J|A|C|S
COMMUNICATIONS

Carboxylic Solvents and O-Donor Ligand Effects on CH Activation by Pt(II)

Vadim R. Ziatdinov,[†] Jonas Oxgaard,[‡] Oleg A. Mironov,[†] Kenneth J. H. Young,[†]
William A. Goddard III,*[,‡] and Roy A. Periana*[,†]

*Department of Chemistry, Loker Hydrocarbon Research Institute, University of Southern California,
Los Angeles, California 90089, and Department of Chemistry, Beckman Institute, California Institute of Technology,
Pasadena, California 91125*

Received February 9, 2006; E-mail: wag@wag.caltech.edu

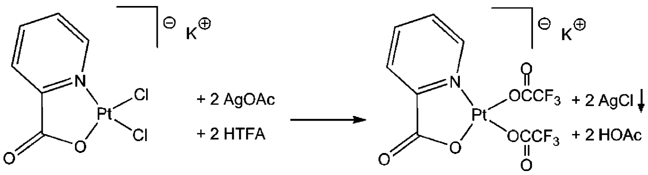
Organometallic coordination catalysts based on the C−H activation reaction currently show the greatest potential for the development of new, selective, hydrocarbon hydroxylation chemistry.[1] Previously, we reported on a platinum catalyst, $Pt(bpym)Cl_2$ (bpym $= \eta^2$-{2,2′-bipyrimidyl}), that converts methane to methanol in concentrated sulfuric acid with a 70% one-pass yield.[2g] The practicality of this system is limited as the average catalyst rate, TOF $\sim 10^{-3}\ s^{-1}$, is below the commercially viable target of $\sim 1\ s^{-1}$. This is due to severe inhibition of the CH activation step (which is the rate-determining step for oxidation in the presence of 1 M water or methanol) by the reaction products, resulting in a maximum methanol concentration to ~1 M rather than the ~5 M required for efficient separation.

On the basis of our understanding of the mechanism of the $Pt(bpym)Cl_2/H_2SO_4$ system,[1h,2] we identified two key steps that contribute to the overall CH activation barrier of ~32 kcal/mol: (A) ~27 kcal/mol for coordination of the hydrocarbon (RH) and (B) ~5 kcal/mol for cleavage of the coordinated CH bond. In designing improved catalysts, it is important that both steps be explicitly considered to ensure that catalyst modifications that decrease the energy requirements for one step *do not* proportionately increase the other. This should be possible since the bonding in the ground state and cleavage transition state should be different.[1h] We now report that using an interplay between computational and experimental methods an efficient system has been designed which catalyzes H/D exchange magnitudes faster than the $Pt(bpym)Cl_2$ system. This improvement results from a reduction in the energetics for coordination *without* a corresponding increase in the energetics for cleavage.

We postulated that replacing the neutral bipyrimidine in $Pt(bpym)(X)_2$ with a monoanionic ligand, such as η^2-N,O-picolinate (pic), would yield a complex which would have reduced energetics for RH coordination due to the increased electron density at the metal center. Furthermore, calculations predicted that use of bidentate TFA ligands in lieu of Cl ligands could facilitate CH cleavage via a six-membered cyclic transition state that is *not* proportionately higher in energy relative to that for the $Pt(bpym)(X)_2$ system, resulting in a predicted lower overall barrier for CH activation for the $K[Pt(pic)(TFA)_2]$ system. Similar six-membered, cyclic transition states have previously been postulated by Ryabov[3] and in a recent computational study for cyclometalation of dimethylbenzylamine.[4]

All calculations utilized the Jaguar 6.5 suite, using B3LYP/LACVP**++ with ZPE and solvent corrections for the TFA medium (Poisson−Boltzmann continuum solvent, with $\epsilon = 8.42$ and radius probe $= 2.479$).[5,6] Diffuse functions were not used for solvents. Furthermore, due to inaccuracies of free energy calculations in solvents, no ΔG results have been included.

Scheme 1



The picolinate ligand was chosen because it is a commercially available monoanionic, chelating N- and O-donor ligand that is stable to protic, thermal, and oxidizing conditions. We have recently shown that O-donor ligands can facilitate the C−H activation reaction as well as selective functionalization of the M−R intermediate,[7] and computational screening indicated that C/H activation should be facile using this ligand.

Solutions of **1** were prepared by treatment of the known $K[Pt(pic)Cl_2]$ with silver acetate in TFA (Scheme 1) and has been characterized by ^1H and ^{13}C NMR, as well as high-resolution electrospray ionization mass spectrometry. Due to the anionic character of **1**, we were unable to isolate it as a pure material without contamination from AgOAc, either by recrystallization or extraction. However, the neutral derivative, $Pt(pic)(Me)(Et_2S)$, has been prepared and fully characterized by ^1H and ^{13}C NMR as well as elemental analysis. Furthermore, in situ NMR confirms that all acetate is present as free HOAc in the TFA solution.

In situ NMR studies of **1** in TFA also showed that **1** was thermally stable in CF_3CO_2H at 70 °C for several days in air. At 100 °C, a slow reaction occurs to quantitatively generate $Pt(pic)_2$ and a black precipitate (believed to be Pt black), with a $t_{1/2}$ of ~10 days. As reactions with methane were found to require temperatures above 100 °C, the CH activation studies were conducted with benzene where reaction could be readily observed at 70 °C. Upon heating a mixture of benzene (0.1 mL) and CF_3CO_2D (1 mL) containing 4 mM of **1** to 70 °C, catalytic incorporation of deuterium into benzene was observed. Analysis by GC/MS shows 43 turnovers after 1 h (TOF of $\sim 1.2 \times 10^{-2}\ s^{-1}$). On the basis of the temperature dependence, a $\Delta G^{\ddagger}$ of ~23 kcal/mol was estimated. Control experiments without catalyst did not lead to any observable H/D exchange (<0.5%) under the same reaction conditions. To compare the catalytic activity of **1** to the Pt(bpym) system, $Pt(bpym)TFA_2$ was prepared and characterized by elemental analysis, high-resolution mass spectroscopy, and ^1H and ^{13}C NMR. H/D exchange with $Pt(bpym)TFA_2$ shows that this complex is 300 times *less* active (TON of 4.6 after 20 h, TOF $\sim 6.4 \times 10^{-5}\ s^{-1}$) than **1** under similar conditions. Unfortunately, direct comparison with $(bpym)PtCl_2$ is not possible as it is not soluble in TFA.

Our theoretical calculations of CH activation with these systems (Figure 1) are consistent with the experimental results. According

---

[†] University of Southern California.
[‡] California Institute of Technology.

10.1021/ja060973k CCC: $33.50 © 2006 American Chemical Society

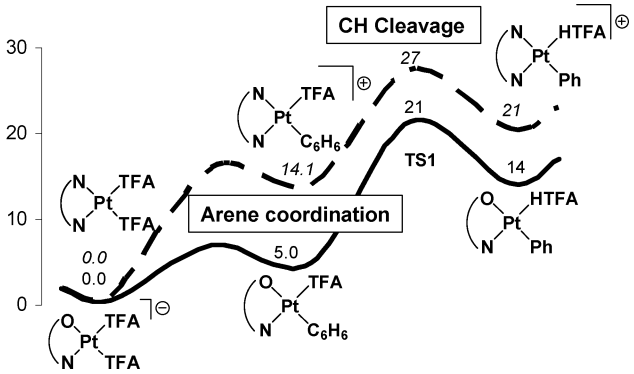


Figure 1. Thermodynamics of the calculated mechanism for the benzene C−H activation: Pt(pic), solid line; Pt(bpym), dashed line.

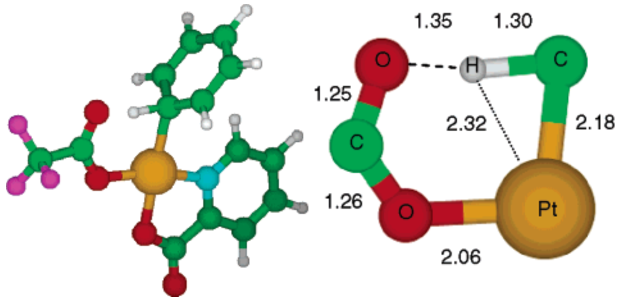


Figure 2. C−H cleavage transition state TS1. Bond lengths in angstroms.

to our calculations, **1** activates benzene C−H bonds with a $\Delta H^{\ddagger} \sim$ 21 kcal/mol, which is significantly lower than the $\sim$27 kcal/mol calculated for Pt(bpym)TFA$_2$ but comparable to the experimental activation barrier of $\sim$23 kcal/mol obtained for **1**.

As can be seen in Figure 1, the calculated resting state of the Pt(bpym) system is a bis-TFA$^-$ complex with an overall neutral charge, Pt(bpym)TFA$_2$. Loss of TFA$^-$ generates a cationic species that coordinates benzene with ΔH of $\sim$14 kcal/mol. The $\Delta H^{\ddagger}$ for the subsequent CH cleavage step, leading to the phenyl complex, is $\sim$13 kcal/mol. The calculations also show that the resting state of the picolinate system is a bis-TFA complex, but in this case, this species is anionic, Pt(pic)TFA$_2^-$. Here, consistent with our original expectation that increasing the electron density at Pt could facilitate substrate binding, the ΔH for loss of a TFA$^-$ and coordination of benzene is considerably less than that for the neutral Pt(bpym)(TFA)$_2$ complex at $\sim$5.0 kcal/mol: a factor of almost 3 times lower! Furthermore, the $\Delta H^{\ddagger}$ for CH cleavage shows only a slight increase to $\sim$16 kcal/mol, leading to an overall decrease in the rate of CH activation for the picolinate complex. Ligand exchange between Pt−HTFA and solvent DTFA is expected to be facile, as the three-coordinate phenyl species is only uphill by 18.2 kcal/mol (not shown). While a five-coordinate ligand exchange, associative transition state cannot be ruled out, the 18.2 kcal/mol can be considered an upper bound.

The C−H cleavage occurs through a six-membered transition state, **TS1** (Figure 2), where the covalent Pt−O and C−H bonds are broken while the Pt−C and O−H bonds are created. Both C−O bonds are 3/2 bond order, with the π-bond transforming into a σ-bond. The reaction is best described as an electrophilic substitution proceeding via addition of the Pt center to the arene ring (as opposed to a σ-bond metathesis involving only the σ-framework). Similar transition states have been implicated in other theoretical works,[4,8] but this is, to the best of our knowledge, the first time this kind of solvent participation has been included by design for CH activation.

It is not clear why the $\Delta H^{\ddagger}$ values for CH cleavage for the Pt(pic) and the Pt(bpym) systems are similar given the dramatic differences in the ΔH for benzene coordination (Figure 1). We are carrying out further studies to understand the fundamental basis for these differences in order to design CH activation-based oxidation catalysts that have low barriers for both coordination and CH cleavage in coordinating media, such as water.

In summary, we have demonstrated that a strong interaction between experimental and theoretical research can lead to deeper understanding as well as fast practical progress. A novel, facile transition state for C−H cleavage has been identified. Enhanced C−H activation reactivity was predicted conceptually for the class of compounds, supported theoretically and shown experimentally for a picolinate platinum system. Specifically, we demonstrated a well-defined, late metal, N,O-ligated complex, which is competent for arene C−H activation, exhibits thermal and protic stability, and is an efficient catalyst for H/D exchange.

Acknowledgment. We thank Dr. W. L. Schinski and Dr. A Kuperman for helpful discussion. We thank the National Science Foundation (CHE-0328121) and Chevron Energy Research & Technology Company for financial support for this research.

Supporting Information Available: Synthetic procedure and spectroscopic details are reported. Computational details, including coordinates, are also included. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560−564. (b) Shilov, A. E.; Shul'pin, G. B. *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*; Kluwer Academic: Dordrecht, The Netherlands, 2000; p 560. (c) Jia, C. G.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633 and references therein. (d) Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2001**, *19*, 2437. (e) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. (f) Jones, W. D. *Acc. Chem. Res.* **2003**, *36*, 140. (g) Periana, R. A.; Mironov, O.; Taube, D.; Bhalla, G.; Jones, C. J. *Science* **2003**, *301*, 814. (h) Conley, B. L.; Tenn, W. J., III; Young, K. J. H.; Ganesh, S. K.; Meier, S. K.; Ziatdinov, V. R.; Mirinov, O.; Oxgaard, J.; Gonzales, J.; Goddard, W. A., III; Periana, R. A. *J. Mol. Catal. A* **2006**, in press.

(2) (a) Xu, X.; Kua, J.; Periana, R. A.; Goddard, W. A., III. *Organometallics* **2003**, *22*, 2057. (b) Kua, J.; Xu, X.; Periana, R. A.; Goddard, W. A., III. *Organometallics* **2002**, *21*, 511.

(3) Ryabov, A. D.; Sakodinskaya, I. K.; Yatsimirsky, A. K. *J. Chem. Soc., Dalton Trans.* **1985**, 2629.

(4) Davies, D. L.; Donald, S. M. A.; Macgregor, S. A. *J. Am. Chem. Soc.* **2005**, *127*, 13754.

(5) There is a discrepancy in the literature regarding the dielectric of TFA, where it is alternatively reported as 8.42 (Dannhauser, W.; Cole, R. H. *J. Am. Chem. Soc.* **1952**, *74*, 6105; Harris, F. E.; O'Konski, C. T. *J. Am. Chem. Soc.* **1954**, *76*, 4317) and 39.0 (Simons, J. H.; Lorentzen, K. E. *J. Am. Chem. Soc.* **1950**, *72*, 1426). As there exists a possibility that the higher dielectric could be a better measure of the polarizability of the TFA, we performed control calculations of bpymPt at both dielectrics. However, the high dielectric yielded unrealistic barriers and were thus discarded.

(6) *Jaguar*, version 6.5; Schrodinger, LLC: New York, 2005. For further details, see Supporting Information.

(7) Bhalla, G.; Liu, X. Y.; Oxgaard, J.; Goddard, W. A.; Periana, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 11372.

(8) Kragten, D. D.; van Santen, R. A.; Neurock, M.; Lerou, J. J. *J. Phys. Chem. A* **1999**, *103*, 2756.

JA060973K