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Comparative Gas-Phase and Solution-Phase Investigations of the Mechanism of C−H Activation by $[(N{-}N)Pt(CH_3)(L)]^+$

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Contrary to previous claims in the literature, there is no solvent assistence by 2,2,2-trifluoroethanol (TFE) in C−H activation reactions by cationic Pt(II) complexes. Both electrospray ionization tandem mass spectrometric studies of isolated gas-phase intermediates and solution-phase kinetic spectroscopy indicate that TFE serves only as an inert diluent. TFE was found in the gas-phase experiment to provide no acceleration of the loss of methane or benzene from preselected $[(N{-}N)Pt(CH_3)(C_6H_6)]^+$ or $[(N{-}N)Pt(CH_4)(C_6H_5)]^+$ ions. In solution, the overall C−H activation reaction of benzene by $[(N{-}N)Pt(CH_3)(H_2O)]^+BF_4^-$ was found to be zero-order in TFE. While it is on one hand disappointing that the claimed facilitation of C−H activation by solvent assistance by TFE at the rate-determining transition state is not supported by the present experimental data, it is on the other hand encouraging that extremely rapid C−H activation (on the time scale of seconds at room temperature) in solution may be achieved in ordinary solvents as long as the solvent is not strongly coordinating.

Introduction

Since the discovery by Shilov[1] that certain platinum salts can catalyze the functionalization of methane, C−H activation has been an active field of investigation.[2] Given the difficulty in working with the poorly defined species that occur in the original Shilov system, model systems that mimic one or more steps of the proposed catalytic cycle have been studied under conditions where the reactions may be cleanly observed and characterized. Previous studies have succeeded in characterizing many of the key steps and reactive intermediates in the catalytic cycle.[2] Experiments by the Caltech and Oslo groups have recently focused on the mechanism of C−H activation of methane and arenes by Pt(II) complexes in 2,2,2-trifluoroethanol (TFE)[3−6] as solvent; the original report claims C−H activation “under the mildest reaction condition yet reported for such processes at cationic Pt complexes”. Subsequent publications assign the rate-determining step in C−H activation of benzene by sterically crowded Pt(II) complexes to the solvent-assisted associative ligand exchange of benzene for coordinated TFE, on the basis of kinetic[4,7] and activation volume[8] measurements. Given the considerable long-term potential of C−H activation reactions and the putative role of TFE in facilitating the reaction, i.e., solvent assistence, a mechanistic investigation to clarify that role is timely. Moreover, given that all of the complexes in the reaction are cationic, the question of mechanism is directly accessible by gas-phase reactions of the complexes in a tandem mass spectrometer where the solvent molecule can be explicitly included or excluded from the reaction. We report both a gas-phase, tandem mass spectrometric study of the C−H activation of benzene by $[(N{-}N)Pt(CH_3)(L)]^+$, **1a**−**d**, (N−N) = Ar−N=C(CH$_3$)−C(CH$_3$)=N−Ar, in which the reaction is performed in both the forward and reverse directions with mass-selected complexes, and an accompanying solution-phase kinetic study of the comparable reaction.

Both sets of experiments strongly suggest that TFE plays no role whatsoever in the rate-determining transition state for the overall C−H activation reaction in either gas phase or solution. The importance of this result for C−H activation is also discussed.

Experimental Section

The preparation of the starting complexes, X-ray structures, and further details on the execution of the experiments are given in the Supporting Information. Complexes **3** and **4** were synthesized as the dimethyl complexes as described in the literature.[4,9] Analytical data matched those previously reported. **1a**−**d** were electrosprayed from a 10^{-5} M solution in

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[1] Shilov, A. E.; Shulpin, G. B. *Chem. Rev.* **1997**, *97*, 2879.

[2] Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2180. Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. Crabtree, R. H. *Chem. Rev.* **1995**, *95*, 987.

[3] Johansson, L.; Ryan, O. B.; Tilset, M. *J. Am. Chem. Soc.* **1999**, *121*, 1974.

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[5] Heiberg, H.; Johansson, L.; Gropen, O.; Ryan, O. B.; Swang, O.; Tilset, M. *J. Am. Chem. Soc.* **2000**, *122*, 10831.

[6] Johansson, L.; Ryan, O. B.; Rømming, C.; Tilset, M. *J. Am. Chem. Soc.* **2001**, *123*, 6579.

[7] Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 1378.

[8] Procelewska, J.; Zahl, A.; van Eldik, R.; Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **2002**, *41*, 2808.

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10.1021/om0209982 CCC: $25.00
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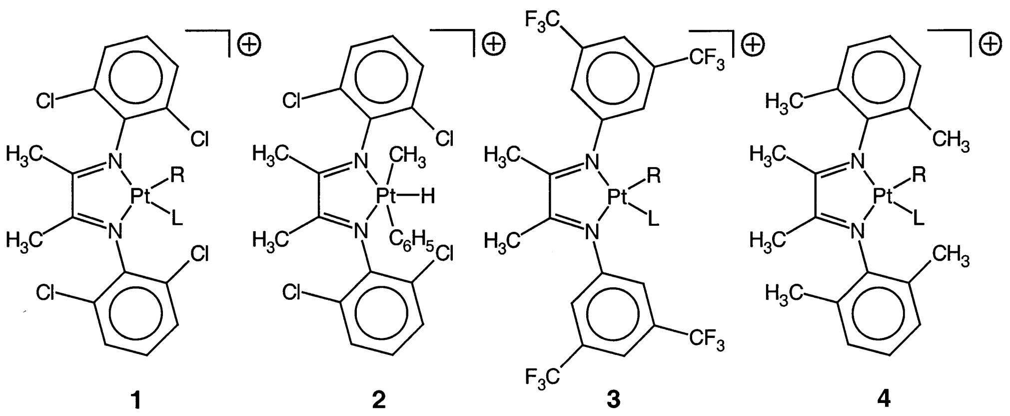
Scheme 1



(a) $R = CH_3$, L = empty coordination site
(b) $R = CH_3$, $L = H_2O$
(c) $R = CH_3$, L = TFE
(d) $R = CH_3$, $L = CH_3CN$
(e) $R = CH_3$, $L = C_6H_6$
(f) $R = C_6H_5$, $L = CH_4$
(g) $R = C_6H_5$, L = empty coordination site
(h) $R = C_6H_5$, $L = H_2O$

TFE to which up to 25% water or acetonitrile was added, depending on the experiment. After desolvation, the ions were mass-selected and reacted in the second octopole region of a modified Finnigan MAT TSQ-700 tandem mass spectrometer, as has been described in previous reports.[10,11]

Solution-phase UV/vis kinetic spectroscopy was done with either a Perkin-Elmer Lambda 6 or a Hitachi U-2010 UV/vis spectrophotometer. The cuvette holders were thermostated by a Haake F3 heat regulator. For the first series of experiments, 0.25 mM (purple) solutions of the dimethyl precursor to **1b** or **4b** in TFE containing 0.16 M water were treated with 1.1 μL of a 50% aqueous solution of HBF_4 in the cuvette. The orange solutions were thermalized and then treated with a measured volume of benzene (at the same temperature). The solution should be observed carefully at the higher benzene concentrations for indications of phase separation, usually evidenced by the appearance of turbidity, which would compromise quantitative rate measurements. For the second series of experiments, benzene was mixed with water and heated to 50 °C. The mixture was cooled; the layers were then separated at 25 °C. The concentration of water in saturated wet benzene has been reported[12] to be 0.029 M. Solutions of 0.25 mM of the dimethyl precursors to **1b** (green) and **4b** (purple) were prepared in the water-saturated benzene and thermalized. Stock solution (40 μL) prepared from 5.7 mg of a 50% aqueous solution of HBF_4, diluted with 1 mL of ether, was added to the cuvette. Spectra were then recorded immediately.

Results

Selection of **1a** versus **1b** (Scheme 1), for example, by *m*/*z* ratio was straightforward. An adduct with benzene having the structure **1e**, **1f**, or **2** could be prepared by reaction of **1a** with benzene vapor (~8.5 mTorr) in the 24-pole ion guide region, followed by selection by mass. While the experiments below do not allow an unambiguous structural assignment to **1e**, **1f**, or **2**, the reactivity of the ion, and particularly, the isotopic scrambling experiment, as detailed below, suggests either that it is **2** or that the interconversion between **1e**, **1f**, and **2** is much faster than elimination to form either **1a** or **1g**. The adduct is therefore designated as **1e**/**1f**/**2**. All reactions in the subsequent octopole were performed at low collision energies.

We find unsurprisingly that addition of benzene to **1b** and **1c** occurs inefficiently under all reactions conditions; **1d** does not react at all. On the other hand, **1a** reacts with benzene with good reaction efficiency at low collision energy to form an adduct, **1e**/**1f**/**2**, as well as a product, **1g**, corresponding to subsequent elimination of methane.[13] Given the coordinative unsaturation of **1a**, the facile product formation is also unsurprising. Figure 1 shows, nevertheless, that this C−H activation reaction is not only facile but also very clean. No ions other than the starting complex **1a**, the adduct **1e**/**1f**/**2**, the product **1g**, and a further benzene complex of **1g** are visible.

With benzene-d_6 instead of benzene as the collision gas, we measure a kinetic isotope effect of 1.18 ± 0.06[14]

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[10] Feichtinger, D.; Plattner, D. A. *Angew. Chem.* **1997**, *109*, 1796. Feichtinger, D.; Plattner, D. A.; Chen, P. *J. Am. Chem. Soc.* **1998**, *120*, 7175. Hinderling, C.; Adlhart, C.; Chen, P. *Angew. Chem.* **1998**, *110*, 2831. Hinderling, C.; Chen, P. *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 Spectrosc. Ion Processes* **2000**, *195/196*, 377. Hinderling, C.; Adlhart, C.; Chen, P. *Chimia* **2000**, *54*, 232. Adlhart, C.; Hinderling, C.; Baumann, H.; Chen, P. *J. Am. Chem. Soc.* **2000**, *122*, 8204. 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. Volland, M. A. O.; Adlhart, C.; Kiener, C. A.; Chen, P.; Hofmann, P. *Chem. Eur. J.* **2001**, *7*, 4621.

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[12] Becker, H. G. O.; Berger, W.; Domschke, G.; Fanghänel, E.; Faust, J.; Fischer, M.; Gentz, F.; Gewald, K.; Gluch, R.; Mayer, R.; Müller, K.; Pavel, D.; Schmidt, H.; Schollberg, K.; Schwetlick, K.; Seiler, E.; Zeppenfeld, G. *Organikum. Organisch-chemisches Praktikum*; Barth Verlaggesellschaft: Leipzig, 1993; p 662.

[13] Quantitative reaction efficiencies as a function of collision energy and collision gas pressure were also recorded; over the range of conditions examined, the isotope effects and product branching ratios did not change appreciably, although the overall reaction efficiency, i.e., yield, increased monotonically with increasing collision energy.

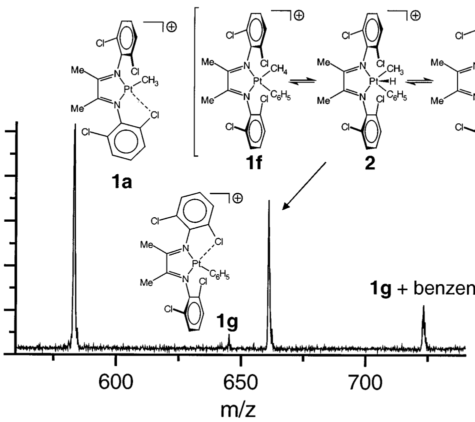

Figure 1. Daughter ion spectrum showing the reaction performed by selection of **1a** and collision of the ion with benzene in the octopole collision cell.

for the overall transformation **1a** → **1g** using product ion peak intensity under standardized conditions as a measure of relative rate. In an independent experiment, we looked at the reaction, benzene (or benzene-d_6) + **1a** → **1e**/**1f**/**2**, and found no detectable isotope effect within experimental error, indicating that the former isotope effect pertains only to the step **1e**/**1f**/**2** → **1g**. Moreover, when **1e**/**1f**/**2**, prepared as above and then isolated by selection according to mass, is collided with argon, one sees only the two products corresponding to loss of methane or loss of benzene, in a 84:16 (±3) ratio.[15] When **1e**/**1f**/**2**-d_6, prepared by reaction of **1a** with benzene-d_6 followed by selection according to mass, is subjected to similar conditions, we find that the deuterium partitions with a slight preference into the departing benzene vis-à-vis methane; precise integrations of the isotopomer peak intensities show a slight deviation from a statistical distribution, i.e., a small partition isotope effect. The spectrum and the derived isotope distribution in the products are shown in Figure 2.

The most important gas-phase experiment with regard to the identity of the rate-determining step in C−H activation of benzene is the comparison of the eliminations of methane or benzene from preselected **1e**/**1f**/**2** induced by collision with either TFE or 1,1,1,2-tetrafluoroethane vapor. In the reaction induced by collision with TFE, one sees neither a TFE-containing adduct nor a TFE-containing product ion. We find that collision of **1e**/**1f**/**2** with TFE vapor or 1,1,1,2-tetrafluoroethane at low energies gives ions corresponding to loss of methane and benzene in a ratio of 83:17 (±2) and 85:15 (±1), respectively, as the only detectable products. As in the case of collision with argon, we find that the branching ratio does not vary much with collision energy, at least within the range in which we typically work (nominally −2 to 14 eV in the laboratory frame). Very interestingly, the collision energy dependence of the summed elimination of methane and benzene is experimentally indistinguishable for the two different collision gases.[16] A superposition of the product yields as a function of collision energy is shown in Figure 3.

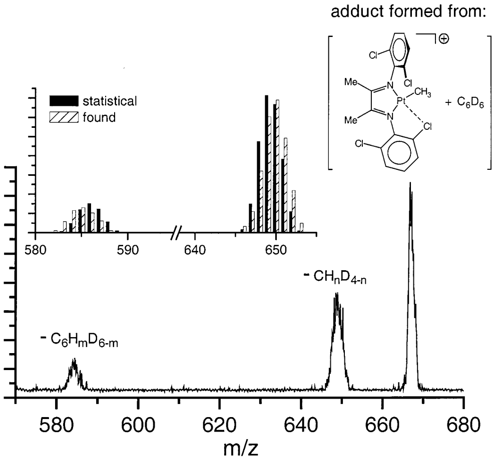

Figure 2. Daughter ion spectrum taken by selecting the **1e**/**1f**/**2**-d_6 ion and performing collision-induced dissociation of the ion with 0.8 mTorr 1,1,1,2-tetrafluoroethane at 7 eV (laboratory frame) collision energy. An extraction of the isotope distribution found in the methane and benzene-loss products is compared with a fully statistical distribution.

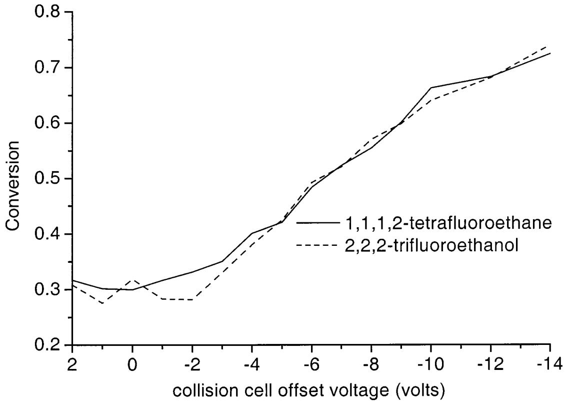

Figure 3. Dependence of the combined yield of benzene and methane-loss products in CID of **1e**/**1f**/**2** on the collision energy varied in steps of 1 eV (laboratory frame, lines connect the data points) for two different collision gases at 0.60 mTorr pressure.

It should be noted that the absolute pressure of collision gas, either TFE or tetrafluoroethane, was reduced successively until the threshold behavior did not change significantly, meaning that we begin to approach the single-collision limit in the octopole collision cell. However, at the pressure of collision gas used, 0.60 mTorr, it cannot be guaranteed that effectively all eliminations follow from a single collision event, although it is certain that most of them do. Accordingly, the extraction of a quantitative threshold, as has been done for some other complexes, would be uninformative.

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[14] The error bound on the isotope effect is computed for 95% certainty and comes from 30 independent measurements.

[15] The error bounds on the branching ratio is computed for 95% certainty and comes from 50 independent measurements. The branching ratios were also constant over the range of collision energies studied, i.e., nominally −2 to 14 eV in the laboratory frame.

[16] In the comparison of elimination from the **1e**/**1f**/**2** complex, the gauge pressures of TFE or tetrafluoroethane were varied between 0.8 and 2.0 mTorr as read from a Pirani gauge attached directly to the housing of the second octopole. Pirani and thermocouple gauges actually measure thermal conductivity rather than pressure. Because thermal conductivity is proportional to the product of heat capacity and pressure, the two gases should have the same actual pressure when the gauge readings are normalized by the ratio of their heat capacities. Computation of the heat capacities from scaled harmonic vibrational frequencies was done and produced a ratio C_v[TFE]/C_v[tetrafluoroethane] of 1.13, which we used to normalize the gauge readings.

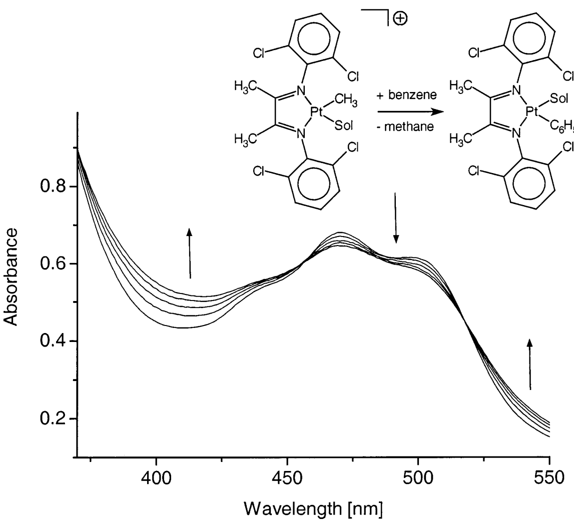

Figure 4. Stacked UV/vis absorption spectra showing the time development of the spectrum of **1b** and benzene at 25 °C in TFE solution containing 3.75 M benzene and 0.14 M water. Two clean isosbestic points are visible. Pseudo-first-order rates were measured for decay of **1b** and rise of **1h** at 310, 400, and 545 nm. The displayed traces were recorded at 5 min intervals.

Nevertheless, the almost complete coincidence of the two plots in Figure 3 suffices for the mechanistic argumentation below.

Solution-phase kinetic studies of the reactions of **1b** and **4b** with benzene in TFE solution were performed primarily by time-dependent UV/vis, with control experiments by ^{1}H NMR and electrospray mass spectrometry to check that the reactions were clean. For both Pt(II) species, protonation of the corresponding dimethyl complexes with HBF_4 afforded the desired aquo complexes, as expected from the work by Tilset, Bercaw, and co-workers. With thorough purification of solvents and reagents, extraneous side-reactions can be suppressed as indicated by the clean isosbestic points visible in Figures 4, 5, 8, and 9.

Kinetics were performed at multiple wavelengths and found to be consistent. As a further control, the rates of disappearance of the cationic methyl complexes **1b** and **4b** were found to be identical with the rates of appearance of the cationic phenyl complexes **1h** and **4h**. Plots of absorbances *A* at the selected wavelengths against time gave good fits to a single exponential over several half-lives in each case, from which a pseudo-first-order rate constant k_{obs} could be extracted.

$$A = A_\infty + (A_0 - A_\infty)\exp(-k_{\mathrm{obs}}t)$$

$$\text{where} \qquad k_{\mathrm{obs}} = k\frac{[\text{benzene}]}{[\text{water}]}$$

Plots of the k_{obs} against [benzene]/[water], shown in Figures 6 and 7, yield the rate constants for C−H activation of benzene in wet TFE solution.

When neat (wet) benzene was used as solvent, the rate of **1b** → **1h** and **4b** → **4h** could also be determined by kinetic spectroscopy. Stacked UV/vis spectra over time for **1b** → **1h** and **4b** → **4h** in neat benzene, i.e., 11.25 M, with 0.029 M water are shown in Figures 8 and 9.

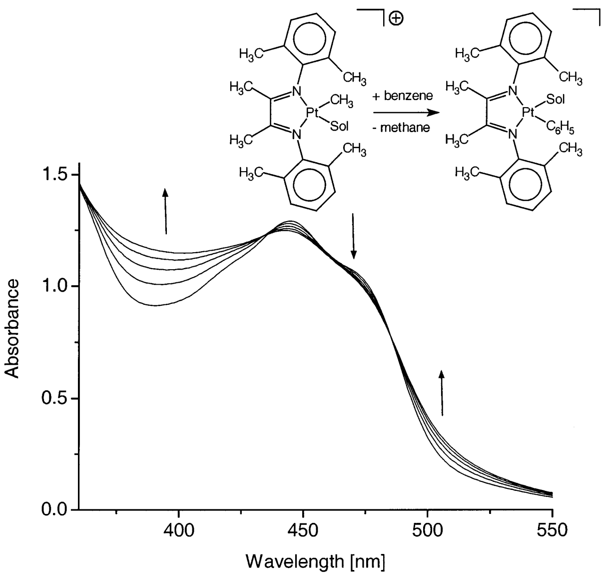

Figure 5. Stacked UV/vis absorption spectra showing the time development of the spectrum of **4b** and benzene at 25 °C in TFE solution containing 1.88 M benzene and 0.17 M water. At least two clear isosbestic points are visible. Pseudo-first-order rates were measured for decay of **4b** and rise of **4h** at 375, 390, and 510 nm. The displayed traces were recorded at 60 min intervals.

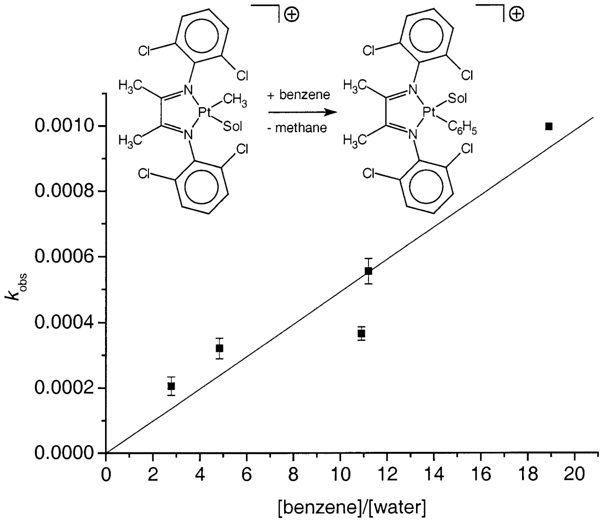

Figure 6. Dependence of the pseudo-first-order rate constant of reaction **1b** → **1h** at 25 °C in TFE solution containing benzene in concentrations between 0.43 and 3.75 M and water between 0.04 and 0.22 M. From the slope of a linear fit, one derives a rate constant of $k = (4.93 \pm 0.42) \times 10^{-5}\ \mathrm{s}^{-1}$.

Figures 10 and 11 show the time development of the absorbances for these two reactions, from which rate constants can be extracted.

Discussion

What are the intermediates and which elementary step is rate determining for the C−H activation of benzene by cationic Pt(II) complexes? Platinum alkyl or aryl complexes have been protonated at low temperature, providing chemical and NMR evidence[4,5,17] for hydridoalkyl and alkane or arene C−H σ- and π-com-

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[17] (17) Wik, B. J.; Lersch, M.; Tilset, M. *J. Am. Chem. Soc.* **2002**, *124*, 12116.

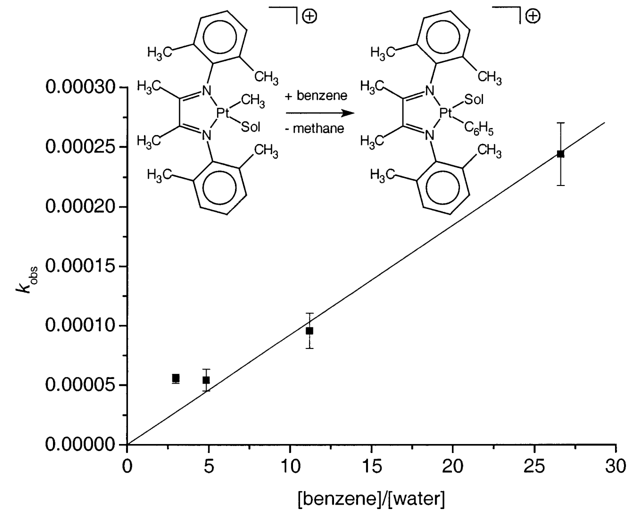

Figure 7. Dependence of the pseudo-first-order rate constant of reaction **4b** → **4h** at 25 °C in TFE solution containing benzene in concentrations between 0.57 and 3.75 M and water between 0.14 and 0.22 M. From the slope of a linear fit, one derives a rate constant of $k = (9.24 \pm 0.60) \times 10^{-6}\ s^{-1}$.

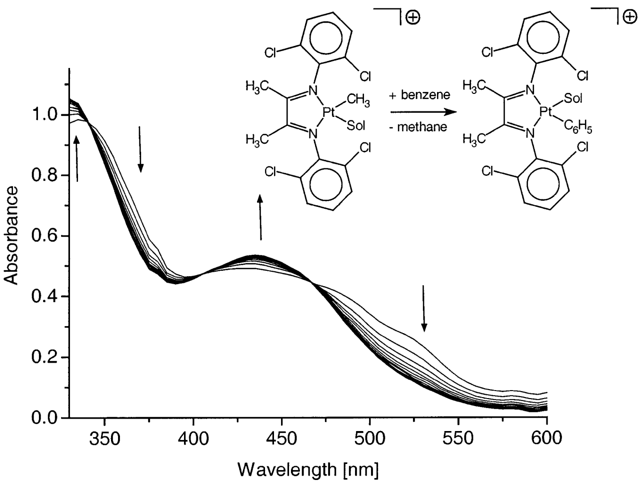

Figure 8. Stacked UV/vis absorption spectra showing the time development of the spectrum **1b** and benzene at 25 °C in neat (11.25 M) benzene containing 0.029 M water. Three clean isosbestic points are visible. Pseudo-first-order rates were measured for decay of **1b** and rise of **1h** at 330, 440, and 520 nm. The displayed traces were recorded at 20 s intervals.

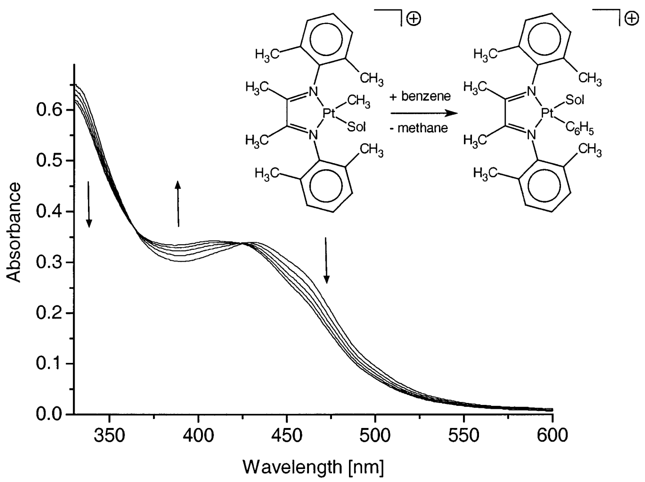

Figure 9. Stacked UV/vis absorption spectra showing the time development of the spectrum of **4b** and benzene at 25 °C in neat (11.25 M) benzene containing 0.029 M water. Two clean isosbestic points are visible. Pseudo-first-order rates were measured for decay of **4b** and rise of **4h** at 390 and 465 nm. The displayed traces were recorded at 20 s intervals.

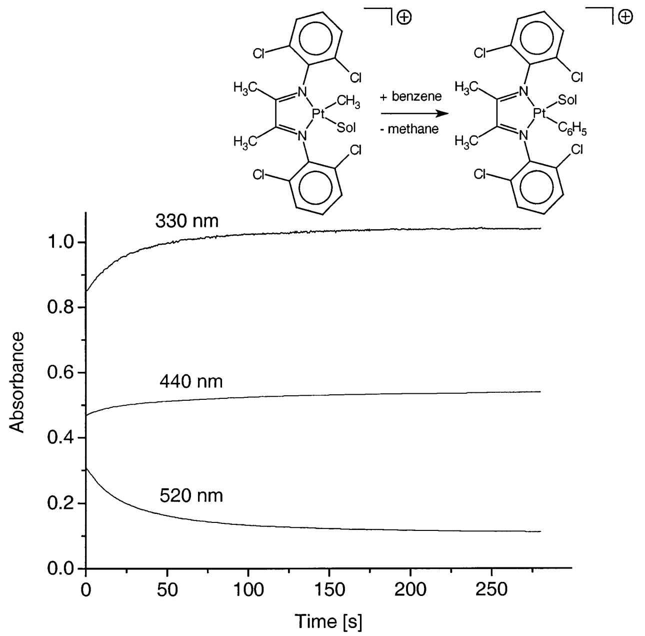

Figure 10. Time dependence of the UV/vis absorbance at three wavelengths for the reaction of **1b** and benzene at 25 °C in neat (11.25 M) benzene containing 0.029 M water. Data points were recorded at 0.5 s intervals and are completely coincident with the fit function and therefore not individually visible. A fit of data from all three wavelengths to an exponential function produced a pseudo-first-order rate constant, which when divided by [benzene]/[water], yields a rate constant of $k = (6.61 \pm 1.66) \times 10^{-5}\ s^{-1}$.

plexes. Oxidative addition was also found to be favored over the alternative σ-bond metathesis reaction in a computational study.[5] Moreover, the putative five-coordinate Pt(IV) intermediate in the reaction of a cationic Pt(II) alkyl complex with alkanes and benzene has been intramolecularly trapped,[18] lending support to an oxidative addition mechanism.

While many of the major features of the overall C−H activation reaction by Pt(II) have been worked out in these previous studies, the claim that the reaction of **3b** or **4b** with methane or arenes in TFE solution is unusually facile begs an explanation, especially in connection to the identification of the rate-determining step for the reaction. The long-term potential of C−H activation makes the identification of those structural or process parameters that confer high activity of considerable interest, especially given the much harsher reaction conditions that needed to be employed in the original Shilov chemistry.

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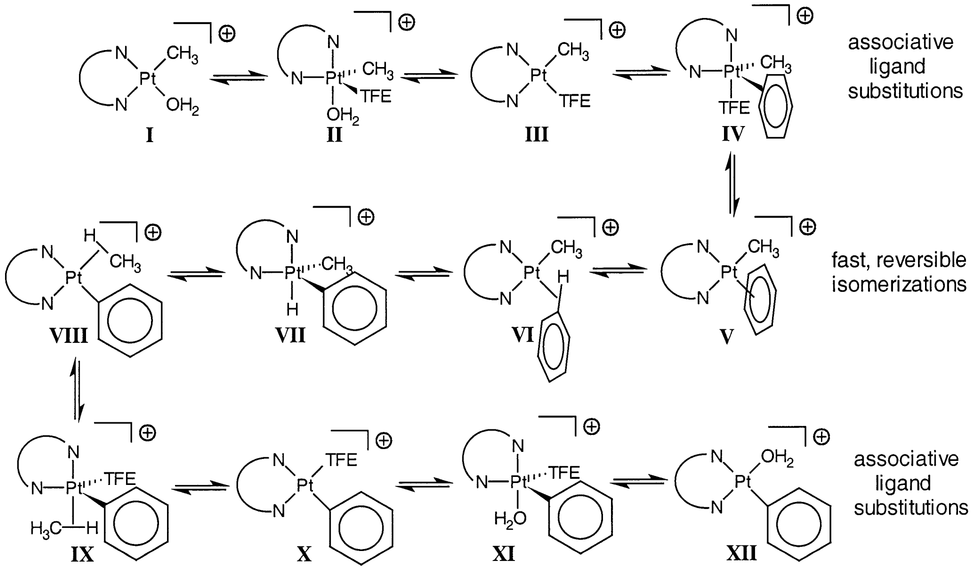
[18] Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235. Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 12724. Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2001**, *20*, 1709. Iron, M. A.; Lo, H. C.; Martin, J. M. L.; Keinan, E. *J. Am. Chem. Soc.* **2002**, *124*, 7041. Lo, H. C.; Haskel, A.; Kapon, M.; Keinan, E. *J. Am. Chem. Soc.* **2002**, *124*, 3226.

Scheme 2



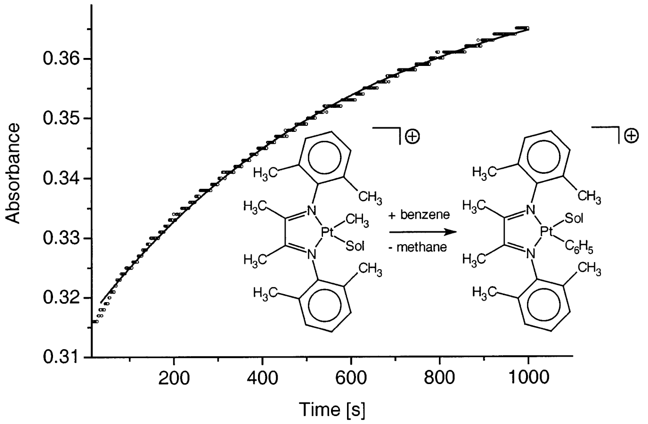
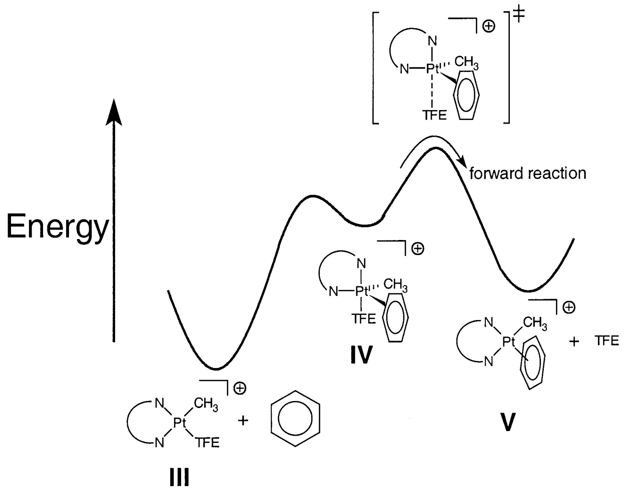


Figure 11. Time dependence of the UV/vis absorbance at 390 nm for the reaction of **4b** and benzene at 25 °C in neat (11.25 M) benzene containing 0.029 M water. Data points are indicated by circles and were recorded at 2 s intervals. A fit to an exponential function produced a pseudo-first-order rate, which when divided by [benzene]/[water], yields a rate constant of $k = (7.50 \pm 3.80) \times 10^{-6}\ s^{-1}$.

The ligand exchange of methane for coordinated solvent in **3d** was shown to be associative by the extent of isotopic incorporation in products from the reaction of $[(N-N)Pt(CH_3)_2]$ with DOTf in TFE in the presence of variable amounts of acetonitrile.[19] This result argues convincingly against the intermediacy of a three-coordinate intermediate in the solution-phase reaction, i.e., against a dissociative mechanism.

Previous studies on square-planar d^8 complexes[20] in general, and Pt(II) complexes[21] in particular, have long provided strong evidence that substitution reactions generally proceed via an associative mechanism. Accordingly, the mechanism in ref 4 can be drawn as indicated in Scheme 2, in which the various ligand substitutions connecting **I**−**V** as well as **IX**−**XII** are formulated as proceeding by associative mechanisms.[22] Isotopic scrambling,[4] as well as equilibration between various isomeric aryl complexes,[6] in solution-phase studies requires that interconversion between the Pt(IV) intermediate **VII**, the two σ-complexes **VI** and **VIII**, and presumably also the π-complex **V** be much faster than elimination of benzene or methane, ruling out either the actual oxidative addition or reductive elimination for the rate-determining step. Therefore, it has been recently proposed[4] that the rate-determining step in the C−H activation of arenes is the solvent-assisted associative ligand exchange reaction **III** → **V**, either as a single concerted step or as a combination of two steps, one of which being actually rate determining. Putting the structures **III**−**V** on a potential energy diagram in Scheme 3, one can argue from the Hammond postulate, applied to the two possible ligand dissociations from **IV**, that the net endothermic transformation **III** → **V** means that the rate-determining transition

Scheme 3



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(22) In Scheme 2, the structures should not be understood to mean that we have assigned a particular stereochemistry to the five-coordinate intermediates. The structures are presumed to undergo facile pseudorotation. The present experiments make no prediction concerning the stereochemistry.

state must be the second step, i.e., the departure of TFE from the five-coordinate intermediate.

This proposition is directly tested in the present experimental report.

While the gas-phase reaction studies formally involve the species very similar to those postulated in solution, the relevance of the present work to C−H activation in solution requires that we first establish that the complexes **1** are good models for the complexes **3** or **4**. We chose the complexes **1** for the gas-phase part of this study because we had found in earlier work that coordinatively and electronically unsaturated complexes often tended to undergo intramolecular C−H activation reactions, i.e., orthometalation, on a ligand.[11] For complexes **3** and **4** that were used in previous solution-phase studies, orthometalation is a possible reaction pathway which could complicate the gas-phase experiment that would interfere because the isolated ion has a comparatively long time to react intramolecularly in the source region of the mass spectrometer as compared to the situation in solution. We therefore employed in this study a ligand in which all ortho positions are blocked by chlorine substitution, which made the unsaturated complex stable against unimolecular reactions in the gas phase. It should be noted that the aryl rings on the ligands of **1**, **3** and **4** are twisted out-of-plane,[23] so the electronic influence of substituents on the rings at the metal center would come only through inductive effects. In this light, the nearly identical values of σ_I for chloro and trifluoromethyl substituents[24] would suggest that **1b** and **3b** would display similar reactivity.[25] The solution-phase kinetics of **3b** and **4b** were reported to be similar as well, with rates differing by less than 1 order of magnitude.[7] It would not be unreasonable to expect therefore broadly similar chemistry for **1b** versus **3b** or **4b**. The expectation is fully borne out by the solution-phase kinetics as illustrated in Figures 4−11. Not only is the chemical behavior for complex **1b** essentially identical to that for **4b**, but even the absolute values of the rates are not too different, e.g., $k = (4.93 \pm 0.42) \times 10^{-5}$ s^{-1} versus $(9.24 \pm 0.60) \times 10^{-6}$ s^{-1} for **1b** and **4b**, respectively. Given that very substantial data have been published for **3b** and **4b**, it is gratifying to see that the rate constant measured in the present work for **4b** is in acceptable agreement with the value of $(1.98 \pm 0.03) \times 10^{-5}$ s^{-1} reported for the same complex under the same conditions by Tilset, Bercaw, and coworkers.[4] Moreover, the clean isosbestic points in Figures 4, 5, 8, and 9 indicate that it is possible to find conditions under which all other side-reactions are much slower than the transformation **1b** → **1h** or **4b** → **4h**. These experiments are important to confirm that the solution-phase studies have been properly performed.

Having established that **1b** behaves like **4b**, we turn first to the gas-phase study. While solvation leads to large changes in the potential surfaces for gas-phase ion−molecule reactions, such as proton exchange, S$_N$2, or carbonyl additions,[26] relative to their congeners in solution, reactions of organometallic complexes electrosprayed into the gas phase[10] have proven surprisingly similar to the corresponding reactions in solution in other cases we have examined,[10,11] leading us to presume that the analogy in this case is also valid. Even so, solution-phase experiments in this report were executed to confirm the expectation (vide infra). Four observations may be made from the ion−molecule reactions. First, we see the same gross reaction in solution and in the gas phase. Second, the overall kinetic isotope effects for the reaction in the two different settings are similar; $k_H/k_D = 1.18 \pm 0.06$ in the gas-phase versus 1.06 ± 0.05 in solution.[4] Third, when benzene-d_6 is used instead of benzene, the distribution of deuterium between methane and benzene products shows nearly full equilibration and, furthermore, shows a small partition isotope effect in the same direction with a similar magnitude as that reported for the solution-phase experiment. Last, in gas-phase experiments, **1e**/**1f**/**2** gives branching ratios close to the reported value of 82:18 for reductive elimination of methane versus benzene observed when [(N−N)Pt(CH$_3$)(C$_6$H$_5$)] is protonated in solution.[4] It might be argued that the reactions of **1a**, a highly unsaturated three-coordinate species, are not directly comparable to those of four-coordinate **3c** or **4c**, or even to those of **1c**, for that matter, and that the gas-phase chemistry makes therefore no relevant prediction for solution-phase mechanisms.[27] The argument fails because one notes that isotope partitioning as well as the product branching ratio is determined not by the addition steps starting from **1a**, but rather by the reactions after formation of **1e**/**1f**/**2**. The presumably equilibrating mixture **1e**/**1f**/**2** in the gas-phase represents exactly those species depicted as **V**, **VI**, **VII**, and **VIII** in solution (with the proviso that one cannot yet distinguish between π- and σ-complexes in the gas phase). These four observations serve to show that the gas-phase chemistry does not differ grossly from that in solution. In particular, the significance of the addition reaction of **1a** should be understood as primarily a gas-phase synthesis of **1e**/

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[23] The X-ray structure of **1** is given in the Supporting Information; for related complexes, the X-ray structure was given in ref 6.

[24] Hines, J. *Structural Effects on Equilibria in Organic Chemistry*; Wiley: New York, 1975.

[25] The Oslo and Caltech groups have remarked in ref 4 that [(N−N)Pt(CH$_3$)(L)]$^+$, (N−N) = Ar−N=C(CH$_3$)−C(CH$_3$)=N−Ar with Ar = *o,o′*-dimethylphenyl, reacts similarly to **3** in TFE solution, only somewhat more slowly and more cleanly. Moreover, ref 6 compares the reactions of the complexes with fluorinated and unfluorinated ligands in their reaction with toluene. While the complex with unfluorinated ligand reacted more slowly, and moreover, produced a product of benzylic C−H activation that was absent in the reactions of **3**, the ratio of *ortho* to *meta* to *para* C−H activation for the two complexes was essentially identical. These observations suggest that, in the reaction of [(N−N)Pt(CH$_3$)(L)]$^+$ with benzene, **1** and **3** should not be expected to show gross mechanistic differences.

[26] Wolf, J. F.; Harch, P. G.; Taft, R. W. *J. Am. Chem. Soc.* **1975**, *97*, 2904. Farneth, W. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 7891. Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 311. Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219. Staley, R. H.; Wieting, R. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 5964. Asubiojo, O. I.; Brauman, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 3715. Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 5993. Arnett, E. M.; Peinta, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 3329. Sharma, S.; Kebarle, P. *J. Am. Chem. Soc.* **1982**, *104*, 19. Bohme, D. K.; MacKay, G. I. *J. Am. Chem. Soc.* **1981**, *103*, 978. Caldwell, G.; Magnera, T. F.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 959. McMahon, T. B.; Heinis, T.; Nicol, G.; Hovey, J. K.; Kebarle, P. *J. Am. Chem. Soc.* **1988**, *110*, 7591.

[27] Given the recent report of a crystal structure for a d^8 ML$_3$ Pt(II) complex stabilized by an agostic interaction at the formally empty fourth coordination site, one cannot lightly discount three-coordinate species on the reaction coordinate. See: Baratta, W.; Stoccoro, S.; Doppiu, A.; Herdtweck, E.; Zucca, A.; Rigo, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 105.

1f/**2**, whose subsequent reactions are shown below to make a relevant prediction for solution-phase mechanisms.

A rate-determining transition state with TFE bound at the metal is ruled out by the present gas-phase experiments: the threshold behaviors in Figure 3 for reductive elimination of benzene and methane from **1e**/**1f**/**2** induced by low-energy collision of the ion with TFE or 1,1,1,2-tetrafluoroethane are identical. The collision of preselected **1e**/**1f**/**2** with TFE corresponds to the reaction of **V** with TFE because both the gas-phase and solution-phase experiments show rapid equilibration of **V**−**VIII** prior to any other reaction. The two collision gases, TFE and 1,1,1,2-tetrafluoroethane, are isoelectronic and isostructural and have almost the same mass, making the kinematics of the collisions similar. They have moreover almost identical dipole moments,[28] making even long-range electrostatic ion−molecule interactions very similar. They do differ, however, in that 1,1,1,2-tetrafluoroethane coordinates much more weakly to electrophilic centers than does TFE, if at all.[29] Moreover, the near-constant branching ratio in the elimination reactions of **1e**/**1f**/**2** as the collision gas is varied from argon to TFE to tetrafluoroethane suggests strongly that TFE participates in the elimination only as a vehicle for energy transfer to **1e**/**1f**/**2**. If *coordination* of TFE were important at the transition state, one would expect to see different thresholds, and perhaps different selectivities, for elimination of benzene or methane from **1e**/**1f**/**2** when one changes the collision gas. By microscopic reversibility, the reaction in the other direction must also have no TFE bound at the transition state. Therefore, a putative solvent-assisted associative mechanism cannot be the explanation for the facile C−H activation reaction. The isotopic scrambling in the gas-phase experiment matches that seen in the analogous reaction in solution, which requires as a minimum conclusion rapid reversible interconversion between **VI**, **VII**, **VIII**, and presumably **V**, just as has been concluded for the solution-phase reaction.[4] This information, combined with the experimental conclusion that TFE is not bound at the rate-determining transition state for either benzene or methane elimination, requires that there exists at least one kinetically significant intermediate between **IV** and **V** for benzene activation and at least one further intermediate between **VIII** and **IX** for methane activation. The rate-determining transition state for C−H activation of benzene by this class of cationic Pt(II) complexes is necessarily the transition state in which this intermediate is transformed into **V**. Similarly, the rate-determining transition state for C−H activation of methane is the transition state in which the intermediate is transformed into **VIII**. The experiment does not specify what the structure of either of the new intermediates is, but their existence, and their crucial position immediately preceding the rate-determining step for the overall C−H activation reaction, is mandatory.

The solution-phase kinetics for **1b** and **4b** fully support the conclusion of the gas-phase study. Examination of Figures 6 and 7 reveals the transformations **1b** → **1h** and **4b** → **4h** are each described by a single rate constant over a broad range of [benzene]/[water] in wet TFE solution. If one makes the decisive comparison of the derived rate constant for benzene activation in TFE solution to the corresponding rate constants in neat (wet) benzene, one finds that, for each of the complexes **1b** or **4b**, the rate constant shows no dependence on TFE concentration at all. We find, for the reaction **1b** → **1h**, $k = (4.93 \pm 0.42) \times 10^{-5}\ \mathrm{s}^{-1}$ in TFE solution, and $(6.61 \pm 1.66) \times 10^{-5}\ \mathrm{s}^{-1}$ with no TFE at all. For **4b** → **4h**, the corresponding rate constants are $k = (9.24 \pm 0.60) \times 10^{-6}$ and $(7.50 \pm 3.80) \times 10^{-6}\ \mathrm{s}^{-1}$. If the rate constant in the complete absence of TFE is experimentally indistinguishable from that when TFE is present as the solvent, i.e., the reaction is zero-order in TFE, it must be concluded that TFE cannot be involved in the rate-determining step for C−H activation. Arguments that complex **1b** is somehow unique in this regard are countered by the corresponding experiments with complex **4b**, which displays identical behavior. One concludes that TFE is nothing more than an inert diluent.

Both the gas-phase and solution-phase experiments compel the existence of at least one additional intermediate immediately prior to the rate-determining step in the C−H activation reactions of either benzene or methane. While the experiment makes no suggestion as to the structure, one may speculate with the proviso that any such structural speculation needs to be validated by further experiment or by computation. Among the candidates for the intermediate in the case of methane activation is the η^2-(H,H) σ-complex, found by computations[5,30] to be another possible binding mode for methane complexes[31] in addition to the more ordinary-looking η^2-(H,C) methane σ-complex. Another possibility for either methane or benzene activation would be a four-coordinate structure in which the fourth site on the cationic Pt(II) center is occupied by the *ortho* substituent on the aryl group of the Schiff base. Coordination of methane or benzene to form a five-coordinate intermediate would then be followed by rate-determining departure of the *ortho* substituent. Variation of substitution on this position can potentially serve as a handle for tuning of reactivity in a rational way. This attractive possibility must wait, though, until the structural speculations are confirmed by further work.

Conclusions

Gas-phase ion−molecule reactions of $[(\mathrm{N{-}N})\mathrm{Pt}(\mathrm{CH_3})(\mathrm{L})]^+$ with benzene show a remarkable similarity to the corresponding solution-phase reactions. We accordingly take advantage of electrospray ionization tandem mass spectrometry to isolate postulated intermediates and investigate the mechanism of C−H activation in the reaction of $[(\mathrm{N{-}N})\mathrm{Pt}(\mathrm{CH_3})(\mathrm{L})]^+$ with benzene. We rule out a rate-determining transition state in which TFE

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[28] From PM3 calculations on optimized geometries, one finds for trifluoroethanol and 1,1,1,2-tetrafluoroethane dipole moments of 2.2 and 2.3 D, respectively.

[29] It should be noted that DFT calculations on model complexes in ref 5 find no evidence that TFE coordinates *to the metal center* in four-coordinate Pt(II) complexes as a fifth ligand.

[30] Hill, G. S.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 1478.

[31] Transition metal alkane complexes have been reviewed: Hall, C.; Perutz, R. *Chem. Rev.* **1996**, *96*, 3125.

solvent is coordinated at the metal and then confirm the result by solution-phase kinetic studies. Given the prior report that benzene activation in TFE solvent by these complexes constitutes the most facile C−H activation reactions yet reported for cationic Pt(II) complexes, it is perhaps disappointing to find that TFE gives no acceleration at all. On the other hand, it should be encouraging to find that C−H activation may be achieved in ordinary solvents in seconds at room temperature as long as the solvent is not strongly coordinating. We plan further studies to clarify the structural basis for this high reactivity.

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Supporting Information Available: Synthesis, characterization, and spectroscopic data for new compounds, experimental details for mass spectrometry, UV/Vis spectroscopy, and X-ray crystallography are available free of charge via the Internet at http://pubs.acs.org.

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