Supplementary material

Synthesis of a Dinucleating Ligand Xanthene-bis(tris(2-pyridylmethyl)amine) and Its Manganese Complex

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Experimental procedures for preparation of 2–5 and 8.

2,7-Bis(1,1-dimethylethyl)-9,9-dimethylxanthene. The preparation method for this compound is identical with that reported by Nowick et al.,[1] except that $AlCl_3$ was used instead of $FeCl_3$. 9,9-Dimethylxanthene (25.2 g, 120 mmol), *tert*-butyl chloride (26.6 g, 288 mmol), and $AlCl_3$ (0.96 g, 7.20 mmol) in 240 ml of CH_2Cl_2 gave 24.3 g (75.4 mmol, 63%) of the desired product. Colorless plate (CH_2Cl_2-EtOH), mp. 185–186°C (lit.[1] 191–192°C). ^{1}H NMR ($CDCl_3$) was identical with the reported data.[1]

4,5-Dibromo-2,7-bis(1,1-dimethylethyl)-9,9-dimethylxanthene. The preparation method for this compound is also identical with that reported by Nowick et al.,[1] except that a mixture of acetic acid and $CHCl_3$ was used instead of CCl_4. 2,7-Bis(1,1-dimethylethyl)-9,9-dimethylxanthene (1.27 g, 3.94 mmol), bromine (1.88 g, 11.8 mmol), Fe powder (10 mg) in acetic acid (10 ml) and $CHCl_3$ (6 ml) gave 1.43 g (2.98 mmol, 76%) of the desired product. Colorless prisms (toluene-hexane), mp. 252–255°C (lit.[1] 259–260°C). ^{1}H NMR ($CDCl_3$) was identical with the reported data.[1]

2,7-Bis(1,1-dimethylethyl)-9,9-dimethylxanthene-4,5-diboronic acid (2). The preparation of this compound has been reported,[2] but the following procedure gave

slightly better yield in our hands. 4,5-Dibromo-2,7-bis(1,1-dimethylethyl)-9,9-dimethylxanthene (1.00 g, 2.08 mmol) was suspended in 7 ml of dry Et_2O under argon. To this suspension, *n*-butyllithium (1.54 M in hexane, 3.0 ml, 4.62 mmol) was added dropwise with stirring at –10 °C. After 1 hour, the mixture was cooled to –78°C and trimethyl borate (2.0 ml, 17.8 mmol) was added dropwise to the solution. Then the reaction mixture was allowed to warm to room temperature. Hydrochloric acid (1 N, 20 ml) was carefully added, and the mixture was stirred overnight at room temperature. The ether layer was separated, and the aqueous layer (containing some white solid) was extracted with CH_2Cl_2. The combined organic phase was evaporated, suspended in 20 ml of Et_2O, and shaken with 60 ml of 3 N NaOH. Cream-yellow precipitates appeared, which were collected by filteration, washed thoroughly with Et_2O, and dissolved in 60 ml of H_2O. The light-yellow solution was carefully acidified with 6 N HCl, and the white precipitates were collected by filteration, washed with water, and dried *in vacuo*. Yield: 662 mg (1.61 mmol, 78%). Colorless needles (acetone-H_2O), mp. 318–320°C (lit.[2] >300°C). ^{1}H NMR (in $CDCl_3$) and IR (KBr) were identical with the reported data.[2] As **2** was only scarcely soluble in $CDCl_3$, DMSO-d_6 was more convenient for ^{1}H NMR measurements: ^{1}H NMR (500 MHz, DMSO-d_6) 8.40 (s, 4H, -OH), 7.68 (d, 2H, arom-H), 7.61 (d, 2H, arom-H), 1.66 (s, 6H, Me), and 1.37 (s, 18H, t-Bu).

4,5-Di(4-pyridyl)-2,7-bis(1,1-dimethylethyl)-9,9-dimethylxanthene di-*N*-oxide (3). The compound **2** (1.03 g, 2.50 mmol), 4-bromopyridine *N*-oxide[3] (957 mg, 5.50 mmol), $Pd(PPh_3)_4$ (231 mg, 0.200 mmol), and Na_2CO_3 (1.06 g, 10.0 mmol) were added to a mixture of 50 ml of toluene, 10 ml of H_2O, and 10 ml of MeOH. The mixture was refluxed overnight under nitrogen and cooled to room temperature. Precipitates formed were collected by filtration. The combined solid was dissolved in CH_2Cl_2 and dried over Na_2SO_4. The solvent was removed by a rotary evaporator and dried *in vacuo*. Yield: 847 mg (1.67 mmol, 67%). Colorless prisms (MeOH), mp. 344°C (dec). ^{1}H NMR (500 MHz, $CDCl_3$) 8.13 (d, 4H, arom-H), 7.52 (d, 2H, arom-H), 7.23 (d, 4H, arom-H), 7.16 (d, 2H, arom-H), 1.72 (s, 6H, Me), and 1.36 (s, 18H, t-Bu). Anal. Found: C, 77.66; H, 7.11; N, 5.50%. Calcd: C, 77.92; H, 7.13; N, 5.51%.

4,5-Bis(2-cyanopyridine-4-yl)-2,7-bis(1,1-dimethylethyl)-9,9-dimethylxanthene (4). The compound **3** (11.6 g, 22.8 mmol) was suspended in 80 ml of CH_2Cl_2. Trimethylsilyl cyanide (11.4 ml, 9.05 g, 91.2 mmol) was added to the suspension at

room temperature under nitrogen and stirred for 30 min. *N,N*-dimethylcarbamoylchloride (8.4 ml, 9.81 g, 91.2 mmol) was then added and the mixture was stirred overnight. Dilute aqueous $NaHCO_3$ (1/10 of saturated solution) was slowly added to the reaction mixture, and the organic layer was separated, washed with dilute aqueous $NaHCO_3$ and water, and dried over Na_2SO_4. The solvent was removed by a rotary evaporator and dried *in vacuo*. Yield: 8.92 g (17.6 mmol, 77%). Colorless prisms (MeOH), mp. 321-323°C. ^{1}H NMR (500 MHz, $CDCl_3$) 8.53 (dd, 2H, arom-H), 7.57 (m, 4H, arom-H), 7.40 (dd, 2H, arom-H), 7.15 (d, 2H, arom-H), 1.75 (s, 6H, Me), and 1.36 (s, 18H, t-Bu). Anal. Found: C, 79.75; H, 6.32; N, 10.59%. Calcd: C, 79.82; H, 6.51; N, 10.64%.

4,5-Bis(2-methoxycarbonylpyridine-4-yl)-2,7-bis(1,1-dimethylethyl)-9,9-dimethylxanthene (5). The compound **4** (2.09 g, 3.97 mmol) and potassium hydroxide (4.20 g, 75 mmol) were suspended in 100 ml of pyridine and 20 ml of water. The suspension was refluxed overnight. The reaction mixture was cooled and carefully neutralized with 1 N HCl with stirring. Precipitates formed were collected by filtration and dried *in vacuo*. ^{1}H NMR (500 MHz, $CDCl_3$) 8.17 (d, 2H, arom-H), 8.12 (s, 2H, arom-H), 7.87 (br, 2H, arom-H), 7.52 (d, 2H, arom-H), 7.18 (d, 2H, arom-H), 1.74 (s, 6H, Me), and 1.35 (s, 18H, t-Bu). This crude dicarboxylic acid (1.53 g) was suspended in 150 ml of methanol, concentrated H_2SO_4 (5.8 ml, 108 mmol) was added to the suspension, and the mixture was refluxed for 2 days. The reaction mixture was poured into water and carefully neutralized with aqueous 1 N NaOH with stirring, and extracted with CH_2Cl_2 five times. The organic layer was washed with brine, and dried over Na_2SO_4. The solvent was removed by a rotary evaporator, and dried *in vacuo*. Yield: 1.32 g (2.23 mmol, 56% for 2 steps). Colorless prisms (MeOH), mp. 250–251°C. ^{1}H NMR (500 MHz, $CDCl_3$) 8.47 (d, 2H, arom-H), 8.04 (d, 2H, arom-H), 7.53 (s, 2H, arom-H), 7.36 (dd, 2H, arom-H), 7.18 (d, 2H, arom-H), 3.03 (s, 3H, CO_2Me), 1.76 (s, 6H, Me), 1.46 (t, 6H, ethyl-CH_3), and 1.36 (s, 18H, t-Bu). Anal. Found: C, 74.78; H, 6.75; N, 4.94%. Calcd: C, 74.98; H, 6.80; N, 4.73%.

Bis(2-pyridylmethyl)amine (8). Pyridine-2-carboxaldehyde (8.25 g, 76.3 mmol) was dissolved in 40 ml of ethanol. 2-(Aminomethyl)pyridine (8.16 g, 76.3 mmol) in 40 ml of ethanol was added slowly to the solution at 0 °C, and the resulting solution was stirred for 1 hour. Then a suspension of $NaBH_4$ (8.76 g, 152 mmol) in 80 ml of ethanol

was added to the mixture, and the mixture was stirred again for 3.5 hours. The mixture was acidified with concentrated HCl at 0 °C. The mixture was filtered, and to the filtrate was added an aqueous NaOH solution until the filtrate was strongly basic. The filtrate was extracted with 50 ml of benzene. The organic layer was washed with brine, and dried over Na_2SO_4. The solvent was removed by a rotary evaporator. Then the product was distilled under reduced pressure (3 mmHg, 150 °C) to give a pale yellow oil. Yield: 10.2 g (51.3 mmol, 67%). ^{1}H NMR (500 MHz, $CDCl_3$) agreed with the reported data:[4] 8.55 (d, 2H, pyridyl-H), 7.64 (m, 2H, pyridyl-H), 7.35 (d, 2H, pyridyl-H), 7.15 (m, 2H, pyridyl-H), 3.98 (s, 4H, CH_2), and 2.27 (br, NH). IR (neat): 3310 (br), 3053 (m), 3009 (m), 2912 (br), 2827 (br), 1591 (s), 1570 (s), 1474 (s), 1435 (s), 1358 (w), 1300 (w), 1225 (w), 1126 (m), 1148 (m), 1047 (m), 993 (m), 846 (m), 756 (s), 627 (w) cm^{-1}.

IR data of new compounds are listed in the following:

1: IR (KBr): 2961 (s), 1599 (s), 1570 (s), 1545 (m), 1475 (s), 1443 (s), 1396 (m), 1366 (m), 1275 (m), 1256 (m), 1126 (w), 1086 (w), 999 (w), 961 (w), 839 (m), 768 (m), 669 (m), 656 (w).

3: IR (KBr): 2958 (m), 1477 (s), 1427 (s), 1257 (vs), 1240 (s), 1173 (m), 1084 (w), 1032 (w), 839 (m), 797 (w), 669 (w), 590 (w) cm^{-1}.

4: IR (KBr): 2963 (s), 1593 (s), 1543 (m), 1447 (s), 1387 (m), 1366 (m), 1277 (s), 1252 (s), 1090 (w), 991 (w), 885 (w), 851 (m), 669 (m), 654 (w) cm^{-1}.

5: IR (KBr): 2958 (s), 1742 (vs), 1595 (s), 1447 (s), 1391 (w), 1366 (m), 1329 (m), 1304 (s), 1277 (s), 1236 (s), 1211 (m), 1140 (s), 1119 (w), 1096 (m), 982 (w), 887 (w), 853 (m), 789 (m), 712 (w), 650 (w), 631 (m) cm^{-1}.

6: IR (KBr): 3383 (br), 2964 (s), 1603 (s), 1549 (m), 1477 (m), 1448 (s), 1400 (m), 1364 (m), 1298 (w), 1279 (m), 1252 (m), 1067 (w), 1045 (w), 885 (w), 849 (w), 831 (w), 669 (w), 654 (w) cm^{-1}.

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