

## Density Functional Theoretical Study on the Oxidative Additions of Silyl Halides to the Rh Pincer Complex

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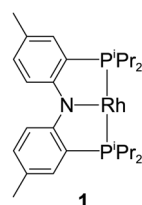
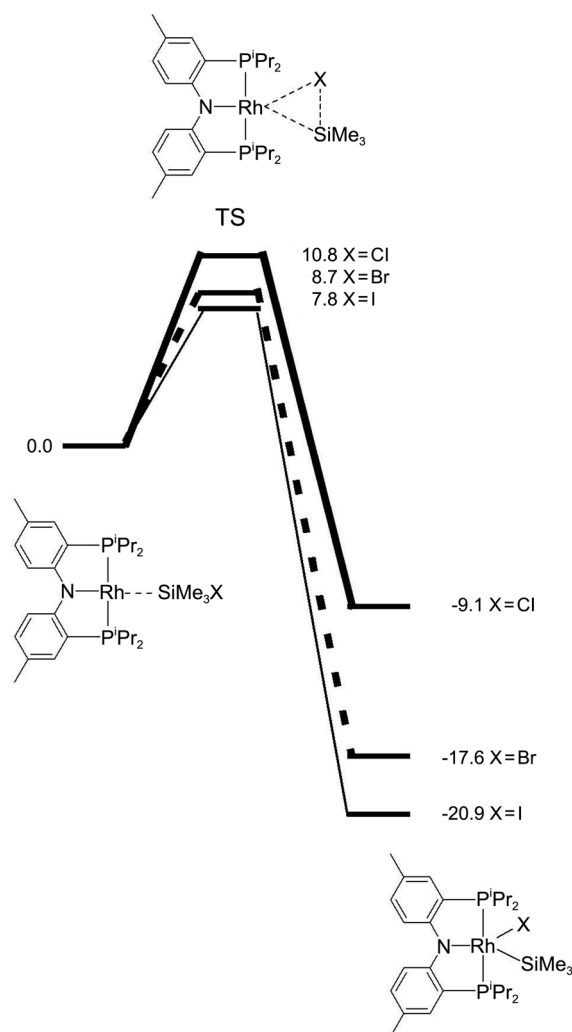
The oxidative addition reactions of C–X bonds in alkyl halides or aryl halides to transition-metal complexes are one of the fundamental reactions in organometallic chemistry.<sup>1</sup> However, the reaction involving silicon receives less attention. Recently oxidative addition reactions involving silicon-halide bonds to a rhodium complex were reported.<sup>2</sup> (PNP)Rh fragment **1** (where PNP is the bis(*o*-diisopropylphosphinophenyl)amide “pincer” ligand), generated from (PNP)Rh(SPr<sup>1</sup><sub>2</sub>), reacts with silyl halides compounds to undergo a silicon-halogen oxidative addition reaction. The fragment **1** has been considered to be convenient for the comparative studies because it is compatible with many reactions which provide several kinetic and thermodynamic parameters of the reactions.<sup>2</sup>

In this study the density functional theoretical (DFT) studies were conducted in order to determine the Gibbs free energy of reaction for the Si–X oxidative addition to **1** and hence to compare the relative stability between the initial adduct and the oxidative addition product. These kinetic and thermodynamic quantities are the key parameters for elucidating the reactivity and the preference toward the chemical species. B3LYP/LACVP\*\* level calculations were chosen because the level of theory was successfully applied to the oxidative addition/reductive elimination reactions involving organometallic pincer complexes.<sup>3,4</sup>

First we examined the dependence of the reactivity and the thermodynamics of the reaction on the halide species. Figure 1 shows the Gibbs free energy diagrams for the reaction between **1** and SiMe<sub>3</sub>X, where X = Cl, Br, or I. The Gibbs activation energy,  $\Delta G^\ddagger$ , were 10.8 kcal/mol for Cl, 8.7 kcal/mol for Br, and 7.8 kcal/mol for I in the gas phase at 298 K. In addition the Gibbs free energy of reaction,  $\Delta G_{\text{reaction}}$ , were –9.1 kcal/mol for Cl, –17.6 kcal/mol for Br, and –20.9 kcal/mol for I, indicating higher stability of the oxidative addition

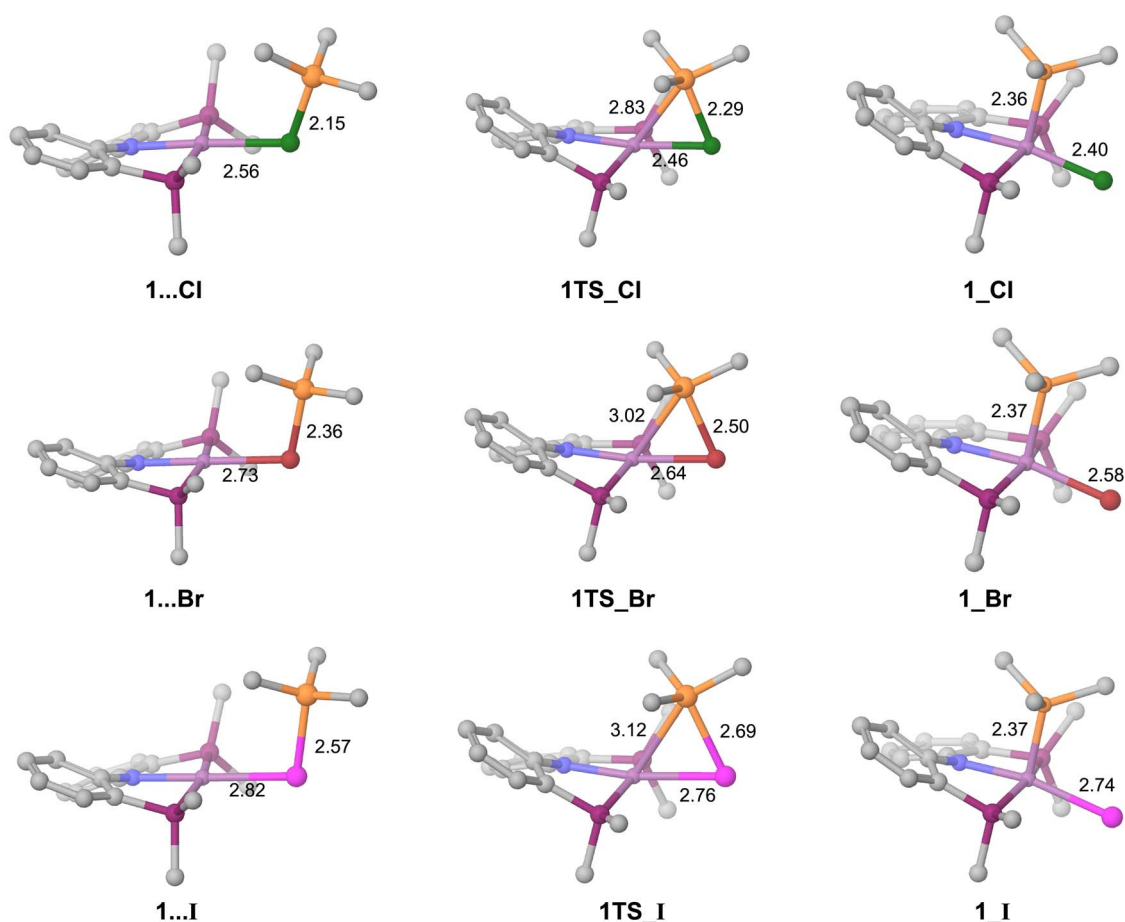
reaction products over the reactants.

The reactivities of silyl halides toward (PNP)Rh fragments are potentially related to the bond dissociation enthalpies of the Si–X bond in the SiMe<sub>3</sub>X molecule. For instance weaker bonds in heavier silyl halides are less inert to the Rh fragment. Furthermore the thermodynamics of the reaction is



**Scheme 1**

**Figure 1.** Relative Gibbs free energy diagram (in kcal/mol) from the B3LYP/LACVP\*\* calculations, where TS denotes the transition state.



**Figure 2.** Optimized structures of the minima and transition states in the Rh complexes from the B3LYP/LACVP\*\* calculations. The hydrogen atoms were not shown for clarity. **1**...X (X=Cl, Br, or I) represents the reactants, **1TS**\_X is the transition state and **1**\_X indicates the final product.

also influenced by the bond dissociation enthalpies of the Si–X bond. In this case heavier complexes are more stable compared to their reactants. Such trends observed in this work are in good agreement with the reported experimental results of both the same compounds<sup>2</sup> and similar reactions in Pt(0) phosphine complexes.<sup>5</sup>

Figure 2 shows the optimized structures from the B3LYP/LACVP\*\* calculations. In **1**...X, the (PNP)Rh fragment and silyl halides interact weakly at relatively large distances of 2.56–2.82 Å. In **1TS**\_X, the Rh–X bond lengths were shortened to 2.46–2.76 Å, and the Si–X bonds were stretched to 2.29–2.69 Å, resulting in the Rh–Si bond formation.

The product Rh complexes **1**\_X (where X = Cl, Br, or I) exhibited distorted square pyramidal geometries with a nearly planar Rh coordination. The Rh–Si bond lengths in **1**\_X were 2.36–2.37 Å, which were comparable to the values found in the X-ray structure of the related Rh complexes.<sup>2,6</sup> Moreover silyl ligands were likely to occupy the apical positions. In addition Rh–X bond lengths were also shortened to the values comparable with the related X-ray structural data.<sup>2,7,8</sup>

Additional calculations were performed in order to investigate the effect of the number of halide atoms in the silyl halides. The second set of compounds with a varying

**Table 1.** Gibbs energy of activation and the reaction between **1** and silyl halides

Silyl halides	SiCl <sub>4</sub>	SiMeCl <sub>3</sub>	SiMe <sub>2</sub> Cl <sub>2</sub>	SiMe <sub>3</sub> Cl
$\Delta G^\ddagger/\text{kcal mol}^{-1}$	3.8	4.9	6.8	10.8
$\Delta G_{\text{reaction}}/\text{kcal mol}^{-1}$	–27.6	–21.5	–15.3	–9.1

number of Cl and subsequently Me groups on Si (SiMe<sub>y</sub>Cl<sub>4–y</sub>, where y = 1, 2, 3, or 4) were utilized for study. The Gibbs free energy of activation and reaction were summarized in Table 1.

Similarly these outcomes agree well with the experimental results of the same compounds<sup>2</sup> and similar reactions in Pt(0) phosphine complexes.<sup>5</sup>

In summary, the DFT calculations were applied to the Si–X oxidative addition reaction to the pincer type Rh complexes. The transition states were successfully constructed, and both the thermodynamic and kinetic results were consistent with the published experimental data and computational results previously reported for the same types of complexes.<sup>2</sup> Furthermore the reactivity due to the thermodynamic preference increases in the series of Cl < Br < I for SiMe<sub>3</sub>X. In addition the reaction for the SiMe<sub>y</sub>Cl<sub>4–y</sub> becomes more favorable with the increasing number of Cl

substituents.

### Computational Details

The geometry of each compound was optimized at the B3LYP/LACVP\*\* level of theory using the Jaguar v5.5 suite.<sup>9</sup> The stability of all of the minima, including the intermediates and the transition states (TSs), was evaluated by calculating the standard Gibbs energy of each species at 298.15 K using the following equation.

$$\Delta G = E_0 + \text{ZPE} + \Delta\Delta G_{0 \rightarrow 298\text{K}}. \quad (1)$$

The total energy of the molecule at 0 K ( $E_0$ ) was calculated at the optimal geometry from the B3LYP/LACVP\*\* computational level. The zero-point energy (ZPE) and the change in the Gibbs free energy from 0 K to 298.15 K ( $\Delta\Delta G_{0 \rightarrow 298}$ ) were studied at the same level of theory. The thermodynamic quantities were investigated according to the rigid-rotor harmonic oscillator approximation using the computed harmonic frequencies from the B3LYP/LACVP\*\* calculations. The local minima and the TSs were identified using the harmonic frequency analysis from the analytical Hessian calculations. The reaction paths were traced from the TSs *via* the intrinsic reaction coordinate (IRC) method in order to confirm that the reactants and products were correct.<sup>10,11</sup> The isopropyl groups attached to the phosphorus

atoms in all of the complexes were replaced with the methyl groups in order to reduce the computational burden.

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