齊魯工業大學（山东省科学院）
QILU UNIVERSITY OF TECHNOLOGY SHANDONG ACADEMY OF SCIENCES

本科毕业设计（论文）

题目： A Theory Study on the Mechanism of Hydrosilylation
硅氢加成机理的理论研究

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Contents

Abstract

Hydrosilylation is a common method to synthesize new Si - C bonds in organic silicon industry. Platinum catalyst is the most commonly used catalyst in hydrosilylation. Although the comprehensive performance of platinum catalyst is suitable for industrial application, there are also problems such as low catalytic selectivity, many by-products and serious platinum pollution. Therefore, the improvement of platinum catalytic technology is popular study. In this experiment, platinum complex catalysts and intermediates in the hydrosilylation reaction mechanism were explored based on density functional theory. The coordination addition mechanism (Chalk-Harrod mechanism, Lewis's mechanism, etc.), ion addition mechanism, radical addition mechanism and photocatalytic mechanism were summarized. The basic contents of density functional theory were briefly introduced. Since the insertion of ligands can reduce the generation of platinum-containing intermediates, the experimental part is based on thermodynamic stability and combined with the Chalk-Harrod mechanism to explore the relatively stable platinum intermediate configuration in the addition reaction process, which provides a theoretical basis for the design of high-selection and low-cost platinum catalysts. Due to time reasons, this paper only studied the oxidative addition reaction between platinum complex catalyst and silicon hydrogen bond.

Key words: hydrosilylation reaction; platinum catalyst; catalytic mechanism

摘　要

硅氢加成反应是有机硅工业合成新 Si—C 键的常用方法。铂催化剂是硅氢加成反应最常用催化剂。尽管铂催化剂的综合性能比较适合工业应用，但是，也存在催化选择性不高，副产物多，铂污染严重等问题。因此，铂催化技术的改进是热门研究。本实验基于密度泛函理论对硅氢加成反应机理中铂络合物催化剂与中间体进行探究，总结了配位加成机理（Chalk-Harrod 机理、Lewis 机理等）、离子加成机理、自由基加成机理与光催化机理，浅要介绍了密度泛函理论的基本内容。由于配体插入的途径可以减少生成含铂中间体，实验部分基于热力学稳定性并与 Chalk-Harrod 机理相结合，来探究加成反应过程存在的相对稳定的铂中间体构型，为高选择低成本铂催化剂的设计提供理论依据。由于时间原因，本课题只研究了铂络合物催化剂与硅氢键的氧化加成反应。

关键词：硅氢加成反应　铂催化剂　催化机理

Introduction

Hydrosilylation, also known as hydrazination, is one of the most useful catalytic reactions leading to the formation of organ silanes and organosilicons, which have a variety of applications in industry and as intermediates in organic chemistry. Hydrosilylation occurs via the addition of H-Si to an unsaturated bond such as carbon-carbon bond, carbon-oxygen bond, carbon-nitrogen bond, nitrogen-nitrogen bond and nitrogen-oxygen bond using a metal catalyst, Lewis Acid, or radical initiator.[1]

With the development of organic carbon chemistry and the emergence of SiF_4, $SiCl_4$ and SiH_4, the interest in an in-depth study of silicon in the same master group as carbon has been greatly stimulated, so as to obtain new silicon materials similar to carbon chemistry. Therefore, chemists began to explore pure silicon chemistry and silicon-carbon binding chemistry. Nowadays, there are many kinds of organic silicon compounds and their organic silicon materials with excellent performance, which have been widely used in industrial and agricultural production, emerging technologies, national defense and military industry, medical and health, and people's daily life. Organic silicon products have become one of the fastest-growing varieties of new chemical materials, and are indispensable chemical materials for society and people to develop production and improve life.[2]

Due to the small electronegativity of Si, there are still some ionization components when the covalent bond is formed. Therefore, the polarization form of $Si^{\delta+}$-$Y^{\delta-}$ (Y =. H, C, Cl, F, etc.) can be taken on the side of the shared electron pair that is biased towards the elements with larger electronegativity than Si. This is the reason why many organic silicon compounds can react with both free radicals and ions.[3]

Compared with other methods for the synthesis of organic silane, hydrosilylation can synthesize the most abundant products, and has the advantages of mild reaction, easy control, fewer side reactions, and pure products. Therefore, hydrosilylation is the most studied and widely used reaction in organic silicon chemistry. For more than sixty years, the hydrosilylation of C-C and carbon-heteroatom multiple bonds has been widely studied not only in the laboratory but also in industrial production. [3] It is necessary to study the catalytic mechanism of hydrosilylation reaction for further searching for high activity, low cost and reusable catalysts.

The preparation and research of its catalyst is also the focus and hot spot in the field of hydrosilylation, especially the preparation and research of anti-poisoning catalyst, which is of great significance to reduce the activation energy of hydrosilylation, promote the reaction and improve the selectivity of products. Transition metal complexes (such as platinum, palladium, ruthenium, rhodium, iron, cobalt, nickel, copper, silver, gold, tungsten, molybdenum, actinides and lanthanide metals) can be used as catalysts for hydrosilylation. [4] For example, $[PtCl_2(C_2H_4)]_2$, $[C_2H_4]_2RhCl]_2$, $RhCL(PPh_3)_3$, $Co_2(Co)_8$ and $Pd(PPh_3)_4$.[15] However, due to the different metal cation centers and metal oxide structure, the catalytic activity is also different, and some varieties of selectivity are not high, resulting in the hydrogenation of unsaturated bonds prone to self-polymerization and other side reactions, the application is greatly limited. At present, hydrosilylation catalysts are mainly developed in the direction of high stability, high catalytic activity, high product selectivity and low cost. Compared with other transition metal complexes, platinum complexes have become the most widely used transition metal catalysts due to their wide source of raw materials, high catalytic activity, high selectivity and obvious catalytic effect. [5] This paper introduces the catalytic mechanism and research progress of platinum complex catalysts for hydrosilylation.

The platinum catalyst is currently the most commonly used catalyst for hydrosilylation and has been widely studied. Hydrosilylation, as one of the most important ways to synthesize organic silicon compounds, has become a research hotspot and difficulty. Since Sommer et al. found the hydrosilylation reaction, a large number of literatures have reported it. [6] Pt and other metals and their salts as catalysts for hydrosilylation were first mentioned in some patents. Wagner first carried out a detailed study on Pt as a catalyst.[7] In 1957, Speier et al. found that chloroplatinic acid($H_2PtCl_6 \cdot 6H_2O$) catalyst, i.e., isopropyl alcohol solution of chloroplatinic acid, had high catalytic activity and catalytic effect on hydrosilylation.[8] However, it has the disadvantages of a large amount of catalyst, low catalytic selectivity, small catalytic range, and chlorine generation in the synthesis process. In 1973, Karstedt found a platinum-based vinyl siloxane complex with high catalytic activity, namely the Karstedt catalyst.[9] Compared with the Speier catalyst, it has better catalytic activity, less dosage, wider application range, and no chlorine production in the synthesis process. However, both of them have the disadvantages of difficult recovery, high cost, difficult control of catalysis, and poor catalytic selectivity, resulting in a serious platinum loss in the industry. With the increasing scarcity of resources, recyclable supported platinum catalysts will become an important new field in the study of hydrosilylation. [10-13] The supported platinum catalyst has the advantages of being recyclable, low cost and good catalytic selectivity. It can be separated by filtration and centrifugation after catalytic reaction, and can be used repeatedly. The amount of supported catalyst is generally relatively small and the number of repeated uses is more, which significantly reduces the cost. The catalytic activity points can be directly contacted with the reactants and can be directly catalyzed, with relatively good catalytic selectivity. At present, inorganic-supported platinum catalysts are the most widely studied. Organic catalysts supported liquid platinum catalysts and other new catalysts have also been reported.[14]

Chiral secondary alcohols can be directly synthesized by hydrosilylation of ketones, in which transition metal complexes are used to catalyze the formation of silyl compounds to protect alcohols. Compared with traditional catalysts, transition metal complexes are more efficient and selective, so the hydrosilylation of carbonyl compounds catalyzed by transition metal complexes has played an important role in the field of hydrogenation. Transition metal complexes as catalysts for hydrosilylation have also attracted the attention of many researchers.[15]

Chapter 1 Hydrosilylation reaction mechanism

Since the discovery of hydrosilylation, there have been many studies on its reaction mechanism, mainly focusing on the platinum catalytic mechanism. The platinum-catalyzed hydrosilylation mechanism mainly includes coordination addition mechanism, nucleophilic–electrophilic catalysis mechanism, free-radical addition mechanism and photocatalytic addition mechanism.

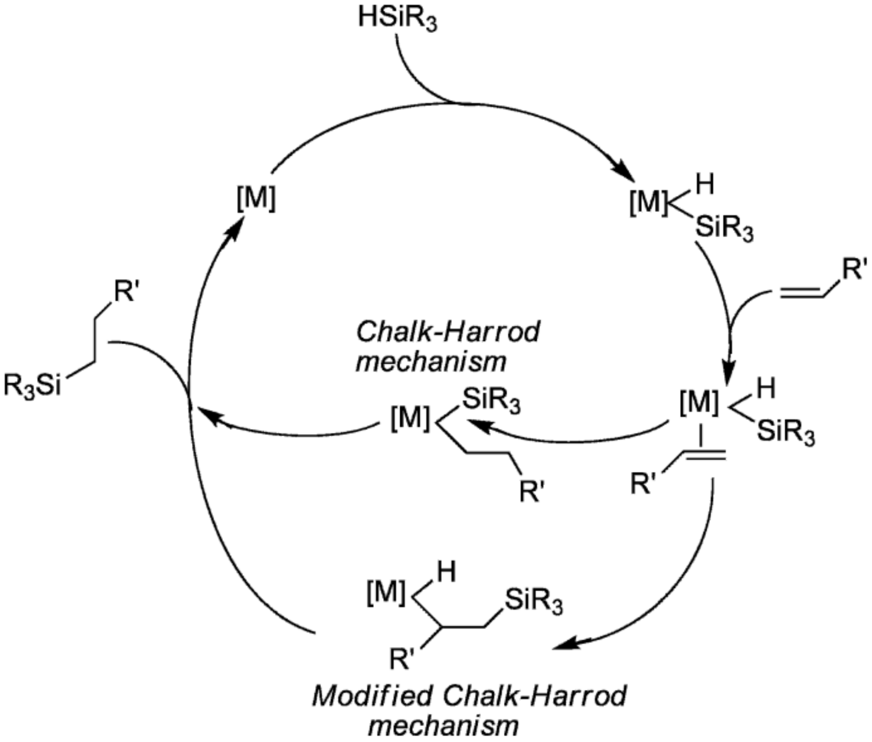
1.1 Coordination addition mechanism

In recent years, with the further study of hydrosilylation reaction, the research of its catalyst has also made some progress. Platinum and its complexes are currently the most widely used and only industrial catalyst in hydrosilylation. Therefore, the coordination addition mechanism has been studied most deeply and controversially, and it is also a widely accepted catalytic theory by researchers. There are generally three recognized mechanisms: Chalk-Harrod mechanism and its correction mechanism, silicon-based migration mechanism and colloidal platinum mechanism. It is generally believed that the catalytic system formed by transition metals and their complexes belongs to the category of coordination addition mechanism.[15]

1.1.1 Chalk-Harrod mechanism

In 1965, Chalk and Harrod studied the hydrosilylation and isomerization of dilute hydrocarbons catalyzed by transition metal complexes Pt (II) and Rh (I), and proposed the hydrosilylation mechanism of dilute hydrocarbons catalyzed by transition metal complexes. [16] The reaction mechanism is shown in four steps: (1) Si-H bond in silane attacks the central metal atom, and the oxidation addition reaction occurs to generate metal oxides; (2) Dilute hydrocarbons attack metal hydrides and coordinate to central metal atoms to form transition metal-olefin complexes; (3) The coordinated olefin molecules were transferred into the metal-hydrogen (Me-H) bond and reduced to alkyl-metal compounds. This step is the rate-determining step; (4) Reductive elimination reaction occurred to generate hydrosilylation products and regenerated catalysts.

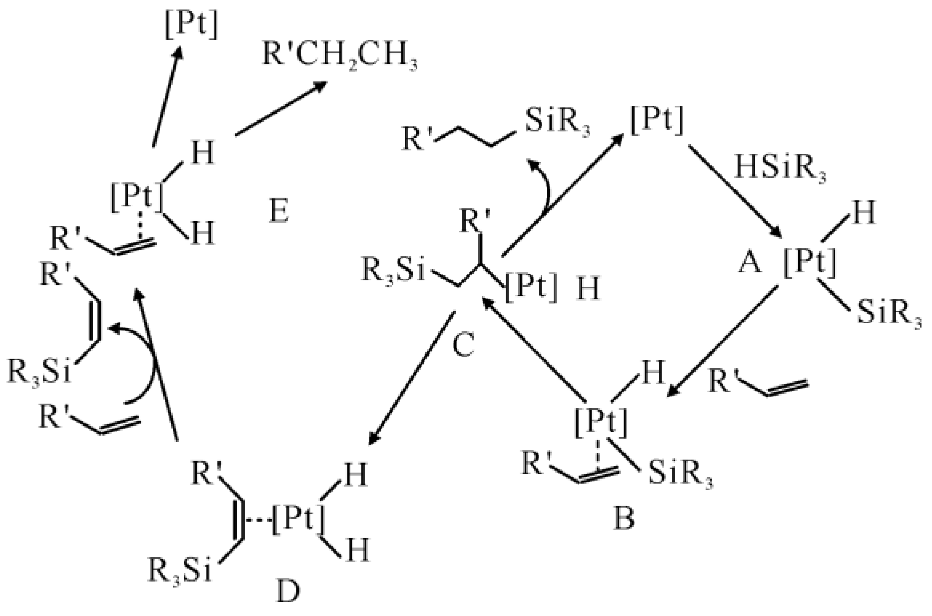
Although this mechanism was proposed based on the study of transition metal Pt and Rh, it provided a basis for the study of other transition metal complexes catalysts.



Scheme 1.1 Chalk-Harrod mechanism for hydrosilylation of olefins catalyzed by late transition metal complexes

In the subsequent Chalk-Harrod improvement mechanism (Scheme 1.1),[17] the migration and insertion of olefins changed from the previous metal hydrogen (Me-H) bond to the metal silicon (Me-Si) bond, and this step was the rate-determining step. After that, many researchers have carried out detailed and in-depth studies on this mechanism. Through the analysis of the research results, they agree that the rate-determining step of the hydrosilylation of olefins catalyzed by transition metals is the migration and insertion of olefin molecules. [18-22] However, the Chalk-Harrod mechanism cannot well explain the experimental phenomena that can be observed in the hydrosilylation of olefins, such as the formation of unsaturated silicone compounds such as vinyl silane in the experiment.

1.1.2 Silyl Migration Mechanism

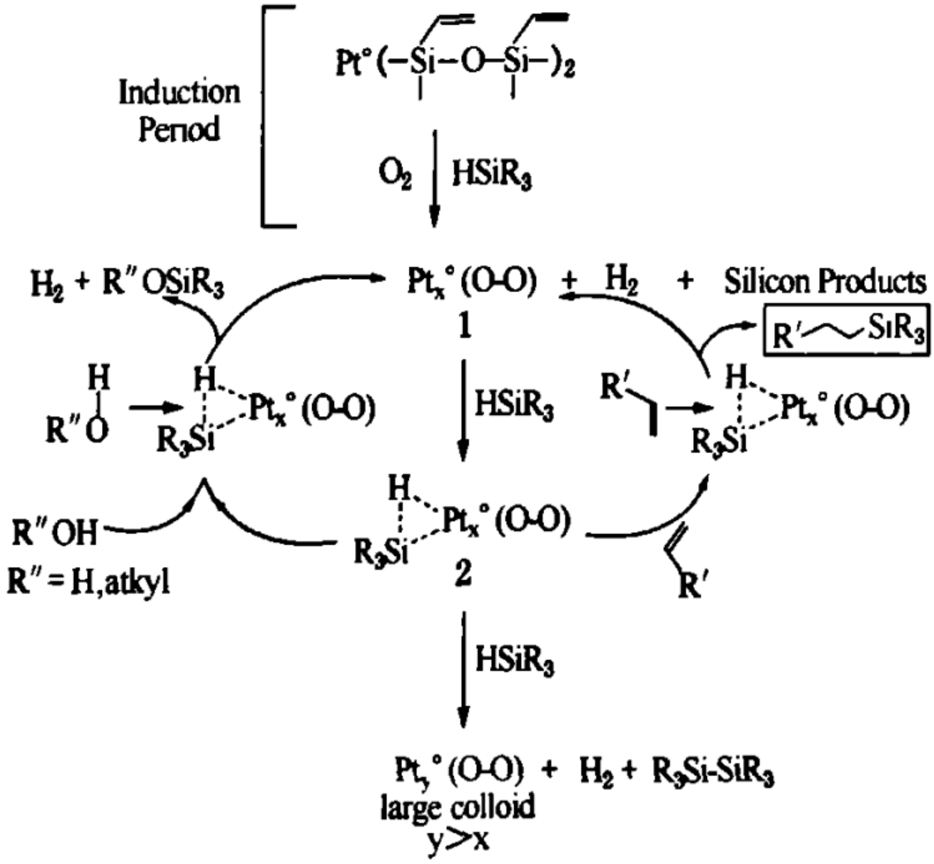


Scheme 1.2 Silicon Migration Mechanism

There are few studies on the mechanism of silicon migration, which mainly provides a theoretical basis for hydro olefins, vinyl silanes and other silane by-products in hydrosilylation reactions. The mechanism of silicon-based migration (Scheme 1.2) [23] can be described as : the platinum active center coordinates with hydrogenated silane to form intermediate A ; intermediate A and unsaturated hydrocarbon generate complex B ; then the transition state C was obtained by the migration of complex B through silicon ; transition state C can react in two different ways : one is dehydrogenation to obtain the target product; the other is that after the formation of intermediate D, the hydrosilylation product of olefins is removed and the olefins are coordinated to form hydro olefin complex E. Finally, the removal of alkanes is completed to obtain platinum active center to complete a catalytic cycle. [24] Many researchers directly attributed the silicon migration mechanism to Chalk-Harrod correction mechanism, but the theoretical depth and mechanism explanation of the silicon migration mechanism are deeper and more comprehensive than the Chalk-Harrod correction mechanism. It can also be seen as the further deepening of Chalk-Harrod correction mechanism. In 1993, M. Brookhart et al. studied the migration path of silicon, providing direct evidence for the migration mechanism of silicon.[23]

1.1.3 Lewis Mechanism

Pt (0) complex is an effective catalyst, but it must be reduced to Pt (0) after an induction period. Characteristic yellow phenomenon in catalytic process; the necessity of O_2 in the reaction process and the phenomena and theories such as the catalytic mechanism of Karstedt platinum complex,[24] which is widely used in the market, cannot be explained by Chalk-Harrod mechanism and its correction mechanism,[25] which promotes the proposal of colloidal platinum mechanism.



Scheme 1.3 Mechanism of metal colloid proposed by Lewis et al

In 1986, Lewis et al. conducted in-depth study on hydrosilylation, observed the liquid after hydrosilylation by transmission electron microscopy, and found the existence of colloidal platinum. Further light scattering and photoelectron spectroscopy tests confirmed and proposed the mechanism of colloidal platinum.[26] This mechanism can well explain the above phenomena and theories. Taking Karstedt catalyst as an example, the reaction process is shown in Scheme 1.3.

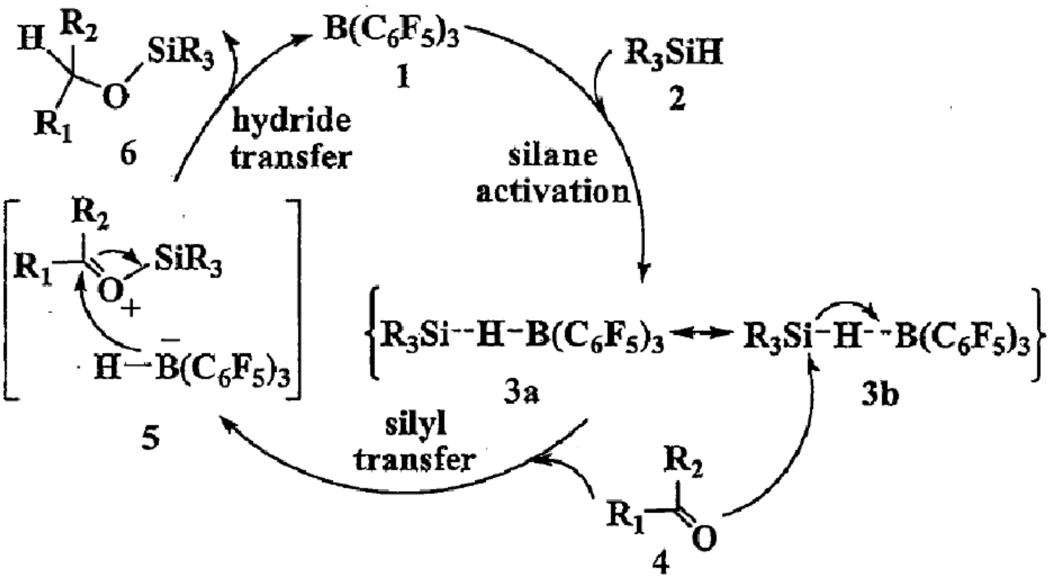
Firstly, the platinum-gold complexes were first reduced to colloidal platinum (1) by HSiR3 during the induction period, and then generated silane and H2. Then HSiR3 was adsorbed on colloidal platinum (1) to form an electrophilic complex (2); then the nucleophilic unsaturated hydrocarbon adsorbed on the complex (2) to form a transition state; the addition product separates from the transition state and resumes colloidal platinum (1) for the next catalytic process.

The mechanism of colloidal platinum explains the role of O_2 as a co-initiator: firstly, aggregation will reduce the reactivity, O_2 can prevent the aggregation of colloidal particles, thereby increasing the electrophilicity of colloidal platinum, unsaturated hydrocarbons are easier to attack. In addition, O_2 can also have weak ligand effect; as for the appearance of characteristic yellow, colloidal platinum is produced during the catalytic process, which is yellow. The higher the molar mass and content of colloidal platinum, the deeper the color of colloid. In addition, the colloidal platinum theory also explains that there is no water in the reaction process system because the nucleophilic water or alcohol can also cooperate with the electrophilic complex (2) to generate by-products.[25,27] In 2017, Kuciński et al. found that the use of colloidal platinum mechanism can well explain the preparation of new bifunctional organosilicon dendritic macromolecules by hydrosilylation, and the functionalized carbosilane dendritic macromolecules (such as $OSiMe_3$, Cl, F and COOCR) can be well maintained, and various functionalized organosilicon materials can be obtained by further reaction of functional groups.[28]

Colloidal platinum mechanism, Chalk-Harrod mechanism and its correction mechanism are two coexist mechanisms, which can explain some experimental phenomena and theories in hydrosilylation. They constitute the two most recognized mechanisms of hydrosilylation. Platinum-gold catalysts are first formed electrophilic complexes with one reagent, and then attacked by another reagent. However, the mechanism of colloidal platinum is completely different. The mechanism of colloidal platinum is that the catalyst is first coordinated with hydrogenated silane to form intermediate complexes, and then the intermediate complexes are attacked by unsaturated hydrocarbons to obtain addition products. However, the Chalk-Harrod mechanism and its correction mechanism are opposite. The catalyst first coordinates with unsaturated hydrocarbons to form intermediate complexes, and then attacks the intermediate complexes by hydro silane to obtain the addition products.[2] When platinum-gold catalyst is low-valent and non-strong coordination catalyst, it is mainly carried out according to colloidal platinum mechanism, represented by Karstedt catalyst; on the contrary, it is mainly based on the Chalk-Harrod mechanism and its correction mechanism, represented by the Speier catalyst. It is generally believed that the catalytic mechanism of polymer-supported platinum catalyst basically follows the Chalk-Harrod mechanism and its correction mechanism.

1.2 Nucleophilic–Electrophilic Catalysis Mechanism

In the 1960s, J. L. Speier et al. found that the electrophilic addition reaction of unsaturated hydrocarbons was similar to the hydrosilylation reaction, and Si-H showed a similar polarization form of Lewis acid. However, this analogy did not introduce platinum catalyst, let alone the efficient activity of the catalyst. [29-30] For general electrophilic – nucleophilic reactions, Lewis's acid electrophilic catalysts are usually added. These catalysts include metal salts (such as $AlCl_3$, $ZnCl_2$, $NiCl_2$, KF, etc.) and non-metallic compounds (such as BF_3, Et_2O, etc.), which can catalyze the hydrosilylation of C=O and C=N without the coordination of alkali. [31]



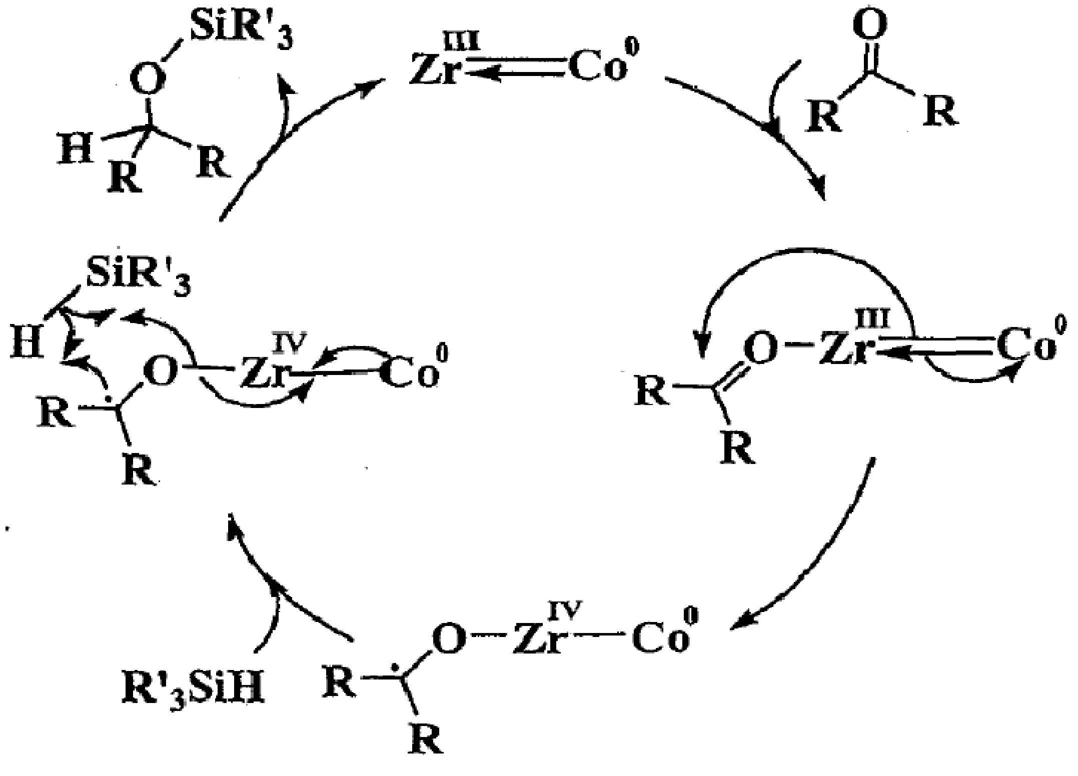
Scheme 1.4 The catalytic cycle of $B(C_6F_5)_3$-catalyzed bydrosilylation of carbonyl compounds.

J. M. Blackwell et al. proposed Lewis's acid catalyzed ionic addition mechanism of C=O compounds in 2003, 2010 and 2015, respectively. They all used $B(C_6F_5)_3$ as catalyst for the preparation of polysiloxane. Through the analysis and comparison of experimental process and results, the addition mechanism was proposed, as shown in scheme 1.4.[15,31] It mainly includes three reaction processes: first, catalyst $B(C_6F_5)_3$ is coordinated with hydro silane to generate two resonant structures 3a and 3b ; then the silane group ($-SiR_3$) approached the O atom on C=O, and the H atom approached the catalyst $B(C_6F_5)_3$ to form the ion pair intermediate 5 ; finally, the H atom was transferred to the C atom on C=O to form the product containing ether silane and release catalyst $B(C_6F_5)_3$, and the next cycle was continued. [32-34]

In 2017, K. Kucinski et al. studied the C=N hydrosilylation of benzothiazoles catalyzed by transition metal ruthenium complexes. Through NMR analysis and calculation, the anionic ruthenium complex $[H_3Ru_4(CO)_{12}]^-$ and the resonant state $[H_4Ru_4(CO)_{11}(SiR_3)]^-$ containing silane R_3SiH complex were obtained. Finally, the addition of benzotriazole was obtained by ion addition mechanism. [35]

1.3 Free-Radical Initiated Mechanism

The Si-H bond energy of silane molecules containing H is relatively low, so the silane molecules containing H are prone to free radical reactions under the conditions of high temperature or super oxidant.[36-37] The free radical addition mechanism of cinnhydration reaction includes two steps: (1) The free radicals are generated by the silane molecules containing H under the action of high temperature or super oxidant; (2) The generated free radicals initiate unsaturated hydrocarbons, which are added to form products and realize carbon chain transfer. This reaction selectivity is low, there will be a lot of by-products, so the researchers for free radical addition reaction research is less.



Scheme 1.5 Schematic diagram proposed by Thomas.

In 2013, Thomas team studied the hydrosilylation of carbonyl compounds catalyzed by transition metal Co, Zr bimetallic complexes. [38] Through quantitative calculation, they found that the bimetallic complexes did not react with phenyl silane ($PhSiH_3$) first, but with phenyl propanone ($PhCOC_2H_5$) to generate free radicals, and then reacted. According to the stoichiometric reaction and isotope labeling methods used by Thomas group, they proposed the possible mechanism of this reaction, as shown in scheme 1.5. The mechanism includes three steps: (1) phenyl propanone is coordinated to the central metal Zr through the carbonyl O atom; (2) Electrons migrate from metal Zr to phenyl propanone to form free radical intermediates; (3) Reduction elimination, the final product of silicon ether, and regeneration catalyst.

1.4 Photo-Initiated Catalysis Mechanism

In recent years, with the proposal and development of photo-curing technology and 3D printing technology, more and more attention has been paid to environmental protection, energy saving and rapid curing. Scientific researchers have gradually focused on the research direction of photo-curing silicone materials. The study of photocatalytic platinum catalyst and its mechanism is very meaningful.

As early as 1992, Boardman proposed cyclopentadiene trialkyl platinum (IV) complex as UV photocatalyst to catalyze UV-curing silicone rubber system. UV-curing could be realized after small-size substrate packaging and line substrate coating, but its catalytic mechanism was not proposed.[39] In 1996, D. C. Neckers et al. studied the catalytic effect of di (acetylacetone) platinum (II) ($Pt(acac)_2$), and proposed the catalytic mechanism of photocatalytic hydrosilylation reaction. The mechanism showed that $Pt(acac)_2$ was not active under dark conditions, but formed a highly active catalyst under near UV light or UV light irradiation. After activation, Lewis colloidal platinum mechanism was used for reference. After photoactivation, there is no need for inert gas protection, and the dissolved air in the raw material has no effect. The subsequent hydrosilylation of Si-H with unsaturated hydrocarbons can be catalyzed sustainably and rapidly. [40-41] In 2013, M. Sangermano et al. studied the thermal catalysis and photocatalysis of $Pt(acac)_2$. It was found that the UV photocuring catalysis of $Pt(acac)_2$ was carried out on the surface of the sample and generated heat. The homogeneous catalyst activated by the catalyst was transformed into Pt (0) heterogeneous catalyst, and the catalytic mechanism of thermal curing of $Pt(acac)_2$ was carried out. The inactivity of $Pt(acac)_2$ under dark conditions was explained by the oxidation-reduction mechanism. [41-42]

Chapter 2 Density functional theory (DFT)

Density functional theory (DFT) is a method to study the electronic structure in multi-electron system. It is pointed out that the density distribution of electrons can determine all the properties of molecules, and the system energy is a functional of the electron density. The main purpose is to take the electron density as the basic quantity of the study rather than the wave function. [43-45] The density functional theory Kohn was proposed based on the electron density distribution (Hohenberg-Kohn (HK) theorem) in 1964. The wave function of the multi-electron system has three times the number of electrons, namely 3N variables, and each electron has three spatial variables in different directions. The variable of electron density is much simpler than the variable of wave function, and it has only three variables. Such substitution can greatly simplify the complexity of the calculation system, and can be more convenient to deal with problems both conceptually and practically.

Density functional theory commonly used methods are B3LYP and B3P86, etc., which are two commonly used hybrid functional forms. Common basis set groups are 6-31G*, 6-311, etc. Guassian09 is a commonly used calculation software for density functional theory.

Chapter 3 Mechanism of reduction elimination of three Pt-catalyst

3.1 Theoretical

Organic chemistry is an important branch of chemistry, which mainly studies the properties, structures, reactions and synthesis of organic materials. With the development of science and technology, the methods of chemical synthesis also have greatly changed, and chemists can synthesize bioactive molecules, polymers and rare natural products through different chemical methods and catalysts. Among the types of catalysts, transition metal complexes are commonly used in organic synthesis reactions based on their high catalytic efficiency. In subsequent studies, chemists were surprised to find that transition metal complexes as catalysts showed many advantages in many organic synthesis reactions. For example, it can simplify the synthesis steps, improve the selectivity of the reaction and appropriately reduce the reaction cost. These advantages make transition metal complexes a hot catalyst. Therefore, in recent years, the focus of international chemistry research began to shift to transition metal complexes catalysts, such as how to prepare transition metal complexes with high catalytic activity, how to detect the catalytic performance of transition metal complexes and its intrinsic catalytic mechanism. However, due to the lack of research on the catalytic mechanism of transition metal complexes, how synthesizing simple and efficient transition metal complexes catalysts is still a problem.

In order to solve this difficulty, researchers have tried to use various research methods to explore the internal reaction mechanism catalyzed by transition metal complexes in recent years, and have made some achievements. For example, if the ligand restrictions on metal complexes are ignored, researchers can correspond specific transition metals to specific catalytic reactions. For reactions involving oxygen atom transfer or oxidation, researchers usually use highly oxidized metal complexes as their efficient catalysts. For hydrogenation reactions, such as hydrosilylation, a series of reduction reactions involving hydrogen atoms, transition metal complexes with low oxidation states are usually used to catalyze these reactions.

The oxidative addition reaction of complexes can be regarded as a process in which the metal atoms are oxidized by the reaction complex to the metal complex. It can be seen from the reaction products that the coordination number and oxidation state of the central metal atom of the complex has changed. The increase of oxidation state is equivalent to oxidation reaction, and the increase of ligand number is equivalent to addition reaction. [47-50] Oxidative addition reaction is a widely used method to generate metal-carbon (Me-C) bond and metal-hydrogen (Me-H) bond.

The reduction elimination reaction is an inverse reaction of the oxidation addition reaction. In the reduction elimination reaction, the central electron density of the transition metal complexes is small, and the oxidation state is high. The oxidation valence state of the metal is reduced, and the coordination number and the total number of electrons are also reduced. During the reduction elimination reaction, the oxidation state and coordination number of metal atoms are reduced. When the central transition metal is lack of electrons and the oxidation state is higher, the reduction elimination reaction is more likely. In addition, the greater the steric hindrance of the two groups to be dissociated, the easier the reductive elimination reaction occurs. [51-54] This reaction is an important step in the homogeneous catalytic reaction catalyzed by soluble metal complexes. Reduction elimination reaction is a common method for generating carbon-oxygen (C-O) bond and carbon-carbon (C-C) bond.

Hydrosilylation is a common method to synthesize new Si - C bonds in organic silicon industry. Platinum catalyst is the most commonly used catalyst in hydrosilylation. Although the comprehensive performance of platinum catalyst is suitable for industrial application, there are also problems such as low catalytic selectivity, many by-products and serious platinum pollution. Therefore, the improvement of platinum catalytic technology is popular study. The mechanism of platinum catalytic hydrosilylation is familiar with the CH mechanism, as shown in Scheme 1.1, which can be divided into three steps. The first step is the oxidation addition reaction of platinum and silane, and then the oxidation addition reaction of olefins (olefin insertion into Pt-H bond belongs to Chalk-harrod mechanism, and insertion into Si-Pt bond belongs to Modified-Chalk-harrod mechanism), and finally the reduction elimination reaction. Due to time reasons, this paper only studied the oxidative addition reaction between platinum complex catalyst and silicon hydrogen bond.

3.2 Computational Methods

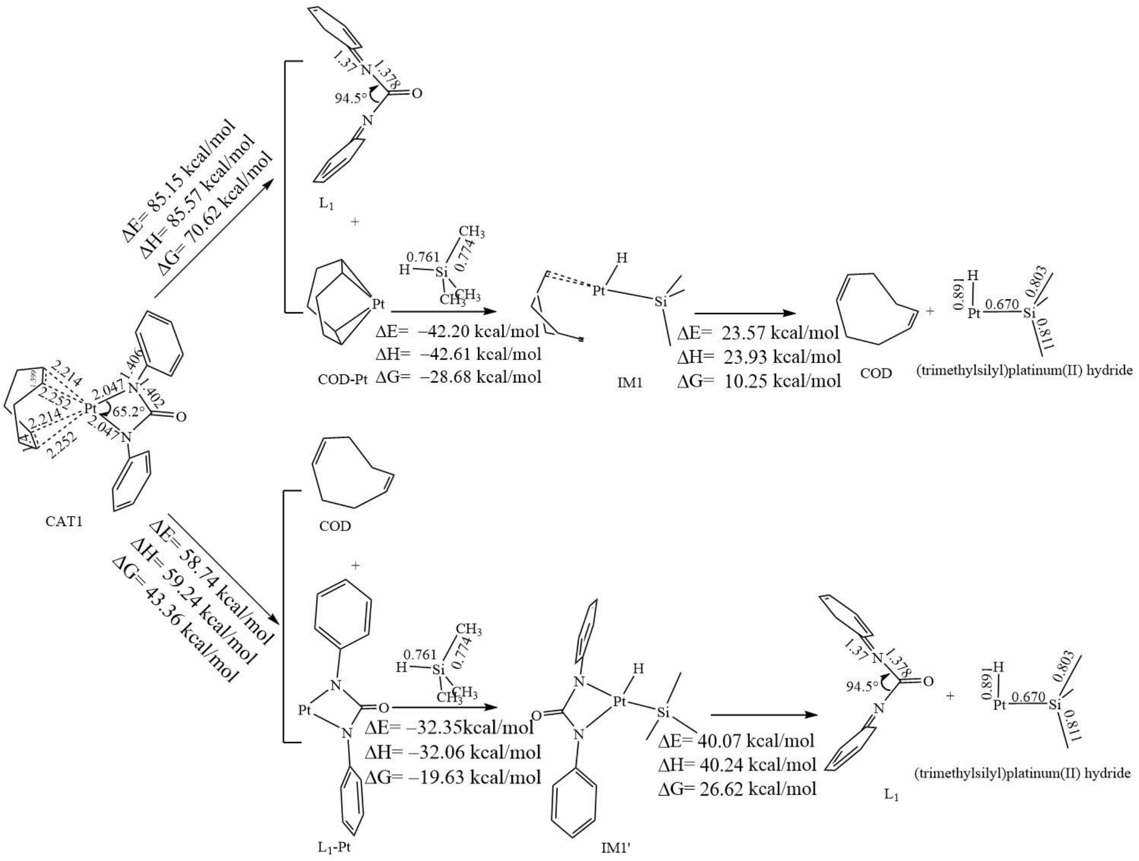
The density functional theory (DFT) was used for quantum chemistry calculation of this study. The geometric configurations of catalysts (CATs), transition states (TSs) an, intermediates (IMs) and ligand (Ls) were optimized using Beche’s three-parameter mixed functional combined with Lee-Yang-Parr correlation functional method (B3LYP). [54-56] Energy corrected to constant pressure, 298 K for zero energy difference. Based on the optimized geometry, the energy changes from reactants to transition states to intermediates were calculated at the 6-31G* basis set level. These calculations are performed using Gaussian09 software packages.

3.3 Results and Discussion

In the experiment, three practical platinum complexes catalysts, CAT1, CAT2 and CAT3, were used to study the possibility of hydrosilylation of ligand complexes and the stability of reaction intermediates through energy calculation. Scheme 2.1, 2.2, 2.3 give the initial part of Chalk-Harrod mechanism. The reaction energy listed in Schemes is represented by ΔG(kcal/mol), and the values of ΔE(kcal/mol) and ΔH(kcal/mol) are also listed as reference energy.

3.3.1 Reaction channel of CAT1

The metal active center platinum of CAT1 was coordinated with 1,5-cyclooctadiene (COD) and L_1 as ligands. According to Scheme 2.1, there are two reaction channels. The first reaction channel is that CAT1 releases L_1 ligand, then COD-Pt reacts with trimethyl silane, the metal active center platinum is inserted into the Si-H bond, and then endothermic reaction generates COD ligand and (trimethylsilyl) platinum (II) hydroxide. Another reaction channel is that the COD ligand in CAT1 is released to form L_1-Pt, which is further oxidized with trimethyl silane to form IM1 ', and then endothermic to form L_1 ligand and (trimethylsilyl) platinum (II) hydroxide.

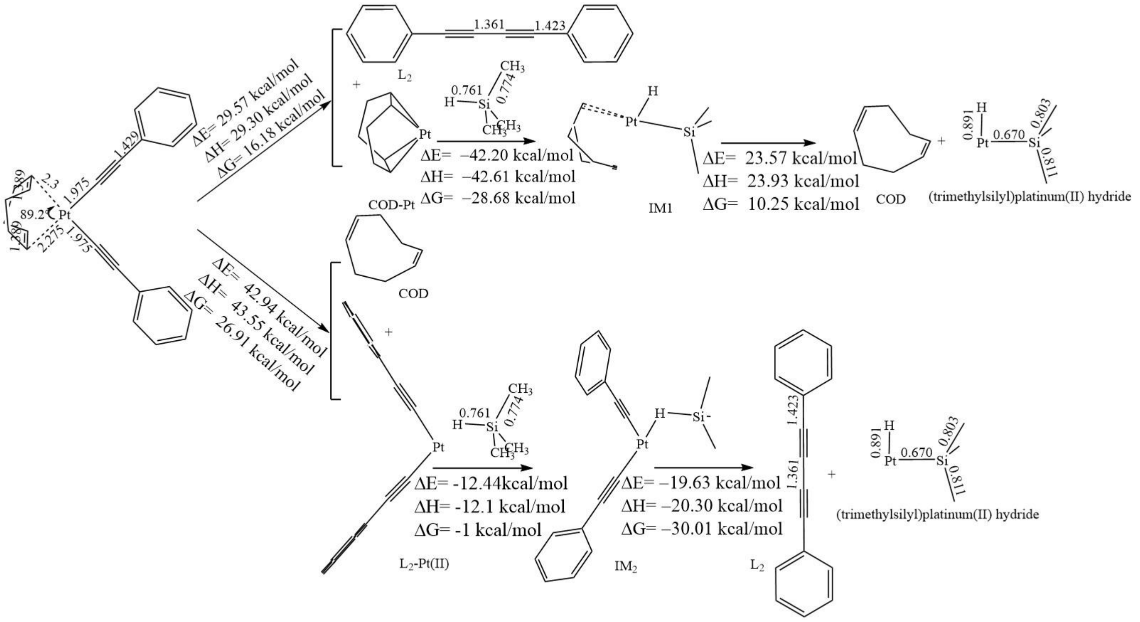


Scheme 2.1 The reaction channels of CAT1

For CAT1, from the ΔG value, the release of COD and L_1 of the two ligands needed to absorb energy, and the release of COD ligand needed less energy than that of L_1. After the release of L_1 ligand, the remaining COD-Pt reacted with silane to form IM_1; after the release of COD ligand, the left L_1-Pt reacted with silane to form IM_1’. The reaction of the two intermediates releasing the corresponding ligands is non-spontaneous, IM_1 and IM_1’ are relatively stable.

3.3.2 Reductive elimination of CAT2

The metal active center platinum of CAT2 selected COD and 1,4-diphenylbutadiyne(L_2) as ligands for coordination. There are two possible reaction channels. According to Scheme 2.2, CAT2 can release L_2 ligand to generate the product COD-Pt which is the same as that of CAT1 released L_1 ligand, and further react with trimethylsilyl to generate IM_1, and then absorb energy to generate COD and (trimethylsilyl) platinum (II) hydroxide. The other reaction path is that COD ligand is released from CAT2 to form L_1-Pt (II) complex, which reacts with trimethylsilyl, and the metal active center platinum is oxidized and added with silane to form the transition state TS_2, which further generates IM_2, and finally the energy is released to spontaneously generate L_2 and (trimethylsilyl) platinum (II) hydroxide.

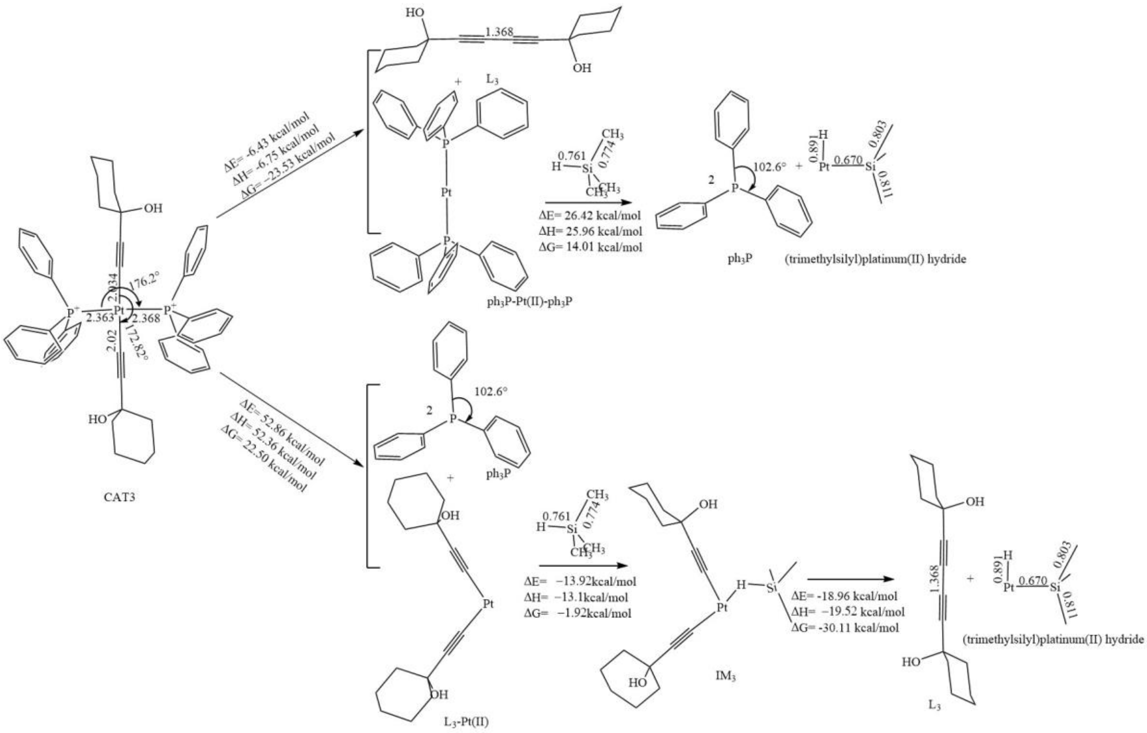


Scheme 2.2 The reaction channels of CAT2

Like CAT1, the release of the two ligands of CAT2 was also non-spontaneous. From the ΔG value, L_2 was more likely to be released. After the ligand was released from CAT2, it would spontaneously react with silane to generate intermediates, but the reaction of IM_1 further releasing COD ligand was non-spontaneous, and the reaction of IM_2 further releasing L_2 ligand was spontaneous, so IM_2 was more stable.

3.3.3 Reductive elimination of CAT3

1,4-Bis(1-hydroxycyclohexyl)-1,3-butadiyne(L_3) and two triphenylphosphine (ph$_3$P) ligands were selected as the metal active center of CAT3. According to scheme 2.3, the channel from CAT3 to the formation of L_3 and ph$_3$P-Pt (II)-ph$_3$P is exothermic and spontaneous, so the L_3 ligand is easy to be released. The resulting ph$_3$P-Pt (II) -ph$_3$P should theoretically be oxidized with trimethyl silane to generate the corresponding transition states and intermediates, but they are not found in the calculation results. Finally, two ph$_3$P and (trimethylsilyl) platinum (II) hydroxide are generated. In the other CAT3 reaction channel, two ph$_3$P were released by absorbing 22.50 kcal/mol energy to form L_3-Pt (II), which was oxidized with silane to form IM_3. Finally, L_3 was reacted with (trimethylsilyl) platinum (II) hydroxide.



Scheme 2.3 The reaction channels of CAT3

The reaction of CAT3 to release L_3 ligand was spontaneous, and two triphenylphosphine (ph_3P-Pt (II) -ph_3P) platinum complex was generated. However, the intermediate between ph_3P-Pt (II) -ph3P and silane was not found, which may be due to the large steric hindrance of two triphenylphosphines, hindering the proximity of ph_3P-Pt (II) -ph_3P to silane. The reaction of CAT3 to release ph_3P was non-spontaneous. L_3 reacted with silane to produce IM_3, but the reaction from IM_3 to release L_3 was spontaneous ($\Delta G < 0$), indicating that IM_3 was unstable, and the released (trimethylsilyl) platinum (II) hydroxide would enter the traditional C-H cycle, which was the result we did not want.

Chapter 4 Conclusions and Outlook

In this study, the stability of platinum intermediates formed by the coordination of five ligands (L1, L2, L3, COD, ph_3P) with metal active center platinum was investigated, and the occurrence of side reactions was reduced by occupying the coordination point of platinum. The first part of this paper mainly studies the mechanism of hydrosilylation under different theories. We first studied the most relevant coordination addition mechanisms (including Chalk-Harrod and Lewis mechanisms etc.), ion addition mechanism, free radical addition mechanism and photocatalytic addition mechanism in this paper. Then the density functional theory used in this experiment is further introduced, which is a quantum mechanical method for studying the electronic structure of multi-electron system. In this paper, based on the density functional theory, this experiment uses the B3LYP functional method to perform the calculation of the 6-31G* basis set level, and the Guassian09 software is used to calculated. In summary, CAT1 and CAT2 are suitable for catalyst, CAT3 is not suitable. This is consistent with the conclusion of the synchronous experimental results (the experimental results are provided by Materials Institute, Shandong Academy of Sciences).

In view of the time reason, the olefin insertion reaction involving the hydrosilylation mechanism has not yet been studied, and the transition state between complex catalysis and hydrosilylation has not been found, which is the next research plan.

We need platinum complexes can remain stable before the formation of (trimethylsilyl) platinum (II) hydroxide, so that the coordination point is still occupied by the ligand, so as to better enter the next Chalk-Harrod cycle reaction, so as to prevent the generation of other intermediates, achieve better selectivity, and form more main products. The main innovation of this study is reflected in the use of DFT theory to study a larger reaction system through a smaller base group and achieve good timeliness. However, there are still some problems in this paper, such as not finding suitable intermediates and transition states. In the future, molecular orbital theory can be used to determine the possible reaction sites and increase the probability of finding transition states of platinum complexes.

Since the discovery that transition metal platinum can catalyze the hydrosilylation reaction, scientists have carried out a series of studies on the reaction mechanism, catalyst screening, yield improvement and industrialization. With the progress of science and technology, these studies have made varying degrees of progress, such as the reaction mechanism and reaction phenomena are mostly reasonably explained, the yield of industrialization has also been greatly improved, and the amount of catalyst and recycling have also made great progress. However, with the development of organic silicon industrialization, the imperfections of the reaction research are gradually revealed. As for the reaction mechanism, some issues remain controversial and unexplainable. In addition, it is particularly important that the industrialization cost of the reaction is too high to be better solved. It is believed that through continuous efforts, through further study of platinum catalyst and its catalytic mechanism for hydrosilylation, we can find a reusable catalyst with less dosage, high activity, good selectivity and easy separation from the reaction system, which can make the research of the reaction more perfect and promote the rapid development of the whole organic silicon industry.

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