

# Barriers for Arene C–H Bond Activation in Platinum(II) $\eta^2$ -Arene Intermediates

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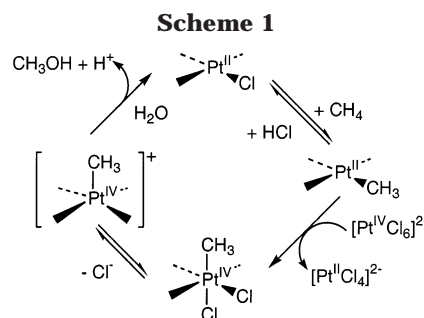
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Received July 8, 2002

Protonation of platinum(IV) complexes of the type  $\text{Tp}'\text{Pt}(\text{Ar})(\text{H})(\text{R})$  [ $\text{Tp}' = \text{hydridotris}(3,5\text{-dimethylpyrazolyl})\text{borate}$ ;  $\text{Ar} = \text{aryl}$ ;  $\text{R} = \text{H}, \text{C}_6\text{H}_5$ ] with  $[\text{H}(\text{OEt}_2)_2][\text{BAR}'_4]$  [ $\text{BAR}'_4 = \text{tetrakis}(3,5\text{-trifluoromethylphenyl})\text{borate}$ ] results in the formation of cationic platinum(II)  $\eta^2$ -arene complexes  $[\kappa^2\text{-}(\text{HTp}')\text{Pt}(\eta^2\text{-HAr})(\text{R})][\text{BAR}'_4]$  [ $\text{Ar} = \text{C}_6\text{H}_5, \text{R} = \text{H}$  (**2**);  $\text{Ar} = \text{MeC}_6\text{H}_4, \text{R} = \text{H}$  (**4**);  $\text{Ar} = 3,6\text{-Me}_2\text{C}_6\text{H}_3, \text{R} = \text{H}$  (**6**);  $\text{Ar} = \text{R} = \text{C}_6\text{H}_5$  (**8**)]. A barrier of 9.4 kcal/mol for platinum migration around the  $\eta^2$ -*p*-xylene ring was calculated for complex **6** at 183 K following variable-temperature NMR measurements. Eyring analysis of hydrogen exchange between the bound benzene and the hydride ligand for cationic benzene complex **2** indicates  $\Delta H^\ddagger = 11.7 \pm 0.5 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -3.8 \pm 2 \text{ cal mol}^{-1} \text{ K}^{-1}$ . This process is assumed to proceed via arene C–H oxidative addition to give the five-coordinate platinum(IV) phenyl dihydride intermediate **2a**. Isolation of ground state  $\eta^2$ -arene adducts with adjacent hydride ligands has allowed the barrier to oxidative addition for arene C–H bonds ( $\Delta G^\ddagger$ ) to be measured as 13.3 kcal/mol for the *p*-hydrogen and 13.6 kcal/mol for the *m*-hydrogens in the toluene adduct **4** and 14.2 kcal/mol for the *p*-xylene adduct **6**. Averaging of the environments for two  $\text{Tp}'$  arms is an NMR observable feature for the  $C_1$  symmetric  $\eta^2$ -benzene phenyl adduct **8**. This dynamic process, which presumably occurs via a five-coordinate platinum(IV) diphenyl hydride intermediate **8a** with  $C_s$  symmetry, allows the barrier for arene C–H oxidative addition to be calculated as 12.9 kcal/mol. Kinetic isotope effects for oxidative addition of the arene C–H(D) bond in the benzene hydride adduct **2** and the benzene phenyl adduct **8** were determined to be  $k_{\text{H}}/k_{\text{D}} = 3.0$  at 259 K and 4.7 at 241 K, respectively. These data provide insight into the energetics of arene C–H bond activation.

## Introduction

The study of C–H bond activation at platinum centers was first undertaken to elucidate the mechanism of the Shilov oxidation.<sup>1–3</sup> The proposed mechanism involves three steps: (1) electrophilic activation of an alkane C–H bond by Pt(II) to form a platinum(II)-alkyl species; (2) oxidation to a platinum(IV)-alkyl complex; (3) reductive elimination of R–X (X = Cl or OH) to release the functionalized alkane and Pt(II) catalyst (Scheme 1).<sup>4–11</sup>



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Much research has focused on the final two steps of the mechanism, oxidation and reductive elimination, whereas, less is known about the C–H activation step, which seems to control the overall reaction rate. Most of our current mechanistic understanding comes from investigations of the microscopic reverse of alkane activation, namely, reductive alkane elimination from platinum(IV) alkyl hydride complexes.<sup>12–14</sup>

Considerable evidence supports the hypothesis that the first step involves coordination of the alkane to the

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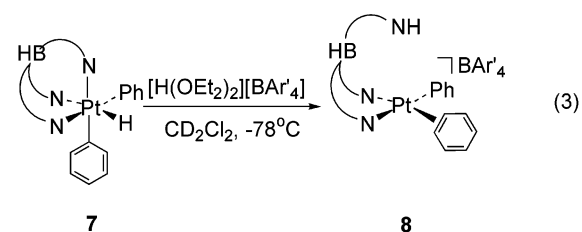
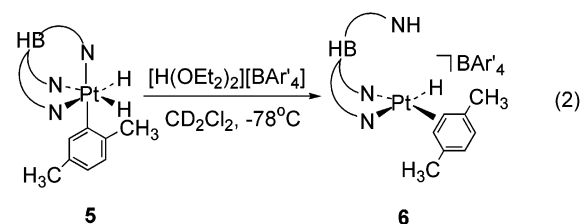
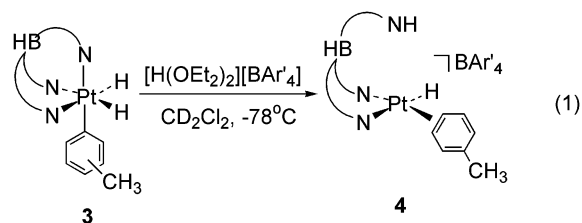
coordinatively unsaturated metal center and leads to two intermediates which are thought to interconvert rapidly: a  $\sigma$ -bound alkane complex  $\text{Pt}^{\text{II}}(\text{R}-\text{H})$  and a  $\text{Pt}^{\text{IV}}(\text{R})(\text{H})$  oxidative addition product.<sup>12,15,16</sup> The existence of these intermediates has been inferred from kinetic data; neither one has been observed directly. Although no platinum alkane complexes have been observed, Ball reported NMR spectroscopic observation of the rhenium alkane complex  $\text{CpRe}(\text{CO})_2(\text{cyclopentane})$ .<sup>17</sup> However, five-coordinate  $\text{Pt}(\text{IV})$  complexes  $[\text{PtMe}_3\{(\text{NArCMe})_2\text{CH}\}]$  [ $\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$ ]<sup>18</sup> and  $[\kappa^2\text{-(HTp')Pt}(\text{H})_2(\text{SiEt}_3)][\text{BAR}'_4]$ <sup>19</sup> [ $\text{Tp}' = \text{hydridotris}(3,5\text{-dimethylpyrazolyl})\text{borate}$ <sup>20</sup> and  $\text{BAR}'_4 = \text{tetrakis}(3,5\text{-trifluoromethylphenyl})\text{borate}$ ]<sup>21</sup> have recently been spectroscopically and structurally characterized. Direct observation of C–H bond activation at a neutral  $\text{Pt}(\text{II})$  center to form a stable platinum(IV) alkyl hydride complex was demonstrated by Goldberg and Wick.<sup>22</sup> Other electrophilic platinum systems for alkane activation have been described recently,<sup>3,23,24</sup> and one is capable of activating methane in aqueous solution,<sup>25</sup> thus resembling the original Shilov system.

Just as a  $\sigma$ -bound alkane complex is a putative intermediate in alkane activation,  $\eta^2$ -arene complexes are key intermediates in aromatic C–H bond activation.<sup>3,12,22,24–32</sup> Although arene C–H bonds ( $E_{\text{C-H}(\text{benzene})}^{\text{diss}} \approx 109 \text{ kcal mol}^{-1}$ )<sup>33</sup> are stronger than alkyl C–H bonds ( $E_{\text{methane}}^{\text{diss}} \approx 104 \text{ kcal mol}^{-1}$ ),<sup>33</sup> oxidative addition of an arene C–H bond to a metal center is often thermodynamically favored relative to alkane C–H oxidative addition, since metal–aryl bonds are generally significantly stronger than metal–alkyl bonds.<sup>34,35</sup> Arene activation is typically favored kinetically relative to alkane activation, too. The barrier for arene C–H bond activation is thought to be lowered by  $\pi$ -coordination of the arene to the metal center prior to oxidative addition.<sup>36</sup> Jones, Perutz, and co-workers measured a barrier

of 12.4 kcal/mol for arene C–H bond activation in a rhodium complex generated by photolysis of a  $\text{Rh}(\text{I})$  precursor.<sup>37,38</sup> The NMR characterization of a  $\text{Pt}(\text{II})$ -benzene adduct was reported by Bercaw and co-workers,<sup>26</sup> and isolation along with an X-ray structure of a  $\text{Pt}(\text{II}) \eta^2$ -benzene adduct was recently communicated.<sup>39</sup> Given the importance of C–H activation by platinum(II) reagents toward the functionalization of hydrocarbons, a study of additional platinum(II) arene adducts has been undertaken.

## Results and Discussion

**Synthesis of  $\eta^2$ -Arene Adducts.** Protonation of  $\text{Tp}'\text{Pt}(\text{C}_6\text{H}_5)(\text{H})_2$  (**1**) with  $[\text{H}(\text{OEt}_2)_2][\text{BAR}'_4]$  generates a cationic platinum(II)  $\eta^2$ -arene complex  $[\kappa^2\text{-(HTp')Pt}(\text{H})(\text{C},\text{C}-\eta^2\text{-C}_6\text{H}_6)][\text{BAR}'_4]$  (**2**).<sup>39</sup> When the neutral platinum(IV) aryl complex  $\text{Tp}'\text{Pt}(\text{Ar})(\text{H})(\text{R})$  [ $\text{Ar} = \text{MeC}_6\text{H}_4$ ,  $\text{R} = \text{H}$  (**3**);  $\text{Ar} = 2,5\text{-Me}_2\text{C}_6\text{H}_3$ ,  $\text{R} = \text{H}$  (**5**);  $\text{Ar} = \text{R} = \text{C}_6\text{H}_5$  (**7**)] is treated with 1.5 equiv of  $[\text{H}(\text{OEt}_2)_2][\text{BAR}'_4]$  in  $\text{CD}_2\text{Cl}_2$  at  $-78^\circ\text{C}$ , the solution turns pale yellow, indicative of protonation to form the cationic  $\eta^2$ -arene product  $[\kappa^2\text{-(HTp')Pt}(\text{C},\text{C}-\eta^2\text{-HAr})(\text{R})][\text{BAR}'_4]$  [ $\text{Ar} = \text{MeC}_6\text{H}_4$ ,  $\text{R} = \text{H}$  (**4**);  $\text{Ar} = 3,6\text{-Me}_2\text{C}_6\text{H}_3$ ,  $\text{R} = \text{H}$  (**6**);  $\text{Ar} = \text{R} = \text{C}_6\text{H}_5$  (**8**)], respectively (eqs 1–3). The spectroscopic features



of the toluene adduct **4**, *p*-xylene adduct **6**, and benzene phenyl adduct **8** are similar to those of the benzene hydride adduct **2** reported previously<sup>39</sup> (Table 1).

While the  $\eta^2$ -benzene adduct **2** remained fluxional at 143 K, migration of platinum around the arene ring can

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Arene C,C- $\eta^2$ -coordination is not necessarily involved in the bond activation process, see refs 30 and 31.

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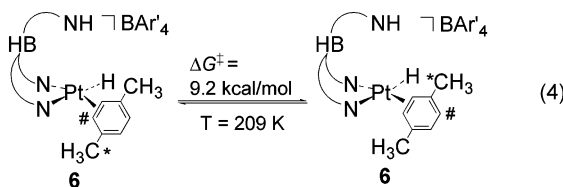
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**Table 1.** NMR Spectroscopic Data (in  $\text{CD}_2\text{Cl}_2$ ) for Complexes **2**, **4**, **6**, and **8**

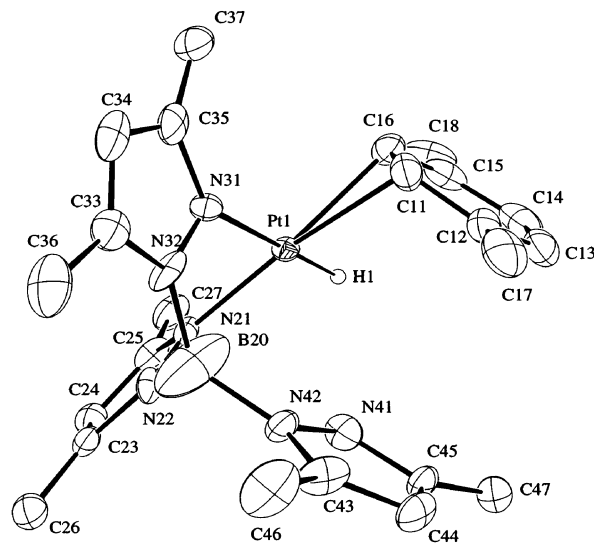
complex	R	arene	$T/K$	$\delta(\text{Pt-H})/\text{ppm}$ $^1J_{\text{Pt-H}}/\text{Hz}$	$\delta(\text{arene-H})$ ppm	$\delta(\text{arene-C})$ ppm
<b>2</b>	H	$\text{C}_6\text{H}_6$	193	-30.13 935	6.88 (6H)	115.3
<b>4</b>	H	$\text{MeC}_6\text{H}_5$	203	-29.79 950	6.87, 6.69 ( <i>o</i> ) 6.61, 6.49 ( <i>m</i> ) 6.55 ( <i>p</i> )	145.9 (CCH <sub>3</sub> ) 125.8, 113.6, 109.0, 104.9, 103.5 (CH) 21.5 (CH <sub>3</sub> )
<b>6</b>	H	<i>p</i> - $\text{Me}_2\text{C}_6\text{H}_4$	183	-29.82 960	6.70, 6.60, 6.54, 5.63	145.6, 143.7 (CCH <sub>3</sub> ) 127.8, 126.9 (CH) 84.9, 81.8 (Pt-CH) 21.0, 20.8 (CH <sub>3</sub> )
<b>8</b>	Ph	$\text{C}_6\text{H}_6$	203		6.85 (6H)	119.2

be frozen out for the *p*-xylene adduct **6** at low temperatures. At 183 K, distinct resonances are observed in the  $^1\text{H}$  NMR spectrum for each of the arene hydrogens. Even more compelling is the  $^{13}\text{C}$  NMR spectrum of **6**, where all six ring carbon atoms are differentiated. Carbon atoms at 84.9 and 81.8 ppm (positive in a DEPT-90 NMR spectrum) resonate upfield relative to the other four ring carbon atoms. Resonances at 127.8 and 126.9 ppm are also positive in the DEPT-90 NMR spectrum, indicating that they are the remaining two CH-carbon atoms of the ring. Chemical shift values identify the upfield signals as due to carbons directly bound to platinum, while the CH carbon signals near 127 and 128 ppm are not directly bound to platinum. At temperatures above 233 K, the platinum center traverses the coordinated *p*-xylene ring rapidly along the C–C double bonds so that one signal results for the two aryl methyl groups, and two resonances are evident for the four aryl hydrogens in the  $^1\text{H}$  NMR spectrum. The observed coalescence of the methyl groups is indicative of double-bond migration on the same face of the arene. In contrast, a face flipping dynamic process would interchange ring hydrogens in a pairwise manner while the methyl groups would remain distinct. One aryl resonance appears as a doublet ( $^3J_{\text{H-H}} = 5$  Hz) with broad platinum satellites ( $^2J_{\text{Pt-H}} = 32$  Hz). A barrier ( $\Delta G^\ddagger$ ) of 9.2 kcal/mol for migration of platinum around the *p*-xylene ring was calculated at  $T_c = 209$  K (eq 4).



Evidence for double migration was also observed by Whitesides and co-workers in their proposed (bisphosphine)( $\eta^2$ -benzene)platinum(0) intermediate.<sup>40</sup> In contrast, double-bond migration in the  $\text{Cp}^*\text{Rh}(\text{L})(\eta^2\text{-arene})$  system, extensively studied by Jones and Feher, is higher in energy than oxidative addition to form the aryl hydride.<sup>35</sup>

Colorless crystals of the *p*-xylene adduct **6** were grown from a concentrated methylene chloride solution layered with pentane at  $-30$  °C. Single-crystal X-ray structural analysis provided the ORTEP diagram of **6** shown in Figure 1. The hydride ligand on platinum was not

**Figure 1.** ORTEP diagram of  $[\kappa^2\text{-(HTp)Pt(H)(}\eta^2\text{-C}_6\text{H}_4\text{-3,6-(CH}_3)_2\text{)]}[\text{BAR}'_4]$  (**6**). Ellipsoids are drawn at the 50% probability level, and the  $\text{BAR}'_4$  counterion is omitted for clarity.

located in the difference Fourier map; it is placed in a calculated position. A disorder phenomenon is evident in the X-ray structure where the boron site is composed of 87% B and 13% Pt and vice versa for the platinum site (see the Supporting Information). Note that the arene ring and the protonated pyrazole ring are parallel to one another, creating a “pseudo  $C_2$  axis” that passes through the center of the six-membered  $\text{Tp}'\text{Pt}$  boat conformation ( $\text{BN}_2\text{PtN}_2$ ). This “pseudo  $C_2$  axis” interchanges the Pt and B atoms in a small fraction of the crystal sites.

The Pt–C (2.27 and 2.25 Å) distances are comparable to other  $\eta^2$ -arene adducts,<sup>39,41–49</sup> while the C11–C16

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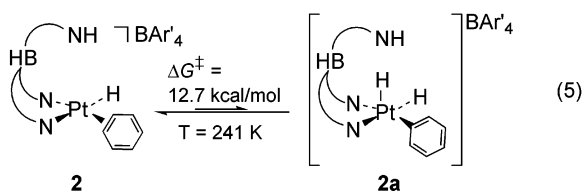
**Table 2.** Comparison of Selected Bond Distances (Å) and Angles (deg) for Complexes **2**<sup>39</sup> and **6**

	benzene adduct ( <b>2</b> )	<i>p</i> -xylene adduct ( <b>6</b> )
Pt1–C11	2.241(11)	2.272(13)
Pt1–C16	2.214(11)	2.253(12)
Pt1–N21	2.037(6)	1.993(9)
Pt1–N31	2.171(8)	2.069(9)
C11–C16	1.360(24)	1.451(21)
C16–C15	1.35(3)	1.396(20)
C11–Pt1–C16	35.5(6)	37.4(5)
C11–Pt1–N21	167.3(5)	163.0(5)
C11–Pt1–N31	99.3(5)	86.3(4)
C16–Pt1–N21	155.6(4)	159.4(5)
C16–Pt1–N31	94.2(4)	108.6(4)
N21–Pt1–N31	87.1(3)	84.8(3)
Pt1–C11–C16	71.2(7)	70.6(7)
C11–C16–C15	119.7(14)	120.2(12)

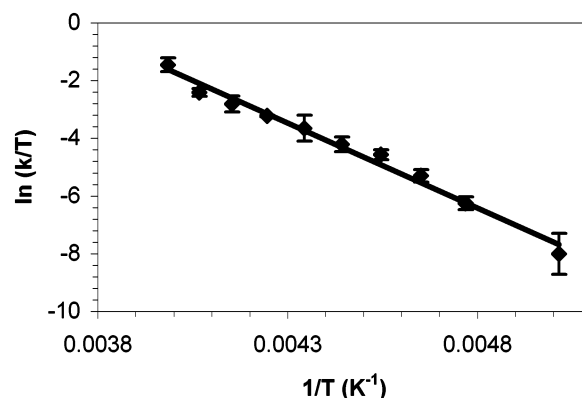
bond length of the coordinated *p*-xylene (1.45 Å) is slightly longer than for free *p*-xylene (1.39 Å)<sup>50</sup> (Table 2). The angle between the plane of the aromatic ring (defined by C11–C16–C15) and the Pt square-plane (defined by N31–Pt1–N21) is almost perpendicular (77.9°), as was seen in the benzene adduct (85.0°).<sup>39</sup> However, the angle between the plane defined by the two carbons directly bound to platinum (defined by C11–Pt1–C16) and the Pt square-plane is 127.3°, which deviates further from 90° than in the benzene adduct (82.5°). This variation from 90° is most likely due to steric interactions between one of the methyl groups of the *p*-xylene ligand and the methyl group of the protonated pyrazole ring. The angle between the aromatic ring and the plane defined by the two carbons directly bound to platinum is 108.8°.

No evidence for dissociation of the bound arene from **4** or **6** was observed up to 273 K. At 273 K, loss of toluene (**4**) or *p*-xylene (**6**) occurs slowly in CD<sub>2</sub>Cl<sub>2</sub> to form a dicationic hydride-bridged dimer.<sup>51</sup> In contrast, dissociation of the bound benzene in **8** occurs slowly at 183 K in CD<sub>2</sub>Cl<sub>2</sub> to form the phenyl-solvated cation [κ<sup>2</sup>-(HTp)Pt(Ph)(solv)][BAR'<sub>4</sub>] [solv = Et<sub>2</sub>O or CD<sub>2</sub>Cl<sub>2</sub>].<sup>52</sup> Complete conversion of **8** to the solvated cation occurs in less than 24 h at 243 K.

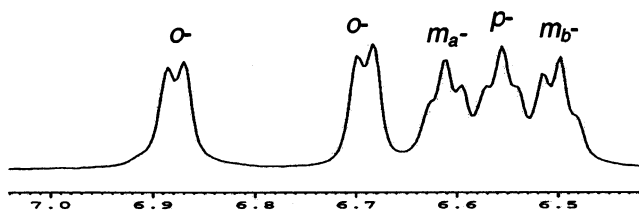
**Kinetics of Arene C–H Bond Activation. Benzene Hydride Adduct.** The barrier (Δ*G*<sup>‡</sup><sub>241K</sub>) to hydrogen exchange between the bound benzene and the hydride position for **2** via arene C–H oxidative addition to give a five-coordinate platinum(IV) aryl dihydride intermediate was reported to be 12.7 kcal/mol,<sup>39</sup> which is similar to the energy of 12.4 kcal/mol calculated at 241 K from the reported Δ*H*<sup>‡</sup> and Δ*S*<sup>‡</sup> values of Jones, Perutz, and co-workers for their rhodium system.<sup>37,38</sup> We have now studied the temperature dependence for the intramolecular C–H oxidative addition of benzene in complex **2** to give the five-coordinate platinum(IV) aryl dihydride intermediate **2a** (eq 5) over the range



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**Figure 2.** Eyring plot for arene C–H exchange with Pt–H of **2** via a five-coordinate platinum(IV) aryl dihydride intermediate **2a**. Calculated activation parameters: Δ*H*<sup>‡</sup> = 11.7 ± 0.5 kcal mol<sup>-1</sup>, Δ*S*<sup>‡</sup> = -3.8 ± 2 cal mol<sup>-1</sup> K<sup>-1</sup>, and Δ*G*<sup>‡</sup><sub>241K</sub> = 12.7 ± 1 kcal mol<sup>-1</sup>.



**Figure 3.** 400 MHz NMR spectrum (in CD<sub>2</sub>Cl<sub>2</sub> at 193 K) of [κ<sup>2</sup>-(HTp)Pt(H)(η<sup>2</sup>-C<sub>6</sub>H<sub>5</sub>Me)][BAR'<sub>4</sub>] (**4**), showing Ar–H resonances.

**Table 3.** Activation Barriers to Arene C–H Oxidative Addition for Complexes **2**, **4**, **6**, and **8**

complex	R	arene	<i>T</i> /K	<i>k</i> /s <sup>-1</sup>	Δ <i>G</i> <sup>‡</sup> /kcal mol <sup>-1</sup>
<b>2</b>	H	C <sub>6</sub> H <sub>6</sub>	241	17	12.7
<b>2-d</b>	D	C <sub>6</sub> D <sub>6</sub>	259	32	13.3
<b>4</b>	H	MeC <sub>6</sub> H <sub>5</sub>	230	0.6 ( <i>m</i> -)	13.6
			230	1.1 ( <i>p</i> -)	13.3
<b>6</b>	H	<i>p</i> -Me <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	272	23	14.2
<b>8</b>	Ph	C <sub>6</sub> H <sub>6</sub>	241	10	12.9
<b>8-d</b>	C <sub>6</sub> D <sub>5</sub>	C <sub>6</sub> D <sub>6</sub>	241	2.2	13.6

199–251 K. Scrambling of the two hydride ligands in **2a** allows for exchange to occur. First-order rate constants were calculated using a spin saturation transfer experiment<sup>53–56</sup> after the longitudinal relaxation times (*T*<sub>1</sub>) for the Pt–H and Pt–C<sub>6</sub>H<sub>6</sub> hydrogens were measured. Activation parameters were calculated from the Eyring plot shown in Figure 2: Δ*H*<sup>‡</sup> = 11.7 ± 0.5 kcal mol<sup>-1</sup>, Δ*S*<sup>‡</sup> = -3.8 ± 2 cal mol<sup>-1</sup> K<sup>-1</sup>, and Δ*G*<sup>‡</sup><sub>241K</sub> = 12.7 ± 1 kcal mol<sup>-1</sup> (Table 3). The entropy of activation is near zero, as is typical for an intramolecular process.

**Toluene Adduct.** Assignment of the protons in the η<sup>2</sup>-coordinated toluene ligand for complex **4** was achieved by observing coalescence of two triplet resonances (*m*-protons) and the two doublet resonances (*o*-protons), while the third triplet remained unchanged (*p*-proton)

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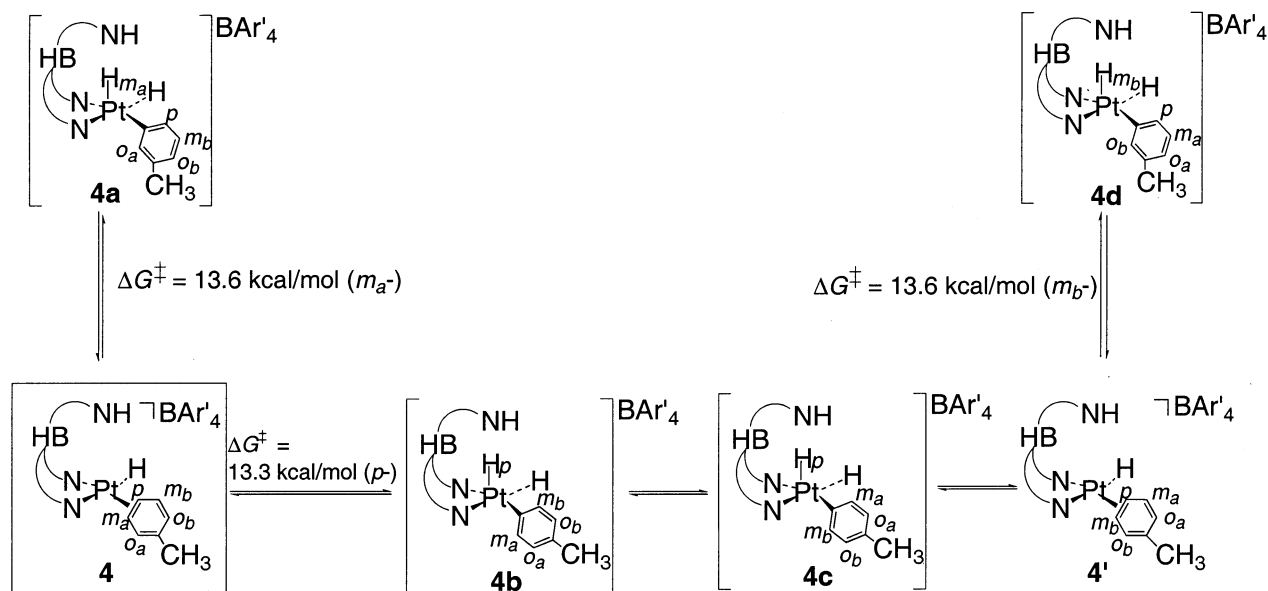
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Scheme 2



(Figure 3). A first-order rate constant  $k = 163 \text{ s}^{-1}$  was calculated at  $T_c = 281 \text{ K}$ , corresponding to a barrier ( $\Delta G^\ddagger$ ) of 13.6 kcal/mol. Averaging of these protons reflects rapid rotation around the Pt–aryl  $\sigma$  bond in the  $p$ -tolyl intermediate **4b** (Scheme 2).

After assignment of the inequivalent aromatic hydrogens in the  $\eta^2$ -toluene ligand, the activation barrier to arene C–H oxidative addition for complex **4** can be measured via a spin saturation transfer experiment<sup>53–56</sup> (Table 3). Irradiation of the hydride resonance at 230 K reveals selective exchange between the hydride and the  $m_a$ -,  $m_b$ -, and  $p$ -hydrogens of the bound toluene (Scheme 2). A first-order rate constant of  $0.60 \text{ s}^{-1}$  was calculated for the  $m_a$ -hydrogen from the experimentally determined longitudinal relaxation time ( $T_1 = 1.0 \text{ s}$ ) and the percentage of signal remaining after saturation (61%) corresponding to a barrier ( $\Delta G^\ddagger$ ) for  $m_a$ -hydrogen activation of 13.6 kcal/mol.

Determination of the rate for hydrogen exchange between the hydride and the  $p$ -hydrogen proved to be more difficult. The  $p$ - and  $m_b$ -hydrogens coincide at 230 K in the  $^1\text{H}$  NMR spectrum, resulting in one broad singlet. At temperatures below 230 K, where these resonances can be separated, no observable saturation transfer can be measured accurately. To apportion the observed saturation of the  $p$ - and  $m_b$ -signal between the  $p$ -hydrogen and the  $m_b$ -hydrogen, we assumed that the barrier for coalescence of the two  $o$ -hydrogens, measured via spin saturation of one  $o$ -hydrogen at 230 K, is an accurate measure of the barrier for C–H activation of the  $p$ -hydrogen ( $\Delta G^\ddagger_{p-H}$ ). This assumption requires that following C–H activation of the  $p$ -hydrogen to give intermediate **4b**, rotation around the Pt–aryl  $\sigma$  bond is fast relative to reductive elimination and exchanges the two  $m$ -hydrogens and the two  $o$ -hydrogens (Scheme 2). The percent saturation due to  $p$ -hydrogen activation in the overlapping  $p$ - and  $m_b$ -resonance was then calculated using the rate of  $o$ -hydrogen exchange, which was characterized by  $\Delta G^\ddagger_{230\text{K}} = 13.3 \text{ kcal/mol}$ . This allowed separation of the total observed saturation in the combined  $p$ - and  $m_b$ -resonance into its two compo-

nents. The rate of  $m_b$ -hydrogen exchange with the platinum hydride, less than either  $p$ - or  $m_a$ -hydrogen exchange, is compatible with activation of the  $m_b$ -hydrogen after rotation places it in the  $m$ -site bound to platinum.

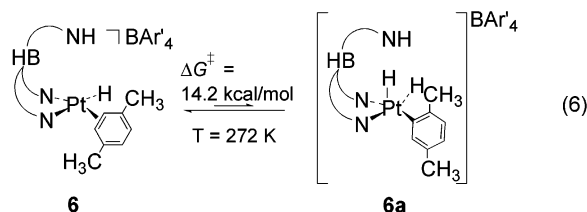
Double-bond migration in the toluene adduct **4** is not an NMR observable process, as all the aromatic hydrogens are inequivalent, a fact that is independent of ring rotation. On the basis of the observable double-bond migration in the  $p$ -xylene adduct **6** at 230 K, the platinum center in the toluene adduct **4** most likely traverses the coordinated toluene as well, but only the thermodynamically favored isomer is significantly populated. We assume that face flipping of the  $\eta^2$ -arene, which is not observed in the  $p$ -xylene adduct **6**, is not responsible for exchange of the two  $m$ -hydrogens here either. These data imply that the rate for C–H activation of the bound  $p$ -hydrogen is slightly faster than that for activation of the bound  $m_a$ -hydrogen. Furthermore,  $p$ -hydrogen activation and ring rotation to place the  $m_b$ -hydrogen in a platinum-bound site is sufficient to account for the spin saturation transfer we observed from the platinum hydride to the  $m_b$ -hydrogen. There was no observable  $o$ -tolyl or benzylic activation.

The preference for  $p$ -hydrogen to  $m$ -hydrogen exchange most likely reflects a kinetic preference similar to the results obtained by Jones and Hessel.<sup>57</sup> They reported a 2:4:3  $m$ -tolyl: $p$ -tolyl:benzyl for the activation of toluene by photolysis of  $\text{Tp}'\text{Rh}(\text{CN-neopentyl})(\eta^2\text{-PhN}=\text{C}=\text{N-neopentyl})$  at 25 °C to give  $\text{Tp}'\text{Rh}(\text{CN-neopentyl})(\text{R})(\text{H})$ .<sup>57</sup> Heating of this sample at 100 °C for 12 h resulted in complete conversion to a statistical 2  $m$ -tolyl:1  $p$ -tolyl ratio.<sup>57</sup>

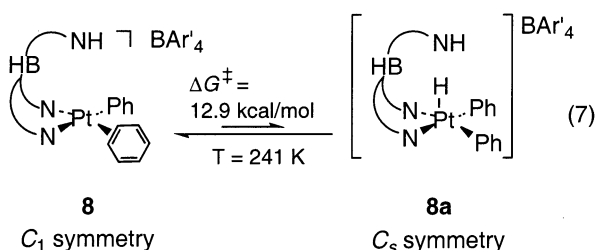
**$p$ -Xylene Adduct.** Hydrogen exchange between the platinum-bound  $p$ -xylene and hydride positions for **6** is evident by broadening of these resonances as the probe temperature is raised (eq 6). Using the slow exchange approximation at 272 K, a first-order rate constant of  $k = 23 \text{ s}^{-1}$  was determined via line broadening of the

(57) Jones, W. D.; Hessel, E. T. *J. Am. Chem. Soc.* **1993**, *115*, 554.

hydride resonance. A barrier ( $\Delta G^\ddagger$ ) for arene oxidative addition of 14.2 kcal/mol was calculated (Table 3).



**Benzene Phenyl Adduct.** In contrast, the benzene phenyl adduct **8** does not have an adjacent hydride ligand that can undergo exchange with the platinum-bound arene aromatic hydrogens as in complexes **2**, **4**, and **6**. However, oxidative addition of the  $\eta^2$ -benzene leads to a hydrido diphenyl intermediate **8a** (eq 7). Such



a process was reflected by averaging of two Tp' arms, as complex **8**, of  $C_1$  symmetry, equilibrates with the oxidative addition product, a five-coordinate platinum(IV) diphenyl hydride intermediate **8a** with  $C_s$  symmetry (Table 3). A first-order rate constant of  $k = 53 \text{ s}^{-1}$  was calculated by observing the coalescence of two Tp'-CH<sub>3</sub> resonances at  $T_c = 256 \text{ K}$ , corresponding to an activation barrier ( $\Delta G^\ddagger$ ) for hydrogen exchange of 12.9 kcal/mol. In addition, hydrogen exchange between the bound benzene and phenyl hydrogens is evident from a spin saturation transfer experiment.<sup>53–56</sup> Irradiation of one Tp'-CH<sub>3</sub> resonance (1.57 ppm) at 241 K reveals the equilibration of two Tp' arms. A first-order rate constant of  $k = 10 \text{ s}^{-1}$  was calculated from the experimentally determined longitudinal relaxation time ( $T_1 = 0.70 \text{ s}$ ) and the percentage of signal remaining after saturation (12%). The calculated barrier ( $\Delta G^\ddagger$ ) for hydrogen exchange of 12.9 kcal/mol was equivalent to the value obtained from Tp' averaging. The oxidative addition barriers for the benzene hydride complex **2** and the benzene phenyl complex **8** are nearly the same, indicating that the hydride and phenyl ligands have similar effects on the barrier to C–H bond activation of benzene in these complexes.

**Kinetic Isotope Effects.** The rate constants ( $k_D$ ) for the perdeuterio complexes [ $\kappa^2$ -(HTp')Pt(D)( $\eta^2$ -C<sub>6</sub>D<sub>6</sub>)]-[BAR'<sub>4</sub>] (**2-d**) and [ $\kappa^2$ -(HTp')Pt(C<sub>6</sub>D<sub>5</sub>)( $\eta^2$ -C<sub>6</sub>D<sub>6</sub>)]-[BAR'<sub>4</sub>] (**8-d**) can be calculated via a spin saturation transfer experiment,<sup>53–56</sup> permitting the calculation of the kinetic isotope effects for arene C–H(D) bond activation. Irradiation of the deuteride resonance (–29.69 ppm) for complex **2-d** at 259 K reveals a first-order rate constant of  $k_D = 32 \text{ s}^{-1}$ . The rate constant for complex **2** at 259 K was determined by line broadening analysis resulting in a  $k_H = 96 \text{ s}^{-1}$ , corresponding to a  $k_H/k_D = 3.0$  at 259 K. Deuterium exchange between the  $\eta^2$ -benzene ligand and the *o*-phenyl group in complex **8-d** is evident by the equilibration of two Tp' arms. Irradiation of one

Tp'-CH<sub>3</sub> resonance (1.60 ppm) at 241 K reveals a first-order rate constant of  $k_D = 2.2 \text{ s}^{-1}$ , corresponding to a  $k_H/k_D = 4.7$  at 241 K.

These  $k_H/k_D$  values, larger than values observed in related systems (vide infra), are consistent with the activation step in which the C–H (or C–D) bond is being cleaved in the transition state. Mayer and co-workers observed a primary kinetic isotope effect for the intramolecular C–H(D) oxidative addition of 1,3,5-C<sub>6</sub>D<sub>3</sub>H<sub>3</sub> to the Re(V) oxo compound TpReO(O)Cl of 4.0(4) at 25 °C, similar to the primary isotope effects seen here.<sup>58</sup> Jones and co-workers observed a primary kinetic isotope effect of 1.4 at –40 °C for intramolecular oxidative addition of benzene with the Rh(I) intermediate Cp\*Rh-(PMe<sub>3</sub>).<sup>59</sup> Caulton and co-workers reported a kinetic isotope effect of 3.2(9) at 47 °C for the C–H(D) bond activation of benzene by an Os(0) intermediate, {OsH(NO)(P'Pr<sub>3</sub>)<sub>2</sub>}.<sup>60</sup>

## Summary and Conclusions

Cationic platinum(II)  $\eta^2$ -arene adducts have been synthesized via protonation of neutral platinum(IV) aryl hydride complexes with [H(OEt<sub>2</sub>)<sub>2</sub>][BAR'<sub>4</sub>]. These  $\eta^2$ -arene platinum(II) adducts exhibit dynamic <sup>1</sup>H NMR spectra which can be attributed to equilibration of the  $\eta^2$ -arene adduct with a five-coordinate platinum aryl hydride intermediate via arene C–H oxidative addition, and the equilibrium favors the platinum(II)  $\eta^2$ -arene structure. No signals for the five-coordinate intermediate, analogous to an isolated silyl derivative,<sup>19</sup> were observed. The three activation energies indicate that increasing methyl substitution from benzene (**2**,  $\Delta G^\ddagger = 12.7 \text{ kcal/mol}$ ) to toluene (**4**,  $\Delta G^\ddagger = 13.6 \text{ kcal/mol}$ ) to *p*-xylene (**6**,  $\Delta G^\ddagger = 14.2 \text{ kcal/mol}$ ) increases the barrier to C–H oxidative addition for each additional methyl substituent. In contrast, the ancillary hydride or phenyl ligand for the benzene hydride adduct **2** ( $\Delta G^\ddagger = 12.7 \text{ kcal/mol}$ ) and the benzene phenyl adduct **8** ( $\Delta G^\ddagger = 12.9 \text{ kcal/mol}$ ), respectively, have similar effects on the barrier to C–H bond activation of benzene, as evident by comparison of activation barriers. The primary isotope effects for intramolecular C–H(D) bond activation in the benzene hydride adduct **2** and the benzene phenyl adduct **8** are 3.0 at 259 K and 4.7 at 241 K, respectively, consistent with significant cleavage of a C–H(D) bond to reach the transition state.

## Experimental Section

**Materials and Methods.** Reactions were performed under an atmosphere of dry nitrogen or argon using standard drybox techniques. Argon and nitrogen were purified by passage through columns of BASF R3-11 catalyst and 4 Å molecular sieves. All glassware was oven-dried prior to use. Methylene chloride and pentanes were purified under an argon atmosphere by passage through a column packed with activated alumina.<sup>61</sup> Deuterated methylene chloride was vacuum transferred from calcium hydride and degassed by several freeze–pump–thaw cycles.

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(60) Yandulov, D. V.; Caulton, K. G. *New J. Chem.* **2002**, *26*, 498.

(61) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

Tp'Pt(C<sub>6</sub>H<sub>5</sub>)(H)<sub>2</sub> (**1**),<sup>62</sup> Tp'Pt(MeC<sub>6</sub>H<sub>4</sub>)(H)<sub>2</sub> (**3**),<sup>62</sup> Tp'Pt(2,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(H)<sub>2</sub> (**5**),<sup>62</sup> Tp'Pt(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(H) (**7**),<sup>63</sup> and [H(OEt<sub>2</sub>)<sub>2</sub>][BAR'<sub>4</sub>]<sup>21</sup> were synthesized according to published procedures. Tp'Pt-(C<sub>6</sub>D<sub>5</sub>)<sub>2</sub> (**2-d**) was synthesized according to a modified published procedure for the synthesis of **1** followed by heating (65 °C) in acetone-*d*<sub>6</sub> in the presence of catalytic lithium diisopropylamide for 18 h.<sup>62</sup> Tp'Pt(C<sub>6</sub>D<sub>5</sub>)<sub>2</sub>D (**7-d**) was synthesized according to a modified published procedure for the synthesis of **1** starting with Tp'PtMe<sub>2</sub>H.<sup>62</sup>

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

**Representative [BAR'<sub>4</sub>]<sup>-</sup> NMR Data.** <sup>1</sup>H and <sup>13</sup>C NMR data for the [BAR'<sub>4</sub>]<sup>-</sup> counterion are reported separately for simplicity. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 193 K,  $\delta$ ): 7.77 (br, 8H, *o*-Ar'), 7.60 (br, 4H, *p*-Ar'). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 193 K,  $\delta$ ): 162.2 (1:1:1:1 pattern, <sup>1</sup>J<sub>B-C</sub> = 50 Hz, C<sub>ipso</sub>), 135.3 (C<sub>ortho</sub>), 129.4 (qq, <sup>2</sup>J<sub>C-F</sub> = 30 Hz, <sup>4</sup>J<sub>C-F</sub> = 5 Hz, C<sub>meta</sub>), 125.1 (q, <sup>1</sup>J<sub>C-F</sub> = 270 Hz, CF<sub>3</sub>), 117.9 (C<sub>para</sub>).

**[ $\kappa^2$ -(HTp')Pt(H)( $\eta^2$ -C<sub>6</sub>H<sub>6</sub>)] [BAR'<sub>4</sub>] (**2**).<sup>39</sup> (a) On a Preparatory Scale.** Tp'Pt(C<sub>6</sub>H<sub>5</sub>)(H)<sub>2</sub> (0.055 g, 0.096 mmol) and [H(OEt<sub>2</sub>)<sub>2</sub>][BAR'<sub>4</sub>] (0.104 mmol) were combined in a 50 mL Schlenk flask and cooled to -78 °C. CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was slowly added through the septum. The reaction mixture was stirred for ca. 5 min and then layered with pentanes (20 mL). The flask was stored in a freezer at -30 °C for 12 h. Colorless needles formed, and these were collected and dried in vacuo. Yield: 124 mg (90%). IR (KBr, room temperature):  $\nu_{\text{BH}} = 2524$  cm<sup>-1</sup>,  $\nu_{\text{PtH}} = 2270$  cm<sup>-1</sup> (br),  $\nu_{\text{BAR}'_4} = 1610$  cm<sup>-1</sup>,  $\nu_{\text{Hpz}'} = 1579$  cm<sup>-1</sup>, and,  $\nu_{\text{pz}'} = 1548$  cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 193 K,  $\delta$ ): 10.09 (s, 1H, pz'NH), 6.95 (s, 6H, C<sub>6</sub>H<sub>6</sub>), 6.33, 5.97, 5.93 (s, 1H each, HTp'CH), 2.36, 2.34, 2.30, 2.27, 1.89, 1.81 (s, 3H, 3H, 3H, 3H, 3H, 3H, HTp'CH<sub>3</sub>), -29.82 (s, 1H, <sup>1</sup>J<sub>Pt-H</sub> = 935 Hz, Pt-H). Anal. Calcd for C<sub>53</sub>H<sub>42</sub>N<sub>6</sub>F<sub>24</sub>B<sub>2</sub>Pt: C, 44.34; H, 2.95; N, 5.85. Found: C, 44.60; H, 3.06; N, 5.38.

(b) **In Situ.** The sample was prepared under an argon atmosphere in a drybox. Tp'Pt(C<sub>6</sub>H<sub>5</sub>)(H)<sub>2</sub> (0.015 g, 0.026 mmol) and [H(OEt<sub>2</sub>)<sub>2</sub>][BAR'<sub>4</sub>] (0.040 g, 0.039 mmol) were weighed into an NMR tube, which was then sealed with a septum and secured with Parafilm. The NMR tube was cooled to -78 °C outside the drybox, and 0.7 mL of CD<sub>2</sub>Cl<sub>2</sub> was slowly added through the septum. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 193 K,  $\delta$ ): 11.67 (s, 1H, pz'NH), 6.88 (s, 6H, C<sub>6</sub>H<sub>6</sub>), 6.27, 5.93, 5.90 (s, 1H each, HTp'CH), 2.31, 2.30, 2.27, 1.86, 1.60 (s, 6H, 3H, 3H, 3H, 3H, HTp'CH<sub>3</sub>), -30.13 (s, 1H, <sup>1</sup>J<sub>Pt-H</sub> = 935 Hz, Pt-H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 193 K,  $\delta$ ): 152.3, 151.6, 148.1, 147.7, 147.2, 143.6 (HTp'CCH<sub>3</sub>), 115.3 (Pt-C<sub>6</sub>H<sub>6</sub>), 109.1, 108.0, 106.4 (HTp'CH), 15.7, 13.8, 12.9, 12.3, 11.0, 10.7 (HTp'CCH<sub>3</sub>).

**[ $\kappa^2$ -(HTp')Pt(D)( $\eta^2$ -C<sub>6</sub>D<sub>6</sub>)] [BAR'<sub>4</sub>] (**2-d**).** The sample was prepared under an argon atmosphere in a drybox. Tp'Pt(C<sub>6</sub>D<sub>5</sub>)(D)<sub>2</sub> (0.017 mmol) and [H(OEt<sub>2</sub>)<sub>2</sub>][BAR'<sub>4</sub>] (0.021 g, 0.021 mmol) were weighed into an NMR tube, which was then sealed with a septum and secured with Parafilm. The NMR tube was cooled to -78 °C outside the drybox, and 0.7 mL of CH<sub>2</sub>Cl<sub>2</sub> was slowly added through the septum. <sup>2</sup>H NMR (CH<sub>2</sub>Cl<sub>2</sub>, 263 K,  $\delta$ ): 7.04 (s, 6D, Pt-C<sub>6</sub>D<sub>6</sub>), -29.69 (s, 1D, Pt-D). *T*<sub>1(Pt-C<sub>6</sub>D<sub>6</sub>)}</sub> = 0.046 s.

**[ $\kappa^2$ -(HTp')Pt(H)( $\eta^2$ -C<sub>6</sub>H<sub>5</sub>Me)] [BAR'<sub>4</sub>] (**4**).** (a) **On a Preparatory Scale.** Tp'Pt(MeC<sub>6</sub>H<sub>4</sub>)(H)<sub>2</sub> (0.010 g, 0.017 mmol) and [H(OEt<sub>2</sub>)<sub>2</sub>][BAR'<sub>4</sub>] (0.019 mmol) were combined in a 50 mL Schlenk flask and cooled to -78 °C. CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was slowly added through the septum. The reaction mixture was stirred for ca. 5 min and then layered with pentanes (20 mL). The

flask was stored in a freezer at -30 °C for 12 h. Colorless needles formed, and these were collected and dried in vacuo. Yield: 15 mg (61%). IR (KBr, room temperature):  $\nu_{\text{BH}} = 2532$  cm<sup>-1</sup>,  $\nu_{\text{PtH}} = 2274$  cm<sup>-1</sup> (br),  $\nu_{\text{BAR}'_4} = 1610$  cm<sup>-1</sup>,  $\nu_{\text{Hpz}'} = 1579$  cm<sup>-1</sup>, and,  $\nu_{\text{pz}'} = 1552$  cm<sup>-1</sup>. Anal. Calcd for C<sub>54</sub>H<sub>44</sub>N<sub>6</sub>F<sub>24</sub>B<sub>2</sub>Pt: C, 44.74; H, 3.06; N, 5.80. Found: C, 44.52; H, 3.17; N, 5.55.

(b) **In Situ.** The sample was prepared under an argon atmosphere in a drybox. Tp'Pt(MeC<sub>6</sub>H<sub>4</sub>)(H)<sub>2</sub> (0.026 mmol) and [H(OEt<sub>2</sub>)<sub>2</sub>][BAR'<sub>4</sub>] (0.040 g, 0.039 mmol) were weighed into an NMR tube, which was then sealed with a septum and secured with Parafilm. The NMR tube was cooled to -78 °C outside the drybox, and 0.7 mL of CD<sub>2</sub>Cl<sub>2</sub> was slowly added through the septum. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 203 K,  $\delta$ ): 11.35 (s, 1H, pz'NH), 6.87, 6.69 (d, 1H each, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, *o*-ArH), 6.61, 6.49 (t, 1H each, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, *m*-ArH), 6.55 (t, 1H, <sup>3</sup>J<sub>H-H</sub> = 6.8 Hz, *p*-ArH), 6.27, 5.94, 5.91 (s, 1H each, HTp'CH), 2.32, 2.30, 2.28, 1.89, 1.67 (s, 9H, 3H, 3H, 3H, 3H, HTp'CH<sub>3</sub> and Pt-MeC<sub>6</sub>H<sub>5</sub>), -29.79 (s, 1H, <sup>1</sup>J<sub>Pt-H</sub> = 950 Hz, Pt-H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 203 K,  $\delta$ ): 152.5, 151.6, 148.3, 147.8, 147.3, 145.9, 143.6 (HTp'CCH<sub>3</sub> and Pt-C<sub>6</sub>H<sub>5</sub>Me, CCH<sub>3</sub>), 125.8, 113.6 (Pt-C<sub>6</sub>H<sub>5</sub>Me, CH), 109.2, 109.0, 108.1, 106.5, 104, 9, 103.5 (HTp'CH and Pt-C<sub>6</sub>H<sub>5</sub>Me, CH), 21.5 (Pt-C<sub>6</sub>H<sub>5</sub>Me, CCH<sub>3</sub>), 15.9, 13.8, 13.0, 12.9, 11.2, 10.9 (HTp'CCH<sub>3</sub>).

**[ $\kappa^2$ -(HTp')Pt(H)( $\eta^2$ -C<sub>6</sub>H<sub>4</sub>-3,6-Me<sub>2</sub>)] [BAR'<sub>4</sub>] (**6**).** (a) **On a Preparatory Scale.** Tp'Pt(2,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(H)<sub>2</sub> (0.020 g, 0.033 mmol) and [H(OEt<sub>2</sub>)<sub>2</sub>][BAR'<sub>4</sub>] (0.038 mmol) were combined in a 50 mL Schlenk flask and cooled to -78 °C. CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was slowly added through the septum. The reaction mixture was stirred for ca. 5 min and then layered with pentanes (20 mL). The flask was stored in a freezer at -30 °C for 12 h. Colorless needles formed, and these were collected and dried in vacuo. Yield: 30 mg (62%). IR (KBr, room temperature):  $\nu_{\text{BH}} = 2532$  cm<sup>-1</sup>,  $\nu_{\text{PtH}} = 2258$ , 2235 cm<sup>-1</sup> (br),  $\nu_{\text{BAR}'_4} = 1610$  cm<sup>-1</sup>,  $\nu_{\text{Hpz}'} = 1575$  cm<sup>-1</sup>, and,  $\nu_{\text{pz}'} = 1552$  cm<sup>-1</sup>. Anal. Calcd for C<sub>55</sub>H<sub>46</sub>N<sub>6</sub>F<sub>24</sub>B<sub>2</sub>Pt-Et<sub>2</sub>O: C, 46.08; H, 3.67; N, 5.46. Found: C, 46.18; H, 3.30; N, 5.65.

(b) **In Situ.** The sample was prepared under an argon atmosphere in a drybox. Tp'Pt(2,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(H)<sub>2</sub> (0.025 mmol) and [H(OEt<sub>2</sub>)<sub>2</sub>][BAR'<sub>4</sub>] (0.037 mmol) were weighed into an NMR tube, which was then sealed with a septum and secured with Parafilm. The NMR tube was cooled to -78 °C outside the drybox, and 0.7 mL of CD<sub>2</sub>Cl<sub>2</sub> was slowly added through the septum. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 183 K,  $\delta$ ): 11.80 (br s, 1H, pz'NH), 6.70, 6.60, 6.54, 5.63 (all br, 1H each, Pt(2,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)), 6.16, 5.97, 5.87 (s, 1H each, HTp'CH), 2.36, 2.35, 2.31, 2.23, 1.89, 1.84 (s, 3H, 3H, 3H, 3H, 3H, 3H, HTp'CH<sub>3</sub>), 2.45, 1.89 (br s, 3H each, Pt(2,5-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)), -29.82 (s, 1H, <sup>1</sup>J<sub>Pt-H</sub> = 960 Hz, Pt-H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 183 K,  $\delta$ ): 152.1, 151.9, 148.4, 147.7, 147.3, 143.8 (HTp'CCH<sub>3</sub>), 145.6, 143.7 (Pt-ArH, CCH<sub>3</sub>), 127.8, 126.9 (Pt-ArH, CH), 109.5, 108.2, 106.4 (HTp'CH), 84.9, 81.8 (Pt-ArH, Pt-CH), 21.0, 20.8 (Pt-ArH, CCH<sub>3</sub>), 15.9, 14.3, 13.0, 12.9, 10.9, 10.8 (HTp'CCH<sub>3</sub>).

**[ $\kappa^2$ -(HTp')Pt(C<sub>6</sub>H<sub>5</sub>)( $\eta^2$ -C<sub>6</sub>H<sub>6</sub>)] [BAR'<sub>4</sub>] (**8**).** The sample was prepared under an argon atmosphere in a drybox. Tp'Pt-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(H) (0.015 mmol) and [H(OEt<sub>2</sub>)<sub>2</sub>][BAR'<sub>4</sub>] (0.023 g, 0.023 mmol) were weighed into an NMR tube, which was then sealed with a septum and secured with Parafilm. The NMR tube was cooled to -78 °C outside the drybox, and 0.7 mL of CD<sub>2</sub>Cl<sub>2</sub> was slowly added through the septum. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 203 K,  $\delta$ ): 10.52 (s, 1H, pz'NH), 6.85 (s, 6H, C<sub>6</sub>H<sub>6</sub>), 6.53, 6.32 (br, 3H, 2H, Pt-Ph), 6.55, 5.94, 5.76 (s, 1H each, HTp'CH), 2.56, 2.50, 2.31, 2.25, 2.09, 1.57 (s, 3H each, HTp'CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 203 K,  $\delta$ ): 153.5, 151.6, 148.8, 148.7, 148.4, 143.8 (HTp'CCH<sub>3</sub>), 124.9, 122.5 (Pt-Ph), 119.2 (Pt-C<sub>6</sub>H<sub>6</sub>), 110.2, 108.6, 108.1 (HTp'CH), 15.3, 15.2, 13.5, 13.1, 12.1, 11.2 (HTp'CCH<sub>3</sub>).

**[ $\kappa^2$ -(HTp')Pt(C<sub>6</sub>D<sub>5</sub>)( $\eta^2$ -C<sub>6</sub>D<sub>6</sub>)] [BAR'<sub>4</sub>] (**8-d**).** The sample was prepared under an argon atmosphere in a drybox. Tp'Pt-(C<sub>6</sub>D<sub>5</sub>)<sub>2</sub>(D) (0.015 mmol) and [H(OEt<sub>2</sub>)<sub>2</sub>][BAR'<sub>4</sub>] (0.023 g, 0.023 mmol) were weighed into an NMR tube, which was then sealed with a septum and secured with Parafilm. The NMR tube was

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cooled to  $-78$  °C outside the drybox, and 0.7 mL of  $\text{CD}_2\text{Cl}_2$  was slowly added through the septum.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 243 K,  $\delta$ ): 10.43 (s, 1H, pz'NH), 6.58, 5.97, 5.79 (s, 1H each, HTp'CH), 2.59, 2.52, 2.34, 2.27, 2.16, 1.60 (s, 3H each, HTp'CH<sub>3</sub>).

**Structural Data for 6.** Crystals from  $\text{CH}_2\text{Cl}_2$ /pentane;  $\text{C}_{55}\text{H}_{45}\text{N}_6\text{F}_{24}\text{B}_2\text{Pt}$ ,  $M = 1435.89$ ; triclinic, space group  $P\bar{1}$ ;  $Z = 2$ ;  $a = 12.7624(12)$  Å,  $b = 12.9020(14)$  Å,  $c = 18.8058(20)$  Å;  $\alpha = 79.368(1)^\circ$ ,  $\beta = 74.497(1)^\circ$ ,  $\gamma = 18.8058(20)^\circ$ ;  $U = 2902.5(5)$  Å<sup>3</sup>;  $D_c = 1.639$  Mg m<sup>-3</sup>;  $T = -100^\circ\text{C}$ ; max  $2\theta$   $50^\circ$ ; Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å); 9271 unique reflections were obtained and 6488 of these with  $I > 2.5\sigma(I)$  were used in the refinement; data were collected on a Bruker SMART diffractometer, using the omega scan method. For significant reflec-

tions merging  $R$ -value 0.037; Residuals:  $R_F$  0.067;  $R_w$  0.072 (significant reflections); GoF 1.8087.

**Acknowledgment.** We gratefully acknowledge the National Science Foundation (Grant CHE-0109655) for support of this research. C.M.N. would also like to thank E. Dawson (UNC-Chapel Hill) for assistance with  $T_1$  measurements.

**Supporting Information Available:** Complete crystallographic data for **6**, 3D-plots of **6** showing the "pseudo  $C_2$ " axis, and plots for the  $T_1$  measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM020526N