

Supporting Information

On the Remarkable Structural Diversity and Kinetic Lability of $\text{Tp}^{\text{C}*}\text{CaX}$ Complexes ($\text{X} = \text{NSi}_2\text{Me}_6, \text{OC}_6\text{H}_4\text{-p-Me}, \text{Tp}^{\text{C}*}$) where $\text{Tp}^{\text{C}*} = \text{tris}[3\text{-(2-methoxy-1,1-dimethylethyl)pyrazolyl}]$ hydroborate.

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General Considerations. The manipulation of air sensitive compounds employed standard Schlenk line techniques and involved the use of anhydrous solvents and dry, deoxygenated nitrogen. $\text{TiTp}^{\text{C}*}$ was prepared as described previously.¹ $\text{Ca}[\text{N}(\text{SiMe}_3)_2](\text{THF})_2$ was prepared according to the literature procedure.² Dimethylmagnesium, MgMe_2 , was prepared according to the literature procedure.³ Dibutylmagnesium, MgBu_2 , was obtained from Aldrich.

Caution. *Thallium metal and its salts are toxic. Extreme care must be employed in the handling of these materials and in disposing of their wastes.*

Measurements. ^1H -, ^{11}B -, and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were recorded in benzene- d_6 , toluene- d_8 , THF- d_8 or chloroform- d on Bruker NMR spectrometers DPX-500, DPX-400 or DPX-250. Elemental analyses for C, H and N were performed by Atlantic Microlab, Inc.

X-ray Structure Determinations.

X-ray diffraction data for compounds **2**, **3** and **4** were collected on a Nonius diffractometer equipped with a Kappa CCD detector. Because of the small size of the crystal for compound **1**, a synchrotron data set was collected at the Advanced Photon Source at Argonne National Laboratory.⁴ Crystal data, data collection, and refinement parameters are summarized in Table

S1. All work was done at low temperature using an Oxford Cryosystems Cryostream Cooler. The structures were solved using direct methods in SHELXS-97⁵ or SIR2004⁶ and standard difference map techniques. Full-matrix least-squares refinements based on F^2 were performed in SHELXL-97,⁷ as incorporated in the WinGX package.⁸ Hydrogen atoms on carbon were included in calculated positions.

*Calcium tris-[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl]hydroborate bistrimethylsilylamide, $Tp^C*CaN(SiMe_3)_2$, 1.* A solution of $TiTp^C*$ (0.953 g, 1.41 mmol) in 40 ml pentane was added dropwise to the solution of $Ca[N(SiMe_3)_2]_2 \cdot (THF)_2$ (0.712 g, 1.41 mmol) in 30 ml pentane at 0°C. $Tp^C*CaN(SiMe_3)_2$ quickly precipitated as a white solid. The ice-water bath was removed and then the reaction mixture was stirred at room temperature overnight to make sure it is complete. Then, the reaction mixture was centrifuged, and then filtered by Schlenk filtration. The solid was washed with cold pentane twice in order to remove $TiN(SiMe_3)_2$, and dried under vacuum. $Tp^C*CaN(SiMe_3)_2$ was obtained as an off-white solid (0.766 g, 81 %). It is redissolved in n-hexane and the single crystals were obtained from cooling of the warm hexane solution overnight. ¹H-NMR (400 MHz, benzene-d₆) δ : 7.89 (H-5, pz, s, 3H), 5.86 (H-4, pz, s, 3H), 3.50(CH₂O, s, 6H), 3.23 (OMe, s, 9H), 1.18 (CMe₂, s, 18 H), 0.336 SiMe₃, s, 18H). ¹³C{¹H}-NMR (400 MHz, benzene-d₆) δ : 159.1(3-C, pz), 136.0 (5-C, pz), 101.2 (4-C, pz), 82.97(CH₂O), 60.97 (OCH₃), 36.81 (CMe₂), 26.45(CMe₂), 6.11 (SiMe₃).

*Calcium tris-[3-(2-methoxy-1,1-dimethylethyl)pyrazolyl]hydroborate} para-methylphenoxide $Tp^C*CaOC_6H_4-p-Me$, 2.* A solution of p-cresol (0.043 μ l, 1.41 mmol) in 5 ml benzene was added dropwise to the solution of compound **1** (0.265 g, 0.400 mmol) in 5 ml benzene at room

temperature. The reaction mixture was stirred for 2 h, and then all volatile materials were removed under vacuum. The white solid was dried under vacuum. X-ray quality single crystals of compound **2** together with one toluene molecule in the asymmetric unit was obtained from toluene solution at -15 °C. ¹H-NMR (250 MHz, benzene-d₆) δ: 7.52 (H-5, pz, d, *J* = 3.6 Hz, 3H), 7.26 (H-3, H-5, C₆H₄-*p*-Me, d, *J* = 8.2 Hz, 2 H), 6.88 (H-2, H-6, C₆H₄-*p*-Me, d, *J* = 8.2 Hz, 2 H), 5.86 (H-4, pz, d, *J* = 3.6 Hz 3H), 3.37 (OMe, s, 9H), 3.35 (CH₂O, s, 6H), 2.42 (*p*-Me, C₆H₄-*p*-Me, s, 3H), 1.25 (CMe₂, s, 18 H); ¹³C{¹H}-NMR (400 MHz, benzene-d₆) δ : 160.8 (C-3, pz), 136.2 (C-5, pz), 130.2 (C-3, C-5, C₆H₄-*p*-Me), 119.9 (C-2, C-6, C₆H₄-*p*-Me), 101.5 (C-4, pz), 83.14 (CH₂O), 61.31 (OCH₃), 36.61 (CMe₂), 26.32 (CMe₂), 20.94 (*p*-Me, C₆H₄-*p*-Me).

Calcium bis{tris-[3-(2-methoxy-1,1-dimethylethyl)pyrazoly]hydroborate}, [Tp^{C}Ca]Tp^{C*}, **3**.*

Compound **1** (1 mmol, 0.672 g) was heated under vacuum at 65 °C for 3 days. Color of the initial solid went from off-white to white upon formation of compound **3**. The ¹H- and ¹³C{¹H}-NMR spectra of the repeatedly recrystallized solid in benzene-d₆ showed signals at 0.413 and 5.45 ppm, respectively, for the SiMe₃ group together with the signals of compound **3**. When one equivalent of Tp^{C*}CaI reacts with one equivalent of KOSiMe₃ or KO^tBu in toluene, compound **3** was determined as a major product, which is confirmed by the same ¹H-NMR signals of the Tp^{C*} ligand. ¹H-NMR(400 MHz, benzene-d₆) δ: 7.52 (d, *J* = 2 Hz, 3H, H-5, pz), 5.86 (d, *J* = 2 Hz, 3H, H-4, pz), 3.47 (s, 9H, OMe), 3.32 (s, 6H, CH₂O), 1.25 (s, 18H, CMe₂); ¹H-NMR(250 MHz, chloroform-d) δ: 7.46 (d, *J* = 2 Hz, 3H, H-5, pz), 5.91 (d, *J* = 2 Hz, 3H, H-4, pz), 3.63 (s, 9H, OMe), 3.54 (s, 6H, CH₂O), 1.35 (s, 18H, CMe₂); ¹H-NMR(250 MHz, dichloromethane-d₂) δ: 7.51 (d, *J* = 2 Hz, 6H, H-5, pz), 5.99 (d, *J* = 2 Hz, 6H, H-4, pz), 3.65 (s, 18H, OMe), 3.59 (s, 12H, CH₂O), 1.38 (s, 18H, CMe₂); ¹H-NMR(250 MHz, THF-d₈) δ: 7.46 (d, *J* = 2 Hz, 6H, H-5,

pz), 5.94 (d, $J = 2$ Hz, 6H, H-4, pz), 3.64 (s, 18H, OMe), 3.58 (s, 12H, CH₂O), 1.37 (s, 36H, CMe₂); ¹³C{¹H}-NMR (400 MHz, benzene-d₆) δ : 160.5 (C-3, pz), 136.2 (C-5, pz), 101.4 (C-4, pz), 83.43 (CH₂O), 61.29 (OCH₃), 36.57 (CMe₂), 26.44 (CMe₂); ¹¹B{¹H}-NMR (250 MHz, benzene-d₆) δ : -2.22 (br); ¹B{¹H}-NMR (250 MHz, THF-d₈) δ : -2.38 (br).

Magnesium bis{tris-[3-(2-methoxy-1,1-dimethylethyl)pyrazoly]hydroborate}, [Tp^{C}Mg]Tp^{C*}, 4.*

A solution of [(CH₂)₃CH₃]₂Mg (3.6 mmol, 3.6 ml, 1 M solution in heptane) was added dropwise to the solution of TITp^{C*} (3.4 mmol, 2.30 g) in 40 ml THF. Immediate formation of Tl metal as a black deposit was observed. The reaction mixture was stirred for 2 h at room temperature. The Tl metal was removed by Schlenk filtration, and the colorless supernatant solution was stripped to dryness under vacuum. Compound **4** was obtained as white solid (1.09 g, 66.1 % experimental yield based on the initial TITp^{C*}). Colorless single crystals were obtained from the concentrated solution of compound **4** in n-hexane at room temperature. ¹H-NMR(400 MHz, benzene-d₆) δ : 7.34 (br, 3H, H-5, pz), 7.26 (d, $J =$ Hz, 3H, H-5, pz), 6.27 (br, 3H, H-5, pz), 5.58 (d, $J = 2$ Hz, 3H, H-4, pz), 3.86 (s, 9H, OMe), 3.67 (br, 6H, CH₂O), 3.54 (s, 6H, CH₂O), 3.20 (br, 9H, OMe), 1.71 (br, 18H, CMe₂), 0.873 (s, 18H, CMe₂); ¹³C{¹H}-NMR (400 MHz, benzene-d₆) δ : 160.9 (C-3, pz, intense), 158.4 (C-3, pz), 137.1 (C-5, pz), 135.7 (C-5, pz), 101.0 (C-4, pz, intense), 99.90 (C-4, pz), 83.30 (CH₂O, intense), 83.10 (CH₂O), 66.07 (OMe), 58.60 (OMe, intense), 37.62 (CMe₂), 36.20 (CMe₂, intense), 26.04 (CMe₂). ¹¹B{¹H}-NMR (250 MHz, benzene-6) δ : -1.85 (br). Anal. Calcd. for C₄₈H₈₀B₂MgN₁₂O₆: C, 59.61; H, 8.34; N, 17.38. Found: C, 59.47; H, 8.32; N, 16.69.

The reaction above was run to obtain Tp^{C*}MgBu so 1.05 eq. of MgBu₂ was reacted with 1.00 equivalent of TITp^{C*}. When 2 eq. of TITp^{C*} reacts with 1 equivalent of MgBu₂ in THF,

compound **4** is obtained in quantitative yield according to the following procedure: To a solution of $\text{TiTp}^{\text{C}*}$ (2.38g, 3.52 mmol) in 25 ml of THF was added dropwise the solution of MgBu_2 (1.76 mmol, 1 ml of 1M solution in n-heptane) at room temperature. The reaction mixture turned gray and then Ti metal was accumulated at the bottom of the Schlenk flask. The reaction mixture was stirred overnight. The solution was filtered, volatiles were removed under vacuum. A gray solid residue was obtained. It was redissolved in n-hexane, filtered and compound **4** was recrystallized from the concentrated n-hexane solution at room temperature (1.46 g, 83.0 %).

Spin Saturation Transfer Experiments

VT ^{13}C $\{^1\text{H}\}$ -NMR spin saturation transfer experiments were carried out on compound **4** in toluene- d_8 . Two sets of ^{13}C signals were observed for the $\text{Tp}^{\text{C}*}$ ligands corresponding to $[\text{Tp}^{\text{C}*}\text{Mg}]^+$ and $[\text{Tp}^{\text{C}*}]^-$ though an absolute assignment of coordinated and free $\text{Tp}^{\text{C}*}$ signals has not been made at this time. The OCH_3 signals with chemical shifts at 66.0 and 58.7 ppm and well separated and were employed in the irradiation experiments. Irradiation of the signal at 66.0 ppm and examination of the signal at 58.7 ppm revealed spin transfer with increasing temperature as shown in Figure 4. Irradiation of the signal at 58.7 ppm also gave rise to the decrease in intensity of the signal at 66.0 ppm with increasing temperature. These experiments confirm the exchange of free and coordinated $\text{Tp}^{\text{C}*}$ ligands.

References

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Table S1. Summary of crystallographic data for compounds **1-4**.

	1	2	3	4
Formula	C ₃₀ H ₅₈ BCaN ₇ O ₃ Si ₂	C ₃₁ H ₄₇ BCaN ₆ O ₄ and toluene	C ₄₈ H ₈₀ B ₂ CaN ₁₂ O ₆	C ₄₈ H ₈₀ B ₂ MgN ₁₂ O ₆

Formula Wt.	671.90	710.77	982.94	967.17
Crystal System	monoclinic	monoclinic	monoclinic	triclinic
a/Å	13.1496(5)	13.390(1)	14.2546(2)	14.3126(1)
b/Å	15.5703(8)	15.831(1)	16.7217(3)	14.5131(2)
c/Å	18.9206(8)	19.583(2)	24.6146(5)	14.9368(2)
α /°				97.536(1)
β /°	99.351(2)	109.058(3)	102.840(1)	115.884(1)
γ /°				99.546(1)
U/Å ³	3822.4(3)	3923.6(6)	5720.4(2)	2679.34(5)
T/K	95(2)	150(2)	230(2)	150(2)
wavelength	0.49595 Å	0.71073	0.71073	0.71073
Space Group	P2 ₁ /c	P2 ₁ /n	P2 ₁ /c	Pī
Z	4	4	4	2
crystal size, mm	0.07 x 0.06 x < 0.01	0.38 x 0.35 x 0.12	0.38 x 0.12 x 0.12	0.27 x 0.19 x 0.15
μ mm ⁻¹	0.080	0.205	0.163	0.090
Reflections Measured	42864	63707	51480	47258
Unique refl., Rint	10864, 0.0513	6918, 0.039	7420, 0.085	9449, 0.038
R1(I>2 σ I)	0.0447	0.0397	0.0885	0.0912
wR2(all data)	0.1117	0.1025	0.2589	0.2891

