Organometallics **2006,** *25,* 809−811

Response to: "C−H Activation by Platinum(II): What Do Gas-Phase Studies Tell Us about the Solution-Phase Mechanism?"

Sir: Because the Correspondence by Labinger et al.[1] directly questions conclusions in our 2003 paper[2] in *Organometallics*, the Editor has solicited a response. There are, at least as far as we can ascertain from the Correspondence, two issues in dispute. (i) Is 2,2,2-trifluoroethanol (TFE) involved in the rate-determining transition state for the overall C−H activation of benzene by Pt(II) complexes [**1**·L] in either the solution or the gas phase? (ii) Do the experiments in our 2003 paper provide any indication of the answer to the first question? Our principal answer is that interested readers should turn to the published literature from the two groups and evaluate the data as presented. Nevertheless, there are two important points that we want to emphasize.

The C−H activation reaction of [1·L] in solution is kinetically zero-order in TFE. First, there are points of agreement that are not in dispute by either side. In most of the cases investigated, and in particular, for the types of complex involved in the present Correspondence, the rate-determining step for the forward-direction C−H activation reaction (Scheme 1) is ligand exchange of benzene for solvent (TFE in Scheme 1).[3]

Both we and Labinger et al. interpret the extensive isotope scrambling in activation of C_6D_6 as indicative of rate-limiting ligand exchange with subsequent fast reversible C−H(D) activation. The resting state is the aquo complex, according to published calculations in addition to some further unpublished DFT calculations done for an upcoming paper, with water bound strongly (measured to be 1.23 eV, or 28 kcal/mol).[4] In support, one sees by ^1H NMR that, even with large molar excesses of benzene, the observed product of the [**1**·H_2O] + benzene reaction in solution is [**2**·H_2O] and not [**2**·benzene]. Also, if [**1**·C_6H_6] were to be the resting state, then it is highly unlikely that the nearly statistical isotopic scrambling would be seen in the activation of C_6D_6. With the aquo complex as the resting state, the rate law must be inverse first order in water if water is not present in the rate-limiting transition state. Moreover, the diagnostic of the involvement of TFE in the rate-limiting transition state would be the kinetic order of the reaction with respect to TFE. Incidentally, transition states for ligand exchange in which TFE is depicted as bound, implied in Labinger's "solvent-assisted" language, are shown explicitly in Figures 4 and 5 of a later publication,[5] even though computational studies by the same authors found no such structure.[6]

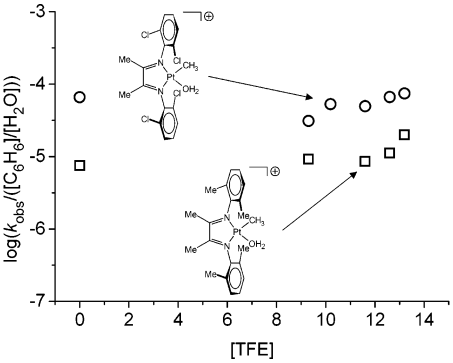
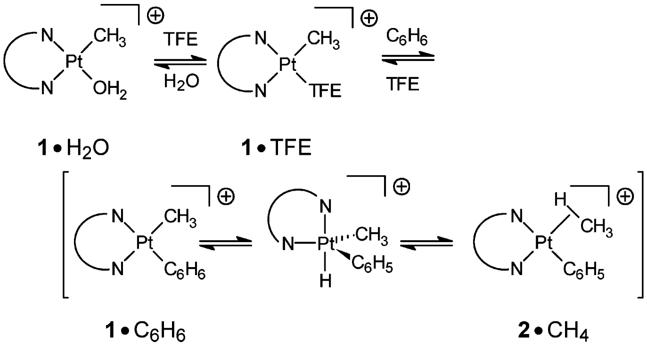


Figure 1. Replotted kinetic data for two Pt(II) complexes in which the observed rate of C−H activation of benzene is confirmed to be zero order in the concentration of TFE.

Scheme 1



The most direct experimental test of the involvement of TFE in the rate-determining transition state is accordingly a measurement of the kinetic order of the C−H activation in Scheme 1. We performed just this experiment.[2] Labinger et al. have not performed any such experiment, so ours are the only experimental data. Replotting the already published data from the 2003 paper produces Figure 1. The observed rate for the solution-phase C−H activation of benzene, divided by the mole ratio of benzene to water, is plotted as a function of [TFE], in ordinary molarity units, for Pt(II) complexes with two different substituents on the ligands. The TFE concentration varies between 0 and 13.2 M. The plots show that the reaction is kinetically zero order in TFE for the two examined complexes.

In the Correspondence, Labinger et al. present no new data at all and simply suggest that the results are coincidence. It is suggested that more low [TFE] points would be needed, which begs the question as to why we have only one low [TFE] point and Labinger et al. none at all. We would welcome more points, too, but there is a reason that there is only one for each complex at low (or zero) [TFE]. TFE is very difficult to dry and even more difficult to keep dry. Because water is kinetically important, any study of rates must control the water concentration. This is done by adding water in a quantity large enough so that the water present in the solvent would be small in comparison. This works in mixed TFE/benzene solution as long as there is a large amount of TFE to keep the solution homogeneous. Mixtures of TFE and benzene with low TFE concentration (or no TFE at all) phase separate when water is added in the necessary quantities. Also, although benzene can be dried, the only point where the concentration of water in benzene is fixed is saturation. We used that point.

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[1] Labinger, J. A.; Bercaw, J. E.; Tilset, M. *Organometallics* **2006**, *25*, 805.

[2] Gerdes, G.; Chen, P. *Organometallics* **2003**, *22*, 2217.

[3] Johansson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 10846.

[4] Hammad, L.; Gerdes, G.; Chen, P. *Organometallics* **2005**, *24*, 1907.

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

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

10.1021/om050785n CCC: $33.50

While Labinger et al. can speculate that we had an odd coincidence, that is no argument against the data. The argument concerning the rate law is covered in the previous paragraph. Both their data and ours indicate that the aquo complex is the resting state, which means our interpretation of the kinetic data is legitimate.

The kinetic order with respect to TFE unambiguously shows that TFE is not involved in the rate-determining transition state for the C−H activation of benzene by [**1**·H_2O] in solution. It cannot therefore provide solvent assistance unless solvent assistance is understood to mean the trivial feature that TFE does not bind more strongly than water. Not only would such a claim be trivial, it is also at odds with the explicit transition-state structures proposed for the putative solvent-assisted ligand exchange.

The gas-phase experiment finds no special role for TFE. In the Correspondence, Labinger et al. have misrepresented the key gas-phase experiment. The important experiment on which we based the conclusion that TFE is not bound at the rate-determining transition state in the gas phase is the attempt to run the microscopic reverse of the reaction in Scheme 1. The ion, assigned to a mixture containing one or more of the species [**1**·C_6H_6], [**2**·CH_4], and the Pt(IV) intermediate connecting the two structures, is subjected to collision-induced dissociation (CID) with several collision gases, among them TFE and the isoelectronic and isostructural analogue 1,1,1,2-tetrafluoroethane. The experiment finds that the threshold curves for the reaction are identical within experimental error for the last two collision partners. If coordination of TFE at the transition state for the microscopic reverse of Scheme 1 were to open a lower energy reaction channel, then one would expect that the two threshold curves to come out differently. We conclude from this experiment that the TFE serves no purpose other than transferring energy to the ion via the collision.

Labinger et al. challenge the conclusion with two assertions in their Correspondence. The first is that the overall reaction in which [**1**·C_6H_6] is dissociated to **1** and benzene does not contain TFE at all and that **1**, without ligand, does not appear in the solution-phase reaction. Second, Labinger et al. asserts that the identity of the two threshold curves could be due to the requirement of an improbable orientation in the ion−molecule collision. Both arguments are wrong. To take the second one first, it has been known for decades that ion−molecule reactions, including CID, proceed by way of long-lived ion−molecule complexes.[7] The complexes are held together by electrostatic forces, charge/dipole or charge/induced dipole, which produce a potential well of 5−10 kcal/mol depth for a generic ion with a generic neutral molecule. For gas-phase bimolecular reactions, this electrostatic well functions analogously to the solvent cage in solution-phase chemistry. Because the interaction is electrostatic and relatively long-ranged, it is not very structure-dependent, meaning that the ion−molecule complexes can explore structure space to find the lowest energy reaction channel. The complexes live long enough to statistically redistribute excess energy, and they allow sampling of all possible geometric orientations, at least for ion−molecule collisions with energies in the range of electronvolts (eV) in the center-of-mass frame. One should note that numerical modeling of the lifetimes for the ion−molecule complexes in our experiments is part of the extraction of energy thresholds for reaction, as we have done in ref 4. For the range of energies in ref 2 where we see reaction, the lifetimes of the ion−molecule complexes formed by collision of the benzene adducts with TFE or tetrafluoroethane range from >50 μs down to approximately 0.1 μs. This is more than enough time to sample configuration space. The orientation argument is simply incorrect, not because our experiments say so, but because ever since Gioumousis and Stevenson confirmed the importance of electrostatic complexes in ion−molecule chemistry almost half a century ago,[8] the model has been verified experimentally and computationally by many groups. Preferred orientation is not a factor in reactions following ion−molecule collisions.

The other gas-phase argument from Labinger et al. is also incorrect. The microscopic reverse of Scheme 1 *does* involve TFE when TFE is the collision gas. The argument is based on the observation of **1** as the final product in the mass spectrometer. Obviously a collision with TFE occurred, or else there would be no CID at all. Moreover, the energy is transferred in a long-lived collision complex, as described above. In the collision complex, there is more than ample opportunity for the TFE to coordinate to Pt if it were to be favorable. If that coordination were to open a lower energy reaction channel, then we would see a lower threshold compared to the case when this new channel did not exist. This is the principle behind the experimental design. The overlapping threshold curves show that the presence of TFE in the collision complex does not open a lower energy exit channel. The mistake by Labinger et al. is that they look at the product, which comes after the (metastable because the total energy exceeds the dissociation limit) collision complex falls apart. The TFE has already departed from the observed product ion, but it is the collision complex that contained all of the components needed for a hypothetical solvent-assisted associative ligand exchange; thus, the CID experiment does provide a direct diagnostic for the proposed solvent-assisted mechanism. The rest of the gas-phase experiments were preparatory and anticipatory to the test of the microscopic reverse reaction. This is important to recognize, because we claim the result on the basis of the reverse, not the forward, reactions.

We should mention that the computations accompanying the gas-phase studies do not indicate that three-coordinate Pt(II) species are important, either in solution or in the gas phase. In our work on the ligand binding energies of Pt(II) complexes,[4] DFT calculations found that unimolecular loss of CH_3CN, H_2O, or TFE from the four-coordinate complexes [**1**·L] produced a four-coordinate product in which what would have been the empty coordination site is filled by whatever group was at the ortho position of the aryl substituents. Similar structures have been observed in other Pt(II) complexes by X-ray crystallography.[9] If such structures were to appear on the reaction coordinate for ligand exchange, then the formally dissociative pathway would actually proceed by a mechanism fully analogous to the ordinary associative ligand exchange in d^8 square-planar complexes. While we do not have independent evidence

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(7) Bowen, R. D.; Williams, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 2752. Morton, T. H. *Tetrahedron* **1982**, *38*, 3195. Bowen, R. D. *Acc. Chem. Res.* **1991**, *24*, 364.

(8) Gioumousis, G.; Stevenson, D. P. *J. Chem. Phys.* **1958**, *29*, 294.

(9) Baratta, W.; Stoccoro, S.; Doppiu, A.; Herdtweck, E.; Zucca, A.; Rigo, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 105. Carr, N.; Dunne, B. J.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1988**, 926. Mole, L.; Spencer, J. L.; Carr, N.; Orpen, A. G. *Organometallics* **1991**, *10*, 49. Carr, N.; Mole, L.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Dalton Trans.* **1992**, 2653. Goel, R. G.; Srivastava, R. C. *J. Organomet. Chem.* **1981**, *204*, C13. Scherer, O. J.; Jungmann, H. *J. Organomet. Chem.* **1982**, *228*, C61. Goel, R. M.; Srivastava, R. C. *Can. J. Chem.* **1983**, *61*, 1352.

that this is the intermediate we suggest for the ligand exchange in solution, it is a plausible candidate.

In summary, if we return to the exchange of comments that is the subject of this text, we would emphasize again that the important data from both sides are published. The community is best served if interested parties simply read the papers and see for themselves what they say.

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