Organometallics **2004,** *23,* 3031−3036

Cationic Platinum(II) Carboxylato Complexes Are Competent in Catalytic Arene C−H Activation under Mild Conditions

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Received December 10, 2003

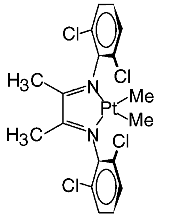
A combination of ESI-MS and kinetic studies establishes that the Pt^{II}-catalyzed H/D exchange between benzene and acetic acid-d_4 proceeds with high turnover number in acetic acid solution. For the catalytic cycle, the resting state is identified as the cationic (diimine)-Pt^{II}(acetato)(acetic acid) complex; the turnover-limiting transition state is the dissociative ligand exchange of benzene for acetic acid. The interconversion of η^2- and η^1-acetato is surprisingly facile, leading to an unexpectedly fast H/D exchange reaction.

Introduction

In recent years, the mechanism of the catalytic conversion of methane to methanol by chloroplatinate salts, the Shilov reaction,[1] reported in 1972,[2] has been investigated using well-defined homogeneous Pt^{II} complexes as model systems.[3] A comparable C−H activation process in which arenes can be deuterated (or tritiated) catalytically by heterogeneous Pt systems (reported in the 1950s),[4,5] as well as homogeneous chloroplatinate salts (first reported in 1967),[6−8] has received much less attention, despite the likelihood that all three processes are mechanistically related. We report a catalytic deuteration of benzene by acetic acid-d_4 in the presence of a well-defined cationic Pt^{II} complex at 85 °C, with the intention to clarify the mechanism of this reaction. We observe that Pt^{II}-acetato complexes are the principal species in solution. The present result, in which over 1500 turnovers are seen, fits into the overall picture in that it shows clearly that an intermediate Pt^{II}-acetato complex is unexpectedly competent in C−H activation, despite the possibility of η^2 coordination by the carboxylate. Moreover, the resting state and turnover-limiting step are unambiguously identified.

Experimental Section

The synthesis of **1** as well as its crystal structure has been described in our previous work.[9] GC−MS spectra were measured on a Fisons MD 800 instrument with a 12 m DB-5MS capillary column. ESI-MS were recorded as previously described[9,10] on either a Finnigan MAT LCQ Deca ion trap or a Finnigan MAT TSQ Quantum triple-quad mass spectrometer, both equipped with electrospray sources. Benzene (OEKANAL grade) was purchased from Riedel de Haen and used as received. It should also be noted that lower grades of benzene produced unreliable kinetic results. The acid $[(Et_2O)_2H]^+[BArF]^-$ (BArF = tetrakis(3,5-bis(trifluoromethylphenyl)borate)) was synthesized according to the procedure of Brookhart.[11] Acetic acid-d_4 was purchased in “100%” quality from Dr. Glaser AG.[12] A mixture of *cis*- and *trans*-decalin was purified according to the literature[13] and degassed immediately prior to use. All glassware and stir bars were washed with alcoholic KOH, water, acetone, and finally p.A. grade MeOH and dried in a 160 °C oven. The hot and dry glassware was then allowed to cool in a nitrogen-filled glovebox (M-Braun Labmaster 130). All chemical operations were performed in the exclusion of air.



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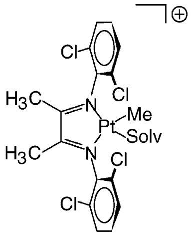

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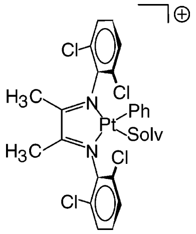

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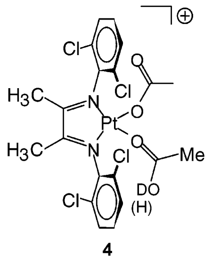

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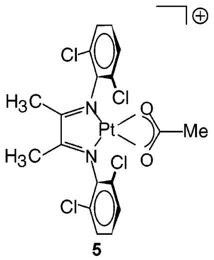

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In the earlier work,[9] activation of **1** to the cationic complex **2** was done by protonation of one methyl group by a strong Brønsted acid such as HBF_4. For electrospray ionization mass spectrometric (ESI-MS) experiments, 0.1 mg of **1** (1.7×10^{-7} mol) was dissolved in 1.5 mL of benzene to give a homogeneous green solution, which was then treated with a slight excess of $[(Et_2O)_2H]^+[BArF]^-$ for 10 min at room temperature,[14] to yield ultimately **3**. Solutions prepared in this fashion were stable

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[1] Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; Reidel: Boston, 1984. Shilov, A. E.; Shulpin, G. B. *Chem. Rev.* **1997**, *97*, 2879.

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[8] Gol’dshleger, N. F.; Tyabin, M. B.; Shilov, A. E.; Shteinman, A. A. *Russ. J. Phys. Chem.* **1969**, *43*, 1222.

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10.1021/om030685m CCC: $27.50
Publication on Web 05/11/2004

and showed no detectable loss of **3** even after heating at 50 °C for greater than 100 h. The clear orange solution of **3** was then treated with 1.5 mL of CH_3COOH (molar ratio Pt to benzene to acetic acid of 1:101 160:158 760) to produce the acetato complex within 1−5 min at room temperature. Samples treated analogously with CD_3COOD instead of CH_3COOH showed progressive deuteration of the bulk benzene solvent over a period of hours. The mixed benzene/acetic acid solution, approximately 56 μM in platinum complexes, was introduced directly into the ESI-MS spectrometer by dipping a sampling capillary directly into the reaction vessel to which an overpressure (1 bar) of nitrogen was applied. The solution behaved well in electrospray.

For kinetic studies, a stock solution of **3** (0.00127 M) was prepared from **1**, a slight excess of $[(Et_2O)_2H]^+[BArF]^-$, and benzene as before. Aliquots were taken from the stock solution, from which nine samples were prepared with various concentrations of **3**, benzene, and CD_3COOD. In each sample, the final volume was taken to 1.4 mL by addition of decalin (a high-boiling solvent inert to C−H activation under these conditions) to produce samples that are less than 1 mM in **3**. The nine sample vessels were sealed with septa and placed in a preheated (85 ± 1.5 °C) bath. From each vessel, five samples of the headspace vapor, taken periodically with a gastight syringe over a period of 23 h, were analyzed by GC−MS. The extent of deuteration was calculated from the mass spectrum of benzene by integration of the isotopic peaks and subtraction of the integrated intensities for unlabeled benzene with natural abundance ^{13}C and ^2H and then expressed as turnover number (TON) in terms of consumption of acetic acid-d_4. Consumption of C_6H_6 was also computed. A further parameter calculated from the mass spectrometric intensities is the Anderson and Kemball's *M* value,[15] which is effectively a measure of the number of deuteriums incorporated into benzene in one "pass" through the catalytic cycle.

The formation of Pt clusters in the reaction mixtures was ruled out by taking aliquots of the reaction mixture after 24 h, dilution with 2,2,2-trifluoroethanol (TFE), and analysis by electrospray. No signals for the protonated, free ligand were observed, which would appear if colloidal Pt were to be formed. On the other hand, addition of excess ligand to these samples gave rise to strong signals of the protonated ligand, ligated Na^+, and dimers thereof while the original Pt signals remained unchanged, which verifies that free ligand would have been detected if present.

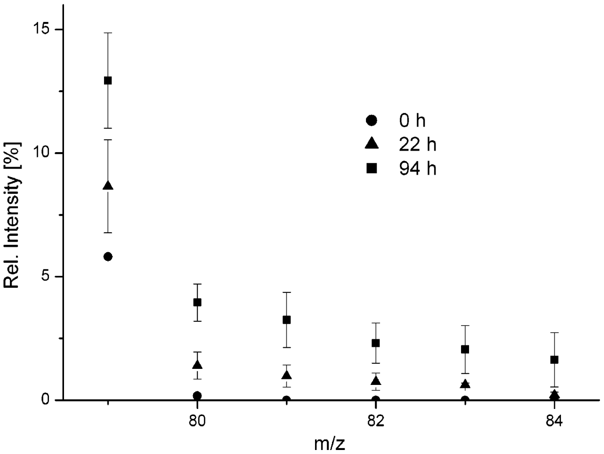

Figure 1. Isotopomer intensities in the mass spectrum of benzene taken at various times during the treatment with acetic acid-d_4 and Pt complex (56 μM) in the ratio Pt to benzene to acetic acid of 1:101 160:158 760 with no other diluent.

Results

The catalytic deuteration of benzene is a clean reaction with no other detectable products other than benzene and acetic acid isotopomers. The isotopomer intensities in the mass spectrum of benzene at several times is shown in Figure 1. It is clear that progressive deuteration occurs with time.

In the kinetic experiments in solutions diluted with decalin, the TON was run up to a maximum of ~1500 so that the kinetics would not be significantly affected by a buildup of deuterated benzene or undeuterated acetic acid.[16] The nine separate sample runs can be organized into three sets in which, for each set, the concentration of only one species, **3**, benzene, or acetic acid, varies in that set. The results are plotted in Figures 2−4. From the data it is clear that the rate of deuteration is first-order in catalyst, first-order in benzene, and inverse first-order in acetic acid. From the slope in plots of each of the nine sets of data, the rate constant k_{358K} in eq 1 can be calculated. The average for the nine samples, $k_{358K} = (4.20 \pm 1.02) \times 10^{-3}\ s^{-1}$ (2σ error bounds), contains all nine of the individual values within the stated bounds.

$$\text{rate} = k_{358K}[\text{catalyst}]\frac{[\text{benzene}]}{[\text{acetic acid}]} \tag{1}$$

A control experiment in which benzene is treated with CD_3COOD identically but with no Pt complex showed no isotopic peaks beyond those expected from natural abundance.

The GC−MS data for benzene isotopomers delivers two rates, the ratio of which contains important mechanistic information. From the background-corrected intensities of the various $C_6H_{6-n}D_n$ species, one calculates

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(10) Hinderling, C.; Plattner, D. A.; Chen, P. *Angew. Chem.* **1997**, *109*, 272. *Angew. Chem. Int. Ed.* **1997**, *36*, 243. Hinderling, C.; Feichtinger, D.; Plattner, D. A.; Chen, P. *J. Am. Chem. Soc.* **1997**, *119*, 10793. Feichtinger, D.; Plattner, D. A. *Angew. Chem.* **1997**, *109*, 1796; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1718. Feichtinger, D.; Plattner, D. A.; Chen, P. *J. Am. Chem. Soc.* **1998**, *120*, 7125. Hinderling, C.; Adlhart, C.; Chen, P. *Angew. Chem.* **1998**, *110*, 2831; *Angew. Chem., Int. Ed.* **1998**, *37*, 2685. Hinderling, C.; Chen, P. *Angew. Chem.* **1999**, *111*, 2393; *Angew. Chem., Int. Ed.* **1999**, *38*, 2253. Kim, Y. M.; Chen, P. *Int. J. Mass Spectrom.* **1999**, *185−7*, 871. Hinderling, C.; Chen, P. *Int. J. Mass Spectrom. Ion Processes* **2000**, *195/196*, 377. Hinderling, C.; Adlhart, C.; Chen, P. *Chimia* **2000**, *54*, 232. Adlhart, C.; Chen, P. *Helv. Chim. Acta* **2000**, *83*, 2192. Adlhart, C.; Volland, M. A. O.; Hofmann, P.; Chen, P. *Helv. Chim. Acta* **2000**, *83*, 3306. Adlhart, C.; Hinderling, C.; Baumann, H.; Chen, P. *J. Am. Chem. Soc.* **2000**, *122*, 8204. Volland, M. A. O.; Adlhart, C.; Kiener, C. A.; Chen, P.; Hofmann, P. *Chem. Eur. J.* **2001**, *7*, 4621. Zhang, X.; Chen, P. *Chem. Eur. J.* **2003**, *9*, 1852. Chen, X.; Zhang, X.; Chen, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 3798.

(11) Brookhart, M.; Grant, B; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.

(12) Acetic acid-d_4 from Cambridge Isotopes contained an unspecified impurity, which could not be reliably removed by standard purification procedures.

(13) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann: Oxford, 1997; p 163.

(14) Solutions prepared in this fashion with benzene purified according to ref 13 and freshly prepared $[(Et_2O)_2H]^+[BArF]^-$ do not exhibit the nonspecific irreversible decay (on the time scale of hours) reported in earlier work from other groups. Similarly stable solutions of the cationic complex **2** can be prepared with the HBF_4 if the benzene solution is extracted several times with water immediately after activation is complete. Evidently, impurities, or perhaps excess acid, in the commercial HBF_4 solution are responsible for destruction of the cationic complexes.

(15) Anderson, J. R.; Kemball, C. *Adv. Catal.* **1957**, *9*, 51.

(16) Mass spectrometric measurements need to be done at low conversions. Golden, J. T.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **2001**, *123*, 5837, p 13 in Suppl.

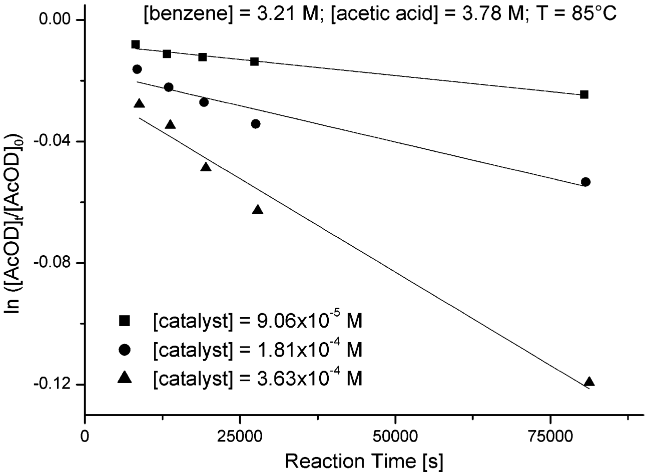


Figure 2. Semilogarithmic plot of the concentration of CD_3COOD against time for three runs in which the catalyst concentration is varied as benzene and acetic acid concentrations are held constant.

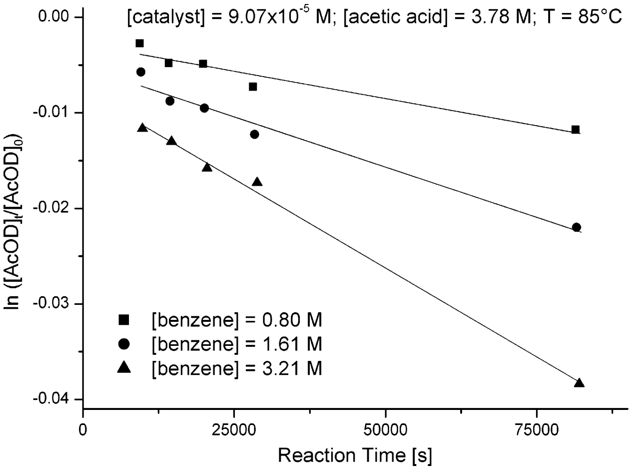


Figure 3. Semilogarithmic plot of the concentration of CD_3COOD against time for three runs in which the benzene concentration is varied as catalyst and acetic acid concentrations are held constant.

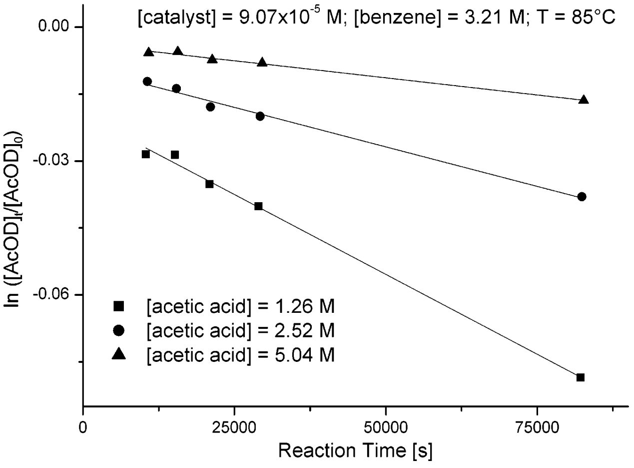


Figure 4. Semilogarithmic plot of the concentration of CD_3COOD against time for three runs in which the acetic acid concentration is varied as benzene and catalyst concentrations are held constant.

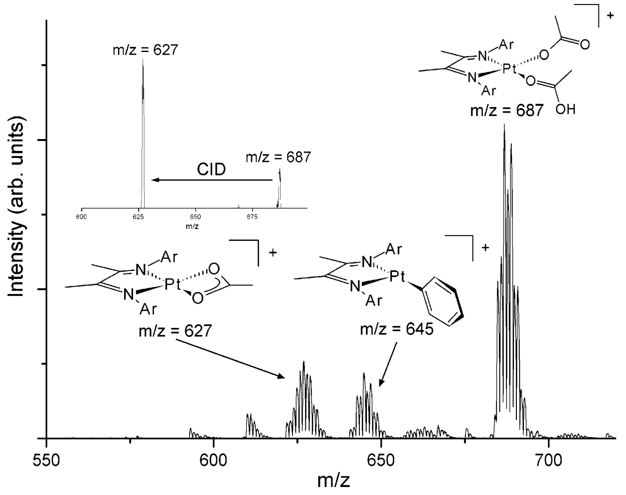


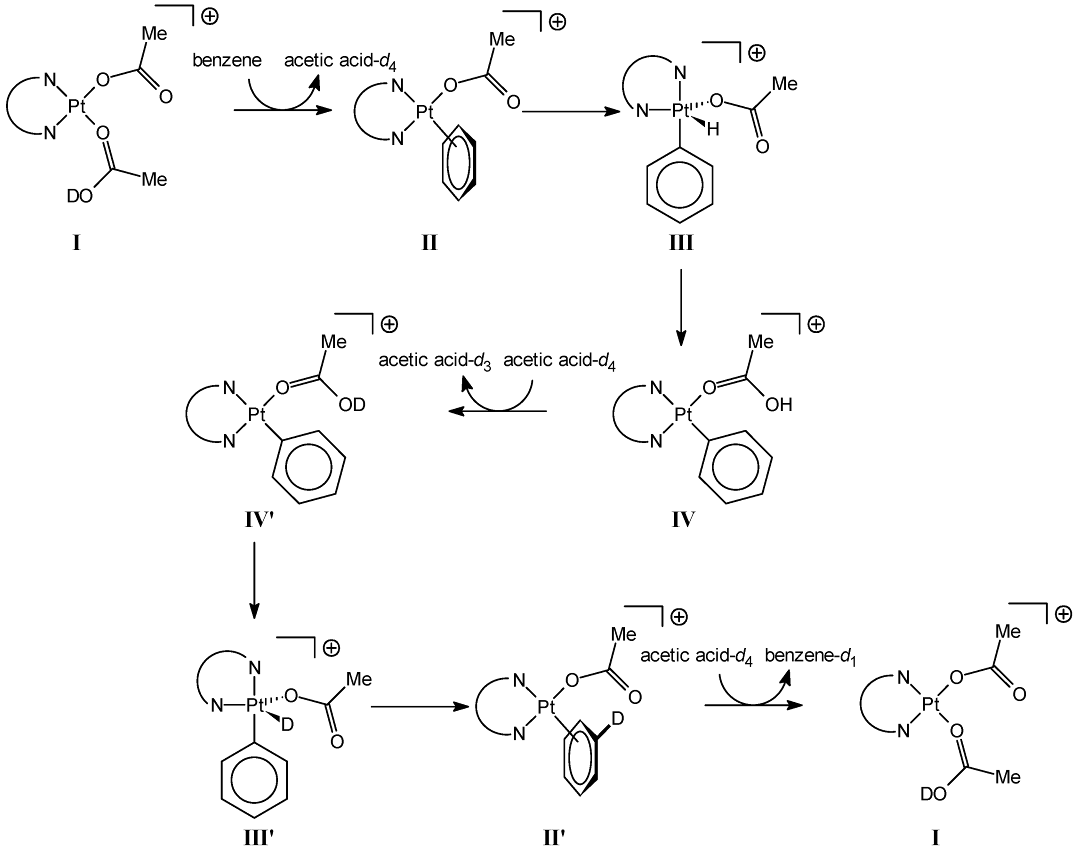
Figure 5. Electrospray mass spectrum (ESI-MS) of the benzene–acetic acid solution with the Pt^{II} complex shortly after initiation of the reaction. The Pt phenyl complex disappears as the reaction reaches steady state. The inset shows the collision-induced dissociation (CID) spectrum of the mass-selected ion at *m*/*z* = 687. A single dominant loss of acetic acid is indicated, even under very gentle conditions of a (lab frame) offset of 0 V and 0.5 mTorr Ar in the octopole collision cell.

the total rate of deuteration, effectively the rate that acetic acid-d_4 is converted to acetic acid-d_3, and the rate of consumption of C_6H_6. If there were only one deuterium incorporated per pass through the catalytic cycle, the two rates would be identical. If, on the other hand, multiple deuteriums were to be incorporated in a single pass, then the rate of deuteration would exceed the rate C_6H_6 consumption. The ratio, termed *M* by Anderson and Kemball,[15] is given in Table 1 in the Supporting Information for each measurement. The total of 45 measurements show consistent *M* values, with a mean value of $M = 2.6 \pm 0.3$ (2σ error bounds).

The electrospray ionization mass spectrum of an active solution directly introduced into the spectrometer, depicted in Figure 5, shows, aside from residual **3**, principally two species in solution, which, by their *m*/*z* ratio, are assignable to structures **4** and **5**. To support this assignment, **5** has been independently synthesized and characterized by ^1H NMR, elemental analysis, and mass spectrometry (see Supporting Information). Collision-induced dissociation (CID) of one isotopomer of **4** gives a clean dissociation to the corresponding isotopomer of **5**; that is, the only reaction is loss of acetic acid. It should be commented that the parent species, **4**, is clearly visible only when the desolvation conditions, e.g., tube lens potential, are set to be very mild. The loss of acetic acid from **4** to form **5** is extremely facile. Studies using the Finnigan MAT LCQ ion trap mass spectrometer rather than the TSQ-Quantum showed no **4**, which is easily understandable if one considers that the ion trap technology, by scanning out stored ions, inherently stores ions under collisional conditions for a much longer time. This longer storage time makes the identification of labile species much more difficult.

ESI-MS of solutions of **2** in benzene with D_2O (two-phase system, organic phase diluted with TFE and sprayed) shows incorporation of deuterium in the metal-bound phenyl group, but the reaction is much slower than the analogue with acetic acid. This is consistent with earlier reports.

Scheme 1



Discussion

C−H activation has been called a “holy grail” of organometallic chemistry,[17] with much activity in Ir and Pt being stimulated by Shilov's reports of catalytic conversion of methane to methanol by chloroplatinate complexes.[3] In particular, the proposed elementary steps in the Shilov chemistry have been studied by means of well-defined cationic Pt^{II} complexes by many groups, both experimentally[18] and computationally.[19] With only a few exceptions,[20,21] though, the well-defined Pt^{II} complexes do not perform catalytic C−H activation with a functionalized hydrocarbon as product, although Periana has reported catalytic C−H activation and functionalization under strongly oxidizing, electrophilic conditions with complexes of Pt and other metals.[22,23]

Interestingly, there were reports both prior[4,6] to, and contemporary[7] with, those from Shilov[8] in which heterogeneous, and later, homogeneous, Pt salts, chloroplatinates included, catalyzed the deuteration of benzene and other arenes with D_2O as the deuterium source in the presence of acetic acid. The process, largely due to Garnett and co-workers,[24] has been applied on the preparative scale for both deuteration and tritiation of arenes in a variety of applications.[25] The process is important from the mechanistic point of view because it is truly catalytic, with each turnover involving C−H activation of the arene. Moreover, the reaction occurs in the presence of coordinating solvents and reagents, which, in the work modeling Shilov chemistry, had been typically considered to be deleterious. The present work is motivated by the desire to model the catalytic cycle in Garnett's reaction by way of well-defined Pt^{II} complexes for which the resting state and turnover-limiting step may then be determined. Renewed interest in the reaction, as seen in recent reports of H/D exchange

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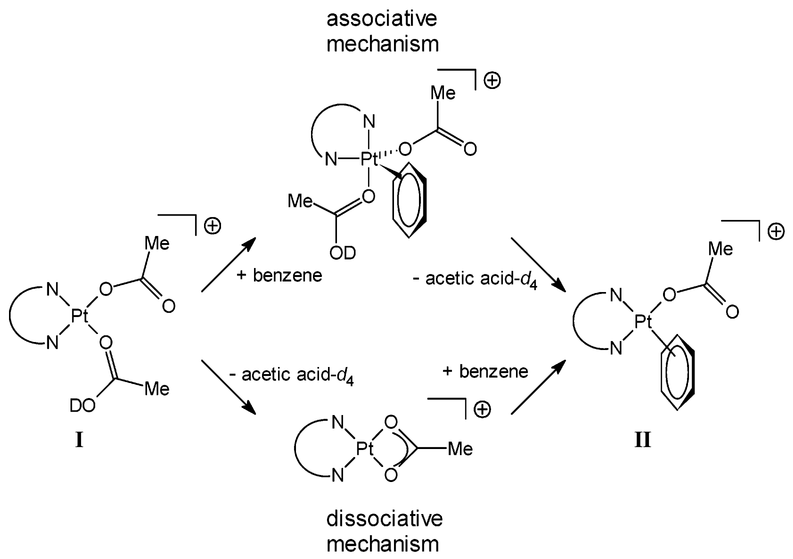
Scheme 2



catalyzed by rhodium[23] and iridium[26] complexes, makes the mechanistic study of well-defined model complexes timely.

One pass through the catalytic cycle is depicted as shown in Scheme 1, starting from the resting state **I**. Each transformation in Scheme 1 may correspond to several elementary steps. For example, the net ligand exchange reaction **I** → **II** may be either dissociative or associative, and the net oxidative addition reaction **II** → **III** may also include changes in benzene from π to σ coordination. Furthermore, no stereochemical claims are made; the structures are meant to denote stoichiometry and connectivity only. Nevertheless, Scheme 1 provides a general framework for discussion of the mechanism and can accommodate the several possible mechanistic possibilities. It should be noted that, whether one considers the reaction **IV′** → **III′** to be an oxidative addition of the metal to an O−H bond or a protonation of the metal by a coordinated Brønsted acid, the result is the same. Furthermore, studies on related Pt^{II} complexes by Tilset show that the site of protonation is in fact the metal.[27]

The mass spectrometric results show clearly that the resting state of the catalytic cycle is a Pt^{II}-acetato complex with a coordinated acetic acid. The observed rate law indicates unambiguously that the turnover-limiting transition state contains one benzene unit more and one acetic acid unit less than does the resting state. It is in principle possible that there are one or more intermediates between the resting state and the turnover-limiting transition state; the transformations involving those intermediates would constitute preequilibria that do not affect the overall rate law.

After the resting state, the second decisive point in the catalytic cycle is the turnover-limiting transition state. The stoichiometry of the resting state and the observed rate law do not alone provide an unambiguous assignment. However, the M value, the mean number of deuteriums incorporated per pass through the catalytic cycle, with a single pass defined to be the reactions starting at the resting state and returning once to the same resting state, provides the necessary additional information. We extract $M = 2.6 \pm 0.3$ (2σ error bounds) from all of the runs in Table 1, which means that between two and three deuteriums are incorporated in benzene per pass under the conditions of the experiment. The tangible consequence is visible in Figure 1, in which one sees qualitatively that, even at low conversion, multiply deuterated benzenes appear. Moreover, the peaks due to multiply deuterated benzene rise approximately parallel, rather than subsequent, to the rise of singly deuterated benzene. For $M = 1$, one would expect to see very little multiple deuteration until the amount of monodeuterated benzene had accumulated to a significant level in the bulk solvent. Hodges and Garnett[7] report $M \approx 2-4$ for the deuteration of benzene by D_2O, catalyzed by $PtCl_4^-$ in the presence of acetic acid and HCl, with the lower bound occurring for solutions with a high mole fraction of acetic acid, such as we have, and higher temperatures. It should be noted that these workers have excluded a simple electrophilic aromatic substitution mechanism for the deuteration, as well as reaction catalyzed by colloidal Pt^0. Considering the resting state and the larger-than-unity M value, and recalling that the potential surface in Scheme 1 is symmetric about its midpoint (aside from zero-point energy effects), one concludes that the turnover-limiting transition state necessarily lies between **I** and **II** (and also **II′** and **I**) for the particular reaction conditions. The observed multiple deuteration per pass requires fast, reversible interconversion of all species between **II** and **II′** through transition states that are not turnover-limiting. Changes in benzene and acetic acid concentration affect the various transition states unequally, so it is of course possible that a different transition state can be rendered turnover-limiting for some other set of reaction conditions, but no evidence for a change in turnover-limiting step is evident in this study.[28]

For the transformation **I** → **II** there are several mechanistic possibilities. Ordinarily, one would expect a ligand exchange in a square-planar d^8 complex to proceed via an associative mechanism.[29] This behavior

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has been reported for similar cationic Pt^{II} diimine complexes in other C−H activation studies,[30,31] although T-shaped, formally 14-electron, Pt^{II} complexes (with an agostic C−H at the "fourth" site), which would be the intermediate in a putative dissociative mechanism, have been prepared.[32] The two possibilities, associative and dissociative[33] ligand substitution, are shown in Scheme 2. For each mechanism there are two further possibilities for the turnover-limiting step, giving a total of four possible turnover-limiting transition states. The stoichiometry of the resting state and the empirical rate law, first-order in benzene and inverse first-order in acetic acid, exclude three of the four. The ligand substitution **I** → **II** must occur by a dissociative mechanism with a turnover-limiting second step. In other words, coordination of benzene with opening of the η^2-acetato complex determines the rate of the overall reaction. One presumes that the otherwise unusual dissociative mechanism for ligand substitution in a square-planar d^8 complex becomes competitive because of the concomitant η^2 coordination of the remaining acetate ligand. While we have done no quantitative collision-induced dissociation (CID) threshold measurement, one can see from the CID experiment that the activation energy for loss of acetic acid from **I** is much lower than that for loss of coordinating solvent molecules, e.g., water, trifluoroethanol, and acetonitrile, from analogous complexes in our earlier work. In principle, the coordination of benzene to the η^2-acetato complex can occur through two steps via yet another five-coordinate intermediate, but the kinetic results do not give enough information to distinguish between this mechanism and a concerted one.

The conclusion that coordination of benzene with opening of the η^2-acetato complex constitutes the turnover-limiting step is itself perhaps not surprising. It is surprising, though, that this step is not so much slower than the other steps in the overall mechanism. The *M* value of 2.6 indicates multiple deuteration per pass through the catalytic cycle, but it also indicates that the turnover-limiting ligand substitution **I** → **II** is not so much slower than the next slower step. If it were, then one would expect a value for *M* approaching 6. One would have ordinarily expected a Pt η^2-carboxylato complex to be a dead end in catalysis, or at least a structure whose stability would deleteriously affect turnover frequency. Such explanations had already been expressed in the literature.[26] The present work indicates that the ligand substitution via such an intermediate is not prohibitively slow. It is interesting to note that the earlier experiments by Garnett and co-workers were also conducted with significant amounts of acetic acid present. Its putative role, however, was always given as cosolvent to keep the benzene/water mixture homogeneous. To the extent that either the heterogeneous or homogeneous catalysts from Garnett are well-modeled by the present system, one can surmise that acetato complexes and acetic acid regulate the turnover frequency in those systems as well.

In principle, the result suggests that complex **I** should be a competent precursor to complex **2** or **3**. An attempted synthesis of **I** from the free ligand and $[Pt(OAc)_2]_4$, prepared by the procedure of Wright,[34] failed, presumably because the 1,2-diimine ligand was not sufficiently coordinating to break up the tetranuclear cluster.[35,36] Nevertheless, ready access to organometallic complexes competent in C−H activation from coordination complexes lacking a metal−carbon bond should be possible, perhaps with sterically more bulky carboxylates. Such a procedure would be in principle synthetically more convenient than the present preparative procedures starting from preformed Pt alkyl complexes.[9]

Conclusions

We have demonstrated that a well-defined cationic Pt^{II}-acetato complex is competent in at least one catalytic C−H activation reaction of benzene. The H/D exchange proceeds with TON in the thousands analogously to H/D exchange reactions reported by Garnett and co-workers for in situ prepared heterogeneous Pt catalysts or chloroplatinate complexes. A combination of ESI-MS, solution-phase kinetics, and analysis of deuteration per turnover unambiguously identifies both the resting state in the cycle and the turnover-limiting step.

Acknowledgment. Technical assistance in the quantitative GC−MS experiments by Mr. G. Grassi (ETHZ) is gratefully acknowledged. This project was supported by the Research Commission of the ETH Zürich and the Swiss National Science Foundation.

Supporting Information Available: Synthesis, characterization, and spectroscopic data for new compounds, experimental details for mass spectrometry, and a complete table of kinetic runs are available free of charge via the Internet at http://pubs.acs.org.

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