

Supporting Information for

Poly(pyrazolyl)aluminate Complexes Containing Aluminum-Hydrogen Bonds

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Preparation of [Li(THF)₂][AlH₂(Ph₂p_z)₂] (1). A 100-mL Schlenk flask, equipped with a stir bar and rubber septum, was charged with Ph₂p_z (1.000 g, 4.54 mmol) and tetrahydrofuran (30 mL). A 4.0 M solution of LiAlH₄ in diethyl ether (0.58 mL, 2.32 mmol) was injected into a separate flask containing tetrahydrofuran (10 mL). The Ph₂p_zH solution was transferred dropwise over about one minute to the LiAlH₄ solution using a thin diameter cannula, which led to immediate gas evolution. After stirring the reaction mixture for 3 h, the solution was concentrated to 10 mL under reduced pressure and was then layered with hexane (50 mL). Crystals formed upon standing at room temperature after 48 hours. The solvent was removed with a cannula and vacuum drying for 0.25 h afforded **1** as colorless crystals (1.396 g, 97 %): mp 110-114 °C (dec); IR (Nujol, cm⁻¹) 1877, 1826 (s, ν_{Al-H}); ¹H NMR (C₆D₆, 23 °C, δ) 8.22-6.86 (m, 20H, aromatic CH), 6.64 (s, 1H, pyrazolyl 4-CH), 5.04 (br, 1H, AlH₂), 3.13 (m, 8H, CH₂CH₂O), 1.01 (m, 8H, CH₂CH₂O); ¹³C{¹H} NMR (C₆D₆, 23 °C, ppm) 155.03 (s, C_q), 155.0 (s, pyrazolyl C-C₆H₅), 128.86 (s, ipso-C of C₆H₅), 128.66 (s, ortho-CH of C₆H₅), 128.50 (s, para-CH of C₆H₅), 128.36 (s, meta-CH of C₆H₅), 103.80 (s, pyrazolyl 4-CH), 103.0 (s, 4-CH''), 68.08 (s, CH₂CH₂O), 25.24 (s, CH₂CH₂O). Note: the ¹H and ¹³C{¹H} NMR spectra of **1** existed as a 50:50 mixture of **1** and **2**; only the resonances for **1** are reported in this section. Anal. Calcd. for C₃₈H₄₀AlLiN₄O₂: C, 73.77; H, 6.53; N, 9.06. Found: C, 73.58; H, 6.59; N, 9.08.

Preparation of [Li(THF)][AlH(Ph₂p_z)₃] (2). In a similar fashion to the preparation of **1**, treatment of Ph₂p_zH (1.500 g, 6.81 mmol) with a 4.0 M solution of LiAlH₄ in diethyl ether (0.57 mL, 2.28 mmol) afforded **2** as colorless crystals (1.940 g, 96%): mp 188-196 °C (dec); IR (Nujol, cm⁻¹) 1934 (s, ν_{Al-H}); ¹H NMR(C₆D₆, 23 °C, δ) 7.65 (m, 12H, ortho-CH), 7.12-7.03 (m, 18H, meta-, para-CH), 6.61 (s, 3H, pyrazolyl 4-CH), 4.66 (br, 1H, AlH), 2.91 (m, 4H, CH₂CH₂O), 0.64 (m, 4H, CH₂CH₂O); ¹³C{¹H} NMR (C₆D₆, 23 °C, ppm) 155.51 (s, pyrazolyl C-C₆H₅), 134.47 (s, ipso-C of C₆H₅), 128.67 (s, ortho-CH of C₆H₅), 128.36 (s, meta-CH of C₆H₅), 127.77 (s, para-CH of C₆H₅), 104.74 (s, pyrazolyl 4-CH), 67.40 (s, CH₂CH₂O), 24.73 (s, CH₂CH₂O). Anal. Calcd. for C₄₉H₄₂AlLiN₆O: C, 76.95; H, 5.55; N, 10.99. Found: C, 76.59; H, 5.60; N, 10.91.

Preparation of [Li(THF)₄][Al(Ph₂p_z)₄]·(THF) (3). In a fashion similar to the preparation of **1**, treatment of Ph₂p_zH (0.352 g, 1.60 mmol) with a 4.0 M solution of LiAlH₄ in diethyl ether (0.10 mL, 0.40 mmol), followed by crystallization from a hot tetrahydrofuran slowly cooled to room temperature over 18 h, afforded colorless crystals (0.483 g, 95%): mp 150-153 °C (dec); IR (Nujol, cm⁻¹) 1604 (ν_{C-N}); ¹H NMR (C₆D₆, 23 °C, δ) 7.42 (m, 16H, ortho-CH), 7.00-6.91 (m, 24H, meta-, para-CH), 6.48 (s, 4H, pyrazolyl 4-CH), 4.66 (br, 1H, AlH), 3.40 (m, 16H, CH₂CH₂O), 1.27 (m, 16H, CH₂CH₂O); ¹³C{¹H} NMR (C₆D₆, 23 °C, ppm) 154.85 (s, pyrazolyl C-C₆H₅), 134.35 (s, ipso-C of C₆H₅), 128.08 (s, meta-CH of C₆H₅), 127.59 (s, ortho-CH of C₆H₅), 127.20 (s, para-CH of C₆H₅), 105.59 (s, pyrazolyl 4-CH), 67.74 (s, CH₂CH₂O), 25.56 (s, CH₂CH₂O). Anal. Calcd. for C₈₀H₈₄AlLiN₈O₅: C, 75.57; H, 6.66; N, 8.81. Found: C, 75.52; H, 6.69; N, 8.75.

Preparation of [Li(THF)][AlH(iPr₂pz)₃] (4): In a fashion similar to the preparation of **1**, treatment of iPr₂pzH (0.770 g, 5.06 mmol) with a 4.0 M solution of LiAlH₄ in diethyl ether (0.42 mL, 1.68 mmol), followed by crystallization from a mixture of tetrahydrofuran (5 mL) and diethyl ether (15 mL) held at -23 °C for 18 h, afforded **4** as colorless crystals (0.841 g, 89%): mp 165-169 °C (dec); IR (Nujol, cm⁻¹) 1869 (s, ν_{Al-H}); ¹H NMR(C₆D₆, 23 °C, δ) 6.00 (s, 3H, pyrazolyl 4-CH), 5.55 (br, 1H, AlH; only observed at < -70 °C), 3.75 (m, 4H, CH₂CH₂O), 3.38 (br s, 6H, CH(CH₃)₂), 1.41 (m, 4H, CH₂CH₂O), 1.28 (d, J = 6.8 Hz, 36H, CH(CH₃)₂); ¹³C{¹H} NMR (C₆D₆, 23 °C, ppm) 160.79 (s, pyrazolyl C-CH(CH₃)₂), 97.10 (s, pyrazolyl 4-CH), 68.73 (s, CH₂CH₂O), 27.76 (s, CH(CH₃)₂), 25.43 (s, CH₂CH₂O), 24.02 (s, CH(CH₃)₂). Anal. Calcd. for C₃₁H₅₄AlLiN₆O: C, 66.40; H, 9.73; N, 14.99. Found: C, 66.60; H, 9.80; N, 15.10.

Preparation of [Zn(AlH(Ph₂pz)₃)(H)] (5). A 100-mL Schlenk flask, equipped with a stir bar and rubber septum, was charged with ZnCl₂ (0.055 g, 0.40 mmol) and diethyl ether (10 mL). A separate 100-mL Schlenk flask was charged with **2** (0.612 g, 0.80 mmol) and diethyl ether (30 mL). The solution of **2** was transferred to the ZnCl₂ solution with a fine cannula over about one minute, resulting in a cloudy white mixture. The reaction mixture was filtered through a pad of Celite and the resulting solution was allowed to stand at ambient temperature for 18 h without stirring. Colorless crystals of **5** formed on the sides of the flask during this time, which were isolated by solvent removal with a fine cannula and then vacuum drying for 0.25 h (0.210 g, 70%): mp 234-237 °C (dec); IR (Nujol, cm⁻¹) 1963 (ν_{Al-H}), 1842 (ν_{Zn-H}); ¹H NMR(C₆D₆, 23 °C, δ) 7.83 (m, 6H, ortho-CH), 7.45-6.88 (broad m, 9H, meta-, para-CH), 6.42 (s, 3H, pyrazolyl 4-CH), 4.72 (s, 1H, Zn-H), 4.52 (broad s, 1H, Al-H); the solubility of **5** was too low in C₆D₆ to permit collection of the ¹³C{¹H} NMR spectrum, and **5** reacted with halogenated and more polar aprotic solvents. Anal. Calc. for C₄₅H₃₅AlN₆Zn: C, 71.85; H, 4.70; N, 11.18. Found: C, 71.61; H, 4.79; N, 11.08.

Preparation of [Mg₂Br₂(Ph₂Pz)₂(THF)₃](THF)₂ (6). A 100-mL Schlenk flask, equipped with a stir bar and rubber septum, was charged with MgBr₂ (0.074 g, 0.40 mmol) and tetrahydrofuran (10 mL). A separate 100-mL Schlenk flask was charged with **2** (0.306 g, 0.40 mmol) and diethyl ether (30 mL). The solution of **2** was carefully layered on the MgBr₂ solution with a fine cannula, and the system was allowed to equilibrate at ambient temperature for 48 h. Colorless crystals of **6** deposited during this time, and were isolated by solvent removal and then vacuum drying for 0.25 h (0.102 g, 25%): mp 320-326 °C (dec); IR (Nujol, cm⁻¹) 1603 (ν_{C-N}); ¹H NMR (DMSO-*d*₆, 23 °C, δ) 7.83 (m, 8H, ortho-CH), 7.25 (m, 8H, meta-CH), 7.07 (t, J = 7.2 Hz, 4H, para-CH), 6.75 (s, 2H, 4-CH), 3.58 (m, 20H, CH₂CH₂O), 1.75 (m, 20H, CH₂CH₂O); ¹³C{¹H} NMR (C₆D₆, 23 °C, ppm) 150.49 (s, pyrazolyl C-C₆H₅), 136.98 (s, ipso-C of C₆H₅), 128.11 (s, overlapping para- and meta-CH of C₆H₅), 124.67 (s, ortho-CH of C₆H₅), 97.85 (s, pyrazolyl 4-CH), 67.13 (s, CH₂CH₂O), 25.25 (s, CH₂CH₂O); the overlapping para-CH and ortho-CH resonances at 128.11 ppm in the ¹³C{¹H} NMR spectrum were confirmed by HMQC analysis. Anal. Calcd. for C₅₀H₆₂Br₂Mg₂N₄O₅: C, 59.61; H, 6.20; N, 5.56. Found: C, 59.75; H, 6.23; N, 5.65.

Preparation of [CoCl(Ph₂Pz)(THF)_{1.5}]₂(THF) (7). In a similar fashion to the preparation of **6**, treatment of CoCl₂ (0.049 g, 0.40 mmol) with **2** (0.306 g, 0.40 mmol) afforded deep blue crystals of **7** (0.042 g, 23%): mp 372-380 °C (dec); IR (Nujol, cm⁻¹) 1603 (ν_{C-N}). Anal. Calcd. for C₄₆H₅₄Cl₂Co₂N₄O₄: C, 60.33; H, 5.94; N, 6.12. Found: C, 60.65; H, 6.28; N, 6.08.