A General High-Yield Route to Bis(salicylaldimine) Zinc(II) Complexes: Application to the Synthesis of Pyridine-Modified Salen-Type Zinc(II) Complexes

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A general, direct, and high-yield synthesis of bis(salicylaldimine) zinc complexes from the ligands and Et_2Zn is reported. This synthetic method is particularly valuable, not only because it allows the efficient preparation of salen-type complexes of zinc but also because it can be used to prepare bifunctional pyridine-modified zinc(II) bis(salicylidene) complexes, which are potentially useful compounds for applications in asymmetric catalysis and materials chemistry. The synthesis and complete structural characterization of a new series of pyridine-modified zinc(II) bis(salicylidene) ligands is discussed.

Introduction

Salen-type ligands derived from salicylaldehydes and diamines have emerged as one of the most important ligand systems in asymmetric catalysis. Over the past decade, the number of applications for metal salen[1] complexes has grown rapidly to encompass an extremely broad range of chemical transformations, including the asymmetric ring-opening of epoxides, aziridination, cyclopropanation, and the epoxidation of olefins.[2] This versatility in chemical reactivity and selectivity is a result of the ability of salen-type ligands to complex a variety of metals with a large number of oxidation states in an easily tunable chiral environment. As such, there has been considerable interest in the synthesis of new salen-type complexes of transition[3−5] and main group[6,7] metals to further develop applications in both catalysis and materials chemistry.

Recently there has been a surge of interest in the use of chiral zinc salen complexes in asymmetric Lewis acid-catalyzed reactions.[8−10] Furthermore, our own search for a bifunctional salen-type template to be used in the synthesis of cyclic supramolecular structures of the Fujita[11,12] and Stang[13] varieties led us to investigate salen complexes of zinc-containing pendant Lewis base groups. Our primary target was zinc(II) salen complex **1**, featuring a pair of pyridyl groups oriented at 180° with respect to each other. By reacting the bifunctional zinc salen "edges" with transition-metal "corners" we envisioned the coordinative self-assembly of such a complex into larger assemblies, e.g., molecular squares, triangles, rectangles, and so on.

Though there are several reports on the preparation of zinc(II) salen complexes from either $Zn(OAc)_2$[14,15] or $ZnCl_2/Et_3N$,[7] we had difficulties isolating pure metalated product following these routes. In our hands, using the common salen-type ligand **2a**, the $ZnCl_2/Et_3N$ method gave a product mixture containing equal amounts of Schiff base ligand and zinc salen complex that could not be readily separated. This observation is consistent with literature reports in which a related zinc Schiff base complex was eventually isolated by a recrystallization procedure that involved cooling the mixture to −30 °C for *2 weeks*.[7]

As a potential solution to the aforementioned synthetic problem, we considered the direct reaction of the salen ligand and Et_2Zn as an alternative method for the preparation of zinc(II) salen-type complexes. Given the highly acidic nature of the ligand's phenolic protons and the highly reactive nature of Et_2Zn, we predicted that the only byproduct for this reaction would be ethane, which could be easily removed to afford pure zinc salen complex in high yield. To our surprise, there have been no direct reports of such a strategy to prepare isolated zinc salen complexes.[16] Herein, we report a general procedure for the direct synthesis of zinc(II) salen-type complexes using this method. We also disclose the successful application of this methodology to the synthesis of the bifunctional complex **1**.

Experimental Section

General Information. Melting points were uncorrected and were determined on a Fisher-Johns melting point apparatus. ^1H and ^{13}C NMR

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10.1021/ic010090o CCC: $20.00
Published on Web 05/24/2001

spectra were recorded on either a Varian Inova 500 (499.773 MHz for ^{1}H, 125.669 MHz for ^{13}C) or a Mercury 400 (400.178 MHz for ^{1}H) spectrometer. ^{1}H NMR data are reported as follows: chemical shift (multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), 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. IR data were collected on a Nicolet 5PC FT-IR spectrometer with PC-IR software. Mass spectra were obtained from the Mass Spectrometry Laboratory, University of Illinois (Urbana, IL). Elemental analyses were provided by Atlantic Microlab, Inc. (Norcross, GA). All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques unless otherwise noted. Flash column chromatography was carried out with 230−400 mesh silica gel, purchased from Merck.

Materials. Schiff base ligands **2a**,[17] **2b**,[18] **2d**,[19] 1,1,2,2-tetramethyl-1,2-ethylenediamine,[20] and aldehyde **6**[21] were synthesized according to published procedures. (1*R*,2*R*)-(−)-1,2-diaminocyclohexane was obtained from Aldrich (at >98% ee). Dichloromethane was distilled over calcium hydride. Tetrahydrofuran (THF) and diethyl ether were distilled over sodium/benzophenone. All solvents were distilled under nitrogen and saturated with nitrogen prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used without further purification. All other reagents were purchased from the Aldrich Chemical Co. and used without further purification, unless otherwise noted.

General Procedure for the Synthesis of 2c, 2e, and 5a−c. A mixture of aldehyde (2.5 g, 9.8 mmol), diamine (0.5 equiv), and EtOH (25 mL) was heated to reflux in a 100 mL round bottom flask equipped with a water-cooled West condenser for 1 h before being allowed to cool to room temperature. If the product precipitated out from the reaction mixture, it was isolated by filtration. If the product was soluble in ethanol, the solvent was removed in vacuo to isolate the product.

***N,N′*-Bis(3,5-di-*tert*-butylsalicylidene)-1,1,2,2-tetramethyl-1,2-diaminoethane (2c):** a yellow solid (mp 190.5−192.0 °C). Yield = 86%. IR (KBr): 2987, 2958, 2904, 2866, 1628, 1592, 1468, 1438, 1389, 1374, 1359, 1272, 1250, 1170, 1128, 976 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 14.41 (s, 2H), 8.43 (s, 2H), 7.37 (d, 2H, J = 2.0 Hz), 7.16 (d, 2H, J = 2.0 Hz), 1.44 (s, 18H), 1.42 (m, 12H), 1.31 (s, 18H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 163.1, 158.7, 140.2, 136.8, 127.1, 126.7, 118.4, 65.5, 35.5, 34.6, 31.8, 29.8, 23.6. FABMS (NBA): *m*/*z* 548 (M^+, 74), 533 (51), 274 (100), 258 (15), 234 (18), 218 (15). Anal. Calcd for $C_{36}H_{56}N_2O_2$: C, 78.78; H, 10.28; N, 5.10. Found: C, 78.70; H, 10.32; N, 5.12.

***N,N′*-Bis(3,5-di-*tert*-butylsalicylidene)-1,3-diaminobenzene (2e):** a yellow solid (mp 209−210 °C). Yield = 89%. IR (KBr): 2954, 2905, 2867, 1619, 1571, 1476, 1467, 1438, 1360, 1272, 1250, 1200, 1174, 965 cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 13.66 (s, 2H), 8.77 (s, 2H), 7.51 (m, 2H), 7.32−7.26 (m, 2H), 7.31 (m, 2H), 1.49 (s, 18H), 1.36 (s, 18H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 164.8, 158.6, 150.1, 141.1, 137.2, 130.7, 128.7, 127.5, 119.8, 118.7, 114.3, 35.6, 34.7, 31.8, 29.8. FABMS (NBA): *m*/*z* 541 (MH^+, 100), 525 (72), 485 (18), 154 (18), 136 (15). HRFABMS (NBA): exact mass calcd for $[C_{36}H_{48}N_2O_2]^+$ 540.3716, found 540.3717. Anal. Calcd for $C_{36}H_{48}N_2O_2$: C, 79.96; H, 8.95; N, 5.18. Found: C, 80.04; H, 9.03; N, 5.24.

***(R,R)*-(−)-*N,N′*-Bis(3-*tert*-butyl-5-(4-pyridyl)salicylidene)-1,2-diaminocyclohexane (5a):** recrystallized from 5:1 hexane/CH_2Cl_2 to give a white solid. An analytical sample was prepared by flash column chromatography [CH_2Cl_2/MeOH 10:1 (6 × 10 cm silica gel)] to give a white solid (mp 212−213 °C). Yield = 73%. IR (KBr): 3400, 3066, 3022, 2936, 2860, 1628, 1592, 1465, 1441, 1273, 1170, 1075, 819, 623 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.57 (d, 4H, J = 5.6 Hz), 8.35 (s, 2H), 7.51 (d, 2H, J = 1.8 Hz), 7.35 (d, 4H, J = 5.6 Hz), 7.27 (d, 2H, J = 1.8 Hz), 3.45 (m, 2H), 2.09−1.48 (m, 8H), 1.44 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.6, 161.8, 150.0, 148.3, 138.5, 128.4, 128.1, 127.4, 121.0, 118.9, 72.5, 35.2, 33.0, 29.4, 24.4. EIMS: *m*/*z* 588 (M^+, 100), 446 (24), 334 (86), 279 (13), 239 (23), 211 (14), 83 (22). HREIMS: exact mass calcd for $[C_{38}H_{44}N_4O_2]^+$ 588.3464, found 588.3460. Anal. Calcd for $C_{38}H_{44}N_4O_2$: C, 77.52; H, 7.53; N, 9.52. Found: C, 77.28; H, 7.54; N, 9.38.

***N,N′*-Bis(3-*tert*-butyl-5-(4-pyridyl)salicylidene)-1,2-diaminobenzene (5b):** an orange solid (mp 268−269 °C). Yield = 95%. IR (KBr): 3467, 2946, 1611, 1592, 1571, 1438, 1254, 1168, 821, 749, 625 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.79 (s, 2H), 8.64 (d, 4H, J = 4.7 Hz), 7.69 (s, 2H), 7.58 (s, 2H), 7.50 (d, 4H, J = 4.7 Hz), 7.40 (m, 2H), 7.33 (m, 2H), 1.49 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.2, 162.0, 150.3, 148.1, 124.3, 139.2, 129.3, 129.3, 128.2, 121.2, 120.0, 119.6, 35.4, 29.5. EIMS: *m*/*z* 582 (M^+, 16), 446 (100), 418 (17), 387 (15), 331 (37). HREIMS: exact mass calcd for $[C_{38}H_{38}N_4O_2]^+$ 582.2995, found 582.2986. Anal. Calcd for $C_{38}H_{38}N_4O_2$: C, 78.32; H, 6.57; N, 9.60. Found: C, 78.38; H, 6.48; N, 9.59.

***N,N′*-Bis(3-*tert*-butyl-5-(4-pyridyl)salicylidene)-1,1,2,2-tetramethyl-1,2-diaminoethane (5c):** a yellow solid (mp 264−265 °C). Yield = 94%. IR (KBr): 3427, 3020, 2988, 2947, 2910, 2866, 1627, 1593, 1466, 1442, 1274, 1256, 819, 622 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 14.83 (s, 2H), 8.60 (d, 4H, J = 5.2 Hz), 8.46 (s, 2H), 7.58 (s, 2H), 7.43 (d, 4H, J = 5.2 Hz), 7.42 (s, 2H), 1.48 (s, 12H), 1.46 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.5, 162.4, 150.3, 148.2, 138.7, 128.7, 128.0, 122.2, 121.0, 119.0, 65.5, 35.2, 29.4, 23.4. FABMS (NBA) *m*/*z* 591 (MH^+, 100), 477 (12), 296 (51), 255 (11), 154 (33). HRFABMS (NBA): exact mass calcd for $[C_{38}H_{47}N_4O_2]^+$ 591.3699, found 591.3700. Anal. Calcd for $C_{38}H_{46}N_4O_2$: C, 77.25; H, 7.85; N, 9.48 Found: C, 77.00; H, 7.87; N, 9.50.

General Procedure for the Synthesis of 1a−c and 3a−e. To a stirred solution of Schiff base ligand (0.91 g, 1.5 mmol) in THF (100 mL) at room temperature was added Et_2Zn (159 μL, 1.5 mmol) in a glovebox under N_2 atmosphere. Compounds **3a−e** were prepared following the same procedure but with hexane as the solvent. The mixture was stirred at room temperature for 12 h, after which the precipitate was filtered and washed with water (200 mL). The solid was dried under reduced pressure.

***(R,R)*-(−)-1,2-Cyclohexanediamino-*N,N′*-bis(3-*tert*-butyl-5-(4-pyridyl)salicylidene) zinc(II) (1a):** a yellow solid (mp 315−316 °C). Yield = 92%. IR (KBr): 3427, 2941, 2860, 1629, 1590, 1548, 1527, 1401, 1383, 1351, 1335, 1297, 1288, 1221, 1159, 815, 794, 773 cm^{-1}. ^{1}H NMR (500 MHz, pyridine-d_5): δ 8.83 (d, 4H, J = 5.5 Hz), 8.62 (s, 2H), 8.01 (d, 2H, J = 2.0 Hz), 7.88 (d, 2H, J = 2.0 Hz), 7.76 (d, 4H, J = 5.5 Hz), 3.13 (m, 2H), 2.37−1.25 (m, 8H), 1.83 (s, 18H). ^{13}C NMR (125 MHz, pyridine-d_5): δ 173.6, 166.5, 151.2, 149.3,-143.9, 133.6, 128.8, 121.2, 120.8, 120.7, 66.0, 36.5, 30.3, 28.6, 24.9. FABMS (NBA): *m*/*z* 651 (MH^+, 50), 589 (50), 307 (20), 289 (15), 154 (100), 136 (82). HRFABMS (NBA): exact mass calcd for $[C_{38}H_{43}N_4O_2Zn]^+$ 651.2677, found 651.2676. Anal. Calcd for $C_{38}H_{42}N_4O_2Zn\cdot{}^1/_2H_2O$: C, 69.03; H, 6.56; N, 8.47. Found: C, 69.12; H, 6.47; N, 8.36.

1,2-Benzenediamino-*N,N′*-bis(3-*tert*-butyl-5-(4-pyridyl)salicylidene) zinc(II) (1b): a yellow solid (mp 327.5−328.5 °C). Yield = 86%. IR (KBr): 3429, 1595, 1577, 1544, 1526, 1383, 1257, 1158, 819, 795, 772, 710 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 2H), 8.31 (d, 4H, J = 5.5 Hz), 7.62 (m, 2H), 7.58 (s, 2H), 7.45 (s, 2H), 7.30 (d, 4H, J = 5.5 Hz), 7.33 (m, 2H), 1.52 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.3, 162.3, 150.0, 149.0, 144.2, 140.0, 133.1, 129.2, 127.7, 120.7, 120.5, 119.7, 115.9, 35.9, 29.6. FABMS (NBA): *m*/*z* 645 (MH^+, 14), 583 (98), 346 (22), 309 (11), 240 (13), 195 (16), 155 (42), 135 (50), 119 (100). HRFABMS (NBA): exact mass calcd for $[C_{38}H_{37}N_4O_2Zn]^+$ 645.2208, found 645.2209. Anal. Calcd for $C_{38}H_{36}N_4O_2Zn\cdot{}^1/_2H_2O$: C, 69.67; H, 5.69; N, 8.55. Found: C, 69.60; H, 5.61; N, 8.40.

1,1,2,2-Tetramethyl-1,2-ethanediamino-*N,N′*-bis(3-*tert*-butyl-5-(4-pyridyl)salicylidene) zinc(II) (1c): a yellow solid (mp 324−325 °C). Yield = 89%. IR (KBr): 3429, 1595, 1577, 1544, 1526, 1383, 1257, 1158, 819, 795, 772, 710 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50 (s, 2H), 8.31 (d, 4H, J = 4.5 Hz), 7.61 (s, 2H), 7.49 (d, 4H, J = 4.5 Hz), 7.46 (s, 2H), 1.43 (s, 18H), 1.28 (s, 12H). ^{13}C NMR (125 MHz,

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$CDCl_3$): δ 173.4, 165.4, 150.1, 149.1, 143.8, 132.7, 127.9, 120.1, 119.8, 65.2, 35.8, 29.5, 23.9. FABMS (NBA): *m*/*z* 653 (MH^+, 100), 294 (15), 278 (13), 262 (15), 237 (14), 195 (16), 155 (42), 135 (50), 119 (100). HRFABMS (NBA): exact mass calcd for $[C_{38}H_{45}N_4O_2Zn]^+$ 653.2834, found 653.2834.

(*R*,*R*)-(−)-1,2-Cyclohexanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) zinc(II) (3a). This compound was isolated from the reaction mixture by the removal of the solvent under reduced pressure and subsequent recrystallization with CH_2Cl_2 to give a yellow solid. Yield = 40%. IR (KBr): 2952, 2904, 2864, 2360, 2336, 1614, 1530, 1460, 1434, 1411, 1327, 1271, 1255, 1165, 1074, 836, 788, 537 cm^{-1}. ^1H NMR (500 MHz, pyridine-d_5): δ 8.50 (s, 2H), 7.72 (s, 2H), 7.36 (s, 2H), 3.04 (s, 2H), 2.28−1.17 (m, 8H), 1.83 (s, 9H), 1.43 (s, 9H). ^{13}C NMR (125 MHz, pyridine-d_5): δ 171.0, 166.8, 142.4, 134.1, 130.5, 128.6, 119.6, 66.2, 36.8, 34.7, 32.5, 30.8, 28.9, 25.3. EIMS: *m*/*z* 608 (M^+, 10), 600 (20), 205 (100), 177 (18), 145 (21), 72 (45). HREIMS: exact mass calcd for $[C_{36}H_{52}N_2O_2Zn]^+$ 608.3320, found 608.3313. Anal. Calcd for $C_{36}H_{52}N_2O_2Zn$: C, 70.86; H, 8.59; N, 4.59. Found: C, 71.16; H, 8.68; N, 4.57.

***rac*-1,2-Cyclohexanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) zinc(II) (*rac*-3a)**. This compound was isolated from the reaction mixture by the removal of the solvent under reduced pressure and subsequent recrystallization with CH_2Cl_2 to give a yellow solid. Yield = 71%.

1,2-Ethanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) zinc(II) (3b). This compound was isolated from the reaction mixture by the removal of the solvent under reduced pressure and subsequent recrystallization with CH_2Cl_2 to give a yellow solid. Yield = 72%. IR (KBr): 2954, 2904, 2866, 2360, 2335, 1608, 1547, 1528, 1459, 1430, 1411, 1384, 1349, 1323, 1253, 1153, 985, 834, 788, 744, 539 cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.91 (s, 2H), 7.41 (d, 2H, J = 2.0 Hz), 6.60 (d, 2H, J = 2.0 Hz), 4.06 (d, 2H, J = 12.8 Hz), 3.75 (d, 2H, J = 12.8 Hz), 1.40 (s, 18H), 1.27 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.2, 168.3, 141.0, 135.4, 130.3, 129.8, 117.5, 57.6, 35.6, 34.1, 31.5, 29.5, 18.9. EIMS: *m*/*z* 554 (M^+, 82), 539 (100), 492 (85), 446 (25), 259 (26), 216 (16). HREIMS: exact mass calcd for $[C_{32}H_{46}N_2O_2Zn]^+$ 554.2851, found 554.2852. Anal. Calcd for $C_{32}H_{46}N_2O_2Zn$: C, 69.11; H, 8.34; N, 5.04. Found: C, 69.02; H, 8.38; N, 5.00.

1,1,2,2-Tetramethyl-1,2-ethanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) zinc(II) (3c): a yellow solid. Yield = 64%. IR (KBr): 2949, 2902, 2864, 2360, 2336, 1627, 1547, 1532, 1464, 1427, 1393, 1381, 1360, 1309, 1256, 1155, 979, 876, 828, 786, 743, 530 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 2H), 7.45 (d, 2H, J = 2.0 Hz), 7.03 (d, 2H, J = 2.0 Hz), 1.48 (s, 18H), 1.33 (m, 12H), 1.32 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.3, 165.8, 142.0, 135.5, 128.9, 128.8, 117.6, 65.1, 36.1, 34.3, 31.3, 31.2, 29.9. EIMS: *m*/*z* 610 (M^+, 100), 595 (35), 554 (15), 538 (18). HREIMS: exact mass calcd for $[C_{36}H_{54}N_2O_2Zn]^+$ 610.3476, found 610.3479. Anal. Calcd for $C_{36}H_{54}N_2O_2Zn\cdot{}^1/_4H_2O$: C, 70.04; H, 8.84; N, 4.54. Found: C, 70.07; H, 8.92; N, 4.69.

1-Methyl-1,2-ethanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) zinc(3d): a yellow solid. Yield = 53%. IR (KBr): 2957, 2904, 2868, 2360, 2336, 1600, 1531, 1457, 1428, 1413, 1360, 1320, 1272, 1256, 1166, 1099, 835, 788, 744, 541 cm^{-1}. ^1H NMR (500 MHz, pyridine-d_5): δ 8.50 (s, 1H), 8.38 (s, 1H), 7.70 (s, 2H), 7.22 (s, 2H), 3.70(m, 2H), 3.20 (m, 1H), 1.80 (s, 18H), 1.41 (s, 18H), 1.44 (d, 3H, J = 6.0 Hz). ^{13}C NMR (125 MHz, pyridine-d_5): δ 171.0, 170.9, 170.3, 168.9, 142.3, 142.2, 134.0, 133.9, 129.9, 129.6, 128.6, 128.5, 119.4, 119.3, 62.9, 60.3, 36.6, 34.5, 32.3, 30.5, 20.8. EIMS: *m*/*z* 568 (M^+, 100), 553 (95), 506 (55), 275 (31), 216 (18), 160 (15). HREIMS: exact mass calcd for $[C_{33}H_{48}N_4O_2Zn]^+$, 568.3007, found 568.3002. Anal. Calcd for $C_{33}H_{48}N_2O_2Zn\cdot 1.5H_2O$: 66.37; H, 8.61; N, 4.69. Found: C, 66.75; H, 8.43; N, 4.65.

1,3-Benzenediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) zinc-(II) (3e). The isolated crude product was washed with cold CH_2Cl_2 to afford a yellow solid. Yield = 84%. IR (KBr): 2952, 2904, 2864, 2360, 2336, 1614, 1530, 1460, 1434, 1411, 1327, 1271, 1255, 1165, 1074, 836, 788, 537 cm^{-1}. ^1H NMR (400 MHz, THF-d_8): δ 8.41 (s, 2H), 7.51 (d, 2H, J = 2.0 Hz), 7.16 (m, 1H), 7.07 (d, 2H, J = 2.0 Hz), 6.85 (m, 2H), 5.94, (s, 1H), 1.48 (s, 18H), 1.31 (s, 18H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 170.0, 169.9, 150.9, 142.2, 136.4, 131.5, 130.3, 130.0, 120.6, 118.1, 114.5, 35.7, 34.0, 31.3, 29.3. Anal. Calcd for $C_{33}H_{50}N_2O_2Zn\cdot CH_2Cl_2$: C, 64.91; H, 7.17; N, 3.98. Found: C, 64.67; H, 7.05; N, 4.05.

X-ray Structure Determination for *rac*-3a·pyridine. Single crystals of *rac*-**3a**·pyridine were obtained by slow evaporation from pyridine. X-ray diffraction analysis was carried out on a Bruker SMART-1000 CCD area detector with graphite-monochromated Mo Kα radiation. The data were collected at a temperature of −120 °C to a maximum 2θ value of 56.6°. Data were collected in 0.30° oscillations with 15.0 s exposures. The crystal-to-detector distance was 50.00 mm. The detector swing angle was 28.00°. The final unit cell was obtained by the least-squares refinement of 7047 reflections. The structure was solved by direct methods (SHELXS97) and expanded using Fourier techniques (DIRDIF94). All non-hydrogen atoms were refined anisotropically. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. The ORTEP drawing of the molecule was realized with thermal ellipsoids at the 50% probability level for non-hydrogen atoms.

X-ray Structure Determination for 1b·piperidine. Single crystals of **1b**·piperidine were obtained in piperidine/hexane (8:1). X-ray diffraction analysis was carried out on a Bruker SMART-1000 CCD area detector with graphite-monochromated Mo Kα radiation. The data were collected at a temperature of −120 °C to a maximum 2θ value of 56.5°. Data were collected 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 final unit cell was obtained by the least-squares refinement of 4911 reflections. The structure was solved by direct methods (SHELXS97) and expanded using Fourier techniques (DIRDIF94). All non-hydrogen atoms were refined anisotropically. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. The ORTEP drawing of the molecule was realized with thermal ellipsoids at the 50% probability level for non-hydrogen atoms.

Further details on the crystal structure investigations 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.

Results and Discussion

We report a general, direct, and high-yield synthesis of zinc salen complexes from salen-type ligands and Et_2Zn. The zinc metalation procedure was first tested on a series of common, easily obtainable salicylidene ligands (**2a**−**e**) prepared from a variety of diamine backbones. The synthesis of ligands **2a**, **2b**, and **2d** are reported in the literature. Two new ligands, **2c** and **2e**, were synthesized by combining aldehyde **4** (2 equiv) with the required diamine (1 equiv) in refluxing ethanol (Scheme 1).

The zinc salen-type complexes **3a**−**e** were then obtained by addition of Et_2Zn to the free diimine ligands **2a**−**e** in hexane. After stirring for 12 h at room temperature, the complexes were isolated by a simple filtration procedure in moderate to good yield (40−84%).[22] Carrying out reactions at −78 °C for 4 h and then gradually warming to room temperature over 12 h did not significantly affect yields.

The structure of *rac*-**3a**·pyridine was confirmed by a single-crystal X-ray diffraction study. An ORTEP representation is shown in Figure 1. Relevant X-ray diffraction data and selected bond lengths and angles are listed in Tables 1 and 2, respectively. The Zn(II) center lies 0.43 Å above the coordination plane in a square pyramidal geometry with the pyridine ligand occupying the axial position. The Zn−N(py) distance (2.108-

(22) Compounds **3a**,**b** were soluble in hexane and were isolated by the removal of solvent under reduced pressure and subsequent recrystallization.

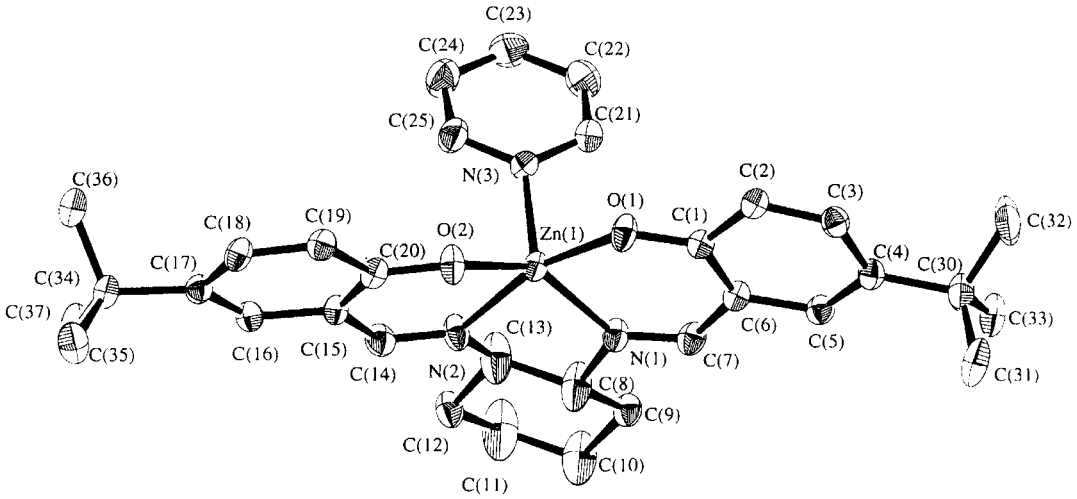
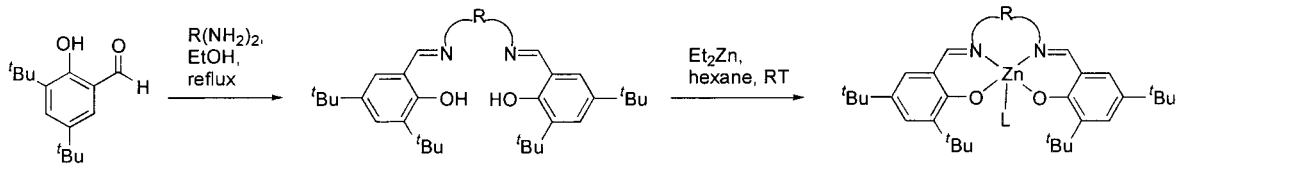


Figure 1. An ORTEP diagram of *rac*-**3a**·pyridine showing the atom-labeling scheme. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms and 3,3′-^{t}Bu groups are omitted for clarity.

Scheme 1



2a: R = (*R*,*R*)-(-)-1,2-cyclohexanediyl
2b: R = 1,2-ethanediyl
2c: R = 1,1,2,2-tetramethyl-1,2-ethanediyl
2d: R = 1-methyl-1,2-ethanediyl
2e: R = 1,3-benzenediyl

3a: R = (*R*,*R*)-(-)-1,2-cyclohexanediyl
3b: R = 1,2-ethanediyl
3c: R = 1,1,2,2-tetramethyl-1,2-ethanediyl
3d: R = 1-methyl-1,2-ethanediyl
3e: R = 1,3-benzenediyl
Depending on the work up conditions, L may be H_2O.

Table 1. Crystal Data and Structure Refinement Parameters for *rac*-1,2-Cyclohexanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) Zinc(II)·pyridine (*rac*-**3a**·pyridine) and 1,2-Benzenediamino-*N*,*N*′-bis(3-*tert*-butyl-5-(4-pyridyl)salicylidene) Zinc(II)·piperidine (**1b**·piperidine)

	1b·piperidine	*rac*-**3a**·pyridine
empirical formula	$C_{48}H_{56}N_6O_2Zn$	$C_{48.5}H_{64.5}N_{4.5}O_2Zn$
fw	814.39	807.95
temp (K)	153(2)	153(2)
wavelength (Å)	0.71069	0.71069
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a (Å)	10.588(2)	14.3373
b (Å)	13.021(3)	16.1799
c (Å)	16.951(3)	19.3730
α (deg)	85.157(3)	
β (deg)	74.477(3)	101.1090
γ (deg)	79.690(3)	
V (Å^3)	2213.7(7)	4409.86(0)
Z	2	4
ρ (calcd) (g/cm^3)	1.222	1.217
μ (mm^{-1})	0.599	0.600
GOF on F^2	1.65	3.30
R1[a]	0.064	0.060
wR2[b]	0.120	0.122

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum(w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

(3) Å) is longer than the Zn−N(ligand) distance (2.087(3) Å). This is similar to what was observed for a (salophen)Zn−pyridine (salophen = *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminobenzene) complex in which the Zn−N(py) distance was 2.103(2) Å, the Zn−N(ligand) distance was 2.099(1) Å, and the Zn atom was displaced by 0.40 Å from the coordination plane.[7]

Table 2. Selected Bond Distances and Angles for *rac*-1,2-Cyclohexanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene) Zinc(II)·pyridine (*rac*-**3a**·pyridine)

Bond Distances (Å)			
Zn(1)−O(1)	1.963(3)	Zn(1)−O(2)	1.953(3)
Zn(1)−N(1)	2.087(3)	Zn(1)−N(2)	2.089(3)
Zn(1)−N(3)	2.108(3)		
Bond Angles (deg)			
N(1)−Zn(1)−N(2)	78.95(12)	N(2)−Zn(1)−O(2)	87.93(12)
N(1)−Zn(1)−O(1)	89.58(12)	N(2)−Zn(1)−N(3)	92.05(13)
N(1)−Zn(1)−O(2)	147.14(13)	O(2)−Zn(1)−O(1)	96.39(11)
N(1)−Zn(1)−N(3)	101.11(13)	O(2)−Zn(1)−N(3)	109.42(12)
N(2)−Zn(1)−O(1)	164.46 (13)	O(1)−Zn(1)−N(3)	100.51(13)

Having demonstrated that the zinc metalation procedure worked well with ordinary salen-type ligands, we were interested in applying this technology to a new series of bifunctional pyridine-modified salen ligands **5a**−**c**. The preparation of pyridyl-containing salen-type ligands required the synthesis of a highly functionalized salicylaldehyde **6**.[21] Aldehyde **6** (2 equiv) was combined with a series of diamines (1 equiv) in refluxing ethanol (Scheme 2) to produce pyridine-modified ligands **5a**−**c** in good yield (73−89%).

Since these salen ligands contain Lewis basic functionalities, we were concerned that self-coordination-induced aggregation[23] might lead to problems with the solubility during the synthesis of the zinc complexes; however, none of these problems was observed. Bifunctional zinc(II) complexes **1a**−**c** were obtained in high yield (86−92%) through a variation of the above procedure where the free diimine ligand was combined with Et_2Zn in THF at room temperature. THF was necessary as a

(23) Fleischer, E. B.; Shachter, A. M. *Inorg. Chem.* **1991**, *30*, 3763−3769.

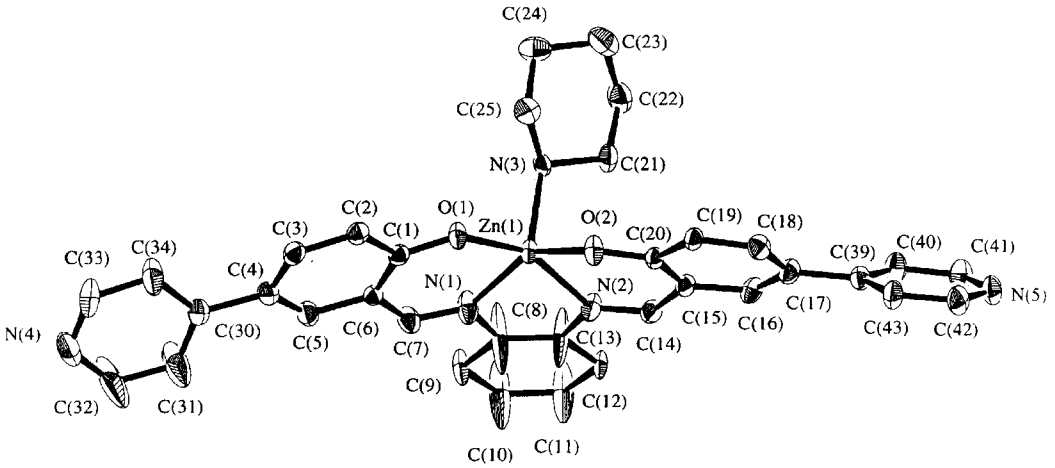
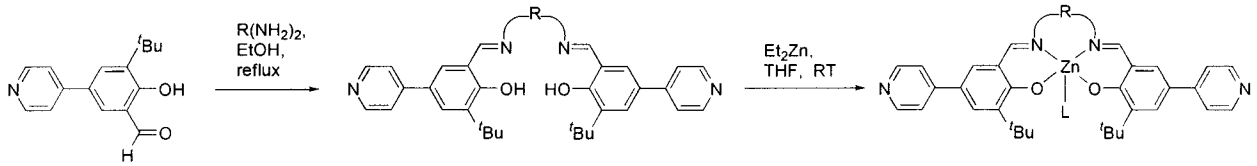


Figure 2. An ORTEP diagram of **1b**·piperidine showing the atom-labeling scheme. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms and ^{t}Bu groups are omitted for clarity.

Scheme 2



6

5a: R = (*R*,*R*)-(-)-1,2-cyclohexanediyl
5b: R = 1,2-benzenediyl
5c: R = 1,1,2,2-tetramethyl-1,2-ethanediyl

1a: R = (*R*,*R*)-(-)-1,2-cyclohexanediyl
1b: R = 1,2-benzenediyl
1c: R = 1,1,2,2-tetramethyl-1,2-ethanediyl
Depending on the work up conditions, L may be either THF or H_2O.

Table 3. Selected Bond Distances and Angles for 1,2-Benzenediamino-*N*,*N*′-bis(3-*tert*-butyl-5-(4-pyridyl)salicylidene) Zinc(II)·piperidine (**1b**·piperidine)

Bond Distances (Å)			
Zn(1)−O(1)	1.986(4)	Zn(1)−O(2)	1.982(4)
Zn(1)−N(1)	2.089(5)	Zn(1)−N(2)	2.094(5)
Zn(1)−N(3)	2.119(5)		
Bond Angles (deg)			
N(1)−Zn(1)−N(2)	77.2(2)	N(2)−Zn(1)−O(2)	87.8(2)
N(1)−Zn(1)−O(1)	87.6(2)	N(2)−Zn(1)−N(3)	99.9(2)
N(1)−Zn(1)−O(2)	145.3(2)	O(2)−Zn(1)−O(1)	93.9(2)
N(1)−Zn(1)−N(3)	109.1(2)	O(2)−Zn(1)−N(3)	104.1(2)
N(2)−Zn(1)−O(1)	155.0(2)	O(1)−Zn(1)−N(3)	103.8(2)

solvent to ensure the reasonable solubility of the ligands. After stirring for 12 h, the solid was filtered and then dried under reduced pressure to yield the compounds as five-coordinate complexes where a THF molecule was bound axially to the zinc center, as evidenced by ^{1}H NMR integration.

The THF ligand could be exchanged through the dissolution of **1b** in piperidine to form **1b**·piperidine. The five-coordinate structure of **1b**·piperidine was confirmed by a single-crystal X-ray diffraction study (Figure 2, Tables 1 and 3). The Zn(II) center lies 0.49 Å above the coordination plane in a square pyramidal geometry with the piperidine ligand occupying the axial position. The Zn−N(piperidine) distance (2.119(5) Å) is longer than the Zn−N(ligand) distance (2.094(5) Å). The dihedral angles between the plane of the pyridine and the salicylidene aromatic ring are 37.9° and 27.5°.

The THF molecule could be removed from **1b**,**c**·THF by heating at 80 °C under high vacuum to give the solvent-free complexes as identified by ^{1}H NMR. We initially expected that removal of the THF molecules would lead to intermolecular aggregation due to the interaction between the distal pyridine groups and the highly electrophilic zinc center, rendering the complexes insoluble or poorly soluble in non-coordinating organic solvents, but this is not the case as **1b**,**c** can be redissolved readily in chloroform.

We suspect that these THF-free zinc salen complexes still contain five-coordinate zinc centers in the solid state but that not all of them have the distal pyridine groups interacting with the zinc centers. It is likely that some adventitious water coordinates to the axial site of a number of the zinc(II) centers and renders the resulting amorphous and complex mixture, containing some (pyridine)zinc salen aggregation and some (water)zinc salen complex, more readily redissolvable in chloroform.[15] A five-coordinate water-ligated zinc salen complex has been described.[24] The presence of water in the solid state is supported by the elemental analysis results for THF-free **1a**,**b** where a submolar amount of water (0.5 equiv) is present. This miniscule amount of water may be enough to disrupt long-range intermolecular aggregation (between the distal pyridines and the zinc center) in the solid state. As a comparison, a 15-fold molar excess of THF is sufficient to compete effectively with pyridine−zinc salen ligation in solution.[25]

The ^{t}Bu group in the THF-free complexes **1b**,**c** appears as a singlet around 1.5 ppm in the ^{1}H NMR spectrum, close to the value observed for the free ligands. The imine protons for each compound are singlets in the range 8.5−8.8 ppm, implying that the structures are symmetrical in solution. Unsymmetric oxygen-bridged dimeric structures, seen in the case of the more flexible salan ligand,[26] give two singlets each for the ^{t}Bu and imine groups.[7] We do not observe clear evidence for coordinated water in the ^{1}H NMR spectrum, presumably due to facile exchange. Surprisingly, pyridyl salen-type complex **1a**, with the flexible *trans*-1,2-cyclohexanediyl backbone, is insoluble in the majority

(24) Hall, D.; Moore, F. H. *Proc. Chem. Soc.* **1960**, 256.
(25) Splan, K. E.; Hupp, J. T. Unpublished results.
(26) Salan ligands are derived by hydrogenating the appropriate salen ligand.

of common organic solvents and could only be characterized in basic solvents such as pyridine that are capable of axially ligating the Zn(II) center.

In conclusion, the direct reaction of a salen-type ligand and Et_2Zn appears to be a versatile method for the synthesis of zinc salen complexes containing a variety of functionalities in good to high yield (40−92%). To the best of our knowledge, this direct metalation method has not been used previously for the preparation of isolated five-coordinate salen complexes of zinc. This new method is significant, in part, because it offers an efficient route to otherwise difficult to access Zn(II) salen complexes containing pendant Lewis base groups, a series of which has been fully characterized. We are currently investigating both the application of chiral zinc salen complexes in asymmetric Lewis acid catalysis and the use of bifunctional pyridine-modified Zn(II) salen complexes as components for the assembly of discrete cyclic nanostructures.[27]

(27) Morris, G. A.; Nguyen, S. T.; Hupp, J. T. Manuscript in preparation.

Acknowledgment. This work was supported by the National Science Foundation's Partnership in Nanotechnology Initiative (NSF Grant No. CHE-9811334) and by the EMSI program of the National Science Foundation and the Department of Energy (NSF Grant No. CHE-9810378) at the Northwestern University Institute for Environmental Catalysis. S.T.N. is an Alfred P. Sloan Research Fellow. We thank the Dreyfus Foundation, the DuPont Company, the Beckman Foundation, and the Packard Foundation for partial financial support. We acknowledge Frontier Scientific, Inc., for providing samples of 4-pyridylboronic acid used to prepare pyridyl-substituted ligands.

Supporting Information Available: Relevant NMR spectra for representative complexes and several different crystallographic views. Two X-ray crystallographic files in CIF format for the structure determination of *rac*-**3a**·pyridine and **1b**·piperidine. This material is available free of charge via the Internet at http://pubs.acs.org.

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