3770 *Organometallics* **2008,** *27,* 3770–3773

The Mechanism by Which Ionic Liquids Enable Shilov-Type CH Activation in an Oxidizing Medium

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Received March 27, 2008

Quantum mechanical studies on methane CH activation catalyzed by $PtCl_2$ in concentrated H_2SO_4 and ionic liquid solution show that the effect of the ionic liquid is to enable Shilov-like chemistry in an oxidizing medium, by solvating the otherwise insoluble $PtCl_2(s)$ in H_2SO_4. Other possible mechanisms have been investigated and discarded.

Introduction

The world's resources in methane are grossly underutilized, mainly due to a lack of efficient low-temperature catalytic processes to convert the methane to transportable liquid forms. The problem is finding a system that can catalyze *both* activation of the CH bond of methane to form a MC bond and the functionalization of MC (i.e., formation of a CX bond). Considerable progress has been made, particularly with the reports of the Shilov[1,2] and the Periana-Catalytica (PC)[3,4] systems, but various problems prevent commercialization.

The Shilov system utilizes an aqueous solution of square-planar Pt(II) complexes $\{[PtCl_{4-n}(H_2O)_n]^{n-2}, n = 0 \text{ to } 2\}$ as the catalytic center for CH activation and uses $PtCl_6^{2-}$ as the stoichiometric oxidant to convert the MC intermediate to methanol and/or chloromethane. The catalytic rate of the Shilov system is very good, but it has two chief drawbacks: (i) the use of an expensive stoichiometric oxidant and (ii) catalyst instability through disproportionation of the Pt^{II} complex to Pt^0 and Pt^{IV}. Consequently, although Sen et al.[5] reported an aerobic variant of the Shilov system to bypass the stoichiometric oxidant issue, the system still appears to be unviable due to this instability.

The PC system uses (bpym)Pt(II)Cl_2 (bpym = η^2-{2,2′-bispyrimidyl}) to convert methane to methyl bisulfate in fuming H_2SO_4, where H_2SO_4 serves also as the oxidant.[3] The PC system displays the highest efficiency and selectivity reported to date, and it is thermally stable under the reaction conditions. However, unlike the Shilov system, the PC catalyst is deactivated by water and the methanol product.[4] Consequently, the PC system does not operate in acid concentration lower than 96% H_2SO_4, severely limiting its commercial utility.

Recently, Cheng et al.[6] reported the effective conversion of methane to methanol using a ternary system containing inorganic Pt salts, concentrated sulfuric acid, and organic ionic liquids (IL) (reaction 1). The activity of this IL system is 50% lower than the PC system in 102% H_2SO_4 [2% oleum], but it is much more tolerant to water than the PC system (~300% higher activity in 96% H_2SO_4 [4% H_2O]).

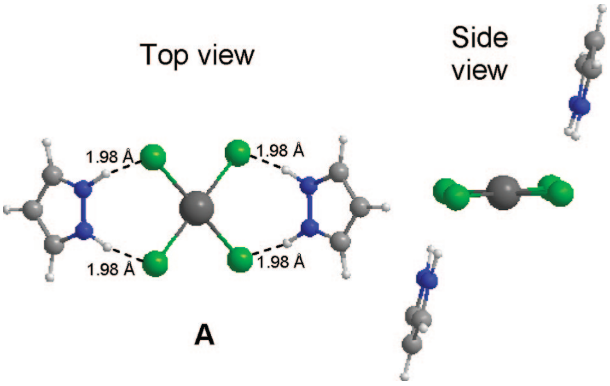

Figure 1. Predicted structure of the neutral complex $[PtCl_4^{2-}][HPzm]_2$ (**A**) The four Pt−Cl bonds are 2.39 Å, and the NH−Cl hydrogen bonds (HB) are 1.98 Å.

$$CH_4 + SO_3 + H_2SO_4 \xrightarrow[\substack{H_2SO_4\ (96\ \%)\\ 220\ ^\circ C}]{\substack{PtCl_2(s)\\ \text{ionic liquid (6 equiv)}}} CH_3OSO_3H + SO_2 + H_2O \quad (1)$$

The amount of IL in this system is low (6 equiv with respect to Pt), and it is not clear what role the IL plays in enabling this chemistry.[6] This prompted us to explore the mechanism for this transformation, and we here report QM studies on the CH activation mechanism carried out by $PtCl_4^{2-}$ in H_2SO_4 with pyrazolium (Pzm)-based IL additives.

We considered the neutral complex $[PtCl_4^{2-}][HPzm]_2$ (structure **A**, Figure 1) as the likely active catalytic species. Including solvation, we calculate that $1/6(PtCl_2)_6 + 2[HPzm][Cl] \rightarrow$ **A** has $\Delta E = -68.3$ kcal/mol, suggesting that the IL would dissolve solid $PtCl_2$ in concentrated H_2SO_4, as experimentally observed. In contrast, we calculate that $1/6(PtCl_2)_6 \rightarrow PtCl_2$ has $\Delta E = +29.4$ kcal/mol *uphill* in water, consistent with the experimental observation that that, without IL, $PtCl_2(s)$ is not soluble in H_2SO_4.[6]

We also calculated the energies required to replace one of the Cl ligands in $[PtCl_4^{2-}][HPzm]_2$ with either HSO_4^- (uphill

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(1) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879.

(2) Lersch, M.; Tilset, M. *Chem. Rev.* **2005**, *105*, 2471.

(3) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560.

(4) Conley, B. L.; Tenn, W. J.; Young, K. J. H.; Ganesh, S. K.; Meier, S. K.; Ziatdinov, V. R.; Mironov, O.; Oxgaard, J.; Gonzales, J.; Goddard, W. A.; Periana, R. A. *J. Mol. Catal. A: Chem.* **2006**, *251*, 8.

(5) Lin, M.; Shen, C.; Garcia-Zayas, E. A.; Sen, A. *J. Am. Chem. Soc.* **2001**, *123*, 1000.

(6) Cheng, J. H.; Li, Z. W.; Haught, M.; Tang, Y. C. *Chem. Commun.* **2006**, 4617.

(7) Siegbahn, P. E. M.; Crabtree, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 4442.

10.1021/om800274f CCC: $40.75

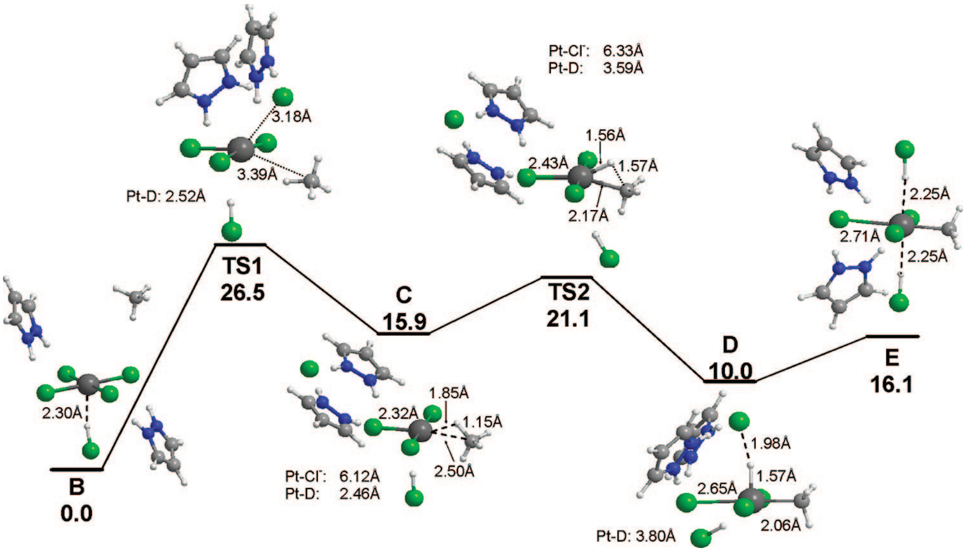

Figure 2. Energy profile and related structures for C−H activation of methane catalyzed by $PtCl_4^{2-}$ in ionic liquid solution. All energies are solvated ΔE (kcal/mol).

by 3.5 kcal/mol) or H_2O (uphill by 3.2 kcal/mol). This higher energy of the $PtCl_3(H_2O)^-$ complex is consistent with previous theoretical results for the $PtCl_4^{2-}$ system under Shilov conditions,[8] but differs from the results on the PC system, where the $Pt(bpym)Cl(H_2O)^+$ complex is more stable than the $Pt(bpym)Cl_2$ complex.[9] This may explain why the $PtCl_2/IL/H_2SO_4$ system is more resistant to water poisoning than the PC system.

Figure 2 shows the energetics we predict for methane activation by $[PtCl_4^{2-}][HPzm]_2$. We included all reacting species throughout the reaction, allowing the two $HPzm^+$ and their Cl^- anions to freely coordinate. To start the reaction we added an explicit methane to **A**, leading to complex **B**, with the CH_4 weakly coordinating to the $PtCl_4[HPzm]_2$ complex (closest Pt−CH_4 distance = 4.1 Å).

Furthermore, since the experiments see rapid H/D exchange, we included an explicit DCl in our calculation, in order to determine the barrier for exchanging a D for the methane H. [Since the experiment is done in concentrated D_2SO_4, the D is likely provided by D_2SO_4 rather than DCl, but we expect the two sources to have similar chemistry.] We found that the explicit DCl coordinates to the Pt^{II} center with a binding energy of 5.3 kcal/mol, significantly greater than expected from a van der Waals complex. Indeed, the D−Pt distance in **B** is only 2.30 Å, indicating that the electropositive D forms a hydrogen bond to the filled Pt d_{z^2} orbital. Consequently, we included an explicit DCl in all complexes, since the implicit solvation model might not account fully for the effect of the highly acidic solvent.

From **B**, the first chemical step is migration of the CH_4 to the first solvation shell of the Pt complex. This leads to **C**, where the displaced Cl remains coordinated to the ILs. **C** is a σ-complex with agostic interactions between Pt and CH_4, as indicated by the elongated (1.15 Å) C−H bond (cf. the normal C−H bond of 1.09 Å in CH_4) and a weak Pt−H interaction (Pt−H = 1.85 Å compared to the value Pt−H = 1.56 Å in a metal hydride).

The transition state for **B** → **C** is **TS1**, with a barrier of ΔE_{solv} = 26.5 kcal/mol). **TS1** is an associative transition state, with two long bonds: Pt−Cl (3.18 Å) and Pt−CH_4 (3.39 Å) (cf. normal PtCl bond distance of 2.17 Å), suggesting that Cl^- leaves as CH_4 approaches. Of interest here is how the two $HPzm^+$ rearrange during the CH_4 association process. They start symmetrically distributed, with each $HPzm^+$ coordinating to a different pair of Cl's. In **TS1**, the $HPzm^+$'s each coordinate to one cis Pt−Cl (r_{H-Cl} = 1.95 Å), while both coordinate to the leaving Cl^- (r_{H-Cl} = 1.94 Å). In **C**, both $HPzm^+$ have moved to the side opposite the CH_4, coordinating only to the trans Pt−Cl (r_{H-Cl} = 2.25 Å) and the dissociated Cl (r_{H-Cl} = 1.92 Å). Thus, the stabilizing cations shuttle the Cl^- from the first coordination sphere to the second.

We also tested whether the first step can occur via a stepwise dissociative mechanism, i.e., forming a T-complex according to $[PtCl_4][HPzm]_2 \rightarrow [PtCl_3][HPzm] + [HPzm][Cl]$ prior to methane coordination.[2] However, the reaction energy for this process is 35.4 kcal/mol, ruling out the T-complex pathway. (This should be contrasted to the low-energy T-complex described by Ziegler et al. in their report on aqueous Shilov CH activation.[8] However, Ziegler et al. use an implicit solvation model, which we believe is not suitable to directly describe a vacant site on a metal.)

The second step involves cleaving one of the CH bonds in **C**, to form the Pt−CH_3 and Pt−H bonds in **D**, via **TS2** (see Figure 2). **TS2** looks like a traditional oxidative addition (OA) transition state, where the C−H bond breaks as the new Pt−C and Pt−H bonds form. Interestingly, the D−Pt distance increases to 3.59 Å in **TS2** and 3.80 Å in **D**, because the d_{z^2} orbital is no longer accessible for hydrogen bonding to the DCl.

The formation of both Pt−CH_3 and Pt−H bonds with normal bond lengths, $R_{Pt\text{-}CH3}$ = 2.06 Å and R_{Pt-H} = 1.57 Å, suggests that the C−H cleavage step is an OA. However, there is little change in electronic character on the Pt. The Mulliken charge on the Pt goes from −0.91 e^- in **C** to −0.93 e^- in **TS2** to −0.70 e^- in **D**, while the population of the 5d orbitals changes from 8.96 e^- to 8.82 e^- to 8.74 e^- and the 5s population changes from 1.07 e^- to 1.14 e^- to 1.09 e^-. Thus, we would describe the electronic state on the Pt as s^1d^9 throughout the reaction. This is different from the Low and Goddard results on OA of CH_4 by $Pt(PH_3)_2$, where they found that the Pt changes from a d^{10} electronic configuration to an s^1d^9 configuration with a covalent Pt−H bond (1.50 Å) and a covalent Pt−CH_3 bond (2.06

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(8) Zhu, H. J.; Ziegler, T. *J. Organomet. Chem.* **2006**, *691*, 4486.
(9) Kua, J.; Xu, X.; Periana, R. A.; Goddard, W. A. *Organomet.* **2002**, *21*, 511.

Å).[12] The wave functions for **B**, **C**, and **D** suggest that Pt makes partially covalent bonds to the two Cl out of the H−Pt−CH_3 plane. Thus, the “oxidation addition” might be viewed as a change of two partially ionic covalent PtCl bonds to one Pt−H and one Pt−CH_3 covalent bond.

We could not find a transition state from **C** for an electrophilic substitution (ES). All attempts to do so collapsed to **C** or **D**. However, the product of such an ES mechanism would be the $[PtCl_3(CH_3)][HPzm]_2$ complex, which we calculate to have an energy of 25.1 kcal/mol. Thus, we do not consider the ES transition state to be energetically competitive.

The last step of the mechanism for H/D exchange involves the replacement of the H with the D from DCl, leading to the deuturated intermediate **D′**. (Going further backward through **TS2′** to **C′** would lead to coordinated CH_3D, and proceeding through **TS1′** to **B′** would lead to the exchanged CH_3D product in solution.)

We here found a concerted mechanism in which the DCl trans to the Pt−H bond in **D** coordinates to the Pt, leading to a linear Cl−D−Pt−H−Cl complex, **E** (see Figure 2), with both DCl and HCl equidistant from the Pt ($R_{Pt-H/D} = 2.25$ Å). The energy of this system is 16.1 kcal/mol, and the QM calculation suggests that **E** should be described as a Pt^{II} complex with two solvent protons strongly hydrogen bonding to the d_{z^2} orbital.

We could not find a transition state for the conversion of **D** to **E**; scanning the Pt−H and Pt−D distances in either direction lead to only monotonous increases in energy. However, we did notice that the positions of the $HPzm^+$ in **D** and **E** are quite different. In **D**, both HPzm’s coordinate to the Cl^-, which stabilizes the negative charge. In **E**, the $HPzm^+$’s are symmetrically distributed, with one $HPzm^+$ coordinating to each HCl and DCl. We could not find a transition state for the movement of the $HPzm^+$ from one side of the complex to the other, (i.e., going from **D** to **E** to **D′**), but on the basis of numerous energy scans we conclude that this barrier for **E** to **D** is less than 5 kcal/mol. This would put the transitions state connecting **D** and **E** at <20.9, below **TS2** at 21.1 kcal/mol. Moreover, under the experimental conditions of ~6 equiv of ionic liquid, it is possible that there may be a third $HPzm^+$ available for an associative ligand rearrangement to decrease this barrier.

The barrier from **C′** to **TS1′** to **B′** is 10.6 kcal/mol, whereas the barrier from **C′** to **TS2′** to **D′** to **E′** is 5.3 kcal/mol. Thus, the system may make multiple traversals of **C** to **E** and back to **C** before the **C** to **B** transition would put the methane product back into solution. Since the deuterated solvent can exchange with the HCl in **C′** on each traversal, the subsequent path from **C′** to **TS2′** to **D′** to **E′** and back to **D″** to **TS2″** to **C″** would lead to CH_2D_2. Subsequent cycles would lead to CHD_3 and then CD_4 products, and it is thus expected that any deuturated CH_4 should be multiply deuturated. Exactly this extensive exchange is observed experimentally in the IL[6] and PC[2] systems. This lower barrier for rapid exchange to form highly deuterated methane was also found in previous computations for the PC[9,10] and Shilov systems ($PtCl_4^{2-}$).[8]

An alternative to this concerted exchange mechanism is a stepwise process in which a free Cl^- abstracts the proton in **D** to form the HCl product, leaving $[Pt^{II}(Cl)_3(CH_3)]^{2-}$ coordinated to the two IL ligands. Replacing the HCl with DCl is isoenergetic, and reversing the mechanism would then give **D′**. However, we find that the energy for the process is 25.1 kcal/mol, much higher than for the concerted pathway.

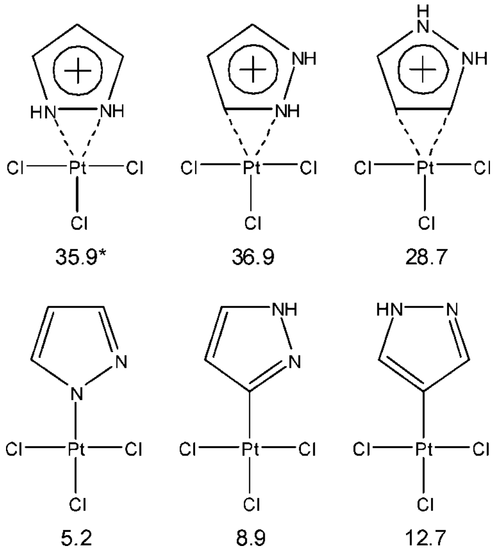

Figure 3. Modes considered for the Pzm to participate in the inner coordination sphere of the catalytic center. Top row omits the spectators $HPzm^+$ and Cl^-. Bottom row omits the spectators $HPzm^+$ and HCl. Total charge of all systems including spectators is 0. All energies are solvated Δ*E* (kcal/mol). *Pzm dissociated from metal.

We also tested the possibility of the $HPzm^+$ participating in the inner coordination sphere of the catalytic center. We found that coordinating an $HPzm^+$ in an η^2 fashion after a Cl^- ligand exchange is prohibitively uphill, with a lowest energy intermediate at $\Delta E_{solv} = 28.0$ kcal/mol. (Minimization of the N,N coordination isomer led to complete ligand dissociation, most likely due to a lack of back-bonding.) However, coordination of $HPzm^+$ followed by H abstraction by Cl^- to generate σ-bonded Pzm ligands (see Figure 3) led to more feasible ΔE_{solv}: 5.2, 8.9, and 12.7 kcal/mol for the three possible coordination modes. However, we found that the energy of the subsequent CH activation step is prohibitively large, with the lowest energy intermediate $\{[(Pzm)PtCl_2CH_3H][HPzm]$, analogous to **D**$\}$ having a $\Delta E_{solv} = 27.2$ kcal/mol. Since this intermediate is higher in energy than the maximum barrier for the $[PtCl_4][HPzm]_2$-catalyzed reaction, we did not explore further mechanisms involving Pzm’s in the inner coordination sphere. However, it is possible that intermediates such as those featured in Figure 3 play a role in the first step of oxidizing the ring of these ionic liquids, responsible for the long-term deactivation observed for many of these IL systems.

The IL system described here differs from the PC system in several ways: First, the overall barrier (26.5 kcal/mol) is considerably lower. Similar calculations for PC lead to 39.2 kcal for the initial catalyst, $Pt(bpym)Cl_2$, and 33.1 for the active catalyst, $Pt(bpym)Cl(HSO_4)$.[9] Second, the CH activation step, **TS2**, proceeds via an OA-like mechanism rather than ES. This barrier of 21.1 kcal/mol is considerably lower than the barrier of 32.4 kcal/mol for PC $[Pt(bpym)Cl(HSO_4)]$. Third, the PC system is poisoned by water through a ground-state inhibition,[3] which is not the case here.

In contrast, our mechanism for CH activation is very similar to mechanisms assumed for the $PtCl_4^{2-}$ Shilov system.[8] Indeed, for the sequence **B** → **D** our calculated reaction energetics are all within 4 kcal/mol of the analogous Shilov steps calculated by Ziegler et al.[8] (ref 8 did not investigate past **D**). Indeed, the

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(10) Paul, A.; Musgrave, C. B. *Organomet.* **2007**, *26*, 793.

(11) Gilbert, T. M.; Hristov, I.; Ziegler, T. *Organometallics* **2001**, *20*, 1183.

(12) Low, J. J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1984**, *106*, 6928.

remaining differences may be due to differences in computational methodology.

We do find two significant differences from the reported Shilov chemistry,[8] however: (1) We observe a strong interaction between the dissociated Cl^- and the hydride in **D** (R_{H-Cl} = 2.07 Å), which enables the facile H/D exchange mechanism in **E**. (Calculations looking for this in the aqueous Shilov system have not been reported.) (2) We observe a surprisingly strong coordination of acidic H to the Pt^{II} d_{z^2} orbital, which disappears in the C−H cleavage transition state **TS2** and returns in **E**. Our preliminary calculations on $PtCl_4^{2-}$(aq) indicate a similar interaction, suggesting that this behavior might occur more generally for Pt^{II} centers in highly acidic media. It is thus not clear whether these observations are unique to the IL system or simply not explored for the Shilov system.

We have not yet considered the issues of oxidation and functionalization, although, most likely, this mechanism will be similar to that for the PC system (as no other oxidant is present). The exact mechanism has not been determined for either the PC or the Shilov systems, and investigations of this are forthcoming. A likely starting point for the IL system is **D**, where we will consider how the oxidant displaces one of the solvent molecules to oxidize the $Pt^{II}-CH_3$ to $Pt^{IV}-CH_3$, followed by functionalization.

Summary

We used QM calculations to derive the mechanism for $PtCl_2$/IL-catalyzed activation of methane in an acidic, oxidizing medium (H_2SO_4). These results suggest that the role of the IL is to enable solvation of the $PtCl_2$ catalyst, through the formation of a $[PtCl_4][HPzm]_2$ tight ion pair and to continue this stabilization as the CH_4 migrates associatively into the first solvation shell and is activated to form the MC bond.

Thus, throughout the reaction, the IL functions much like the highly charge-stabilizing water solvent in the traditional Shilov system. Consequently, it appears that the function of the IL is to migrate the Shilov C−H activation process from water into the oxidizing media characteristic of the Periana-Catalytica system. This ionic liquid system provides an exciting new alternative to the field of C−H *functionalization*, and it may prove useful for enabling coupling of other previously incompatible chemistries.

Computational Details

All QM calculations used the B3LYP type of hybrid density functional theory (DFT) [the Becke three-parameter functional[13] (B3) with the correlation functional of Lee, Yang, and Parr[14] (LYP)] as implemented in the Jaguar 6.5 program package.[15] B3LYP is known to produce good descriptions of reaction profiles for transition metal containing compounds.[16,17] We used the lacv3p**++ basis sets for all calculations.

All geometries were optimized in the gas phase. Transition states and intermediates were verified by calculating the analytic Hessian to validate a single negative eigenvalue or all positive eigenvalues, respectively. Transition states were also evaluated using IRC calculations. Solvent effects were evaluated using the Poisson−Boltzmann (PBF) continuum approximation (with $\varepsilon = 99.0$ and $R_{solv} = 2.205$ Å for sulfuric acid) as implemented in Jaguar v6.5.[18,19] The solvation energies were calculated at the B3LYP/lacv3p** level using the geometries from the gas-phase optimizations.

Acknowledgment. We thank Dr. Yongchun Tang and J. H. Cheng for helpful discussions. This research was supported by the DOE (DE-PS36-03GO93015, William Prymak). In addition, the computational resources were provided by ARO-DURIP and ONR-DURIP.

Supporting Information Available: Energies, solvation energies, *xyz* coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(14) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(15) *Jaguar, v.6.5*; Schrodinger, LLC: New York, NY, 2005.

(16) Baker, J. M.; Andzelm, M. J.; Scheiner, A. *ACS Symposium Series 629*; Laird, B. B., Ross, R. B., Ziegler, T., Eds.; American Chemical Society: Washington, DC, 1996.

(17) Niu, S. Q.; Hall, M. B. *Chem. Rev.* **2000**, *100*, 353.

(18) Marten, B.; Kim, K.; Cortis, C.; Friesner, R. A.; Murphy, R. B.; Ringnalda, M. N.; Sitkoff, D.; Honig, B. *J. Phys. Chem.* **1996**, *100*, 11775.

(19) Tannor, D. J.; Marten, B.; Murphy, R.; Friesner, R. A.; Sitkoff, D.; Nicholls, A.; Ringnalda, M.; Goddard, W. A.; Honig, B. *J. Am. Chem. Soc.* **1994**, *116*, 11875.