd for $C_{16}H_{10}Br_6N_2O_2Sn$: C, 22.44; H, 1.18; N, 3.27. Found: C, 22.36; H, 1.12; N, 3.20. ^{1}H NMR (pyridine-d_6): δ 8.38 (s, 1H), 7.94 (s, 1H), 7.69 (d, 1H, J = 2.5 Hz), 7.69 (s, 1H), 7.30 (s, 1H), 7.13 (s, 2H), 4.37 (s, 4H). EIMS: *m*/*z* 780.4 ([M − Br]$^+$, 28), 699.6 (66), 621.7 (14), 421.7 (70), 395.7 (64), 198.9 (100).

General Procedure for the Synthesis of 4a−e. I_2 (127 mg, 0.5 mmol) was added to a hexanes (20 mL) slurry of the corresponding (salen)Sn(II) complex, **1a**−**e**, (0.5 mmol) in a 50-mL Schlenk flask equipped with a magnetic stirbar under nitrogen. The reaction mixture was allowed to stir for 18 h and filtered via cannula. The remaining solid product was washed with hexanes (2 × 10 mL) and dried under vacuum.

1,2-Ethanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) Tin(IV) Diiodide (4a). Yellow solid, yield = 369 mg (84%). Anal. Calcd for $C_{32}H_{46}I_2N_2O_2Sn\cdot{}^1/_4CH_2Cl_2$: C, 43.73; H, 5.30; N, 3.16; Found: C, 43.67; H, 5.31; N, 3.20. ^{1}H NMR (CD_2Cl_2): δ 8.17 (s, 2H, J_{Sn-H} = 32.6 Hz), 7.68 (d, 2H, J = 2.8 Hz), 7.13 (d, 2H, J = 2.8 Hz), 4.16 (s, 4H), 1.49 (s, 18H), 1.34 (s, 18H). ^{13}C NMR (CD_2Cl_2): δ 171.0 (*C*H═N), 162.3, 142.7, 141.1, 133.1, 130.7, 117.1, 51.0, 35.9, 34.7, 31.5 (C(*C*H$_3$)$_3$), 30.2 (C(*C*H$_3$)$_3$). ^{119}Sn NMR (CD_2Cl_2): δ −805.1. FABMS Calcd: *m*/*z* 736.3. Found: *m*/*z* 737 ([M − I]$^+$).

1-Methyl-1,2-ethanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) Tin(IV) Diiodide (4b). Yellow solid, yield = 377 mg (86%). Anal. Calcd for $C_{33}H_{48}I_2N_2O_2Sn\cdot CH_2Cl_2$: C, 42.44; H, 5.24; N, 2.91. Found: C, 42.58; H, 5.21; N, 2.92. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 2H, J_{Sn-H} = 34.6 Hz), 7.64 (s, 2H), 7.07 (d, 2H, J = 4.4 Hz), 4.67 (b, 1H), 4.08 (b, 1H), 3.91 (b, 1H), 1.64 (d, 3H), 1.51 (s, 18H), 1.28 (s, 18H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 170.6 (*C*H═N), 163.0, 142.9, 142.8, 140.8, 133.1, 132.9, 130.7, 117.0, 56.9, 35.6, 34.4, 31.8, 31.5, 31.4 (C(*C*H$_3$)$_3$), 30.1 (C(*C*H$_3$)$_3$), 16.7 (*C*H$_3$). ^{119}Sn NMR (CD_2Cl_2): δ −1015.9. FABMS Calcd: *m*/*z* 750.4. Found: *m*/*z* 751 ([M − I]$^+$).

1,2-Benzenediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) Tin(IV) Diiodide (4c). Orange solid, yield = 420 mg (92%). Anal. Calcd for $C_{36}H_{46}I_2N_2O_2Sn\cdot{}^1/_4C_6H_{14}$: C, 48.20; H, 5.34; N, 3.00. Found: C, 48.12; H, 35; N, 2.87. ^{1}H NMR (CD_3OD): δ 9.55 (s, 2H, J_{Sn-H} = 38.4 Hz), 8.31 (q, 2H), 7.96 (d, 2H, J = 2.0 Hz), 7.79 (m, 4H, J = 2.0 Hz), 1.62 (s, 18H), 1.47 (s, 18H). ^{13}C NMR (CD_3OD): δ 168.3 (*C*H═N), 164.8, 144.3, 144.1, 136.4, 134.0, 133.5, 131.8, 119.5, 118.7, 36.7, 31.6 (C(*C*H$_3$)$_3$), 30.7 (C(*C*H$_3$)$_3$). ^{119}Sn NMR (CD_3OD): δ −783.8. APCIMS (MeCN) Calcd: *m*/*z* 784.4. Found: *m*/*z* 785 ([M − I]$^+$).

(*R*,*R*)-(−)-1,2-Cyclohexanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) Tin(IV) Diiodide (4d). Yellow solid, yield = 262 mg (57%). Anal. Calcd for $C_{36}H_{52}I_2N_2O_2Sn\cdot{}^1/_2C_6H_{14}$: C, 48.69; H, 6.19; N, 2.91. Found: C, 48.61; H, 6.11; N, 3.01. ^{1}H NMR (CD_2Cl_2): δ 8.09 (s, 2H, J_{Sn-H} = 39.3 Hz), 7.67 (d, 2H, J = 2.4 Hz), 7.17 (d, 2H, J = 2.4 Hz), 4.25 (b, 2H), 2.56 (m, 2H), 2.09 (m, 2H), 1.6−1.9 (b, 4H), 1.50 (s, 18H), 1.35 (s, 18H). ^{13}C NMR (CD_2Cl_2): δ 167.8 (*C*H═N), 162.6, 142.9, 141.3, 133.2, 131.5, 117.1, 60.8, 35.9, 34.7, 31.5 (C(*C*H$_3$)$_3$), 30.2 (C(*C*H$_3$)$_3$), 26.8, 24.0, ^{119}Sn NMR (CD_2Cl_2): δ −992.1. APCIMS (MeCN) Calcd: *m*/*z* 790.4. Found: *m*/*z* 791 ([M − I]$^+$).

(*S*,*S*)-(+)-1,2-Cyclohexanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) Tin(IV) Diiodide (4e). Yellow solid, yield = 408 mg (89%). Anal. Calcd for $C_{36}H_{52}I_2N_2O_2Sn\cdot{}^1/_4C_6H_{14}$: C, 47.89; H, 5.95; N, 2.98. Found: C, 48.11; H, 6.05; N, 2.98. ^{1}H NMR ($CDCl_3$): δ 8.05 (s, 2H, J_{Sn-H} = 39.4 Hz), 7.64 (d, 2H, J = 2.4 Hz), 7.07 (d, 2H, J = 2.4 Hz), 4.25 (b, 2H), 2.57 (m, 2H), 2.11 (m, 2H), 1.66 (m, 4H), 1.52 (s, 18H), 1.33 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 167.0 (*C*H═N), 162.4, 142.7, 142.7, 140.5, 132.7, 130.8, 116.7, 60.3, 35.7, 34.5, 31.6 (C(*C*H$_3$)$_3$), 30.2 (C(*C*H$_3$)$_3$), 26.6, 23.8. ^{119}Sn NMR (CD_2Cl_2): δ. −992.1. FABMS Calcd: *m*/*z* 790.4. Found: *m*/*z* 791 ([M − I]$^+$).

General Procedure for the Synthesis of 5a−e. AgOTf (51.4 mg, 0.2 mmol) was added to a CH_2Cl_2 solution (20 mL) of the corresponding (salen)Sn(IV) complex, **3a**−**e**, (0.1 mmol) in a 50-mL Schlenk flask equipped with a magnetic stirbar under nitrogen. The reaction mixture was allowed to stir for 12 h. The solution was filtered via cannula into another 50-mL Schlenk flask, and the filtrate was evaporated in vacuo to give a solid product.

1,2-Ethanediamino-*N,N′*-bis(3,5-di-*tert*-butylsalicylidene) Tin(IV) Bis(triflate) (5a). Pale yellow-green solid, yield = 430 mg (97%). Anal. Calcd for $C_{34}H_{46}F_6N_2O_8S_2Sn\cdot{}^1/_4CH_2Cl_2$: C, 44.23; H, 5.04; N, 3.01. Found: C, 44.37; H, 5.11; N, 3.07. ^{1}H NMR (CD_2Cl_2): δ 8.60 (s, 2H, J_{Sn-H} = 55.2 Hz), 7.78 (d, 2H, J = 2.4 Hz), 7.22 (d, 2H, J = 2.4 Hz), 4.33 (s, 2H), 1.48 (s, 18H), 1.34 (s, 18H). ^{119}Sn NMR (CD_2Cl_2): δ 662.3. ^{19}F NMR (CD_2Cl_2): δ 54.52. APCIMS (MeCN) Calcd: *m*/*z* 759.2. Found: *m*/*z* 760 ([M − OTf]$^+$).

1-Methyl-1,2-ethanediamino-*N,N′*-bis(3,5-di-*tert*-butylsalicylidene) Tin(IV) Bis(triflate) (5b). Pale yellow-green solid, yield = 364 mg (79%). Anal. Calcd for $C_{35}H_{48}F_6N_2O_8S_2Sn\cdot{}^3/_4CH_2Cl_2$: C, 43.55; H, 5.06; N, 2.84. Found: C, 43.41; H, 5.40; N, 2.84. ^{1}H NMR ($CDCl_3$): δ 8.53 (d, 2H, J_{Sn-H} = 56.2 Hz, 54.4 Hz), 7.74 (s, 2H), 7.15 (d, 2H, J = 11.2 Hz), 4.56 (b, 1H), 4.16 (b, 2H), 1.70 (d, 3H, J = 4.0 Hz), 1.50 (s, 18H), 1.34 (s, 18H). ^{13}C NMR (CD_2Cl_2): δ 174.8 (*C*H═N), 172.8 (*C*H═N), 163.9, 163.3, 142.8, 142.4, 134.6, 134.4, 131.3, 130.8, 120.5, 117.3, 117.0, 116.8, 57.1, 54.9, 35.9, 34.6, 31.4 (C(*C*H$_3$)$_3$), 29.7 (C(*C*H$_3$)$_3$), 16.8. The quartet peak of the triflate carbon was not observed. ^{119}Sn NMR (CD_2Cl_2): δ −659.8. ^{19}F NMR (CD_2Cl_2): δ 55.1. APCIMS (MeCN) Calcd: *m*/*z* 773.2. Found: *m*/*z* 773 ([M − OTf]$^+$).

1,2-Benzenediamino-*N,N′*-bis(3,5-di-*tert*-butylsalicylidene) Tin(IV) Bis(triflate) (5c). Pale yellow-green solid, yield = 344 mg (72%). Anal. Calcd for $C_{38}H_{46}F_6N_2O_8S_2Sn\cdot{}^3/_4CH_2Cl_2$: C, 45.63; H, 4.70; N, 2.75. Found: C, 45.32; H, 5.03; N, 2.80. ^{1}H NMR (CD_2Cl_2): δ 9.11 (s, 2H, J_{Sn-H} = 56.0 Hz), 7.92 (q, 2H, J = 3.2 Hz), 7.88 (d, 2H, J = 2.4 Hz), 7.65 (d, 2H), 7.40 (d, 2H, J = 2.0 Hz), 1.53 (s, 18H), 1.37 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 165.8 (*C*H═N), 164.7, 143.1, 142.2, 136.4, 135.4, 132.2, 131.8, 130.1, 129.9, 117.3, 117.2, 116.5, 116.3, 35.8, 34.5, 31.2 (C(*C*H$_3$)$_3$), 29.8 (C(*C*H$_3$)$_3$). The quartet peak of the triflate carbon was not observed. ^{119}Sn NMR (CD_2Cl_2): δ −652.9. ^{19}F NMR (CD_2Cl_2): δ 54.42. APCIMS (MeCN) Calcd: *m*/*z* 807.2. Found: *m*/*z* 807 ([M − OTf]$^+$).

(*R,R*)-(−)-1,2-Cyclohexanediamino-*N,N′*-bis(3,5-di-*tert*-butylsalicylidene) Tin(IV) Bis(triflate) (5d). Pale yellow-green solid, yield = 361 mg (75%). Anal. Calcd for $C_{38}H_{52}F_6N_2O_8S_2Sn$: C, 47.39; H, 5.45; N, 2.91. Found: C, 47.34; H, 5.40; N, 2.88. ^{1}H NMR ($CDCl_3$): δ 8.42 (s, 2H, J_{Sn-H} = 60.0 Hz), 7.72 (s, 2H), 7.15 (d, 2H), 4.05 (b, 2H), 2.69 (m, 2H), 2.17 (m, 2H), 1.62 (b, 4H), 1.49 (s, 18H), 1.34 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 171.5 (*C*H═N), 163.8, 142.9, 142.5, 134.4, 131.3, 116.8, 62.5, 35.8, 34.5, 31.3 (C(*C*H$_3$)$_3$), 29.6 (C(*C*H$_3$)$_3$), 26.8, 23.5. The quartet peak of carbon of triflate was not observed. ^{119}Sn NMR (CD_2Cl_2): δ −663.5. ^{19}F NMR (CD_2Cl_2): δ 55.09. APCIMS (MeCN) Calcd: *m*/*z* 812.6. Found: *m*/*z* 813 ([M − OTf]$^+$).

(*S,S*)-(+)-1,2-Cyclohexanediamino-*N,N′*-bis(3,5-di-*tert*-butylsalicylidene) Tin(IV) Bis(triflate) (5e). Pale yellow-green solid, yield = 313 mg (65%). Anal. Calcd for $C_{38}H_{52}F_6N_2O_8S_2Sn$: C, 47.39; H, 5.45; N, 2.91. Found: C, 47.34; H, 5.40; N, 2.88. ^{1}H NMR (CD_2Cl_2): δ 8.09 (s, 2H, J_{Sn-H} = 60.2 Hz), 7.67 (d, 2H, J = 2.4 Hz), 7.17 (d, 2H, J = 2.4 Hz), 4.25 (b, 2H), 2.56 (m, 2H), 2.09 (m, 2H), 1.60−1.90 (b, 4H), 1.50 (s, 18H), 1.35 (s, 18H). ^{13}C NMR (CD_2Cl_2): δ 171.8 (*C*H═N), 163.6, 142.83, 142.75, 134.6, 131.6, 117.1, 63.0, 36.1, 34.8, 31.4 (C(*C*H$_3$)$_3$), 29.8 (C(*C*H$_3$)$_3$), 27.2, 23.9. The quartet peak of the triflate carbon was not observed. ^{119}Sn NMR (CD_2Cl_2): δ −661.5. ^{19}F NMR (CD_2Cl_2): δ 54.53. APCIMS (MeCN) Calcd: *m*/*z* 812.6. Found: *m*/*z* 813 ([M − OTf]$^+$).

1,2-Ethanediamino-*N,N′*-bis(3,5-di-*tert*-butylsalicylidene) Tin(IV) Bromide Triflate (6a). AgOTf (51.4 mg, 0.2 mmol) was added to a CH_2Cl_2 solution (20 mL) of **3a** (0.2 mmol) in a 50-mL Schlenk flask equipped with a magnetic stirbar under nitrogen. The reaction mixture was allowed to stir for 12 h and filtered via cannula into another 50-mL Schlenk flask. The filtrate was then evaporated in vacuo to give a yellow solid product. Yield = 145 mg (86%). Anal. Calcd for $C_{33}H_{46}BrF_3N_2O_5Sn$: C, 47.28; H, 5.53; N, 3.34. Found: C, 47.49; H, 5.51 N, 3.35. ^{1}H NMR (CD_2Cl_2): δ 8.43 (s, 2H, J_{Sn-H} = 47.0 Hz), 7.72 (d, 2H, J = 2.0 Hz), 7.17 (d, 2H, J = 1.6 Hz), 4.22 (m, 4H), 1.49 (s, 18H), 1.33 (s, 18H). ^{13}C NMR (CD_2Cl_2): δ 173.5 (*C*H═N), 163.4, 142.8 142.0, 133.8, 130.9, 117.4, 51.8, 36.1, 34.7, 31.5 (C(*C*H$_3$)$_3$), 29.9 (C(*C*H$_3$)$_3$). The quartet peak of the triflate carbon was not observed. ^{119}Sn NMR (CD_2Cl_2): δ −662.6. ^{19}F NMR (CD_2Cl_2): δ 53.99. APCIMS (MeCN) Calcd: *m*/*z* 689.2. Found: *m*/*z* 689 ([M − OTf]$^+$).

General Procedure for the Synthesis of 2a, 2e, 4a, and 4e from 5a and 5e. Either NaCl or NaI (5 equiv) was added to a CH_2Cl_2/THF solution (1:1.5 v/v, 15 mL) of the corresponding (salen)Sn(OTf)$_2$, **5a** or **5e** (0.3 mmol), in a 50-mL Schlenk flask equipped with a magnetic stirbar. The reaction mixture was allowed to stir for 18 h, and then hexanes (15 mL) was added to the mixture. The reaction was stirred for an additional 10 h and filtered via cannula into another 50-mL Schlenk flask. The filtrate was then evaporated in vacuo to give a solid product that was washed with hexanes (2 × 10 mL). Yield for **2a** = 90%. Yield for **2e** = 87%. Yield for **4a** = 90%. Yield for **4e** = 80%.

Synthesis of 4a from 3a. NaI (5 equiv) was added to a CH_2Cl_2 solution (10 mL) of **3a** (0.3 mmol) in a 50-mL Schlenk flask equipped with a magnetic stirbar. The reaction mixture was allowed to stir for 28 h and filtered via cannula into another 50-mL Schlenk flask. The filtrate was collected and then evaporated in vacuo to give a solid product that was washed with hexanes (2 × 10 mL). Yield = 82%.

X-ray analysis of 1c, 1e, 2a·CHCl$_3$, 3c·CH$_2$Cl$_2$, 3e·C$_6$H$_6$CH$_3$, and 5a·2CH$_2$Cl$_2$. Single crystals of **1c** and **1e** were obtained by recrystallizing these compounds in ethanol. Single crystals of **2a·CHCl$_3$** were grown in chloroform. Crystals of **3c·CH$_2$Cl$_2$**, **3e·toluene**, and **5a·2CH$_2$Cl$_2$** were grown from a solvent mixture consisting of CH_2Cl_2/toluene/hexanes (2:1:1 v/v/v). X-ray diffraction analyses were carried out on a Bruker SMART-1000 CCD area detector with graphite monochromated Mo Kα radiation. The data were collected at −120 °C to a maximum 2θ value of 56.5° in 0.30° oscillations with 25.0 s exposures. The crystal-to-detector distance was 50.00 mm. The detector swing angle was 28.00°. The structure was solved by direct methods (SIR92) and expanded using Fourier techniques (DIRDIF94). All non-hydrogen atoms of crystals **2a·CHCl$_3$**, **3c·CH$_2$Cl$_2$**, and **5a·2CH$_2$Cl$_2$** were refined anisotropically. The carbon atoms of the phenyl backbone of crystal **1c** were refined isotropically, while the remaining non-hydrogen atoms were refined anisotropically. The disordered *tert*-butyl carbon atoms of crystals **1e** and **3e·toluene** were refined with a group isotropic thermal parameter. Hydrogen atoms were included in idealized positions but not refined except for those on the disordered *tert*-butyl methyl carbons. All calculations were performed using the teXan crystallographic software package of Molecular Structure Corporation. Further details on the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge, U.K., on quoting the full journal citation.

General Procedure for Carrying Out Catalytic Propylene Carbonate Synthesis from Propylene Oxide and CO$_2$. In a nitrogen-filled glovebox, propylene oxide (PO, 3.8 mL, 1700 equiv) was transferred, using a 5-mL gastight syringe, to a 200-mL Parr pressure reactor which was equipped with a magnetic stirbar. Next, the DMAP cocatalyst (0.0195 g, 5 equiv) was added to the pressure reactor, followed by (salen)Sn catalyst (0.032 mmol, 1 equiv).

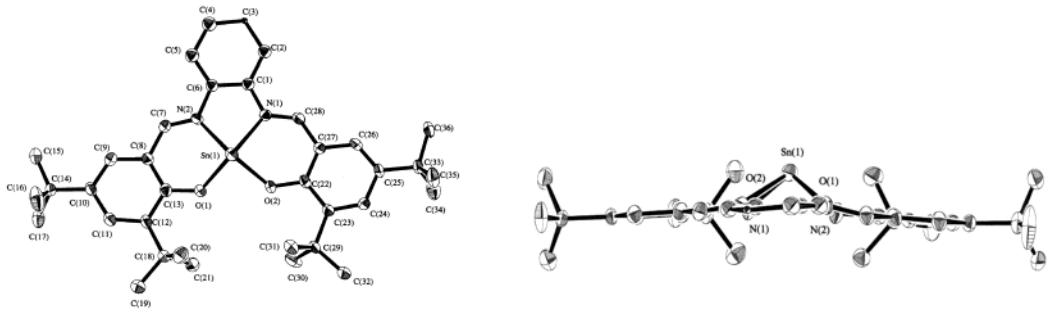


Figure 1. Two ORTEP views of the crystal structure of complex **1c** showing the atom labeling scheme and the asymmetric subunit. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

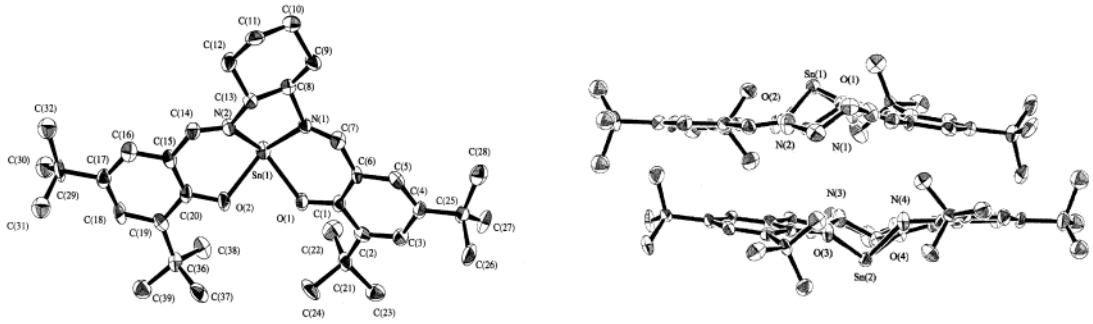
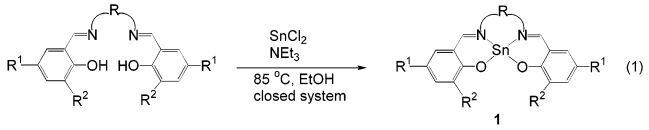


Figure 2. Two ORTEP views of the crystal structure of complex **1e** showing the atom labeling scheme and the asymmetric subunit. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

Finally, CH_2Cl_2 (0.5 mL) was added to the reactor, which was then sealed, brought out of the glovebox, and attached to a CO_2 tank via a Swagelok manifold that had been purged with carbon dioxide. Next, the reactor was pressurized to 100 psig of carbon dioxide, allowed to stand for 2 min, sealed, and disconnected from the carbon dioxide manifold. The reactor was immersed in an oil bath that had been preheated to the desired temperature and allowed to stir for 4 h and 15 min. Prior to immersing the reactor, it was wrapped with a cloth so that the portion of the reactor not submerged in the oil bath would remain heated at a constant temperature. When the desired reaction time had been reached, the reactor was quickly removed from the oil bath and immediately cooled by immersing it in a cold-water bath. The reaction mixture was transferred to a round-bottom flask, and the excess PO and CH_2Cl_2 were removed on a rotary evaporator. The crude product was analyzed by ^{1}H NMR spectroscopy ($CDCl_3$) to determine if any polymer, PO, or CH_2Cl_2 was present. In all cases where there was catalytic activity, propylene carbonate was the only product observed. Hence, the yield of propylene carbonate was calculated by subtracting the catalyst and cocatalyst weights from the weight of the crude product. Our prior experience with another catalyst system has shown that this method of determining yield is quite accurate when compared against that obtained using the isolated pure propylene carbonate (obtained via Kugelrohr distillation of the crude product mixture).[13] For high-temperature experiments (>100 °C), a background reaction can occur, leading to a small amount of cyclic carbonate product. Thus, the control experiments were carried out in the absence of the catalyst/cocatalyst system and the yield of the background reaction was substracted from the total yield.

Results and Discussion

Synthesis and Properties of (Salen)Sn(II) Complexes. Of the known methods for (salen)Sn(II) synthesis, some have relied on the use of alkali salen salts,[8] while others have used expensive tin precursors such as $Sn[((CH_3)_3Si)_2N]_2$.[8,10] Hobday and Smith have utilized the direct reaction of $SnCl_2$ with salen ligands in the presence of sodium ethoxide in refluxing ethanol,[7] albeit with unsubstituted salen ligands. When we applied this procedure to more substituted and more soluble salen ligands, mixtures of the desired product and the bis-ligand complex, $(salenH)_2Sn$, were formed that were difficult to separate (vide infra). However, the (salen)-Sn(II) compounds **1a**−**i** could be obtained in moderate to good yields (50−93%) following the method reported by Parkin et al.[10] In a closed system, stoichiometric amounts of the appropriate salen ligand, $SnCl_2$, and NEt_3 as a base were combined in absolute ethanol (eq 1). We did not observe the formation of any bis-ligand complex under these conditions.



(1)

a: R = 1,2-ethanediyl; $R^1 = R^2 = {}^t$Bu
b: R = 1-methyl-1,2-ethanediyl; $R^1 = R^2 = {}^t$Bu
c: R = 1,2-benzenediyl; $R^1 = R^2 = {}^t$Bu
d: R = (*R*,*R*)-(-)-1,2-cyclohexanediyl; $R^1 = R^2 = {}^t$Bu
e: R = (*S*,*S*)-(+)-1,2-cyclohexanediyl; $R^1 = R^2 = {}^t$Bu
f: R = 1,2-ethanediyl; R^1 = Br; R^2 = H
g: R = (*S*,*S*)-(+)-1,2-cyclohexanediyl; $R^1 = R^2$ = Br
h: R = 1,2-ethanediyl; R^1 = H; R^2 = OMe
i: R = 1,2-ethanediyl; $R^1 = R^2$ = Br

(Salen)Sn(II) compounds **1a**−**i** do not have sharp melting points and tend to decompose in air between 200 and 300 °C. These compounds are very air-sensitive in solution but are stable in the solid state. It was observed that under nonanhydrous conditions a THF solution of compound **1a** slowly changed color from orange to pale yellow-green concurrently with the formation of $Sn(OH)_2$ as a white precipitate. The bis-ligand complex $(salenH)_2Sn$ (**1a′**) was isolated from the resulting pale yellow-green solution and was identified by ^{1}H NMR and FABMS (eq 2). Further

Table 1. Crystallographic Data for **1c**, **1e**, **2a·CHCl$_3$**, **3c·CH$_2$Cl$_2$**, **3e·toluene**, and **5a·2CH$_2$Cl$_2$**

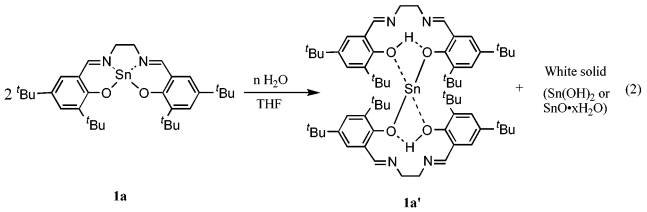
param	1c	1e	2a·CHCl$_3$	3c·CH$_2$Cl$_2$	3e·toluene	5a·2CH$_2$Cl$_2$
chemical formula	$C_{36}H_{46}N_2O_2Sn$	$C_{36}H_{52}N_2O_2Sn$	$C_{33}H_{47}Cl_5N_2O_2Sn$	$C_{37}H_{48}Br_2Cl_2N_2O_2Sn$	$C_{43}H_{60}Br_2N_2O_2Sn$	$C_{36}H_{50}Cl_4F_6N_2O_8S_2Sn$
fwt	659.48	663.51	799.70	902.20	915.46	1077.41
T/K	153(2)	153(2)	153(2)	153(2)	153(2)	153(2)
cryst syst	triclinic	orthorhombic	orthorhombic	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$	$P2_1$	$C2/c$
a/Å	9.692(2)	10.741(1)	9.9933(7)	11.419(2)	12.444(2)	12.778(3)
b/Å	12.177(2)	23.4428(10)	12.6633(9)	13.057(2)	26.662(4)	26.361(6)
c/Å	15.156(3)	26.698(4)	29.922(2)	13.845(3)	12.924(2)	13.618(3)
α/deg	88.413(3)	90	90	75.089(3)	90	90
β/deg	84.678(3)	90	90	76.771(3)	94.354(3)	90
γ/deg	69.280(3)	90	90	89.064(3)	90	90
U/Å^3	1665.7(5)	6724.4(10)	3786.6(4)	1939.8(6)	4275.8(9)	4582.9(15)
Z	2	8	4	2	4	4
μ/cm^{-1}	7.99	7.92	10.57	29.0	25.1	9.5
D_{calcd}/g·cm^{-3}	1.311	1.311	1.403	1.311	1.423	1.311
R1[a]	0.049	0.050	0.039	0.049	0.039	0.046
wR2[b]	0.107	0.093	0.088	0.107	0.070	0.086

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$, where $w = 1/[2(F_o^2) + (0.0530P)^2 + 0.30P]$ with $P = (\max F_o^2 + 2F_c^2)/3$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1c** and **1e**

	1c	1e
Sn1−N1	2.352(4)	2.325(9)
Sn1−N2	2.351(4)	2.379(7)
Sn1−O1	2.107(3)	2.102(7)
Sn1−O2	2.101(4)	2.124(8)
O1−Sn1−N1	118.63(13)	78.1(3)
O1−Sn1−N2	77.42(13)	119.4(3)
O1−Sn1−O2	79.97(13)	80.3(3)
N1−Sn1−N2	67.7(1)	69.0(3)
O2−Sn1−N1	77.86(13)	120.9(3)
O2−Sn1−N2	121.5(1)	75.6(3)

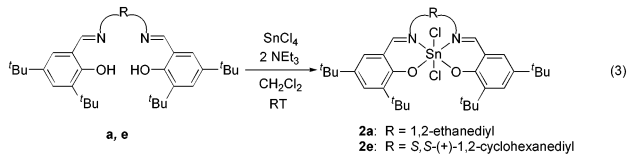
exposure of **1a′** to nonanhydrous conditions gave an amorphous white solid (which could be either $Sn(OH)_2$ or SnO·xH$_2$O) and salenH$_2$ ligand.



(2)

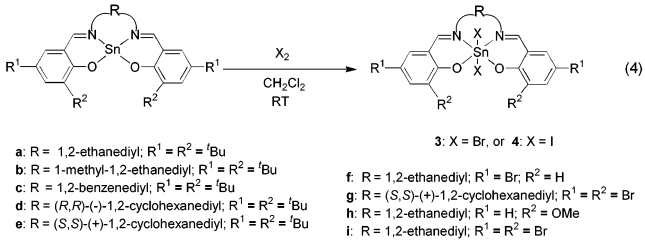
Crystal Structures of 1c and 1e. The crystal structures of **1c** (Figure 1) and **1e** (Figure 2) show that the Sn(II) centers lie above the respective N_2O_2 planes in a geometry that is roughly square pyramidal. This geometry was also observed by Parkin and co-workers for a similar (salen)Sn(II) complex.[10] Complex **1c** has a planar salen N_2O_2-base with the Sn−N_2O_2 plane distance being 1.097 Å. On the other hand, the cyclohexyl backbone of complex **1e** leads to a slightly distorted salen N_2O_2 plane. Complex **1e** crystallizes in a large orthorhombic unit cell ($Z = 8$) with each asymmetric subunit containing two molecules oriented in a face-to-face manner. The Sn(1)−N_2O_2 plane distance was determined to be 1.100 Å, and the Sn(2)−N_2O_2 plane distance was measured as 1.085 Å. The relevant crystallographic data for **1c** and **1e** are listed in Tables 1 and 2.

Synthesis and Properties of (Salen)Sn(IV) Complexes. The preparation of a few Lewis acidic (salen)Sn(IV) complexes has been previously described.[7,8,12,23] Specifically, the reaction of SnX_4 and salenH$_2$ either with[12] or without[23] a base has been reported. However, following the former procedure whereby $SnCl_4$ was added to a CH_2Cl_2 solution of the corresponding salen ligand and NEt_3 (eq 3), we obtained **2a** and **2e** only in low yields (15−20%). Another method for making dihalogenated (salen)Sn(IV) complexes used the transmetalation reaction between (salen)Co and SnX_4.[7] Unfortunately, this procedure required the preparation and handling of an air-sensitive Co(II) precursor.



(3)

A more facile method for synthesizing a (salen)Sn(IV) compound was described by Barrau et al., where (salen)Sn (salen = 1,2-ethanediamino-*N*,*N*′-bis(salicylidene)) was directly oxidized to (salen)SnI_2 with I_2.[8] We successfully expanded this direct oxidation methodology to incorporate a variety of ligand environments with not only iodine but also bromine as the oxidizing agent. Thus, (salen)$SnBr_2$, **3a**−**i**, and (salen)SnI_2, **4a**−**e**, were easily obtained in high yields (∼90%) at room temperature (eq 4).



(4)

We did not carry out the direct oxidation of (salen)Sn(II) compounds with Cl_2 due to the toxicity of the latter reagent. Attempted oxidation of (salen)Sn(II) compounds with $CuCl_2$,

(23) Sakuntala, E. N.; Vasanta, E. N. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1985**, *40B*, 1173−1176.

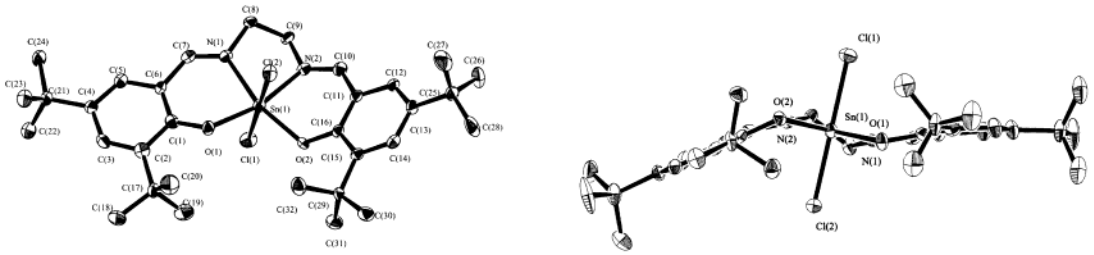


Figure 3. Two ORTEP views of the crystal structure of complex **2a·CHCl$_3$** showing the atom labeling scheme and the asymmetric subunit. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

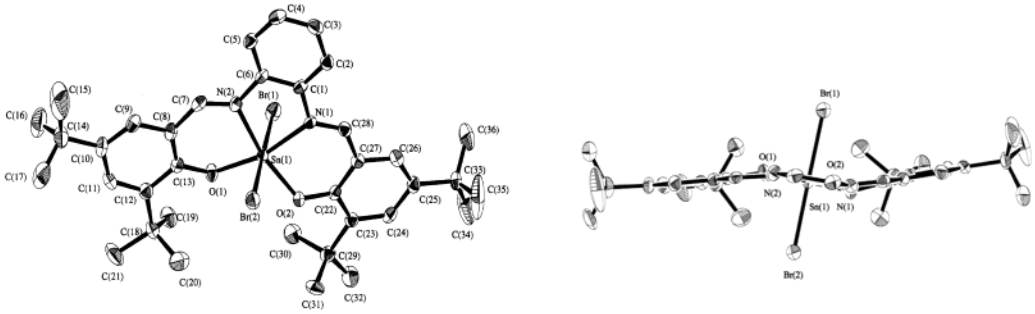
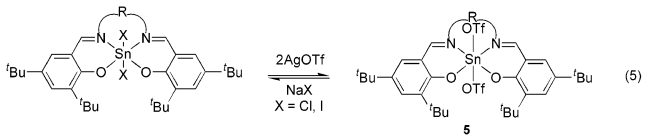


Figure 4. Two ORTEP views of the crystal structure of complex **3c·CH$_2$Cl$_2$** showing the atom labeling scheme and the asymmetric subunit. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

a good chlorinating agent,[24,25] yielded a mixture of insoluble products. Other chlorinating agents such as PCl_5 also yielded inseparable product mixtures. Hence, we decided to access the (salen)$SnCl_2$ using an anion-exchange reaction instead of an oxidative addition. We were also interested in bis-triflate (salen)Sn(IV) complexes due to the well-known lability of the triflate ligand which could be advantageous in catalysis.

(Salen)Sn(OTf)$_2$ complexes **5a**−**e** were obtained from either the corresponding (salen)SnI_2 or (salen)$SnBr_2$ complexes by combining these starting materials with 2 equiv of AgOTf at room temperature (eq 5). (Salen)$SnCl_2$ complexes **2a** and **2e** could then be prepared in excellent yields (90% and 87%, respectively) from (salen)Sn(OTf)$_2$ and excess NaCl (eq 5). We note that direct exchange between the dihalide (salen)Sn with other alkali salts is also possible. (Salen)SnI_2 complexes **4a** and **4e** could be synthesized from either (salen)Sn(OTf)$_2$ or (salen)$SnBr_2$ with excess NaI (eq 5).



We were able to synthesize a mixed ligand complex (salen)Sn(Br)(OTf), **6a**, from the corresponding (salen)$SnBr_2$ complex **3a** and 1 equiv of AgOTf at room temperature. However, this method was unsuccessful when applied to complex **3e** to make the corresponding (salen)Sn(Br)(OTf) complex **6e** with the cyclohexyl backbone.

In contrast to (salen)Sn(II) complexes, (salen)Sn(IV) complexes are six-coordinate and are stable in air both in solution and as solids. These complexes are only slightly sensitive to moisture over extended exposure. All (salen)-Sn(IV) complexes reported herein do not have sharp melting points and tend to decompose in air between 200 and 300 °C.

Crystal Structures of 2a·CHCl$_3$, 3c·CH$_2$Cl$_2$, 3e·toluene, and 5a·2CH$_2$Cl$_2$. The crystal structures of **2a·CHCl$_3$** (Figure 3), **3c·CH$_2$Cl$_2$** (Figure 4), **3e·toluene** (Figure 5), and **5a·2CH$_2$Cl$_2$** (Figure 6) show that the Sn(IV) atoms are at centers of slightly distorted octahedrons formed by the anionic ligands and the salen N_2O_2 plane. Unlike the corresponding (salen)Sn(II) complexes, the Sn(IV) centers are located in the N_2O_2 plane of the salen ligand. Interestingly, the unit cells of compounds **3c** and **3e** contain different solvent molecules even though their single crystals were grown in similar solvent mixtures. This discrepancy is probably due to the difference in packing forces as indicated by the different space groups. The cocrystallized solvent molecules could be removed from the crystal samples under vacuum. Similar to that observed for compound **1e**, the asymmetric subunit of the unit cell of compound **3e** also contains two different molecules. The crystallographic data of **3c·CH$_2$Cl$_2$**, **3e·toluene**, and **5a·2CH$_2$Cl$_2$** are listed in Tables 3 and 4.

^{1}H NMR Spectra. (Salen)Sn(II) complexes exhibit very interesting spectroscopic characteristics. The *tert*-butyl groups in the ^{1}H NMR spectra of **1a** and **1c** appear as two singlets around 1.5 and 1.3 ppm, close to the value observed for the free ligands. The imine protons for each compound give rise to singlets at 8.67 and 8.41 ppm, respectively. In addition,

(24) Onoe, A.; Uemura, S.; Okano, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 345−346.
(25) Taylor, P. H.; Wehrmeier, A.; Sidhu, S. S.; Lenoir, D.; Schramm, K. W.; Kettrup, A. *Chemosphere* **2000**, *40*, 1297−1303.

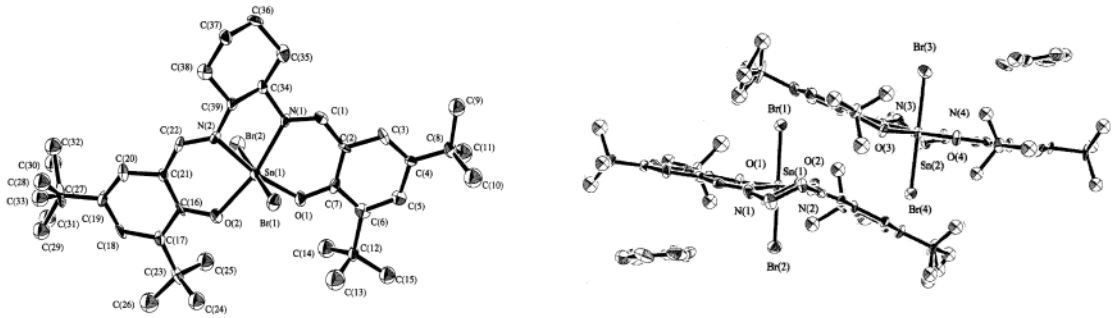


Figure 5. Two ORTEP views of the crystal structure of complex **3e·$C_6H_6CH_3$** showing the atom labeling scheme and the asymmetric subunit. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

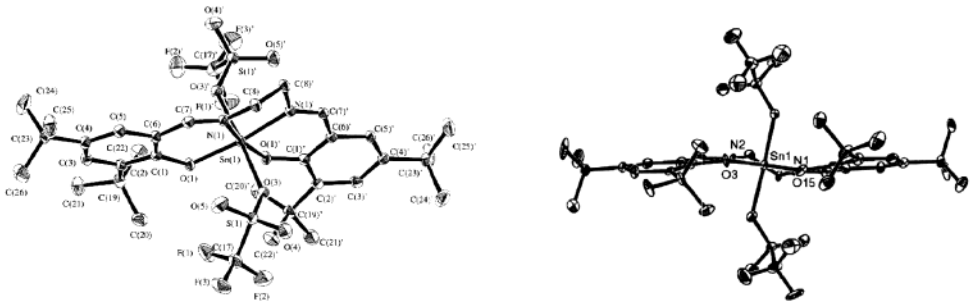


Figure 6. An ORTEP view of the crystal structure of complex **5a·2CH_2Cl_2** showing the atom labeling scheme. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) for **2a·$CHCl_3$**, **3c·CH_2Cl_2**, **3e·toluene**, and **5a·2CH_2Cl_2**

	2a·$CHCl_3$	**3c·CH_2Cl_2**	**3e·toluene**	**5a·2CH_2Cl_2**[a]
Sn1−N1	2.146(3)	2.148(5)	2.146(9)	2.108(2)
Sn1−N2	2.151(3)	2.154(5)	2.159(10)	2.108(2)
Sn1−O1	2.007(3)	2.000(4)	2.018(9)	1.969(2)
Sn1−O2	2.010(3)	2.001(4)	2.003(8)	1.969(2)
Sn1−X1	2.4134(11)	2.5862(11)	2.580(2)	2.143(2)
Sn1−X2	2.4188(11)	2.5626(11)	2.587(2)	2.143(2)

[a] For **5a**, X1 = O3, X2 = O4.

Table 4. Selected Bond Angles (deg) for **2a·$CHCl_3$**, **3c·CH_2Cl_2**, **3e·toluene**, and **5a·2CH_2Cl_2**

	2a·$CHCl_3$	**3c·CH_2Cl_2**	**3e·toluene**	**5a·2CH_2Cl_2**[a]
O1−Sn1−N1	87.38(12)	165.6(2)	90.7(3)	90.72(8)
O1−Sn1−N2	164.63(12)	89.0(2)	167.8(4)	169.25(8)
O1−Sn1−O2	108.96(11)	105.1(2)	104.3(4)	99.83(11)
N1−Sn1−N2	77.26(13)	77.4(2)	77.2(4)	78.83(12)
O2−Sn1−N1	163.65(11)	88.8(2)	87.9(4)	169.25 (8)
O2−Sn1−N2	86.40(12)	165.7(2)	165.0(4)	90.72(8)
X1−Sn1-X2	178.18(4)	178.87(4)	179.63(6)	177.33(11)
X1−Sn1−O1	89.12(9)	88.99(13)	89.6(2)	92.68(7)
X1−Sn1−O2	88.82(8)	89.47(13)	90.1(2)	85.60(7)
X1−Sn1−N1	91.09(10)	87.2(1)	91.2(2)	90.18(8)
X1−Sn1−N2	91.52(9)	93.5 (1)	88.9(3)	91.88(8)
X2−Sn1−O1	89.73(9)	90.92(13)	90.2(2)	85.60(7)
X2−Sn1−O2	90.21(8)	89.46(13)	90.3(2)	92.68(7)
X2−Sn1−N1	90.27(10)	87.6(1)	88.5(2)	91.88(8)
X2−Sn1−N2	89.96(9)	93.2(1)	91.2(3)	90.18(8)

[a] For **5a**, X1 = O3, X2 = O4.

there are only two sets of the aryl protons for each complex in the range 6.9−7.6 ppm, suggesting that the structures of these complexes have a perpendicular mirror plane that bisects the backbone of the salen ligand. The protons of the ligand backbone for **1a** appear as two sets of doublets, indicating that the Sn(II) center does not lie in the salen N_2O_2 coordination plane, a conclusion which is also supported by X-ray diffraction structural studies of two other members of this class of Sn(II) compounds (Figures 1 and 2). The unsymmetrical monomethyl backbone of compound **1b** results in two distinct resonances for the imine protons in its ^{1}H NMR spectrum. However, the ^{1}H NMR spectrum of compound **1e** exhibits double resonances for each group of chemically similar protons, suggesting a very unsymmetrical structure which is possible if the Sn(II) center lies above the asymmetric N_2O_2 "plane" (Figure 2). This phenomenon was also described by Parkin et al.[10] and Barreau and coworkers[8] for similar asymmetric (salen)Sn(II) complexes.

On the other hand, (salen)SnX_2 compounds **3a**−**i**, **4a**−**e**, **5a**−**e**, and **6a** all have simple ^{1}H NMR spectra presumably due to a symmetrical solution structure where the Sn(IV) atom is coplanar with the salen N_2O_2 coordination framework. This hypothesis is further substantiated by our X-ray diffraction studies of three members of this class of Sn(IV) compounds (Figures 3−6).

^{13}C NMR Spectra. As expected, compounds **1a**−**6a** and **1c**−**5c** give simple spectra consistent with the symmetrical salen backbone. In contrast, compounds **1b**−**5b, 1d**−**5d,** and **1e**−**5e** all have complicated spectra due to the asymmetric salen backbone.

^{119}Sn NMR Spectra. All compounds reported herein have a single ^{119}Sn resonance with chemical shifts that agree well with those observed in prior work for other (salen)Sn(II)[8,11] and (salen)Sn(IV)[8] complexes (Table 5). From a simple electronic argument, Sn(IV), being at a higher oxidation state, should be more Lewis acidic than Sn(II) and, thus, should have ^{119}Sn chemical shifts further downfield.[26] However, the

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Table 5. ^{119}Sn Chemical Shifts of (Salen)Sn Compounds

		[Sn]					
		1	**2**	**3**	**4**	**5**	**6**
	R =	Sn^{II}	$Sn^{IV}Cl_2$	$Sn^{IV}Br_2$	$Sn^{IV}I_2$	$Sn^{IV}(OTf)_2$	$Sn^{IV}Br(OTf)$
A		-516.7	-595.5	-719.1	-805.1	-662.3	-662.6
B		-526.5	–	-714.6	-1015.9	-659.8	–
C		-501.4	–	-720.4	-783.8	-652.9	–
D		-524.5[a]	–	-711.8	-992.1	-663.5	–
E		-521.5	-593.9	-709.7	-992.1	-661.5	–

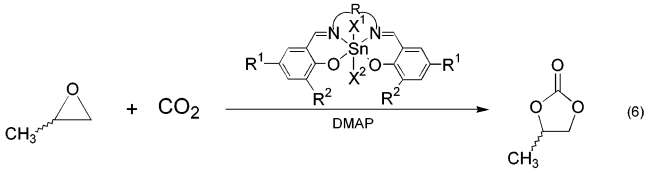
[a] Data cited from literature.[8]

chemical shifts for (salen)SnX_2 complexes are often higher upfield than those for the corresponding (salen)Sn(II) complexes. This observation can be attributed to an increase in the coordination number of the metal[27] in going from (salen)Sn to (salen)SnX_2, which leads to an increase in tin shielding of up to several hundred ppm.[28] The ^{119}Sn chemical shifts for the (salen)SnX_2 family shift progressively higher upfield in the order Cl < OTf < Br < I, corresponding to increasing electron density at the metal center with the softer I^- ligands contributing the most electron density.

Mass Spectrometry. Due to the air-sensitive nature of the (salen)Sn(II) complexes **1a**−**1i**, EIMS and FABMS are better characterization techniques than APCIMS because the corresponding M^+ ion can be observed more frequently. (Salen)SnX_2 complexes could be characterized with FABMS, EIMS, or APCIMS but often lost one anionic ligand to give only the $[M - X]^+$ ion. For (salen)Sn$(OTf)_2$, the standard APCIMS solvent mixture (acetonitrile/formic acid = 9:1) led to rapid anion replacement, and only the $[M - (OTf)_2 + \text{formate}]^+$ ion was observed. The $[M - (OTf)]^+$ ion could only be seen when pure acetonitrile was used. This observation demonstrates the lability of the triflate ligands in (salen)-Sn$(OTf)_2$.

Catalytic Properties of (Salen)Sn Complexes in the Coupling of CO_2 and Propylene Oxide. The use of (salen)-Sn complexes as catalysts is a relatively unexplored area. Belokon et al. have used a variety of salen metal complexes as catalysts in the phase-transfer asymmetric alkylation of the Schiff base derived from benzaldehyde and the isopropyl ester of racemic alanine.[19] Among the various metal-salen compounds used, the catalytic activity of the Sn(II) complex was investigated. Relatively low yields (35%) and ee's (6%) were obtained as the uncharged Sn(II) complex was not prone to coordination by substrates. In another report, methanol was converted to acetic acid or methyl acetate in a one-pot synthesis with $FeCl_3$, $SnCl_2$, and a salen ligand.[20] It is, however, ambiguous whether the corresponding salen(Sn) or salen(Fe) complex was formed in the process and what the actual active catalytic species was. Additionally, the synthesis of siloxypropane from an aryl trialkylsilyl ether and (*R*)-propylene oxide can be catalyzed by a variety of complexes including Sn(II or IV) inorganic salts and salen ligands.[18] The formation of (salen)Sn compounds was not reported, nor was the structure of the active catalyst species.

The catalytic coupling of propylene oxide (PO) and CO_2 to form cyclic carbonate (eq 6) is a reaction of great interest due to its exceptional atom-economy and the value of the cyclic carbonate product.[29] Although Sn(IV) catalysts have been used for organic carbonate activation,[30] decarboxylation,[31] and polymerization,[32] relatively little work has been done to examine the use of tin-based catalysts for cyclic carbonate synthesis. In 1976, Harada[17] employed tin(II) alkoxide catalysts in the catalytic formation of cyclic carbonates. However, the turnover frequency (TOF) was quite low ($\sim$15 h^{-1}).[17] Later on, Baba and co-workers examined reaction 6 with a $Bu_3SnI-Bu_4PI$ catalyst system.[33] These researchers noted that neither Bu_3SnI nor Bu_4PI alone showed any catalytic activity[33] and hinted at the necessity of a Lewis acid/Lewis base complex in the cycloaddition of oxiranes to heterocumulenes.[34,35] Given our prior success in effecting reaction 6 using a (salen)Cr−DMAP catalyst system, we employed our (salen)Sn compounds as the Lewis acid catalyst component along with a Lewis base for the coupling of propylene oxide with CO_2. Our ability to synthesize (salen)Sn complexes of two different oxidation states and with a variety of substituents and anionic ligands (in the case of Sn(IV)) afforded a unique opportunity for investigating catalyst activity as a function of the Lewis acidity at the tin metal center.



(6)

As expected from the Baba Lewis acid/Lewis base dual-site model[34,35] and our own work,[13] (salen)Sn compounds alone did not catalyze reaction 6. However, good catalytic

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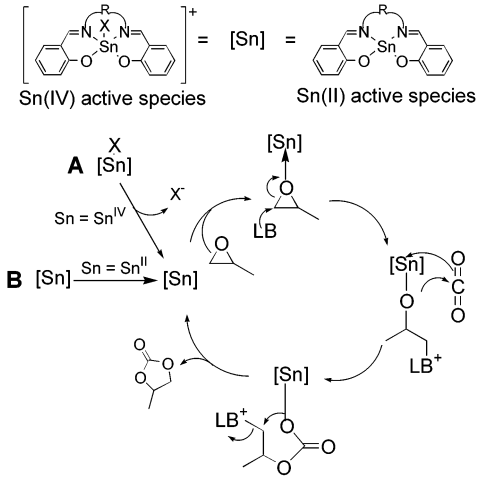
Table 6. Effect of DMAP Loading on TOF Using **3i** as Catalyst[a]

DMAP (equiv)	TON	TOF (h^{-1})
0	0	0
2	129	25
5	2786	531

[a] Reaction conditions: [Cat] = 0.02 mmol; PO = 4000−6500 equiv relative to **3i**; CH_2Cl_2 = 0.5 mL; $P(CO_2)$ = 100 psig; 5 h 15 min; 120 °C.

Scheme 1. Proposed Mechanism for the Cyclic Carbonate Formation Using (Salen)Sn(II or IV) Compounds[a]



[a] (A) Sn(IV) mechanism. (B) Sn(II) mechanism. Substituents on salen ligands omitted for clarity.

activity was observed for several (salen)Sn compounds, at catalyst loadings as low as 0.03 mol % relative to PO, in the presence of DMAP as the Lewis base cocatalyst. DMAP was chosen as the ideal Lewis base over PPh_3, PPh_3O, imidazole, pyridine, and NEt_3 based on our (salen)Cr work where DMAP was shown to be the best Lewis base cocatalyst.[36] For up to 5 equiv, the catalyst activity increased with higher DMAP loading (Table 6).

The work of the Shi[37] and Kim[38] groups has led to the proposal of similar reaction mechanisms for the Lewis acid catalyst and the Lewis base cocatalyst. Their experimental evidence suggests that the epoxide first coordinates to the Lewis acid followed by the ring-opening of the epoxide by the Lewis base cocatalyst and CO_2 insertion. It is most likely that our (salen)Sn/DMAP system behaves in a similar fashion: the Sn(salen) acts as the Lewis acid and DMAP is the Lewis base component (Scheme 1). Mechanistic studies are currently underway to elucidate the reactive intermediates and the catalytic pathway.

Kim and co-workers have shown the effects of varying the nucleophilicity of the pyridinyl base for the cyclic carbonate reaction.[38,39] They report that minor alterations of the pyridine (from unsubstituted to the 2-methyl pyridine) can greatly affect the cyclic carbonate yield. Others have investigated the effects of varying the Lewis acidity of the catalyst. Wang and co-workers found that $ZnCl_2$, a stronger Lewis acid, is a more active catalyst than ZnI_2 in their ZnX_2−Bu_4NI system.[40] The opposite relationship was observed by Baba et al. for the Bu_3SnX−Bu_3PI catalyst (X = Cl, Br, I)[33] and by Kim et al. for ZnX_2Py_2 complexes.[38] In the latter example, the authors suggested that the more electronegative halide ligands may decrease the dissociation rate of the pyridine ligand, thereby hindering the coordination of the epoxide in the first activation step. For our (salen)Sn system, the ability to employ various salen frameworks and the accessibility of two oxidation states at the tin metal center can potentially afford a more detailed understanding of the effect Lewis acidity has on reaction 6.

We first examined a series of (salen)Sn(IV) compounds composed of the same ligand framework and various axial counterions, **2a**−**6a**, as catalysts in the cyclic carbonate reaction (Table 7). For the (salen)SnX_2 catalysts, we observed that the more electronegative the axial halogen counterion, the higher the catalytic activity of the complex. One possible explanation for this invokes the dissociation of only one axial ligand from the parent (salen)SnX_2 compound (Scheme 1A), resulting in a cationic (salen)XSn^+ complex as the active species, which then activates the epoxide. The remaining axial ligand affects the Lewis acidity of the tin metal center and hence the extent that the epoxide is activated. Thus, a more electronegative halide ligand would lead to a more Lewis acidic Sn center and would result in a more reactive tin/epoxide complex. For example, the (salen)SnI_2 compound **4a**, having the most electron-rich axial ligand, is less active (TOF = 62 h^{-1}) than all of the other dihalogenated (salen)-SnX_2 compounds. This possible mechanism is also supported by the results found for the mixed anion complex **6a**, which contains Br and OTf counterions. This compound has the highest activity (TOF = 174 h^{-1}) of all the complexes with the same ligand framework (**2a**−**6a**). According to our hypothesis, the labile OTf ligand of **6a** would quickly dissociate generating the Lewis acidic $[(salen)SnBr]^+$ species. In contrast, the dibrominated compound, **3a**, would have the same active $[(salen)SnBr]^+$ species but a lower activity (TOF = 119 h^{-1}) due to the slower rate of bromine dissociation over triflate. Interestingly, the compound with two triflate counterions was the least active. In the case of (salen)Sn-$(OTf)_2$ one possible reason for its lower activity is that both of the labile OTf ligands disassociate forming a very electron-deficient Sn^{2+} species which would bind strongly to the Lewis base cocatalyst and become unavailable for epoxide activation.

For (salen)Sn(IV) catalysts with the same ligand backbone and axial counterions, we observed higher catalytic activity for catalysts with more electron-withdrawing salen ligand framework. This is also consistent with increased Lewis acidity at the metal center having a greater affect on epoxide activation. Thus, complex **3i**, which was brominated in the 3,3′ and 5,5′ positions of the phenyl groups, was more active than **3f**, which had bromines only in the 5,5′ positions (Table

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Table 7. Catalytic Results of (Salen)Sn Complexes[a]

	R	R^1	R^2	TOF (h^{-1})		R	R^1	R^2	X^1	X^2	TOF (h^{-1})
					2a		^{t}Bu	^{t}Bu	Cl	Cl	150
					3a		^{t}Bu	^{t}Bu	Br	Br	119
1a		^{t}Bu	^{t}Bu	49	**4a**		^{t}Bu	^{t}Bu	I	I	62
					5a		^{t}Bu	^{t}Bu	OTf	OTf	29
					6a		^{t}Bu	^{t}Bu	Br	OTf	174
1d		^{t}Bu	^{t}Bu	71	**3d**		^{t}Bu	^{t}Bu	Br	Br	71
					2e		^{t}Bu	^{t}Bu	Cl	Cl	216
1e		^{t}Bu	^{t}Bu	71	**4e**		^{t}Bu	^{t}Bu	I	I	74
					5e		^{t}Bu	^{t}Bu	OTf	OTf	52
1g		Br	Br	190	**3f**		Br	H	Br	Br	271
1h		H	OMe	114	**3h**		H	OMe	Br	Br	301
1i		Br	Br	187	**3i**		Br	Br	Br	Br	524

[a] Reaction conditions: [Cat] = 0.03 mmol; [Cat]/PO = 1/1700; [Cat]/[DMAP] = 1/5; CH_2Cl_2 = 0.5 mL; 120 °C; $P(CO_2)$ = 100 psig; 4 h 15min.

Table 8. Effect of Temperature on TOF Using **3a** as Catalyst[a]

temp (°C)	TON	TOF (h^{-1})
100	344	81
120	507	119
140	768	181

[a] Reaction conditions: [Cat] = 0.03 mmol; [Cat]/PO = 1/1700; [Cat]/[DMAP] = 1/5; CH_2Cl_2 = 0.5 mL; $P(CO_2)$ = 100 psig; 4 h 15 min.

7). Complex **3f** in turn had higher activity than **3a**, which had *tert* butyl substituents in the 3,3′ and 5,5′ positions. Overall, the most efficient catalyst was (3,3′,5,5′-Br_4-salen)-$SnBr_2$, **3i**, with an excellent turnover frequency of 524 h^{-1}.

The same relationship between the electron-withdrawing nature of the salen ligand and catalytic activity was observed for (salen)Sn(II) catalysts. The most active (salen)Sn(II) catalyst of the series, **1g**, had electron-withdrawing bromine moieties in both the 3,3′ and 5,5′ positions of the salen phenyl rings (TOF = 190 h^{-1}). The more electron-rich Sn(II) compounds, however, were less active than their corresponding Sn(IV) analogues (Table 7).

We propose that both the Sn(II) and Sn(IV) catalysts have similar reaction mechanisms (Scheme 1). Although the Sn(II) compounds do not have to undergo a ligand dissocation step prior to epoxide binding (Scheme 1B), they are less Lewis acidic and hence do not activate the epoxide as strongly as the corresponding Sn(IV) species, resulting in lower activities.

Our system requires moderately low CO_2 pressures (100 psig), low catalyst loading (0.032 mol % relative to PO), and short reaction times (4 h 15 min). The (salen)Sn complexes, however, require higher temperatures than our (salen)Cr system.[13] As would be expected, higher reaction temperatures led to better catalyst activity (Table 8).

Overall, the TOFs reported herein for our Sn(II) and Sn(IV) salen compounds are competitive with many catalytic systems in the literature.[29] For a Co binaphthyldiamine salen system, the best catalytic results (TOF = 57 h^{-1}) were obtained with NEt_3 at 100 °C under higher CO_2 pressures (500 psi) and longer reaction times (16 h).[37] Kim and coworkers' most active $ZnBr_2L_2$ catalyst $ZnBr_2(DMAP)_2$ operates at a slightly milder temperature (T = 100 °C) but requires higher pressure (continuous feeding of CO_2 at 493 psi) and catalyst loading (1 mol % relative to PO) to give a TOF of 516 h^{-1}.[38] Very recently, they have reported the use of imidazolium zinc tetrahalides which are more active (TOF = 1846 h^{-1}) albeit at much higher pressure (508 psi) than ours.[41] Although tin salens are not the most active cyclic carbonate catalysts known for cyclic carbonate formation, their activity is quite respectable, and they have great promise as a class of tunable Lewis acids for use in cyclic carbonate formation or other types of catalysis.

Conclusions. The direct oxidation reaction of (salen)Sn(II) compounds with halogens is a versatile method for the synthesis of (salen)Sn(IV) compounds in high yields. The (salen)SnX_2 compounds can be interconverted either by direct exchange with simple alkali halide salts or via (salen)Sn(OTf)$_2$ compounds as intermediates. This strategy is significant because it offers an efficient route to otherwise difficult-to-obtain six-coordinate (salen)Sn(IV) dihalide or mixed halide complexes. Further, these facile syntheses are applicable to a wide range of ligand environments allowing us ready access to (salen)Sn complexes with varying electronic and steric properties.

The availability of a wide range of tin salen compounds allowed us a unique opportunity to test the catalytic activity of (salen)Sn complexes as a function of ligand environment, metal oxidation state, and Lewis acidity. We found that the more Lewis acidic (salen)Sn(IV) compounds displayed higher activity than their corresponding (salen)Sn(II) counterparts in the formation of propylene carbonate. In addition, we found that increasing the electron-withdrawing ability of the salen framework and the axial ligands also increased the catalyst performance. To the best of our knowledge, this work

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is one of the first comprehensive examinations of salen(Sn) compounds as a promising class of tunable Lewis acid catalysts.

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Supporting Information Available: Relevant NMR spectra for representative complexes. Combined X-ray crystallographic file in CIF format for the structure determination of **1c**, **1e**, **2a·CHCl$_3$**, **3c·CH$_2$Cl$_2$**, **3e·C$_6$H$_6$CH$_3$**, and **5a·2CH$_2$Cl$_2$**. This material is available free of charge via the Internet at http://pubs.acs.org.

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