# Detailed Mechanistic Information on Methane Elimination from a Methyl(hydrido)platinum(IV) Complex. Relevance for the Mechanism of Methane Activation

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*Received March 1, 1999*

The kinetics of methane reductive elimination from both isomers of the methyl(hydrido)-platinum(IV) complex $[Pt(H)(CH_3)_2(BPMA)]^+$ (BPMA = bis(pyridylmethyl)amine) were studied by $^1H$ NMR spectroscopy. The application of high-pressure techniques enabled the determination of the activation volume for methane elimination (+6 $cm^3$/mol for the *cis* isomer, ca. +8 $cm^3$/mol for the *trans* isomer). The low activation volume together with results on the rate and stereochemistry of deuterium incorporation into one methyl group of the *cis* isomer provides the basis for a suggested mechanism that involves five-coordinate platinum as a steady-state intermediate.



## Introduction

The catalytic oxidation of methane to methanol at low temperatures in homogeneous solution remains an important challenge. Considerable efforts were invested in the search for catalytic systems and in the understanding of the underlying reaction mechanisms. Impressive progress has been made in the study of the mechanism of methane activation by $Pt^{II}/Pt^{IV}$ complexes in aqueous solution (Shilov's reaction[1,2]) or other protic solvents.[3] The activation of methane can involve methyl(hydrido)platinum(IV) complexes, although they need not necessarily be involved in all catalytic systems. These have been postulated as crucial intermediates both in the protonolysis of some methyl $Pt^{II}$ complexes and in the activation of methane by several platinum complexes and were therefore synthesized.[4−9] The mechanism of Shilov's reaction, in accord with Shilov's original proposal and the mechanistic conclusions drawn by Bercaw et al.,[3,7] is shown in Scheme 1, which depicts a methane activation mechanism involving oxidative addition. A labile solvated $Pt^{II}$ species (**A**) binds methane to give an $\eta^2$-methane complex (**B**),[10] which can interconvert into a five-coordinate methyl(hydrido)platinum(IV) complex (**C**). Five-coordinate $Pt^{IV}$ is unstable, but can be stabilized by an additional ligand to give a complex of type **D**. In Scheme 1, the additional ligand is chloride, but in similar systems nitrogen donors have instead been used successfully.

We are interested in the initial steps of alkane activation via oxidative addition and the microscopic reverse of these steps. It is important to note that methyl(hydrido)platinum(IV) complexes are less likely as intermediates in cases where Pt(IV) is not stabilized sufficiently. A viable pathway for methane activation is then the direct deprotonation of the $\eta^2$-methane complex (**B**) to form the methylplatinum(II) complex (**E**). However, alkane activation proceeds via oxidative addition when Pt(IV) is stabilized strongly. This was demonstrated in an elegant way by showing that alkanes can add to labilized Pt(II) complexes to give alkyl(hydrido)platinum(IV) complexes in a stoichiometric reaction.[11] A pendant nitrogen donor arm was used for the stabilization of Pt(IV). The use of nitrogen donor ligands in alkane activating systems is of increasing importance, as also recently illustrated for the CATALYTICA system,[12] which is based on a bipyrimidine−Pt(II) complex. We do not address the question in this study whether the CATALYTICA system involves methyl(hydrido)platinum(IV) complexes or (more likely) direct deprotonation. The present investigation serves

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(10) The $\eta^2$-methane complex is consistently shown throughout this paper with a symmetrically (via two hydrogen atoms) bonded methane. This is an arbitrarily chosen convention. It may also be unsymmetrically bonded, such that basically one C−H bond functions as a donor. Since rotation of bonded methane is extremely facile and practically activationless (see ref 42), our conclusions concerning H/D exchange (see discussion) do not depend on the exact geometry of $\eta^2$-bonded methane.

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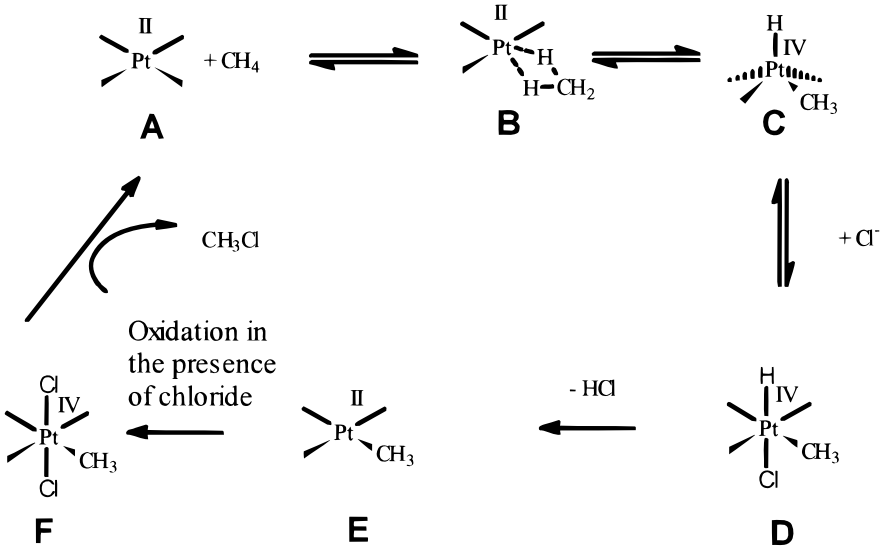
10.1021/om9901426 CCC: $15.00 
Publication on Web 09/04/1999

**Scheme 1**






as a model study for systems that are known to proceed via oxidative addition. Since it still remains extremely difficult to obtain direct mechanistic information on the initial steps of alkane activation via oxidative addition, we follow a proposal[7] that the study of methane reductive elimination can contribute to the understanding of this type of methane activation mechanism, since both processes must pass through the same transition state on the basis of microscopic reversibility.

This paper reports high-pressure kinetic data for methane elimination from $[Pt(H)(CH_3)_2(BPMA)]^+$ (BPMA = bis(pyridylmethyl)amine), first synthesized by Puddephatt and co-workers.[13] Earlier studies on related systems have shown that oxidative addition reactions are characterized by significantly negative volumes of activation, whereas reductive elimination is characterized by strongly positive volumes of activation.[14−19] We report a surprisingly low positive volume of activation for methane elimination from $[Pt(H)(CH_3)_2(BPMA)]^+$. From this value together with results from a deuterium isotope scrambling study, the conclusion is drawn that breakage of the bond *trans* to hydride contributes significantly to the observed rate constant, but the reverse (ring closure) reaction cannot be neglected, since its rate is of the same order of magnitude as the intramolecular proton transfer to give an $\eta^2$-methane complex.

## Results

**Isomerization of the Complex $[Pt(H)(CH_3)_2(BPMA)]^+$.** We selected the complex $[Pt(H)(CH_3)_2(BPMA)]^+$ (**2**) (see Scheme 2) for our mechanistic studies, since it is known to eliminate methane on a convenient time scale. We observed two remarkable facts concerning the formation of the *cis* and *trans* forms of **2** (referring to the position of the hydride relative to the amine nitrogen). First, the protonation to give the *cis* isomer **2a** is much faster than the protonation to give the *trans* isomer **2b**. Second, the isomerization cannot occur intramolecularly, but only in the presence of unprotonated $[Pt(CH_3)_2(BPMA)]$ (**1**). The deprotonation/protonation mechanism shown in Scheme 2 is suggested to account for isomerization. A bimolecular reaction between **1** and **2** is a mechanistic alternative for isomerization. However, we found no evidence for this pathway, e.g., no binuclear complex in the reaction mixture, although methyl(hydrido)platinum(IV) complexes involving a bridging hydride can be very stable.[20,21] The observed isomerization behavior allowed us to study the reductive elimination of methane from **2a** and **2b** independently. We could completely prevent the formation of the *trans* isomer **2b**: the formation of the *cis* isomer **2a** is kinetically controlled when **1** is protonated by a strong acid in dichloromethane or acetone. If an excess of acid is used (5−10% is sufficient), no *trans* isomer **2b** can form. This excess acid is consumed within seconds to give $[Pt(BPMA)X]^+$ (**4**), which has no further influence on the actual reaction of interest. The net result is that **1** is completely protonated to give **2a**, but no excess acid is present in the reaction mixture. However, the use of a small excess of acid at the start of the reaction guaranteed that no complex **1** is left. Since the absence of **1** makes isomerization impossible, the only reaction then observed is the elimination of methane from **2a** to give **3**. This can be seen from Figure 1. On the other hand, addition of a substoichiometric amount of acid (e.g., 0.7 equiv) leads to a situation where a fraction of the platinum is still in the form of complex **1** (30% of the total platinum concentration in our example). As mentioned above, **1** efficiently mediates the isomerization between the Pt(IV) isomers. Under these conditions, the two isomers are in equilibrium

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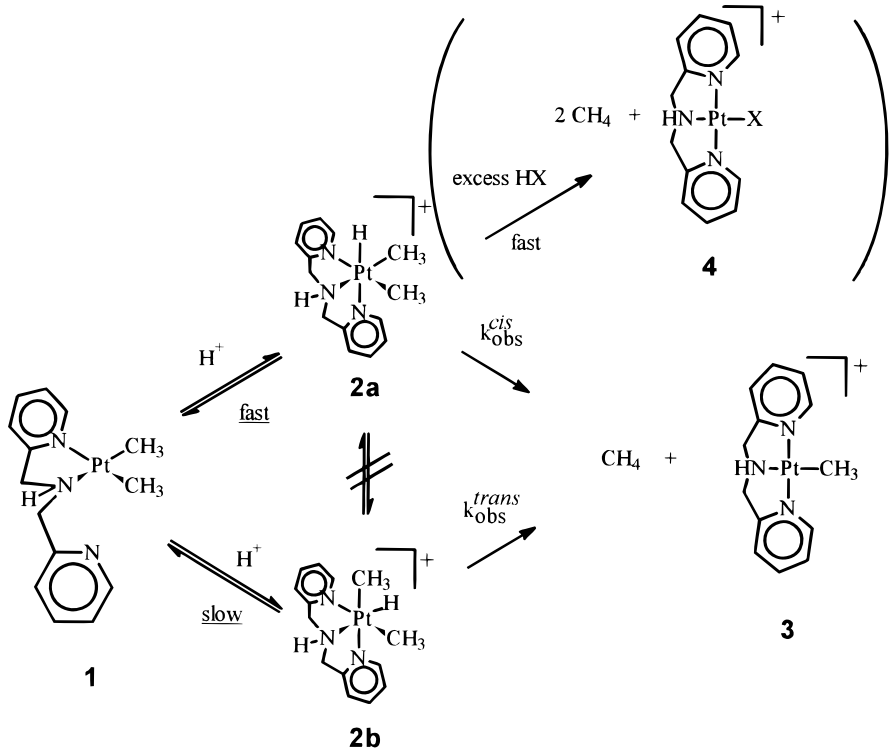
**Scheme 2**



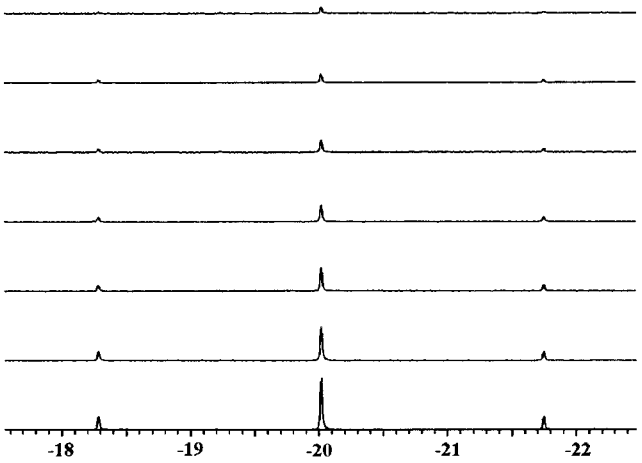




**Figure 1.** Consecutive $^1$H NMR spectra (400 MHz, Pt−H region) for the elimination of methane from **2a**-$BF_4$ in $CD_2Cl_2$ at 25 °C, time interval = 1 h. Note that no *trans* isomer **2b** (signal at −19.2 ppm) is formed since 10% excess of acid was used.

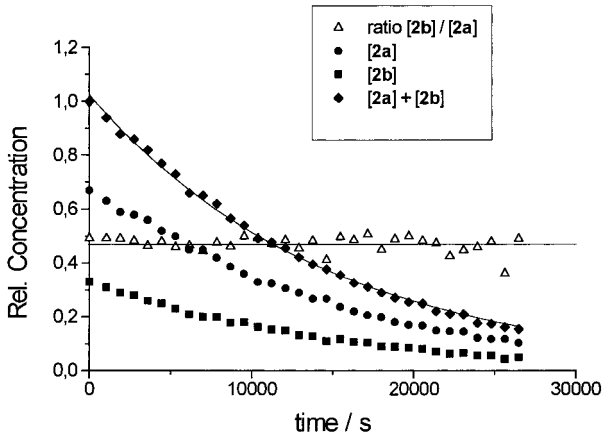



**Figure 2.** Elimination of methane from an equilibrium mixture of **2a** and **2b**. The fast equilibration was achieved by addition of 0.65 equiv of $HBF_4$ to **1**, such that 35% of unprotonated **1** (which mediates the isomerization, see Scheme 2) was available. The observed rate fits very well to a single exponential.

during methane elimination, as shown in Figure 2. From the integrated NMR signals the equilibrium constant for isomerization was determined to be $K$ = [**2b**]/[**2a**] = 0.470(5) at 25 °C in $CD_2Cl_2$. The method of preventing isomerization by addition of a small excess of acid also works for mixtures of **2a** and **2b**. An equilibrium mixture of **2a** and **2b** can be prepared as described above. Addition of an extra amount of acid such that nothing of **1** is left immediately quenches the isomerization process. Elimination from the isomer **2a** can then be seen with a rate constant $k_{obs}^{cis}$, which is identical to the rate constant obtained for a solution containing only **2a**. Elimination from **2b** occurs as a totally independent process, is much slower, and results in $k_{obs}^{trans}$.

**Kinetics of Methane Reductive Elimination. Rate Constants, Temperature, and Pressure Dependence.** To obtain kinetic data on the reductive elimination of methane, at least 15 $^1$H NMR spectra were recorded during at least 3 half-lives of the reaction. The concentration of the hydride was followed by integration of the hydride signal, and a clean first-order behavior was found. Control experiments showed that the reaction rate observed did not depend on the initial platinum concentration employed. If intermediates are involved in these reactions, they must be very reactive and do not accumulate to a concentration that makes them observable by NMR.

We found the rate constants for methane elimination[22] from **2a** and **2b** to be $k_{obs}^{cis} = 1.10(2) \times 10^{-4}$ and $k_{obs}^{trans} = 4.83(5) \times 10^{-6}$ s$^{-1}$ at 25 °C in dichloro-

**Table 1. Kinetic Parameters for Methane Elimination from 2a and 2b in $CD_2Cl_2$[a]**

| | 2a | 2b |
|---|---|---|
| $k_{25\,°C}/s^{-1}$ | $(1.10 \pm 0.02) \times 10^{-4}$ | $(4.83 \pm 0.05) \times 10^{-6}$ |
| $\Delta H^{\#}$/kJ mol$^{-1}$ | $104 \pm 3$ | $133 \pm 5$ |
| $\Delta S^{\#}$/J K$^{-1}$ mol$^{-1}$ | $+28 \pm 10$ | $+101 \pm 17$ |
| $\Delta V^{\#}$/cm$^3$ mol$^{-1}$ | $+6.2 \pm 0.3$ | $+8 \pm 1$, limited pressure range available[24] |

[a] For further information see supporting Figures S1−S4.

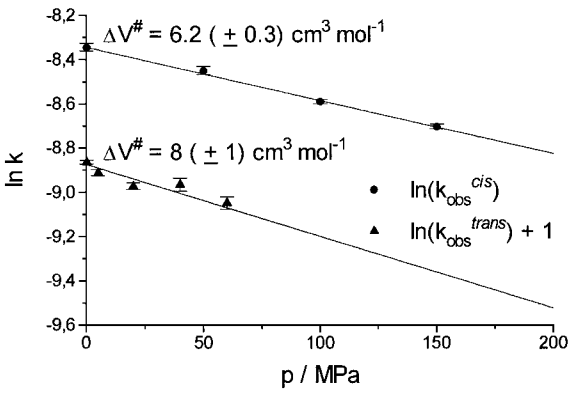



**Figure 3.** Pressure dependence of the elimination of methane from **2** in $CD_2Cl_2$. For graphical reasons, 1.0 is added to $\ln(k_{obs}{}^{trans})$. $\Delta V^{\#}$ is obtained according to $\delta(\ln k)/\delta p = -\Delta V^{\#}/RT$. The measurements were done at 30.0 °C ($k_{obs}{}^{cis}$) and 38.0 °C ($k_{obs}{}^{trans}$).[24]

methane-$d_2$. The fact that the *trans* isomer eliminates methane much slower by a factor of 20 has important implications for the mechanism of methane elimination discussed below. The temperature dependence of these reactions was studied over the range[23] 20−40 °C and 25−38 °C for **2a** and **2b**, respectively. The calculated thermal activation parameters are summarized in Table 1. Kinetic studies were conducted under pressure up to 150 MPa in order to obtain the activation volume for the elimination of methane. The dependence of (ln *k*) on the applied pressure, which appears to be linear in the pressure range accessible, is shown in Figure 3, which results in $\Delta V^{\#}_{obs} = +6.2(3)$ cm$^3$ mol$^{-1}$ for the *cis* isomer and + 8(1) cm$^3$ mol$^{-1}$ for the *trans* isomer.[24] The observed low positive activation volumes contrast the high positive activation volumes usually found for reductive eliminations, e.g., +17 cm$^3$ mol$^{-1}$ for elimination of ethane[18] from (phen)Pd(I)(Me)$_3$ or +20 cm$^3$ mol$^{-1}$ for elimination of $H_2$ from a ruthenium cluster.[16] It should further be kept in mind that the molar volume of liquid methane[25] is ca. 40 cm$^3$ mol$^{-1}$. The mechanistic implication of the low activation volume will be discussed below. The interpretation of activation entropies can be more difficult and is often subjected to larger experimental errors than activation volumes. It should, however, be noted that the activation entropy for elimination from the *cis* complex shows the same peculiarity as the activation volume. A positive value of 28 ± 10 J K$^{-1}$ mol$^{-1}$ was found, which is very low for a reductive elimination reaction.[26]

**Deuterium Scrambling and Kinetic Deuterium Effect for the *Cis* Complex.** The incorporation of deuterium into the methyl groups of $[Pt(D)(CH_3)_2(BPMA)]^+$ (**2a-Pt-D**) has been shown by Puddephatt et al.[13] to depend on the way the deuterated acid (DCl was used) is generated. When a stoichiometric amount of MeCOCl and excess $CD_3OD$ were used, deuterium scrambling was observed, while generation of DCl using $Me_3SiCl$ and $D_2O$ did not lead to scrambling. We preferred to avoid the presence of protic solvents in the reaction mixture, since it is known that protic hydrogens can form strong hydrogen bonds with metal-bonded hydrides.[27] This could lead to additional pathways for scrambling. On the other hand, the chloride ion in DCl could complicate the reaction, since chloride is a relatively good nucleophile and could coordinate to platinum in some short-lived intermediate species. Therefore we preferred to protonate N-deuterated **1** with water-free $F_3CSO_3D$ in acetone-$d_6$ to give **2a-Pt-D** (compare Scheme 3).

Following this procedure, it could be demonstrated that deuterium scrambling occurs with high selectivity into the methyl group *trans* to amine. This is shown in Figure 4, where the methyl region of the $^1$H NMR spectrum after ca. 3 half-lives of **2a** can be seen. The $CH_3$ signal *trans* to amine has a "twin signal" at higher field strength, which appears only in the deuteration experiments. At high resolution, H−D coupling can be observed, confirming the assignment as $CH_2D$. Since the overlap of the $CH_3$ and $CH_2D$ signals does not allow exact integration, the degree of deuteration (discussed below) was determined from the integration of the hydride signal. $CHD_2$ signals are not observed. In contrast to the observation for the *trans* group, deuteration *cis* to amine occurs only to a negligible extent. Notably, the methyl group of the elimination product is deuterated considerably. We observed the formation of $CH_4$ and $CH_3D$ but not of $CH_2D_2$ under these conditions, indicating again that the protonation is irreversible if excess acid is used. This observation also suggests that deuterium scrambling, like the elimination process, occurs intramolecularly. In agreement with the suggested isomerization mechanism given above, multiple deuterium incorporation occurs and $CH_2D_2$ is formed (at a later stage in the reaction) only if a substoichiometric amount of acid is used. In order not to complicate the kinetic scheme, an excess of acid was used in the deuterium scrambling studies.

It is of interest to compare the deuterium scrambling rate with the rate of methane elimination. Starting from the Pt-deuterated complex, two parallel reactions oc-

(22) $k_{cis}$ was determined using 5−10% excess of $HBF_4$·$OEt_2$ ($F_3CSO_3H$ gave identical kinetics), whereas for the measurement of $k_{trans}$, 0.65 equiv of acid was first added, leading to the formation of an equilibrium mixture of **2a** and **2b**. Then the equilibration was "frozen" by adding an excess of acid. The reaction of **2a** and the much slower reaction of **2b** were thus followed separately. Alternatively, $k_2$ could be obtained (but with less accuracy) from the kinetic time trace of an equilibrium mixture along with the known values of $k_1$ and *K*.

(23) For the limitations of the temperature range, see the Supporting Information.

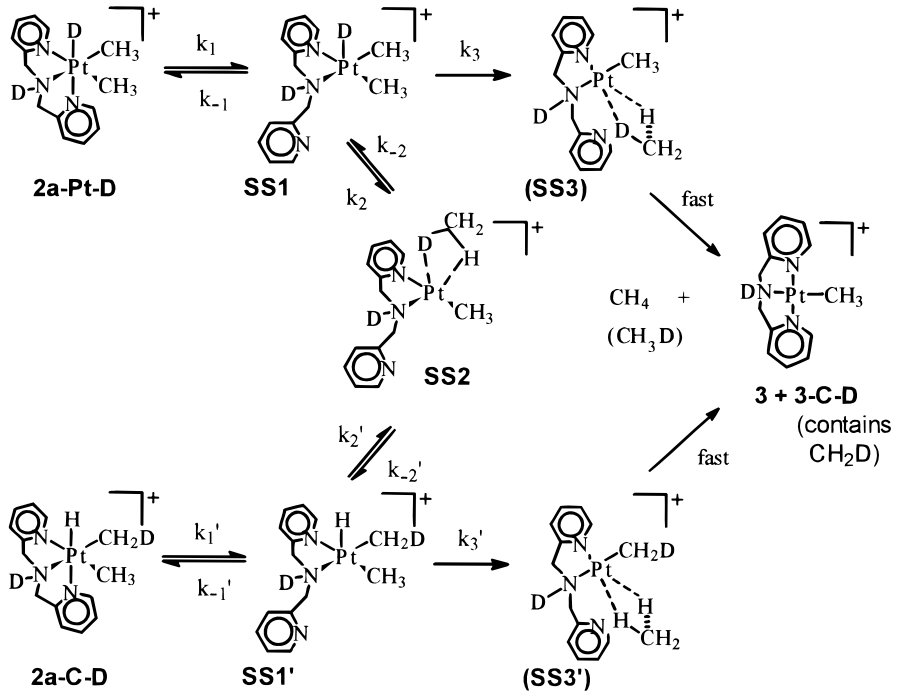
(24) The more restricted pressure range for the *trans* isomer stems from the fact that the glass walls accept protons under high pressure, which leads to isomerization to give the more reactive *cis* isomer. An enhancement in reactivity was observed under pressures higher than those plotted in Figure 3.

(25) Terry, M. J.; Lynch, J. T.; Bunclark, M.; Mansell, K. R.; Staveley, L. A. K. *J. Chem. Thermodyn.* **1969**, *1*, 413.

(26) Although elimination reactions are generally accompanied by a very positive activation entropy, the $\Delta S^{\#}$ values for alkane elimination cover a wide range (Gould, G. L.; Heinekey, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 5502), which is indicative of different rate-determining steps or composite rate laws.

(27) Crabtree, R. H.; Siegbahn, P. E. M.; Eisenstein, O.; Rheingold, A. L.; Koetzle, T. F. *Acc. Chem. Res.* **1996**, *29*, 348.

**Scheme 3**



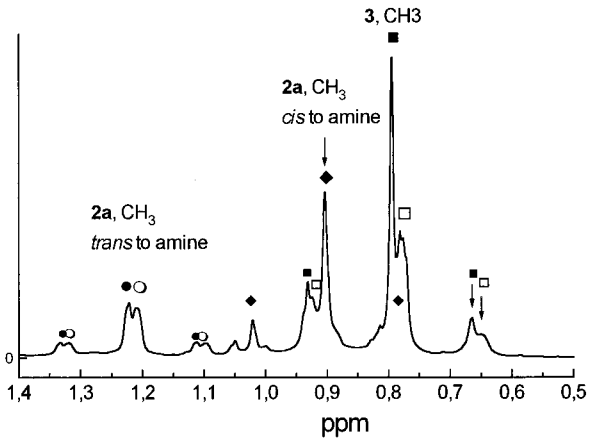




**Figure 4.** $^1$H NMR spectrum (300 MHz, $CH_3$ region) of the reaction mixture obtained from **2a-Pt-D** (see Scheme 3) after a reaction time of 5 h at 30 °C in acetone-$d_6$. The symbols refer to $CH_3$ *trans* to amine (filled circles) in **2a-Pt-D**, $CH_3$ *cis* to amine in **2a-Pt-D** (filled diamonds), and $CH_3$ in **3** (filled squares). The corresponding symbols of smaller size designate the $^{195}$Pt satellites. The open symbols refer to the corresponding $CH_2D$ groups of the complexes **2a-C-D** and **3-C-D**. It can be seen that **2a-Pt-D** selectively incorporates deuterium in its methyl group *trans* to amine. The methyl group of the product, complex **3**, is deuterated to considerable extent, implying that the methyl group *cis* to amine is eliminated during the reaction and not the *trans* group.

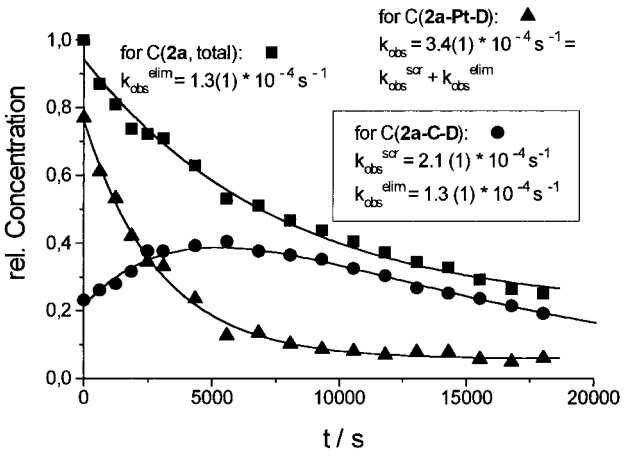



**Figure 5.** Concentration profile (as followed by NMR, at 30 °C in acetone-$d_6$) for the reaction of complex **2a-Pt-D** (shown as triangles). It undergoes two parallel reactions: deuterium scrambling into the methyl group *trans* to amine to give **2a-C-D** and reductive elimination to give **3**. The scrambling product **2a-C-D** eliminates at a rate very close to that of **2a-Pt-D** and gives **3-C-D**. The fact that the scrambling is almost 2 times faster than the elimination has implications for the suggested mechanism, which is discussed in the text.

cur: the irreversible elimination of methane and the essentially irreversible migration of deuterium from Pt to $CH_3$ *trans* to amine, shown in Figure 5 (see Experimental Section for more details). It was observed that the rate constant for scrambling ($k_{obs}^{scr}$) is significantly larger (by a factor of 1.6) than the rate constant for methane elimination ($k_{obs}^{elim}$). Noteworthy, the concentration−time trace for the reaction of the sum of Pt−H and Pt−D fits well to a single exponential, and the same rate constant of $1.3 \times 10^{-4}$ s$^{-1}$ (at 30 °C in acetone) is obtained compared to when the kinetics of the Pt−H complex **2a** are followed in acetone-$H_6$. From this the mechanistically important conclusion can be drawn that $k_H/k_D$ is close to 1. From the initial slope, $k_H/k_D$ can be estimated[28] to be higher than 0.7 but lower than 1.2.

(28) It might be suggested that preparation of an analogous complex containing deuterated methyl groups would lead to a better determination of $k_H/k_D$, since it prevents formation of the Pt−H complex. However, the secondary isotope effect of six deuterium atoms will lead to a systematic error that could be as large as the uncertainty of our determination.

## Discussion

**Suggested Reaction Mechanism.** The observation that the isomers **2a** and **2b** eliminate methane at significantly different rates has important implications for the reaction mechanism. It has been proposed before that elimination from Pt(IV) and other octahedral $d^6$ complexes takes place via a five-coordinate intermediate and thus is favored when a ligand easily dissociates.[29,30] In the system under study, the amine nitrogen cannot dissociate easily, but the pyridyl residues can dissociate to form a five-coordinate species. This is shown in Scheme 3 (for the *cis* isomer **2a**, as structure **SS1**). The observation that the *trans* isomer **2b** eliminates methane by a factor of 20 slower confirms this assumption. Breakage of the bond *trans* to a strong $\sigma$-donor (like hydride or methyl) is facile. It is known that the *trans* influence of hydride even exceeds the *trans* influence of methyl.[9,31] In **2a**, the pyridyl residue is *trans* to hydride, whereas in **2b**, it is *trans* to the weaker $\sigma$-donor methyl. This certainly contributes to the lower reactivity of **2b**. In addition, elimination from complex **2b** must involve a more complicated geometrical rearrangement, since a methyl group in the position *trans* to amine exists in the common product **3** and in **2a**, but not in **2b**, where the hydride is *trans* to amine. The mechanism for elimination from **2b** is probably similar to elimination from **2a**, as indicated by the similar volume of activation. However, it might involve an additional isomerization step. For this reason we discuss the elimination from **2a** in more detail, since it is the simpler system.

On the basis of the high-pressure kinetic and deuterium isotope effect data we propose the mechanism shown in Scheme 3, which presents a unified view for deuterium scrambling and methane elimination. It offers a straightforward explanation for the fact that deuterium is incorporated selectively *trans* to amine. The formation of an $\eta^2$-bound methane *trans* to amine must be reversible, since no fast and irreversible step leads to methane elimination.[32] On the other hand, a similar $\eta^2$-bound methane formed *cis* to amine can be substituted very rapidly by the uncoordinated pyridylmethyl residue. The fact that the scrambling and elimination rates are of the same order of magnitude confirms the hypothesis that a common mechanism is operative. A detailed analysis of the scrambling rate versus elimination rate will reveal semiquantitative information on the relative values of $k_1$, $k_{-1}$, $k_2$, and $k_3$. It should again be noted that scrambling is observed, but no isomerization. This implies that the five-coordinate species **SS1** and **SS2** are stereochemically rigid on the time scale of the ring-closure and intramolecular proton-transfer reactions they undergo.

**Steady-State Treatment.** First, we consider the methane elimination from nondeuterated **2a**, where scrambling does not complicate the treatment. The upper half of Scheme 3 (omit **SS2** and do not distinguish between H and D) resembles that situation. We consider the possibility that **2a** is in a preequilibrium with the $\eta^2$-methane complex and that the extrusion of methane from the latter is the rate-determining step (this mechanism would be analogous to the mechanism for benzene elimination[33] from [Tp′Rh(H)(Ph)(*N*-neopentyl)]). This would lead to deuterium incorporation *cis* to amine prior to elimination, which was not observed. A back reaction can be ruled out for the $\eta^2$-bound methane *cis* to amine; thus a rate constant $k_{-3}$ need not be considered. The five-coordinate complex is treated as a steady-state intermediate (**SS1**), which leads to the expression for the observed rate constant for methane elimination (eq 1).

$$k_{\mathrm{obs}}^{\ \mathrm{elim}} = \frac{k_1 k_3}{k_{-1} + k_3} \qquad (1)$$

In many cases further simplifications of the steady-state expression are possible. These will be tested in the following discussion. If $k_3 \ll k_{-1}$, eq 1 would reduce to $k_{\mathrm{obs}} = k_3(k_1/k_{-1}) = k_3 K_{\mathrm{preeq}}$. The formation of the $\eta^2$-methane complex would be rate determining following a rapid preequilibration between **2a** and **SS1**. This possibility would lead to a kinetic isotope effect in the range[34] between 3 and 5, stemming from the $k_3$ term, while $K_{\mathrm{preeq}}$ should not show a significant deuterium isotope effect. This possibility is ruled out by the observed isotope effect of close to unity.

On the other hand, if $k_3 \gg k_{-1}$, eq 1 would reduce to $k_{\mathrm{obs}} = k_1$. Thus ring opening, that is dissociation of the pyridine residue, would be rate determining. Although this possibility would lead to the observed isotope effect of close to unity and the observed high activation enthalpy, it is also discarded for the following reasons. From high-pressure studies on pyridine dissociation from octahedral complexes it is known that an activation volume of close to 20 $\mathrm{cm^3\ mol^{-1}}$ can be expected,[35−38] which contrasts the low activation volume of 6 $\mathrm{cm^3\ mol^{-1}}$ observed here.

Furthermore, this simplification is disproved by the deuterium scrambling results, which are discussed on the basis of the complete mechanism shown in Scheme 3. Deuterium scrambling is essentially irreversible[39] (see Figure 5); omitting $k_{-2}$ and applying steady-state conditions leads to eq 2:

(29) Goldberg, K. I.; Yan, J.; Breitung, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 6889.
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(32) It is important to note that isomerization to give the *trans* hydride **2b** was not observed under these conditions. Although the equilibrium is not too unfavorable for interconversion of **2a** into **2b**, there is no low-energy path for an intramolecular isomerization. Obviously, the kinetic barrier for placing the methane hydrogen in **SS2** *trans* to amine is higher than for the migration of the hydrogen into the *cis* position. This may be due to the kinetic *trans* effect of the amine donor, quite similar to the effect discussed below.
(33) Jones, W. D.; Hessell, E. T. *J. Am. Chem. Soc.* **1992**, *114*, 6087.
(34) A $k_{\mathrm{H}}/k_{\mathrm{D}}$ of 5 at room temperature is the maximum kinetic isotope effect calculated from the Pt−H vibration frequency, whereas a value close to 3 was reported experimentally: Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961.
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$$-\frac{\mathrm{d}[\text{2a-Pt-D}]}{\mathrm{d}t} = [\text{2a-Pt-D}]\,\frac{k_1(k_2 + k_3)}{k_{-1} + k_2 + k_3} \qquad (2)$$

If $k_2$ or $k_3$ (or both) $\gg k_{-1}$, it follows that $k_{obs} = k_1$. However, we observed experimentally that the rate constant for the disappearance of **2a-Pt-D** is ca. 3 times larger than the rate constant for methane elimination, and deuterium scrambling is almost 2 times faster than methane elimination. It follows that these observations are not consistent with this proposal.

We are now left with the conclusion that eq 1 describes the observed rate constant for elimination, but cannot be simplified further. This steady-state expression is consistent with both the observed kinetic isotope effect and the activation volume data. To verify the former statement, a $k_H/k_D$ of 3 could be expected for $k_3$ in eq 1. One can easily show that a "dilution" of the kinetic isotope effect[40] occurs due to the contributions of $k_1$ and $k_{-1}$. The proton-transfer step associated with $k_3$ may, of course, be faster than ring closure ($k_{-1}$), but of the same order of magnitude. For example, if $k_3 = 4k_{-1}$, the observed $k_H/k_D$ reduces to 1.15.

Equation 1 also accounts for the low positive activation volume found. Although the ring-opening step should be accompanied by a very positive volume of activation, a pronouncedly negative volume of activation is expected for the proton transfer which reduces the coordination number of platinum. The observed volume of activation is given by $\Delta V^{\#}_{obs} = -RT[\delta(\ln k)/\delta p]$. Applied to eq 1, it follows that $\Delta V^{\#}_{obs} = \Delta V^{\#}(k_1) + \Delta V^{\#}(k_3) + RT\{\delta[\ln(k_{-1} + k_3)]/\delta p\}$, and the apparent activation volume will depend on the hydrostatic pressure. The expected nonlinearity of the ln $k$ versus $p$ plot, however, is in most cases not seen in the pressure range accessible. Important to note, however, is that the apparent activation volume will be much lower than $\Delta V^{\#}(k_1)$. The observed low activation volume, therefore, disproves the assumption that $k_1$ is rate determining, which again shows that $k_3$ cannot be much faster than $k_{-1}$.

It is important to discuss the question why the scrambling rate is higher than the elimination rate. Substitution of $k_3$ by $k_2$ in eq 1 results in the corresponding expression for the scrambling rate constant (see Scheme 3). The fact that scrambling is faster by a factor of 1.6 than elimination gives a lower limit for the ratio $k_2/k_3$. Using steady-state treatment and the simplification that deuterium incorporation into the methyl group is irreversible (which is well founded, see Figure 5), it can be shown that eq 3 applies:

$$\frac{k_2}{k_3} = \frac{k_{obs}{}^{scr}}{k_{obs}{}^{elim}}\,\frac{k_1 - k_{obs}{}^{elim}}{k_1 - k_{obs}{}^{scr}} \qquad (3)$$

It must be noted that the second term of the product on the right-hand side of eq 2 is larger than 1, since the observed rate constant for scrambling is larger than the observed rate constant for elimination. From $k_{obs}{}^{scr}/k_{obs}{}^{elim} = 1.6$ (at 30 °C), it follows that the ratio $k_2/k_3$ must be larger than 1.6. We can offer a plausible reason for why proton (or deuterium) transfer to the $CH_3$ group *trans* to amine ($k_2$) is faster than *cis* to amine ($k_3$). Amines are stronger $\sigma$-donors than pyridyl residues, as can be seen for example from basicities. The stronger the donor *trans* to a methyl group, the weaker the platinum−carbon bond will be and the faster proton transfer could be. This seems to be true in our case, as suggested by the $^{195}Pt-^{1}H$ coupling constant of the methyl groups. An $^{2}J_{Pt-H}$ of 67 Hz for $CH_3$ *trans* to amine versus 71 Hz for $CH_3$ *trans* to pyridyl suggests that the bond *trans* to amine is indeed weaker. Since significant bond weakening is required in the transition state, this possibly can account for the different proton-transfer rates and the observed ratio $k_2/k_3$.

## Conclusion and Outlook

The present study provides information on the intimate mechanism of the reactions of the methyl(hydrido)platinum(IV) complex $[Pt(H)(CH_3)_2(BPMA)]^+$. Kinetic data for deuterium scrambling into the methyl group *trans* to amine and reductive elimination of methane that involves the methyl group *cis* to amine are provided. Several mechanistic studies on deuterium scrambling and alkane elimination from somewhat related rhodium and iridium complexes have been published.[41] The present work, however, gives information on a platinum system that adds a new feature: The reactivities of two nonequivalent methyl groups are different and can be separated kinetically. The study presented here also includes the first high-pressure kinetic data on this type of reaction. Although the rate law is a composite function in the present case, and a complete deconvolution is not possible, mechanistically valuable semiquantitative information is obtained. From the relative values of the rate constants for the steps involved, a qualitative reaction energy profile can be derived, as shown in Figure 6. Following microscopic reversibility arguments, this allows conclusions to be drawn for the methane activation process (the diagram must then be read from right to left). Interestingly, methane activation may be regarded as almost accomplished when the $\eta^2$-methane complex is formed. The highest activation energy is required for the substitution of a strong donor ligand by methane. Following this step, both the interconversion into the five-coordinate methyl(hydrido)platinum(IV) complex and ring closure to give a stable six-coordinate complex are extremely facile, which is also supported by theoretical studies for the interconversion process.[42]

Recently, this concept received direct support from the demonstration that the generation of a very good leaving group using a strong Lewis acid enables the addition of alkanes to Pt(II) to give stable alkyl(hydrido)platinum(IV) complexes, if the ligand has an "open arm" in the reactant complex.[11] We now have the means, at least theoretically, to control the different steps in methane

(39) A treatment of the complete system is possible, but unfortunately not simple. We treated the complete system shown in Scheme 3 using the computer algebra system MAPLE (Maple V.3, student version, 1981−1994, Waterloo Maple Software and University of Waterloo) The evaluation of [**SS1**], [**SS2**], and [**SS1′**] in terms of the rate constants is possible. The calculation of the rates for formation of intermediate (**2a-C-D**) and product leads to a system of two linear differential equations that can be solved. However, the solution is so complex (a multiterm expression that fills several pages) that no meaningful conclusion could be drawn.

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(42) Hill, G. S.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 1478.

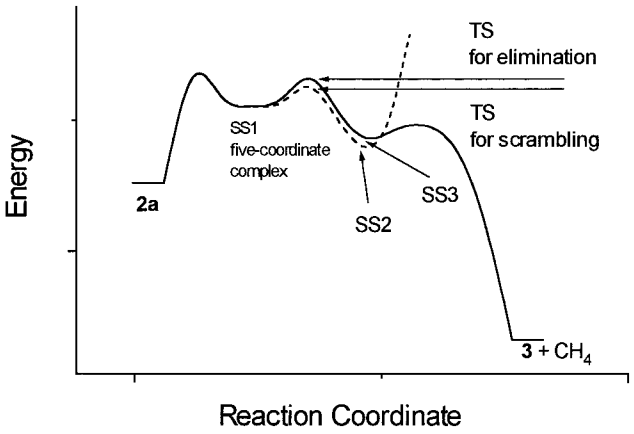


**Figure 6.** Qualitative reaction coordinate diagram for the unimolecular reactions of **2a** and its deuterated analogue **2a-Pt-D**. Following the formation of the five-coordinate intermediate **SS1**, two reaction paths are possible: formation of $\eta^2$-bound methane *cis* to amine (**SS3**) leads to elimination; formation of $\eta^2$-bound methane *trans* to amine (**SS2**) leads to deuterium/proton scrambling.

activation: The substitution of a ligand by methane strongly depends on the leaving group, which must preferably be a weak ligand. The interconversion between the $\eta^2$-methane complex and the five-coordinate methyl(hydrido)platinum(IV) complex can be controlled utilizing the *trans* labilizing effect of strong donors. This is suggested by the present study, and clearly much more can be done in this area. The stabilization of the Pt(IV) hydrido species depends on the donor strength and the geometrical requirements of pendant arms or, alternatively, on the donor strength and concentration of additional ligands. If a catalytic process is desired, this stabilization must be balanced and not too strongly, otherwise a "dead-end" situation will arise.

In our opinion the construction of reaction coordinate diagrams for these important reactions is much aided by kinetics which include not only the use of isotope labeling but also the application of high pressure as an additional kinetic parameter. Currently, we are working on systems that should reveal the activation volume for processes where elimination from the $\eta^2$-methane complex is rate determining. The ultimate goal would be to gain insight into the volume changes associated with alkane activation itself.

## Experimental Section

The NMR spectra were acquired on a BRUKER Avance DRX 400WB or DPX 300 spectrometer. Chemical shifts are reported in ppm relative to TMS. Elemental analyses were performed on a Carlo Erba elemental analyzer, type 1106 (C, H, N) or 1108 (C, H, N, S).

**Syntheses. [Pt(CH$_3$)$_2$(BPMA)] (1).** The title complex was prepared in water-free form using a modified procedure from the literature:[13] Instead of [Me$_2$Pt($\mu$-SMe$_2$)$_2$PtMe$_2$], [Me$_2$Pt($\mu$-SEt$_2$)$_2$PtMe$_2$] (which was synthesized in a procedure similar to that given by Scott and Puddephatt[43]) was used. When the reaction was complete (within 1 h), the reaction mixture was cooled to 0 °C. The complex **1** precipitated as a yellow microcrystalline powder, which was filtered off under argon and dried in vacuo. Yield: 75%. Anal. Calcd for $C_{14}H_{19}N_3Pt$: C, 39.6; H, 4.5; N, 9.9. Found: C, 39.7; H, 4.6; N, 9.8.

**[PtCl$_2$(SEt$_2$)$_2$] (mixture of *cis* and *trans* isomer).** Since this complex is a widely used precursor for [Me$_2$Pt($\mu$-SEt$_2$)$_2$-PtMe$_2$], we found that it can be prepared conveniently and cost-effectively directly from PtCl$_2$ instead of using[44] [PtCl$_4$]$^{2-}$. In general, PtCl$_2$ is not suitable for synthesizing Pt$^{II}$ complexes directly because of its strong tendency to disproportionate. This problem, however, was not encountered in the following procedure: To PtCl$_2$ (4 g, 15 mmol) was added diethyl sulfide (5 mL, 46 mmol) in 120 mL of water. The suspension was heated under reflux and vigorously stirred for 2 h. The resulting yellow solution was extracted 6 times with 50 mL of dichloromethane. Removing the solvent in vacuo left the complex in the form of yellow crystals. Yield: 6.2 g, 93%.

**[Pt(BPMA)(F$_3$CSO$_3$)][F$_3$CSO$_3$] (4).** A 10 mg sample of **1** was dissolved in 1 mL of dichloromethane. Addition of 1.1 equiv of triflic acid led to the formation of **2a**. When an additional 1 equiv of triflic acid was added, the formation of gas bubbles (methane) was immediately observed. The reaction was complete within 10 s. The solvent was reduced to one-third (in vacuo) and the reaction mixture cooled to 0 °C. Microcrystalline **4** was obtained in essentially quantitative yield. Anal. Calcd for $C_{14}H_{13}N_3PtF_6S_2O_6$: C, 24.3; H, 1.9; N, 6.1; S, 9.3. Found: C, 23.9; H, 2.0; N, 5.9; S, 9.1.$^1$H NMR ($CD_2Cl_2$): $\delta$ 8.47 (dd, $J_{H-H}$ = 1.5 Hz, 6.3 Hz, $^3J_{Pt-H}$ = 30 Hz, 1 H, H *ortho* to N), 8.11 (dt, $J_{H-H}$ = 1.4 Hz, 8 Hz, 1 H, H *para*), 7.56 (m, 2 H, H *meta*), 4.7 (m, 2 H, $CH_2$). IR (KBr): $\nu$[SO$_3$]: 1255(s), 1288(s), 1337(m) cm$^{-1}$, characteristic for triflate, consistent with the presence of both coordinated and ionic triflate.[45,46]

**In Situ Characterization.** The $^1$H NMR data of [Pt(CH$_3$)$_2$-(BPMA)] (**1**), *cis*-[Pt(H)(CH$_3$)$_2$(BPMA)](BF$_4$) (**2a**), *trans*-[Pt(H)-(CH$_3$)$_2$(BPMA)] (BF$_4$) (**2b**), and [Pt(CH$_3$)(BPMA)](BF$_4$) (**3**) were identical with those reported in the literature.[13] Similar spectra were obtained for the triflate salts.

**General Procedures and High-Pressure NMR.** The reactions were performed under inert conditions (dry argon) using standard glovebag and high-vacuum line techniques. The glassware was flame dried in vacuo prior to use. $CD_2Cl_2$ was dried using $CaH_2$ and freshly distilled. For a typical run, a sufficient amount of **1**, typically 2−5 mg, was weighed and transferred to a WILMAD screw cap NMR tube equipped with a PTFE-septum, and 1 mL of solvent was added. The appropriate amount of acid (HBF$_4$·OEt$_2$, 85% in OEt$_2$, or F$_3$-CSO$_3$H, both obtained from Aldrich in the highest purity available) was added using a microliter syringe, and the NMR spectra were recorded after 10 min (after which the final temperature was reached and the shimming was completed).

For the high-pressure studies, the DRX 400WB spectrometer was used together with a homemade high-pressure probe.[47] In addition to the published design, a $^2$H lock channel was implemented to stabilize the magnetic field during the experiment. The magnetic field inhomogenity over the sample volume was reduced to $3 \times 10^{-9}$. The high-pressure NMR tube was sealed with a MACOR plug and an O-ring made of VITON. Plug and O-ring were shown to be stable in the employed solvent and acid. For the high-pressure studies on **2b**, the procedure described in the paper was used, with the exception that the equilibration and the "freezing" of the equilibrium (by excess acid) were done in a dry Schlenk tube. The solution was then transferred to the high-pressure NMR tube. The spectra were evaluated (Fourier transformed and integrated) using the WIN-NMR program package. Kinetic data of the observed first-order reactions were obtained by fitting the data (standard nonlinear least-squares procedure) to the integrated rate law: $C = C_0 \exp(-kt)$.

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**Deuterium Scrambling Studies.** N-deuterated [$Pt(CH_3)_2$(BPMA)] **(1)** was prepared using a procedure similar to that given for **1** above. The BPMA ligand used for this purpose was deuterated at the nitrogen position by adding 2 mL of $CD_3OD$ to 0.1 mL of the ligand. Exchange of the amine proton was complete after 24 h (followed by NMR). After removal of the solvent, the ligand was used as described above. Acetone-$d_6$ (Aldrich, highest quality available) and $F_3CSO_3D$ (Aldrich, 98 atom % D) were used for the protonation to generate **2a-Pt-D**. The NMR tubes were pretreated for several days using $CD_3OD$ and dried in vacuo. The sum of **2a-Pt-D** and **2a-C-D** concentration was obtained from the integration of the aromatic signal at 7.8 ppm, corresponding to the two *para* protons of **2a**. Since integration of the hydride signal allowed direct determination of **2a-C-D**, the concentration of **2a-Pt-D** was determined from the difference in concentration.

**Acknowledgment.** The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, and the Max-Buchner-Forschungsstiftung. We thank Dr. S. Schindler (Erlangen) for a gift of the BPMA ligand and Dr. K. Goldberg (Seattle) for valuable discussions.

**Supporting Information Available:** Kinetic time traces and Eyring plots for $k_{obs}^{cis}$ and $k_{obs}^{trans}$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9901426