Density Functional Study on the Reductive Elimination at an (NCN)Pt(IV) Center

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The formation of C-C bond catalyzed by metal complex has been a subject of intensive studies. Recently competitive sp^3-sp^3 and sp^2-sp^3 carbon-carbon reductive elimination from a platinum(IV) center was reported.[1] A platinum complex of tridentate "pincer" ligand of the form (NCN) (**1**) has been synthesized, and the addition of trifluoromethanesulfonic acid (HOTf) resulted in complexes from reductive elimination. (Scheme 1) The rate of sp^3-sp^3 coupling forming **3** is comparable to that of sp^2-sp^3 coupling leading to **4**, which is not expected from the earlier works.[2,3]

Here we report density functional studies on the mechanism of those two reductive elimination reactions of the intermediate (**2**) formed from **1**. The ethyl groups attached to N of **1** (and other chemical species) were replaced by methyl groups to reduce computational burden and extra complexity from conformational degree of freedom due to ethyl groups. Geometry optimization was carried out at the B3LYP/LACVP** level of theory using Jaguar v5.5 suite.[4] The stability of all the minima including intermediates and transition states (TSs) was evaluated by calculating the standard Gibbs free energy of each species at 233.15 K at which the experiments were performed. The standard Gibbs free energy of a molecule was evaluated by

$$\Delta G = E_0 + ZPE + \Delta\Delta G_{0 \to 233}. \quad (1)$$

The total energy of the molecule at 0 K (E_0) is calculated at the optimum geometry from B3LYP/LACVP** level of theory. Zero-point energy (ZPE), and Gibbs free energy change from 0 K to 233.15 K ($\Delta\Delta G_{0\to233}$) were evaluated at the same level of theory. Thermodynamic quantities were evaluated according to rigid-rotor harmonic oscillator approximation using the computed harmonic frequencies. The local minima and TSs were identified by the analysis of harmonic frequencies from analytical Hessian calculation. Reaction paths were traced by the intrinsic reaction coordinate (IRC) method[5,6] starting from the TSs to confirm that the reactants and products are correct. Poison-Boltzmann (PB) continuum model[7,8] was used to describe the solvent (CH_2Cl_2) at the B3LYP/6-31G** level with solvent probe radius of 2.34 Å and the solvent dielectric constant of 9.1.[9] The solvation effects were calculated at gas phase geometries optimized with B3LYP/6-31G** level. We focused on the C-C reductive elimination step. Five-coordinate Pt(IV) cationic intermediate is conjectured to be the chemical species from

which the C-C reductive coupling occurs rather than from a six-coordinate Pt(IV) solvento species.[10] Previous studies on reductive elimination reaction to form C-C and C-X bonds from Pt(IV) or Pd(IV) showed that five-coordinated intermediates are formed before the reductive coupling occurs.[11]
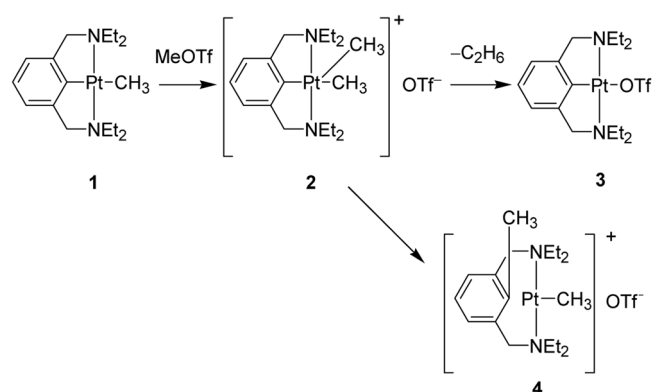
In Figure 1, showed is the Gibbs free energy diagram relative to intermediate 2^+ (+ denotes the five-coordinated cationic species) and the optimized structures from B3LYP/LACVP** calculations. For the comparison, the gas-phase thermodynamic quantities are also included.

Two conformers exist for 2^+, one is C_2-symmetric and the other is C_s-symmetric. The computation results showed that C_2-form is more stable than C_s-form, both in the gas phase (by 1.7 kcal/mol) and in CH_2Cl_2 (by 1.3 kcal/mol). The energy barrier for the conversion between two forms was calculated to be 3.7 kcal/mol in CH_2Cl_2 (4.1 kcal/mol in the gas phase). Pt-C_{ph} distance was calculated to be 2.02 Å for both forms, and Pt-C_{Me} distances were 2.15 Å (C_2) and 2.13 and 2.17 Å (C_s).

Two conformers also exist for 3^+. C_2-form is more stable by 1.6 kcal/mol in the gas phase, and C_s-form is more stable by 4.2 kcal/mol in CH_2Cl_2. Pt-C_{ph} distance was calculated to be 1.93 Å.

Only C_s-symmetric form can exist for 4^+, since phenyl ring is subject to a boat-type puckering and thus considerably tilted from the metal-ligand coordination plane, as found in other similar compounds.[12,13] The complex can be regarded as a frozen intermediate toward C_{sp2}-C_{sp3} bond activation.[12,13] The steric repulsion between two methyl rings in the TS also contribute to the relative instability of the Cs form, if exists. Pt-C_{ph} distance is calculated to be 2.39 Å, which is much longer than 2.18 Å found in PtI(MeC$_6$H$_3$(CH$_2$NMe$_2$)$_2$-o,o')]$^+$.[12]

Unlike the previous calculation and speculations,[2,3] $\Delta G^{\dagger}$ for sp^2-sp^3 coupling is similar to that for sp^3-sp^3 coupling, which is consistent with the experimental data.[1] (experimental rate of 7:1 at −40 °C) Gibbs free energy of activation for sp^3-sp^3 coupling was calculated to be 6.1 kcal/mol in CH_2Cl_2 (6.3 kcal/mol in the gas phase). It is much smaller than 23-28 kcal/mol for ethane reductive coupling from *fac*-[(L$_2$)PtMe$_3$X] (where X = halide, L$_2$ = a bidentate diphosphine or two monodentate phosphines).[10,14] Earlier theoretical model calculation with GVB level estimated ~35

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Scheme 1

Scheme 2

are considered.

We performed additional DFT calculations on model complexes of **5** and **6** in order to compare the Gibbs free energy of activation for the reductive elimination for sp^2-sp^2 coupling and the effect of the restraints due to pincer type ligand.

The activation barriers for sp^2-sp^2 and sp^2-sp^3 couplings in model complex **5** were calculated to be 15.0 and 7.4 kcal/mol in CH_2Cl_2 (14.7 and 7.4 kcal/mol in the gas phase). In model **6**, the activation barriers were 12.7 and 7.0 kcal/mol both in CH_2Cl_2 and in the gas phase. These results show that the main factor in determining the activation barrier is the steric hindrance between Ph group attached to Pt and Me groups attached to N, which affects optimal orbital overlap between sp^2 and sp^2 (or between sp^2 and sp^3).

In summary, we performed DFT calculations on reductive elimination reaction from a Pt(IV) center. We located transition states and intermediates successfully, and the results were consistent with the existing experimental data.

kcal/mol of activation.[3] Low energy of activation indicates that the intermediate $\mathbf{2}^+$ is rather unstable and is reflected by low temperature condition of the experiment. The activation barrier for sp^2-sp^3 coupling was calculated to be located at 8.6 kcal/mol in CH_2Cl_2 (9.3 kcal/mol in the gas phase) relative to the C_2 form of the intermediate. Conversion to C_s form must be preceded for this coupling since it is not occur in C_2 form due to the steric hindrance. This results was not expected in the previous works. It is anticipated that sp^2-sp^2 and sp^2-sp^3 couplings for Pt(IV) have lower activation energy since the increased s character of the sp^2 hybrids makes the orbital less directional,[3] even though the numeral data have not reported. As for Pt(II), the Gibbs free energies of activation were calculated to be 45.0, 37.5 and 26.2 kcal/mol for sp^2-sp^3, sp^2-sp^3, and sp^2-sp^2 coupling for $PtCl_2R_2$, where R = Me or Ph.[2]

Considering the estimated accuracy of ~ 3 kcal/mol for stable intermediates, ~ 5 kcal/mol for transition states, and even larger uncertainty for solvation energy calculations associated with the current level of theory,[15] the computational results are in good agreement with the experimental data.

Another point to be noticed is that the relative independence on the reaction media, which is related to the current model in which the five coordinated cationic intermediates
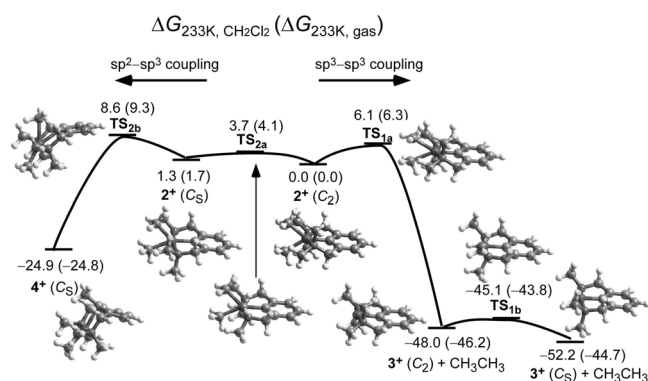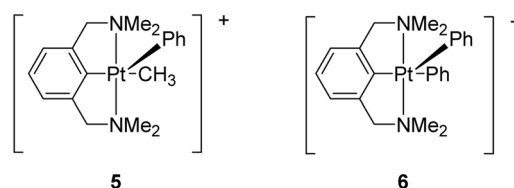
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Figure 1. Relative Gibbs free energy diagram and the optimized structures of minima and transition states from B3LYP/LACVP** level of theory calculations (Values in parentheses are the gas-phase data).