# Theoretical Elucidation of the Platinum-Mediated Arene C−H Activation Reactions

Ji-Lai Li,† Cai-Yun Geng,† Xu-Ri Huang,*,† Xiang Zhang,‡ and Chia-Chung Sun†

*State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, People's Republic of China, and State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China*

*Received January 14, 2007*

The complete reaction mechanism of the platinum-mediated arene [(N−N)$PtPh_2$ (N−N = diimine ArN=CMe−CMe=NAr with Ar = 2,6-$Me_2C_6H_3$)] C−H activation has been investigated by using the B3LYP density functional theory method. The calculations show that the protonation should occur at the metal center, giving a coordinately unsaturated five-coordinate Pt(IV) hydride which is trapped by acetonitrile; otherwise monophenyl solvento cations (N−N)Pt(Ph)(NCMe)$^+$ should be isolated and characterized spectroscopically. Of the H exchange process, oxidative addition−reductive elimination and $\sigma$-bond metathesis mechanisms (including direct $\sigma$-bond metathesis and indirect $\sigma$-bond metathesis) are considered. The indirect $\sigma$-bond metathesis, which goes through a two-step H migration, is dramatically higher in energy than that of the direct one, so we can safely rule it out. The barrier associated with direct $\sigma$-bond metathesis is 14.70 kcal/mol, to be compared with 20.56 kcal/mol found in oxidative addition. So, unlike the methane C−H activation, the direct $\sigma$-bond metathesis pathway is predicted to take place predominantly. Furthermore, the solvent-induced associative elimination of benzene is also confirmed by the current theoretical studies for the first time. The trigonal bipyramidal transition states offer substantial evidence for this process, and the principle of microscopic reversibility then implies that benzene coordination will also be a solvent-assisted, associative process for a C−H activation reaction. For the different rates of benzene elimination, our calculations show that nucleophiles with higher electron-donating abilities and small steric effects of the diimine ligands will favor elimination greatly.

## Introduction

Since the early work by Garnett and Shilov established that aqueous Pt(II) salts are capable of activating C−H bonds of arenes and alkanes,[1−3] the quest to understand and utilize this "C−H activation" reaction has been the focus of intense research effort, as evidenced by numerous recent reviews.[4−10] In fact, the recent development of promising catalytic systems highlights the potential of organometallic chemistry for useful C−H bond activation strategies and will ultimately allow us to exploit Earth's alkane resources more efficiently and cleanly.[4−11]

Previous studies have succeeded in characterizing many of the key steps and reactive intermediates in the catalytic cycle.[4−6,11]

First, numerous experimental[12−23] and theoretical[17,24−31] studies of relevant Pt systems have focused mostly on the initial C−H activation step, which is considered to yield a Pt(IV) hydrido alkyl species by oxidative addition of R−H. The microscopic reverse of the initial C−H activation is examed by investigating the protonlysis of an alkylplatinum(II) complex.

---

* To whom correspondence should be addressed. Fax: (+86) 431-8894-5942. E-mail: tcclab@gmail.com.

† Jilin University.

‡ Dalian Institute of Chemical Physics.

(1) Garnett, J. L.; Hodges, R. J. *J. Am. Chem. Soc.* **1967**, *89*, 4546.

(2) Gol'dshleger, N. F.; Shteinman, A. A.; Shilov, A. E.; Eskova, V. V. *Zh. Fiz. Khim.* **1972**, *46*, 1353.

(3) Gol'dshleger, N. F.; Tyabin, M. B.; Shilov, A. E.; Shteinman, A. A. *Zh. Fiz. Khim.* **1969**, *43*, 2174.

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

(5) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2181.

(6) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154.

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

(8) Fekl, U.; Goldberg, K. I. *Adv. Inorg. Chem.* **2003**, *54*, 259.

(9) Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2001**, 2437.

(10) Crabtree, R. H. *J. Organomet. Chem.* **2004**, *689*, 4083.

(11) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507.

(12) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 9371.

(13) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961.

(14) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848.

(15) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235.

(16) Holtcamp, M. W.; Henling, L. M.; Day, M. W.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chim. Acta* **1998**, *270*, 467.

(17) Heiberg, H.; Johansson, L.; Gropen, O.; Ryan, O. B.; Swang, O.; Tilset, M. *J. Am. Chem. Soc.* **2000**, *122*, 10831.

(18) Johansson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 10846.

(19) Johansson, L.; Ryan, O. B.; Rømming, C.; Tilset, M. *J. Am. Chem. Soc.* **2001**, *123*, 6579.

(20) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2001**, *123*, 5100.

(21) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 12724.

(22) Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 1378.

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

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

(25) Hill, G. S.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 1478.

(26) Heiberg, H.; Swang, O.; Ryan, O. B.; Gropen, O. *J. Phys. Chem. A* **1999**, *103*, 10004.

(27) Mylvaganam, K.; Bacskay, G. B.; Hush, N. S. *J. Am. Chem. Soc.* **2000**, *122*, 2041.

(28) Bartlett, K. L.; Goldberg, K. I.; Borden, W. T. *J. Am. Chem. Soc.* **2000**, *122*, 1456.

10.1021/om070039d CCC: \$37.00

For example, the Bercaw group has first established on a tmeda−Pt(II) model system[12] that hydridoalkylplatinum(IV) species can indeed mediate the protonlysis reaction, contrary to a previous proposal which suggested the proton attack at the platinum−carbon bond leads directly to a $\sigma$-complex intermediate/transition state.[32] Other studies[12−14,17,33−37] also have observed the hydridoalkylplatinum(IV) species during low-temperature protonation. On the other hand, the protonation site is another important question pertaining to these protonation reactions. The mere observation of Pt(IV) hydrides at low temperature does not provide conclusive evidence that metal protonation occurs since that only identifies the thermodynamic site of protonation. Recently, the Tilset group has presented evidence that the metal center of Pt(II) dialkyl complexes is also the kinetically preferred site of protonation with using the competitive trapping technique.[23]

Second, two mechanistic possibilities are originally favored in the multiple H/D exchange: one possibility is reversible oxidative cleavage, which operates for reactions at electron-rich, low-oxidation-state complexes, and the other offers an alternative for reactions at electron-deficient metal centers, in particular at $d^0$ complexes, which is called $\sigma$-bond methathesis. However, interestingly, Webster[38] offers a reminder that $\sigma$-bond metathesis warrants consideration also at lower oxidation state and for "late" transition metals. Numerous experimental[39] and theoretical[17,24,26−27,30,40−41] studies on Pt system have focused on the H/D exchange mechanism, and they have offered substantial evidence for which possibility is preferred. For example, DFT calculations on $(NH_3)_2PtCl_2$ using a dielectric continuum to model solvation are used by Hush et al. to study oxidative addition vs electrophilic substitution.[27] They suggest that in the case of cisplatin the C−H activation is expected to occur by both $\sigma$-bond metathesis and oxidative addition. However, in the transplatin system the C−H activation process is predicted to take place predominantly by oxidative addition, as the $\sigma$-bond metathesis is found to be associated with a much higher barrier, in further contrast with the Shilov reaction where the two pathways are found to be comparable with regard to their activation energies.[27]

Third, understanding the mechanism of ligand substitution is also crucial for the C−H activation. Does the reacting hydrocarbon enter or leave the coordination sphere by an associative or dissociative mechanism? The pentafluoropyridine complex $[(tmeda)Pt(CH_3)(C_5F_5N)]^+$, which activates C−H bonds,[14] appears to undergo dissociative substitution of pentafluoropyridine,[42] while Johansson has addressed evidence that associative substitution pathways operate for methane loss following protonation of $(diimine)Pt^{II}(CH_3)_2$ complexes.[43] The principle of microscopic reversibility implies associative hydrocarbon coordination, which was also inferred from detailed mechanistic studies of the benzene activation reaction,[18,22] but some of the evidence is subjected to significant experimental uncertainty and/or alternative interpretation.[44] Recently, Procelewska et al.[44] have conducted the first example of an activation volume measurement for C−H activation which offers a powerful tool for resolving such ambiguities. The significantly negative value for the activation volume, as well as the significantly negative activation entropy determined previously, clearly supports the operation of an associative mechanism and clarifies the nature of the mechanism for the C−H activation step in a model for the Shilov alkane oxidation system.[44]

Very recently, Tilset and co-workers have described the low-temperature protonation chemistry of $(N-N)PtPh_2$ complexes.[45] It demonstrates that the choice between Pt(II) and Pt(IV) products is depending on the reaction conditions. The Pt(II) phenyl/$\pi$-benzene complexes $(N-N)Pt(C_6H_5)(\eta^2\text{-}C_6H_6)^+$ are only formed in the absence of a strongly bonded ligand, acetonitrile. In this contribution, we have used density-functional theory calculations to investigate the benzene activation by the $(N-N)PtPh_2$ ($N-N$ = diimine ArN=CMe−CMe=NAr with Ar = $2,6\text{-}Me_2C_6H_3$) system, in an effort to gain useful insight and understanding of the factors that affect every step of the C−H activation process. Our aims are 3-fold as listed in the following:

(1) Does the protonation occur at Pt or at the phenyl group? Various mechanisms have been proposed, and the process is probably dependent on the nature of the substrate, acid, solvent, and other parameters.[13,24,32,46−48] (2) Does the multiple H/D exchange take the reversible oxidative cleavage mechanism or the $\sigma$-bond metathesis mechanism? (3) Reductive elimination often serves as the critical product release step in homogeneously catalyzed organic reactions and metal-mediated stoichiometric transformation. In the title reactions, does the benzene elimination apply the solvent-assisted associative mechanism as suggested by experiments? Do the reasonable transition states which take the trigonal bipyramidal structure proposed by Lars Johansson et al.[19] exist on the PES of the theoretical study? Do the nucleophiles and steric effects of the diimine ligands greatly affect the reactivity of the metal center?

The thorough investigation on the benzene activation in the title reactions may be helpful for further theoretical and experimental studies of C−H activation. It must be stressed that the trigonal bipyramidal transition state which affirms the solvent-assisted associative mechanism appears to be the first time found in the theoretical calculation and gives substantial evidence for the associative mechanism.

---

(29) Bartlett, K. L.; Goldberg, K. I.; Borden, W. T. *Organometallics* **2001**, *20*, 2669.

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

(31) Iron, M. A.; Lo, H. C.; Martin, J. M. L.; Keinan, E. *J. Am. Chem. Soc.* **2002**, *124*, 7041.

(32) Alibrandi, G.; Minniti, D.; Romeo, R.; Uguagliati, P.; Calligaro, L.; Belluco, U.; Crociani, B. *Inorg. Chim. Acta* **1985**, *100*, 107.

(33) Jenkins, H. A.; Yap, G. P. A.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1946.

(34) Fekl, U.; Zahl, A.; van Eldik, R. *Organometallics* **1999**, *18*, 4156.

(35) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966.

(36) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chim. Acta* **1997**, *265*, 117.

(37) Hinman, J. G.; Baar, C. R.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2000**, *19*, 563.

(38) Webster, C. E.; Fan, Y.; Hall, M. B.; Kunz, D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 858.

(39) Johansson, L.; Ryan, O. B.; Tilset, M. *J. Am. Chem. Soc.* **1999**, *121*, 1974.

(40) Siegbahn, P. E. M. *J. Phys. Chem.* **1995**, *99*, 12723.

(41) Kua, J.; Xu, X.; Periana, R. A.; Goddard, W. A., III. *Organometallics* **2002**, *21*, 511.

(42) Rostovtsev, V. V. Ph.D. Dissertation, California Institute of Technology, 2001.

(43) Johansson, L.; Tilset, M. *J. Am. Chem. Soc.* **2001**, *123*, 739 and references cited therein.

(44) Procelewska, J.; Zahl, A.; van Eldik, R.; Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **2002**, *41*, 2808.

(45) Wik, B. J.; Lersch, M.; Krivokapic, A.; Tilset, M. *J. Am. Chem. Soc.* **2006**, *128*, 2682.

(46) Belluco, U.; Croatto, U.; Uguagliati, P.; Pietropaolo, R. *Inorg. Chem.* **1967**, *6*, 718.

(47) Alibrandi, G.; Minniti, D.; Romeo, R.; Uguagliati, P.; Calligaro, L.; Belluco, U. *Inorg. Chim. Acta* **1986**, *112*, L15.

(48) Jawad, J. K.; Puddephatt, R. J.; Stalteri, M. A. *Inorg. Chem.* **1982**, *21*, 332.

## Computational Method

Density functional theory (DFT) is used throughout the study with the hybrid density functional, B3LYP,[49,50] which is considered by and large as a reliable quantum chemical method for large molecules, especially when transition metals are included.[17,25,27−29,31,41] Two kinds of basis set systems (B1, LANL2DZ[51−53] for Pt, 6-31G for the nonmetal atoms; B2, LANL2DZ for Pt, 6-31+G(d) for the atoms directly involved in reactions (see Supporting Information sketch map), 6-31G for the rest of the nonmetal atoms) are used for the geometry optimizations. All of the geometries were fully optimized, normally without symmetry constrains. Harmonic vibrational frequencies were computed to verify the nature of the stationary points. Therefore, the minimum structures reported in this paper show positive eigenvalues of the Hessian matrix, whereas the transition states (TSs) have only one negative eigenvalue. To corroborate which are the correspondent minima linked by the considered transition states, normal coordinate analyses were performed on these TS structures by intrinsic reaction coordinate (IRC) routes[54] in both reactant and product directions. Additional geometry optimizations starting from the last IRC structures were carried out when the IRC calculations did not converge themselves.

For the purpose of obtaining more reliable energies of various structures, the B1 optimized geometries were reevaluated by single point energy calculation with the B3 (LANL2DZ for Pt, 6-311+G-(d,p) for the nonmetal atoms) basis set and B2 optimized geometries were reevaluated by the B4 (LANL2DZ for Pt, 6-311++G(d,p) for nonmetal atoms) basis set. To take into account the role of the solvent, single point calculations are carried out on some important B2-optimized structures using the polarized continuum model (PCM),[55−57] acetonitrile and ether being considered as the solvent for the protonation process and H exchange process, respectively.[58] Unscaled vibrational frequencies were used to calculate zero-point energy (ZPE) corrections to the total energies.

The thermodynamic functions ($\Delta H$, $\Delta S$, and $\Delta G$) were estimated within the ideal gas, rigid-rotor, and harmonic oscillator approximations. Two temperatures of 195.15 and 233.15 K and a pressure of 1 atm were assumed.

## Results and Discussion

The discussion of the theoretical results of the platinum-mediated arene C−H activation reaction is divided into four subsections. In the first subsection some important structures are discussed. From the second to the fourth subsections, all mechanisms included in the reaction are discussed. The initial step of the protonation is discussed in the second subsection, and the H exchange process is discussed in the third. In the fourth subsection, benzene eliminations with different nucleophiles and steric effects are investigated. An overview of the optimized stable structures and transition states is depicted in Figures 1 and 2, respectively.

**A. Important Stable Structures.** The starting complex is (N−N)PtPh$_2$ complex A$_a$. As expected, complex A$_a$ shows a square-planar environment around Pt(II). The Pt−N bonds are 2.173 Å long, while the Pt−C bonds are 2.029 Å long, which agree well with the values of 2.1050 (2.1036) Å and 2.0150 (2.0056) Å observed by X-ray crystallography.[45] The N$_1$−Pt−N$_2$ angle is compressed, as is typical for square-planar Pt(II) diimine complexes, from the ideal 90 to 74.6°, and the C$_1$−Pt−C$_2$ angle is also compressed to 86.2°. It should be noted that the computed structure A$_a$ is not perfectly symmetric, as well as the crystal structure.

$\eta^2$-Arene complexes are key intermediates in aromatic activations,[5,59−69] although this is not always the case.[70−71] A Pt benzene complex with an $\eta^2$-(C,C) coordination mode has recently been characterized by X-ray crystallography.[21] With DFT methods, we obtained two possible conformers of a Pt(II) $\pi$-benzene complex (B$_a$ and B$_a$′) as suggested by Johansson et al.[18] In conformer B$_a$, the benzene orients toward the phenyl ligand, while, in B$_a$′, the benzene orients toward the 2,6-dimethyl-substituted N−aryl group. In both conformers, the coordinated C=C bonds are almost oriented perpendicular to the coordination plane and the platinum atom is almost equidistant to the carbon atoms (C$_1$ and C$_3$) of the benzene. The Pt−N$_2$ bond trans to the benzene is shorter (0.150−0.188 Å) than Pt−N$_1$ bond trans to the phenyl ligand, in accordance with the greater trans influence of phenyl versus benzene ligand. Conformer B$_a$′ lies about 2.7 kcal/mol higher in energy than B$_a$ on steric grounds, and the relative population of the two conformers is expected to be temperature dependent.[18] B$_a$′ may be an intermediate at low temperature, and it could easily transform to B$_a$ through a $\eta^1$-bonded transition state TS-B$_a$′B$_a$ (energy barrier: 4.47−4.66 kcal/mol). So B$_a$ is thermodynamically predominate, and only in this conformer, we may explain the high-field shifts of the phenyl signal, since the platinum phenyl group should lie in the shielding region created by the benzene ring current effects.[18]

The five-coordinate complex C$_a$ or C$_a$′, which takes a square-pyramidal structure may, in principle, be formed by the oxidative addition of benzene within the $\pi$-benzene complex (B$_a$ and B$_a$′). C$_a$ and C$_a$′ are enantiomorphic structures. The five-coordinate C−H oxidative products have never been directly observed, presumably because of the unfavorable thermodynamics of their formation relative to that of the precursors as well as a low barrier (2.9−3.0 kcal/mol) against reductive elimination.

C,H-$\eta^2$-alkane adducts are commonly invoked intermediates in oxidative addition and reductive elimination of C−H bonds,[18]

---

[49] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

[50] Stephens, P. J.; Devlin, J. F.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

[51] Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

[52] Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.

[53] Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

[54] Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.

[55] Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117−129.

[56] S. Miertus, J. Tomasi, *Chem. Phys.* **1982**, *65*, 239−245.

[57] Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *Chem. Phys. Lett.* **1996**, *255*, 327−335.

[58] We should mention that the geometry parameters and relative energies predicted by B3LYP/B1 and B3LYP/B2 are in excellent agreement. (See Table S4 (Supporting Information); we only compared the energy of protonation on the phenyl ligand.) The relative energies with solvent effects also agree well with them. For the sake of saving computational resources and convenience of comparison of the couple systems, all of the discussion in this paper is based on the results at the B3LYP/B3//B3LYP/B1 levels of theory.

[59] Chin, R. M.; Dong, L.; Duckett, S. B.; Jones, W. D. *Organometallics* **1992**, *11*, 871.

[60] Chin, R. M.; Dong, L.; Duckett, S. B.; Partridge, M. G.; Jones, W. D.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 7685.

[61] Cronin, L.; Higgitt, C. L.; Perutz, R. N. *Organometallics* **2000**, *19*, 672.

[62] Iverson, C. N.; Lachicotte, R. J.; Mueller, C.; Jones, W. D. *Organometallics* **2002**, *21*, 5320.

[63] Churchill, D. G.; Janak, K. E.; Wittenberg, J. S.; Parkin, G. *J. Am. Chem. Soc.* **2003**, *125*, 1403.

[64] Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 305.

[65] Sweet, J. R.; Graham, W. A. G. *Organometallics* **1983**, *2*, 135.

[66] Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1989**, *111*, 8722.

[67] Cordone, R.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 8101.

[68] Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814.

[69] Chin, R. M.; Dong, L.; Duckett, S. B.; Jones, W. D. *Organometallics* **1992**, *11*, 871.

[70] Vigalok, A.; Uzan, O.; Shimon, L. J. W.; Ben-David, Y.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 12539.

[71] Peterson, T. H.; Golden, J. T.; Bergman, R. G. *J. Am. Chem. Soc.* **2001**, *123*, 455.

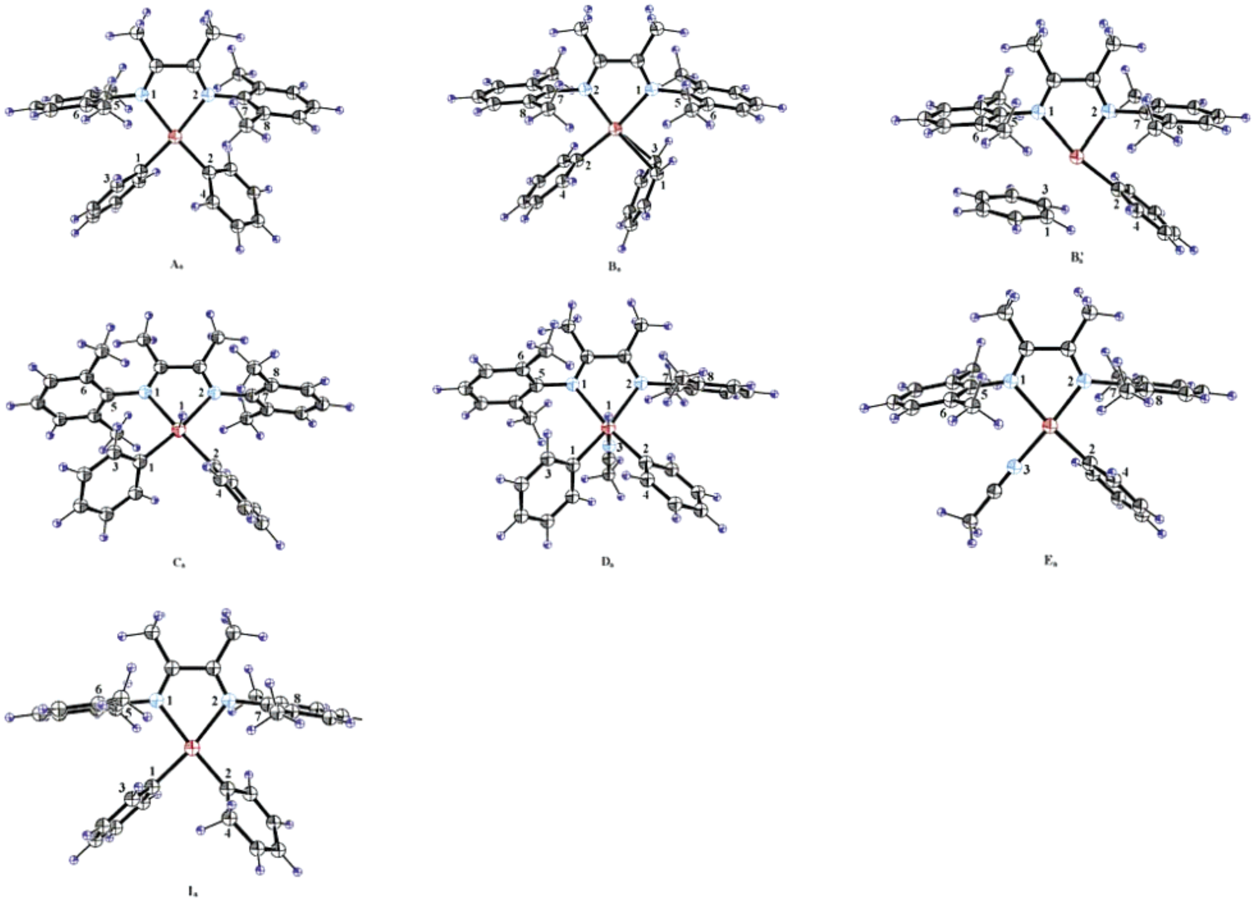


**Figure 1.** Important optimized stable structures of benzene C−H activation.

starting from the $\eta^2$-(C,C) precomplexation of the arene[5,59−69] and then probably followed by an arene "slip" to an $\eta^2$-(C,H)[18,63,70] or even $\eta^1$-(C)[72] coordination mode from which the oxidative cleavage of the C−H bond occurs.[45] However, it must be emphasized that, for the Pt case, all attempts to find such coordination mode adducts led directly to the $\eta^2$-$\pi$-benzene complex. We only locate transition states (TS-$B_aC_a$ and TS-$B_a'C_a'$; vide infra) for the direct transformation of $\pi$-benzene complex ($B_a$ and $B_a'$) to (N−N)Pt(Ph)$_2$(H) ($C_a$ and $C_a'$). That is to say, the $\eta^2$-$\pi$-benzene adducts and the phenyl hydride derivative $C_a$ interconvert directly without the intermediacy of a $\sigma$-complex.[63] Becaw et al. also offered several grounds for the impossible existence of the C,H-$\eta^2$ benzene coordination,[18] and there is no reporting of the Pt($\sigma$-HPh) complex up to the present.

Trapping of the five-coordinate (N−N)Pt(Ph)$_2$(H)$^+$ by L, in our case, acetonitrile, was done to get the thermodynamically favored six-coordinate hydrido alkyl Pt(IV) species.[73] Those species have been observed during low-temperature protonations.[12−14,17,33−37] In our calculated six-coordinate structure $D_a$, the hydride and MeCN ligands occupy the apical coordination sites.[13,33−35,74−75]

Cationic square planar Pt(II) complex (N−N)Pt(Ph)(NCMe)$^+$, $E_a$, is the product of the associative process. In this complex, one can also see the great trans effect of the phenyl ligand as compared with that of the MeCN ligand. The nitrogen trans to the MeCN ligand is much closer to the metal center than the one trans to the phenyl ligand. The formation of $E_a$ is strongly thermodynamically favored.

**B. Protonation of (N−N)PtPh$_2$ Complexes in the Presence of Acetonitrile at Low Temperature.** Ascertaining the preferred site of protonation is a prerequisite to the following studies. To the best of our knowledge, this is the first time elucidating the question theoretically. For the title reaction, two limiting mechanisms can be considered: protonation at the phenyl ligand leading to a $\pi$ complex, Pt$^{II}$($C_6H_6$) ($B_a$ or $B_a'$), or at platinum, generating an intermediate Pt$^{IV}$(Ph)(H) ($C_a$). We now utilize the reduction to absurdity method to characterize that the metal center is the preferred protonation site: We suppose that the phenyl ligand is the protonation site, and therefore, the $\pi$-benzene complex $B_a$ (or $B_a'$) is commonly considered as the intermediate in the protonation process. Starting from the $\pi$-benzene complex, there are two possible reactions that may occur (see sections C and D for more details): (1) C−H oxidative addition; (2) benzene elimination. As summarized in Figure 3, it is readily apparent that either from $B_a$ or $B_a'$ benzene elimination is more favorable than C−H oxidative addition. In the benzene elimination pathway, the energy barrier is about 11−15 kcal/mol. This is at least 5 kcal/mol lower than the oxidative addition. This therefore suggests that if the protonation occurs at the phenyl group, the monophenyl solvento cations (N−N)Pt(Ph)(NCMe)$^+$ ($E_a$) should be isolated and characterized spectroscopically. This conflicts with the experimental phenomenon, where hexacoordinated Pt(IV) hydride (N−N)PtPh$_2$(H)(NCMe)$^+$ ($D_a$) is the only intermediate at low temperature. So the metal center should be the preferred protonation site and the proposed protonation mechanism is

---

[72] Krumper, J. R.; Gerisch, M.; Magistrato, A.; Rothlisberger, U.; Bergman, R. G.; Tilley, T. D. *J. Am. Chem. Soc.* **2004**, *126*, 12492.

[73] Puddephatt, R. J. *Coord. Chem. Rev.* **2001**, *157*, 219−221.

[74] Hill, G. S.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 8745.

[75] Hill, G. S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1209.

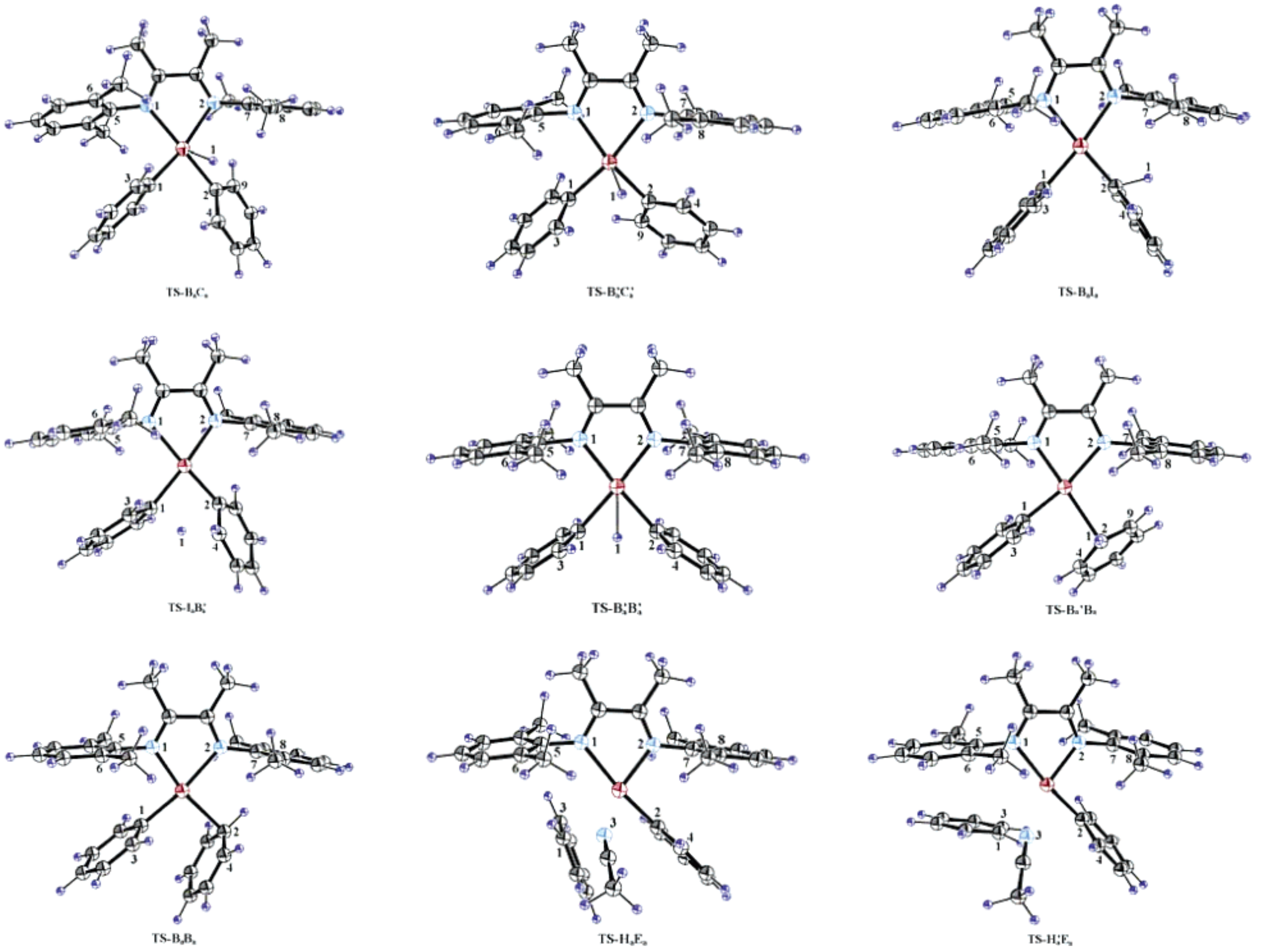


**Figure 2.** Important optimized transition states of benzene C−H activation.

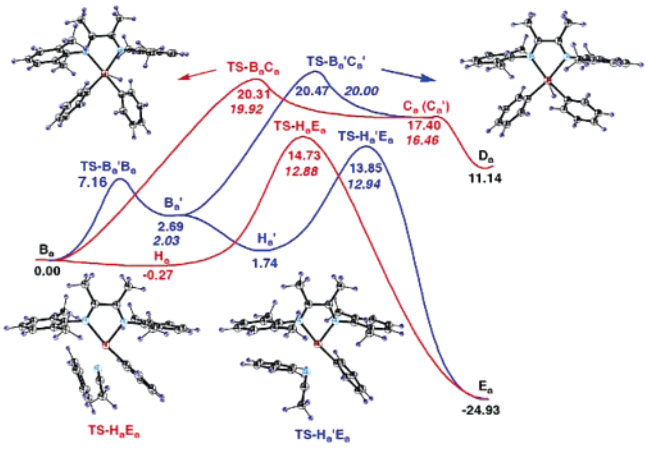


**Figure 3.** Schematic Gibbs free energy ($\Delta G$) energy surface (kcal/mol) for protonation on the phenyl ligand. Energies in italics include the solvent effects, acetonitrile being considered as the solvent.

depicted in Scheme 1. First, protonation at Pt to give a coordinately unsaturated five-coordinate Pt(IV) hydride and then the presence of strongly bonded acetonitrile may inhibit its isomerization[19] and trap it associatively[4] to give the hexacoordinated Pt(IV) hydride ($D_a$). $D_a$ is stable at low temperature, and when heated, it may first dissociate the MeCN ligand and then lead to the elimination of benzene.

On the other hand, while protonation occurs in the absence of a strongly bonded ligand, ether, for example, $C_a$ ($C_a'$) may surmount a small barrier of 2.91 kcal/mol (3.07 kcal/mol) to directly form the thermodynamically stable $\pi$-benzene complex $B_a$ ($B_a'$). In this circumstance, we will study the H exchange process in the $\pi$-benzene complex in the following paragraph.

**C. H Exchange Processes: Oxidative Addition vs $\sigma$-Bond Metathesis.** Clearing the C−H activation step is important part of our study. Two different mechanisms have been suggested for this activation. Of the oxidative addition mechanism, two reaction pathways are found in the study of the PES of this reaction, as shown in Figure 4. Actually, they are the same pathways. One is the reverse reaction of the other. Taking one for example, starting from $B_a$, the first step is the hydrogen migration to the platinum ion, effectively oxidizing it to Pt(IV) ($C_a$). Transition state TS-$B_aC_a$, corresponding to the C−H oxidative addition and the formation of five-coordinate complex $C_a$, is similar to $C_a$, but with the hydrogen ($H_1$) bent toward the phenyl group forming a $C_2$−Pt−$H_1$ angle of 56.5°. The Pt−$H_1$ (1.57 Å) and Pt−$C_2$ (2.09 Å) distances are only modestly increased, which are much longer in the final benzene complexes. The calculated energy barrier of this step is 20.43 kcal/mol. To complete the exchange of carbon atoms, the hydrogen ligand must undergo a reductive elimination process to another benzene ligand. Unlike the alkane C−H activation, in which it will be the reverse of the oxidative addition by something very close to symmetry, the arrangement of the two benzene ligands makes it a different situation, which leads to another conformer, $B_a'$. This necessitates a further step of $B_a'$ to $B_a$ conversion to complete the H exchange process.

An alternative mechanism to oxidative addition is that of $\sigma$-bond metathesis. Two pathways are also considered: (a) direct $\sigma$-bond metathesis; (b) indirect $\sigma$-bond metathesis. As shown in Figure 5, the indirect pathway b, which goes through a two-

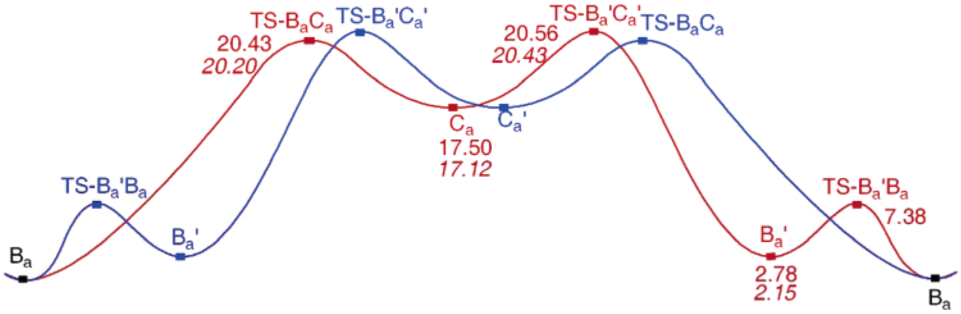


**Figure 4.** Schematic Gibbs free energy ($\Delta G$) energy surface (kcal/mol) for the C−H activation steps following oxidative addition pathways. Energies in italics include the solvent effects, ether being considered as the solvent.

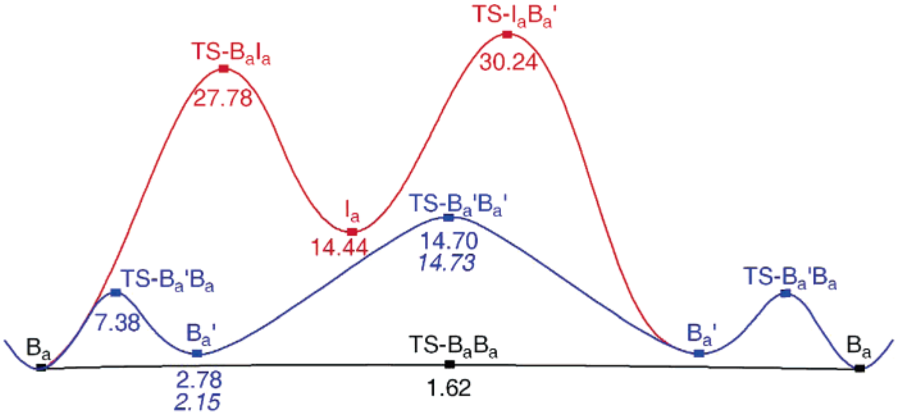


**Figure 5.** Schematic Gibbs free energy ($\Delta G$) energy surface (kcal/mol) for the C−H activation steps following $\sigma$-bond metathesis pathways. Energies in italics include the solvent effects, ether being considered as the solvent.

step H migration (via TS-$B_aI_a$ and TS-$I_aB_a{}'$, respectively) is dramatically higher in energy than that of pathway a, so we can safely rule it out. Pathway a features the direct H transfer between the two phenyl groups. The transition state, TS$B_a{}'B_a{}'$, corresponding to this process is located. In this transition state, the hydrogen is located within the equatorial plane and the Pt−H distance is 1.836 Å, which implies that the platinum atom interacts weakly with the hydrogen atom to "pass it along" to the other phenyl ligand. Calculations give an activation energy barrier of 14.70 kcal/mol (relative to $B_a$), to be compared with the previously found 20.56 kcal/mol for oxidative addition. The results are therefore in favor of the $\sigma$-bond metathesis pathway over oxidative addition.

The second coordination sphere of the solvent is found to play an important role in the Shilov reaction.[24] Ether, as an electron donor, may coordinate to the vacant site of the oxidative addition TS structure and stabilize it more efficiently than that of $\sigma$-bond metathesis. However, the solvent effects in the title reaction are greatly attenuated by the steric effect. The essentially perpendicular 2,6-dimethyl-substituted N−aryl groups and the arrangement of the benzene ligands make the ether hardly accessible to the metal center. Thus, the relative energies of species under study are not strongly influenced by the presence of ether. This is also confirmed by the polarized continuum model (PCM) calculations.

Before we draw a conclusion for the H exchange process, another two important questions pertaining to it, rotation of Pt−($\pi$-benzene) ligand and benzene elimination, are necessary to make clear here. For the former, we get a symmetrical $\eta^1$-(C) transition state TS-$B_aB_a$, which separates the two $\eta^2$-(C,C) minima with a barrier of only 1.62 kcal/mol. So, it can be safely assumed that the rate of rotation of the $\pi$-benzene ring is fast relative to the exchange rate. And for the latter, our theoretical calculations[76] indeed support the scenario[45] that the equilibration of all intermediates involved in H exchange process is fast compared to benzene loss; i.e., the hydrogen is capable of rapid exchange between the phenyl and benzene ligands.

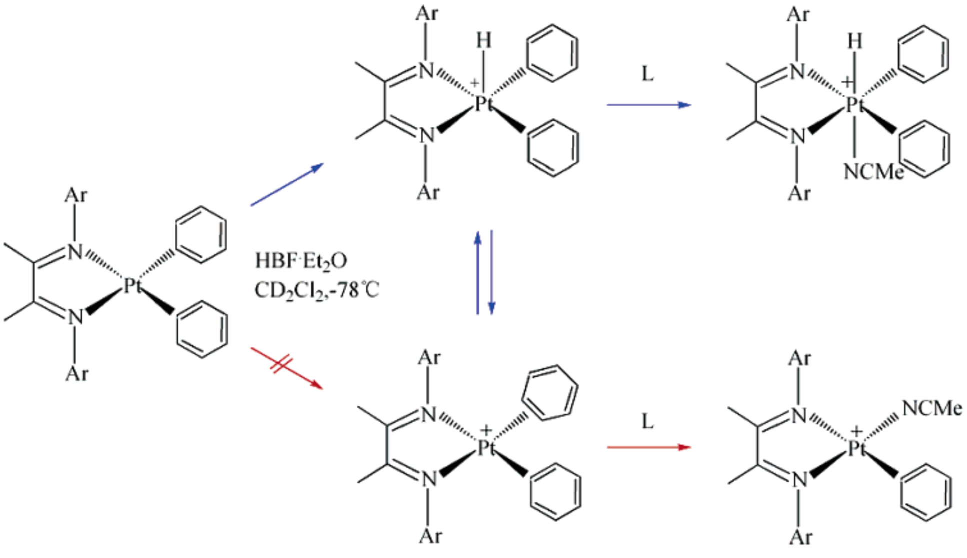
In summary, unlike the alkane C−H activation,[17] the most reasonable mechanism scenario for the H exchange process is the $\sigma$-bond metathesis mechanism; i.e., hydrogen transfers directly between the couple of phenyl groups. The scenario is depicted in Scheme 2. Finally, the facile rotation of the $\pi$-benzene complex allows the different C−H bonds to interact with the metal, and this would then eventually lead to scrambling of all of the six hydrogen atoms.

**D. Benzene Elimination: An Associative Process.** To address the issue of whether it is a trigonal bipyramidal transition state that is on the direct energy surface for the benzene elimination, which offer substantial evidence for the associative mechanism, we first put an acetonitrile molecule in the second coordinate shell of the $\pi$-benzene complex $B_a$ and then a series of geometry optimization calculations that progressively couples the Pt−N bond were performed. On account of finding a "hill" (the character of transition state) on the scan curve, there should be a transition state on the energy surface. After numerous full reoptimizations of the structures around the hill, a pentacoordinated transition state TS-$H_aE_a$ was well-established. It has an

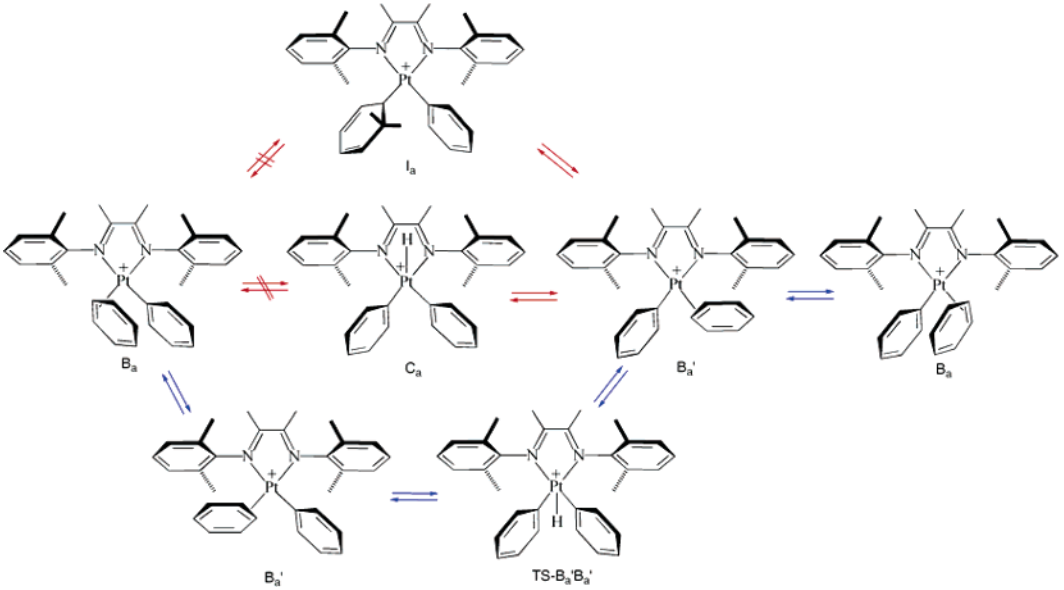
---

(76) Although we get almost the same scan curve with the 3,5-sustituted system, the transition state accounting for the $Et_2O$ attacking the 2,6-substituted system cannot be located. It was a really hard work locating the trigonal bipyramidal transition state, especially the most crowed TS-$He_aEe_a$. Anyway, it may exist in principle on the following grounds: the obvious associative mechanism for benzene substitution and the other existing trigonal bipyramidal transition states, especially the transition state for $Et_2O$ attacking the 3,5-sustituted system, TS-$He_bEe_b$. We can also speculate that the energy barrier of TS-$He_aEe_a$ lies at least 5 kcal/mol higher than that of TS-$He_bEe_b$ (see Figure 6), following the trends of MeCN and THF attacking the two systems.

**Scheme 1**



**Scheme 2**



imaginary frequency of 88.9i cm$^{-1}$, and the animation of the imaginary frequency corresponds to the movement of MeCN and the benzene ring. When MeCN moves toward the platinum center, the benzene ring would move away from it; that is to say, the formation of the Pt−N bond is concomitant with the breaking of the Pt−C bond. A corollary is the formation of the Pt−C bond would be concomitant with the breaking of the Pt−N bond. So this establishes that benzene entering or leaving the coordination sphere is a solvent-assisted, associative process. This is in accordance with the high-pressure studies that give a negative activation volume.[44] With the same method, a series of trigonal bipyramidal transition states with different nucleophiles and diimine ligands are located (see Figure S1, Supporting Information).

Now, we discuss two different effects on benzene elimination.

(1) The first effect is different nucleophiles. As we known, increasing the electron-donating ability of the nucleophiles obviously acts to favor the nucleophiles attacking on Pt. The electron-donating ability of the nucleophiles decreases in the order MeCN > THF > Et$_2$O, consistent with the observation that the substitution of benzene occurs fastest in MeCN and slowest in Et$_2$O[76] (see Figure 6). Expectedly and interestingly, as shown in Table S2 (Supporting Information), the distances of Pt···M (M denote N, O, O) are 2.634 and 2.639 Å in TS-H$_a$E$_a$ and TS-Ht$_a$Et$_a$ and about 3.30 Å in TS-He$_a$Ee$_a$,[77] increasing gradually, which is in line with the trend of their relative energies. The small steric effects of the nucleophiles may also account for these trends. MeCN, with the smallest steric effect, should have easier access to Pt compared with the other two nucleophiles, while the Et$_2$O molecule, with the smallest electron-donating ability and the greatest bulk, can hardly have access to Pt and may only form a loose transition state.[76,77]

(2) We also have steric effects. As shown in Figure 6, the energy barriers of TS-H$_b$E$_b$, TS-Ht$_b$Et$_b$, and TS-He$_b$Ee$_b$ are 11.92, 17.68, and 20.43 kcal/mol, respectively, which are lower than those with the 2,6-dimethyl-substituted system.[78] This is in accordance with Bercaw's observation[22] that the reactions

---

[77] As we can see from Table S2 (Supporting Information), in the two transition states of the same nucleophile attacking the two systems, the N−Pt(O−Pt) distances are almost equal, while Pt−C values in the 2,6-substituted system are 0.13−0. 14 Å longer than that in the 3,5-substituted system. Given the existence of TS-He$_a$Ee$_a$, the O−Pt distance might be about 3.30 Å and the Pt−C distance around 3.44 Å.

[78] Norris, C. M.; Reinartz, S.; White, P. S.; Templeton, J. L. *Organometallics* **2002**, *21*, 5649.

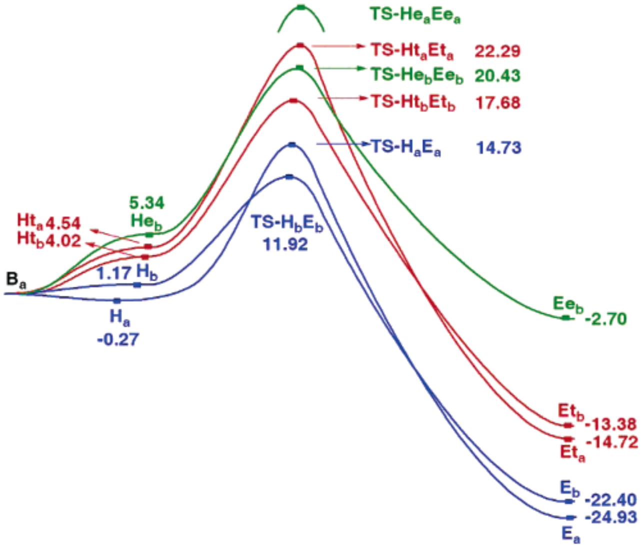


**Figure 6.** Schematic Gibbs free energy ($\Delta G$) energy surface (kcal/mol) for the nucleophilic molecules attacking the Pt metal center.

of benzene with complexes containing 2,6-dimethyl-substituted aryls are considerably slower than those with no such substitution, for example, the 3,5-dimethyl-substituted complexes. A steric explanation appears the most probable. The essentially perpendicular N−aryl groups increase the steric demands of the 2,6-dimethyl-substituted systems (the torsion angles are 89, 81, and 84° for 2,6-dimethyl-substituted aryls and 77, 56, and 46° for the 3,5-dimethyl-substituted complexes). So when the nucleophiles progressively access the metal center, the steric interactions with 2,6-dimethyl-substituted N−aryl groups are expected to be more significant than those with 3,5-dimethyl-substituted N−aryl groups. Hence, these lead to a significant destabilization of the transition-state structures which contain the 2,6-dimethyl-substituted N−aryl groups. Electronic effects may be neglectable as the facts are the aryl rings are twisted out of the coordination plane so as to attenuate some resonance effects.[45] NBO[79−80] calculations for natural population analysis (NPA) show that the natural charges on Pt are almost equal (0.71222 for $B_a$ and 0.70090 for $B_b$), from which we can safely rule out the electronic effects.

In summary, the calculated trigonal bipyramidal transition states offer substantial evidence for the associative process. Nucleophiles with higher electron-donating abilities and small steric effects of the diimine ligands will favor benzene elimination.

## Concluding Remarks

The calculations reported in this study address some of the points raised in the Introduction. First, the initial step is the protonation of the (N−N)$PtPh_2$ complex in the presence of acetonitrile at low temperature; we found the protonation site Pt, which suggested by experiments is supported by the present theoretical results. Second, the H exchange process is expected to occur by both $\sigma$-bond metathesis and oxidative addition. Our calculations show that this process is predicted to take place predominantly by $\sigma$-bond metathesis, as the oxidative addition is found to be associated with a much higher barrier. Third, a valuable finding of our study is that the associative mechanism for benzene elimination is confirmed by current calculation. The trigonal bipyramidal transition states, which provide strong support for that, are well-established. For the different rate of benzene elimination, nucleophiles with higher electron-donating abilities and small steric effects of the diimine ligands will favor it greatly.

**Acknowledgment.** This work is supported by the National Natural Science Foundation of China (Grant Nos. 20073014 and 20103003), Excellent Young Teacher Foundation of the Ministry of Education of China, Excellent Young Foundation of Jilin Province, and Technology Development Project of Jilin Province (Grant No. 20050906-6). We are thankful for the reviewers' invaluable comments.

**Supporting Information Available:** Structures for benzene elimination with different nucleophiles and diimine ligands, tables of energy data for protonation on phenyl ligands, the H exchange process, and the benzene elimination process, and selected bond distances and angles for all of the structures. This material is available free of charge via the Internet at http://pubs.acs.org.

OM070039D

---

(79) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. *NBO 5.0*; Theoretical Chemistry Institute, University of Wisconsin: Madison, WI, 2001; http://www.chem.wisc.edu/~nbo5.

(80) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.