Supporting Information

C–H Activation of Arenes and Heteroarenes by Early Transition Metallaborane, $[(Cp^*Ta)_2B_5H_{11}]$ ($Cp^* = \eta^5$-C_5Me_5)

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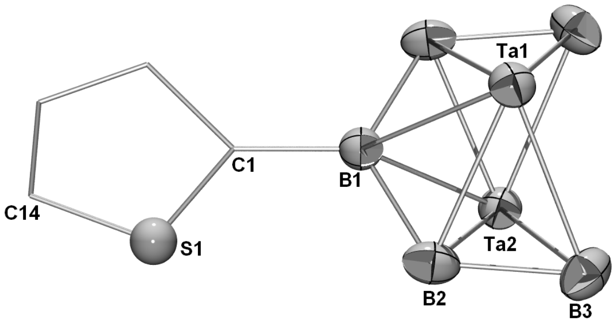


Figure S1: Molecular structure of **5** (30% probability ellipsoids). Cp* ligands, Ta–Ta bond, Ta–H–B and B–H hydrogens are excluded for clarity. Selected bond lengths (Å): Ta1–Ta2, 2.9318(3); Ta1–B1, 2.289(6); B1–B2, 1.750(6); B1–C1, 1.551(11); C1–S1, 1.613(7).

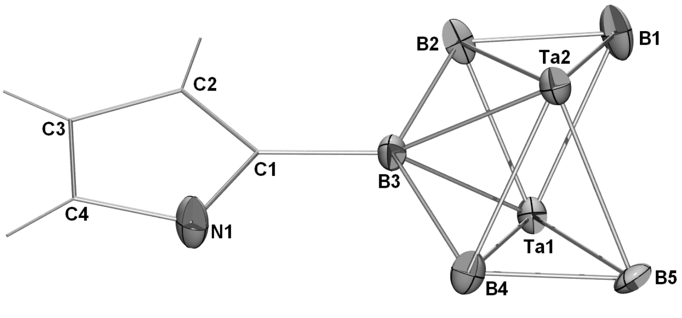
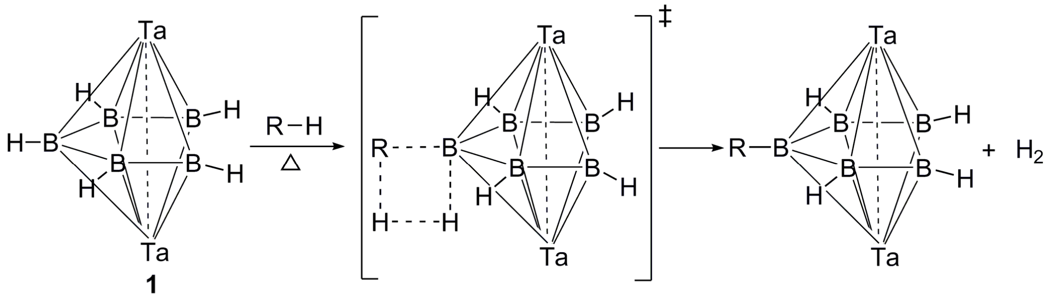


Figure S2: Molecular structure of **6** (30% probability ellipsoids). Cp* ligands and Ta–Ta bond are excluded for clarity. Selected bond lengths (Å): Ta1–Ta2, 2.9171(9); Ta1–B1, 2.44(2); B1–B2, 1.89(3); B3–C1, 1.57(2).



1

Ta = Cp*Ta R = aryl or heteroaryl

Scheme S1: A plausible mechanism for the CH activation of arenes and heteroarenes by **1** (Ta–H–B protons are not shown for clarity).

General consideration: All syntheses were carried out under an argon atmosphere with standard Schlenk and glovebox techniques. Solvents were dried by common methods and distilled under N_2 before use. Compound **1** was prepared according to literature method.[1] While other chemicals were obtained commercially and used as received. The external reference for the ^{11}B NMR, $[Bu_4N(B_3H_8)]$, was synthesized with the literature method.[2] Thin layer chromatography was carried on 250 mm dia aluminum supported silica gel TLC plates (MERCK TLC Plates). NMR spectra were recorded on a 400 and 500 MHz Bruker FT-NMR spectrometer. Residual solvent protons were used as reference (δ, ppm, [D$_6$]benzene, 7.16), while a sealed tube containing $[Bu_4N(B_3H_8)]$ in [D$_6$]benzene (δ_B, ppm, –30.07) was used as an external reference for the ^{11}B NMR. Infrared spectra were recorded on a Nicolet 6700 FT spectrometer. Microanalyses for C, H and N were performed on Perkin Elimer Instruments series II model 2400. Mass spectra were obtained on a Jeol SX 102/Da-600 mass spectrometer with argon/xenon (6kv, 10 mÅ) as FAB gas.

Synthesis of 2-6. In a typical reaction, solution of **1** (0.120 g, 0.17 mmol) in benzene (4 mL) was thermolyzed at 80 ºC for 12 h. The solvent was evaporated in vacuo; residue was extracted into hexane and passed through Celite. After removal of solvent from filtrate, the residue was subjected to chromatographic work up using silica gel TLC plates (eluent: hexane/CH_2Cl_2 = 90:10 *v/v*) yielded yellow **2** (0.084 g, 63%). Further, in a similar fashion, the isolated yields of **3-6** from **1** were 75% (0.102 g), 42% (0.058 g), 65% (0.087 g) and 80% (0.105 g) respectively.

[(Cp*Ta)$_2$B$_5$H$_{10}$(C$_6$H$_5$)], 2: ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ = 7.67-7.46 (m, 5H; C_6H_5), 5.43 (partially collapsed quartet (pcq), 2BH_t), 4.39 (pcq, 2BH_t), 2.16 (s, 30H; Cp*), –3.75 (br, 2Ta–*H*–B), –7.21 ppm (br, 4Ta–*H*–B). ^{11}B NMR (128 MHz, C_6D_6, 22 °C): δ = 51.0 (s, 1B), 20.2 (d, 2B), 3.5 ppm (br, 2B). ^{13}C NMR (100 MHz, C_6D_6, 22 °C): δ = 132.0, 130.7, 128.2, 124.4 (C_6H_5), 111.4 (s; C_5Me_5), 14.1 ppm (s; C_5Me_5). IR (hexane) ν/cm^{-1}: 2443 (B–H$_t$). MS (FAB) P$^+$(max): *m/z*(%) 773. Elemental analysis (%) calcd for $C_{26}H_{45}B_5Ta_2$: C 40.37, H 5.86; found: C 40.56, H 5.98.

[(Cp*Ta)$_2$B$_5$H$_{10}$(C$_6$H$_4$CH$_3$)], 3: The proton chemical shifts of the two isomers (*meta*:*para* in 1:1 ratio) were determined by selective decoupling of peaks in the aromatic region. *m*-($C_6H_4CH_3$)(Cp*Ta)$_2$B$_5$H$_{10}$. ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ = 6.80-6.52 (m, 3H; C_6H_4), 6.59 (s, 1H; C_6H_4), 5.33 (pcq, 2BH_t), 4.25 (pcq, 2BH_t), 2.30 (s, 3H; $C_6H_4CH_3$), 2.08 (s, 30H; Cp*), –3.35 (br, 2Ta–*H*–B), –6.81 ppm (br, 4Ta–*H*–B). ^{11}B NMR (128 MHz, C_6D_6, 22 °C): δ = 51.3 (s, 1B), 20.8 (br, 2B), 4.1 ppm (br, 2B). ^{13}C NMR (100 MHz, C_6D_6, 22 °C): δ = 134.2, 133.8, 131.2, 130.0, 128.2, 124.9 (C_6H_4Me), 110.2 (s; C_5Me_5), 21.6 (C_6H_4Me), 13.0 ppm (s; C_5Me_5). *p*-($C_6H_4CH_3$)(Cp*Ta)$_2$B$_5$H$_{10}$. ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ = 6.75 (d, 2H; C_6H_4), 6.64 (d, 2H; C_6H_4), 5.33 (pcq, 2BH_t), 4.25 (pcq, 2BH_t), 2.24 (s, 3H; $C_6H_4CH_3$), 2.08 (s, 30H; Cp*), –3.35 (br, 2Ta–*H*–B), –6.81 ppm (br, 4Ta–*H*–B). ^{11}B NMR (128 MHz, C_6D_6, 22 °C): δ = 51.3 (s, 1B), 20.8 (br, 2B), 4.1 ppm (br, 2B). ^{13}C NMR (100 MHz, C_6D_6, 22 °C): δ = 135.1, 134.0, 126.0, 125.5 (C_6H_4Me), 110.2 (s; C_5Me_5), 21.0 (C_6H_4Me), 13.0 ppm (s; C_5Me_5). IR (hexane) ν/cm^{-1}: 2458 (B–H$_t$). MS (FAB) P$^+$(max): m/z(%) 787. Elemental analysis (%) calcd for $C_{27}H_{47}B_5Ta_2$: C 41.17, H 6.01; found: C 41.32, H 6.13.

[(Cp*Ta)$_2$B$_5$H$_{10}$(C$_6$H$_4$Cl)], 4: The proton chemical shifts of the two isomers (*meta*:*para* in 2:1 ratio) were determined by selective decoupling of peaks in the aromatic region. *m*-(C$_6$H$_4$Cl)(Cp*Ta)$_2$B$_5$H$_{10}$. ^{1}H NMR (400 MHz, C$_6$D$_6$, 22 °C): δ = 7.72-7.00 (m, 3H; C$_6$*H*$_4$), 7.02 (s, 1H; C$_6$*H*$_4$), 5.21 (pcq, 2B*H*$_t$), 4.18 (pcq, 2 B*H*$_t$), 2.12 (s, 30H; Cp*), –3.05 (br, 2Ta–*H*–B), –6.98 ppm (br, 4Ta–*H*–B). ^{11}B NMR (128 MHz, C$_6$D$_6$, 22 °C): δ = 49.5 (s, 1B), 21.0 (br, 2B), 4.1 ppm (d, 2B). ^{13}C NMR (100 MHz, C$_6$D$_6$, 22 °C): δ = 136.1, 135.9, 132.7, 132.0, 128.8, 125.9 (*C*$_6$H$_4$Cl), 111.2 (s; *C*$_5$Me$_5$), 13.6 ppm (s; C$_5$*Me*$_5$). *p*-(C$_6$H$_4$Cl)(Cp*Ta)$_2$B$_5$H$_{10}$. ^{1}H NMR (400 MHz, C$_6$D$_6$, 22 °C): δ = 7.46 (d, 2H; C$_6$*H*$_4$), 7.04 (d, 2H; C$_6$*H*$_4$), 5.21 (pcq, 2B*H*$_t$), 4.18 (pcq, 2B*H*$_t$), 2.12 (s, 30H; Cp*), –3.05 (br, 2Ta–*H*–B), –6.98 ppm (br, 4Ta–*H*–B). ^{11}B NMR (128 MHz, C$_6$D$_6$, 22 °C): δ = 49.5 (s, 1B), 21.0 (br, 2B), 4.1 ppm (d, 2B). ^{13}C NMR (100 MHz, C$_6$D$_6$, 22 °C): δ = 138.1, 134.4, 131.5, 126.4, (*C*$_6$H$_4$Cl), 111.2 (s; *C*$_5$Me$_5$), 13.6 ppm (s; C$_5$*Me*$_5$). IR (hexane) ν/cm^{-1}: 2445 (B–H$_t$). MS (FAB) P$^+$(max): *m/z*(%) 808. Elemental analysis (%) calcd for C$_{26}$H$_{44}$B$_5$Cl$_1$Ta$_2$: C 38.65, H 5.49; found: C 38.92, H 5.62.

[(Cp*Ta)$_2$B$_5$H$_{10}$(C$_4$H$_3$S)], 5: ^{1}H NMR (400 MHz, C$_6$D$_6$, 22 °C): δ = 6.91 (d, 1H; C$_4$*H*$_3$S), 6.74 (dd, 1H; C$_4$*H*$_3$S), 6.27 (d, 1H; C$_4$*H*$_3$S), 4.65 (pcq, 2B*H*$_t$), 3.91 (pcq, 2B*H*$_t$), 2.20 (s, 30H; Cp*), –3.65 (br, 2Ta–*H*–B), –7.12 ppm (br, 4Ta–*H*–B). ^{11}B NMR (128 MHz, C$_6$D$_6$, 22 °C): δ = 45.9 (s, 1B), 20.6 (br, 2B), 3.2 ppm (d, 2B). ^{13}C NMR (100 MHz, C$_6$D$_6$, 22 °C): δ = 131.0, 129.0, 127.2, 124.7 (*C*$_4$H$_3$S), 111.6 (s; *C*$_5$Me$_5$), 12.8 ppm (s; C$_5$*Me*$_5$). IR (hexane) ν/cm^{-1}: 2450 (B–H$_t$). MS (FAB) P$^+$(max): *m/z*(%) 779. Elemental analysis (%) calcd for C$_{24}$H$_{43}$B$_5$S$_1$Ta$_2$: C 36.97, H 5.56; found: C 37.15, H 5.71.

[(Cp*Ta)$_2$B$_5$H$_{10}$(C$_4$H$_3$NH)], 6: ^{1}H NMR (400 MHz, C$_6$D$_6$, 22 °C): δ = 6.47 (d, 1H; C$_4$*H*$_3$NH), 5.96 (dd, 1H; C$_4$*H*$_3$NH), 5.45 (d, 1H; C$_4$*H*$_3$NH), 4.80 (pcq, 2B*H*$_t$), 4.13 (br, C$_4$H$_3$N*H*), 3.79 (pcq, 2B*H*$_t$), 2.18 (s, 30H; Cp*), –4.15 (br, 2Ta–*H*–B), –6.96 ppm (br, 4Ta–*H*–B). ^{11}B NMR (128 MHz, C$_6$D$_6$, 22 °C): δ = 45.4 (s, 1B), 20.9 (br, 2B), 2.5 ppm (br, 2B). ^{13}C NMR (100 MHz, C$_6$D$_6$, 22 °C): δ = 118.1, 115.0, 114.2, 108.7 (*C*$_4$H$_3$NH), 111.5 (s; *C*$_5$Me$_5$), 12.7 ppm (s; C$_5$*Me*$_5$). IR (hexane) ν/cm^{-1}: 3417 (N–H), 2454 (B–H$_t$).

MS (FAB) P^+(max): *m/z*(%) 762. Elemental analysis (%) calcd for $C_{24}H_{44}B_5N_1Ta_2$: C 37.80, H 5.82; found: C 37.53, H 5.64.

[(Cp*Ta)$_2$B$_5$H$_{10}$(C$_6$H$_4$Br)] (Table 1, entry 4): The proton chemical shifts of the two isomers (*meta*:*para* in 2:1 ratio) were determined by selective decoupling of peaks in the aromatic region. *m*-(C_6H_4Br)(Cp*Ta)$_2$B$_5$H$_{10}$. ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ = 7.75-7.18 (m, 3H; C_6H_4), 7.21 (s, 1H, C_6H_4), 5.20 (pcq, 2BH_t), 4.18 (pcq, 2BH_t), 2.22 (s, 30H; Cp*), –3.45 (br, 2Ta–*H*–B), –7.08 ppm (br, 4Ta–*H*–B). ^{11}B NMR (128 MHz, C_6D_6, 22 °C): δ = 47.1 (s, 1B), 22.1 (br, 2B), 4.3 ppm (d, 2B). *p*-(C_6H_4Br)(Cp*Ta)$_2$B$_5$H$_{10}$. ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ = 7.51 (d, 2H; C_6H_4), 7.19 (d, 2H; C_6H_4), 5.20 (pcq, 2BH_t), 4.18 (pcq, 2BH_t), 2.22 (s, 30H; Cp*), –3.45 (br, 2Ta–*H*–B), –7.08 ppm (br, 4Ta–*H*–B). ^{11}B NMR (128 MHz, C_6D_6, 22 °C): δ = 47.1 (s, 1B), 22.1 (br, 2B), 4.3 ppm (d, 2B). IR (hexane) ν/cm^{-1}: 2474 (B–H_t). MS (FAB) P^+(max): *m/z*(%) 852. Elemental analysis (%) calcd for $C_{26}H_{44}B_5Br_1Ta_2$: C 36.63, H 5.20; found: C 35.81, H 4.96.

[(Cp*Ta)$_2$B$_5$H$_{10}$(C$_6$H$_4$I)] (entry 5): The proton chemical shifts of the two isomers (*meta*:*para* in 2:1 ratio) were determined by selective decoupling of peaks in the aromatic region. *m*-(C_6H_4I)(Cp*Ta)$_2$B$_5$H$_{10}$: ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ = 7.80-7.15 (m, 3H; C_6H_4), 7.32 (s, 1H, C_6H_4), 5.08 (pcq, 2BH_t), 4.38 (pcq, 2BH_t), 2.34 (s, 30H; Cp*), –3.23 (br, 2Ta–*H*–B), –6.41 ppm (br, 4Ta–*H*–B); ^{11}B NMR (128 MHz, C_6D_6, 22 °C): δ = 46.8 (s, 1B), 20.8 (br, 2B), 5.5 ppm (br, 2B); *p*-(C_6H_4I)(Cp*Ta)$_2$B$_5$H$_{10}$: ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ = 7.38 (d, 2H; C_6H_4), 7.08 (d, 2H; C_6H_4), 5.08 (pcq, 2BH_t), 4.38 (pcq, 2BH_t), 2.34 (s, 30H; Cp*), –3.23 (br, 2Ta–*H*–B), –6.41 ppm (br, 4Ta–*H*–B); ^{11}B NMR (128 MHz, C_6D_6, 22 °C): δ = 46.8 (s, 1B), 20.8 (br, 2B), 5.5 ppm (br, 2B); IR (hexane) ν/cm^{-1}: 2499 (B–H_t). Elemental analysis (%) calcd for $C_{26}H_{44}B_5I_1Ta_2$: C 34.72, H 4.93; found: C 33.81, H 4.45.

[(Cp*Ta)$_2$B$_5$H$_{10}$(C$_6$H$_3$Me$_2$)] (entry 6): ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ = 7.20-7.15 (m, 3H; C_6H_3), 5.01 (pcq, 2BH_t), 4.51 (pcq, 2BH_t), 2.29 (s, 3H; $C_6H_3Me_2$), 2.24 (s, 3H; $C_6H_3Me_2$), 2.18 (s, 30H;

Cp*), –3.68 (br, 2Ta–*H*–B), –7.08 ppm (br, 4Ta–*H*–B). ^{11}B NMR (128 MHz, C_6D_6, 22 °C): δ = 50.5 (s, 1B), 21.8 (br, 2B), 4.5 ppm (br, 2B). IR (hexane) ν/cm^{-1}: 2451 (B–H_t). MS (FAB) P^+(max): *m/z*(%) 801.

[(Cp*Ta)$_2$B$_5$H$_{10}$(C$_4$H$_2$MeS)] (entry 9): ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ = 6.53 (d, 1H; C_4H_2), 5.74 (d, 1H; C_4H_2), 5.16 (pcq, 2BH_t), 4.07 (pcq, 2BH_t), 2.42 (s, 3H; C_4H_2Me), 2.17 (s, 30H; Cp*), –3.02 (br, 2Ta–*H*–B), –6.98 ppm (br, 4Ta–*H*–B). ^{11}B NMR (128 MHz, C_6D_6, 22 °C): δ = 46.5 (s, 1B), 20.0 (d, 2B), 2.9 ppm (br, 2B). IR (hexane) ν/cm^{-1}: 2468 (B–H_t). MS (FAB) P^+(max): *m/z*(%) 793.

[(Cp*Ta)$_2$B$_5$H$_{10}$(C$_4$H$_2$IS)] (entry 10): ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ = 7.38 (d, 1H; C_4H_2), 6.95 (d, 1H; C_4H_2), 5.10 (pcq, 2BH_t), 4.22 (pcq, 2BH_t), 2.11 (s, 30H; Cp*), –3.32 (br, 2Ta–*H*–B), –6.74 ppm (br, 4Ta–*H*–B). ^{11}B NMR (128 MHz, C_6D_6, 22 °C): δ = 46.2 (s, 1B), 21.2 (d, 2B), 3.4 ppm (br, 2B). IR (hexane) ν/cm^{-1}: 2485 (B–H_t). MS (FAB) P^+(max): *m/z*(%) 905.

[(Cp*Ta)$_2$B$_5$H$_{10}$(C$_4$HMe$_2$S)] (entry 11): ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ = 6.79 (s, 1H; C_4H), 5.32 (pcq, 2BH_t), 4.28 (pcq, 2BH_t), 2.47 (m, 6H; C_4HMe_2), 2.08 (s, 30H; Cp*), –3.75 (br, 2Ta–*H*–B), –7.14 ppm (br, 4Ta–*H*–B). ^{11}B NMR (128 MHz, C_6D_6, 22 °C): δ = 45.0 (s, 1B), 21.8 (br, 2B), 6.2 ppm (br, 2B). IR (hexane) ν/cm^{-1}: 2492 (B–H_t). Elemental analysis (%) calcd for $C_{26}H_{47}B_5S_1Ta_2$: C 38.66, H 5.87; found: C 37.65, H 5.16.

[(Cp*Ta)$_2$B$_5$H$_{10}$(C$_4$HBr$_2$S)] (entry 12): ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ = 7.12 (d, 1H; C_4H), 5.12 (pcq, 2BH_t), 4.10 (pcq, 2BH_t), 2.33 (s, 30H; Cp*), –3.90 (br, 2Ta–*H*–B), –7.05 ppm (br, 4Ta–*H*–B). ^{11}B NMR (128 MHz, C_6D_6, 22 °C): δ = 49.6 (s, 1B), 20.1 (br, 2B), 4.3 ppm (d, 2B). IR (hexane) ν/cm^{-1}: 2462 (B–H_t). MS (FAB) P^+(max): *m/z*(%) 937. Elemental analysis (%) calcd for $C_{24}H_{41}B_5Br_2S_1Ta_2$: C 30.75, H 4.41; found: C 29.94, H 4.05.

[(Cp*Ta)$_2$B$_5$H$_{10}$(C$_4$HMe$_2$NH)] (entry 13): ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ = 5.94 (d, 1H; C_4H), 5.22 (pcq, 2BH_t), 5.08 (br, 1H, C_4HMe_2NH), 4.28 (pcq, 2BH_t), 2.18 (s, 30H; Cp*), 2.04 (m, 6H; C_4HMe_2NH), –3.81 (br, 2Ta–*H*–B), –7.15 ppm (br, 4Ta–*H*–B). ^{11}B NMR (128 MHz, C_6D_6, 22 °C): δ =

43.4 (s, 1B), 22.0 (br, 2B), 5.3 ppm (d, 2B). IR (hexane) ν/cm^{-1}: 3450 (N–H), 2465 (B–H$_t$). Elemental analysis (%) calcd for $C_{26}H_{48}B_5N_1Ta_2$: C 39.50, H 6.12; found: C 38.94, H 5.85.

[(Cp*Ta)$_2$B$_5$H$_{10}${C$_4$H$_3$NSi(*i*Pr)$_3$}] (entry 14): ^{1}H NMR (400 MHz, C_6D_6, 22 °C): δ = 6.49 (s, 1H; C$_4$*H*$_3$), 5.94 (d, 1H; C$_4$*H*$_3$), 5.61 (d, 1H; C$_4$*H*$_3$), 5.00 (pcq, 2B*H$_t$*), 4.20 (pcq, 2B*H$_t$*), 2.28 (s, 30H; Cp*), 1.34 (m, 3H; 3C*H*Me$_2$), 1.01 (d, 18H; 3CH*Me$_2$*), –4.19 (br, 2Ta–*H*–B), –7.25 ppm (br, 4Ta–*H*–B). ^{11}B NMR (128 MHz, C_6D_6, 22 °C): δ = 46.6 (s, 1B), 22.2 (br, 2B), 3.3 ppm (br, 2B). IR (hexane) ν/cm^{-1}: 2448 (B–H$_t$). MS (FAB) P$^+$(max): *m/z*(%) 918.

Isotope Effect Measurement. The tantalaborane **1** (0.050 g, 0.07 mmol) was added to an NMR sample tube as a solid. Equimolar amounts of benzene (0.30 mL) and benzene-*d*$_6$ (0.30 mL) were added to the tube by syringe, and the tube was flame-sealed. The reaction was monitored by ^{1}H NMR spectroscopy at 80 °C. The rate constants were benzene, $k = 41.25 \times 10^{-2}$ hr^{-1}; benzene-*d*$_6$, $k = 29.45 \times 10^{-2}$ hr^{-1}. These rate constants correspond to a kinetic isotope effect k_H/k_D of 1.4.

X-ray Structure Determination. Crystallographic informations for **2**, **5** and **6** are listed in Table S1. The crystal data for **2** were collected and integrated using Bruker Axs kappa apex2 CCD diffractometer, with graphite monochromated Mo–Kα (λ = 0.71073 Å) radiation at 293 K. Several attempts to grow good X-ray-quality single crystals of **6** by the slow evaporation of hexane at –5 °C were unsuccessful. However, by using a mixed-solvent system (hexane/toluene, 9:1 v/v) we managed to grow crystals of **6** at –20 °C. Crystal data for **5** and **6** were collected on an OXFORD DIFFRACTION XCALIBUR-S CCD system equipped with graphite-monochromated Mo$_{K\alpha}$ radiation at 150 K. The structures were solved by heavy atom methods using SHELXS-97 or SIR92[3] and refined using SHELXL-97.[4,5] CCDC-814966 (**2**), CCDC-814964 (**5**) and CCDC-814965 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac. uk/data_request/cif.

Table S1. Crystallographic Data and Structure Refinement Information for **2**, **5** and **6**.

	2	**5**	**6**
empirical formula	$C_{26}H_{45}B_5Ta_2$	$C_{24}H_{43}B_5STa_2$	$C_{24}H_{43}B_5NTa_2$
formula weight	773.57	779.59	761.54
crystal system	monoclinic	monoclinic	triclinic
Space group	*C*2/*c*	*C*2/*c*	$P\overline{1}$
a (Å)	16.7619(4)	16.7674(8)	8.5841(4)
b (Å)	17.2045(4)	17.0966(14)	10.1872(6)
c (Å)	10.0036(2)	10.1063(6)	17.2208(10)
α (º)	90	90	98.965(5)
β (°)	100.8740(10)	101.068(5)	104.066(5)
γ (°)	90	90	106.012(5)
V(Å^3)	2833.04(11)	2843.2(3)	1363.39(13)
Z	4	4	2
D_{calc} (g/cm^3)	1.814	1.821	1.855
F (000)	1488	1496	730
μ (mm^{-1})	7.732	7.775	8.032
Crystal size (mm)	0.18 x 0.15 x 0.12	0.23 x 0.18 x 0.13	0.33 x 0.24 x 0.18
θ Range (°)	2.47– 28.31	3.44–32.76	3.55–25.00
no. of total refins collected	10619	15722	8713
no. of unique refins [$I > 2\sigma(I)$]	3368	4870	4794
max and min transmission	0.492 and 0.388	0.4314 and 0.2679	0.367 and 0.212
data/restraints/parameters	3368 / 12 / 198	4870 / 7 / 165	4794 / 43 / 299
goodness-of-fit on F^2	1.021	0.858	1.114
final *R* indices [$I > 2\theta(I)$]	R1 = 0.0245 wR2 = 0.0468	R1 = 0.0307 wR2 = 0.0713	0.0790 0.2192
R indices (all data)	R1 = 0.0421 wR2 = 0.0518	R1 = 0.0614 wR2 = 0.0769	0.0870 0.2284
largest difference in peak and hole (e/ Å^3)	0.868 and –0.543	1.812 and –0.927	7.549 and –7.509

^{11}B NMR Spectra

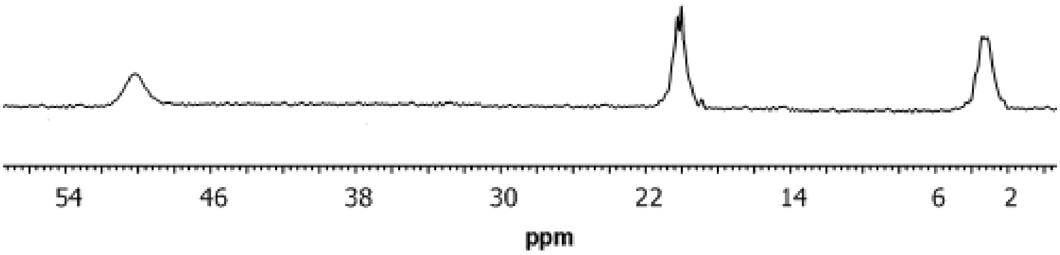


Figure S3. ^{11}B NMR (128 MHz, [d_6]benzene) spectrum of $[(Cp^*Ta)_2B_5H_{10}(C_6H_5)]$ **2**.

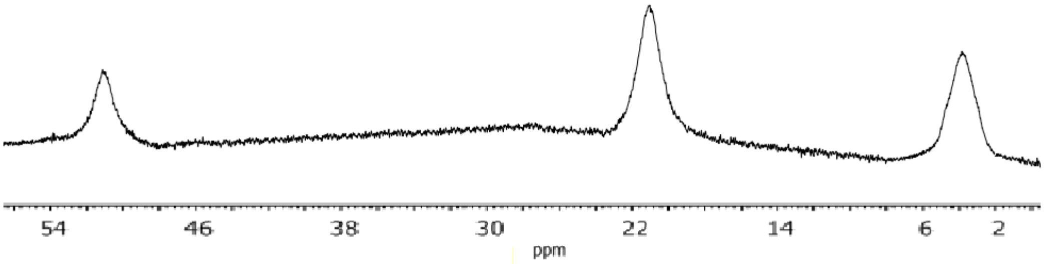


Figure S4: ^{11}B NMR (128 MHz, [d_6]benzene) spectrum of $[(Cp^*Ta)_2B_5H_{10}(C_6H_4CH_3)]$ **3**.

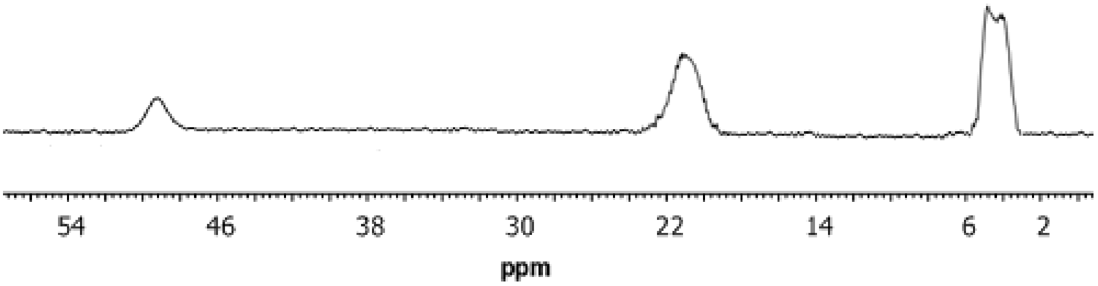


Figure S5: ^{11}B NMR (128 MHz, [d_6]benzene) spectrum of [$(Cp^{*}Ta)_2B_5H_{10}(C_6H_4Cl)$] **4**.

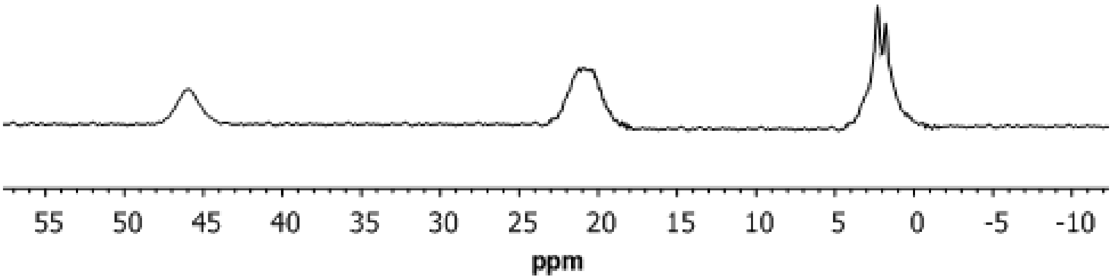


Figure S6: ^{11}B NMR (128 MHz, [d_6]benzene) spectrum of [$(Cp^{*}Ta)_2B_5H_{10}(C_4H_3S)$] **5**.

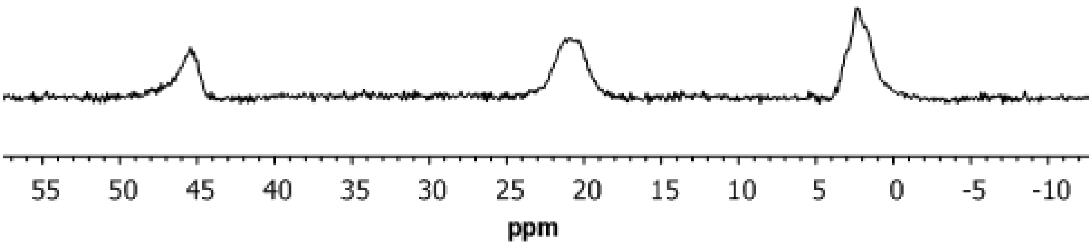


Figure S7: ^{11}B NMR (128 MHz, [d_6]benzene) spectrum of [$(Cp^*Ta)_2B_5H_{10}(C_4H_3NH)$] **6**.

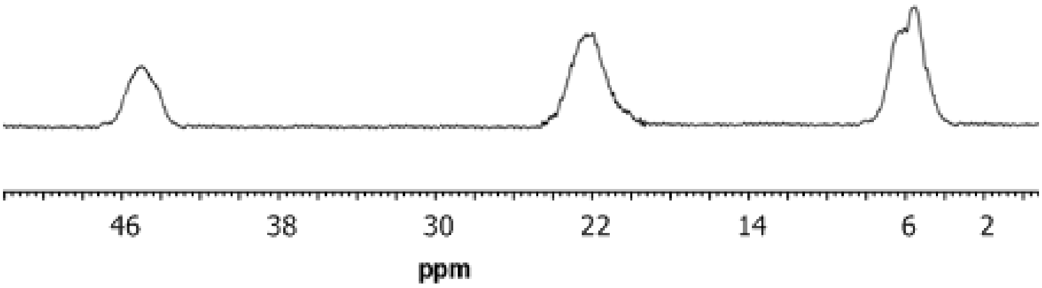


Figure S8: ^{11}B NMR (128 MHz, [d_6]benzene) spectrum of [$(Cp^*Ta)_2B_5H_{10}(C_6H_4Br)$] .

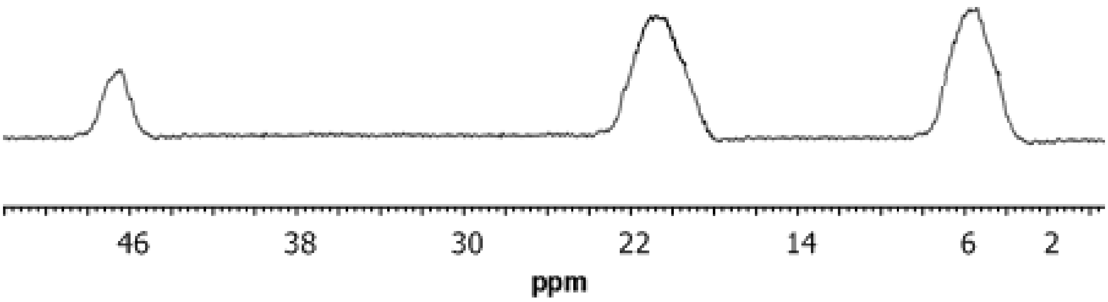


Figure S9: ^{11}B NMR (128 MHz, [*d*$_6$]benzene) spectrum of $[(Cp^*Ta)_2B_5H_{10}(C_6H_4I)]$.

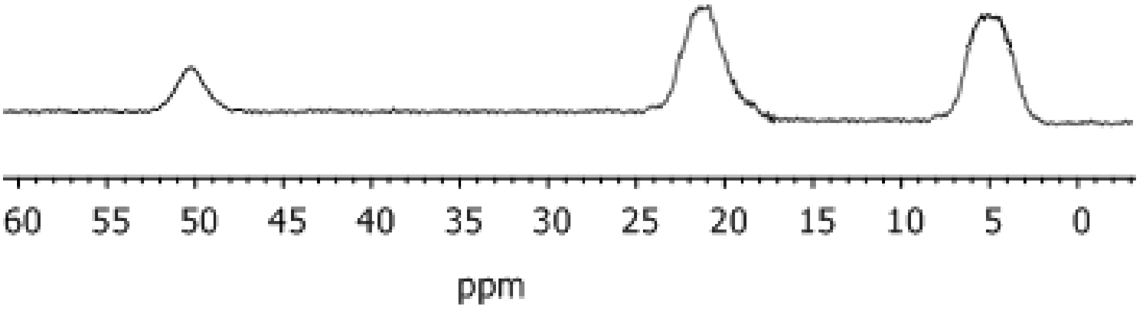


Figure S10: ^{11}B NMR (128 MHz, [*d*$_6$]benzene) spectrum of $[(Cp^*Ta)_2B_5H_{10}(C_6H_3Me_2)]$.

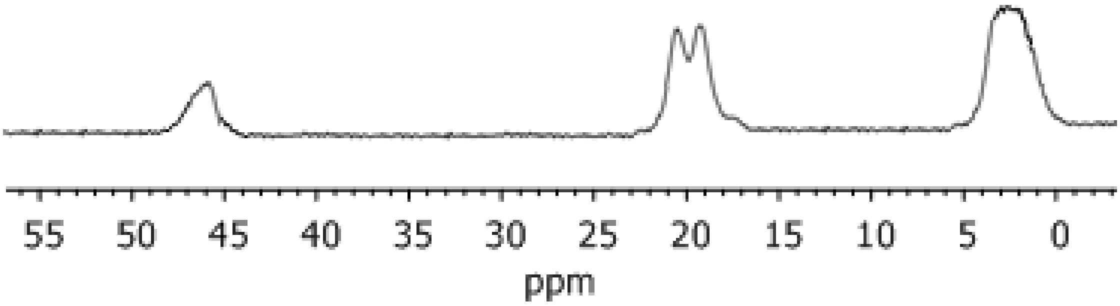


Figure S11: ^{11}B NMR (128 MHz, [d_6]benzene) spectrum of [$(Cp^*Ta)_2B_5H_{10}(C_4H_2MeS)$] .

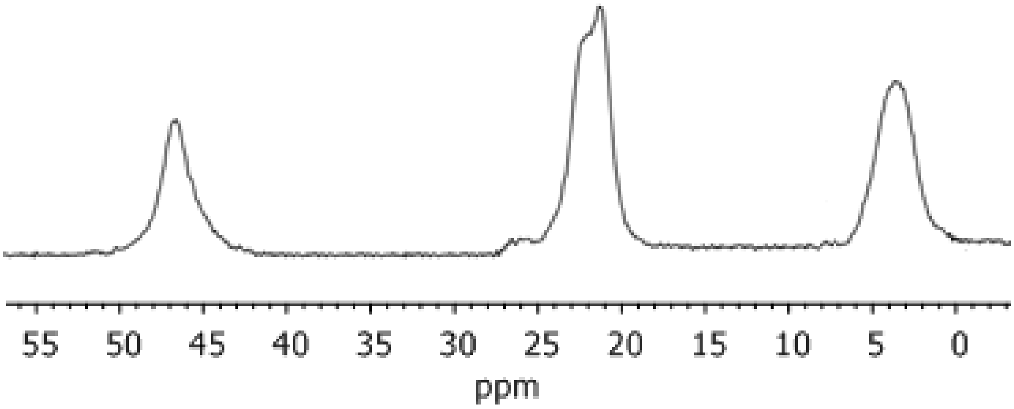


Figure S12: ^{11}B NMR (128 MHz, [d_6]benzene) spectrum of [$(Cp^*Ta)_2B_5H_{10}(C_4H_2IS)$] .

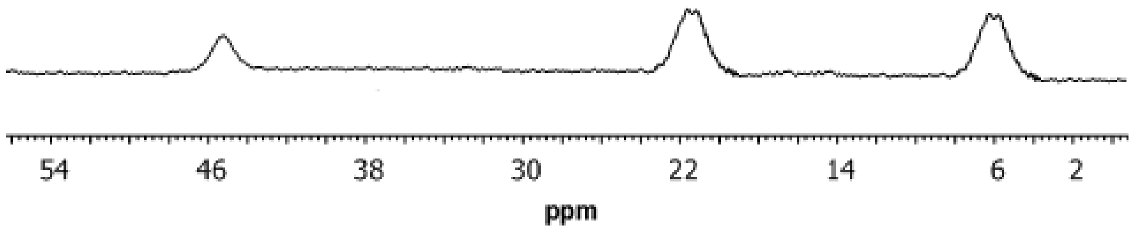


Figure S13: ^{11}B NMR (128 MHz, [d_6]benzene) spectrum of [$(Cp^*Ta)_2B_5H_{10}(C_4HMe_2S)$] .

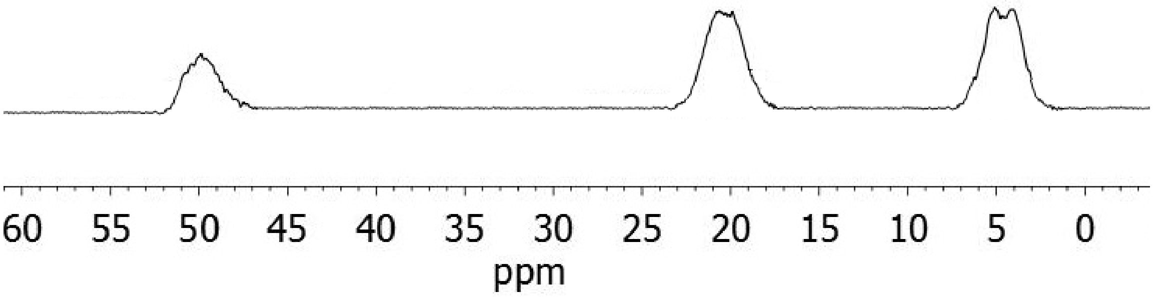


Figure S14: ^{11}B NMR (128 MHz, [d_6]benzene) spectrum of [$(Cp^*Ta)_2B_5H_{10}(C_4HBr_2S)$] .

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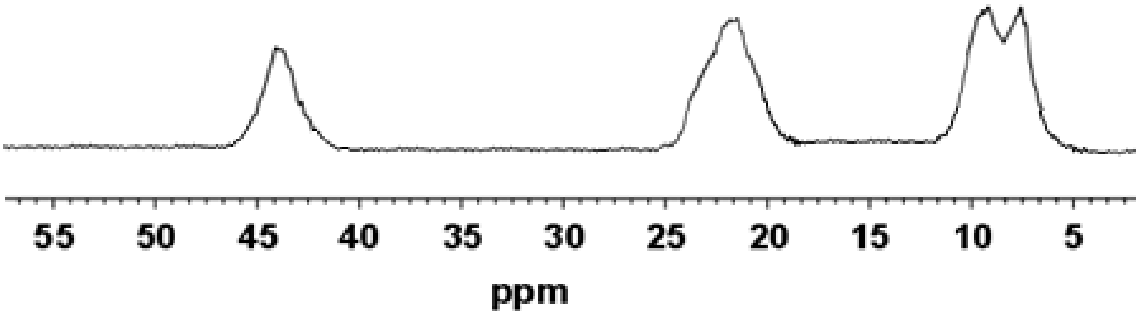

Figure S15: ^{11}B NMR (128 MHz, [d_6]benzene) spectrum of [$(Cp^*Ta)_2B_5H_{10}(C_4HMe_2NH)$] .

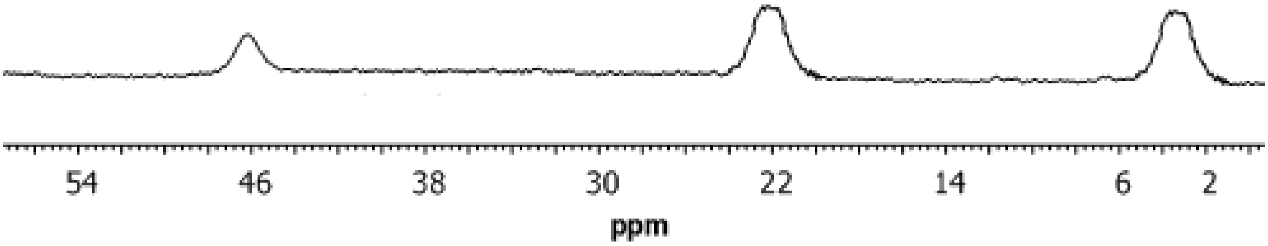

Figure S16: ^{11}B NMR (128 MHz, [d_6]benzene) spectrum of [$(Cp^*Ta)_2B_5H_{10}\{C_4H_3NSi(i Pr)_3\}$] .

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