

Syntheses of Platinum(IV) Aryl Dihydride Complexes via Arene C–H Bond Activation

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Summary: $Tp'PtMeH_2$ (**1**) reacts with substoichiometric amounts of $B(C_6F_5)_3$ in aromatic solvents to yield platinum(IV) aryl dihydride complexes via borane-induced reductive elimination of methane from **1** and subsequent C–H activation of the aromatic solvent.

Introduction

Platinum(IV) alkyl hydride complexes of the general formula $TpPt(R)(R')H^{1-8}$ [Tp = hydridotris(pyrazolyl)borate; Tp' = hydridotris(3,5-dimethylpyrazolyl)borate;⁹ R, R' = combinations of alkyl, hydride, and aryl groups] have been extensively studied in the context of C–H bond activation at platinum.^{10–15} Noteworthy in particular are the syntheses of stable hydrido(dialkyl)platinum(IV) complexes via oxidative addition of alkanes to the $[Tp'Pt(II)Me]$ fragment, demonstrated by Wick and Goldberg.⁶ The hapticity of the Tp' ligand is changed from κ^2 in the platinum(II) species, which was obtained by methide abstraction from $[Tp'Pt(II)Me_2]^-$ by $B(C_6F_5)_3$,^{16,17} to κ^3 in the platinum(IV) product. Reductive elimination of R–H from octahedral Pt(IV), which has been demonstrated to occur from a five-coordinate intermediate generated by ligand dissociation,^{18–28} is thus prevented.

Reductive elimination of methane from $Tp'PtMe_2H$ requires high temperatures and is presumably initiated by dissociation of one of the pyrazole rings. Thermolysis

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Table 1. List of the Different Isomers of Complexes 2–6

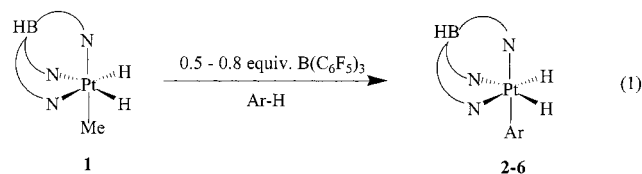
complex	Ar	$\delta(Pt-H)/ppm$	isomer	isomer ratio
2	Ph	–18.65		single isomer
3a	tol	–18.79	3-methyl	2
3b	tol	–18.81	4-methyl	1
3c	tol	–19.09	2-methyl	0.2
4	<i>o</i> -xyl	–18.83	3,4-dimethyl	single isomer
5a	<i>m</i> -xyl	–18.83	3,5-dimethyl	1
5b	<i>m</i> -xyl	–19.13	2,4-dimethyl	trace
6	<i>p</i> -xyl	–19.16	2,5-dimethyl	single isomer

of $Tp'PtMe_2H$ in benzene leads to the formation of $Tp'PtPh_2H$ via double reductive elimination of methane with subsequent C–H activation of the solvent.²⁹ The observation that substoichiometric amounts of a Lewis acid such as $B(C_6F_5)_3$ ³⁰ catalyzed the transformation at room temperature in seconds prompted us to investigate this reaction as a route to new platinum(IV) compounds.³¹ We report here the syntheses of several platinum(IV) aryl dihydrides from $Tp'PtMe_2H$ (**1**) via $B(C_6F_5)_3$ -induced methane elimination and subsequent aromatic C–H activation.

Results and Discussion

Reaction of the methyldihydride complex **1** with substoichiometric amounts of $B(C_6F_5)_3$ in different aromatic solvents (benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene), removal of volatiles, chromatography of the resulting residue on alumina, and recrystallization from pentane result in the formation of the platinum(IV) aryl dihydride complexes **2–6** as white, air-stable powders in moderate to good yields [eq 1 and Table 1]. Methane

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evolution is observed during the reaction, as verified by NMR scale experiments.

The solution IR spectrum of $\text{Tp}'\text{Pt}(\text{C}_6\text{H}_5)(\text{H})_2$, **2** (hexanes), shows a sharp absorption at 2524 cm^{-1} for the B–H stretch of the Tp' ligand, indicative of a κ^3 coordination mode.³² A single sharp absorption at 2262 cm^{-1} is seen for the Pt–H stretches, suggesting small vibrational coupling between the hydride ligands.^{4,8,33,34} Solution IR data for the other aryl dihydrides **3–6** are identical. The ^1H NMR spectrum of **2** displays a 2:1 pattern for the resonances of the Tp' ligand, indicative of mirror symmetry, and the hydrides resonate at -18.65 ppm ($^1J_{\text{Pt-H}} = 1280\text{ Hz}$). Rotation of the phenyl ring can be frozen out at low temperature; doublets are observed for the two ortho protons of the platinum-bound phenyl ring at 7.61 ppm ($^3J_{\text{Pt-H}} = 77\text{ Hz}$) and 6.47 ppm ($^3J_{\text{Pt-H}} = 40\text{ Hz}$). The large chemical shift difference can be explained by assuming a geometry in which the ortho proton at 6.47 ppm lies in the shielded area between two pyrazole rings.

The ^1H NMR spectrum of $\text{Tp}'\text{Pt}(\text{tol})(\text{H})_2$ (**3**) displays a signal pattern indicative of three tolyl regioisomers as evidenced by the presence of three distinct hydride resonances. The meta-activated tolyl complex **3a** and the para-activated tolyl complex **3b** are present in about a 2:1 ratio. We tentatively assign the third and minor product to the ortho-activated tolyl species **3c**. Thus, C–H activation of the meta and para C–H bonds of toluene occurs in an almost statistical ratio, while ortho activation is disfavored because of steric hindrance.³⁵ Rotation of the tolyl ring can be frozen out at low temperature. This leads to a complex signal pattern in the aromatic region of the ^1H NMR spectrum because of additional rotamers present in solution. We were able to assign all four species (two rotamers of **3a**, **3b**, and **3c**) by comparing the aromatic region with the aromatic regions of the xylyl spectra (vide infra) and by supplementing the ^1H NMR data with a correlation spectrum. Thus, complex **3a** exists as a mixture of rotamers in about a 2:1 ratio, the major rotamer having the meta-methyl group oriented away from the Tp' ligand. This result is analogous to the result obtained in the case of *o*-xylylene activation (vide infra). Both the fully assigned aromatic region of the low-temperature ^1H NMR spectrum and the correlation spectrum are included in the Supporting Information.

Since toluene activation favors meta and para positions, the prognosis for single isomer products from the three xylenes deserved investigation. Discounting ortho activation, the two ring positions available for C–H activation in *o*-xylylene are equivalent while *m*-xylylene should activate preferentially at only one site [Figure

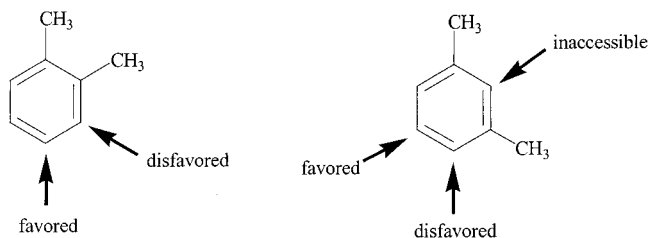


Figure 1. Accessible Sites for C–H activation in *o*- and *m*-xylylene.

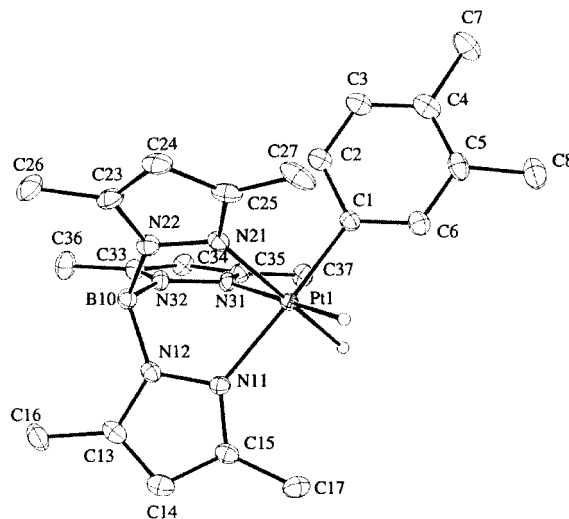


Figure 2. ORTEP diagram of $\text{Tp}'\text{Pt}(\text{o-xylyl})(\text{H})_2$, **4**. Ellipsoids are drawn with 50% probability. Selected bond distances (Å) and angles (deg) are the following: Pt1–C1 2.033(6), Pt1–N11 2.132(5), Pt1–N21 2.145(5), Pt1–N31 2.149(4); C1–Pt1–N11 177.46(22), C1–Pt1–N21 93.40(23), C1–Pt1–N31 93.49(20), N11–Pt1–N21 84.83(19), N11–Pt1–N31 84.65(17), N21–Pt1–N31 88.80(19), Pt1–C1–C2 118.2(5), Pt1–C1–C6 124.1(5).

1]. Likewise C–H activation of *p*-xylylene should yield only one product (of necessity metalation can only occur ortho to a methyl group) because of equivalence of all four aromatic C–H bonds.

Reaction of the methyl dihydride complex **1** with $\text{B}(\text{C}_6\text{F}_5)_3$ in *o*-xylylene leads to the formation of complex **4** in 44% isolated yield; a C–H bond para to one and meta to the other methyl group has been activated. The ^1H NMR spectrum of **4** displays a hydride resonance at -18.87 ppm ($^1J_{\text{Pt-H}} = 1290\text{ Hz}$). Two xylyl rotamers can be frozen out in a 1:1.8 ratio upon cooling an NMR sample to 253 K ; the major rotamer has the meta-methyl group pointed away from the methyl groups of the Tp' ligand.

To support the spectroscopic evidence, a single crystal of the *o*-xylyl dihydride **4**, obtained by slow evaporation of a methylene chloride solution, was subjected to X-ray structural analysis; an ORTEP diagram is shown in Figure 2. The hydride ligands on platinum could not be located in the difference Fourier map and were placed in calculated positions. As evident from the ORTEP diagram, the solid-state structure of complex **4** is almost perfectly octahedral. The xylyl ligand exerts about the same trans influence as the hydride ligands, so the Pt–N distance trans to the xylyl ligand of 2.132(5) Å is only marginally shorter (0.01 Å) than the Pt–N distances of 2.145(5) and 2.149(4) Å trans to the hydride ligands. The Pt–C bond length of 2.033(6) Å is similar

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to those in other platinum(IV) aryl complexes.^{36–40} The solid-state structure of **4** supports the assignment of the low-temperature NMR solution structure; the xylyl plane bisects the N21–Pt1–N31 angle, thus placing the proton on C2 between two pyrazole rings. One small geometrical peculiarity should be pointed out: the Pt1–C1–C2 angle of 118.2(5)° is distinctly smaller than the Pt1–C1–C6 angle of 124.1(5)°. Cauty and co-workers have reported a similar, although smaller, effect in the crystal structure of TpPt(p-tol)₂OH.³⁶ The fact that the xylyl ligand is tilted slightly toward the Tp' ligand may be the cause of the dramatic difference in platinum coupling to the two ortho protons: 40 Hz for H_o on C2 and 79 Hz for H_o on C6 in the major rotamer.

Tp'Pt(m-xylyl)(H)₂ (**5**) has been isolated in 51% yield; the C–H bond that is meta to both methyl groups has been activated.⁴¹ Rotation of the meta-xylyl ring can be frozen out at low temperature; three singlets are observed for the three protons of the platinum-bound xylyl ring at 7.30 ppm (³J_{Pt–H} = 81 Hz), 6.53 ppm, and 6.20 ppm (³J_{Pt–H} = 41 Hz). Again, the xylyl proton that is placed between the pyrazole rings is shielded and resonates upfield from the other two protons.

The ¹H NMR spectrum of the *p*-xylyl dihydride **6**, the only product from the reaction of **1** with B(C₆F₅)₃ in *p*-xylene, is unique in that no dynamic behavior is evident at room temperature. A hydride resonance at –19.16 ppm (¹J_{Pt–H} = 1279 Hz) and a singlet at 6.50 ppm (³J_{Pt–H} = 42 Hz) upfield from the other aromatic signals are observed, indicating that the ortho-methyl group is proximal to the platinum-bound hydride ligands.

The mechanism of the borane-induced methane elimination from the methyldihydride complex **1** is currently unknown. One possibility would be borane-assisted dissociation of one of the pyrazole rings, in analogy to our previous protonation results.³ This would generate the necessary open coordination site for methane elimination,²⁸ and subsequent C–H activation would yield, after borane dissociation, the final product. This mechanistic pathway is in agreement with the experimental observation that only substoichiometric amounts of the borane Lewis acid are needed.⁴²

In summary, we have isolated and characterized several platinum(IV) aryl dihydride complexes via an arene C–H bond activation route.

Experimental Section

Materials and Methods. Reactions were performed under an atmosphere of dry nitrogen or argon using standard Schlenk and drybox techniques. Argon and nitrogen were purified by passage through columns of BASF R3-11 catalyst

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(41) A second hydride species (–19.13 ppm, ca. 3% relative to **5a**) is present after chromatography of the crude product. We believe that this species is the product of C–H activation ortho to one and para to the other methyl group in *m*-xylene.

(42) We cannot exclude the possibility that the reaction is catalyzed by small amounts of protic acid generated from B(C₆F₅)₃ and water.

and 4 Å molecular sieves. All glassware was oven-dried prior to use. Toluene, methylene chloride, pentanes, and hexanes were purified under an argon atmosphere by passage through a column packed with activated alumina.⁴³ Benzene, *o*-xylene, *m*-xylene, and *p*-xylene (Aldrich, sure seal) were used as purchased. Deuterated methylene chloride was vacuum-transferred from calcium hydride and degassed by several freeze–pump–thaw cycles.

Tp'Pt(CH₃)(H)₂ was synthesized according to a modification of the published procedure for the Tp analogue.^{8,44} B(C₆F₅)₃ was used as obtained from Strem.

¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. ¹H NMR and ¹³C NMR chemical shifts were referenced to residual ¹H and ¹³C signals of the deuterated solvents. Infrared spectra were recorded on an ASI ReactIR 1000. Chemical analyses were performed by Atlantic Microlabs of Norcross, GA.

General Procedure for the Syntheses of Tp'PtAr(H)₂ Complexes (2–6). In a typical experiment, 0.10 g of Tp'Pt-(CH₃)(H)₂ (**1**) and 75 mg of B(C₆F₅)₃ were weighed into a 100 mL Schlenk flask. Then about 15 mL of the aromatic solvent was added via syringe through the septum. Gas evolution occurred upon solvent addition. The reaction mixture was stirred for ca. 20 min. Small amounts of an unknown pink oil were present in the flask. After solvent removal and trituration with pentanes, the residue was chromatographed on alumina (CH₂Cl₂ as eluent) and a white solid was obtained, which was recrystallized from pentanes at –30 °C and extensively dried.

Tp'Pt(C₆H₅)(H)₂ (2**).** Tp'Pt(CH₃)₂H (0.15 g, 0.29 mmol) and 0.075 g of B(C₆F₅)₃ (0.15 mmol) were combined as described above with 15 mL of anhydrous C₆H₆. Yield: 115 mg (69%). IR (hexanes): ν_{BH} = 2524 cm^{–1}, ν_{PtH} = 2262 cm^{–1}. ¹H NMR (CD₂Cl₂, 193 K, δ): 7.61 (d, 1H, ³J_{H–H} = 5.5 Hz, ³J_{Pt–H} = 77 Hz, Pt–Ph, H_o), 6.87, 6.70 (m, 2H, 1H, Pt–Ph, H_m and H_p), 6.47 (d, 1H, ³J_{H–H} = 7.7 Hz, ³J_{Pt–H} = 40 Hz, Pt–Ph, H_o), 5.84, 5.80 (s, 1H, 2H, Tp'CH), 2.37, 2.30, 2.14, 1.54 (s, 6H, 3H, 3H, 6H, Tp'CH₃), –18.65 (s, 2H, ¹J_{Pt–H} = 1280 Hz, Pt–H). ¹³C NMR (CD₂Cl₂, 293 K, δ): 150.1 (2C, J_{Pt–C} = 21 Hz, Tp'CCH₃), 150.0 (1C, J_{Pt–C} = 25 Hz, Tp'CCH₃), 145.1, 144.6 (1C, 2C, Tp'CCH₃), 127.2 (J_{Pt–C} = 56 Hz, Pt–Ph), 123.2 (J_{Pt–C} = 10.7 Hz, Pt–Ph), 122.2 (¹J_{Pt–C} = 815 Hz, Pt–Ph, C_{ipso}), 106.2 (2C, ³J_{Pt–C} = 9.7 Hz, Tp'CH), 105.6 (1C, ³J_{Pt–C} = 9.7 Hz, Tp'CH), 16.0 (1C, J_{Pt–C} = 33 Hz, Tp'CH₃), 14.4 (2C, J_{Pt–C} = 18.4 Hz, Tp'CH₃), 12.7 (Tp'CH₃). Anal. Calcd for C₂₁H₂₉N₆BPt: C, 44.14; H, 5.12; N, 14.70. Found: C, 44.27; H, 5.17; N, 14.41.

Tp'Pt(tol)(H)₂ (3**).** Tp'Pt(CH₃)₂H (0.10 g, 0.20 mmol) and 0.075 g of B(C₆F₅)₃ (0.15 mmol) were combined as described above with 15 mL of dry toluene. Yield: 65 mg (57%). IR (hexanes): ν_{BH} = 2524 cm^{–1}, ν_{PtH} = 2262 cm^{–1}. ¹H NMR (CD₂Cl₂, 293 K, δ): 7.55, 6.71, 6.66, 6.40 (br, Pt-tol), 5.84, 5.82 (s, 1H, 2H, Tp'CH), 2.44, 2.37, 2.21, 1.66 (s, 6H, 3H, 3H, 6H, Tp'CH₃, tol-CH₃ too broad), –18.79, –18.81, –19.09 (s, 2H, ca. 2:1:0.2, ¹J_{Pt–H} = 1290 Hz, Pt–H). ¹³C NMR (CD₂Cl₂, 293 K, δ): 150.2 (2C, J_{Pt–C} = 21 Hz, Tp'CCH₃), 150.0 (1C, J_{Pt–C} = 25 Hz, Tp'CCH₃), 145.1, 144.5 (1C, 2C, Tp'CCH₃), 136.3 (J_{Pt–C} = 58 Hz, Pt-tol), 132.3 (J_{Pt–C} = 8.7 Hz, Pt-tol), 128.2 (J_{Pt–C} = 57 Hz, Pt-tol), 126.9 (J_{Pt–C} = 55 Hz, Pt-tol), 124.0 (J_{Pt–C} = 8.7 Hz, Pt-tol), 122.0 (¹J_{Pt–C} = 812 Hz, Pt-tol, C_{ipso}), 106.2 (2C, ³J_{Pt–C} = 9.5 Hz, Tp'CH), 105.5 (1C, ³J_{Pt–C} = 9.7 Hz, Tp'CH), 21.4 (tol-CH₃), 16.0 (1C, J_{Pt–C} = 33 Hz, Tp'CH₃), 14.5 (2C, J_{Pt–C} = 17.3 Hz, Tp'CH₃), 12.7 (Tp'CH₃). Anal. Calcd for C₂₁H₂₉N₆BPt: C, 45.13; H, 5.34; N, 14.35. Found: C, 45.46; H, 5.36; N, 14.04.

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(44) A slurry of Tp'PtMe(CO)₃ in a basic 1:1 acetone/water mixture was heated to a light reflux for several hours, and the methyldihydride complex **1** was filtered off. Experimental and spectroscopic data for **1** will be published elsewhere. Reinartz, S.; Baik, M.-H.; White, P.; Brookhart, M.; Templeton, J. L. Manuscript submitted for publication.

Tp'Pt(3,4-Me₂C₆H₃)(H)₂ (4). Tp'Pt(CH₃)₂H (0.12 g, 0.24 mmol) and 0.085 g of B(C₆F₅)₃ (0.10 mmol) were combined as described above with 12 mL of anhydrous *o*-xylene. Yield: 62 mg (44%). IR (hexanes): $\nu_{\text{BH}} = 2524 \text{ cm}^{-1}$, $\nu_{\text{PtH}} = 2262 \text{ cm}^{-1}$. ¹H NMR (CD₂Cl₂, 293 K, δ): 7.45, 6.55, 6.25 (br, 1H each, Pt-*xy*l), 5.84, 5.81 (s, 1H, 2H, Tp'CH), 2.44, 2.37, 2.20, 1.66 (s, 6H, 3H, 3H, 6H, Tp'CH₃), 2.15 (br, 6H, CH₃ on Pt-*xy*l), -18.87 (s, 2H, ¹J_{Pt-H} = 1290 Hz, Pt-*H*). ¹H NMR (CD₂Cl₂, 253 K, δ): 7.44 (s, ca. 0.6 H, ³J_{Pt-H} = 79 Hz, Pt-*xy*l, *H_o* major), 7.33 (d, ca. 0.4 H, ³J_{H-H} = 6.8 Hz, ³J_{Pt-H} = 41 Hz, Pt-*xy*l, *H_o* minor), 6.65 (d, ca. 0.4 H, ³J_{H-H} = 6.8 Hz, Pt-*xy*l, *H_m* minor), 6.49 (d, ca. 0.6 H, ³J_{H-H} = 6.8 Hz, Pt-*xy*l, *H_m* major), 6.35 (s, ca. 0.4 H, ³J_{Pt-H} = 38 Hz, Pt-*xy*l, *H_o* minor), 6.21 (d, ca. 0.6 H, ³J_{H-H} = 6.8 Hz, ³J_{Pt-H} = 40 Hz, Pt-*xy*l, *H_o* major), 5.84, 5.80 (s, 1H, 2H, Tp'CH), 2.41, 2.34, 2.18, 2.12, 1.63 (s, 6H, 3H, 6H, 3H, 6H, Tp'CH₃ and *xy*-CH₃), -18.83 (s, 2H, ¹J_{Pt-H} = 1286 Hz, Pt-*H*). ¹³C NMR (CD₂Cl₂, 293 K, δ): 150.1 (2C, J_{Pt-C} = 22 Hz, Tp'CCH₃), 149.9 (1C, J_{Pt-C} = 25 Hz, Tp'CCH₃), 145.0, 144.5 (1C, 2C, Tp'CCH₃), 135.0 (J_{Pt-C} = 62 Hz, Pt-*xy*l), 130.9 (J_{Pt-C} = 9.7 Hz, Pt-*xy*l), 128.4 (J_{Pt-C} = 53 Hz, Pt-*xy*l), 118.3 (Pt-*xy*l), 106.1 (2C, ³J_{Pt-C} = 10.7 Hz, Tp'CH), 105.5 (1C, ³J_{Pt-C} = 9.7 Hz, Tp'CH), 19.5, 19.1 (CH₃ on Pt-*xy*l), 16.0 (1C, J_{Pt-C} = 33 Hz, Tp'CH₃), 14.5 (2C, J_{Pt-C} = 17.4 Hz, Tp'CH₃), 12.69, 12.65 (2C, 1C, Tp'CH₃). Anal. Calcd for C₂₃H₃₃N₆BPT: C, 46.08; H, 5.55; N, 14.01. Found: C, 46.47; H, 5.49; N, 13.55.

Tp'Pt(3,5-Me₂C₆H₃)(H)₂ (5). Tp'Pt(CH₃)₂H (0.07 g, 0.14 mmol) and 0.05 g of B(C₆F₅)₃ (0.10 mmol) were combined as described above with 10 mL of anhydrous *m*-xylene. Yield: 42 mg (51%). IR (hexanes): $\nu_{\text{BH}} = 2524 \text{ cm}^{-1}$, $\nu_{\text{PtH}} = 2262 \text{ cm}^{-1}$. ¹H NMR (CD₂Cl₂, 253 K, δ): 7.30 (s, 1H, ³J_{Pt-H} = 81 Hz, Pt-*xy*l, *H_o*), 6.53 (s, 1H, Pt-*xy*l, *H_p*), 6.20 (s, 1H, ³J_{Pt-H} = 41 Hz, Pt-*xy*l, *H_o*), 5.84, 5.80 (s, 1H, 2H, Tp'CH), 2.41, 2.34, 2.17, 1.63 (s, 6H, 3H, 3H, 6H, Tp'CH₃), 2.20, 1.94 (s, 3H each, slightly broad, CH₃ on Pt-*xy*l), -18.83 (s, 2H, ¹J_{Pt-H} = 1287 Hz, Pt-*H*). ¹³C NMR (CD₂Cl₂, 253 K, δ): 149.7 (2C, J_{Pt-C} = 21 Hz, Tp'CCH₃), 149.5, 144.8, 144.3 (1C, 1C, 2C, Tp'CCH₃), 141.9, 135.7, 135.6 (Pt-*xy*l), 133.5 (J_{Pt-C} = 17.4 Hz, Pt-*xy*l), 124.6 (J_{Pt-C} = 9.7 Hz, Pt-*xy*l), 121.5 (¹J_{Pt-C} = 808 Hz, C_{ipso}, Pt-*xy*l), 105.8 (2C, ³J_{Pt-C} = 9.7 Hz, Tp'CH), 105.2 (1C, ³J_{Pt-C} = 9.7 Hz, Tp'CH), 21.05, 20.98 (CH₃ on Pt-*xy*l), 15.8 (1C, J_{Pt-C} = 32 Hz, Tp'CH₃), 14.3 (2C, J_{Pt-C} = 17.4 Hz, Tp'CH₃), 12.6, 12.5 (2C, 1C, Tp'CH₃). Anal. Calcd for C₂₃H₃₃N₆BPT: C, 46.08; H, 5.55; N, 14.01. Found: C, 46.18; H, 5.52; N, 13.80.

Tp'Pt(2,5-Me₂C₆H₃)(H)₂ (6). Tp'Pt(CH₃)₂H (0.12 g, 0.24 mmol) and 0.09 g of B(C₆F₅)₃ (0.18 mmol) were combined as

described above with 15 mL of anhydrous *p*-xylene. Yield: 66 mg (46%). IR (hexanes): $\nu_{\text{BH}} = 2524 \text{ cm}^{-1}$, $\nu_{\text{PtH}} = 2262 \text{ cm}^{-1}$. ¹H NMR (CD₂Cl₂, 293 K, δ): 6.94 (d, 1H, ³J_{H-H} = 7.6 Hz, ³J_{Pt-H} = 23 Hz, Pt-*xy*l, *H_m*), 6.66 (d, 1H, ³J_{H-H} = 7.6 Hz, Pt-*xy*l, *H_p*), 6.50 (s, 1H, ³J_{Pt-H} = 42 Hz, Pt-*xy*l, *H_o*), 5.86 (s, 1H, ⁴J_{Pt-H} = 7.7 Hz, Tp'CH), 5.81 (s, 2H, Tp'CH), 2.45, 2.39, 2.26, 1.95, 1.56 (s, 9H, 3H, 3H, 3H, 6H, Tp'CH₃ and CH₃ on Pt-*xy*l), -19.16 (s, 2H, ¹J_{Pt-H} = 1279 Hz, Pt-*H*). ¹³C NMR (CD₂Cl₂, δ): 150.0 (1C, J_{Pt-C} = 27 Hz, Tp'CCH₃), 149.9 (2C, J_{Pt-C} = 20 Hz, Tp'CCH₃), 144.9, 144.5 (1C, 2C, Tp'CCH₃), 140.1 (J_{Pt-C} = 58 Hz, Pt-*xy*l, CCH₃), 137.7 (J_{Pt-C} = 27 Hz, Pt-*xy*l, CH), 132.9 (J_{Pt-C} = 35 Hz, Pt-*xy*l, CCH₃), 127.0 (J_{Pt-C} = 41 Hz, Pt-*xy*l, CH), 124.3 (J_{Pt-C} = 7.8 Hz, Pt-*xy*l, CH), 126.3 (¹J_{Pt-C} = 827 Hz, C_{ipso}, Pt-*xy*l), 106.1 (2C, ³J_{Pt-C} = 10.7 Hz, Tp'CH), 105.5 (1C, ³J_{Pt-C} = 10.7 Hz, Tp'CH), 32.7 (³J_{Pt-C} = 126 Hz, Pt-*xy*l, *o*-CH₃), 20.8 (Pt-*xy*l, *m*-CH₃), 15.9 (1C, J_{Pt-C} = 35 Hz, Tp'CH₃), 14.3 (2C, J_{Pt-C} = 18.4 Hz, Tp'CH₃), 12.8, 12.7 (2C, 1C, Tp'CH₃). Anal. Calcd for C₂₃H₃₃N₆BPT: C, 46.08; H, 5.55; N, 14.01. Found: C, 45.89; H, 5.23; N, 13.91.

Structural Data for 4. Crystals from CD₂Cl₂; C₂₃H₃₃N₆BPT, MW = 599.45; triclinic, space group *P* $\bar{1}$; *Z* = 2; *a* = 7.8819(3) Å, *b* = 9.8686(4) Å, *c* = 16.3539(6) Å; α = 74.229(1)°, β = 77.422(1)°, γ = 84.148(1)°; *V* = 1193.56(8) Å³; *D_c* = 1.668 Mg m⁻³; *T* = -100 °C; max 2θ = 60°; Mo K α radiation (λ = 0.710 73 Å); 5996 unique reflections were obtained and 5137 of these with *I* > 2.5 $\sigma(I)$ were used in the refinement. Data were collected on a Bruker SMART diffractometer using the ω scan method. For significant reflections: merging *R* value, 0.027; residuals, *R_F*, 0.039; *R_w*, 0.045 (significant reflections); GOF, 1.8552.

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Supporting Information Available: Complete crystallographic data for complex 4, ¹H NMR spectra (aryl region) of complex 2 at 193 and 313 K, and low-temperature correlation spectra and ¹H NMR spectra (aryl region) of complex 3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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