Supplementary Material (ESI) for Chemical Communications

Supplementary Information For

A New Bis(imidazolyl)(alkylthiolate) Tripodal Ligand and the Spontaneous Formation of a Disulfide-Linked, Hydroxo-Bridged Dinuclear Zinc Complex

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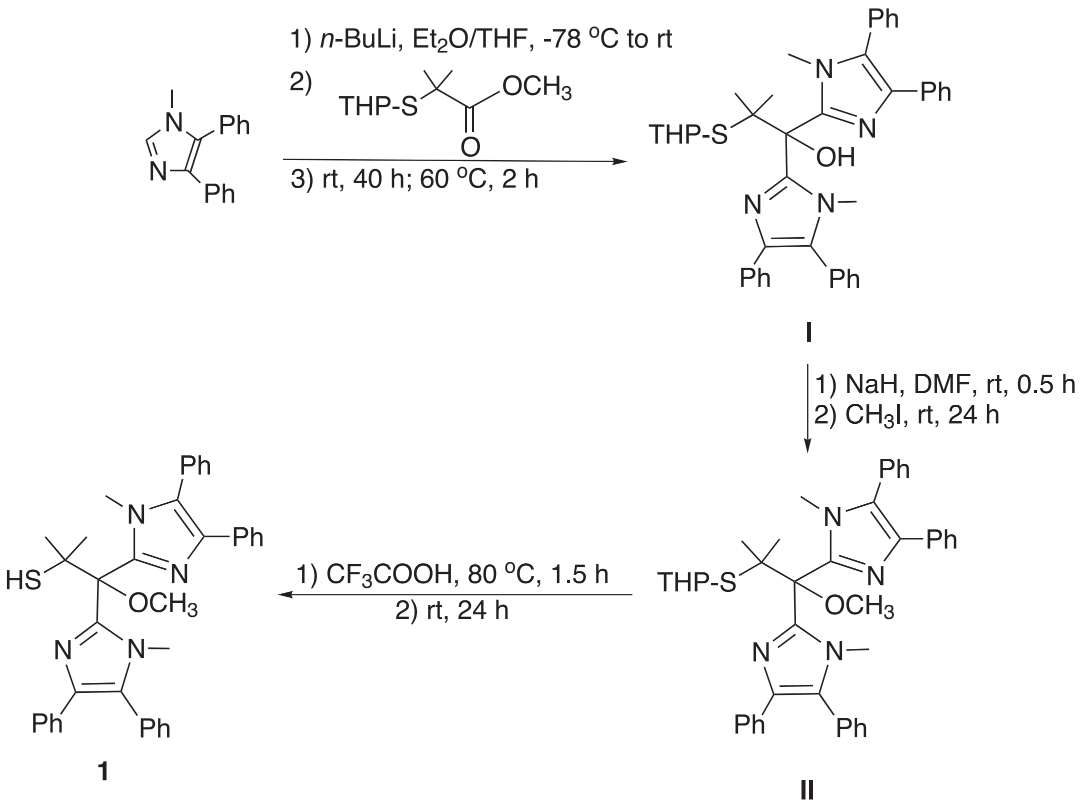
Experimental Section

General Procedures: Methyl 2-(tetrahydropyran-2-ylthio)-2-methylpropionate[1] and *N*-methyl-4,5-diphenylimidazole[2] were prepared according to literature procedures. Commercially available reagents were used as received. Column chromatography was performed with Natland International Corp. silica gel 60, 200-400 mesh. ^{1}H NMR spectra in $CDCl_3$ were recorded on a Varian Unity Plus 400 spectrometer (400 MHz) at ambient probe temperature with tetramethylsilane as the internal reference, whereas ^{1}H NMR spectra in CD_3CN and ^{13}C NMR spectra in $CDCl_3$ were recorded with the solvent peak as the internal reference. Mass spectra were recorded at the Mass Spectrometry Laboratory, Department of Chemistry, The Johns Hopkins University, using a VG-70-S mass spectrometer. Elemental analyses were recorded at Atlantic Microlab, Inc., Norcross, GA.

The synthesis of **1** was carried out according to Scheme S1:



Scheme S1

2-Methyl-1,1-bis-(1-methyl-4,5-diphenyl-1*H*-imidazol-2-yl)-2-(tetrahydro-pyran-2-ylsulfanyl)-propan-1-ol (I): *N*-methyl-4,5-diphenylimidazole (14.0 g, 0.06 mol) in dry THF (100 mL) was added to n-BuLi (37.6 mL, 1.60 M in hexanes, 0.06 mol) in dry Et_2O (100 mL) at –78 °C under argon. The resulting orange-red solution was stirred at –78 °C for 1 h, and allowed to warm slowly to room temperature. To this solution methyl 2-(tetrahydropyran-2-ylthio)-2-methylpropionate (6.6 g, 0.03 mol) in dry THF (80 mL) was added dropwise. The resulting dark red reaction mixture was stirred at room temperature for 40 h to give a yellow solution and then refluxed for 2 h at 60 °C. The resulting orange solution was then cooled to room temperature, quenched with deionized water (150 mL) and extracted with Et_2O (2 x 150 mL). The organic layers were washed with deionized water (200 mL) and dried over Na_2SO_4. Removal of Et_2O

under reduced pressure gave **I** as a foamy solid (21.4 g), which was used in the next step without further purification. Analytical data were obtained after silica gel chromatography ($MeOH/CH_2Cl_2$ 5% v/v). ^1H NMR (400 MHz, $CDCl_3$): δ 7.53-7.10 (m, 20H, C_6H_5), 5.86 (s, 1H, -OH), 4.6-4.5 (br, 1H, O-C(H)-S), 4.08-4.04 (m, 1H, S-C-CH_2), 3.48-3.41 (m, 1H, S-C-CH_2), 3.08 (s, 3H, N-CH_3), 3.05 (s, 3H, N-CH_3), 2.12 (s, 3H, C-CH_3), 2.02 (s, 3H, C-CH_3), 1.85-1.34 (m, 6H, THP). FAB-MS: m/z 655.4 ($[M+H]^+$, calcd. 655.3).

1-Methoxy-2-methyl-1,1-bis-(1-methyl-4,5-diphenyl-1*H*-imidazol-2-yl)-2-(tetrahydro-pyran-2-ylsulfanyl)-propane (II): Sodium hydride (1.70 g, 60% mineral oil suspension, 0.04 mol) was washed with anhydrous hexane and suspended in anhydrous DMF (50 mL) under argon. Crude **I** (20.4 g, 0.03 mol) was dissolved in anhydrous DMF (100 mL) to give an orange-brown solution which was added dropwise to the NaH suspension over 45 minutes and the resulting mixture was stirred for 0.5 h at room temperature. Methyl iodide (2.64 mL, 0.04 mol) was added dropwise and the reaction mixture was stirred for 24 h and then quenched by the addition of deionized water (200 mL), resulting in a white precipitate. The precipitate was dissolved by the addition of methylene chloride (200 mL) and then the organic layer was separated and dried over Na_2SO_4. The volatile solvents were removed under reduced pressure giving a brown oil. Residual amounts of DMF were removed by heating the brown oil to 140 °C under vacuum for 2 h, affording **II** as a yellow solid (18.86 g) which was used in the next step without further purification. Analytical data were obtained after silica gel chromatography ($MeOH/CH_2Cl_2$ 5% v/v). ^1H NMR (400 MHz, $CDCl_3$): δ 7.54-7.10 (m, 20H, C_6H_5), 4.02 (br, 2H, THP), 3.72 (br, 1H, THP), 3.28 (br, 6H, N-CH_3), 2.74 (br, 3H, O-CH_3), 2.32 (br, 3H, C-CH_3), 2.23 (br, 3H, C-CH_3), 1.74-1.46 (m, 6H, THP). FAB-MS: m/z 669.4 ($[M+H]^+$, calcd. 669.3).

1-Methoxy-2-methyl-1,1-bis-(1-methyl-4,5-diphenyl-1*H*-imidazol-2-yl)-propane-2-thiol (1, L^{Im_2SH}): Crude **II** (3.0 g) was dissolved in 95% trifluoroacetic acid (TFA) (30 mL) and heated to 80 °C under argon for 1.5 h. The reaction mixture was cooled to room temperature and stirred for 24 h, and then the TFA was removed under reduced pressure. The resulting dark viscous oil was dissolved in benzene (250 mL), extracted with aq. NaOH (100 mL, 2 M), and the organic layer was dried over Na_2SO_4. Benzene was removed under reduced pressure to give a brown solid. Pure **1** was obtained after flash chromatography on silica gel ($MeOH/CH_2Cl_2$ 1% v/v) as a pale yellow crystalline solid (0.7 g, 27%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.54-7.11 (m, 20H C_6H_5), 4.3 (br, 1H, SH), 3.53 (s, 6H, N-CH_3), 2.80 (br, 3H, O-CH_3), 1.60 (s, 6H, C-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 134.9, 131.5, 131.3, 130.4, 129.2, 128.9, 128.2, 126.7, 126.2, 85.5, 56.0, 54.5, 34.0, 31.7, 29.5. Anal. Calcd. for $C_{37}H_{36}N_4OS$: C, 76.00; H, 6.21; N, 9.58. Found C, 75.36; H, 6.33; N, 9.45. FAB-MS: m/z 585.3 ($[M+H]^+$, calcd. 585.3).

(L^{Im_2S})$ZnCH_3$ (2): An amount of **1** (204 mg, 0.35 mmol) was dissolved in anhydrous toluene (5 mL) and transferred to a solution of $Zn(CH_3)_2$ (250 μL, 2.0 M in toluene, 0.50 mmol) in anhydrous toluene (3 mL) under argon. A white solid precipitated by the time the addition was over. The reaction mixture was stirred under argon for 3 h. The white solid was filtered in air, washed with Et_2O and dried under vacuum (199 mg, 86%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.47-7.17 (m, 20H C_6H_5), 3.87 (s, 6H, N-CH_3), 3.57 (s, 3H, O-CH_3), 1.64 (s, 6H, C-CH_3), -1.31 (s, 3H, Zn-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 131.6, 131.4, 129.4, 129.3, 129.2, 127.9, 127.5, 92.9, 56.3, 54.7, 35.4, 32.3, -13.0. FAB-MS: m/z 685.3 ($[M+Na]^+$, calcd. 685.2).

[(L^{Im_2S})$_2$Zn] (3): An amount of **2** (31 mg, 0.05 mmol) was suspended in anhydrous toluene (3 mL), to which deionized water (25 μL, 1.4 mmol) was added. The reaction mixture was stirred at room temperature under argon for 6 days at which point the volatiles were removed under reduced pressure to give **3** as a white powder (27 mg, 94%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.53-6.81 (m, 40H C_6H_5), 3.87 (s, 6H, N-CH$_3$), 2.95 (s, 6H, N-CH$_3$), 2.62 (s, 6H, C-CH$_3$), 2.57 (s, 6H, O-CH$_3$), 2.06 (s, 6H, C-CH$_3$). FAB-MS: m/z 1231.4 ([M+H]$^+$, calcd. 1231.4).

[(L^{Im_2S})$_2$Zn$_2$(OH)(CH$_3$CN)$_2$](BF$_4$)$_3$ (4): An amount of **2** (71 mg, 0.11 mmol) was suspended in acetonitrile (3 mL) to which HBF$_4$ (26.6 μL, 50% by wt. in water, 0.21 mmol) was added under an argon atmosphere. The solution instantaneously became clear, and was stirred for 24 h at room temperature. The volatiles were removed under reduced pressure to give a glassy, yellow solid. Colorless crystals of **4** were obtained in air from a CH$_3$CN/Et$_2$O solution (62 mg, 70%). ^{1}H NMR (400 MHz, CD$_3$CN): δ 7.54-6.62 (m, 40H C_6H_5), 3.95 (s, 12H, N-CH$_3$), 3.56 (s, 6H, O-CH$_3$), 1.79 (s, 6H, C-CH$_3$), 1.54 (s, 6H, C-CH$_3$). Anal. Calcd. for $C_{80}H_{80}$ $B_3F_{12}N_{11}O_3S_2Zn_2$ (**4**•CH$_3$CN): C, 56.56; H, 4.74; N, 9.07. Found C, 56.08; H, 4.89; N, 9.32.

[(L^{Im_2S})$_2$Zn$_2$(OH)(CH$_3$CN)$_2$](CF$_3$SO$_3$)$_3$ (5): An amount of **2** (46 mg, 0.07 mmol) was suspended in acetonitrile (3 mL) to which CF$_3$SO$_3$H (12.3 μL, 0.14 mmol) was added under an argon atmosphere. Upon addition of the acid, the suspension cleared. The reaction mixture was stirred for 24 h, and the volatiles were removed under reduced pressure to give a glassy, yellow solid. Colorless crystals of **5** were obtained in air from a CH$_3$CN/Et$_2$O solution (45 mg, 63%). ^{1}H NMR (400 MHz, CD$_3$CN): δ 7.53-6.62 (m, 40H, C_6H_5), 3.95 (s, 12H, N-CH$_3$), 3.56 (s, 6H, O-CH$_3$), 1.79 (s, 6H, C-CH_3), 1.54 (s, 6H, C-CH_3). Anal. Calcd. for $C_{82}H_{78}N_{10}O_{15}S_6F_{12}Zn_2$ (**5**•CF_3SO_3H): C, 49.38; H, 3.94; N, 7.02. Found C, 49.70; H, 4.13; N, 7.30.

References:

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