

Mechanistic Study of Alkene Hydrosilylation Catalyzed by Phenalenyl Based Fe Complex

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by

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May, 2022

DECLARATION

I, Piyali Ray, hereby declare that this thesis titled ‘Mechanistic Study of Alkene Hydrosilylation Catalyzed by Phenalenyl Based Fe Complex’ is my own work and to the best of my knowledge, it contains no material previously published or written by any other person, or substantial proportions of material which have been accepted for the award of any other degree or diploma at IISER Kolkata or any other educational institution, except where due acknowledgement is made in the thesis.

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CERTIFICATE

This is to certify that the thesis entitled ‘Mechanistic Study of Alkene Hydrosilylation Catalyzed by Phenalenyl Based Fe Complex’ has been carried out by Ms. Piyali Ray under my supervision at IISER-Kolkata. The work presented here is original and has not been submitted so far, in part or full, for any degree or diploma of any other university/institute.



24/5/22

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ABSTRACT

Alkene hydrosilylation is an organic reaction of significant industrial interest. At present, rare heavy metal-based compounds are used as catalysts for this reaction. To reduce the production cost and the environmental impact, earth-abundant metals such as iron have been proposed to replace the heavy metals in these catalysts. But the mechanism of alkene hydrosilylation with iron-based catalysts is not well understood. In this dissertation, the catalytic cycle of polymethylhydrosiloxane (PMHS) functionalization by a recently developed $(\text{Fe}(\text{O}, \text{O-PLY})_3)$ catalyst is studied using computational methods. Electronic structure calculations based on density functional theory have uncovered the thermodynamical stability of individual intermediates and have identified the most energetically favorable pathways for the reaction. This study will provide key insight into the design and understanding of the role of iron-based organometallic catalysts in hydrosilylation reactions.

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Chapter 1

INTRODUCTION

1.1 Target Reaction:

Alkene hydrosilylation reaction is a common type of organic reaction between aliphatic or aromatic alkenes (arenes) and a silane molecule to produce functionalized silanes. This work is a part of a project aimed at developing a new reaction scheme for polymethylhydrosiloxane (PMHS) functionalization by alkene hydrosilylation reaction using an iron based homogeneous catalyst.

1.2 Why PMHS?

PMHS is a commonly used reducing agent in chemical laboratories for its excellent hydride donation capacity. Being a by-product of the silicon industry, it is inexpensive and widely available. Alkene or arene group substitution on this polymer significantly alters its physical properties, such as viscosity, density, and surface tension, and chemical properties such as solubility, chain flexibility and silicon curing process. The new polymer produced has potential for commercial application if the synthetic procedure is suitable for industrial scale. Thus, the reaction between alkene and PMHS is a significant field of research in reducing industrial chemical waste.

1.3 Catalyst for the Reaction:

There are many successful reports of alkene hydrosilylation reaction by PMHS using Co, Pt, Mn based organometallic homogeneous and heterogeneous

catalysts, and nano catalysts ^[1]. However, these metal catalysts are expensive and not ideal for large scale industrial application. Earth abundant, inexpensive iron complex catalysts are the new developments in this area. This year Aaron M. Tondreau *et. al.* ^[2]. reported an iron complex that catalyses alkene hydrosilylation by heptamethyltrisiloxane (HMTS), the monomer of PMHS, with excellent yield in gas chromatography. Now the Fe(O, O-PLY)₃ complex, previously developed by S. Chakroborty *et. al.* ^[3], is being studied as catalyst for this reaction. In this work a possible mechanism of the reaction was proposed and examined through density functional theory.

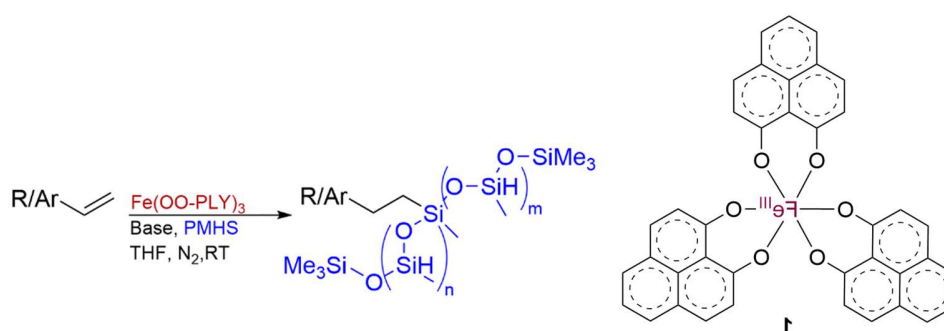


Figure 1: Reaction scheme of the experimental project and the catalyst Fe(O, O-PLY)₃ **1**

1.4 PLY Ligand:

Phenalenyl(PLY) is the three benzene ring component of graphene. It has one non-bonding molecular orbital having one unpaired electron ^[4]. It has three charge states, positively charged, neutral radical, and negatively charged. PLY can also accept or donate electron from its NBMO to another molecule without compromising its structure, thus, acting as a catalyst itself.

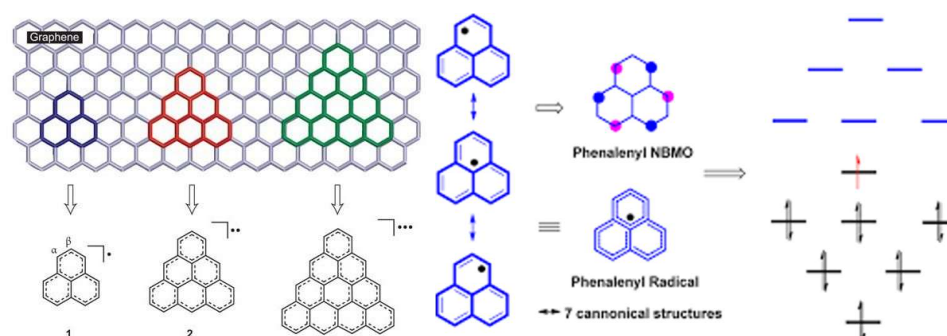


Figure 2: Structure of POLY molecule ^[4] and the distribution of the non-bonding molecular orbital on POLY ^[5].

The NBMO of POLY is distributed over the α carbons (Fig 2). heteroatomic substitution on one or more of these α carbons can tune the energy of the NBMO, modifying its reactivity towards desired substrates. 9-hydroxyphenalenone (O, O-POLY) is a catalyst of this group ^[6]. The catalytic activity of O, O-POLY takes place by accepting electron from base into its NBMO and undergoing SET to the substrate of the reaction ^[5]. A metal complex is also expected to catalyze reactions through the same mechanism. Introduction of a transition metal serves the same purpose of tweaking the NBMO energy level.

1.5 Proposed Mechanism:

A typical alkene hydrosilylation reaction by a homogeneous organometallic catalyst involves oxidative addition of the silane to the metal centre, followed by metal coordination with the alkene, hydrogen atom transfer and finally reductive elimination of the final product, hydrosilylated alkene. But our catalyst with OOPOLY ligand is expected to follow a pathway involving SET from one of the OOPOLY ligands.

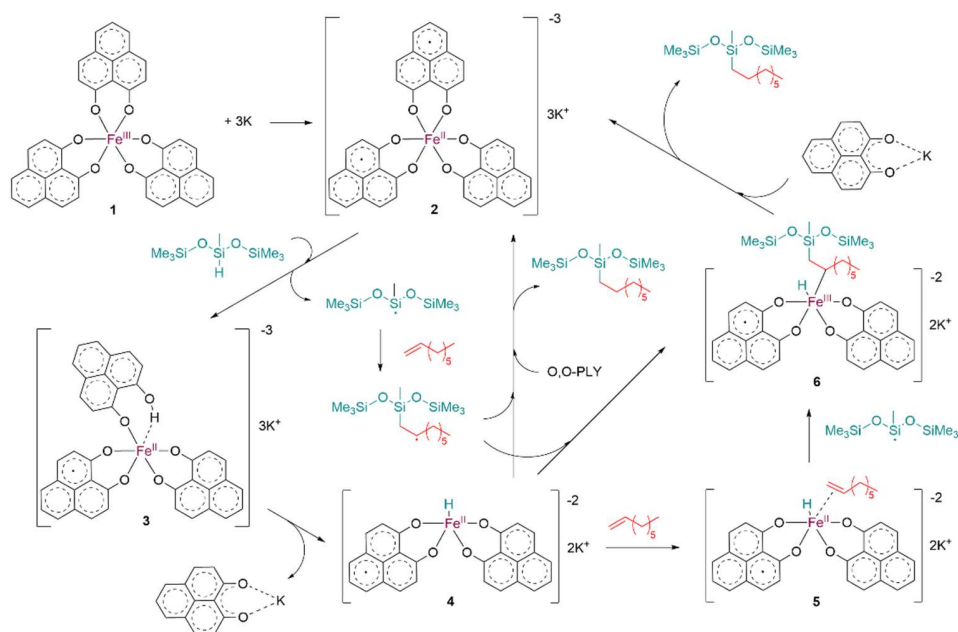


Figure 3: Proposed mechanism of the hydrosilylation reaction.

The mechanism of $\text{Fe}(\text{O},\text{O-PLY})_3$ catalyzed hydrosilylation was inspired by a similar reaction with Ni catalyst developed by Gonela Vijaykumar *et. al.* [7]. Here we propose that the catalyst **1** is reduced by metallic potassium to form the active catalyst **2**. The active catalyst then transfers one electron to HMTS causing homolytic cleavage of the Si-H bond. The silyl radical produced, undergoes anti-Markonikov selective addition to octene, one of the alkene substrates studied for this reaction. The remaining valance on carbon is fulfilled by the hydride broken from the HMTS. During this reaction the complex **2** can capture the free hydride to form complex **3**. It can also further facilitate the reaction by pi coordination with alkene to form complex **4**, which after reacting with silyl radical forms complex **5**. After hydrogen atom transfer (HAT) the complex **5** returns to complex **2** eliminating the final product alkyl siloxane.

Chapter 2

METHODS

For mechanistic study only the reaction between octene for alkene substrate and HMTS as hydrosilylating agent was considered to reduce computational cost (Fig 4). The active catalyst and the Fe complexes throughout the mechanism Fe (II) metal center. Fe (II) can be in high spin (HS) or low spin (LS) state based on the structure (Fig 5). Geometry optimization and single point energy calculations were performed for all the molecules involved in the proposed mechanism, including both high spin and low spin Fe (II) complexes, using the Gaussian09 program. These calculations were done using the B3LYP functional with LANL2Z basis set for Fe and 6-31G* basis set for other atoms. The CPCM model with LANL2Z basis set for Fe and 6-311++g** basis set was used to calculate single point energy in THF solvent.

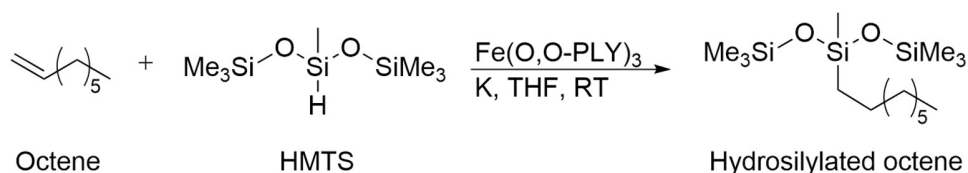


Figure 4: Reaction scheme studied in this work.

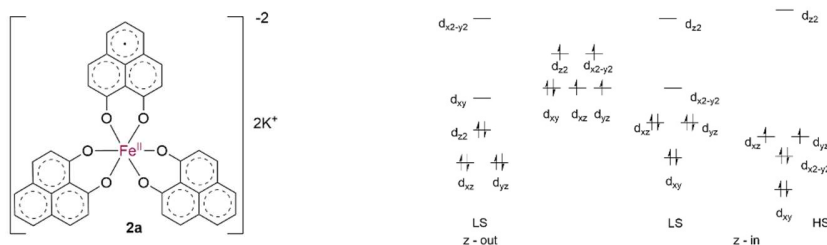


Figure 5: High spin and low spin electronic configuration of the active catalyst **2a**

Chapter 3

RESULTS & DISCUSSION

3.1 Optimized Molecules:

During the limited timespan of this work only the following molecules were successfully optimized, **1**, **2a** HS and LS, **2b** HS and LS, **3a** HS and LS, **4a** HS and LS, **5a** LS, HMTS, HMTS radical, octene, octyl HMTS radical, heptamethyl octyl trisiloxane (final product), K, K⁺, O, O-PLY, and O, O-PLY–K complex.

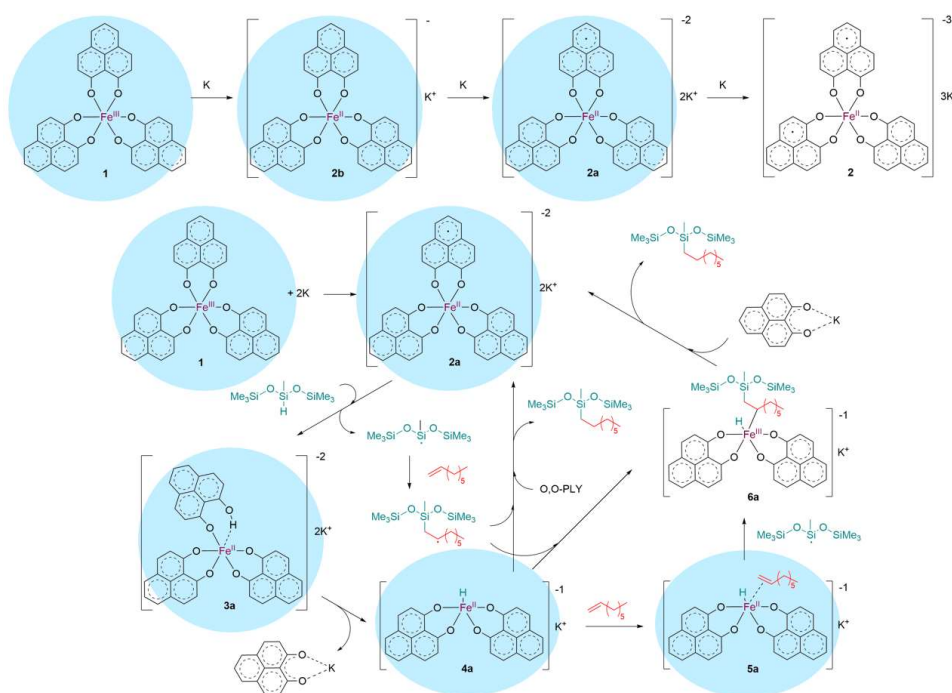


Figure 6: Molecules optimised so far presented in blue colour.

With these molecules three possible mechanistic cycles were deduced.

3.2 Mechanistic Cycle 1:

The electronic energy, enthalpy, and free energy of each step in the mechanistic cycle 1, shown in fig 7, are given in table 1.

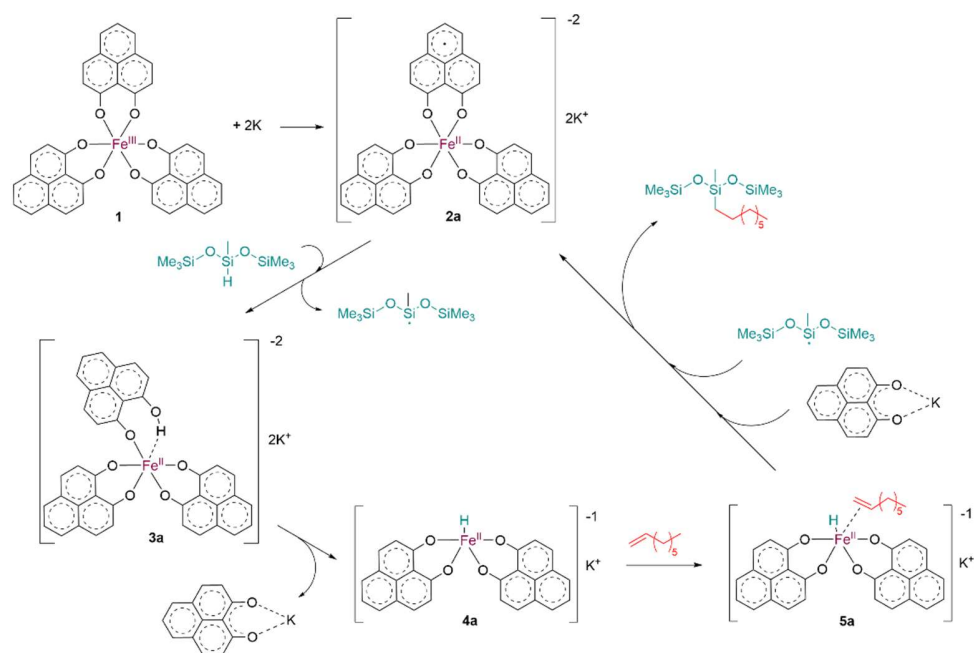


Figure 7: Mechanistic cycle 1.

Table 1: Gas phase and solvated electronic energy, enthalpy, and free energy change for all the steps in cycle 1. All energies are in kcal/mol unit.

Step	ΔE_g	ΔH_g	ΔG_g	ΔE_{sol}	ΔH_{sol}	ΔG_{sol}
1 to 2a	-12.711	-12.250	-12.798	3.859	4.320	3.771
2a to 3a	58.732	59.595	57.356	-565.167	-564.305	-566.544
3a to 4a	-54.481	-55.176	-60.699	-24.201	-24.895	-30.419
4a to 5a	-47.528	-46.727	-42.447	-4.437	-3.637	0.643
5a to 2a	16.454	16.001	30.465	80.826	80.373	94.837

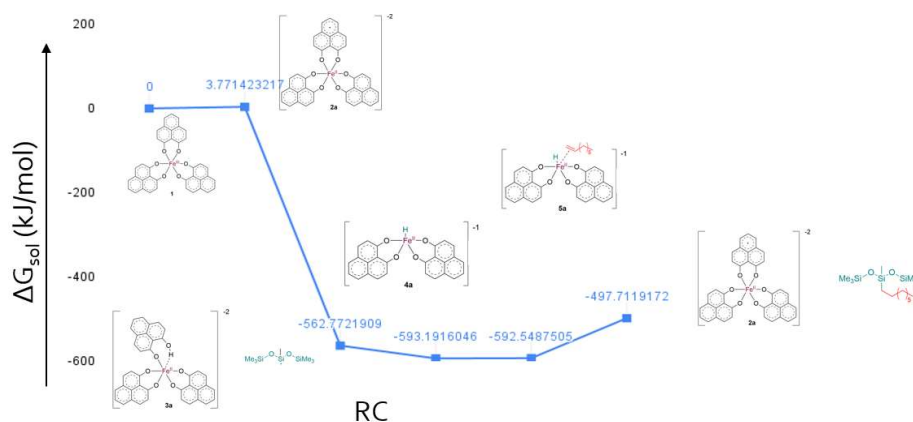


Figure 8: Free energy diagram of cycle 1.

All the Fe (II) complexes in this cycle are low spin complexes. The second step in this cycle has a big negative free energy change of -566.544 kcal/mol in THF solution. This is expected since it is a radical reaction. The free energy change in the final step of this cycle is positive and very high. So, this mechanistic cycle is not feasible for the reaction.

From the optimized geometry of **5a** LS complex it is seen that the C=C bond length of octene is 1.386Å, which is slightly higher than an uncoordinated C=C bond length of 1.348Å.

This indicates a possible weak coordination between the Fe center and octene in **5a**.

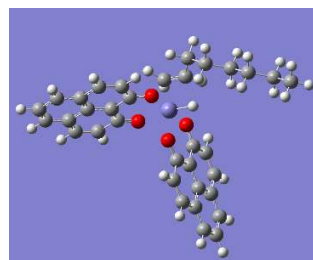


Figure 9: Optimized geometry of **5a** LS complex.

3.3 Mechanistic cycle 2:

The electronic energy, enthalpy, and free energy of each step in the mechanistic cycle 2, shown in fig 10, are given in table 2.

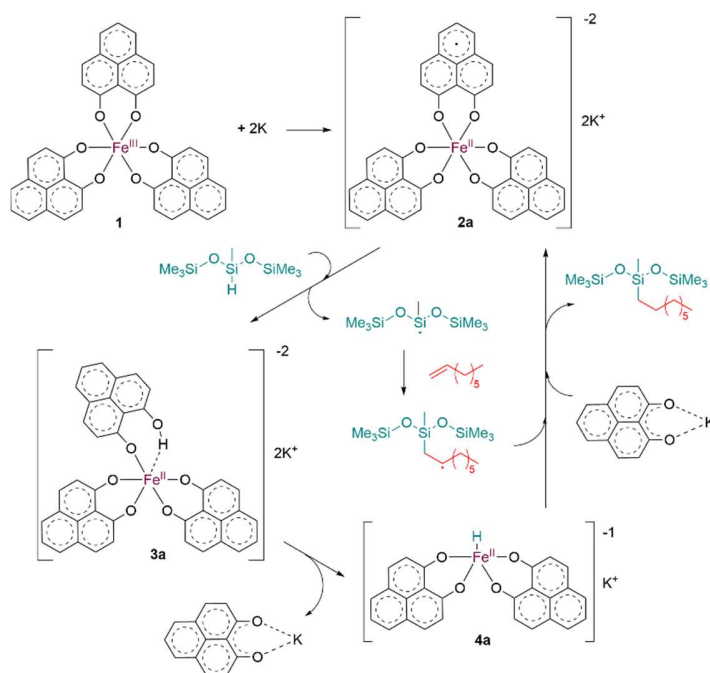


Figure 10: Mechanistic cycle 2 for LS Fe (II) and mechanistic cycle 3 for HS Fe (II).

Table 2: Gas phase and solvated electronic energy, enthalpy, and free energy change for all the steps in cycle 2. All energies are in kcal/mol unit.

Step	ΔE_g	ΔH_g	ΔG_g	ΔE_{sol}	ΔH_{sol}	ΔG_{sol}
1 to 2a	-12.711	-12.250	-12.798	3.859	4.320	3.771
2a to 3a	58.732	59.595	57.356	-565.167	-564.305	-566.544
3a to 4a	-54.481	-55.176	-60.699	-24.201	-24.895	-30.419
4a to 2a	-13.021	-12.802	-6.177	96.876	97.095	103.720

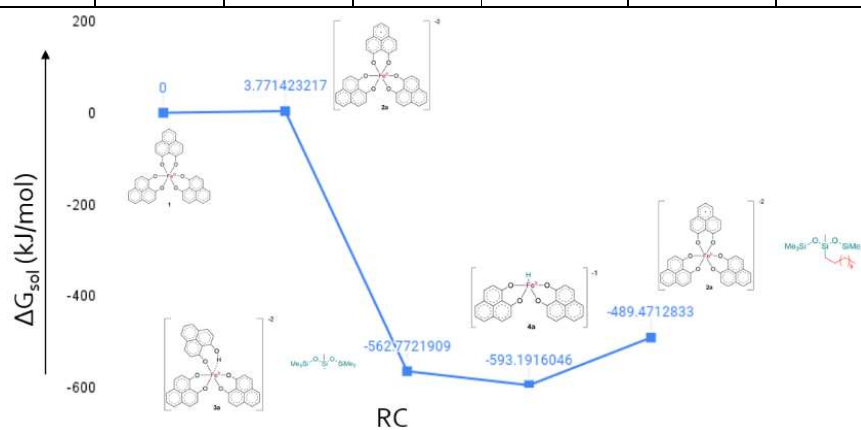


Figure 11: Free energy diagram of cycle 2.

All the Fe (II) complexes in this cycle are low spin complexes. The second step in this cycle is also highly stabilized as it is a radical reaction. The free energy change in the final step of this cycle is also positive and very high. So, this mechanistic cycle is not feasible as well for the reaction.

3.4 Mechanistic Cycle 3:

This mechanistic cycle is the same as cycle 2 but the Fe (II) complexes in cycle3 are high spin in nature. The electronic energy, enthalpy, and free energy of each step in cycle 3, shown in fig 10, are given in table 3.

Table 3: Gas phase and solvated electronic energy, enthalpy, and free energy change for all the steps in cycle 3. All energies are in kcal/mol unit.

Step	ΔE_g	ΔH_g	ΔG_g	ΔE_{sol}	ΔH_{sol}	ΔG_{sol}
1 to 2a	2.481	2.100	5.468	-113.903	-114.284	-110.916
2a to 3a	41.295	42.282	38.909	-438.038	-437.052	-440.424
3a to 4a	-58.440	-58.872	-64.933	-34.944	-35.376	-41.436
4a to 2a	8.375	8.208	16.503	-19.510	-19.677	-11.382

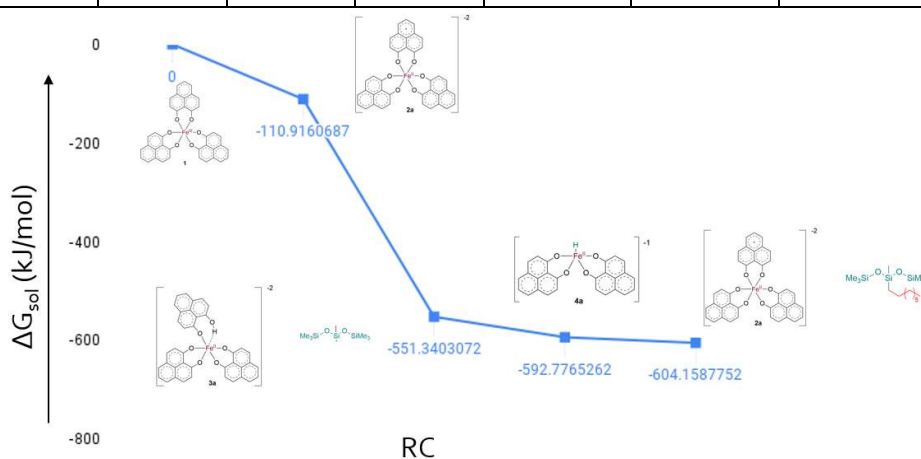


Figure 12: : Free energy diagram of cycle 3.

All the steps in cycle 3 have negative free energy difference. So, mechanistic cycle 3 is a possible pathway for target hydrosilylation reaction.

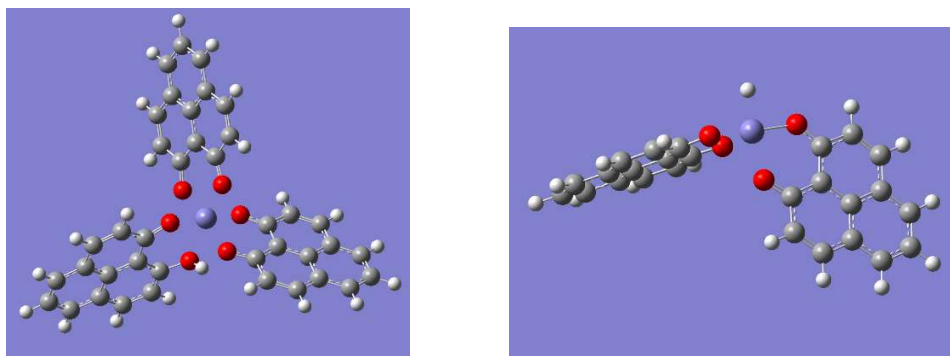


Figure 13: Optimized geometry of complexes **3a** HS (left), and **4a** HS (right)

From the optimized geometry of **3a** it is observed that the O – H bond length is 0.9997Å, slightly higher than that of free O, O-PLY (0.974Å) and C – O bond length is 1.387Å, slightly higher than that of phenol (1.36Å). Also, the Fe – H bond length is 2.186Å, whereas a typical terminal Fe – H bond length ranges from 1.5Å to 1.8Å. However, the optimized geometry of **4a** shows a Fe – H bond length of 1.586 Å, well within the normal range. This indicates that in the hydride abstraction step of cycle 3, one of the O, O-PLY ligands take the hydride from HMTS to form complex **3a** and HMTS radical. Only after ligand dissociation in the following step a terminal hydride is formed in complex **4a**.

3.5 Active Catalyst SOMO:

The active catalyst **2a** has three singly occupied molecular orbitals (SOMO). SOMO 1 is delocalized mostly on only one of the ligands and the Fe metal center but both SOMO 2 and SOMO 3 are delocalized over all three ligands and metal center. Therefore, the radical in the active catalyst is present in SOMO 1

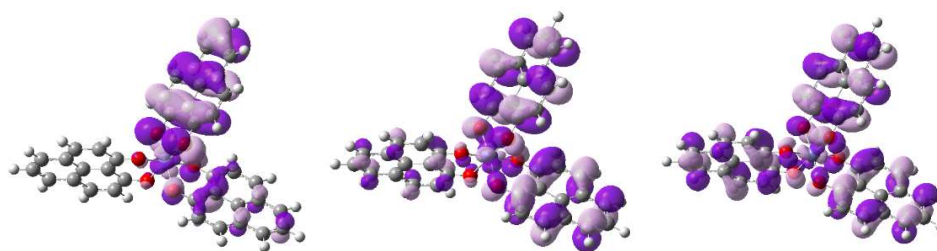


Figure 14: Orbital visualisation for active catalyst **2a**: SOMO 1, SOMO 2, and SOMO 3 respectively.

Chapter 4

CONCLUSION

Finally, from this work it is established that the hydrosilylation reaction of octene by HMTS using $\text{Fe}(\text{O}, \text{O-PLY})_3$ catalyst can go via mechanistic cycle 3, where high spin Fe complex **2a** is the active catalyst.

It is also shown that the Fe (II) complexes in this reaction mechanism with high spin configuration are more favorable than low spin.

Chapter 5

LIMITATION & FUTURE DIRECTION

The active catalyst for the target reaction is more likely to be complex **2** having two radicals in two O, O-PLY ligands instead of complex **2a**. So, calculations should be performed for all the molecules involved in the mechanistic cycle starting with active catalyst **2**. The cycles starting with active catalyst **2a** should be completed with calculations for **5a** HS, and **6a** HS and LS complexes. The possible contribution of K throughout the mechanistic cycle and the solvent THF should also be calculated with explicit models.

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