

Notes

Density Functional Theoretical Study on the Carbon-Halide Oxidative Additions to a Rh Pincer Complex[†]

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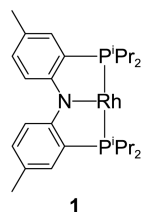
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The oxidative addition reactions of C-X bonds in alkyl or aryl halides to transition-metal complexes are some of the fundamental reactions in organometallic chemistry.¹ Reactions involving silicon, however, have received less attention. Recently, oxidative addition reactions involving silicon-halide bonds to a rhodium complex were reported. (PNP)Rh fragment **1** (where PNP is the bis(*o*-diisopropylphosphinophenyl) amide “pincer” ligand), which is generated from (PNP)Rh (SPrⁱ₂), reacts with silyl halides compounds to undergo a silicon-halogen oxidative addition reaction.² Fragment **1** is considered convenient for comparative studies because it is compatible with many reactions that provide several kinetic and thermodynamic parameters of the reactions.^{3,4} Density functional theoretical (DFT) studies were carried out to determine the Gibbs free energy of the reaction for Si-X oxidative addition to fragment **1**, and compare the relative stability of the initial adduct and oxidative addition product. These kinetic and thermodynamic quantities are the key parameters for determining the reactivity and preference toward chemical species.



Scheme 1

In this study, DFT calculations for the C-X oxidative addition to **1** were carried out to compare the thermodynamic and kinetic parameters with those of Si-X oxidative addition.

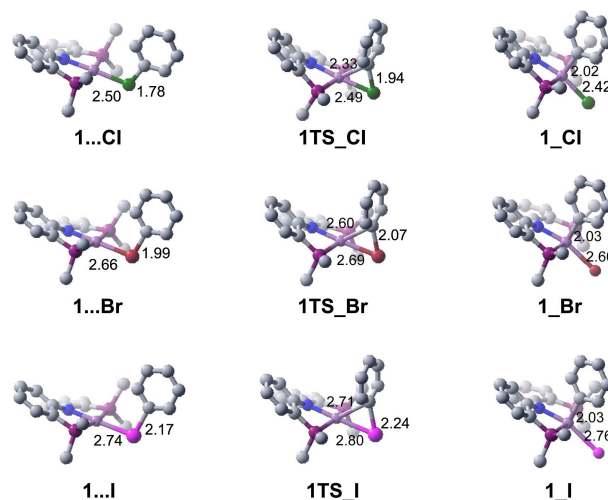


Figure 1. Optimized structures of the minima and transition states in the Rh complexes from B3LYP/LACVP** calculations. The hydrogen atoms are not shown for clarity. **1...X** (X=Cl, Br, or I) represents the reactants, **1TS_X** is the transition state and **1_X** indicates the final product.

The B3LYP/LACVP** level calculations were chosen because the level of theory has been applied successfully to oxidative addition/reductive elimination reactions involving organometallic pincer complexes.^{5,6}

Figure 1 presents the optimized structures from B3LYP/LACVP** calculations. In **1...X**, the (PNP)Rh fragment and phenyl halides interact weakly at relatively large distances of 2.50–2.74 Å. In **1TS_X**, the Rh–X bond lengths were shortened to 2.49–2.80 Å, and the C–X bonds were stretched to 1.94–2.24 Å, resulting in Rh–C bond formation. Note that the phenyl ring was rotated ~90° to allow Rh–C bond formation.

The product Rh complexes **1_X** (where X = Cl, Br, or I) exhibited distorted square pyramidal geometries with almost planar Rh coordination. The Rh–C bond lengths in **1_X** were

[†]This paper is to commemorate Professor Kook Joe Shin's honourable retirement.

Table 1. Gibbs energy of activation and the reaction between **1** and methyl and t-butyl halides

| Alkyl halides | Me-Cl | Me-Br | Me-I |
|---|--------------------|--------------------|-------------------|
| ΔG^\ddagger / kcal mol ⁻¹ | 18.1 | 13.3 | 13.5 |
| $\Delta G_{\text{reaction}}$ / kcal mol ⁻¹ | -25.0 | -30.7 | -28.1 |
| Alkyl halides | ^t Bu-Cl | ^t Bu-Br | ^t Bu-I |
| ΔG^\ddagger / kcal mol ⁻¹ | 24.4 | 19.8 | 19.5 |
| $\Delta G_{\text{reaction}}$ / kcal mol ⁻¹ | -9.7 | -14.4 | -13.9 |

2.02–2.03 Å, which are comparable to the values obtained from the X-ray structure of **1-Br**.³ Phenyl ligands occupied the apical positions, as found in the X-ray structure. In addition, the Rh–X bond lengths were also shortened to the values comparable to the related X-ray structural data.^{3,7}

The Gibbs activation energy, ΔG^\ddagger , for X = Cl, Br and I in the gas phase at 298K were 14.9, 11.7 and 12.6 kcal/mol, respectively. In addition, the Gibbs free energy of reaction, $\Delta G_{\text{reaction}}$, for X = Cl, Br and I were -24.0, -31.0 and -28.7 kcal/mol, respectively, indicating that the oxidative addition reaction products have higher stability than the reactants.

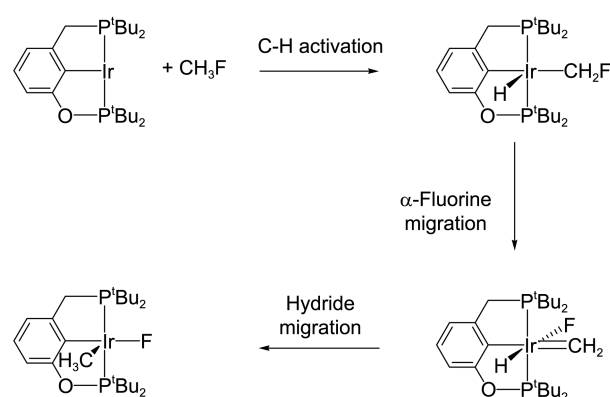
The reactivity of silyl halides toward (PNP)Rh fragments are potentially related to the bond dissociation enthalpies of the C–X bond in the substituted phenyl molecule. For example, weaker bonds in heavier phenyl halides are less inert to the Rh fragment. Furthermore, the thermodynamics of the reaction is also influenced by the bond dissociation enthalpy of the C–X bond. In this case, heavier complexes are more stable than their reactants. These trends are in good agreement with the reported experimental results of both the same compounds and similar reactions in Pt(0) phosphine complexes.⁸

When compared to the Si–X bond, the trend was almost the same but the thermodynamic data involving carbon is greater than that with silicon, indicating that it is more difficult to activate the C–X bond in phenyl halides than a Si–X bond in SiMe₃X. This is in good agreement with the experimental data.⁴

Additional calculations of the oxidative addition of methyl halides and t-butyl halides were performed to compare the results with the C–X bond involving aliphatic carbon.

Similarly, the dependence of halide species agrees well with the experimental results of the same compounds. Unlike the general oxidative addition/reductive elimination reaction cases, the results for the aliphatic carbon and aromatic carbon are similar. Similar results were also obtained in other pincer complexes.^{5,6} Steric hindrance plays an important role in the thermodynamics and kinetics reflecting the higher activation energy and lower Gibbs energy for the ^tBu cases.

Recently, it was reported that the C–F bond, which is generally believed to be inert due to the strong bond strength, would be activated through a mechanism involving C–H oxidative addition and F migration for iridium complexes.⁹ (Scheme 2) In this study, DFT calculation of the same mechanism of C–F addition to the Rh pincer complex **1**

**Scheme 2**

were also performed to determine if the mechanism is applicable to **1**. On the other hand, the computation gave the activation Gibbs energy for the F migration reaction (35.3 kcal/mol), which is the rate determining step of the reaction. This activation Gibbs energy is greater than the energy for direct C–F bond activation (27.0 kcal/mol), which indicates that the newly suggested mechanism in Scheme 2 is not applicable at least to this Rh complex **1**.

In summary, DFT calculations were applied to the C–X oxidative addition reaction to the pincer type Rh complex. The transition states were constructed successfully. Both the thermodynamic and kinetic results were consistent with the published experimental data and computational results reported previously for similar complexes. The reactivity is less favorable when compared to silicon compounds.

Computational Details

The geometry of each compound was optimized at the B3LYP/LACVP** level of theory using the Jaguar v5.5 suite.¹⁰ 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 energy from 0 K to 298.15 K ($\Delta \Delta G_{0 \rightarrow 298\text{K}}$) 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 TSs were identified using harmonic frequency analysis from analytical Hessian calculations. The reaction paths were traced from the TSs *via* the intrinsic reaction coordinate (IRC) method^{11,12} to confirm that the reactants and products were correct. 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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