

General Considerations. Synthetic operations and physical measurements were conducted using protocols described previously (A. Kayal, A. F. Ducruet and S. C. Lee, *Inorg. Chem.* 2000, **39**, 3696). Microanalyses have proven accurate for carbon and hydrogen, but are consistently low for nitrogen (ca. 1-3%, on multiple attempts) due to the high nitrogen content of the samples.

Tp₂Ti (1). KTp (6.048 g, 24 mmol) was added to a rapidly stirred brown solution of TiCl₂(TMEDA)₂ (4.212 g, 12 mmol) in benzene (250 mL) resulting in an instantaneous solution color change to dark red. The reaction mixture was stirred for 12 h, filtered to remove KCl, and evaporated in vacuo to yield a dark red residue. The residue was washed with 4 × 30 mL *n*-pentane and dried in vacuo to give 5.130 g (90 %) of complex **1** as a dark-red microcrystalline solid. Dark red crystalline blocks suitable for x-ray diffraction were grown by slow evaporation of a saturated benzene solution over 5 d. ¹H NMR (500 MHz, C₆D₆) δ -43.07 (s, 6H), 1.18 (s, 6H), 13.10 (d, br, B-H, 2H), 16.09 (s, 6H). UV-Vis (CH₂Cl₂) λ_{max}(ε_M): 256 (7400); 390 (sh, 1650); 513 (3170); 590 (sh, 1610): Anal. Calcd for C₁₈H₂₀B₂N₁₂Ti: C, 45.61; H, 4.25; N, 35.46; Ti, 10.10. Found: C, 45.45; H, 4.28; N, 35.05; Ti, 10.18.

[Tp₂Ti](PF₆) (2). A stirred dark red solution of **1** (0.400 g, 0.84 mmol) in 15 mL CH₂Cl₂ was treated with AgPF₆ (0.213 g, 0.84 mmol), resulting in an instantaneous solution color change to yellow and precipitation of a brown solid. The reaction mixture was stirred for 2 h, then filtered and concentrated in vacuo to a minimal volume. Vapor diffusion of several vol equiv of *n*-pentane over 12 h yielded transparent-yellow crystalline blocks that were collected, washed with *n*-pentane, and dried in vacuo to give 0.390 g (78%) of complex **2**. ¹H NMR (500 MHz, CD₂Cl₂) δ 2.21-3.90 (very br); 4.35-5.20 (br), 6.10-6.85 (br), 7.32-8.20 (br). UV-Vis (CH₂Cl₂) λ_{max}(ε_M): 259 (26380); 307 (sh, 4470); 429 (13). Anal. Calcd for C₁₈H₂₀B₂N₁₂PF₆: C, 34.93; H, 3.26; N, 27.16. Found: C, 34.72; H, 3.27; N, 26.04.

[(κ²-Tp)(κ³-Tp)Ti]₂(μ-O) (3). A dark red solution of **1** (0.150 g, 0.32 mmol) in

benzene (2 mL) was treated with a solution of pyridine-N-oxide (0.030 g, 0.32 mmol) in benzene (2 mL), resulting in an instantaneous color change to orange. The solution was stirred for 2 h, then evaporated in vacuo to afford an orange-red residue. This material was redissolved in a minimal amount of benzene; vapor diffusion of several vol equiv of *n*-pentane over 2 d yielded orange crystals that were collected, washed with *n*-pentane and dried in vacuo to give 0.100 g (61%) of **3**•C₆H₆. ¹H NMR (500 MHz, C₆D₆) δ 2.25-4.98 (v br), 5.24-6.26 (d, br), 6.42 (br), 7.45-8.16 (v br), 8.32 (br), 10.05-13.00 (v br), 15.18-19.05 (v br). Anal. Calcd for C₃₆H₄₀B₄N₂₄OTi₂•C₆H₆: C, 48.41; H, 4.45; N, 32.26. Found: C, 47.99; H, 4.35; N, 29.59.

(κ²-Tp)(κ³-Tp)Ti=Se (4-Se). Se powder (0.040 g, 0.506 mmol) was added to a stirred dark-red solution of **1** (0.240 g, 0.506 mmol) in benzene (10 mL) resulting in a brown solution color. The reaction mixture was stirred for 30 min, filtered, concentrated in vacuo to a minimal volume, and layered with two vol equiv of *n*-pentane. The brown crystals that grew overnight were collected, washed with *n*-pentane, and dried in vacuo to give 0.200 g (71%) of complex **4**. ¹H NMR (500 MHz, C₆D₆) δ 4.40 (d, br, B-H, 1H), 5.07 (d, *J* = 2 Hz, 1H), 5.27 (d, *J* = 2 Hz, 1H), 5.77 (t, *J* = 2 Hz, 2H), 5.87 (t, *J* = 2 Hz, 2H), 6.43 (t, *J* = 2 Hz, 1H), 6.65 (v br, B-H, 1H), 6.73 (d, *J* = 2 Hz, 2H), 6.86 (d, *J* = 2 Hz, 1H), 7.26 (d, *J* = 2 Hz, 2H), 7.68 (d, *J* = 2 Hz, 2H), 8.12 (d, *J* = 2 Hz, 1H), 8.17 (d, *J* = 2 Hz, 1H), 8.55 (d, *J* = 2 Hz, 2H). Anal. Calcd for C₁₈H₂₀B₂N₁₂SeTi: C, 39.11; H, 3.65; N, 30.39. Found: C, 39.47; H, 3.78; N, 28.85.

(κ²-Tp)(κ³-Tp)Ti=S (4-S). A procedure analogous to the synthesis of **4-Se** was followed using 0.239 g (0.504 mmol) of **1** and 0.0162 g (0.505 mmol) of S in benzene (5 mL). The product was isolated as a green microcrystalline solid (0.189 g, 74%). Complex **4-S** is accompanied by formation of limited amounts of disulfido complex **5**; difficulties in dispensing exact, milligram quantities of sulfur are probably at fault. ¹H NMR (400 MHz, C₆D₆) δ 4.40 (d, br, B-H, 1H), 5.19 (t, *J* = 2 Hz, 1H), 5.39 (d, *J* = 1.6 Hz, 1H), 5.78 (t, *J* = 2 Hz, 2H), 5.87 (t, *J* = 2 Hz, 2H), 6.44 (t, *J* = 1.6 Hz, 1H), 6.74 (d, *J* = 2 Hz,

2H), 6.96 (d, $J = 2$ Hz, 1H), 7.26 (d, $J = 2$ Hz, 2H), 7.68 (d, $J = 2$ Hz, 2H), 8.13 (d, $J = 0.08$ Hz, 1H), 8.16 (d, $J = 2$ Hz, 1H), 8.45 (d, $J = 1.6$ Hz, 2H).

(κ^2 -Tp)(κ^3 -Tp)TiS₂ (5). A stirred dark red solution of **1** (0.150 g, 0.316 mmol) in benzene (5 mL) was treated with an excess of S (0.120 g, 3.74 mmol) resulting in an immediate color change to green. The reaction mixture was stirred for 24 h, concentrated, and filtered. The filtrate was evaporated in vacuo to afford complex **6** (0.135 g, 76%) as a blue-green microcrystalline solid. Blue-green crystalline blocks suitable for x-ray diffraction can be grown by benzene/*n*-pentane layering over a period of 12 h. ¹H NMR (500 MHz, C₆D₆) δ 4.45 (d, br, B-H); 5.28 (br), 5.55–6.00 (br), 6.32 (d, br), 6.67–7.09 (br), 7.20–7.52 (br), 7.90–8.41 (br). Anal. Calcd for C₁₈H₂₀B₂N₁₂S₂Ti: C, 40.18; H, 3.75; N, 31.23. Found: C, 39.96; H, 3.61; N, 29.18.