Experimental and Theoretical Study of the Silicon-Hydrogen Bond Activation by Rhodium Dicarbonyl Complex in Solution

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Abstract

The photoreactivity of hydrotris-(3,5-dimethylpyrazolyl)boratedicarbonylrhodium(I) or HB(Pz*)3Rh(CO)2 complex has been studied at room-temperature n-pentane solution in the presence of 0.05 M Et3SiH (Et = C2H5). The IR spectra show that the decline of vco parent complex at 1980 and 2054 cm⁻¹ is followed by growing bands at 2029 and 2020 cm⁻¹. In light of the photolysis of the parent complex in neat n-pentane solution the feature at 2020 cm⁻¹ is tentatively assigned to the vco band of the Si-H bond activation product. Upon standing in the dark, the 2020 cm⁻¹ increases slightly in contrast with the 2029 cm⁻¹ peak which decreases over time. These observations raise question whether the intensity increase of the 2020 cm⁻¹ peak occurs unimolecularly resulting from the intramolecular rearrangement of the C-H bond activation of Et3SiH or bimolecularly as a result of the elimination of the C-H bond activation of the solvent and subsequent re-addition of the Si-H bond of the Et3SiH ligand. To gain more insight to reaction dynamics of the Si-H bond activation, the experimental results are compared to the photolysis of the parent complex in neat Et3SiH. The quantum efficiency (ϕps-1) of this photoreaction yields a low value of 0.16. The results indicate that the Si-H bond activation is facilitated by intramolecular rearrangement mode. In addition, a theoretical study was conducted using density functional study at B3LYP/LanL2DZ level of theory, and the findings implicate that the final complex product was produced by the Si-H bond activation of Et3SiH.

Comparison of energy stability among dicarbonyl parent complex, C-H bond activation of ethyl moieties, and Si-H bond activation of triethylsilane. The optimized structure clearly shows that the Si-H bond activation has the lowest energy (thermodynamically the most stable of the final product). The later is believed to be coming from the more kinetically accessible C-H bond activation of ethyl moieties of triethylsilane, which has higher energy than the corresponding Si-H bond activation product. Clearly, it shows that the intramolecular rearrangement of the C-H bond activation leading to the Si-H bond activation is the mode of reaction mechanism.

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Acknowledgment
Introduction

The photoreactivity of organometallic complexes have been the subject of intense study due to their importance in many synthetic and catalytic processes. It has been established that a coordinatively unsaturated metal center can bind to a nonreactive solvent molecule such as an alkane [1]. In this related particular interest, for example, the photochemical oxidative addition of a Si-H bond to certain transition metal complexes has been the focus of many research efforts. This type of bond activation reaction is critical in hydrosilylation processes and provides a comparison to oxidative reactions by metal complexes [2]. Previously, we reported our results on the photochemical C-H bond activation of HB(Pz*)Rh(CO): in saturated alkane solution, in which Pz* is 3,5-dimethylpirazolyl. It was confirmed that the metal complex formed stable C-H activated product upon photolysis with appreciable quantum efficiency [3,4].

The general accepted reaction mechanisms of C-H bond activation by metal complexes has been reported in literature; the primarily photoproduct of this Rh complex, the monocarbonyl, forms a solvent complex and this species, subsequently, undergoes a thermal reaction which breaks one of the Rh-N bonds to form a $\eta^2$-Pz* complex. The later complex crosses a barrier of 8.3 kcal/mol to form C-H bond activation complex, and then the unchelated pz* ligand rebound to the metal center and produces alkylhidridomonocarbonyl final complex [5].

There have been many reports for reaction mechanism schemes of silane Si-H bond activation; different metal complexes may exhibit unique routes. Organometallic complexes of group 7 (d8) have been explored extensively to undergo photochemical Si-H bond activation; different routes of Si-H activation reaction mechanisms were reported [5-7]. Moreover, the computational works did for these systems support effectively the photochemical decarbonylation mechanism [8]. Different mode of Si-H bond activation has also been thermally shown by metal complexes [9].

The role spin flip model in the photochemical reaction mechanism has also been investigated. Both Co and Rh complexes have undergone difference multiplicity in reaction mechanism [10,11]. Interestingly, the reactivity in these complexes has been dominated by triplet state in explaining the general interaction between unsaturated metal complexes and substrates. In so far as electronic multiplicity concerned, other types of organometallic complexes have been reported to undergo photochemical Si-H bond reaction activation [12].

In trimethylsilane, both of C-H and Si-H bond activation are possible, even though it is generally accepted that the Si-H bond activation is the more stable final product. Many studies have been conducted to explaining the reaction mechanism pathway. The interaction between metal fragments and solvent molecules may take place both intermolecularly [13] and/or intramolecularly [14]. Different mode of reaction mechanism has also been proposed in explaining the activation of Si-H bond in these molecules [15]. For this reason a theoretical study was needed to clarify which mode of reaction mechanism is more plausible.

Results and Discussion

Photolysis of HB(Pz*)Rh(CO): were carried out in n-pentane containing 0.05 M EtSiH as well as in neat EtSiH at room temperature, and the progress of the reactions were monitored by UV-visible and FTIR spectroscopy. Figure 1 shows absorption band of dicarbonyl, centered at 356 nm, steadily decreases in intensity upon photolysis. Table 1 represents the same experiment that reveals the progressive decline of the $\nu$(CO) at 2054 and 1980 cm$^{-1}$ of the parent dicarbonyl complex, and subsequence appearance bands at 2029 and 2020 cm$^{-1}$ of the photoproduct [4].

Table 1. Absorption spectra following 366-nm photolysis of HB(Pz*)Rh(CO): in n-pentane containing 0.05 M EtSiH at 293 K.

<table>
<thead>
<tr>
<th>UV-Visible, $\lambda_{max}$</th>
<th>FTIR of HB(Pz*):Rh (CO)$_2$</th>
<th>FTIR of HB(Pz*)Rh(CO)- Hbond(solvent, $\nu$(CO))</th>
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<tbody>
<tr>
<td>356 nm</td>
<td>2054 and 1980 cm$^{-1}$</td>
<td>2029 and 2020 cm$^{-1}$</td>
</tr>
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</table>

After the light experiment is completed the 2020 cm$^{-1}$ band stays relatively constant and even increases slightly upon standing in the dark. This behavior is in contrast with the 2029 cm$^{-1}$ peak which decreases over time, representative of a different thermal reaction. This observation raises a question whether the intensity increase of the 2020 cm$^{-1}$ band occurs unimolecularly resulting from the intramolecular rearrangement of the C-H bond activation of EtSiH or bimolecularly as a result of the elimination of the C-H bond activation of the solvent and subsequent re-addition of the Si-H bond of the EtSiH ligand. However, the 2020 cm$^{-1}$ band is not observed upon
addition of the Et₃SiH to a freshly prepared HB(Pz*)₃Rh(CO)(H)(pentyl) solution, appearing to rule out the bimolecular process.

Observation of the photolysis of the dicarbonyl complex in neat Et₃SiH apparently supports the intramolecular rearrangement pathway. In this experiment the decrease of the IR band of the parent complex followed by a new growing band at 2020 cm⁻¹ and a fluctuation of the new higher band located at 2029 cm⁻¹. The electronic absorption spectral sequences for the same photolysis reveal that the reaction is very clean, that is the smooth decline of band intensity of dicarbonyl parent complex is followed by appearance of isobestic point at the higher energy tail (see Fig. 1). Moreover, the HB(Pz*)₃Rh(CO)(H)(SiEt₃) final product is successfully isolated and its IR spectrum in n-pentane mimics the one from the in situ measurement, that is the observation of a strong sharp band at 2020 cm⁻¹.

In order to gain more insight to dynamics of the Si-H bond activation, the quantum efficiency of the Si-H bond activation is measured. It was calculated to be 0.16 at the 366 nm photolysis in neat Et₃SiH [4]. This value is about one half of the quantum efficiency of the C-H bond activation in alkane solution. It is initially somewhat surprising to observe the difference of the quantum efficiencies.

In Et₃SiH molecule, there are the C-H and Si-H bond that might be activated. The question is which one of them is more favored. Although it is generally accepted that in silanes the C-H bond is stronger than the Si-H bond [16], but the strength of these bond does not play a role in this oxidative-addition reaction as the cleavage of the bonds is not the rate-determining step. So, the bond strength difference is unlikely to be the reason for the lower quantum efficiency.

In order to support the findings of experimental studies, theoretical studies were carried out using the density functional study at B3LYP/LanL2DZ method level of theory to determine the species formed in complex intramolecular rearrangement processes. The optimized structures of complex compounds formed are depicted in Figure 2. A theoretical study showing the existence of intramolecular rearrangements as demonstrated by the Si-H bond activation product has lower energy than the C-H bond one. The product formed due to the Si-H bond activation has stability energy of -4.31 x 10⁶ kJ mol⁻¹, -3.22 x 10⁶ kJ mol⁻¹, and -2.42 x 10⁶ kJ mol⁻¹, respectively.
while the C-H activated product has stability energy of $-4.21 \times 10^4$ kJ mol$^{-1}$ (Figure 3). This result shows the lower quantum yield of Si-H bond activation is compatible with the dynamic energy level of the species.

![Figure 3. Trends in complex stability energies.](image)

**Conclusions**

Solution photolysis of rhodium dicarbonyl parent complex in triethyisilane results in Si-H bond activation product. The lower quantum efficiency of this photolysis, as compared to the C-H bond activation in alkane solution, is due to the unique route of this interaction. The reaction mechanism is preceded by solvation through C-H bond of the ethyl moiety and is followed by intramolecular rearrangement channel to produce the more thermodynamically stable Si-H bond activation species. The DFT calculations fully support the proposed mechanism.

**Experimental Section**

All reagents and procedures to synthesize HB(Pz$^*$)Rh(CO)$_2$ complex have been described in detail elsewhere [4]. In general, UV photolysis was carried out with medium-pressure 200-W mercury arc lamp using band interference filter to isolate the excitation wavelength. UV-visible spectra were recorded from solutions held in regular 1-cm quartz cuvettes. Infrared spectra were also obtained from solutions using a NaCl cell of 1-mm path length.

Computational calculations of the studied systems were obtained using density functional theory calculations. All calculations were performed using Gaussian 09 software [18]. The LanL2DZ ECP basis set was used referring to the suitability of theoretical and experimental data on the system being studied. The polarized continuum model (PCM) was used to apply the solvent system. Optimization of inhibitor structure was not carried out in solvents because it would only have a minimal effect on structural parameters and electronic energy [18-20].

**Conflict of Interest**

The authors declare that there is no conflict of interest.

**References**


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