

# Mechanistic Investigation of Benzene C–H Activation at a Cationic Platinum(II) Center: Direct Observation of a Platinum(II) Benzene Adduct

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**Abstract:** The platinum(II) methyl cation  $[(N-N)Pt(CH_3)(solv)]^+BF_4^-$  ( $N-N = ArN=C(Me)C(Me)=NAr$ ,  $Ar = 2,6-(CH_3)_2C_6H_3$ ,  $solv = H_2O$  (**2a**) or TFE =  $CF_3CH_2OH$  (**2b**)) is prepared by treatment of  $(N-N)Pt(CH_3)_2$  with 1 equiv of aqueous  $HBF_4$  in TFE. Reaction of a mixture of **2a** and **2b** with benzene in TFE/ $H_2O$  solutions cleanly affords the platinum(II) phenyl cation  $[(N-N)Pt(C_6H_5)(solv)]^+BF_4^-$  (**3**). Investigations of the kinetics and isotopic labeling experiments indicate that reaction of **2** with benzene proceeds via benzene coordination, reversible oxidative addition of benzene C–H bonds, reversible formation of a methane C,H- $\sigma$  complex, and final dissociation of methane. Under conditions where  $[(N-N)Pt(CH_3)(H_2O)]^+BF_4^-$  (**2a**) is the major starting complex, rate-determining benzene coordination to **2b** is implicated by the observed kinetic rate law (inverse first order in  $[H_2O]$  and first order in  $[C_6H_6]$  to 3.8 M) and the small kinetic deuterium isotope effect for  $C_6H_6$  vs  $C_6D_6$  ( $k_H/k_D = 1.06 \pm 0.05$  at 25 °C). When deuterated benzenes  $C_6D_6$  and 1,3,5- $C_6H_3D_3$  are used, almost full statistical scrambling of deuterium from one benzene into methane is achieved, indicating that the energetic barriers for dissociating benzene and methane are considerably higher than interconversions of intermediate hydrocarbon complexes and  $[(N-N)Pt(C_6H_5)(CH_3)H]^+$ . Protonation of  $(N-N)Pt(CH_3)(C_6H_5)$  with  $HBF_4$  in TFE, which provides an independent route into the manifold of postulated intermediates, gives a mixture of **3** +  $CH_4$  (82%) and **2** +  $C_6H_6$  (18%). Protonation of  $(N-N)Pt(CH_3)(C_6H_5)$  with triflic acid in methylene chloride/diethyl ether mixtures at  $-69$  °C allows direct low-temperature NMR observation of a fluxional  $\pi$  benzene complex,  $[(N-N)Pt(CH_3)(C,C-\eta^2-C_6H_6)]^+$ .

## Introduction

The reactions of hydrocarbon C–H bonds with organo-transition metal complexes have been a major focus of research over the last two decades, motivated in large part by the tantalizing possibility of direct utilization of alkanes as chemical feedstocks. Many examples of C–H activation, some remarkably efficient, have been reported,<sup>2</sup> but relatively few have been incorporated into schemes for overall alkane functionalization. Selective oxidation is a particularly attractive target, but the majority of alkane-activating complexes are unstable to oxidizing conditions. Most exceptions to this limitation are found in the class of electrophilic activations by late transition metals.<sup>3</sup> The most extensively studied example of the latter is the so-called Shilov system, consisting of aqueous Pt(II) and Pt(IV) salts, which converts alkanes to alcohols at 120 °C. Earlier work in the Caltech group<sup>4</sup> and elsewhere<sup>5</sup> has delineated the scope of this reaction, and established the mechanism depicted in Scheme 1.

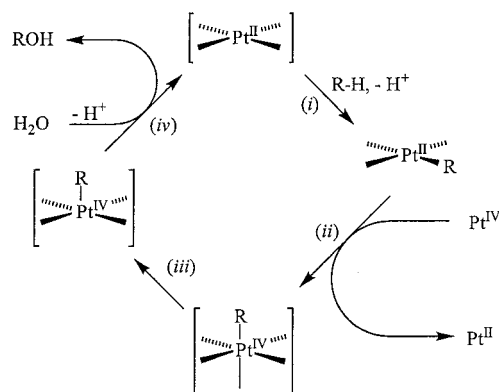
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## Scheme 1



Mechanistic details of the actual C–H activation, step (i) in Scheme 1, cannot be obtained by direct examination of the working catalytic system, so we resorted to models. Studies of protonolysis of complexes  $L_2PtRX$ , the formal microscopic reverse of the C–H activation step, provide evidence for the involvement of two intermediates—a Pt(II) C,H- $\eta^2$ -alkane

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complex and a Pt<sup>IV</sup>(R)(H) oxidative addition product—which interconvert rapidly.<sup>6</sup> These model complexes differ from the Shilov system in that they include stabilizing (nitrogen or phosphorus) ligands, raising the question of their relevance to the catalytic alkane oxidations. But relevance has been demonstrated, perhaps most dramatically by the finding that such a complex with L<sub>2</sub> = 2,2'-bipyrimidyl catalyzes the oxidation of methane to methyl bisulfate by concentrated sulfuric acid in over 70% yield, by far the most effective example of homogeneously catalyzed alkane functionalization yet reported.<sup>7</sup>

While the above-mentioned model studies concentrated on the reverse of the reaction of interest, the deduced scheme indicated that C–H activation might be observed in the chemistry of [L<sub>2</sub>PtR(solv)]<sup>+</sup>, where solv is a weakly bonded solvent molecule or other ligand. This was first achieved for the case L<sub>2</sub> = tetramethylethylenediamine (tmeda), R = methyl, and solv = pentafluoropyridine: this cationic Pt(II) complex reacts with hydrocarbons such as benzene and <sup>13</sup>CH<sub>4</sub> at 85 °C, generating methane and the corresponding new organoplatinum(II) product.<sup>8</sup> More recently the Oslo group<sup>9</sup> found that the analogous diimine complex [(N<sup>f</sup>-N<sup>f</sup>)Pt(CH<sub>3</sub>)(OH<sub>2</sub>)]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (N<sup>f</sup>-N<sup>f</sup> = Ar<sup>f</sup>N=C(Me)C(Me)=NAr<sup>f</sup>, Ar<sup>f</sup> = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) exhibits the same reactivity under milder conditions in trifluoroethanol (TFE), readily activating benzene and methane C–H bonds at 25 and 45 °C, respectively.

These stoichiometric C–H activations offer the possibility of gaining information about several key mechanistic questions.

(1) Does activation proceed via oxidative addition, giving the Pt<sup>IV</sup>(R)(H) intermediate implicated by the protonolysis studies (as well as by a related system wherein a Pt<sup>IV</sup>(R)(H) species generated by C–H activation is the stable final product<sup>10</sup>), or by some alternative route such as σ-bond metathesis? Calculations on a cationic Ir(III) system which had earlier been shown to undergo similar transformations<sup>11</sup> support oxidative addition,<sup>12</sup> whereas several theoretical studies on the Shilov system and models have been interpreted as supporting a variety of detailed C–H activation mechanisms.<sup>13</sup>

(2) What is the rate-limiting step—coordination of the incoming hydrocarbon, the actual C–H activation, or something else?

(3) Does the reacting hydrocarbon enter the coordination sphere by an associative or dissociative mechanism? The iridium system mentioned above, [Cp\*Ir(PMe<sub>3</sub>)(Me)(CH<sub>2</sub>Cl<sub>2</sub>)]<sup>+</sup>, is an

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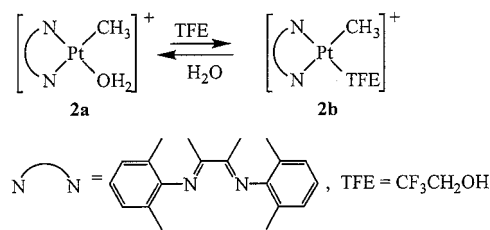
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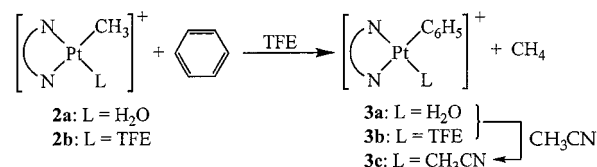
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## Scheme 2



## Scheme 3



18-electron species and presumably reacts dissociatively, but [L<sub>2</sub>PtR(solv)]<sup>+</sup> is an open-shell 16-electron complex, so either mechanism is in principle possible.

As part of an ongoing study into the effects of ligand variations, we discovered that [(N–N)Pt(CH<sub>3</sub>)(solv)]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (N–N = ArN=C(Me)C(Me)=NAr, Ar = 2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, solv = H<sub>2</sub>O or TFE) (**2**) undergoes similar C–H activation in TFE, but the reactions are somewhat cleaner and the products more stable than in the previous cases. We report here a detailed kinetic and mechanistic investigation of the C–H activation of benzene reaction by **2**.

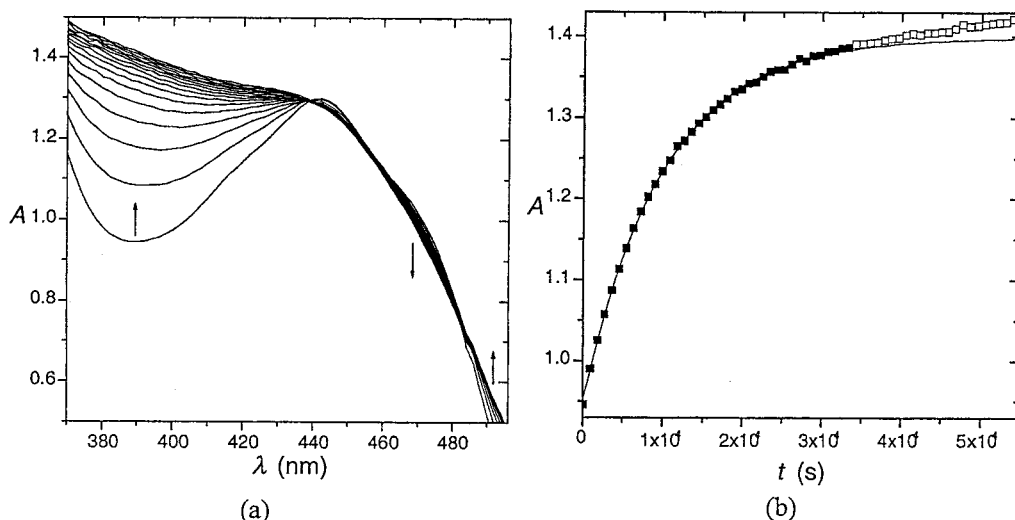
## Results and Discussion

**Preparation of Platinum Complexes and C–H Activation of Benzene.** Following the procedure for preparation of (N<sup>f</sup>-N<sup>f</sup>)Pt(CH<sub>3</sub>)<sub>2</sub>,<sup>9</sup> protonolysis of (N–N)Pt(CH<sub>3</sub>)<sub>2</sub> (**1**) with 1 equiv of aqueous HBF<sub>4</sub> in TFE and evaporation of solvent give an air-stable orange-brown powder. When the product is dissolved in dry TFE-*d*<sub>3</sub>, the <sup>1</sup>H NMR data show the presence of a mixture of *two* [(N–N)Pt(CH<sub>3</sub>)(L)]<sup>+</sup> species, in an approximately 3:1 ratio. Addition of water to the solution results in an increase in the peaks of the major species and a corresponding decrease of the minor species. We attribute this observation to an equilibrium between the expected aqua complex [(N–N)Pt(CH<sub>3</sub>)(OH<sub>2</sub>)]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (**2a**) and a minor solvento adduct [(N–N)Pt(CH<sub>3</sub>)(TFE)]<sup>+</sup>BF<sub>4</sub><sup>-</sup> (**2b**) (Scheme 2). The equilibrium constant  $K_{eq} = [2b][H_2O]/[2a][TFE]$  was estimated at  $(1.2 \pm 0.3) \times 10^{-3}$  at 25 °C by <sup>1</sup>H NMR analysis of the ratio between **2a** and **2b** at different water concentrations in TFE. Analytical data indicate the isolated solid is primarily **2b**.

Addition of ca. 30 equiv of benzene (ca. 0.4 M) to a solution of **2** in TFE-*d*<sub>3</sub> at ambient temperature results in clean formation of the corresponding phenyl species **3** (“**2**” and “**3**” denote the equilibrium mixture of **2a/b** and **3a/b**, respectively) with concurrent production of methane, as observed by <sup>1</sup>H NMR spectroscopy (Scheme 3).<sup>14</sup>

Complete conversion to **3** is achieved after approximately 16 h. No intermediates can be observed during the course of the reaction, and the ratio between **3a** and **3b** is constant and approximately the same as for **2a** and **2b** (3:1). Addition of water after complete reaction leads to an increased **3a:3b** ratio, confirming that the major species **3a** is the aqua adduct. Subsequent addition of acetonitrile to the product mixture

(14) An X-ray crystal structure determination for [(N–N)Pt(C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>-CN)]<sup>+</sup>BF<sub>4</sub><sup>-</sup> has been carried out. Its description will be reported separately.



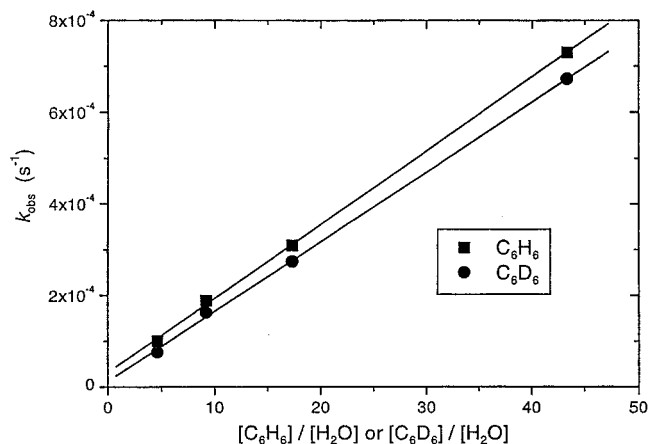
**Figure 1.** (a) UV/vis spectral changes for the reaction of benzene with **2a** in TFE. Isosbestic points appear at 439 and 484 nm. (b) Absorbance at 390 nm versus time: (■) points used for the first-order kinetics least-squares fit (—); (□) points omitted from the fit, which illustrate the “background” increase in absorbance attributed to slow degradation of the Pt species.

quantitatively produces  $[(N-N)Pt(C_6H_5)(NCMe)]^+BF_4^-$  (**3c**). The spectroscopic data for **3c** are identical to those of an authentic sample independently synthesized from  $(N-N)Pt-(C_6H_5)_2$  (**4**) and  $HBF_4$  in  $CH_3CN$ . Benzene activation by the mixture of **2a** and **2b** in TFE thus appears to proceed at a lower rate, but otherwise in a fashion very similar to that of the analogous reaction of  $[(N^f-N^f)Pt(CH_3)(H_2O)]^+$ .<sup>9</sup>

**Kinetics of the Benzene Activation Reaction.** Since the diimine platinum species described above are intensely colored, the reaction can be conveniently followed by UV/vis spectroscopy. The typical spectral change over time for the reaction between **2a** (excess  $H_2O$ ) and benzene in TFE is shown in Figure 1a. The appearance of isosbestic points (439 and 484 nm) is consistent with the conclusion from  $^1H$  NMR that no intermediates accumulate to a significant level.

Kinetic data are obtained by following the absorbance at 390 nm as a function of time. Benzene concentrations in these experiments were always high enough to ensure pseudo-first-order conditions ( $[C_6H_6] > 10[Pt]$ ). Constant ionic strength in the system was maintained by the addition of excess of an inert salt ( $Me_4N^+BF_4^-$ ). Control experiments showed that the presence of salt has no measurable effect on the reaction rate. As described above, at low water concentrations substantial amounts of the solvento species **2b** and **3b** are present in the reaction mixture. To simplify analysis, the kinetic experiments were performed at water concentrations where at least 90% of the platinum species are present as the aqua adducts **2a** and **3a** ( $[H_2O] > 0.11$  M), so that the data can be treated in terms of a simple transformation of **2a** to **3a**. Of course, the potential role of the solvento species **2b/3b** must be taken into account with regard to mechanistic interpretation.

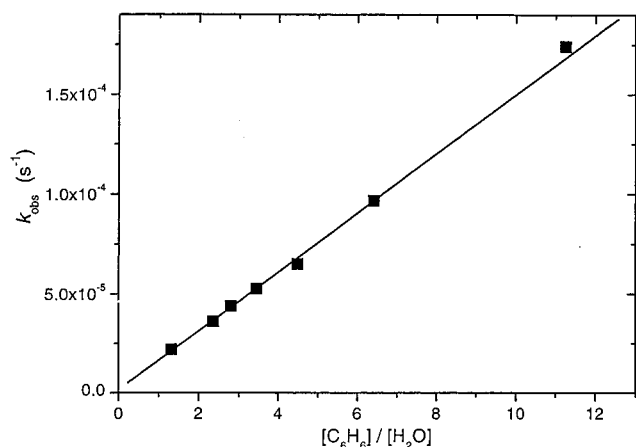
The change in absorbance at 390 nm over time exhibited clean first-order behavior over 3–4 half-lives (Figure 1b); control experiments showed that the reaction rate was independent of the initial platinum concentration. When the absorbance was followed for more than 4 half-lives, deviation from first-order behavior was manifested by a slow additional increase in intensity. We believe that this deviation is due to slow degradation of **2** and **3**. In control experiments, slow decomposition of **2** and **3** in TFE- $d_3$  could indeed be observed by  $^1H$  NMR over several days, accompanied by elimination of methane and benzene, respectively, and formation of complex patterns



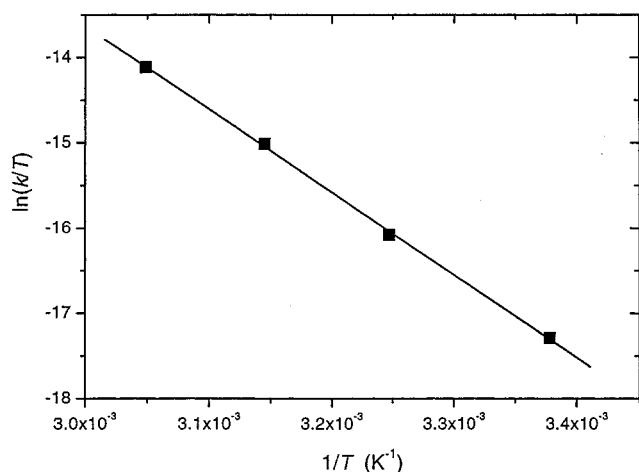
**Figure 2.**  $k_{obs}$  versus  $[C_6H_6]/[H_2O]$  or  $[C_6D_6]/[H_2O]$  for the benzene activation at **2a** in TFE at various benzene concentrations ( $[C_6H_6]$  and  $[C_6D_6] = 0.6$ – $3.8$  M) and almost constant water concentration ( $[H_2O] = 0.11$ – $0.15$  M).  $[Pt] = 5.3$ – $7.6 \times 10^{-3}$  M;  $[Me_4N^+BF_4^-] = 0.13$ – $0.19$  M;  $T = 25$  °C. Calculated rate constants:  $k_H = (1.98 \pm 0.03) \times 10^{-5} s^{-1}$  and  $k_D = (1.87 \pm 0.04) \times 10^{-5} s^{-1}$ . Calculated kinetic isotope effect:  $k_H/k_D = 1.06 \pm 0.05$ .  $k_{obs} = k[C_6H_6]/[H_2O]$ .

of new  $^1H$  NMR signals in both cases. Furthermore, a TFE solution of **2** (no benzene present) exhibited a small increase in absorbance at 390 nm over 15 h. The exact nature of these decomposition pathways is not fully understood, but the absence of incorporation of deuterium in the liberated methane (in TFE- $d_3$  solutions) suggests some kind of inter- or intramolecular C–H activation of the diimine ligand. However, the rate of the decomposition, and more importantly the rate of the corresponding increase in absorbance at 390 nm, for **2a/3a** is at least 1 order of magnitude lower than that of the benzene C–H activation reaction and therefore should not affect the observed rate constants to any significant extent.

Two sets of experiments were performed: varying benzene (both  $C_6H_6$  and  $C_6D_6$ ) concentration, keeping water concentration nearly constant, and the converse. The first-order rate constants thus obtained,  $k_{obs}$ , are plotted as a function of the ratio  $[benzene]/[water]$  in Figures 2 and 3, respectively. The reaction rate exhibits first-order dependence on benzene concentration, with no signs of saturation kinetics in the concentration range investigated (0.6–3.8 M), and inverse first-order



**Figure 3.**  $k_{\text{obs}}$  versus  $[\text{C}_6\text{H}_6]/[\text{H}_2\text{O}]$  for the benzene activation at **2a** in TFE at various water concentrations ( $[\text{H}_2\text{O}] = 0.13\text{--}1.08\text{ M}$ ) and almost constant benzene concentration ( $[\text{C}_6\text{H}_6] = 1.42\text{--}1.50\text{ M}$ ).  $[\text{Pt}] = 6.7 \times 10^{-3}\text{ M}$ ;  $[\text{Me}_4\text{N}^+\text{BF}_4^-] = 0.15\text{ M}$ ;  $T = 25\text{ }^\circ\text{C}$ . Calculated rate constant:  $k = (1.53 \pm 0.03) \times 10^{-5}\text{ s}^{-1}$ .  $k_{\text{obs}} = k[\text{C}_6\text{H}_6]/[\text{H}_2\text{O}]$ .



**Figure 4.** Eyring plot for the reaction of benzene with **2a** in TFE.  $[\text{C}_6\text{H}_6] = 1.50\text{ M}$ ;  $[\text{H}_2\text{O}] = 0.24\text{ M}$ ;  $[\text{Pt}] = 6.7 \times 10^{-3}\text{ M}$ ;  $[\text{Me}_4\text{N}^+\text{BF}_4^-] = 0.15\text{ M}$ ;  $T = 23, 35, 45,$  and  $55\text{ }^\circ\text{C}$ . Calculated activation parameters:  $\Delta H^\ddagger = 19 \pm 0.3\text{ kcal mol}^{-1}$ ,  $\Delta S^\ddagger = -16 \pm 1\text{ cal mol}^{-1}\text{ K}^{-1}$ , and  $\Delta G^\ddagger_{298\text{ K}} = 24 \pm 1\text{ kcal mol}^{-1}$ .

dependence on water concentration, giving the rate law shown as eq 1. The kinetic isotope effect is close to unity;  $k_{\text{H}}/k_{\text{D}} =$

$$-\frac{d[\mathbf{2a}]}{dt} = k \frac{[\text{C}_6\text{H}_6]}{[\text{H}_2\text{O}]}[\mathbf{2a}] \quad (1)$$

$1.06 \pm 0.05$ . The temperature dependence of the reaction was studied over the range  $23\text{--}55\text{ }^\circ\text{C}$ , and the activation parameters were calculated from the Eyring plot shown in Figure 4:  $\Delta H^\ddagger = 19 \pm 0.3\text{ kcal mol}^{-1}$ ,  $\Delta S^\ddagger = -16 \pm 1\text{ cal mol}^{-1}\text{ K}^{-1}$ , and  $\Delta G^\ddagger_{298\text{ K}} = 24 \pm 1\text{ kcal mol}^{-1}$ .

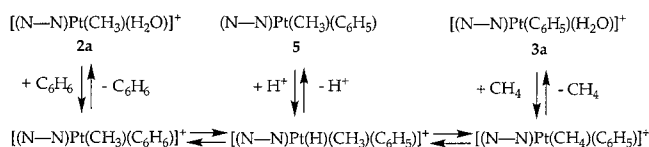
**Deuterium Scrambling.** As in the previously reported studies on the closely related species  $[(\text{tmeda})\text{Pt}(\text{CH}_3)(\text{NC}_5\text{F}_5)]^+[\text{B}\{3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2\}_4]^-$  and  $[(\text{N}^i\text{-N}^i)\text{Pt}(\text{CH}_3)(\text{OH}_2)]^+\text{BF}_4^-$ ,<sup>8,9</sup> reaction with deuterated hydrocarbon substrates leads to multiple incorporation of deuterium in the liberated methane. In three parallel NMR tube experiments,  $\text{C}_6\text{H}_6$ ,  $1,3,5\text{-C}_6\text{H}_3\text{D}_3$ , and  $\text{C}_6\text{D}_6$ , respectively, were allowed to react with **2a** in TFE- $d_3$ , and the methane isotopomer distributions after complete reaction were determined from  $^1\text{H}$  NMR analysis.<sup>15</sup> Results are summarized in Table 1.

**Table 1.** Methane Isotopomer Distributions Obtained in Reactions with  $\text{C}_6\text{H}_6$ ,  $1,3,5\text{-C}_6\text{H}_3\text{D}_3$ , and  $\text{C}_6\text{D}_6$

isotopomer	$\text{C}_6\text{H}_6$		$1,3,5\text{-C}_6\text{H}_3\text{D}_3$		$\text{C}_6\text{D}_6$	
	found (%)	calcd (%) <sup>a</sup>	found (%)	calcd (%) <sup>a</sup>	found (%)	calcd (%) <sup>a</sup>
$\text{CH}_4$	100	31	12	< 1 <sup>b</sup>	—	—
$\text{CH}_3\text{D}$	—	37	47	17	5	5
$\text{CH}_2\text{D}_2$	—	20	36	32	36	36
$\text{CHD}_3$	—	11	5	32	47	47
$\text{CD}_4$	—	—	—	19	12	12
total % D	—	28	33	63	67	67

<sup>a</sup> Calculated statistical distribution. <sup>b</sup> Presumably formed due to slow concurrent decomposition of **2a**.

#### Scheme 4



The absence of deuterium in methane generated in the reaction with  $\text{C}_6\text{H}_6$  rules out any H/D exchange between intermediates and either solvent or water.<sup>16</sup> In contrast, the reactions with  $1,3,5\text{-C}_6\text{H}_3\text{D}_3$  and  $\text{C}_6\text{D}_6$  produce substantial amounts of  $\text{CH}_3\text{D}$ ,  $\text{CH}_2\text{D}_2$ , and  $\text{CHD}_3$  (easily detected by  $^1\text{H}$  NMR spectroscopy) and, in the latter case, significant amounts of  $\text{CD}_4$  (identified by  $^2\text{H}$  NMR spectroscopy). This behavior may be explained by an extension of the same mechanism previously proposed,<sup>8</sup> shown in Scheme 4.

Isotope scrambling is effected by two processes: interconversion between the hydrocarbon complex intermediates  $[(\text{N-N})\text{Pt}(\text{II})(\text{CH}_3)(\text{C}_6\text{H}_6)]^+$  and  $[(\text{N-N})\text{Pt}(\text{II})(\text{CH}_4)(\text{C}_6\text{H}_5)]^+$  by way of the platinum(IV) methyl/phenyl/hydride, and rearrangement of the C,H- $\eta^2$ -coordinated benzene and methane adducts from one C–H bond to another. Three additional features should be noted. First, no discernible incorporation of deuterium into the Pt– $\text{CH}_3$  group of **2a** could be observed by  $^1\text{H}$  NMR during the course of the reaction.<sup>17</sup> Second, when the total extent of deuterium incorporation in these experiments is calculated, *almost full statistical scrambling of deuterium into methane is achieved* (63% in the reaction with  $\text{C}_6\text{D}_6$  and 28% in the reaction with  $1,3,5\text{-C}_6\text{H}_3\text{D}_3$ ), assuming one molecule of benzene exchanges isotopes with one molecule of **2a**. Third, the deprotonation of  $[(\text{N-N})\text{Pt}(\text{H})(\text{CH}_3)(\text{C}_6\text{H}_5)]^+$  must be relatively slow, a difference from the tetramethylenediamine system.<sup>6a</sup> These findings imply that (a) once a molecule of benzene has coordinated and undergone C–H activation, initiating the exchange process, loss of benzene to regenerate **2a** is considerably slower than loss of methane to produce **3a**, i.e., scrambling involving more than one molecule of benzene prior to methane loss is not significant, and (b) the energetic barriers for elimination of benzene and methane from the respective

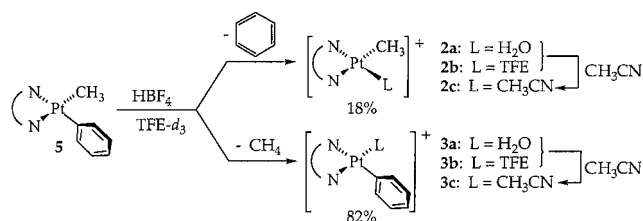
(15) The relative amounts of the different isotopomers were determined by NMR integration with one of the diimine arene methyl signals in the product serving as internal standard. The quantity of the  $^1\text{H}$  NMR inactive isotopomer  $\text{CD}_4$  was calculated from the total amount of methane generated (as determined in the reaction with  $\text{C}_6\text{H}_6$ ).

(16) Water is mainly present as  $\text{D}_2\text{O}$  in the solution due to facile H/D exchange with TFE- $d_3$ .

(17) More recent studies of the reaction of benzene- $d_6$  with a related platinum methyl complex reveals at partial reaction a very weak 1:1:1 triplet slightly upfield of the  $^1\text{H}$  NMR signal for  $[\text{Pt}-\text{CH}_3]$ , indicative of  $[\text{Pt}-\text{CH}_2\text{D}]$ . The NMR data for reaction of **2a** with deuterated benzenes is not of sufficient quality to reveal this minor signal, but we believe that there is a small extent of deuterium incorporation into the methyl group, as is expected from the relative rates of loss of benzene and methane on protonation of  $(\text{N-N})\text{Pt}(\text{II})(\text{CH}_3)(\text{C}_6\text{H}_5)$  (vide infra). Zhong, A. H.; Labinger, J. A.; Bercaw, J. E. Unpublished results.



## Scheme 5



intermediates must be much higher than the barriers involved in the interconversion between these species.

**Synthesis and Protonation of (N–N)Pt(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>) (5). Generation of [(N–N)Pt(CH<sub>3</sub>)(C,C-η<sup>2</sup>-C<sub>6</sub>H<sub>6</sub>)]<sup>+</sup> at Low Temperature.** Protonation of the methyl phenyl complex **5** offers an alternate route to the manifold of postulated intermediates involved in the H/D scrambling process (Scheme 4). Given the relative activation barrier heights discussed above, it is not implausible that one or more intermediates might be sufficiently long-lived for direct observation by NMR at low temperature, as has been accomplished for several platinum(IV) alkyl hydride species.<sup>6</sup> Furthermore, the relative amounts of the final products (**2**, **3**, benzene, and methane) resulting from the protonation of **5** in TFE should give a direct measure of the difference in energy barriers for benzene and methane loss.

Attempted preparation of **5** by direct reaction of (N–N)Pt(C<sub>6</sub>H<sub>5</sub>)(Cl) with methyl lithium or (N–N)Pt(CH<sub>3</sub>)(Cl) with phenyllithium led to extensive decomposition and formation of platinum black. This does not take place with the corresponding tetramethylethylenediamine complexes, and may be due to low-lying diimine-centered LUMOs facilitating reduction of the platinum species by the lithium reagents. We therefore decided to perform the arylation at platinum *before* the introduction of the diimine ligand.

Reaction between Pt(CH<sub>3</sub>)(Cl)(SMe<sub>2</sub>)<sub>2</sub> and phenyllithium gave Pt(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)(SMe<sub>2</sub>)<sub>2</sub><sup>18</sup> as the major product. Small amounts of Pt(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(SMe<sub>2</sub>)<sub>2</sub> were also formed in the reaction. Attempts to isolate Pt(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)(SMe<sub>2</sub>)<sub>2</sub> by recrystallization at this stage were unsuccessful. Subsequent reaction of the crude Pt(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)(SMe<sub>2</sub>)<sub>2</sub> with the diimine ligand (N–N) gave a mixture of about 90% **5** and 10% byproduct (N–N)Pt(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (**4**). Separation of the desired product was achieved by flash chromatography on basic alumina. Analytically pure **5** was obtained in 31% overall yield.

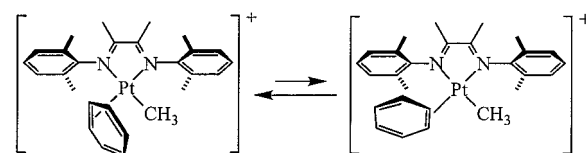
In an NMR tube, **5** was protonated with 1 equiv of aqueous HBF<sub>4</sub> in TFE-*d*<sub>3</sub> at 25 °C. <sup>1</sup>H NMR spectroscopy revealed that 18% methyl species (**2a** + **2b**) and 82% phenyl species (**3a** + **3b**) were formed in the reaction (Scheme 5). Subsequent addition of acetonitrile to the product mixture led to the more stable **2c** and **3c**, in the same 18:82 ratio. This result implies that the transition state for elimination of benzene from **iii** in Scheme 7 lies about 0.9 kcal/mol higher (ΔΔ*G*<sup>‡</sup>) than that for elimination of methane.

In a second NMR tube experiment, 10 equiv of HOTf was added to **5** at –78 °C in dichloromethane.<sup>19</sup> A reaction took place immediately upon addition of the acid, resulting in a pale orange-yellow solution. The <sup>1</sup>H NMR spectrum at –69 °C

(18) The <sup>1</sup>H NMR spectrum of the product is highly complex. We presume that this is due to the formation of a mixture of *cis*-Pt(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)(SMe<sub>2</sub>)<sub>2</sub> (major species), *trans*-Pt(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)(SMe<sub>2</sub>)<sub>2</sub>, *cis*-Pt<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(μ-SMe<sub>2</sub>)<sub>2</sub>, and *trans*-Pt<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(μ-SMe<sub>2</sub>)<sub>2</sub>. Selected <sup>1</sup>H NMR data for *cis*-Pt(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)(SMe<sub>2</sub>)<sub>2</sub>: (300 MHz, dichloromethane-*d*<sub>2</sub>) δ 0.56 (s, <sup>2</sup>*J*(<sup>195</sup>Pt–H) = 84.5 Hz, 3 H, PtMe), 2.11 (s, <sup>3</sup>*J*(<sup>195</sup>Pt–H) = 24.3 Hz, 6 H, PtSMe<sub>2</sub>), 2.39 (s, <sup>3</sup>*J*(<sup>195</sup>Pt–H) = 22.8 Hz, 6 H, PtSMe<sub>2</sub>).

(19) Low-temperature experiments at –78 °C cannot be performed in TFE due to its high freezing point (–45 °C).

## Scheme 6



reveals clean formation of what appears to be a single species (**i**), stable at this temperature, which we formulate as the benzene adduct [(N–N)Pt(CH<sub>3</sub>)(C,C-η<sup>2</sup>-C<sub>6</sub>H<sub>6</sub>)]<sup>+</sup>, on the basis of the following: (1) No signals attributable to free methane or benzene, or to any platinum hydride, can be detected in the <sup>1</sup>H NMR spectrum. (2) The platinum methyl group (integrating for 3 H) appears as a broad signal at δ –1.59, far upfield from where methyl groups coordinated to neutral or cationic {(N–N)Pt(II)} and {(N–N)Pt(IV)} normally resonate<sup>20</sup> (Figure 5). (3) In the aromatic region, a singlet is observed at δ 6.96 integrating for 6 H, in addition to signals for the diimine aryl protons. (4) At –33 °C (by which temperature **i** has begun to convert to new species) the singlet in the aromatic region exhibits <sup>195</sup>Pt satellites (*J*(<sup>195</sup>Pt–H) = 23.5 Hz); the platinum methyl signal also exhibits satellites, as well as a substantial shift downfield (δ –1.35, <sup>2</sup>*J*(<sup>195</sup>Pt–H) = 65.9 Hz).

These observations suggest that **i** contains a C,C-η<sup>2</sup>-benzene coordinated to the Pt(II) center. By analogy to platinum(II) olefin complexes, the coordinated C=C bond would be expected to be oriented perpendicular to the coordination plane. As shown in Scheme 6, there are two possible conformers, of which the one on the left appears likely to be more favorable on steric grounds. In this conformer, the platinum methyl group should lie in the shielding region created by the benzene ring current effect, accounting for the abnormally high upfield shift of the methyl signal.

This interpretation would also explain the large temperature dependence of that shift, since the relative population of the two conformers would be expected to be temperature dependent, as well as the fact that the methyl signal is relatively broad, if the interconversion between conformers is not extremely fast on the NMR time scale at these low temperatures. In addition to the conformer interconversion, of course, the platinum must also be rapidly interchanging among the six possible C,C-η<sup>2</sup> coordination modes for the benzene ligand to render all the hydrogens apparently chemically equivalent.

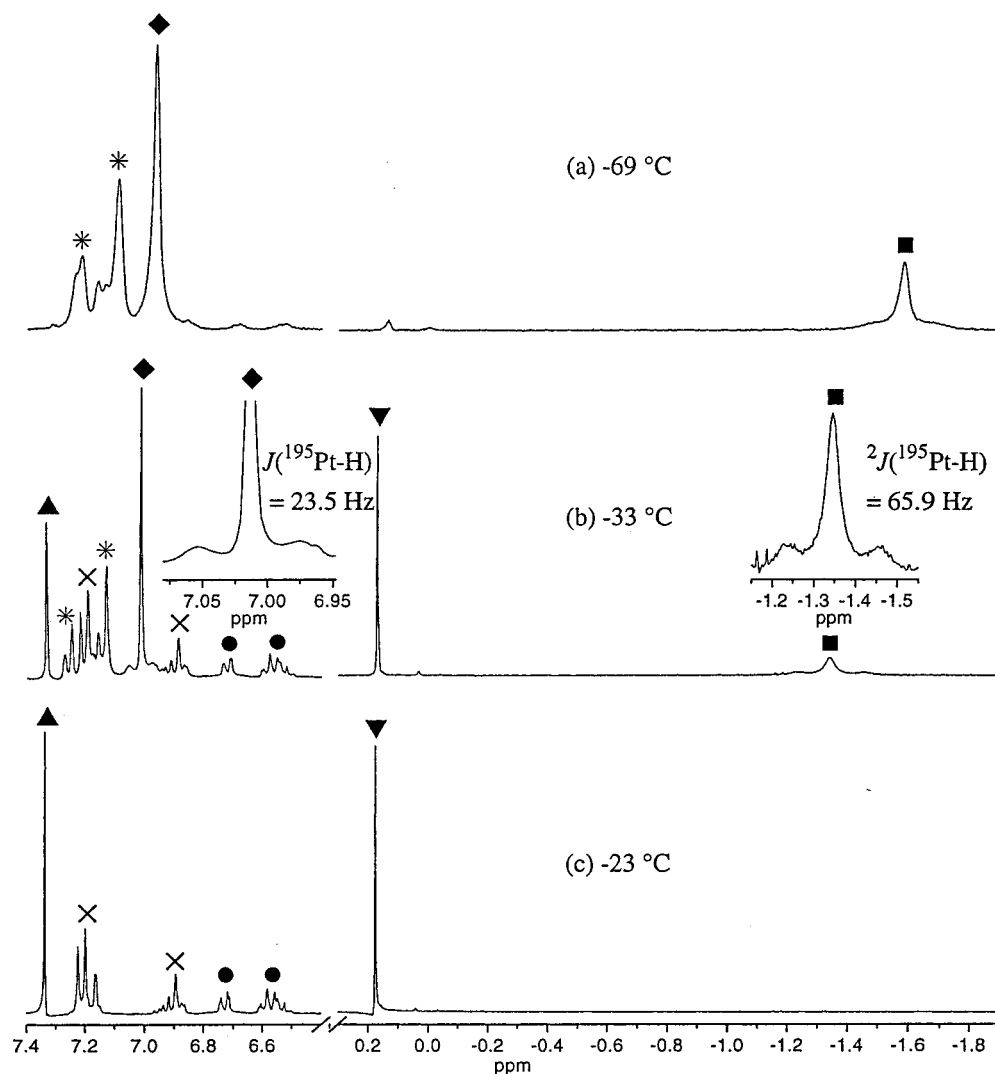
Although C,H-η<sup>2</sup> benzene coordination is also possible in principle, it seems to us much less likely on several grounds. First, there is no obvious reason a conformation placing the coordinated benzene in a position to shield the methyl group would be favorable; alternatives wherein the benzene ring lies outside the coordination plane seem at least as attractive. Second, such a structure would be expected to give a substantially higher value for *J*(<sup>195</sup>Pt–H). Third, there is no good precedent for such a coordination mode—several determined attempts to generate a C,H-η<sup>2</sup>-methane complex from analogous platinum methyl complexes were unsuccessful<sup>21</sup>—whereas a C,C-η<sup>2</sup>-benzene species has been isolated in a related Rh system where the C–H activation step is sterically blocked.<sup>22</sup>

At temperatures above ca. –40 °C, elimination of methane and benzene is observed. At –23 °C, all of the benzene adduct **i** is cleanly converted to products within an hour. Presumably

(20) See for instance compounds **2a–c** and **5**, or similar complexes reported in ref 9.

(21) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **1998**, *37*, 2422–31.

(22) Jones, W. D.; Feher, F. H. *J. Am. Chem. Soc.* **1984**, *106*, 1650.



**Figure 5.** Selected parts of the  $^1\text{H}$  NMR spectra showing the species formed after protonation of **5** with HOTf in dichloromethane- $d_2$  at  $-78\text{ }^\circ\text{C}$ : (a) at  $-69\text{ }^\circ\text{C}$ ; the benzene adduct  $[(\text{N}-\text{N})\text{Pt}(\text{CH}_3)(\text{C}_6\text{H}_6)]^+$  (**i**); ( $\blacksquare$ )  $\text{PtCH}_3$ , ( $\blacklozenge$ )  $\text{PtC}_6\text{H}_5$ , ( $*$ )  $\text{ArH}$ ; (b) at  $-33\text{ }^\circ\text{C}$ ; a mixture of **i** and the products  $(\text{N}-\text{N})\text{Pt}(\text{CH}_3)(\text{OTf})$  (**6**),  $(\text{N}-\text{N})\text{Pt}(\text{C}_6\text{H}_5)(\text{OTf})$  (**7**), benzene, and methane; ( $\times$ ) **6** and **7**,  $\text{ArH}$ ; ( $\bullet$ ) **7**,  $\text{PtC}_6\text{H}_5$ ; ( $\blacktriangledown$ )  $\text{CH}_4$ ; ( $\blacktriangle$ )  $\text{C}_6\text{H}_6$ ; (c) at  $-23\text{ }^\circ\text{C}$ ; after full conversion to the products.

the latter are the corresponding methyl and phenyl triflates **6** and **7**, although we have not yet isolated them in pure form.<sup>23</sup> The ratio of **6**:**7** is about 40:60, indicating that loss of benzene is relatively less disfavored compared to that of methane at these low temperatures in dichloromethane than in TFE at room temperature. No other intermediates could be observed prior to methane/benzene elimination by  $^1\text{H}$  NMR.

**Proposed Mechanism.** All of the above results may be accounted for in terms of Scheme 7, where the manifold of intermediates may be accessed either by protonation of **5** or by substitution of benzene for water in **2a**.

We can construct a qualitative reaction coordinate diagram, shown in Figure 6. The details are based on the following observations of the kinetics and isotopic exchange: (1) The observation of almost complete statistical scrambling of deuterium into the produced methane in the reactions between **2a** and  $\text{C}_6\text{D}_6/1,3,5\text{-C}_6\text{H}_3\text{D}_3$  implies a rapid dynamic equilibrium between the benzene adducts **i** and **ii** and methane adduct **v**

(23) The closely related complex  $(\text{N}^f\text{-N}^f)\text{Pt}(\text{CH}_3)(\text{OTf})$  can be generated in dichloromethane- $d_2$  by protonation of the corresponding platinum dimethyl complex with 1 equiv of HOTf and characterized by  $^{19}\text{F}$  NMR, but it is unstable at ambient temperature. Johansson, L.; Tilset, M. Preceding paper in this issue.

and, therefore, that the barriers between these intermediates are considerably lower than those for elimination of either methane or benzene. The relative height of the two latter barriers may be determined from the ratio of products obtained in the protonolysis of **5** (methane:benzene = 82:18 at room temperature). (2) The diagram implies that substitution of benzene for water in **2a** to afford **i** should be the rate-limiting step in benzene activation, consistent with the rate law, which is first-order in benzene as well as **2a**. If initial coordination of benzene involves C=C interaction rather than C–H, as argued above, this is also consistent with the very small kinetic isotope effect found.

The observed inverse first-order dependence on the water concentration precludes a direct, associative pathway for the water–benzene exchange at **2a**, but there are still (at least) two possible scenarios that agree with the observed kinetics: either a dissociative pathway via the coordinatively unsaturated  $14\text{e}^-$  intermediate  $[(\text{N}-\text{N})\text{Pt}(\text{Me})]^+$  (Scheme 8) or a solvent-assisted associative pathway via the TFE complex **2b** (Scheme 9). Utilizing steady-state and fast preequilibrium approximations, the corresponding rate laws for the two alternative mechanisms can be formulated as given in eqs 2 and 3, respectively.

For situations where  $k_{-1}[\text{H}_2\text{O}] \gg k_2[\text{C}_6\text{H}_6]$  and  $[\text{H}_2\text{O}] \gg$

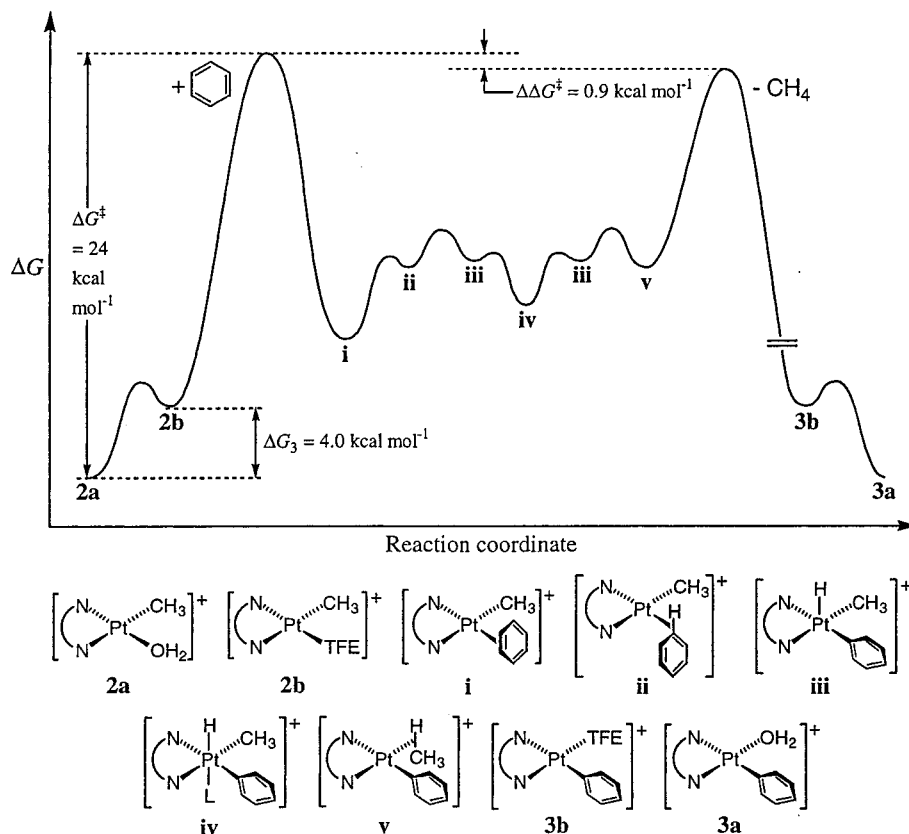
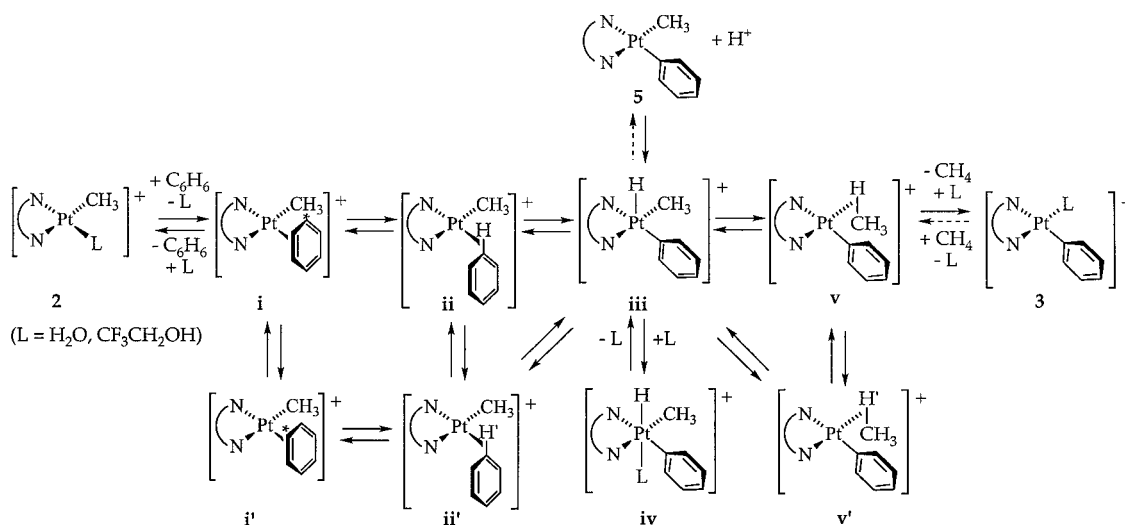
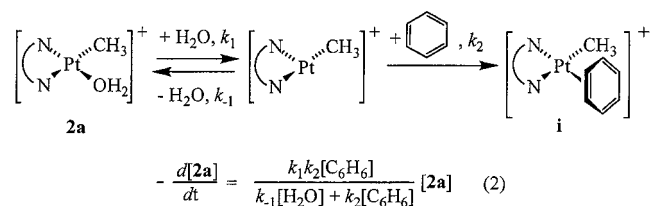


Figure 6. Qualitative reaction coordinate diagram for the reaction between **2a** and benzene.

#### Scheme 7



#### Scheme 8



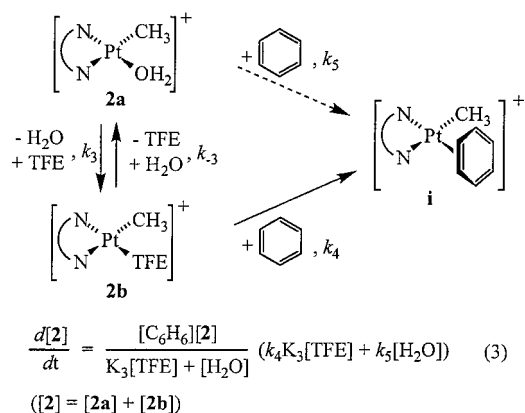
$K_3[TFE]$ , and neglecting any contribution from a direct associative  $H_2O$ –benzene substitution on **2a** ( $k_5$ ), both rate laws are in agreement with the observed kinetics (eq 1). The absence of rate saturation in  $[C_6H_6]$  appears to support eq 3, but of course it might just be that sufficiently high benzene concentrations

were not reached. The rather negative activation entropy obtained from the Eyring plot ( $-16 \text{ cal mol}^{-1} \text{ K}^{-1}$ ) also argues against a dissociative pathway; however, solvation effects might contribute to a significant extent to this value. Thus, while the solvent-assisted associative route seems somewhat more consistent with observations, we do not want to draw any definitive conclusion at this time.<sup>24</sup>

Once the benzene adduct **i** is formed, a dynamic equilibrium between it and the postulated intermediates **ii–v** is established.<sup>25</sup> From the protonation experiment of **5** at low temperature we

(24) After experiments described in this paper, two of us have obtained evidence supporting associative rather than dissociative substitution of methane for acetonitrile for **2c** (Johansson, L.; Tilsted, M. *J. Am. Chem. Soc.*, in press).

## Scheme 9



have direct  $^1\text{H}$  NMR evidence for the benzene adduct **i** in dichloromethane, and we assume that this species is formed in TFE as well. On the basis of the  $^1\text{H}$  NMR features of **i**, we also propose that benzene is rapidly rotating in this complex, and is probably C=C  $\pi$ -coordinated in its energetically most stable form. However, a  $\sigma$ -coordinated benzene intermediate **ii**, coordinated through a C–H bond, also likely lies on the reaction coordinate for the subsequent breaking of a C–H bond in benzene. This process yields a transient 5-coordinated platinum(IV) hydride intermediate (**iii**)<sup>26</sup> which can eliminate methane via **v**.

We have no direct evidence for the relative energy, or even the existence, of the ligand-stabilized six-coordinate platinum(IV) hydride **iv** (L = water or TFE). Analogous compounds may be generated by low-temperature protonation or other routes<sup>10,27</sup> with different nitrogen ligand systems. One might suppose that, in the absence of an  $\eta^2$ -benzene alternative, a species such as **iv** might be observable, but on protonolysis of the dimethyl complex (N–N)Pt(CH<sub>3</sub>)<sub>2</sub> with HBF<sub>4</sub> at low temperature, no intermediates at all could be observed prior to methane loss. However, when an analogous experiment was performed with (N<sup>f</sup>–N<sup>f</sup>)Pt(CH<sub>3</sub>)<sub>2</sub> and HBF<sub>4</sub> in dichloromethane/diethyl ether at –78 °C, clean formation of [(N<sup>f</sup>–N<sup>f</sup>)Pt(CH<sub>3</sub>)<sub>2</sub>(H)(L)]<sup>+</sup> (stable up to ca –40 °C) was observed by  $^1\text{H}$  NMR.<sup>28</sup> When the temperature was gradually increased, no other intermediates were observed prior to methane loss, suggesting that the platinum(IV) hydride is energetically more stable than any putative [(N<sup>f</sup>–N<sup>f</sup>)Pt(CH<sub>3</sub>)( $\sigma$ -CH<sub>4</sub>)]<sup>+</sup> intermediate. If we assume that the same trend applies to the present benzene activation system, the order of stability would be **i** > **iv** > **ii**  $\approx$  **v**. In any case, as long as intermediate **iv** is less stable than **i**, it will not be detectable either by direct observation or by affecting the interconversion between **ii** and **v** in the present system.

(25) One might also argue that there exists only one benzene adduct, that is to say that intermediates **i** and **ii** in Scheme 7 should be collapsed into one, the C,C- $\eta^2$ -benzene isomer. But C,H- $\eta^2$ -alkane adducts (as for **v**) are commonly invoked intermediates in oxidative addition and reductive elimination of C–H bonds. Moreover, it is difficult to envision how the C,C- $\eta^2$ -coordinated benzene would undergo direct C–H oxidative addition, or how reductive elimination of the C–H bond of the phenyl hydride intermediate would lead directly to the C,C- $\eta^2$ -benzene isomer. Thus, we prefer the interpretation shown in Scheme 7.

(26) It has been shown that reductive elimination from 6-coordinated Pt(IV) species with a labile ligand L takes place via initial dissociation of L to a 5-coordinated Pt(IV) intermediate. By the principle of microscopic reversibility, we assume that **iii** is the intermediate formed after insertion into a C–H bond in **ii** and **v**, respectively. See: Crumpton, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2000**, *122*, 962 and references therein.

(27) (a) Fekl, U.; Zahl, A.; van Eldik, R. *Organometallics* **1999**, *18*, 4156. (b) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966.

(28) Johansson, L.; Tilset, M. Preceding paper in this issue.

The reaction is completed by loss of methane from **v** to give **3a**. By microscopic reversibility, this may proceed either dissociatively (via the coordinatively unsaturated 14 e<sup>–</sup> intermediate **vi**) or associatively (via the solvento species **3b**). Although Scheme 4 shows this step as reversible, we have seen no evidence for the reverse reaction under our conditions, partly because the concentration of methane is very low. But we expect that the rate of methane activation by **3a** is inherently very low, as this process (measured by isotope exchange) is generally slower than benzene activation;<sup>9</sup> also **3a** is likely to be more stable than **2a**, further increasing the reaction barrier.

In conclusion, the ArN=C(Me)C(Me)=NAr (Ar = 2,6-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) ligand-stabilized methylplatinum(II) cation undergoes relatively clean reactions with benzene. Rate-determining benzene coordination leads to isomeric C,C- $\eta^2$ - and C,H- $\eta^2$ -benzene adducts that rapidly interconvert via the platinum(IV) methyl/phenyl/hydride complex with a C,H- $\eta^2$ -methane adduct. Loss of methane to afford the phenylplatinum(II) cation, although somewhat faster than loss of benzene, is surprisingly much slower than interconversions of the isomeric benzene and methane adducts.

## Experimental Section

**General Considerations.** Trifluoroethanol (TFE) and TFE-*d*<sub>3</sub> were distilled from CaSO<sub>4</sub> and a small amount of NaHCO<sub>3</sub> and stored over 3 Å molecular sieves. All other solvents were dried according to standard procedures. The UV/vis experiments were performed on an HP 8452A spectrophotometer; the cuvette holder was electronically thermostated with an HP 89090A instrument (Peltier element).  $^1\text{H}$  NMR spectra were recorded on General Electric QE300, Bruker Advance DXP 300, and Innova 500 instruments.  $^1\text{H}$  NMR chemical shifts are reported in parts per million relative to tetramethylsilane, with the residual solvent proton resonance as internal standard. Elemental analyses were carried out at the Caltech Elemental Analysis Facility by Fenton Harvey or Ilse Beetz, Mikroanalytisches Laboratorium, Kronach, Germany. Pt(CH<sub>3</sub>)<sub>4</sub>( $\mu$ -SMe<sub>2</sub>)<sub>2</sub>,<sup>29a</sup> Pt(CH<sub>3</sub>)(Cl)(SMe<sub>2</sub>)<sub>2</sub>,<sup>26a</sup> Pt-(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(SMe<sub>2</sub>)<sub>2</sub>,<sup>26b</sup> and the diimine ligand N–N = ArN=C(Me)C–(Me)=NAr, Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>4</sub>,<sup>30</sup> were prepared as described in the literature. (N–N)Pt(CH<sub>3</sub>)<sub>2</sub> (**1**) was prepared according to the procedure developed by Scollard et al.<sup>31</sup>

[(N–N)Pt(CH<sub>3</sub>)(OH<sub>2</sub>)<sub>2</sub>]<sup>+</sup>(BF<sub>4</sub><sup>–</sup>) (**2a**(BF<sub>4</sub><sup>–</sup>)) and [(N–N)Pt(CH<sub>3</sub>)(TFE)]<sup>+</sup>(BF<sub>4</sub><sup>–</sup>) (**2b**(BF<sub>4</sub><sup>–</sup>)). A 100 mL Schlenk flask loaded with **1** (111 mg, 0.214 mmol) was cooled to –15 °C, whereupon a cooled mixture of TFE (25 mL) and a 48% solution of HBF<sub>4</sub> in H<sub>2</sub>O (28  $\mu$ L, 0.21 mmol) was added with a syringe. The solution was slowly heated to 0 °C and stirred until all starting material had reacted to give an orange solution. The solution was cooled to –15 °C, and the solvent was slowly removed by vacuum transfer. The residue was dried in vacuo at ambient temperature to give an orange-brown powder:  $^1\text{H}$  NMR (300 MHz, TFE-*d*<sub>3</sub>) (**2a**)  $\delta$  0.63 (s, <sup>2</sup>J(<sup>195</sup>Pt–H) = 73.1 Hz, 3 H, PtMe), 1.64 (s, 3 H, NCMeC'MeN), 1.83 (s, 3 H, NCMeC'MeN), 2.21 (s, 6 H, ArMe), 2.31 (s, 6 H, Ar'Me), 7.19–7.28 (m, 6 H, ArH); (**2b**)  $\delta$  0.65 (s, 3 H, PtMe), 1.76 (s, 3 H, NCMeC'MeN), 1.91 (s, 3 H, NCMeC'MeN), 2.21 (s, 6H, ArMe), 2.34 (s, 6H, Ar'Me) 7.19–7.28 (m, 6 H, ArH). Anal. Calcd for C<sub>21</sub>H<sub>29</sub>BF<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Pt (**2a**): C, 41.53; H, 4.81; N, 4.61. Anal. Calcd for C<sub>23</sub>H<sub>30</sub>BF<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Pt (**2b**): C, 40.07; H, 4.39; N, 4.06. Found: C, 39.93; H, 4.50; N, 4.11.

(N–N)Pt(CH<sub>3</sub>)(NCMe)]<sup>+</sup>(BF<sub>4</sub><sup>–</sup>) (**2c**(BF<sub>4</sub><sup>–</sup>)). To a solution of **1** (127 mg, 0.245 mmol) in 12 mL of acetonitrile was added a 54% solution of HBF<sub>4</sub> in diethyl ether (34  $\mu$ L, 0.25 mmol), and the reaction mixture was stirred for 15 min. The solvent was removed, and the residue was washed with several portions of diethyl ether. The product was obtained

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as an orange powder (152 mg, 98%) after drying in vacuo:  $^1\text{H}$  NMR (300 MHz, TFE- $d_3$ )  $\delta$  0.57 (s,  $^2J(^{195}\text{Pt}-\text{H}) = 75.2$  Hz, 3 H, PtMe), 1.85 (s, 3 H,  $^4J(^{195}\text{Pt}-\text{H}) = 12.1$  Hz, PtNCMe), 1.88 (s, 3 H,  $^4J(^{195}\text{Pt}-\text{H}) = 9.2$  Hz, NCMeC'MeN), 1.94 (s, 3 H, NCMeC'MeN), 2.18 (s, 6 H, ArMe), 2.29 (s, 6 H, Ar'Me), 7.21–7.31 (m, 6 H, ArH);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz, dichloromethane- $d_2$ )  $\delta$  -13.2 ( $^1J(^{195}\text{Pt}-\text{C}) = 671$  Hz, PtMe), 2.7 ( $^3J(^{195}\text{Pt}-\text{C}) = 13.8$  Hz, PtNCMe), 17.4 and 17.6 (ArMe and Ar'Me), 19.2 ( $^3J(^{195}\text{Pt}-\text{C}) = 17.4$  Hz, NCMeC'MeN), 20.1 ( $^3J(^{195}\text{Pt}-\text{C}) = 46.9$  Hz, NCMeC'MeN), 118.9 ( $^2J(^{195}\text{Pt}-\text{C}) = 290$  Hz, PtNCMe), 127.9 (Ar C<sub>p</sub>), 128.5 ( $^3J(^{195}\text{Pt}-\text{C}) = 10.0$  Hz, Ar C<sub>o</sub>), 128.8 (Ar' C<sub>m</sub>), 128.9 (Ar' C<sub>m</sub>), 129.0 (Ar' C<sub>p</sub>), 129.8 ( $^3J(^{195}\text{Pt}-\text{C}) = 14.9$  Hz, Ar C<sub>o</sub>), 142.7 ( $^2J(^{195}\text{Pt}-\text{C}) = 11.1$  Hz, Ar C<sub>ipso</sub>), 142.8 ( $^2J(^{195}\text{Pt}-\text{C}) = 30.5$  Hz, Ar' C<sub>ipso</sub>), 174.6 ( $^2J(^{195}\text{Pt}-\text{C}) = 60.0$  Hz, NCMeC'MeN), 183.3 (NCMeC'MeN). Anal. Calcd for C<sub>23</sub>H<sub>30</sub>BF<sub>4</sub>N<sub>3</sub>Pt: C, 43.82; H, 4.80; N, 6.67. Found: C, 44.11; H, 4.50; N, 6.37.

**(N-N)Pt(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(4).** A solution of Pt(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(SMe<sub>2</sub>)<sub>2</sub> (358 mg, 0.756 mmol) and the diimine ligand (221 mg, 0.756 mmol) in toluene (40 mL) was stirred at 45 °C for 18 h. Pentane (ca 100 mL) was added to let the product precipitate, and the mixture was slowly cooled to ambient temperature. The mother liquid was decanted, and the product was washed with several portions of pentane and finally dried in vacuo. The product was obtained as a dark purple powder (436 mg, 90%):  $^1\text{H}$  NMR (300 MHz, dichloromethane- $d_2$ )  $\delta$  1.64 (s, 6 H, NCMeC'MeN), 2.20 (s, 12 H, ArMe), 6.40 (m, 2H, PhH<sub>p</sub>), 6.49 (m, 4H, PhH<sub>m</sub>), 6.86 ("d",  $^3J(\text{H}-\text{H}) = 7.2$  Hz,  $^3J(^{195}\text{Pt}-\text{H}) = 70.3$  Hz, 4H, PhH<sub>o</sub>), 6.88–6.92 (m, 6 H, ArH). Anal. Calcd for C<sub>32</sub>H<sub>34</sub>N<sub>2</sub>Pt: C, 59.89; H, 5.34; N, 4.37. Found: C, 59.68; H, 5.10; N, 4.07.

**[(N-N)Pt(C<sub>6</sub>H<sub>5</sub>)(NCMe)]<sup>+</sup>(BF<sub>4</sub><sup>-</sup>) (3c(BF<sub>4</sub><sup>-</sup>)).** To a solution of **4** (104 mg, 0.162 mmol) in 10 mL of dichloromethane and 1 mL of acetonitrile was added a 54% solution of HBF<sub>4</sub> in diethyl ether (23  $\mu\text{L}$ , 0.17 mmol), and the reaction mixture was stirred for 30 min. The solvent was removed, and the residue was washed with several portions of diethyl ether. The product was obtained as an orange powder (108 mg, 94%) after drying in vacuo:  $^1\text{H}$  NMR (300 MHz, TFE- $d_3$ )  $\delta$  1.77 (s, 3 H, PtNCMe), 2.00 (s, 3 H, NCMeC'MeN), 2.10 (s, 3 H, NCMeC'MeN), 2.14 (s, 6 H, ArMe), 2.38 (s, 6 H, Ar'Me), 6.68–6.71 (m, 3H, PhH<sub>m</sub> and PhH<sub>p</sub>), 6.75–6.80 (m, 2H, PhH<sub>o</sub>), 6.88–6.99 (m, 3 H, ArH), 7.25–7.35 (m, 3 H, Ar'H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz, dichloromethane- $d_2$ )  $\delta$  2.8 ( $^3J(^{195}\text{Pt}-\text{C}) = 12.5$  Hz, PtNCMe), 17.8 and 17.8 (ArMe and Ar'Me), 19.5 ( $^3J(^{195}\text{Pt}-\text{C}) = 16.7$  Hz, NCMeC'MeN), 20.4 ( $^3J(^{195}\text{Pt}-\text{C}) = 47.4$  Hz, NCMeC'MeN), 118.2 (PtNCMe), 124.3 (PtPh C<sub>p</sub>), 126.7 ( $^2J(^{195}\text{Pt}-\text{C}) = 48.7$  Hz, PtPh C<sub>o</sub>), 128.3 (Ar C<sub>p</sub>), 128.4 (Ar C<sub>o</sub>), 128.6 (Ar C<sub>m</sub>), 129.0 (Ar' C<sub>m</sub>), 129.1 (Ar' C<sub>p</sub>), 129.4 ( $^3J(^{195}\text{Pt}-\text{C}) = 15.4$  Hz, Ar' C<sub>o</sub>), 132.2 ( $^1J(^{195}\text{Pt}-\text{C}) = 894$  Hz, PtPh C<sub>ipso</sub>), 135.1 (PtPh C<sub>m</sub>), 142.5 ( $^2J(^{195}\text{Pt}-\text{C}) = 12.0$  Hz, Ar C<sub>ipso</sub>), 143.2 (Ar' C<sub>ipso</sub>), 176.8 ( $^2J(^{195}\text{Pt}-\text{C}) = 59.6$  Hz, NCMeC'MeN), 183.5 (NCMeC'MeN). Anal. Calcd for C<sub>28</sub>H<sub>32</sub>BF<sub>4</sub>N<sub>3</sub>Pt: C, 48.57; H, 4.66; N, 6.07. Found: C, 48.64; H, 4.92; N, 5.88.

**(N-N)Pt(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>) (5).** A suspension of Pt(CH<sub>3</sub>)(Cl)(SMe<sub>2</sub>)<sub>2</sub> (228 mg, 0.617 mmol) in 40 mL of diethyl ether was cooled to -20 °C, and a 1.8 M solution of phenyllithium in diethyl ether/cyclohexane (360  $\mu\text{L}$ , 0.65 mmol) was added dropwise with a syringe. After the resulting solution was stirred for 45 min, 100 mL of water was added. The layers were separated, and the aqueous phase was extracted with diethyl ether (2  $\times$  75 mL). A small amount of charcoal was added to the combined organic phases, which were then dried over MgSO<sub>4</sub>. After filtration the diethyl ether solution was added to a 45 °C solution of the diimine ligand (200 mg, 0.68 mmol) in 50 mL of toluene, and the reaction mixture was stirred for 26 h at this temperature. The solvent was removed and the residue washed with several portions of pentane. To separate **5** from the byproduct (**4**, ca. 10%), flash chromatography (basic alumina, diethyl ether/hexanes, 1:1) was employed. The desired product was collected as the first dark purple fraction. The solvent was removed, and the product was washed with pentane and dried in vacuo, giving a dark purple powder (111 mg, 31%):  $^1\text{H}$  NMR (300 MHz, dichloromethane- $d_2$ )  $\delta$  0.75 (s,  $^2J(^{195}\text{Pt}-\text{H}) = 87.8$  Hz, 3 H, PtMe), 1.41 (s, 3 H, NCMeC'MeN), 1.52 (s, 3 H, NCMeC'MeN), 2.10 (s, 6 H, ArMe), 2.24 (s, 6 H, Ar'Me), 6.44–6.57 (m, 3 H, PhH<sub>m</sub> and PhH<sub>p</sub>), 6.72 ("d",  $^3J(\text{H}-\text{H}) = 8.1$  Hz,  $^3J(^{195}\text{Pt}-\text{H}) = 66.4$  Hz, 2 H, PhH<sub>o</sub>),

6.85–6.94 (m, 3 H, ArH), 7.12–7.25 (m, 3 H, Ar'H). Anal. Calcd for C<sub>27</sub>H<sub>32</sub>N<sub>2</sub>Pt: C, 55.95; H, 5.56; N, 4.83. Found: C, 55.62; H, 5.38; N, 4.44.

**Protonation of (N-N)Pt(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>) (5).** To an NMR tube loaded with **5** (4.9 mg,  $8.5 \times 10^{-3}$  mmol) was added a 48% solution of aqueous HBF<sub>4</sub> (1.2  $\mu\text{L}$ ,  $9 \times 10^{-3}$  mmol) dissolved in 0.7 mL of TFE- $d_3$ .  $^1\text{H}$  NMR showed a product composition consisting of **2a** (14%), **2b** (4%) **3a** (70%), and **3b** (12%). After addition of acetonitrile- $d_3$  (1.0  $\mu\text{L}$ , 0.02 mmol) to the solution,  $^1\text{H}$  NMR revealed clean formation of **2c** (18%) and **3c** (82%).

**Generation of [(N-N)Pt(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)<sup>+</sup>(OTf<sup>-</sup>)] (i(OTf<sup>-</sup>)) at Low Temperature.** To an NMR tube loaded with a solution of **5** (3.0 mg,  $5.2 \times 10^{-3}$  mmol) in 400  $\mu\text{L}$  of dichloromethane- $d_2$  was slowly added 150  $\mu\text{L}$  of dichloromethane  $d_2$  to form an upper, separate layer. After subsequent slow addition of a solution of HOTf (4.5  $\mu\text{L}$ ,  $5.2 \times 10^{-2}$  mmol) in 100  $\mu\text{L}$  of dichloromethane- $d_2$ /40  $\mu\text{L}$  of diethyl ether, the tube was sealed and cooled to -78 °C. The tube was shaken to mix the reactants (care was taken to minimize any heating of the sample), and a pale orange-yellow solution was immediately obtained. The tube was then transferred to a precooled NMR probe:  $^1\text{H}$  NMR (300 MHz, -69 °C)  $\delta$  -1.58 (s, 3 H, PtMe), 1.99 (s, 3 H, NCMeC'MeN), 2.04 (s, 3 H, NCMeC'MeN), 2.10 (s, 6 H, ArMe), 2.33 (s, 6 H, Ar'Me), 6.96 (s, 6 H, PtC<sub>6</sub>H<sub>6</sub>), 7.09–7.28 (m, 6 H, ArH and Ar'H); (300 MHz, -33 °C)  $\delta$  -1.35 (s,  $^2J(^{195}\text{Pt}-\text{H}) = 65.9$  Hz, 3 H, PtMe), 1.98 (s, 3 H, NCMeC'MeN), 2.02 (s, 3 H, NCMeC'MeN), 2.12 (s, 6 H, ArMe), 2.32 (s, 6 H, Ar'Me), 7.01 (s,  $J(^{195}\text{Pt}-\text{H}) = 23.5$  Hz, 6 H, PtC<sub>6</sub>H<sub>6</sub>), 7.13–7.27 (m, 6 H, ArH and Ar'H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz, dichloromethane- $d_2$ , -62 °C)  $\delta$  not obsd (PtMe), 17.1 and 17.3 (ArMe and Ar'Me), 19.5 (NCMeC'MeN), 19.8 (NCMeC'MeN), 120.7 (br, Pt-(C<sub>6</sub>H<sub>6</sub>)), 127.6, 127.9, 128.2, 128.2 (?), 128.6, 129.2 (Ar and Ar' C<sub>o</sub>, C<sub>m</sub>, and C<sub>p</sub>), 139.6 and 142.0 (Ar and Ar' C<sub>ipso</sub>), not obsd (NCMeC'MeN and NCMeC'MeN).

**NMR Data of the Products (N-N)Pt(CH<sub>3</sub>)(OTf) (6) and (N-N)Pt(C<sub>6</sub>H<sub>5</sub>)(OTf) (7).**  $^1\text{H}$  NMR (300 MHz, -23 °C) (**6**) (40%)  $\delta$  0.71 (s,  $^2J(^{195}\text{Pt}-\text{H}) = 73.9$  Hz, 3 H, PtMe), 1.53 (s, 3 H, NCMeC'MeN), 1.78 (s, 3 H, NCMeC'MeN), 2.18 (s, 6 H, ArMe), 2.25 (s, 6 H, Ar'Me), 7.14–7.24 (m, 6 H, ArH and Ar'H); (**7**) (60%)  $\delta$  1.66 (s, 3 H, NCMeC'MeN), 1.94 (s, 3 H, NCMeC'MeN), 2.14 (s, 6 H, ArMe), 2.34 (s, 6 H, Ar'Me), 6.49–6.61 (m, 3 H, PhH<sub>m</sub> and PhH<sub>p</sub>), 6.75 ("d",  $^3J(\text{H}-\text{H}) = 7.9$  Hz, 2 H, PhH<sub>o</sub>), 6.85–6.96 (m, 3 H, ArH), 7.14–7.24 (m, 3 H, Ar'H).

**UV/Vis Kinetics. General Procedure for the Preparation of Stock Solutions.** A Schlenk flask loaded with **1** (51.8 mg, 0.100 mmol) was cooled to -15 °C. A mixture of HBF<sub>4</sub> (48% in water, 13.1  $\mu\text{L}$ , 0.10 mmol) in 10 mL of 0.2 M Me<sub>4</sub>NBF<sub>4</sub> in TFE was added to the flask, and the reaction mixture was slowly allowed to warm to ambient temperature and stirred for 30 min. An appropriate amount of water was then added to the thus generated solution of **2a**. The actual water concentration in the stock solution was determined as follows: Two oven-dried NMR tubes were loaded with a known amount of ferrocene dissolved in 600  $\mu\text{L}$  of dichloromethane- $d_2$ . To one of the tubes was added 100  $\mu\text{L}$  of the stock solution. From the  $^1\text{H}$  NMR integration of the water signal in the two samples (the ferrocene signal serving as internal standard), the actual water concentration in the stock solution was calculated. The stock solutions were stored under argon at -20 °C.

**Varying Benzene Concentration.** A 500  $\mu\text{L}$  portion of stock solution ([H<sub>2</sub>O] = 0.16 M) was transferred to a 0.1 cm UV Pyrex cell. Benzene or benzene- $d_6$  (27, 53, 100, and 250  $\mu\text{L}$ ) (caution: cancer suspect agent) was then added to the cell with a syringe. The cell was sealed with a Teflon plug and shaken thoroughly. The reactions were followed by UV/vis spectroscopy at 390 nm at 25 °C over at least 3 half-lives.

**Varying Water Concentration.** A 400  $\mu\text{L}$  portion of stock solution ([H<sub>2</sub>O] = 0.20 M) was transferred to a 0.1 cm UV Pyrex cell. To seven different 2 mL solutions containing 4.5 M benzene in TFE were added 0, 11, 22, 32, 43, 54, and 108  $\mu\text{L}$  of water, respectively. Then, 200  $\mu\text{L}$  of the appropriate water/benzene/TFE solution was added to the UV cell with a syringe, and the reaction was followed as described above.

**Varying Temperature.** A 1.50 mL portion of stock solution ([H<sub>2</sub>O] = 0.36 M) was transferred to a 1 cm UV Pyrex cell equipped with a

magnetic stirbar. A 750  $\mu\text{L}$  portion of a 4.5 M solution of benzene in TFE was then added to the cell with a syringe. The cell was sealed with a Teflon screwcap and shaken thoroughly. The reactions were followed by UV/vis spectroscopy at 390 nm at 23, 35, 45, and 55  $^{\circ}\text{C}$  over at least 3 half-lives. Rate constants were obtained from a first-order three-parameter ( $k_{\text{obsd}}$ ,  $A_0$ , and  $A_{\infty}$ ) least-squares fit of the absorbance at 390 nm ( $A$ ) versus time ( $t$ ) data employing the equation  $A = A_{\infty} + (A_0 - A_{\infty})e^{-k_{\text{obsd}}t}$ . The activation parameters for the reaction were derived from a linear least-squares analysis of  $\ln(k/T)$  versus  $T^{-1}$

data, where  $k = k_{\text{obsd}}[\text{H}_2\text{O}]/[\text{C}_6\text{H}_6]$ .

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