

**CATALYTIC ACTIVITY OF METAL CARBENES,  
SYNTHESIZED WITH ATOMIC CARBON AND TUNGSTEN  
HEXACHLORIDE (WCl<sub>6</sub>), IN OLEFIN METATHESIS  
REACTIONS**

**ATOMİK KARBON VE TUNGSTEN HEKZAKLORÜR (WCl<sub>6</sub>)  
İLE OLUŞTURULAN METAL KARBENLERİN OLEFİN  
METATEZ TEPKİMELERİNDEKİ KATALİTİK AKTİVİTESİ**

**DİLEK YÜKSEL**

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To my family

# **ACTIVITY OF METAL CARBENES, SYNTHESIZED WITH ATOMIC CARBON AND TUNGSTEN HEXACHLORIDE (WCl<sub>6</sub>), IN OLEFIN METATHESIS REACTIONS**

Dilek YÜKSEL

## **ABSTRACT**

In this study, the synthesis of tungsten based carbenes was achieved via the reaction of tungsten hexachloride (WCl<sub>6</sub>) and atomic carbon in a carbon arc reactor, which was cooled by liquid nitrogen at 77 K under high vacuum.

It was found that the tungsten carbene formed under these conditions had a structure as [W]=CCl<sub>2</sub> and catalyzed the self metathesis reactions of terminal and internal acyclic olefins, 1-octene, 2-octene, 1-heptene, 2-heptene, 1-pentene and 2-pentene.

It was also investigated theoretically, the structure and the mechanism of formation of the tungsten carbene, [W]=CCl<sub>2</sub>, within the WCl<sub>6</sub>/ C atom system and the energetics of the metathesis of 1-octene, in the presence of this tungsten carbene, with respect to the metal carbene metallocyclobutane mechanism proposed by Chauvin and Herisson (1971).

For this purpose, DFT calculations at B3LYP /LANL2DZ level was performed.

**KEY WORDS:** Carbon arc, Olefin Metathesis, Tungsten Carbene, DFT.

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# ATOMİK KARBON VE TUNGSTENHEKZAKLORÜR ( $WCl_6$ ) İLE OLUŞTURULAN METAL KARBENLERİN OLEFİN METATEZ TEPKİMELERİNDEKİ KATALİTİK AKTİVİTESİ

Dilek YÜKSEL

## ÖZ

Bu çalışmada, tungsten heksaklorür ( $WCl_6$ ) ve atomik karbonun, sıvı azotla 77 K' e soğutulan bir karbon ark reaktöründe ve yüksek vakum altında gerçekleşen tepkimesi yoluyla tungsten karben sentezi başarılmıştır.

Bu koşullarda oluşturulan tungsten karbenin,  $[W]=CCl_2$  şeklinde bir yapıya sahip olduğu ve düz zincirli iç ve uç olefinler, 1-okten, 2-okten, 1-hepten, 2-hepten, 1-penten ve 2-pentenin metatez tepkimelerini katalizlediği saptanmıştır.

Ayrıca  $WCl_6/ C$  atomu sistemi içinde  $[W]=CCl_2$  nin oluşma mekanizması, bu türün geometrisi ve bu metal karben varlığında, Chauvin ile Herisson (1971) tarafından önerilen metal karben metalosiklobütan mekanizması esas alınarak, 1-okten metatez tepkimesinin mekanizması teorik olarak incelenmiş, bu amaçla B3LYP/LANL2DZ seviyesinde DFT hesaplamaları gerçekleştirilmiştir.

ANAHTAR KELİMELER: Karbon arkı, Olefin Metatezi, Tungsten Karben, DFT.

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## ABBREVIATIONS

ADMET	Acyclic Diene Metathesis Polymerization
B3LYP	Becke 3-term functional with Lee-Yang-Parr exchange correlation
CM	Cross Metathesis
DBA	Double Bond Addition
DFT	Density Functional Theory
GC-MS	Gas Chromatography- Mass Spectrometry
HF	Hartree Fock
IRC	Intrinsic Reaction Coordinates
LANL2DZ	Los Alamos National Laboratories-2 Double Zeta
PES	Potential Energy Surface
RCM	Ring Closing Metathesis
RHF	Restricted Hartree Fock
RMS	Root Mean Square
ROHF	Restricted Open shell Hartree Fock
ROM	Ring Opening Metathesis
ROMP	Ring Opening Metathesis and Polymerization
RT	Retention Time
SCF	Self Consistent Field
STO	Slater Type Orbital
UHF	Unrestricted Hartree Fock
ZPE	Zero Point Energy

## 1. INTRODUCTION

Olefin metathesis is an extremely important and useful reaction, so that it brought to its pioneers, Yves Chauvin, Robert H. Grubbs and Richard R. Schrock, the Nobel Prize in Chemistry *“for the development of the metathesis method in organic synthesis”* (2005).

The discoveries of the Nobel laureates have had great effects on academic research, the development of new drugs and other biologically active compounds, polymeric materials and industrial syntheses. The reaction has found a very wide range of application area.

Since its discovery (Eleuterio, 1956) and understanding (Calderon, 1967), olefin metathesis has shown a rapid and great improvement. Utility of the reaction has triggered many investigations on catalyst systems for olefin metathesis reactions and it has been found that these catalyst systems almost always contain a transition metal complex acting through formation of a metal carbene, which initiate and then propagate the reaction (Schrock, 1986).

After many attempts for explaining the mechanism of catalysis by metal carbenes, the metal carbene metallocyclobutane mechanism for olefin metathesis, which was first proposed by Yves Chauvin and his student Jean-Louis Hérisson (1971), is greatly accepted.

From 1980 onwards, well-defined carbene complexes of W, Ta, Mo, Re and Ru have been reported, which act as initiators without the need for activation by heat, light or co-catalyst. Various transition metal complexes and organic synthesis methods such as photochemical, electrochemical etc., have been used to develop the efficiency of these metal carbene catalyst systems (Ivin and Mol, 1997).

With this study of thesis, it is intended to contribute to these methods of the synthesis of metal carbenes with a new one. The method, which was used for this purpose is the direct combination of a highly energetic carbon atom with a transition metal complex in a carbon arc reactor at 77 K and under high vacuum.

By using tungsten hexachloride,  $WCl_6$ , as the transition metal complex, a tungsten carbene species was synthesized and after in situ addition of an acyclic olefin (1-

octene, 2-octene, 1-heptene, 2-heptene, 1-pentene or 2-pentene), the system was allowed to warm to the room temperature. Then the reaction mixtures were analyzed by instrumental analysis methods and formation of metathesis products for each of the olefins was observed.

Structure of the active species in these metathesis reactions was investigated by using benzaldehyde as a trap molecule and it was found that the tungsten carbene species had a structure as  $[W]=CCl_2$ .

The mechanism of formation of this species and the energetics of metathesis of 1-octene were also investigated by DFT calculations at the B3LYP/LANL2DZ level of the theory.



## **2. GENERAL INFORMATION**

### **2.1. Properties of Atomic Carbon**

Although there are numerous carbon containing compounds known, in pure bulk forms such as diamond and graphite, carbon is very unreactive towards organic and inorganic substrates. The reason for this unreactivity is that carbon-carbon bonds are very strong. Actually, carbon has the highest melting/ sublimation points of all elements regardless of its allotropic form. It has no melting point at atmospheric pressure and only above 3800 °C it sublimates. Therefore a great deal of energy is needed to generate atomic carbon from its pure condensed phase, i.e. graphite.

Despite the difficulty, once the forces keeping carbon atoms together are broken and the carbon is atomized, it becomes very reactive and lead to a variety of reactions. There are few intermediates possessing more energy than atomic carbon. Carbon atoms at triplet and singlet states have a heat of formation of 171 kcal/mol and 233 kcal/mol, respectively.

### **2.2. Generation of Atomic Carbon**

There are several ways of generating carbon atoms, such as photolytic, photochemical, nuclear recoil methods and graphite vaporization methods. The latter has two type:

- i) Heating of graphite
- ii) Carbon arc method

All these methods involve the formation of molecular carbon species as side products besides the atomic carbon. Investigations on the composition and the physical properties of carbon vapor had indicated that carbon vapor, evaporating from a graphite surface, contained C<sub>3</sub> and C<sub>4</sub> molecules, besides the atomic and diatomic species (Honig, 1953, Chupka and Inghram, 1953, Glockler, 1954). When the amounts of arc generated species are concerned, atomic carbon is the most prominent in the mixture and C<sub>3</sub> molecules are relatively more abundant than C<sub>2</sub> molecules.

### 2.2.1. Carbon Arc Method

In this method, the carbon arc, produced as a result of the high temperature attained on the graphite electrodes of a carbon atom reactor, provides both the energy needed for the atomization and the source of carbon. The method is pioneered by Philip Skell and his coworkers (Skell et al., 1965, 1971, 1973).

Using the reactor, shown in Figure 2.1., carbon vapor is produced between the two graphite electrodes by intermittent arcing. Afterwards they are condensed on the surface of the reactor, which is cooled with liquid nitrogen at  $-196\text{ }^{\circ}\text{C}$  under high vacuum ( $\sim 5 \times 10^{-5}$  torr).

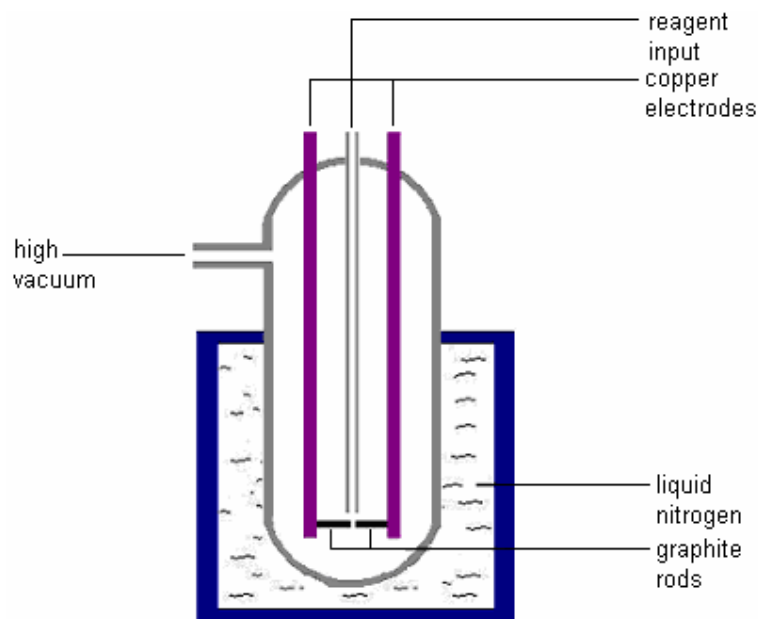


Figure 2.1. Carbon arc reactor

On the other hand, the substrate molecules, which were sent into the reactor in gas phase are also condensed with atomic carbon. Thus, the reactions between atomic carbon and the substrate molecules in the reactor can take place at any temperature between  $\sim 2500\text{ }^{\circ}\text{C}$ , at which the arc is produced, and  $-196\text{ }^{\circ}\text{C}$ . Nevertheless, it is believed that the reactions take place in condensed phase, because the carbon atoms are produced at a low pressure and the probability of collisions between carbon atoms and substrate molecules during the flight to the walls is small.

## 2.3. Reactions of Atomic Carbon

The high energy and unfilled valencies of atomic carbon make it similar to carbenes in reactivity. In fact the primary products of carbon atom reactions with organic substrates are often carbenes. These carbenes can further react with other substrates or rearrange to stable products. There are three types of reactions that atomic carbon and carbenes can undergo:

- i) Insertion into single bonds
- ii) Addition to double bonds (DBA)
- iii) Intramolecular rearrangements

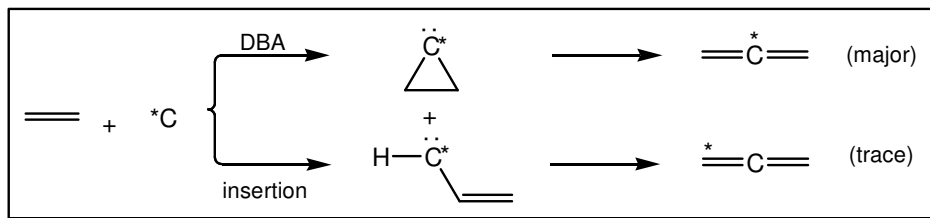
### 2.3.1 Insertion into Single Bonds

Atomic carbons at triplet and singlet states can insert into primary or secondary C-H bonds yielding triplet and singlet carbene intermediates, respectively. Triplet carbenes, as diradicals, abstract two hydrogens to form a methyl group, while singlet carbenes react by migration of hydrogen atoms or alkyl groups to give olefins, and also by intramolecular insertions to produce cyclopropanes (Skell and Engel, 1966).

### 2.3.2 Addition to Double Bonds

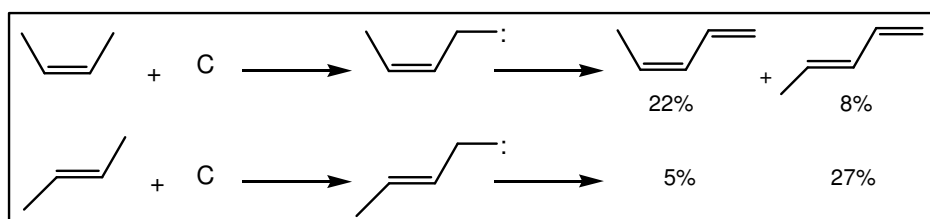
When electron deficient atomic carbon reacts with olefins, the carbon carbon double bond is the favored position of attack and the double bond addition intermediates, cyclopropylidenes, which are known to arrange to cumulenes are formed. The other mode of attack is =C-H bond insertion which gives vinyl carbene intermediates.

Reaction of atomic carbon with ethylene produces propyne and allene as the major products (Skell, 1971). When  $^{13}\text{C}$  was used, the labeling (\*) was found mostly on the middle carbon for both allene and propyne, which originated from the double bond addition. However, small amount labeling was found on the terminal carbons, indicating a C-H insertion as seen in Scheme 2.1.



Scheme 2.1. Reaction of atomic carbon with ethylene

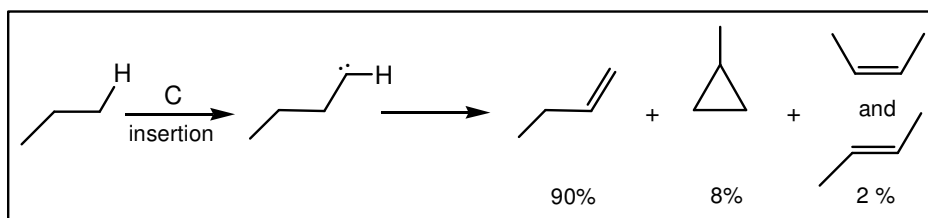
Cis- and trans-2-butenes react with atomic carbon to give 2,3-pentadiene and also a mixture of the 1,3-pentadienes (Plonka, 1970). 1,3-pentadienes are formed with predominant retention of stereochemistry about the double bond, but some cis-trans interconversion does occur (Scheme 2.2.). The intermediates leading to isomerization of the double bonds are thought to be vibrationally excited crotyl carbenes.



Scheme 2.2. Reactions of atomic carbon with cis- and trans -2-butenes

### 2.3.3 Intramolecular Rearrangements

Rearrangements and interconversions of atomic carbon and carbenes are common in gas phase organic reactions as seen in Scheme 2.3. (Skell et al., 1973).



Scheme 2.3. Intramolecular rearrangements after carbene formation

## 2.4. Carbene Chemistry

Starting as chemical interests in the pioneering works of Curtius (Buchner et al., 1885) and Staudinger (1912), carbenes have played an important role as transient intermediates over the last five decades (Kirmse, 1964, 1971, Regitz et al., 1989, Brinker et al., 1998, Arduengo, 1998).

Introduced by Doering into organic chemistry in the 1950s (Doering and Hoffmann, 1954) and by Fischer into organometallic chemistry in 1964 (Fischer et al., 1964), these fascinating species are involved in many reactions of high synthetic interest.

### 2.4.1. Carbenes in Organic Chemistry

Carbenes are neutral species featuring a divalent carbon atom with six electrons in its valence shell. Carbenes have the general formula as  $R_1-\ddot{C}-R_2$ , the carbon atom can either be linear or bent and each geometry can be explained by a certain degree of hybridization.

The linear geometry implies an  $sp$ -hybridized carbene center with two nonbonding degenerate orbitals ( $p_x$  and  $p_y$ ) as seen in Figure 2.2.

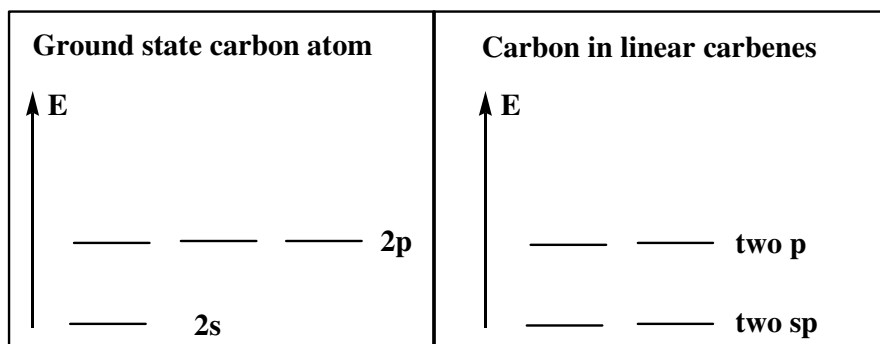


Figure 2.2. Orbitals in linear carbene

Bending the molecule breaks this degeneracy and the carbon atom adopts an  $sp^2$  type hybridization. In Figure 2.3, orbitals in the bent carbene structure and the lone pair electrons in an  $sp^2$  type hybrid is shown.

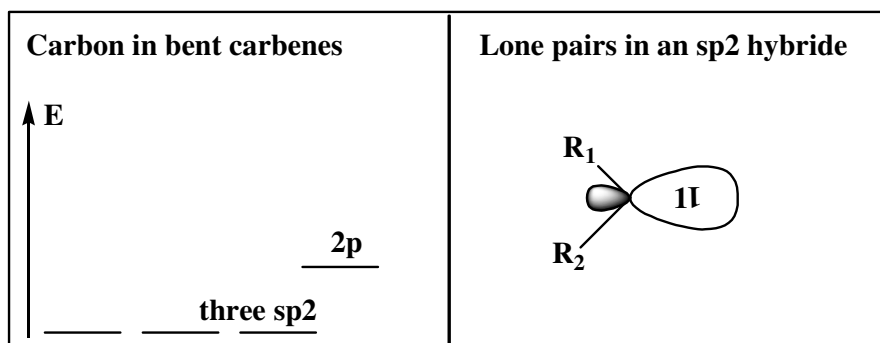


Figure 2.3. Orbitals in bent carbene

The  $p_y$  orbital remains almost unchanged (it is usually called  $p_{\Pi}$ ), while the orbital that starts as pure  $p_x$  orbital is stabilized. Because this  $p_x$  orbital acquires some  $s$  character it is called  $\sigma$ . The linear geometry is an extreme case; most carbenes are bent and their frontier orbitals will be systematically called as  $\sigma$  and  $p_{\Pi}$  as shown in Figure 2.4.

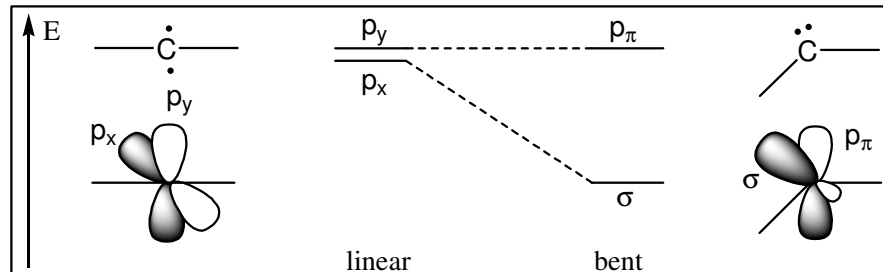


Figure 2.4. Relationship between the carbene bond angle and the nature of the frontier orbitals.

As depicted in Figure 2.5., four electronic configurations can be envisaged. The two nonbonding electrons can be in two different orbitals with parallel spins (triplet state); hence, the molecule is correctly described by the  $\sigma^1 p_{\Pi}^1$  configuration ( $^3B_1$  state). In contrast, for singlet carbenes, the two nonbonding electrons can be paired in the same  $\sigma$  or  $\Pi$  orbital. Therefore, there are two different  $^1A_1$  states, the

$\sigma^2$  being generally more stable than the  $p_{\pi}^2$ . Last, an excited singlet state with  $\sigma^1 p_{\pi}^1$  configuration can also be envisaged ( $^1B_1$  state).

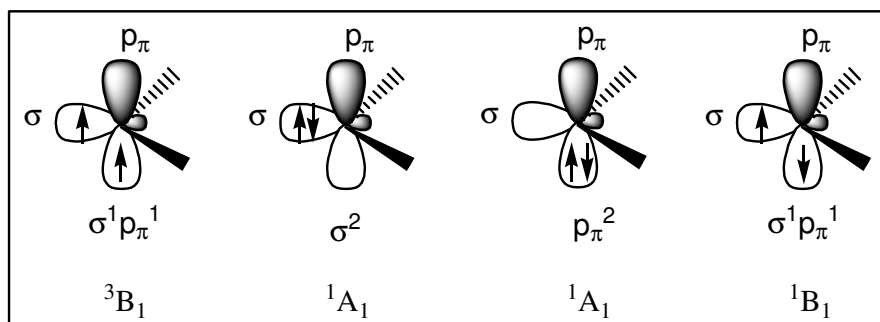


Figure 2.5. Electronic configurations of carbenes

The carbene ground-state multiplicity is related to the relative energy of the  $\sigma$  and  $p$  orbitals. The singlet ground state is favored by a large  $\sigma$ - $p_{\pi}$  separation. Hoffmann determined that a value of at least 2 eV is necessary to impose a singlet ground state, whereas a value below 1.5 eV leads to a triplet ground state (Gleiter et al., 1968).

The ground state spin multiplicity is a fundamental feature of carbenes that dictates their reactivity (Schuster, 1986). Indeed, singlet carbenes feature a filled and a vacant orbital, and therefore, they should possess an ambiphilic character. On the other hand, triplet carbenes have two singly occupied orbitals and are generally regarded as diradicals.

Singlet and triplet carbenes do not demonstrate the same reactivity. Singlet carbenes generally participate in cheletropic reactions as either electrophiles or nucleophiles. Singlet carbenes with the unfilled  $p$ -orbital should be electrophilic, whereas triplet carbenes should be considered as diradicals, and participate in stepwise radical additions. Triplet carbenes have to go through an intermediate with two unpaired electrons, whereas singlet carbene can react in a single concerted step. Addition of singlet carbenes to olefinic double bonds is more stereoselective than that of triplet carbenes. Addition reactions with olefins can be used to determine whether the singlet or triplet carbene is involved.

## 2.4.2. Carbenes In Organometallic Chemistry

Organometallic carbenes are compounds with an organic group, which is double bonded to the metal atom. These transition metal carbene complexes fall into two clearly defined groups:

i) Fischer Type Carbenes

ii) Schrock Type Carbenes

Both the Fischer type and the Schrock type carbenes are shown in Figure 2.6.

In Fischer-type carbenes, the metal center is typically a late transition metal with a low oxidation state, such as  $W(CO)_5(=CMe(OMe))$  (Dötz et al., 1983 and Schubert, 1984) and the ligands are  $\pi$ -acceptors with  $\pi$ -donor substituents (OR groups) attached to the metal center. The carbon atom in Fischer-type carbenes is electrophilic, behaving like it has a  $\delta+$  charge, and will react with nucleophiles such as phosphines.

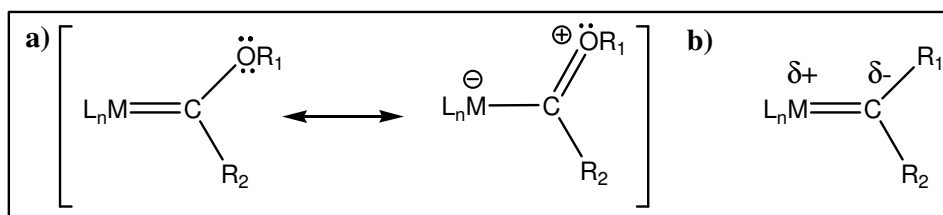


Figure 2.6. a) Fischer carbene and b) Schrock carbene

In Schrock carbenes, on the other hand, the metal center is an early transition metal with a high oxidation state, the ligands are non- $\pi$ -acceptors, and the carbene ligand has R groups that are not  $\pi$ -donating. The chemistry of Schrock type carbenes is distinct from that of the Fischer-type, since the  $\alpha$  carbon is nucleophile, behaving like it has a  $\delta-$  charge, as in Wittig-type reactions.

The first nonheteroatom-stabilized carbene,  $(Me_3CCH_2)_3Ta(=CHCMe_3)$ , is characterized in 1974 by Schrock (Schrock, 1974). This and related compounds, called "Schrock type carbenes" or alkylidene complexes, were shown to be active



in olefin metathesis and polymerization and for the conversion of carbonyl compounds into olefins (Schrock et al., 1974-1987).

## **2.5. Olefin Metathesis**

Olefin metathesis was first observed in the 1950s by industrial chemists. They observed many products that could not be explained by the reactions of olefins known at the time.

In 1967, Nissim Calderon and coworkers at Goodyear Tire & Rubber, Akron, Ohio, figured out that the unexpected products are due to the cleavage and reformation of the double bonds of olefins. One carbon of the double bond of one olefin, along with everything attached to it, exchanges place with one carbon of the double bond of the other olefin, along with everything attached to it. The Goodyear researchers named the reaction "olefin metathesis" (1967).

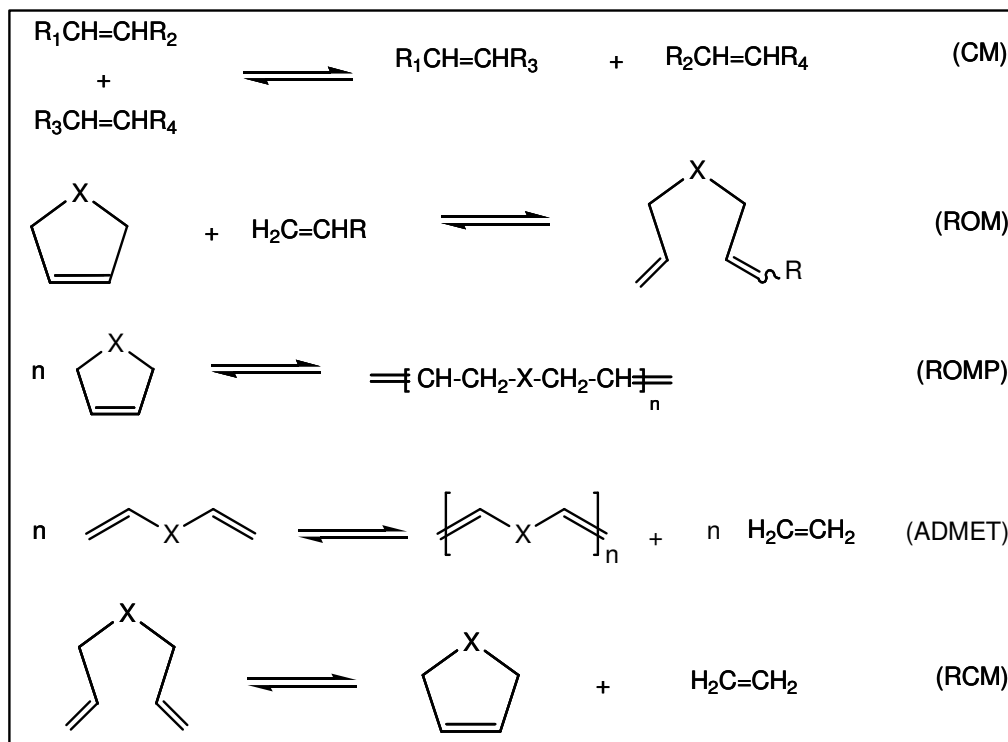
### **2.5.1. Some Important Features of Metathesis**

Olefin metathesis is a popular and useful reaction. In the presence of certain transition-metal compounds, including various metal carbenes, olefins exchange the groups around the double bonds, resulting in several outcomes such as straight swapping of groups between two acyclic olefins (cross-metathesis, CM), closure of large rings (ring-closing metathesis, RCM), formation of dienes from cyclic and acyclic olefins (ring-opening metathesis, ROM), polymerization of cyclic olefins (ring-opening metathesis polymerization, ROMP), and polymerization of acyclic dienes (acyclic diene metathesis polymerization, ADMET) as depicted in Scheme 2.5. (Trnka and Grubbs, 2001).

When the cross metathesis reaction takes place between the two molecule of the same olefin, it is called as self metathesis. These reactions may either be productive or regenerative, by yielding starting olefins (Grubbs, 1982, Ivin, 1983).

Isotopic labeling studies have shown that productive metathesis of terminal olefins are much more faster than that of regenerative metathesis (Tanaka, 1979).

The reaction products of cross metathesis are highly important as raw material. Industrial production of olefins is based on cross-metathesis using heterogeneous catalysts.



Scheme 2.4. Metathesis possibilities

## 2.6. Catalyst Systems For Metathesis

The power of olefin metathesis is that it transforms the carbon-carbon double bond, a functional group that is unreactive toward many reagents that react with many other functional groups. With certain catalysts, new carbon-carbon double bonds are formed at or near room temperature even in aqueous media from starting materials that bear a variety of functional groups.

The number of catalyst systems that initiate olefin metathesis is very large. A single compound is sometimes effective but more commonly the catalyst system contains two or more components. The systems may be homogeneous or heterogeneous.

The most important catalyst systems are derived from compounds of the transition elements, Mo, W, Re, Ru, Rh, Os and Ir., those of the first three are generally the most effective. Among these, it is possible that there are more known tungsten based catalysts than all others together. Many examples for metathesis of terminal and internal olefins in the literature by using tungsten based catalysts. Primary metathesis products were obtained in many cases via different methods. Some of these methods were presented in Table 2.1. (Ivin and Mol, 1997).

Table 2.1. Examples for metathesis of acyclic olefins with other methods

Reactant	Product	Catalyst system	Reference
1-octene	7-tetradecene	WCl <sub>2</sub> (OAr) <sub>4</sub> / EtAlCl <sub>2</sub>	Dodd, 1982
2-octene	6-dodecene	WCl <sub>6</sub> / EtAlCl <sub>2</sub> / EtOH	Calderon,1968
1-heptene	6-dodecene	WCl <sub>6</sub> / Sn Ph <sub>4</sub>	Balcar, 1983
2-heptene	5-decene	WCl <sub>6</sub> / SnBu <sub>4</sub>	Nishiguchi, 1981
1-pentene	4-octene	WCl <sub>6</sub> / Bu/ MeCN <sub>4</sub> Sn	Ichikawa, 1976
2-pentene	3-hexene	WCl <sub>6</sub> / Al anode/ e <sup>-</sup>	Gilet, 1979

### 2.6.1. Metal Carbene Catalysts

Use of olefin metathesis in organic synthesis has been directly correlated to improvements in metal carbene catalysts. As mentioned above, most early work in olefin metathesis was done using multicomponent catalyst systems (Warwel et al.,1983, Leymet et al.,1989, Liaw et al., 1993).

It is only in recent years that well-defined single component metal carbene complexes have been prepared and utilized in olefin metathesis. The chemists most responsible for developing such catalysts are chemistry professors Robert H.Grubbs and Richard R.Schrock. The so called Grubbs and Schrock catalysts were developed through focused research programs going back to the 1970s.

- **Schrock W and Mo and Catalysts**

Tungsten and molybdenum, are obviously the most active metals in olefin metathesis and, around 1980, Schrock and his group increased their efforts in the search for stable molecular alkylidene and alkylidyne complexes of these metals that could catalyze the metathesis of unsaturated hydrocarbons. This search was successful and eventually produced a whole family of tungsten- and molybdenum-alkylidene complexes of the general formula  $[M(=CHCMe_2Ph)(=N-Ar)(OR_2)]$ , R being bulky groups. These compounds presently are the most active olefin metathesis catalysts (Schrock et al., 1974, 1979, 1990, Bazan et al., 1990, 1991).

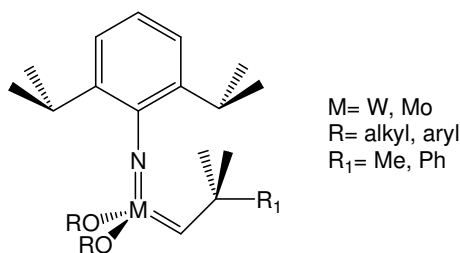


Figure 2.7. Schrock catalysts

- **Grubbs Ru Catalysts**

In the early 1990's Robert Grubbs developed a series of Ru catalysts that differ from the previous generations in several distinct ways. First, the metal is not in its highest oxidation state and is supported by phosphine ligands. Second, these catalysts are so tolerant of functionality that some of them can operate even in water on the benchtop. Such functional group tolerance comes at the expense of lower metathesis rates than the Schrock catalysts, but these systems are extremely promising.

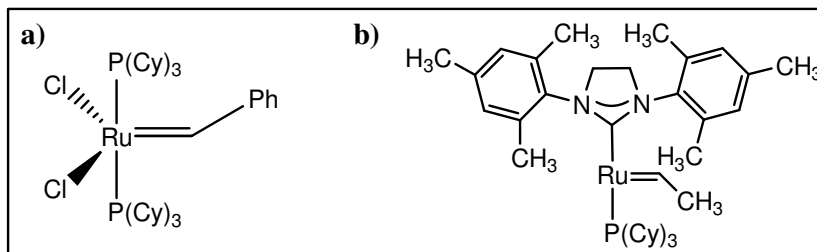


Figure 2.8. a) The first and b) The second generation Grubbs catalysts

### 2.6.2. The Nature of the Initiating Species in Catalytic Metathesis

The nature of the initiating species, i.e. metal carbene, in catalytic olefin metathesis reactions is studied in many cases and similar results have been stated for a variety of both homogeneous and heterogeneous catalyst systems.

For example in the  $W(CO)_6/ CCl_4/ h\nu$  system, in the reaction with 1-ethoxynorbornene, the product contains the  $=CCl_2$  entity, suggesting that  $[W]=CCl_2$  is formed (Rudler, 1980). However, in the reaction of 4-octene and 7-tetradecene, no  $RCH=CCl_2$  is detected during cross metathesis (Karan and İmamoğlu, 1989). There is again no evidence for metathesis initiation by  $[W]=CCl_2$  in the reaction with 2-pentene (Schilder, 1992). In the last case it appears that  $[W]=CCl_2$  is destroyed before it can react with the substrate and the metathesis reaction is initiated from the surface of a precipitate and the nature of the initiating species is not clear.

In  $WCl_6/ Me_4Sn$  system the  $^1H$  NMR spectrum of the mixture in  $CD_2Cl_2$  at  $20^\circ C$  develops a singlet at 10.52 ppm, reaching the maximum after 25 min, then slowly declining. When  $(^{13}CH_3)_4Sn$  is used as cocatalyst, this signal appears as a doublet ( $J=134$  Hz) and a second, much weaker doublet is seen at about 9 ppm. Corresponding peaks are seen in in the  $^{13}C$  NMR spectrum at 298.7 and 285.2 ppm, respectively. The low field  $^1H$  and  $^{13}C$  NMR signals are assigned to  $[W]=CH_2$  by analogy with the shifts for known tungsten carbene complexes. It seems likely that the main initiating species is  $W(=CH_2) Cl_4$  formed by elimination of methane from  $(CH_3)_2W Cl_4$  (Ivin, 1987, Wei, 1994).

The nature of the initiating complex can also sometimes be deduced from the product of its reaction with a carbene trap. For example the 7-coordinate, 18-electron complex  $WCl_2(CO)(AsPh_3)_2$  catalyzes the ROMP of norbornene in benzene at  $80^\circ C$ , presumably through loss of a CO ligand followed by coordination of the norbornene and rearrangement to a tungsten carbene complex which then propagates the ROMP. In the presence of benzaldehyde as carbene trap, polymerization is inhibited and the main product is 2-benzylidenenorbornane (Bencze, 1985).

Similarly the carbene ligands generated in the systems  $W(CO)_6/ CCl_4/ h\nu$  and  $W(CO)_6/ Ph_2CCl_2/ h\nu$  have been identified as  $=CCl_2$  and  $=CPh_2$ , respectively, from the products of reaction with 2-ethoxynorbornene (Garnier, 1980).

## 2.7. Mechanism of Metathesis

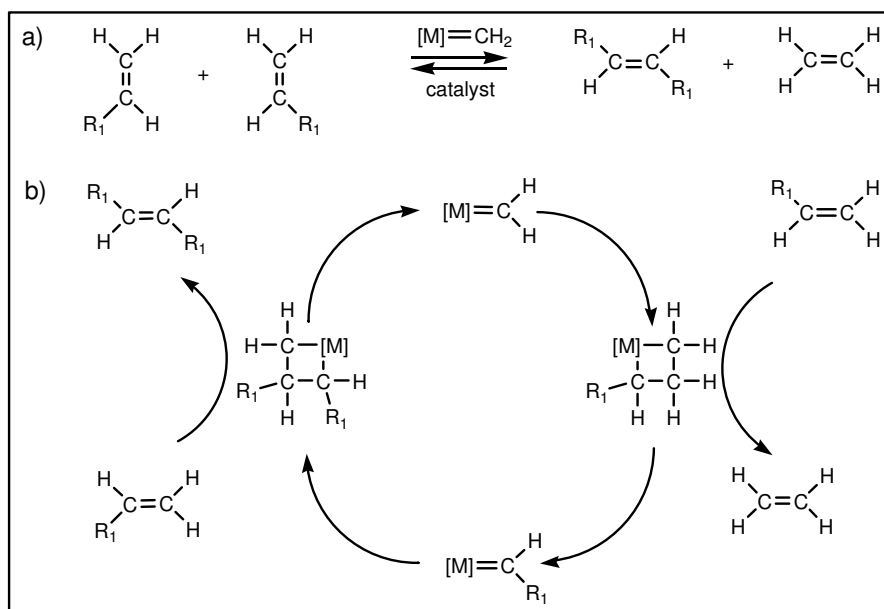
More and more chemists started to realise that metathesis could offer great potential in organic synthesis. But no one suspected how great it was to become. Though many researchers put forward proposals as to how metathesis could take place, the breakthrough came in 1971 with a publication by Yves Chauvin (Hérison and Chauvin, 1971). He and his student Jean-Louis Hérisson proposed that the catalyst was a metal carbene. In later literature metal carbene came to be termed metal alkylide. Other metal carbenes had been discovered some years earlier by Ernst Otto Fischer (Nobel Prize in Chemistry 1973).

Chauvin also presented an entirely new mechanism for how the metal compound functions as a catalyst in the reaction. His new experimental results tallied with this new mechanism and could not be explained by any previously proposed mechanism.

As shown in Scheme 2.5.a., a metal carbene acts as catalyst for the exchange of alkylidenes between two different olefins and the result is two entirely new olefins (the square brackets round the M show that the metal, apart from being bound with a double bond to methylene, is also bound to other groups).

Scheme 2.5.b. shows the mechanism. In the first stage of the reaction, metal methylene combines with one olefin to form a ring of four atoms. The ring consists

of the metal atom and three carbon atoms bound to one another with single bonds. In the next step two of the single bonds are broken and a new olefin (ethylene) and a new metal alkylidene is obtained. In the third step of the reaction this new metal alkylidene unites with one of the original olefins to form a new metallocyclobutane. In the last stage of the catalytic cycle, this transition molecule is broken apart and gives a metathesis product and the re-formation of the metal methylene molecule. It is now ready to act as a catalyst in another metathesis reaction. The end result of the reaction cycle is that the two substrate molecules have exchanged alkylidene groups with each other; they have undergone metathesis.



Scheme 2.5. Chauvin mechanism for metathesis

Chauvin's mechanism explained at one stroke all earlier outcomes of olefin metathesis. His mechanism received strong support from experimental investigations by Robert H. Grubbs, Thomas J. Katz and Richard R. Schrock, and is now generally accepted (Grubbs et al., 2001).

## 2.8. Computational Chemistry

The term theoretical chemistry is defined as a mathematical description of chemistry, whereas computational chemistry is usually used when a mathematical method is sufficiently well developed that it can be automated for implementation on a computer.

Computational chemistry is a branch of chemistry that uses the results of theoretical chemistry incorporated into efficient computer programs to calculate the structures and properties of molecules and solids, applying these programs to real chemical problems. Examples of such properties are structure (i.e. the expected positions of the constituent atoms), energy and interaction energy, charges, dipoles and higher multipole moments, vibrational frequencies, reactivity or other spectroscopic quantities, and cross sections for collision with other particles.

### 2.8.1. Quantum Mechanics

One of the primary goals in molecular quantum mechanics is to solve the time-independent Schrödinger equation and to determine the electronic structures of atoms and molecules.

To solve the electronic Schrödinger equation (1) for electrons in molecules, a series of computational techniques and approximations have been developed that make the computations feasible.

$$H\Psi(r; R) = E(R)\Psi(r; R) \quad (1)$$

For a fixed set of locations  $R$  of the nuclei, the electronic wavefunction,  $\Psi$ , depends on the electronic coordinates  $r$  and parametrically on  $R$ .  $E(R)$  is the electronic energy.

The electronic Hamiltonian operator,  $H$ , contains three terms, namely kinetic energy, electrostatic interaction between electrons and nuclei, and electrostatic repulsion between electrons.

In order to simplify expressions and to make the theory independent of the experimental values of physical constants, atomic units are introduced.



Derived atomic units of length and energy are given in Equations (2) and (3), where  $a_0$  is the Bohr radius,  $e$  is the charge and  $m$  is the mass of one electron.

$$1 \text{ bohr} = a_0 = \frac{\hbar^2}{me^2} = 0.529 \text{ \AA} \quad (2)$$

$$1 \text{ hartree} = \frac{e^2}{a_0} = 4.3598 \times 10^{-18} \text{ J/mol} = 627.51 \text{ kcal/mol} \quad (3)$$

In molecular structure calculations it is conventional not to include the nucleus-nucleus repulsion term in H, but to add it as a classical term at the end of the calculation.

### 2.8.2. Molecular Mechanics

In many cases, large molecular systems can be modeled successfully while avoiding quantum mechanical calculations entirely. Molecular mechanics simulations, for example, use a single classical expression for the energy of a compound, for instance the harmonic oscillator. All constants appearing in the equations must be obtained beforehand from experimental data or ab initio calculations.

The database of compounds used for parameterization, where the resulting set of parameters and functions is called the force field, is crucial to the success of molecular mechanics calculations.

A force field parameterized against a specific class of molecules, for instance proteins, would be expected to only have any relevance when describing other molecules of the same class.

### 2.8.3. Semi Empirical Methods

A semiempirical method makes use of a simplified form for the hamiltonian and adjustable parameters obtained from experimental data. In both cases it is a challenging task to compute chemically accurate energies, that is, energies calculated within about 0.05 eV (about 5 kJ mol<sup>-1</sup>) of the exact values.

#### 2.8.4. The Born-Oppenheimer Approximation

Even for the simplest molecule,  $\text{H}_2^+$ , the Schrödinger equation can not be solved analytically. To overcome this difficulty, reasonable approximations should be made. Born-Oppenheimer approximation takes note of the great difference in masses of electrons of nuclei. It consists of two steps:

In the first step, the nuclear kinetic energy is neglected, that is, the corresponding operator is subtracted from the total molecular Hamiltonian. In the remaining electronic Hamiltonian the nuclear positions enter as parameters.

The electron-nucleus interactions are not removed and the electrons still feel the Coulomb potential of the nuclei clamped at certain positions in space. This first step of the Born-Oppenheimer approximation is therefore often referred to as the clamped nuclei approximation.

The electronic Schrödinger equation is solved, out of necessity approximately, with a fixed nuclear geometry as input. The quantity stands for all electronic coordinates. Obviously, the electronic energy eigenvalue depends on the chosen positions of the nuclei. Varying these positions in small steps and repeatedly solving the electronic Schrödinger equation, one obtains the electronic energy as a function of the position of the nuclei. This is called as the potential energy surface (PES) of the electron. Because this procedure of recomputing the electronic wave functions as a function of an infinitesimally changing nuclear geometry is resembling of the conditions for the adiabatic theorem, this manner of obtaining a PES is often referred to as the adiabatic approximation and the PES itself is called an adiabatic surface.

In the second step of the Born-Oppenheimer approximation the nuclear kinetic energy, containing partial derivatives with respect to the components of the position of the nuclei, is reintroduced and the Schrödinger equation for the nuclear motion is solved. This second step of the Born-Oppenheimer approximation is far from trivial and involves separation of vibrational and rotational motion. The total energy of the molecule, includes contributions from electrons, nuclear vibrations, and rotations.

### 2.8.5. Molecular Structure

A given molecular formula can represent a number of molecular isomers. Each isomer is a local minimum on the PES created from the total energy (electronic energy plus repulsion energy between the nuclei) as a function of the coordinates of all the nuclei.

A stationary point is a geometry such that the derivative of the energy with respect to all displacements of the nuclei is zero. A local energy minimum is a stationary point where all such displacements lead to an increase in energy.

The local minimum that is lowest is called the global minimum and corresponds to the most stable isomer. If there is one particular coordinate change that leads to a decrease in the total energy in both directions, the stationary point is a transition structure and the coordinate is the reaction coordinate. This process of determining stationary points is called geometry optimization. The positions of the stationary points on a PES is shown in Figure 2.9.

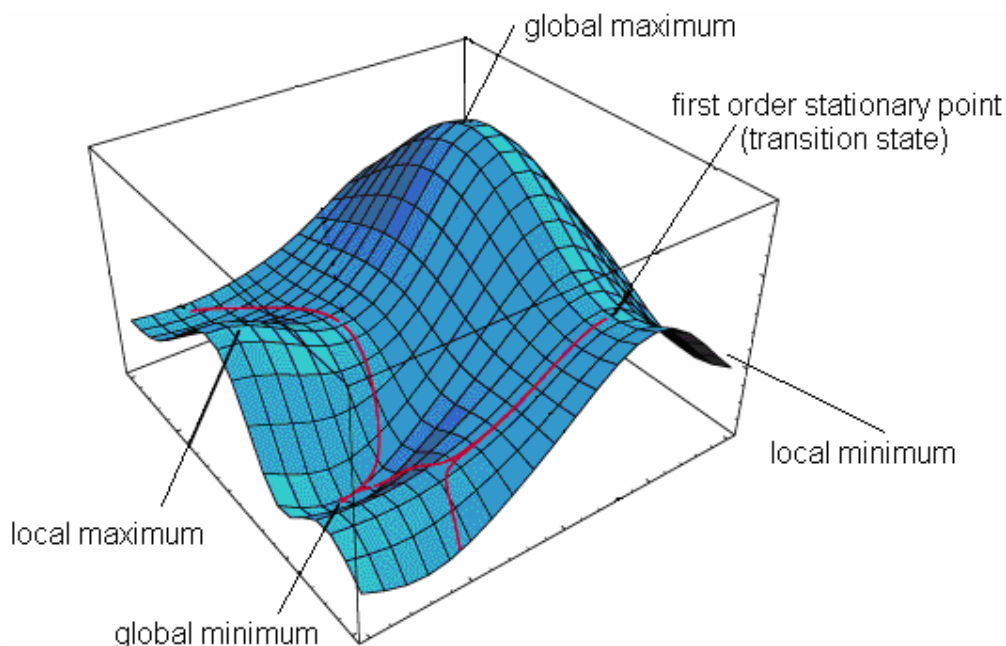


Figure 2.9. Stationary points on PES

The determination of molecular structure by geometry optimization became routine only when efficient methods for calculating the first derivatives of the energy with respect to all atomic coordinates became available. Evaluation of the related second derivatives allows the prediction of vibrational frequencies if harmonic motion is assumed. In some ways more importantly it allows the characterization of stationary points.

The frequencies are related to the eigenvalues of the matrix of second derivatives (the Hessian matrix). If the eigenvalues are all positive, then the frequencies are all real and the stationary point is a local minimum. If one eigenvalue is negative (an imaginary frequency), the stationary point is a transition structure. If more than one eigenvalue is negative the stationary point is a more complex one, and usually of little interest.

The total energy is determined by approximate solutions of the time-dependent Schrödinger equation, usually with no relativistic terms included, and making use of the Born-Oppenheimer approximation which, based on the much higher velocity of the electrons in comparison with the nuclei, allows the separation of electronic and nuclear motions, and simplifies the Schrödinger equation as mentioned before. This leads to evaluating the total energy as a sum of the electronic energy at fixed nuclei positions plus the repulsion energy of the nuclei. A notable exception are certain approaches called direct quantum chemistry, which treat electrons and nuclei on a common footing. Density functional methods and semi-empirical methods are variants on the major theme. For very large systems the total energy is determined using molecular mechanics.

### **2.8.6. The Hartree-Fock Approximation**

The Hartree-Fock method assumes that the exact, N-body wavefunction of the system can be approximated by a single Slater determinant (in the case where the particles are fermions) or by a single permanent (in the case of bosons) of N spin-orbitals. Invoking the variational principle one can derive a set of N coupled equations for the N spin-orbitals. Solution of these equations yields the Hartree-Fock wavefunction and energy of the system, which are approximations of the exact ones.

The Hartree-Fock method finds its typical application in the solution of the electronic Schrödinger equation of atoms, molecules and solids but it has also found widespread use in nuclear physics.

The Hartree-Fock method is also called, especially in the older literature, the self-consistent field method (SCF) because the resulting equations are almost universally solved by means of an iterative, fixed-point type algorithm (see the following section for more details). This solution scheme is not the only one possible and is not specific of the Hartree-Fock method. Therefore self-consistent field is a potentially ambiguous denomination.

The discussion here is only for the Restricted Hartree-Fock method, where the atom or molecule is a closed-shell system with all orbitals (atomic or molecular) are doubly occupied. Open shell systems, where some of the electrons are not paired, can be dealt with by one of two Hartree-Fock methods:

- **Restricted Open-Shell Hartree-Fock (ROHF)**

ROHF theory is a variant of Hartree-Fock theory for open shell molecules. It uses doubly occupied molecular orbitals as far as possible and then singly occupied orbitals for the unpaired electrons.

In contrast to Unrestricted Hartree-Fock (UHF), the ROHF wave function is a satisfactory eigenfunction of the total spin operator.

- **Unrestricted Hartree-Fock (UHF)**

UHF theory is the most common molecular orbital method for open shell molecules where the number of electrons of each spin are not equal. While restricted Hartree-Fock theory uses a single molecular orbital twice, once multiplied by the  $\alpha$  spin function and once multiplied by the  $\beta$  spin function in the Slater determinant, unrestricted Hartree-Fock theory uses different molecular orbitals for the  $\alpha$  and  $\beta$  electrons. This has been called a different orbitals for different spins method.

Unrestricted Hartree-Fock theory was developed by John Pople (Pople and Nesbet, 1954) and it is found in almost all ab initio programs.

### **2.8.7 Ab Initio Methods and Density Functional Theory**

The term ab initio comes from the Latin words for 'from the beginning'. In an ab initio calculation, a model is chosen for the electronic wavefunction and the electronic Schrödinger equation is solved using as input only the values of the fundamental constants and the atomic numbers of the nuclei.

The accuracy of this approach is determined primarily by the model chosen for the wavefunction. For large molecules, accurate ab initio calculations are computationally time consuming and semiempirical methods have been developed to treat a wider variety of chemical species.

Density functional theory (DFT) methods are often considered to be ab initio methods for determining the molecular electronic structure, even though many of the most common functionals use parameters derived from empirical data, or from more complex calculations. This means that they could also be called semi-empirical methods. It is best to treat them as a class on their own. In DFT, the total energy is expressed in terms of the total electron density rather than the wave function. In this type of calculation, there is an approximate Hamiltonian and an approximate expression for the total electron density. DFT methods can be very accurate for little computational cost. The drawback is, that unlike ab initio methods, there is no systematic way to improve the methods by improving the form of the functional.

### **2.8.8. Basis Sets**

Generically, a basis set is a collection of vectors which defines a space in which a problem is solved, whereas a basis set in chemistry is a set of functions used to create the molecular orbitals, which are expanded as a linear combination of such functions with the weights or coefficients to be determined.

Usually these functions are atomic orbitals, in that they are centered on atoms, but functions centered in bonds or lone pairs have been used as have pairs of functions centered in the two lobes of a p orbital.

In modern computational chemistry, quantum chemical calculations are typically performed within a finite set of basis functions. In these cases, the wavefunctions

under consideration are all represented as vectors, the components of which correspond to coefficients in a linear combination of the basis functions in the basis set used. The operators are then represented as matrices in this finite basis.

There are numerous types of basis sets. A few of them can be defined as:

- **Minimal basis set** : Contains one basis function (Slater type orbitals, STO, or Gaussian type orbitals ) for each atomic orbital in the atom.
- **Double-zeta basis set** : Contains two basis functions for each atomic orbitals.
- **Triple-zeta basis set** : Contains three basis functions for each atomic orbitals and this continues for quadruple-zeta , 5z, 6z, etc.

Having different-sized functions allows the orbital to get bigger or smaller when other atoms approach it. A split-valence basis uses only one basis function for each core atomic orbitals, and a larger basis for the valence of atomic orbitals.

While choosing the basis set for the computation it is important that a basis set should be able to describe the actual wave function well enough to give chemically useful results, and accuracy must be weighed against computational cost.

### 3. THE AIM OF THE WORK

The primary objective of this thesis is to try a new method in generating transition metal carbene species, which would be active in olefin metathesis reactions and in particular metathesis of acyclic olefins.

For this purpose, experiments in carbon arc reactor were conducted. As the transition metal complex tungsten hexachloride,  $WCl_6$ , and as terminal and internal acyclic olefins 1-octene, 2-octene, 1-heptene, 2-heptene, 1-pentene and 2-pentene were chosen.

It is also aimed to determine the structure and the mechanism of formation of the tungsten carbene species, which initiate the metathesis reaction. To do this both trapping experiments and theoretical calculations at B3LYP/ LANL2DZ level of DFT were performed.

Furthermore, again by computational means with the same methods, to illuminate the structures and energetics of all of the transition states and intermediates involved in both productive and nonproductive steps of the self metathesis of 1-octene is intended.



## 4. EXPERIMENTAL

### 4.1. Properties of Chemicals

Most of the chemicals used in our experiments were purchased from Merck, Aldrich and Sigma. Solvents were either reagent or technical grade and when necessary they were purified by distillation.

- **Graphite rods**

For all carbon arc experiments, 99.995 % pure high density graphite rods (Aldrich) with 6 mm diameter and 150 mm length were used.

- **Liquid nitrogen**

Liquid nitrogen at 77 K was used for the cooling of the reactor during the carbon arc.

- **Vacuum grease**

Connection parts of the experimental equipment were oiled with Dove Corning high vacuum grease.

- **Tungsten hexachloride ( $WCl_6$ )**

$WCl_6$  (Aldrich) was used as starting material for metal carbene synthesis. This dark violet blue species exists as a volatile solid under standard conditions with melting point at 275 °C and boiling point at 346 °C. It is an important starting reagent in the preparation of tungsten compounds.  $WCl_6$  is a rare example of a neutral charged hexachloride. In the presence of moisture or oxygen,  $WCl_6$  easily oxidizes to  $WOCl_4$ , thus to prevent from oxidation, it was filled into graphite rods, placed immediately into the reactor and the air in the reactor was evacuated by vacuum pump.

- **Acyclic olefins**

For metathesis reactions both terminal and internal acyclic olefins (Sigma-Aldrich), 1-octene, 2-octene, 1-heptene, 2-heptene, 1-pentene and 2-pentene, were used. These olefins were purified by distillation before the experiments.

- **Benzaldehyde**

Benzaldehyde is a common terminating agent for metathesis reactions (Bencze et al., 1985, Wallace et al., 1989, Park et al., 1991, Fox et al., 1994). In this work, benzaldehyde (Aldrich) was used as the trapping molecule for the tungsten carbene species.

- **Cyclohexane**

HPLC grade cyclohexane (Labscan) was used as solvent for the metathesis products of 1-octene, 2-octene, 1-heptene, 2-heptene and 1-pentene. It was placed in the flask of the reactor before the experiment and sent into the reactor by vaporizing after the reaction mixture reached to the room temperature and metathesis reactions occurred.

- **Chlorobenzene**

Technical grade chlorobenzene (Riedel de Haën) was used for taking low molecular weight metathesis products of 2-pentene into solution.

- **Other solvents**

Chloroform (Riedel de Haën), dichloromethane (Labscan) and extra pure toluene (Merck) were also used as solvent .

## **4.2. Experimental Procedure**

### **4.2.1. Metal Atom Vaporization Technique**

The carbon atom reactor is modeled after that described by Philip Skell (Skell et al., 1965).

The technique, metal atom vapor chemistry, generates single atoms of metal, which behave quite differently from their more familiar bulk metal forms and reacting these metal atoms may generate valuable new materials. Skell pioneered the technique in the early 1970s (Skell et al., 1973).

Some chemists and materials scientists are using it to produce catalysts for difficult chemical reactions and synthesize new compounds. Other scientists are

looking at the technique as a way to produce novel materials with a variety of applications that include refining petrochemical products and improving information storage and processing.

In metal atom vaporization, metal is heated in a vacuum and condensed on the cooled walls of the reactor in which the process takes place. As the metal atoms are deposited, solvent or reactant molecules are also condensed and deposited on the reactor walls, which have been chilled by immersion in liquid nitrogen. When what is now a frozen mixture of metal atoms and solvent or reactants warms, compounds form, some of which can not be prepared by any other known synthetic technique. Surrounding a metal atom with a solvent blocks its natural tendency to agglomerate to form bulk metal.

Metal atom vapor chemistry has allowed organometallic chemists to synthesize some compounds that were predicted to exist, but couldn't be made by other means. In recent years, it has made some significant contributions to heterogeneous catalysis. Metal atom vaporization has been used to create heterogeneous catalysts such as a metal fixed to an inorganic support.

In this work, pure graphite was vaporized in the reactor and carbon atoms were generated. These high energy atomic carbons were interacted with the tungsten salt  $WCl_6$  and tungsten carbene species were synthesized in situ.

#### **4.2.2. Set-up of Equipment and the Experiment**

Before the experiment, the carbon arc reactor shown in Figure 4.1. was connected with a series of equipment containing an U-trap to a vacuum pump as in Figure 4.2. The ends of two 6 cm high purity graphite rods were drilled to open a hollow with 3 mm diameter and 2 cm length. Then they were filled with powdered  $WCl_6$ , attached to the copper electrodes and the electrodes were placed into the reactor.

1 ml olefin is placed into one of the flasks of the reactor and about 5 ml of the solvent, into the other. The taps connecting the flasks to the reactor were closed and that of connecting the reactor to the vacuum pump were opened. After that the vacuum pump was turned on.

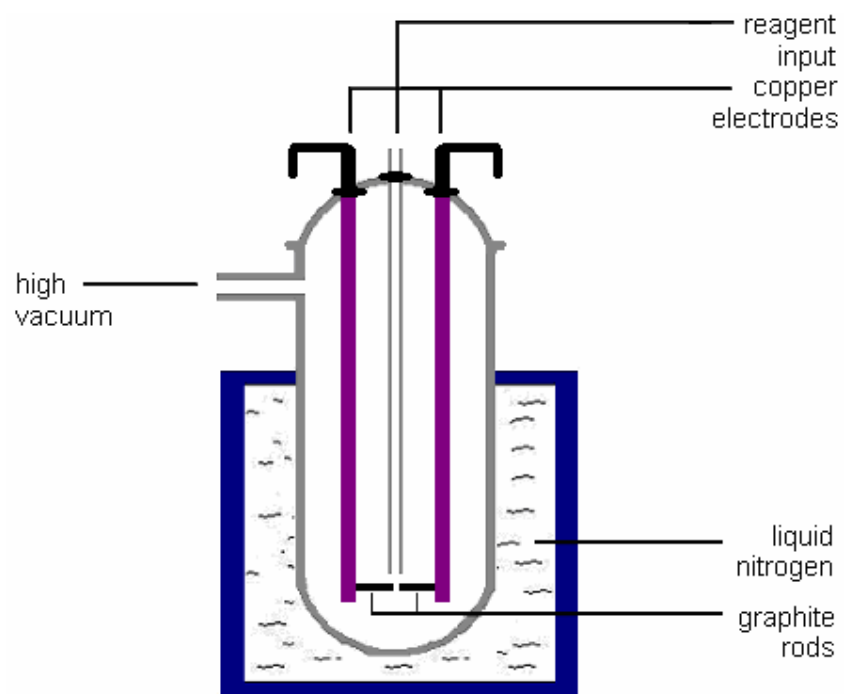


Figure 4.1. Detailed representation of carbon arc reactor

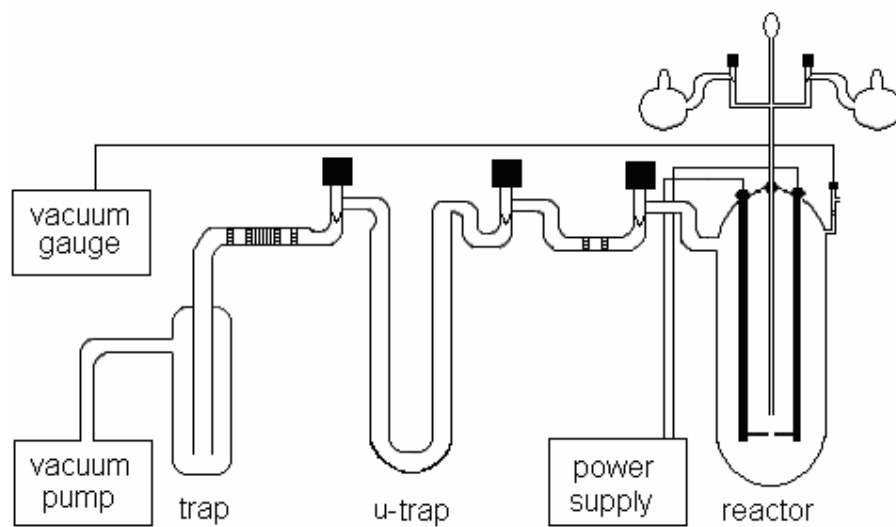


Figure 4.2. Experimental equipment of carbon arc reactor

When the pressure of the system decreased below 10 mtorr, experiments could be started.

Firstly, to remove the dissolved oxygen from the olefin and from the solvent, degas procedure was applied to both liquids in flasks. To do this, flasks were cooled with liquid nitrogen and when the liquids were frozen, taps of the flasks were opened to vacuum. Then taps were closed and frozen liquids were allowed to warm. This procedure was repeated until the change in pressure due to the gas evolved from flasks was negligible.

When the pressure of the system decreased below 10 mtorr again, the system was cooled with liquid nitrogen at 77 K. To do this, besides the reactor, both traps of the system were immersed into liquid nitrogen and then the power of the electrodes was turned on. To prevent powdered  $WCl_6$  from dispersing and venting off to vacuum, graphites were kept connected until they melted and stuck. Then they were parted and an arc (at an 80 A current and an alternating (~12-64 V) voltage) was struck intermittently between the graphite rods. The temperature attained on the electrodes at the instant of arc is above 2500 °C, thus electrodes of the reactor were cooled by running water during the experiment.

After a while poles of the electrodes were exchanged for using both rods efficiently. When the graphite rods were used up, the tap of the reactor was closed, the power of electrodes and the vacuum pump were turned off, and the tap of the olefin flask was opened to the reactor. The liquid olefin in the flask vaporized and then condensed on the walls of the reactor with help of the low temperature and high vacuum in the reactor.

Finally, liquid nitrogen was removed and the reactor was allowed to warm to room temperature. At room temperature reactions between C atom,  $WCl_6$  and olefin occurred.

After 30 minutes, the solvent was sent into the reactor with the same way as the olefin and then the vacuum was released. Finally, the contents of the reactor analyzed for any metathesis product by GC/MS.

### 4.3. Analysis Methods

#### 4.3.1. GC-MS Analyses

The gas chromatography is an efficient tool for separation and identification of components from a mixture of organic compounds. Characterization of unknown components is often possible from retention times appropriate to the particular column used.

Mass spectrometry, on the other hand, because of high sensitivity and fast scan speeds, is the technique most suitable to provide definite structural information from the small quantities of material eluted from gas chromatography.

The association of these two techniques has therefore provided a powerful means of structure identification.

Qualitative analysis of the reaction mixtures of the metathesis experiments were made by GC-MS. Basic properties of the GC-MS system used in this work are given in Table 4.1.

Table 4.1. Properties and working conditions of the GC-MS system

---

Gas chromatograph	: Shimadzu GC17A
Mass spectrometer	: Shimadzu GCMS-QP5050A
Column	: Optima-5
Column length	: 50 m
Column diameter	: 0.32 mm
Column flow	: 2.3 ml/min
Injection	: 1 $\mu$ l sample
Linear velocity	: 42.6
Split ratio	: 10
Oven temperature	: 50 °C
Injection temperature	: 275 °C
Interface temperature	: 280 °C
Initial temperature	: 50 °C
Rate	: 8 °C/min
Final temperature	: 250 °C/min

---

#### 4.4. Computational Methods

The quantum chemical calculations were carried out by density functional theory (DFT) (Kohn et al., 1964, 1965, Parr and Yang, 1989, Becke, 1992, Gill et al., 1992, Pople et al., 1992,1998) since it usually gives realistic geometries, relative energies and vibrational frequencies for transition metal compounds.

All calculations presented in this work were performed with the Gaussian 03 Revision B.03 molecular modeling program (Frisch et al., 2003).

All geometries were fully optimized, without any symmetry restrictions, by using Becke 3-term functional with Lee-Yang-Parr exchange correlation (B3LYP) (Lee et al., 1988, Becke, 1993) in combination with the Los Alamos National Laboratory 2-Double-zeta, (LANL2DZ) basis set (Hay and Wadt, 1985).

The convergence criteria for the optimizations consisted of threshold values of  $4.5 \times 10^{-4}$  ,  $3 \times 10^{-4}$  ,  $1.8 \times 10^{-3}$  and  $1.2 \times 10^{-3}$  for maximum force, root-mean-square (RMS) of the forces, maximum displacement and RMS displacement convergence, respectively.

The geometries optimized were also subjected to full frequency analyses at the same level of theory to verify the nature of the stationary points. Equilibrium geometries were characterized by the absence of imaginary frequencies, whereas the transition structure geometries exhibited only one imaginary frequency in the reaction coordinate.

For transition state (TS) geometries, confirmation calculations, involving intrinsic reaction coordinates (IRC) calculations, were performed in which the path connecting reagents, TS and products are mapped.

The energy values that are given in the results are the electronic energies at 298 K for an isolated system in the gas phase and therefore only the electronic effects are considered in this study.

## 5. RESULTS AND DISCUSSION

### 5.1. Experimental Results

Olefin metathesis (both self and cross metathesis) and isomerization reactions can take place during the self metathesis of acyclic olefins to form a variety of products. As an example, some of the possible reactions 1-octene can undergo in the presence of a metathesis catalyst are given in Table 5.1.

Table 5.1. Possible reactions of 1-octene in the presence of metathesis catalysts

Reaction	Substrate	Products
<i>Primary metathesis</i>		
Self metathesis	$\text{H}_2\text{C}=\text{C}_7\text{H}_{14}$	$\text{H}_2\text{C}=\text{CH}_2 + \text{H}_{14}\text{C}_7=\text{C}_7\text{H}_{14}$
<i>Isomerization</i>	$\text{H}_2\text{C}=\text{C}_7\text{H}_{14}$	$\text{H}_4\text{C}_2=\text{C}_6\text{H}_{12} + \text{H}_6\text{C}_3=\text{C}_5\text{H}_{10} +$ $\text{H}_8\text{C}_4=\text{C}_4\text{H}_8$
<i>Secondary metathesis</i>		
Self metathesis	$\text{H}_4\text{C}_2=\text{C}_6\text{H}_{12}$	$\text{H}_4\text{C}_2=\text{C}_2\text{H}_4 + \text{H}_{12}\text{C}_6=\text{C}_6\text{H}_{12}$
Cross metathesis	$\text{H}_2\text{C}=\text{C}_7\text{H}_{14} + \text{H}_4\text{C}_2=\text{C}_6\text{H}_{12}$	$\text{H}_2\text{C}=\text{C}_2\text{H}_4 + \text{H}_2\text{C}=\text{C}_6 + \text{H}_4\text{C}_2=\text{C}_7\text{H}_{14} +$ $\text{H}_{12}\text{C}_6=\text{C}_7\text{H}_{14}$

Three major groups of products, i.e. primary metathesis products, isomerization products and secondary metathesis products are possible. Following the double bond isomerization of 1-octene to 2-octene, secondary cross metathesis reactions between the two olefins can take place yielding 1-heptene, which in turn can undergo the same series of reactions. This gives rise to a cascade of reactions eventually leading to a range of  $\text{C}_2\text{-C}_{14}$  olefin products. Similarly each olefin used in this work is supposed to give its own isomerization, primary metathesis and secondary metathesis products.

According to our experimental results, for each of the acyclic olefins that we used as substrate, the formation of expected primary metathesis product was obtained.

Some of secondary metathesis and isomerization products were also found to exist in resulting reaction mixtures.



GC-MS analysis results of reaction mixture of each olefin are given in figures and tables below. The peaks in the chromatograms of the reaction mixtures were identified by comparison of retention times with that of authentic samples, which are recorded by using the same GC-MS device at the same working conditions. The characteristic mass spectra of olefins were also very helpful for identification.

The list of the retention times (RT) in minutes (min) and molecular masses of the authentic samples of expected metathesis products is given in Table 5.2.

Table 5.2. Retention times of authentic samples of olefins

Olefin	Mass	RT(min)
1-/ 2-pentene, C <sub>5</sub>	70	2.700/ 2.760
3-hexene, C <sub>6</sub>	84	3.625
1-/ 2-heptene, C <sub>7</sub>	98	6.100/ 5.500
1-/ 2-octene, C <sub>8</sub>	112	7.085/ 7.775
nonene, C <sub>9</sub>	126	9.824
decene, C <sub>10</sub>	140	11.838
undecene, C <sub>11</sub>	154	14.100
dodecene, C <sub>12</sub>	168	16.200
tridecene, C <sub>13</sub>	182	18.200
tetradecene, C <sub>14</sub>	196	20.110

### 5.1.1. Products of 1-Octene

As explained above, from ethylene to tetradecene, in varying amounts, formation of all olefins is expected as a result of the metathesis and isomerization reactions that 1-octene undergoes. GC-MS analysis results confirmed the formation of C<sub>14</sub>, C<sub>10</sub> and C<sub>13</sub> olefins with retention times at 20.100, 11.750, and 18.208 minutes respectively on the gas chromatogram given in Figure 5.1.

It is also seen that besides these olefins, chlorinated side products arised from  $WCl_6$  were formed. The chlorinated product, namely chlorooctane, has a retention time at 12.248 min on the chromatogram. Product distribution of  $WCl_6$ / C atom / 1-octene system is given in Table 5.3.

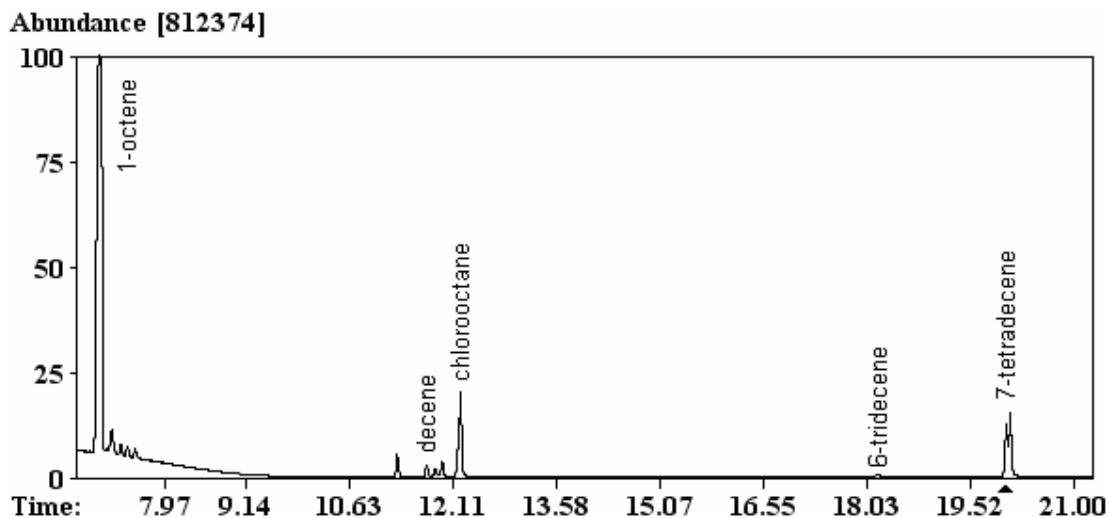


Figure 5.1. Gas chromatogram of  $WCl_6$ / C atom / 1-octene system

Table 5.3. GC-MS analysis results for  $WCl_6$ / C atom/ 1-octene system

RT(min)	% area	mass	corresponding species
7.250	44.98	112	1-octene
11.750	0.70	140	decene
12.248	4.24	148	chlorooctane
18.208	0.06	182	6-tridecene
20.100	3.53	196	7-tetradecene

When the mass spectra of the relevant peaks on the gas chromatogram are examined, it is seen that mass spectra of metathesis products are characterized by distinct molecular ion peaks and clusters of peaks at intervals of 14 units.

The mass spectrum of 7-tetradecene, with a molecular ion peak at mass-to-charge ratio ( $m/z$ ) 196, is shown in Figure 5.2. The peaks at  $m/z$  55, 69, 83, 97, 111, 125, 139, 153 and 168 also correspond to the molecule. These values are matching with that of the authentic sample.

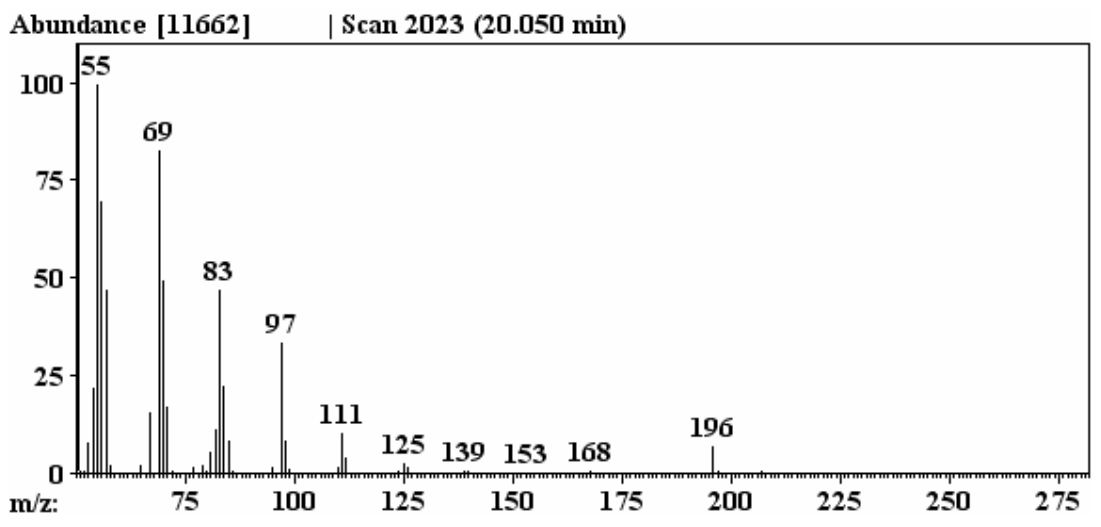


Figure 5.2. Mass spectrum of 7-tetradecene from 1-octene

### 5.1.2. Products of 2-Octene

Expected products of metathesis and isomerization reactions of 2-octene are 6-dodecene, as primary metathesis product, and all the olefins from ethylene to dodecene as secondary metathesis or isomerization products.

As seen in Figure 5.3., the peak of 6-dodecene was observed at retention time 12.933 min on the gas chromatogram of the reaction mixture. Again formation of the chlorinated product was observed at 11.100 min and methyl octene was also observed as a side product which was produced due to C atom reactions of 1-octene. Important peaks from GC-MS of  $WCl_6$ / C atom/ 2-octene system are given in Table 5.4.

The mass spectrum of 6-dodecene, shown in Figure 5.4, is similar to that of 7-tetradecene. Molecular ion peak appears at  $m/z$  168. The mass spectrum is in agreement with that of the authentic sample.

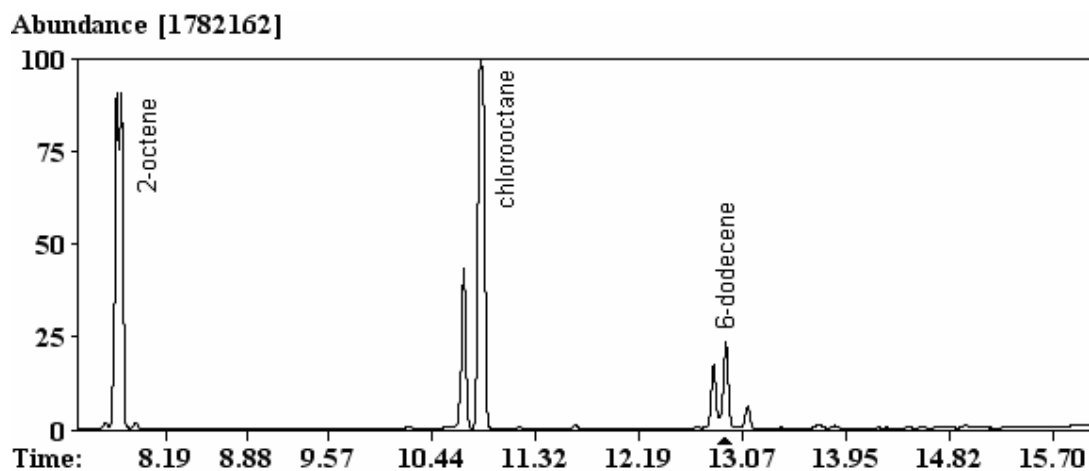


Figure 5.3. Gas chromatogram of  $WCl_6$ / C atom/ 2-octene system

Table 5.4. GC-MS analysis results for  $WCl_6$ / C atom/ 2-octene system

RT(min)	% area	mass	corresponding species
7.700	45.83	112	2-octene
10.900	5.70	126	methyl octene
11.100	39.08	148	chlorooctane
12.933	2.85	168	6-dodecene

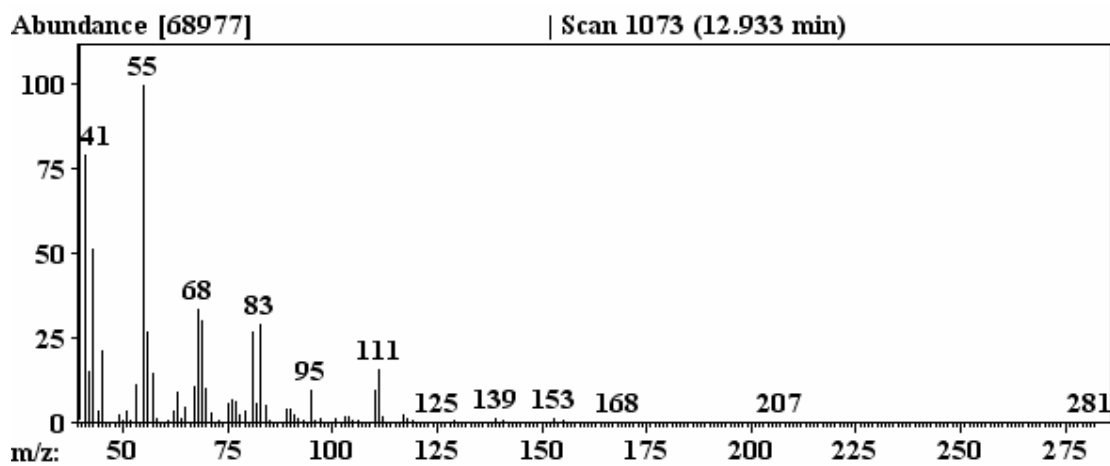


Figure 5.4. Mass spectrum of 6-dodecene from 2-octene

### 5.1.3. Metathesis Products of 1-Heptene

Primary metathesis product of 1-heptene is also 6-dodecene with a peak at 13.142 min retention time on the gas chromatogram of  $WCl_6$ / C atom / 1-heptene reaction mixture shown in Figure 5.5. The chlorination product, chloroheptane appears with a large peak at 9.300 min. The products observed are given in Table 5.5 with respect to their retention times, molecular mass and percent peak areas on the gas chromatogram.

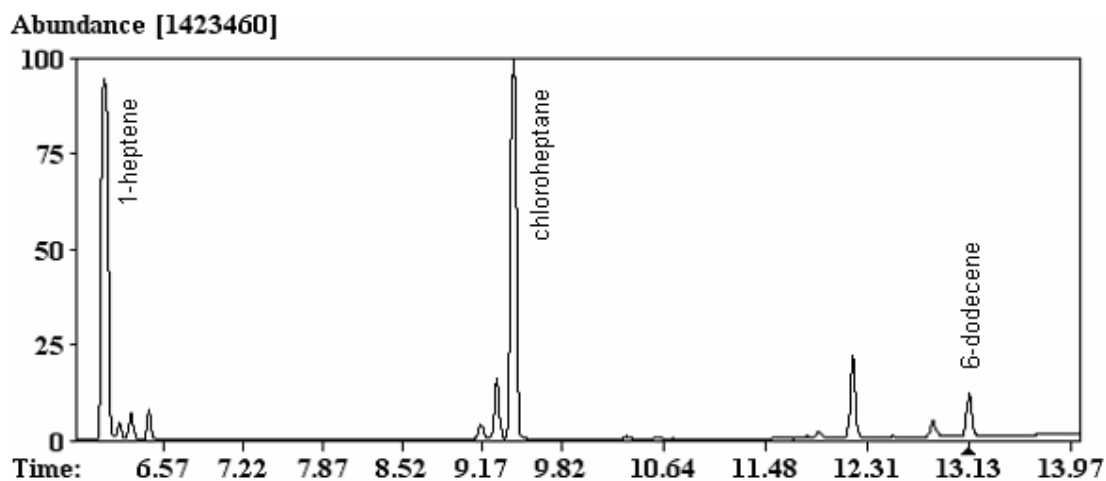


Figure 5.5. Gas chromatogram of  $WCl_6$ / C atom / 1-heptene system

Table 5.5. GC-MS analysis results for  $WCl_6$ / C atom/ 1-heptene system

RT(min)	% area	mass	corresponding species
5.400	40.31	98	heptene isomers
9.433	34.22	134	chloroheptane
10.601	0.22	140	5-decene
13.142	2.44	168	6-dodecene

Molecular ion peak appears at  $m/z$  168. The other peaks involved in the spectrum are at  $m/z$  41,55, 69, 83, 97, 111, 125,139 and 153.

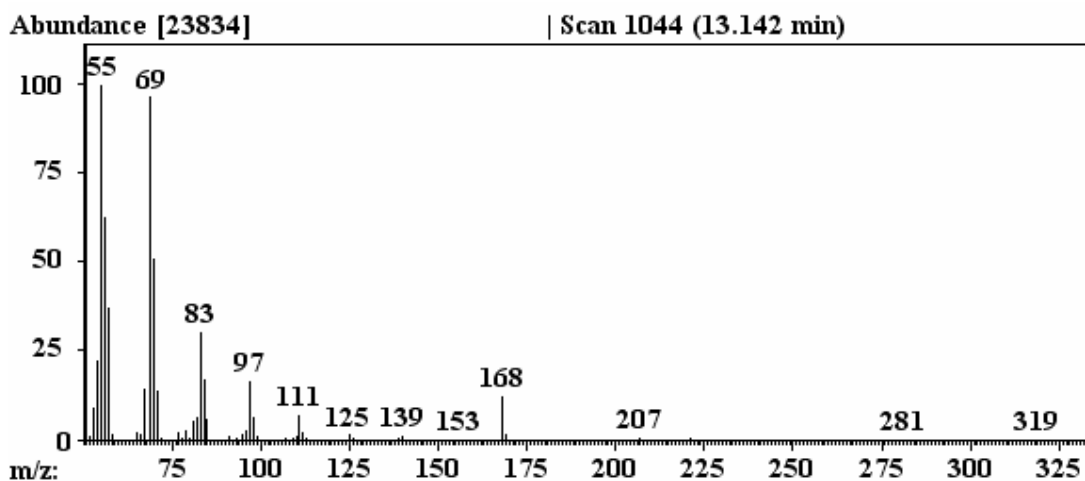


Figure 5.6. Mass spectrum of 6-dodecene from 1-heptene

#### 5.1.4. Metathesis Products of 2-Heptene

The self metathesis of 2-heptene was the most successful metathesis reaction which was carried out in this work. There were little isomerization products and therefore, product distribution was narrow. As seen in the gas chromatogram in Figure 5.7., the primary metathesis product of 2-heptene is 5-decene and unlike the metathesis products of other olefins, 5-decene from 2-heptene has a greater peak area, at 11.850 min, than the chlorination product.

The only secondary metathesis product is 4-nonene, appearing on the chromatogram with a peak at 9.482 retention time. This product may have been produced by the cross metathesis reaction of 3-heptene and 2-heptene. Important peaks in the chromatogram and the corresponding species are given in Table 5.6.

The mass spectrum of the primary metathesis product, 5-decene is shown in Figure 5.8. The molecular ion peak appears at  $m/z$  140 and the other peaks have  $m/z$  41, 55, 69, 83, 97, 111, 125 values as expected.

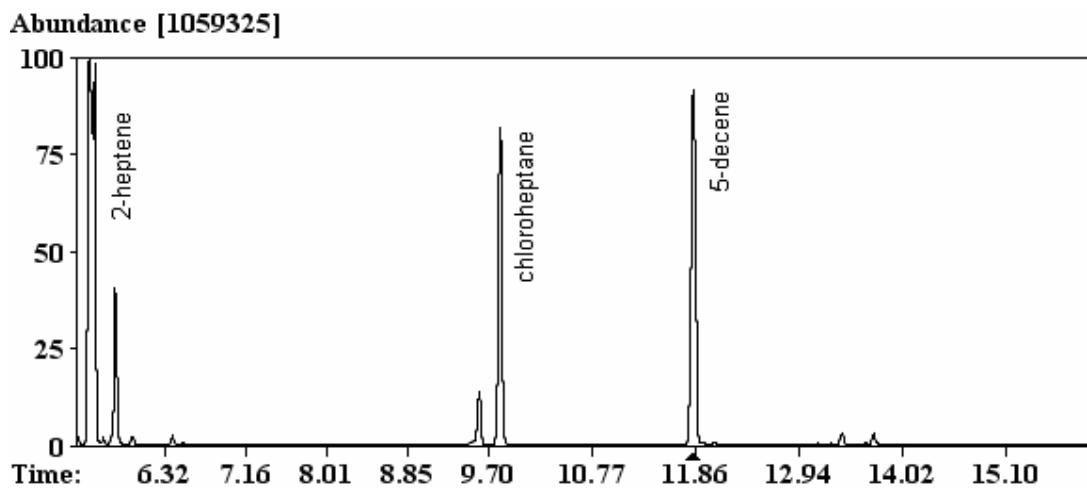


Figure 5.7. Gas chromatogram of  $WCl_6$ / C atom/ 2-heptene system

Table 5.6. GC-MS analysis results for  $WCl_6$ / C atom/ 2-heptene system

RT(min)	% area	mass	corresponding species
5.508	20.97	98	2-heptene
9.482	0.96	126	4- nonene
9.825	8.10	134	chloroheptane
11.850	10.80	140	5-decene

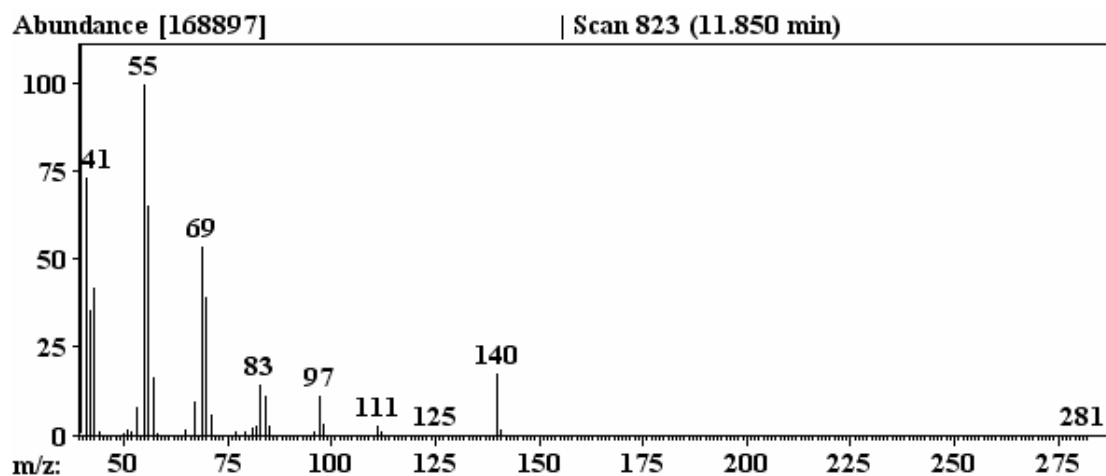


Figure 5.8. Mass spectrum of 5-decene from 2-heptene

### 5.1.5. Metathesis Products of 1-Pentene

In most cases, since the isomerization and the secondary metathesis reactions predominate the primary metathesis, obtaining the primary metathesis products of acyclic pentenes has been difficult (Ivin and Mol, 1997). After a few attempts we succeeded in doing this.

The main peaks belong to the chlorinated products within a retention time range of 5.317-5.917 min. The primary metathesis product of 1-pentene is 4-octene and its isomers, which has several peaks at about 7.25 min retention time on the gas chromatogram shown in Figure 5.9. Production of nonene and heptene was also observed as given in Table 5.7.

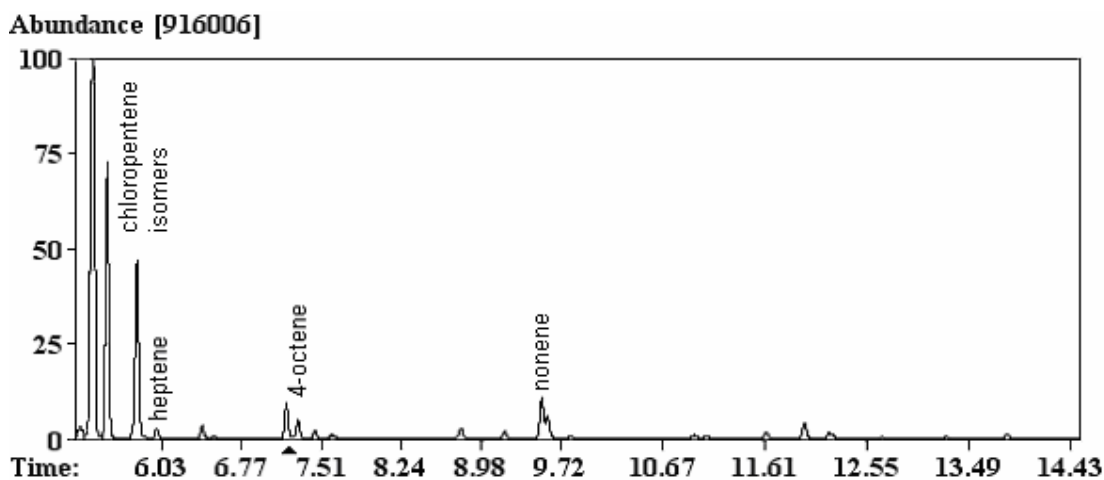


Figure 5.9. Gas chromatogram of  $WCl_6$ / C atom/ 1-pentene system

Table 5.7. GC-MS analysis results for  $WCl_6$ / C atom/ 1-pentene system

RT(min)	% area	mass	corresponding species
5.450	37.92	104	chloropentene isomers
6.000	0.45	98	heptene
7.275	1.53	112	4-octene
9.550	1.66	126	nonene



The mass spectrum of 4-octene from 1-pentene, taken at a retention time 7.275 min is given in Figure 5.10. The molecular ion peak at  $m/z$  112 is stable. Other peaks are at  $m/z$  55, 69 and 83 as expected.

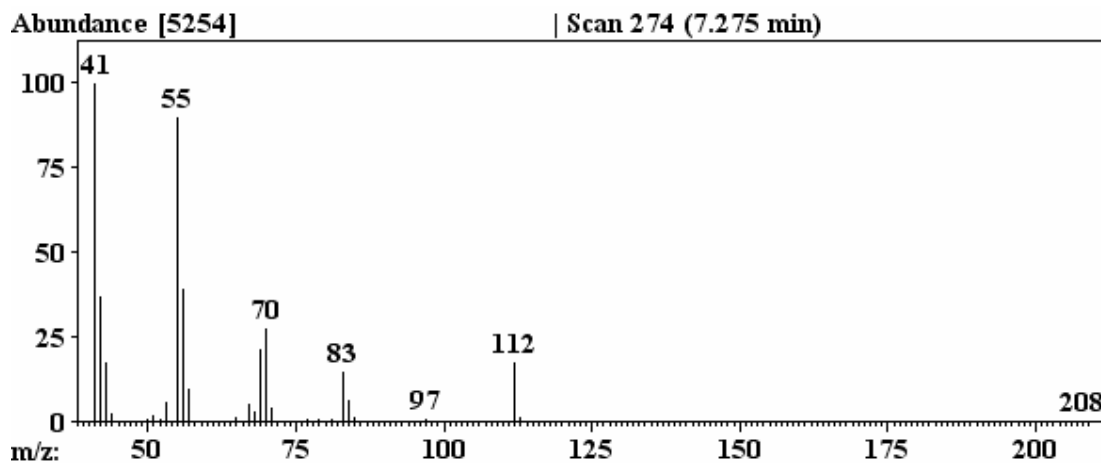


Figure 5.10. Mass spectrum of 4-octene from 1-pentene

### 5.1.6. Metathesis Products of 2-Pentene

The observed metathesis products of 2-pentene are 3-hexene as primary metathesis product and 3-heptene as secondary metathesis product. Since retention time of cyclohexane may coincide with that of 3-hexene, chlorobenzene was used as solvent in this experiment.

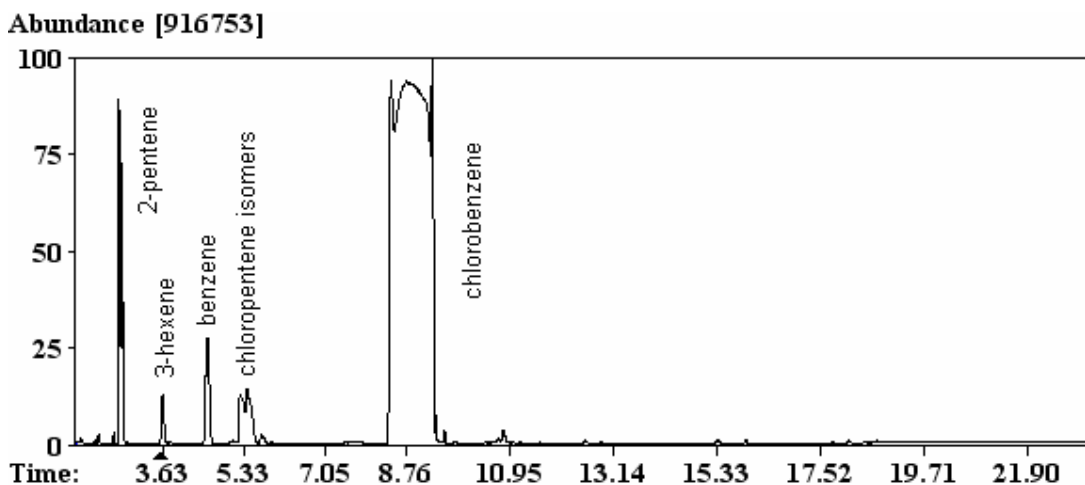


Figure 5.11. Gas chromatogram of  $WCl_6$  / C atom / 2-pentene system

The gas chromatogram of 2-pentene reaction mixture is given in Figure 5.11. 3-hexene appears at 3.592 min, whereas 3-heptene has a small peak at 5.750 min. Other peaks with amounts as percent area on the chromatogram are listed in Table 5.8.

Table 5.8. GC-MS analysis results for  $WCl_6$ / C atom/ 2-pentene system

RT(min)	% area	mass	corresponding species
2.640	9.87	70	2-pentene
3.625	0.80	84	3-hexene
4.600	2.91	78	benzene
5.300	3.25	104	chloropentene
5.750	0.30	98	3-heptene
8.853	37.06	112	chlorobenzene

The mass spectrum of 3-hexene given in Figure 5.12 is simple. The molecular ion peak has a mass to charge ratio 84.

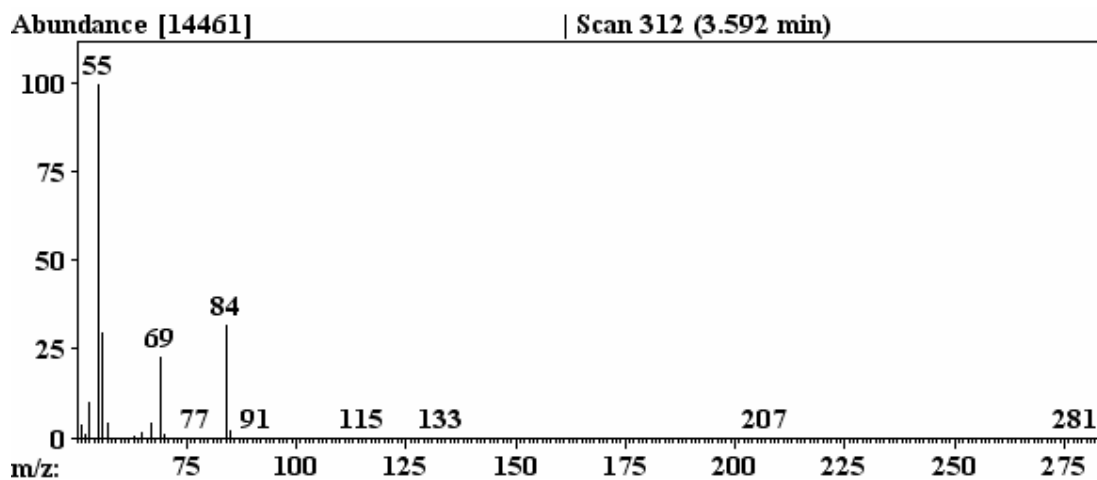


Figure 5.12. Mass spectrum of 3-hexene from 2-pentene

### 5.1.7. Results of Blank Experiment

To confirm the catalytic activity of  $WCl_6/C$  atom system in olefin metathesis reactions a blank experiment was applied.

The same experimental procedure as in the metathesis of 1-octene, was conducted without using  $WCl_6$  and as depicted in Figure 5.13., no metathesis product was obtained from GC-MS analysis of the reaction mixture. This result demonstrates that without  $WCl_6$ , metathesis reactions do not take place in our system.

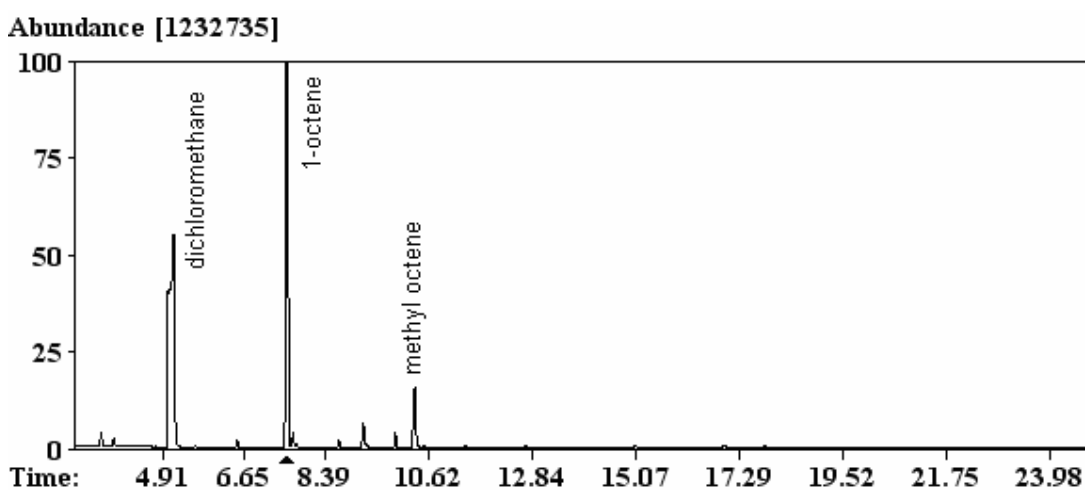


Figure 5.13. Gas chromatogram of blank reaction mixture of 1-octene

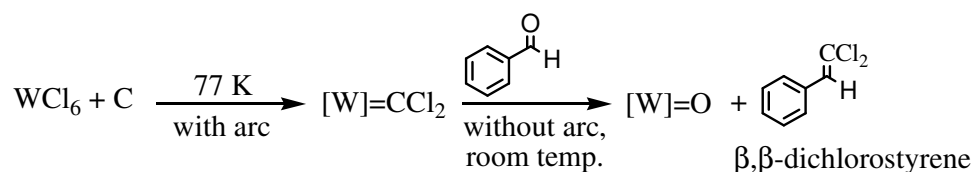
Since it is known that  $WCl_6$  itself has no catalytic activity either (Düz, 1997), this result shows that, when combined with atomic carbon,  $WCl_6$  forms an active species catalyzing olefin metathesis reactions.

### 5.1.8. Trapping of the Tungsten Carbene Species with Benzaldehyde

Previously, information regarding the nature of the initiating metal carbene has been obtained in many cases by examining the first formed products in the reactions of olefins. It is also possible trapping of the initiating molecule with a terminating agent for metathesis. Aldehydes and ketones are known terminating agents for metathesis of acyclic olefins (Ivin and Mol, 1997).

With respect to these facts, and other studies assuming that the initiating species contains a =CH<sub>2</sub> moiety (Rudler, 1980, Schilder, 1992), it was presumed that the active species within WCl<sub>6</sub>/ C atom system was [W]=CCl<sub>2</sub> and thus benzaldehyde was used as a carbene trap to catch this tungsten carbene species.

The reactions given in Scheme 5.1 were taken as the route for the experiment and repeating the usual experimental procedure with carbon arc reactor for olefin metathesis, in order to the olefin, benzaldehyde was sent into the reactor after arc.



Scheme 5.1. Formation of β,β-dichlorostyrene

When the temperature of the reactor came to the room temperature, the reaction mixture was dissolved in cyclohexane and analyzed by GC/MS.

As seen in Figure 5.14, the formation of β, β-dichlorostyrene was detected by GC-MS analysis with a peak at 17.575 min on the gas chromatogram.

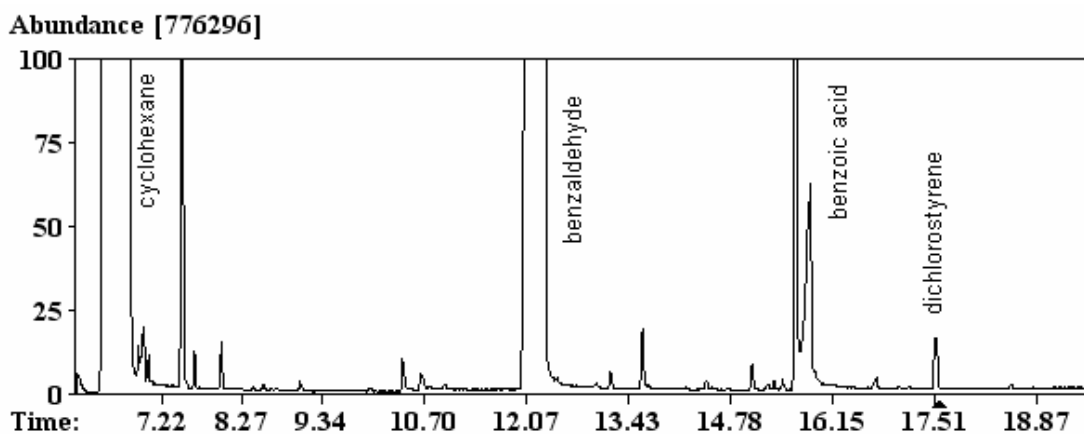


Figure 5.14. Gas chromatogram of WCl<sub>6</sub>/ C atom/ benzaldehyde system

When the mass spectrum of the product, given in Figure 5.15 is studied, it is seen that the molecular ion peak appears at  $m/z$  172 and the other fragmentations are at  $m/z$  137, 112, 102, 101, 68 and 51. The peaks at  $m/z$  174 and 176 correspond to  $[M+2]^+$  and  $[M+4]^+$  isotopic ions, respectively and with the peaks at  $m/z$  137 and 102 corresponding chlorine losses, it is clear that the structure contains two chlorine atoms.

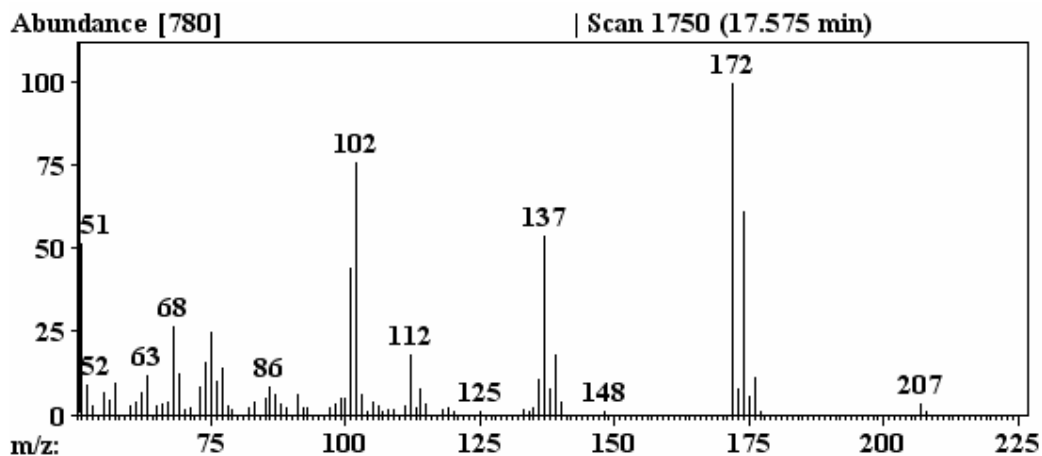
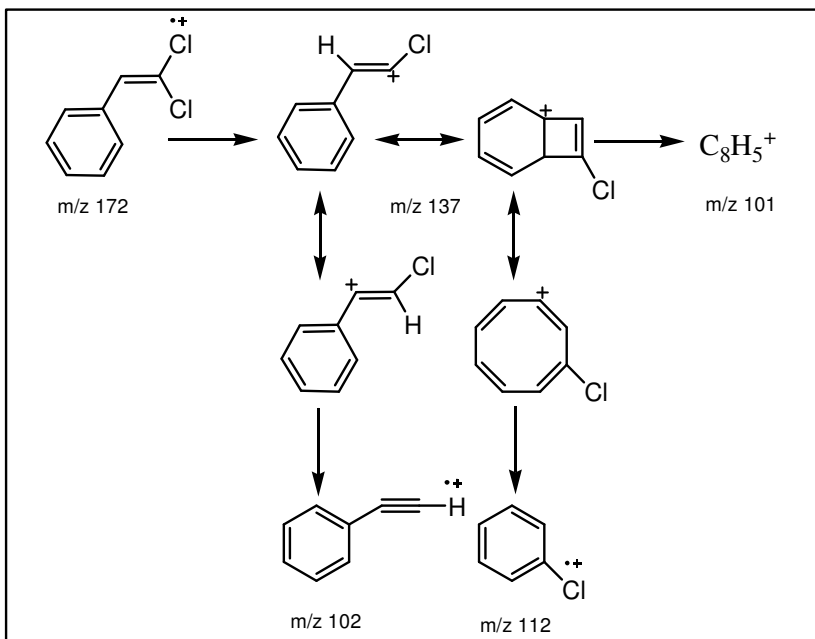


Figure 5.15. Mass spectrum of  $\beta,\beta$ -dichlorostyrene



Scheme 5.2. Possible fragmentation pathway for  $\beta,\beta$ -dichlorostyrene

For further characterization, recent studies on dichloro styrenes (Shastin et al., 2000, Li et al., 2003, Lin et al., 2004) were examined and it was seen that results of these studies were in agreement with the results of this study (Düz et al., 2006).

According to the work of Lin (Lin et al., 2004),  $\beta,\beta$ -dichlorostyrene has an abundant molecular ion, with primary fragments involving consecutive losses of chlorine and a base peak at  $m/z$  102 as seen in Scheme 5.2.

In order to retain the chlorobenzene ion as one of major fragment ions, formation of a four membered ring cation, then isomerization to a cyclooctatetraene cation, followed by loss of an acetylene molecule are the essential processes.

## 5.2. Computational Results

Conceptually the formation of a tungsten carbene precatalyst, within the  $WCl_6/C$  atom system and productive and regenerative metathesis reactions of 1-octene in the presence of this species is illustrated in Schemes 5.3, 5.4 and 5.5.

This mechanistic model is mainly based on the metal carbene metallocyclobutane mechanism proposed by Chauvin and Hérisson (1971) and our experimental results. The generic labels **1-10** are given to the individual tungsten carbene and derived species involved in the reaction mechanism.

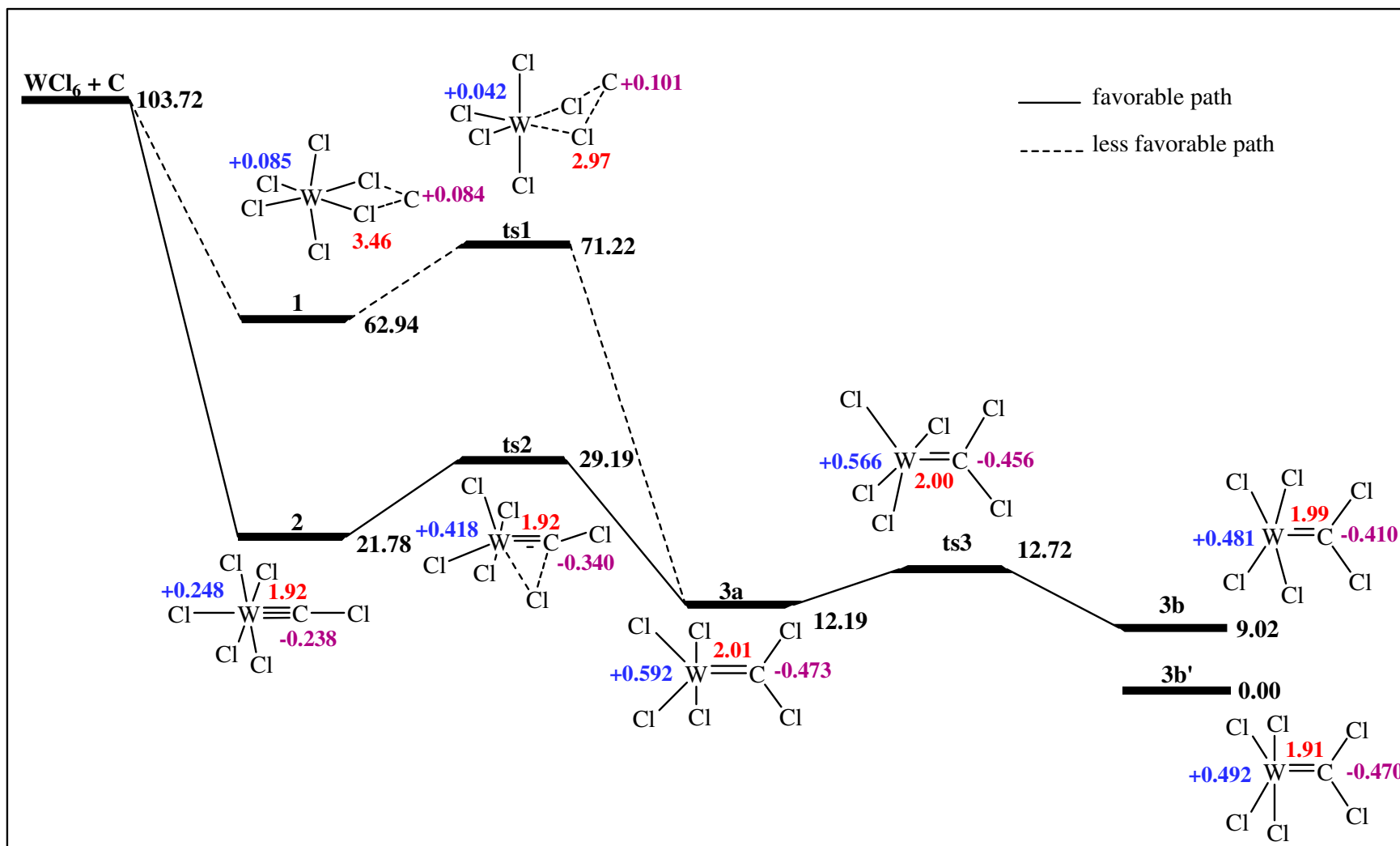
### 5.2.1. Formation and Structure of the Tungsten Carbene

In the first course of the reactions,  $WCl_6$  reacts with a C atom via carbon arc to form a tungsten carbene species. According to our experimental results, the active species that initiates the metathesis was found to be the tungsten carbene,  $[W]=CCl_2$  (Düz et al., 2006).

To gain insight into the exact structure of this tungsten carbene species and the mechanism of its formation from  $WCl_6$  and a C atom, we performed a potential energy surface scan on the  $WCl_6/C$  atom system. Geometries, relative energies as to the most stable structure, **3b'**, (kcal/mol), W-C bond lengths (Å, red) and the partial charges on W (blue) and C atoms (magenta) for the structures found on the potential energy surface of the  $WCl_6/C$  atom system are given in Scheme 5.3.

In triplet state, there are two possible pathways leading to the formation of tungsten carbenes. In the energetically less favorable path, shown with dash lines in Scheme 5.3., C atom forms a complex structure, **1**, with  $WCl_6$  and this complex transforms into the more stable structure **3a** with trigonal bipyramidal geometry and a 2.01 Å W=C bond, which is a double bond within experimental results (Cundari et al., 1992, Cho and Andrews, 2005), through **ts1** with an activation energy of 8.28 kcal/ mol.

In the way from the structure **1** to the structure **3a**, the W-C bond distance decreases steadily from 3.46 to 2.01 Å and a W=C double bond forms. The charge on the W atom increases from -0.037 to +0.592 and the charge on the C atom decreases from 0.00 to -0.473.



Scheme 5.3. Formation of tungsten carbenes



The other pathway leading to **3a** starts with structure **2**. Since there is not any complex present leading to the formation of the structure **2**, it is assumed that it had formed directly from  $WCl_6$  and a C atom via insertion of the highly energetic C atom into the W–Cl bond. This structure converts then, through **ts2** with an activation energy 7.41 kcal/mol, to **3a**. Finally, with a geometric isomerization and an activation energy 0.53 kcal/mol, the tungsten carbene **3a** adopts its least energetic form, **3b**, through **ts3**. This path is energetically more favorable.

In the singlet state, a stepwise mechanism leading to the formation of a tungsten carbene does not exist. All attempts gave only one significant zero order stationary point corresponding to the structure **3b'**, which is very similar to **3b**.

**3b** and **3b'** are the most stable structures on the potential energy surface. In comparison, although charge distributions are different, in both **3b** and **3b'**, tungsten atom has an electrophilic character with  $\delta^+$  charges, +0.481 and +0.492, and the carbon behaves as a nucleophile with  $\delta^-$  charges, -410 and -470, respectively. At singlet state W=C bond is shorter by 0.08 Å.

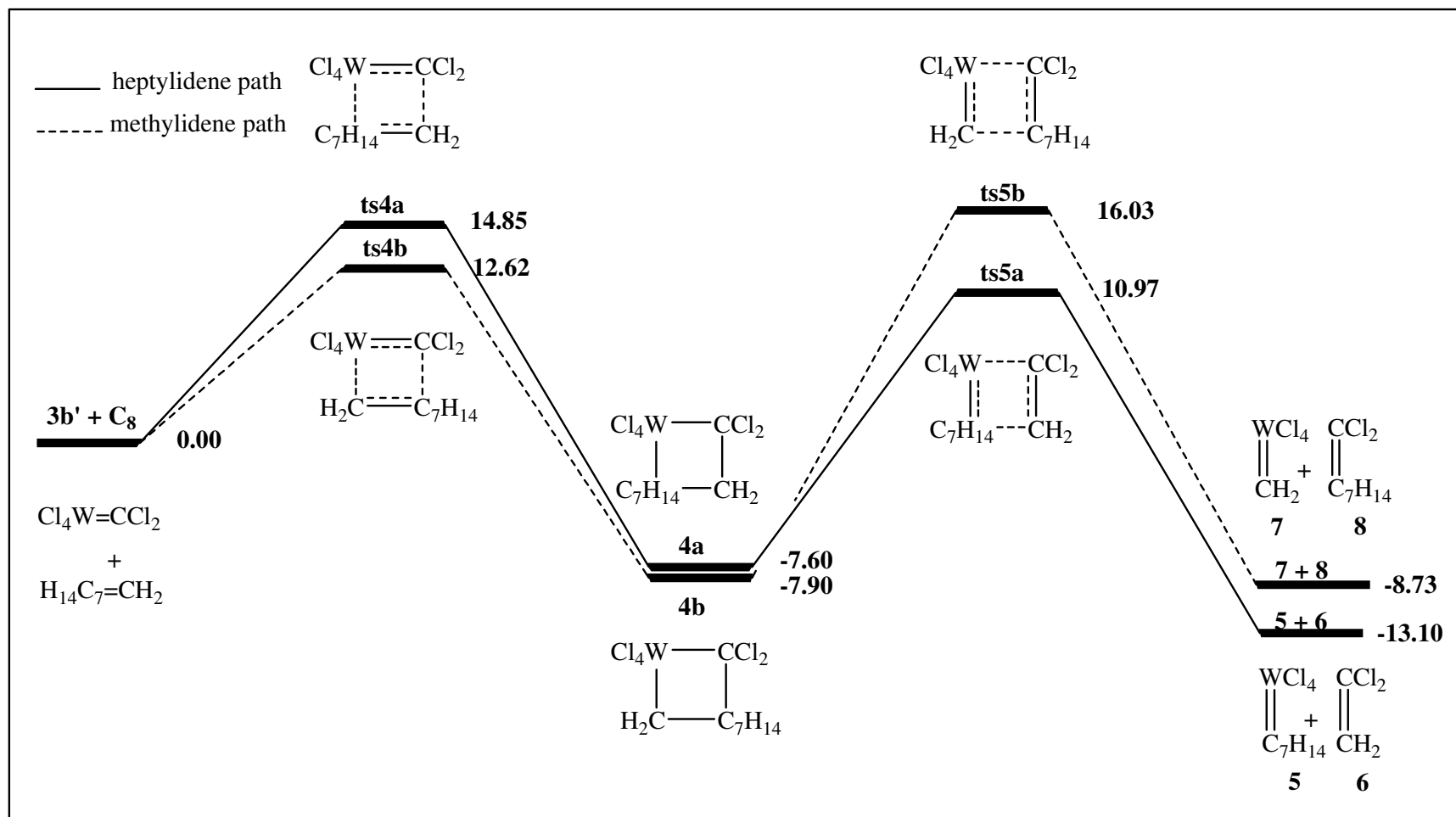
As predicted, singlet state is more stable than the triplet state by 9.02 kcal/mol and therefore further calculations for metathesis were performed at singlet state.

### 5.2.2. Metathesis Mechanism of 1-Octene

There have been a few recent studies that calculated mechanistic parameters or combined experimental work with computational studies on the olefin metathesis with metal carbenes (Sanford et al., 2001, Adlhart et al., 2000, 2002, 2004, Burdett et al., 2004, Bernardi et al., 2003, Jordaan et al., 2006).

In many of these studies, ethylene was used as model olefin to mainly reduce the computing cost. However the calculated results were not in a good agreement with experimental results in these simplified systems. Therefore the theoretical calculations that was employed in this study were applied to 1-octene as olefin to gain more realistic results.

The different geometrical approaches of 1-octene (**C<sub>8</sub>**) towards the catalytically active species, **3b'** and **5**, lead to four activation steps given with **a** and **b** notations in Schemes 5.4. and 5.5.



Scheme 5.4. Initiation step of metathesis of 1-octene

These steps consist of several successive formation of metallocyclobutane structures (**4a**, **4b**, **9a** and **9b**) and cycloreversions to form the respective catalytically active intermediates (**5** and **7**) or side products (**6** and **8**).

In the first step, there is an initiation phase, in which the precatalyst is converted from the  $\text{Cl}_4\text{W}=\text{CCl}_2$  complex, **3b'**, to the heptylidene, **5** or the methyldiene, **7** complex. This takes place through the coordination of 1-octene to the metal center of **3b'** to form a transition state (**ts4a** or **ts4b**) with activation energies 14.85 and 12.62 kcal/mol, respectively.

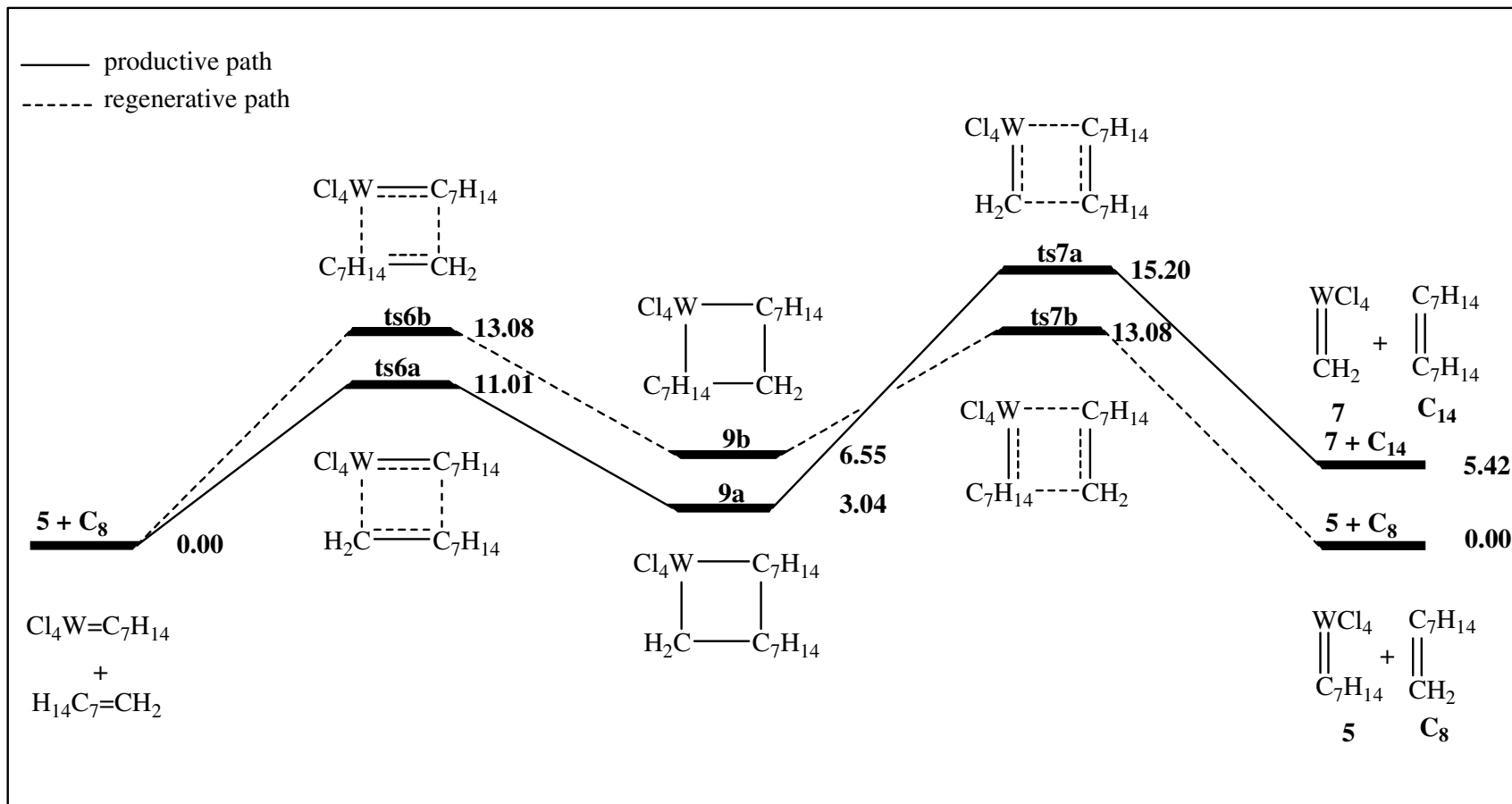
Afterwards, the transition structure undergoes formation of a metallocyclobutane ring (**4a** or **4b**) and then it reverts into **5** or **7**, through a second transition state, (**ts5a** or **ts5b**), with activation energies, 18.57 and 23.93 kcal/mol, respectively.

Schematic representation of the structures involved in the initiation step and their relative energies (kcal/mol) as to the starting structures **3b'** and **C<sub>8</sub>** are as given in Scheme 5.4.

In the second step, the heptylidene, **5** and the methyldiene, **7** enter the same set of the reactions as the initiation step with 1-octene. Productive and regenerative metathesis reactions of 1-octene in the presence of the heptylidene is given in Scheme 5.5.

Relative to the geometrical approach of 1-octene, **C<sub>8</sub>**, towards the tungsten carbene **5**, metallocyclobutane intermediates **9a** and **9b** are formed through the transition states **ts6a** and **ts6b** with the activation energies, 11.01 kcal/mol and 13.08 kcal/mol, respectively.

The metallocyclobutane **9a** produces the metathesis product 7-tetradecene, **C<sub>14</sub>**, through **ts7a** with an activation energy of 12.16 kcal/mol, while **9b** regenerates the starting structures, **5** and **C<sub>8</sub>**, through **ts7b** with an activation energy 6.53 kcal/mol.



Scheme 5.5. Productive and regenerative metathesis of 1-octene

## 6. CONCLUSION

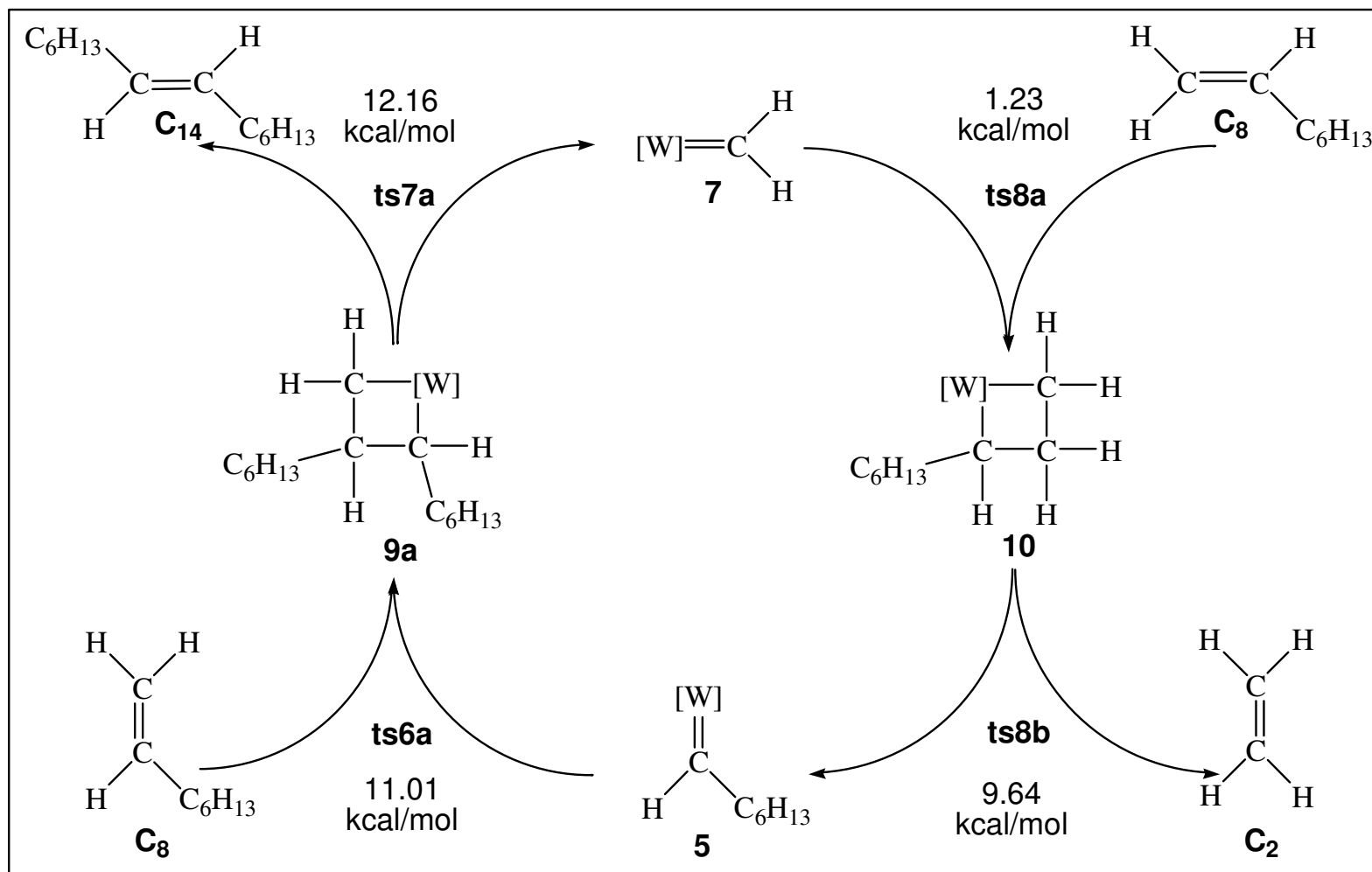
This thesis consists of the experimental studies of the self metathesis reactions of acyclic olefins (1-octene, 2-octene, 1-heptene, 2-heptene and 1-pentene) by a tungsten carbene species synthesized from  $WCl_6$  via carbon arc reactions in situ, and the complementary computational studies explaining the energetics of reaction paths involved in the related reactions.

- In the experimental part of the work, the metal atom vaporization technique was applied to graphite and  $WCl_6$  to synthesize a tungsten carbene species in a carbon arc reactor. After in situ addition of olefin, reaction mixtures were analyzed by GC-MS.
- GC-MS analysis results of reaction mixtures of  $WCl_6$ / C atom/ olefin system mixtures showed that the formation of metathesis products from each olefin indicating the catalytic activity of the  $WCl_6$ / C arc system. When the percent peak areas of the metathesis products for each olefin were compared, it was seen that the highest peak area for the primary metathesis product was achieved by 2-heptene with 10.8 %.
- To confirm that the catalytic activity had arisen from the generation of tungsten carbenes in our system, a blank experiment was conducted via the same experimental procedure as in the metathesis of 1-octene, without using  $WCl_6$ . No metathesis product was observed from the blank experiment. Methyl octene was formed as a result of the carbon atom reactions of 1-octene.
- The presence of the tungsten carbene species was also proved by using a trap molecule, namely benzaldehyde, in order to olefin in the same reaction conditions. This time the GC-MS analysis results of the reaction mixture showed that tungsten carbene species contained the  $=CCl_2$  entity and it had a structure as  $[W]=CCl_2$  (Düz et al., 2006).

Computational part of the study consists of three steps, starting with the formation of the tungsten carbene from  $WCl_6$  and atomic carbon, and ending with the formation of the metathesis product.

- Firstly, the potential energy surface of  $WCl_6/C$  atom system was scanned for the stationary points to clarify the geometry of the tungsten carbene.
- Among tungsten carbenes which were optimized both in singlet and triplet states, it is found that the singlet tungsten carbene,  $Cl_4W=CCl_2$ , in square pyramidal geometry is the most stable structure on the potential energy surface of  $WCl_6/C$  atom system. This species is the most probable structure which can provide the catalytic activity to our system.
- In the first step of metathesis of 1-octene,  $Cl_4W=CCl_2$ , reacts with 1-octene via two competitive pathways yielding methylidene or heptylidene species, both having catalytic activity. Heptylidene formation is energetically more favorable than methylidene formation by means of 4.37 kcal/mol.
- In the second step, the energetics of productive and regenerative metathesis of 1-octene in the presence of the heptylidene species formed in the first step was examined. These two paths are also competitive within a range of about 2 kcal/mol and it is found that the regenerative pathway is slightly more favorable.
- Finally, when these values are applied to the Chauvin mechanism of metathesis, it is seen that within the catalytic cycle, the heptylidene, **5**, is converted to the methylidene, **7**, which in turn converted back to the heptylidene until all the 1-octene, **C<sub>8</sub>**, has been consumed. During the conversion of **5** to **7**, the metathesis product of **C<sub>8</sub>**, 7-tetradecene is formed, while ethylene is formed when **5** is converted to **7** with activation energies given in Scheme 6.1. Detailed data about the geometries and the energetics of the structures computed are available in the appendix .

In summary, with this study, we have found a new route for the generation of metathetic active tungsten carbenes in the reaction of a C atom with  $WCl_6$ .




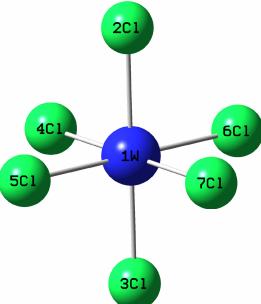
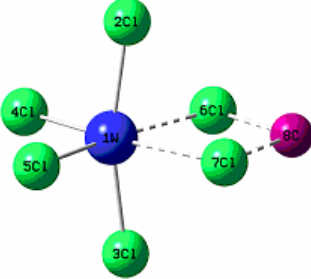
Scheme 6.1. Chauvin mechanism for metathesis of 1-octene

## **APPENDIX**

### **Selected Geometric Parameters from Computational Results**



Appendix : Selected geometric parameters

Molecule		Bond Length (Å)	Mulliken Charges	E (UB+HF-LYP) (a.u.)	ZPE (a.u.)	Total Energy (a.u.)	Total Energy (kcal/mol)
<b>C</b> atom		-	0.000	-37.853417	-	-37.853417	-23753.38
<b>WCl<sub>6</sub></b>		W <sub>1</sub> -Cl <sub>2</sub> : 2.37 W <sub>1</sub> -Cl <sub>3</sub> : 2.37 W <sub>1</sub> -Cl <sub>4</sub> : 2.41 W <sub>1</sub> -Cl <sub>5</sub> : 2.41 W <sub>1</sub> -Cl <sub>6</sub> : 2.41 W <sub>1</sub> -Cl <sub>7</sub> : 2.41	W <sub>1</sub> : 0.004 Cl <sub>2</sub> : 0.019 Cl <sub>3</sub> : 0.019 Cl <sub>4</sub> : -0.010 Cl <sub>5</sub> : -0.010 Cl <sub>6</sub> : -0.010 Cl <sub>7</sub> : -0.010	-157.0605044	0.005420	-157.599624	-98895.26
<b>1</b>		W <sub>1</sub> -C <sub>8</sub> : 3.46 W <sub>1</sub> -Cl <sub>2</sub> : 2.33 W <sub>1</sub> -Cl <sub>3</sub> : 2.33 W <sub>1</sub> -Cl <sub>4</sub> : 2.33 W <sub>1</sub> -Cl <sub>5</sub> : 2.33 W <sub>1</sub> -Cl <sub>6</sub> : 2.61 W <sub>1</sub> -Cl <sub>7</sub> : 2.61 C <sub>8</sub> -Cl <sub>6</sub> : 2.14 C <sub>8</sub> -Cl <sub>7</sub> : 2.14	W <sub>1</sub> : 0.085 C <sub>8</sub> : 0.084 Cl <sub>2</sub> : -0.021 Cl <sub>3</sub> : -0.021 Cl <sub>4</sub> : -0.050 Cl <sub>5</sub> : -0.050 Cl <sub>6</sub> : -0.013 Cl <sub>7</sub> : -0.013	-195.581254	0.008811	-195.572443	-122723.57

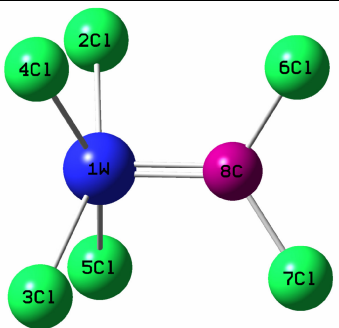
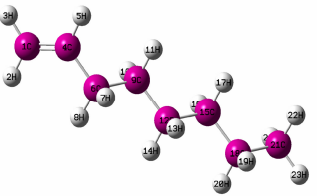
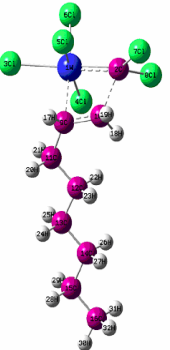
Appendix : Selected geometric parameters continued

	Molecule	Bond Length (Å)	Mulliken Charges	E (UB+HF-LYP) (a.u.)	ZPE (a.u.)	Total Energy (a.u.)	Total Energy (kcal/mol)
ts1		W <sub>1</sub> -C <sub>8</sub> : 2.97 W <sub>1</sub> -Cl <sub>2</sub> : 2.37 W <sub>1</sub> -Cl <sub>3</sub> : 2.36 W <sub>1</sub> -Cl <sub>4</sub> : 2.31 W <sub>1</sub> -Cl <sub>5</sub> : 2.33 W <sub>1</sub> -Cl <sub>6</sub> : 2.68 W <sub>1</sub> -Cl <sub>7</sub> : 2.65 C <sub>8</sub> -Cl <sub>6</sub> : 2.05 C <sub>8</sub> -Cl <sub>7</sub> : 2.09	W <sub>1</sub> : 0.042 C <sub>8</sub> : 0.102 Cl <sub>2</sub> : -0.050 Cl <sub>3</sub> : -0.056 Cl <sub>4</sub> : -0.045 Cl <sub>5</sub> : -0.048 Cl <sub>6</sub> : 0.028 Cl <sub>7</sub> : 0.028	-195.567570	0.008313	-195.559257	-122715.29
2		W <sub>1</sub> -C <sub>8</sub> : 0.92 W <sub>1</sub> -Cl <sub>2</sub> : 2.40 W <sub>1</sub> -Cl <sub>3</sub> : 2.40 W <sub>1</sub> -Cl <sub>4</sub> : 2.39 W <sub>1</sub> -Cl <sub>5</sub> : 2.40 W <sub>1</sub> -Cl <sub>7</sub> : 2.40 C <sub>8</sub> -Cl <sub>6</sub> : 1.68 C <sub>8</sub> -Cl <sub>7</sub> : 3.02	W <sub>1</sub> : 0.248 C <sub>8</sub> : -0.238 Cl <sub>2</sub> : -0.032 Cl <sub>3</sub> : -0.032 Cl <sub>4</sub> : -0.075 Cl <sub>5</sub> : -0.032 Cl <sub>6</sub> : 0.195 Cl <sub>7</sub> : -0.032	-195.648763	0.010784	-195.637979	-122764.69
ts2		W <sub>1</sub> -C <sub>8</sub> : 1.92 W <sub>1</sub> -Cl <sub>2</sub> : 2.44 W <sub>1</sub> -Cl <sub>3</sub> : 2.36 W <sub>1</sub> -Cl <sub>4</sub> : 2.33 W <sub>1</sub> -Cl <sub>5</sub> : 2.38 W <sub>1</sub> -Cl <sub>7</sub> : 2.69 C <sub>8</sub> -Cl <sub>6</sub> : 1.70 C <sub>8</sub> -Cl <sub>7</sub> : 2.28	W <sub>1</sub> : 0.418 C <sub>8</sub> : -0.340 Cl <sub>2</sub> : -0.056 Cl <sub>3</sub> : -0.050 Cl <sub>4</sub> : -0.050 Cl <sub>5</sub> : -0.087 Cl <sub>6</sub> : 0.206 Cl <sub>7</sub> : -0.041	-195.636118	0.009899	-195.626219	-122757.31

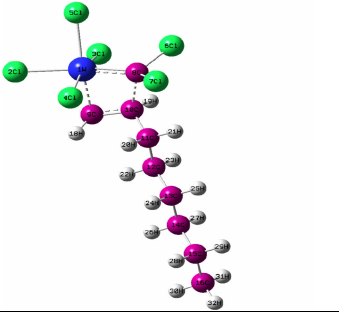
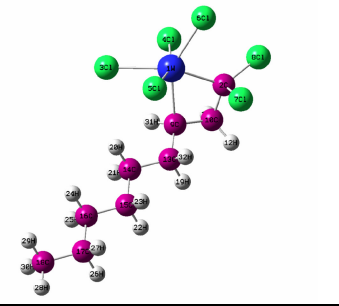
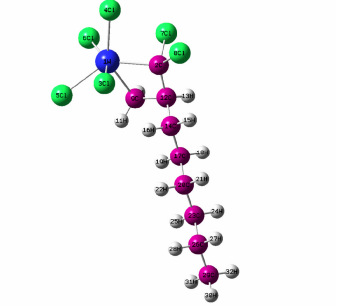
Appendix : Selected geometric parameters continued

Molecule		Bond Length (Å)	Mulliken Charges	E (UB+HF-LYP) (a.u.)	ZPE (a.u.)	Total Energy (a.u.)	Total Energy (kcal/mol)
3a		W <sub>1</sub> -C <sub>8</sub> : 2.01 W <sub>1</sub> -Cl <sub>2</sub> : 2.42 W <sub>1</sub> -Cl <sub>3</sub> : 2.42 W <sub>1</sub> -Cl <sub>4</sub> : 2.32 W <sub>1</sub> -Cl <sub>5</sub> : 2.32 C <sub>8</sub> -Cl <sub>6</sub> : 1.77 C <sub>8</sub> -Cl <sub>7</sub> : 1.77	W <sub>1</sub> : 0.592 C <sub>8</sub> : -0.473 Cl <sub>2</sub> : -0.116 Cl <sub>3</sub> : -0.116 Cl <sub>4</sub> : -0.070 Cl <sub>5</sub> : -0.070 Cl <sub>6</sub> : 0.128 Cl <sub>7</sub> : 0.128	-195.664369	0.011054	-195.653315	-122774.31
ts3		W <sub>1</sub> -C <sub>8</sub> : 2.00 W <sub>1</sub> -Cl <sub>2</sub> : 2.44 W <sub>1</sub> -Cl <sub>3</sub> : 2.38 W <sub>1</sub> -Cl <sub>4</sub> : 2.33 W <sub>1</sub> -Cl <sub>5</sub> : 2.34 C <sub>8</sub> -Cl <sub>6</sub> : 1.78 C <sub>8</sub> -Cl <sub>7</sub> : 1.78	W <sub>1</sub> : 0.566 C <sub>8</sub> : -0.456 Cl <sub>2</sub> : -0.105 Cl <sub>3</sub> : -0.098 Cl <sub>4</sub> : -0.076 Cl <sub>5</sub> : -0.070 Cl <sub>6</sub> : 0.125 Cl <sub>7</sub> : 0.122	-195.663407	0.010940	-195.652467	-122773.78
3b		W <sub>1</sub> -C <sub>8</sub> : 1.99 W <sub>1</sub> -Cl <sub>2</sub> : 2.37 W <sub>1</sub> -Cl <sub>3</sub> : 2.37 W <sub>1</sub> -Cl <sub>4</sub> : 2.37 W <sub>1</sub> -Cl <sub>5</sub> : 2.37 C <sub>8</sub> -Cl <sub>6</sub> : 1.78 C <sub>8</sub> -Cl <sub>7</sub> : 1.78	W <sub>1</sub> : 0.481 C <sub>8</sub> : -0.410 Cl <sub>2</sub> : -0.078 Cl <sub>3</sub> : -0.078 Cl <sub>4</sub> : -0.078 Cl <sub>5</sub> : -0.078 Cl <sub>6</sub> : 0.120 Cl <sub>7</sub> : 0.120	-195.669549	0.011187	-195.658362	-122777.48

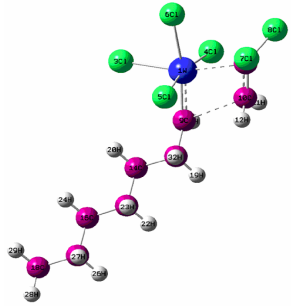
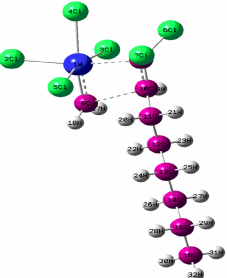
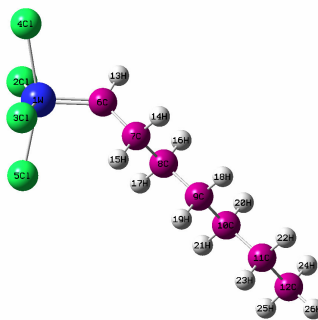
Appendix : Selected geometric parameters continued

	Molecule	Bond Length (Å)	Mulliken Charges	E (RB+HF-LYP) (a.u.)	ZPE (a.u.)	Total Energy (a.u.)	Total Energy (kcal/mol)
<b>3b'</b>		W <sub>1</sub> -C <sub>8</sub> : 1.99 W <sub>1</sub> -Cl <sub>2</sub> : 2.37 W <sub>1</sub> -Cl <sub>3</sub> : 2.37 W <sub>1</sub> -Cl <sub>4</sub> : 2.37 W <sub>1</sub> -Cl <sub>5</sub> : 2.37 C <sub>8</sub> -Cl <sub>6</sub> : 1.78 C <sub>8</sub> -Cl <sub>7</sub> : 1.78	W <sub>1</sub> : 0.481 C <sub>8</sub> : -0.410 Cl <sub>2</sub> : -0.078 Cl <sub>3</sub> : -0.078 Cl <sub>4</sub> : -0.078 Cl <sub>5</sub> : -0.078 Cl <sub>6</sub> : 0.120 Cl <sub>7</sub> : 0.120	-195.684353	0.011614	-195.672740	-122786.50
<b>C<sub>8</sub></b>		C <sub>1</sub> -C <sub>4</sub> : 1.35 C <sub>1</sub> -H <sub>2</sub> : 1.09 C <sub>1</sub> -H <sub>3</sub> : 1.09 C <sub>4</sub> -H <sub>5</sub> : 1.09 C <sub>4</sub> -C <sub>6</sub> : 1.51	C <sub>1</sub> : -0.585 C <sub>4</sub> : -0.032 H <sub>2</sub> : -0.211 H <sub>3</sub> : -0.205 H <sub>5</sub> : -0.202 C <sub>6</sub> : -0.411	-314.425085	0.223380	-314.201714	-197164.56
<b>ts4a</b>		W <sub>1</sub> -C <sub>8</sub> : 2.08 W <sub>1</sub> -C <sub>10</sub> : 2.15 C <sub>8</sub> -C <sub>9</sub> : 1.89 C <sub>9</sub> -C <sub>10</sub> : 1.53 C <sub>10</sub> -C <sub>11</sub> : 1.54 C <sub>11</sub> -C <sub>12</sub> : 1.55	W <sub>1</sub> : 0.202 C <sub>8</sub> : -0.526 C <sub>9</sub> : -0.473 C <sub>10</sub> : -0.280 C <sub>11</sub> : -0.379 C <sub>12</sub> : -0.328	-510.088527	0.237747	-509.850780	-319936.21

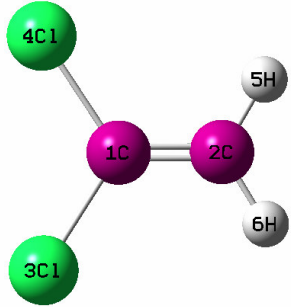
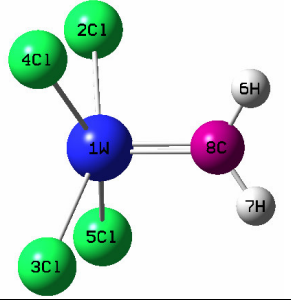
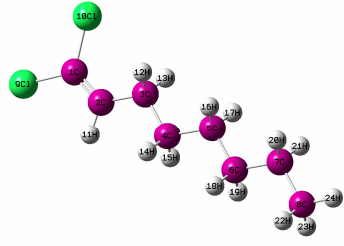
Appendix : Selected geometric parameters continued

	Molecule	Bond Length (Å)	Mulliken Charges	E (RB+HF-LYP) (a.u.)	ZPE (a.u.)	Total Energy (a.u.)	Total Energy (kcal/mol)
ts4b		W <sub>1</sub> -C <sub>8</sub> : 2.07 W <sub>1</sub> -C <sub>10</sub> : 2.13 C <sub>8</sub> -C <sub>9</sub> : 1.91 C <sub>9</sub> -C <sub>10</sub> : 1.53 C <sub>10</sub> -C <sub>11</sub> : 1.54 C <sub>11</sub> -C <sub>12</sub> : 1.55	W <sub>1</sub> : 0.149 C <sub>8</sub> : -0.584 C <sub>9</sub> : -0.118 C <sub>10</sub> : -0.588 C <sub>11</sub> : -0.386 C <sub>12</sub> : -0.332	-510.092077	0.237746	-509.854330	-319938.44
4a		W <sub>1</sub> -C <sub>8</sub> : 2.20 W <sub>1</sub> -C <sub>10</sub> : 2.21 C <sub>8</sub> -C <sub>9</sub> : 1.52 C <sub>9</sub> -C <sub>10</sub> : 1.55 C <sub>10</sub> -C <sub>11</sub> : 1.54 C <sub>11</sub> -C <sub>12</sub> : 1.54	W <sub>1</sub> : 0.053 C <sub>8</sub> : -0.431 C <sub>9</sub> : -0.383 C <sub>10</sub> : -0.216 C <sub>11</sub> : -0.384 C <sub>12</sub> : -0.353	--510.125673	0.239113	-509.886559	-319958.66
4b		W <sub>1</sub> -C <sub>8</sub> : 2.20 W <sub>1</sub> -C <sub>10</sub> : 2.20 C <sub>8</sub> -C <sub>9</sub> : 1.53 C <sub>9</sub> -C <sub>10</sub> : 1.55 C <sub>10</sub> -C <sub>11</sub> : 1.55 C <sub>11</sub> -C <sub>12</sub> : 1.55	W <sub>1</sub> : 0.017 C <sub>8</sub> : -0.551 C <sub>9</sub> : 0.142 C <sub>10</sub> : -0.574 C <sub>11</sub> : -0.414 C <sub>12</sub> : -0.346	-510.126361	0.239320	-509.887041	-319958.96

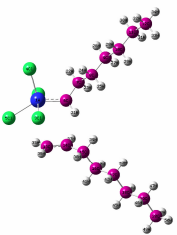
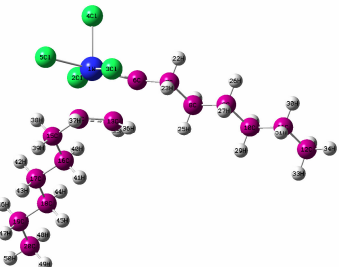
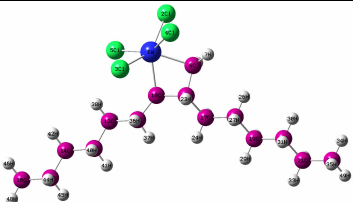
Appendix : Selected geometric parameters continued

	Molecule	Bond Length (Å)	Mulliken Charges	E (RB+HF-LYP) (a.u.)	ZPE (a.u.)	Total Energy (a.u.)	Total Energy (kcal/mol)
ts5a		$W_1-C_8$ : 2.42 $W_1-C_{10}$ : 2.00 $C_8-C_9$ : 1.41 $C_9-C_{10}$ : 2.53 $C_{10}-C_{11}$ : 1.49 $C_{11}-C_{12}$ : 1.57	$W_1$ : 0.062 $C_8$ : -0.289 $C_9$ : -0.360 $C_{10}$ : -0.330 $C_{11}$ : -0.456 $C_{12}$ : -0.340	-510.093713	0.236737	-509.856976	-319940.10
ts5b		$W_1-C_8$ : 2.41 $W_1-C_{10}$ : 1.97 $C_8-C_9$ : 1.42 $C_9-C_{10}$ : 2.55 $C_{10}-C_{11}$ : 1.51 $C_{11}-C_{12}$ : 1.54	$W_1$ : 0.040 $C_8$ : -0.469 $C_9$ : 0.071 $C_{10}$ : -0.594 $C_{11}$ : -0.402 $C_{12}$ : -0.356	-510.084695	0.235783	-509.848912	-319935.04
5		$W_1-C_6$ : 1.87 $C_6-C_7$ : 1.52 $C_7-C_8$ : 1.55 $C_9-C_{10}$ : 1.54 $C_{10}-C_{11}$ : 1.54 $C_{11}-C_{12}$ : 1.54	$W_1$ : 0.307 $C_6$ : -0.366 $C_7$ : -0.407 $C_8$ : -0.330 $C_9$ : -0.322 $C_{10}$ : -0.317 $C_{11}$ : -0.313 $C_{12}$ : -0.652	-402.882999	0.201040	-402.681959	-252686.75

Appendix : Selected geometric parameters continued

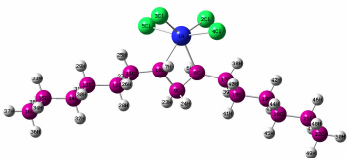
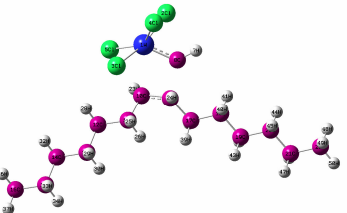
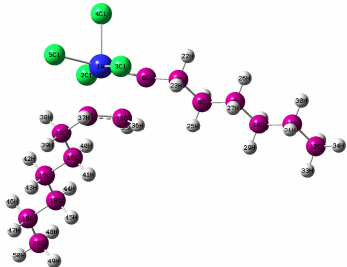
	Molecule	Bond Length (Å)	Mulliken Charges	E (RB+HF-LYP) (a.u.)	ZPE (kcal/mol)	Total Energy (a.u.)	Total Energy (kcal/mol)
6		C <sub>1</sub> -C <sub>2</sub> : 1.34 C <sub>2</sub> -H <sub>5</sub> : 1.09 C <sub>2</sub> -H <sub>6</sub> : 1.09 C <sub>1</sub> -Cl <sub>3</sub> : 1.80 C <sub>1</sub> -Cl <sub>4</sub> : 1.80	C <sub>1</sub> : -0.102 C <sub>2</sub> : 0.370 Cl <sub>3</sub> : -0.010 Cl <sub>4</sub> : -0.010 H <sub>1</sub> : -0.246 H <sub>2</sub> : -0.246	-107.246785	0.033420	-107.213364	-67277.40
7		W <sub>1</sub> -C <sub>8</sub> : 1.87 W <sub>1</sub> -Cl <sub>2</sub> : 2.37 W <sub>1</sub> -Cl <sub>3</sub> : 2.37 W <sub>1</sub> -Cl <sub>4</sub> : 2.37 W <sub>1</sub> -Cl <sub>5</sub> : 2.37 C <sub>8</sub> -H <sub>6</sub> : 1.10 C <sub>8</sub> -H <sub>7</sub> : 1.10	W <sub>1</sub> : 0.385 C <sub>8</sub> : -0.635 Cl <sub>2</sub> : -0.077 Cl <sub>3</sub> : -0.077 Cl <sub>4</sub> : -0.077 Cl <sub>5</sub> : -0.077 H <sub>6</sub> : 0.279 H <sub>7</sub> : 0.279	-167.027585	0.028702	-166.998883	-104793.39
8		C <sub>1</sub> -C <sub>2</sub> : 1.34 C <sub>2</sub> -C <sub>3</sub> : 1.52 C <sub>3</sub> -C <sub>4</sub> : 1.54 C <sub>1</sub> -Cl <sub>9</sub> : 1.81 C <sub>1</sub> -Cl <sub>10</sub> : 1.81	C <sub>1</sub> : -0.357 C <sub>2</sub> : 0.099 C <sub>3</sub> : -0.403 C <sub>4</sub> : -0.359 Cl <sub>9</sub> : -0.015 Cl <sub>10</sub> : -0.034	-343.094194	0.204712	-342.889481	-215166.41

Appendix : Selected geometric parameters continued

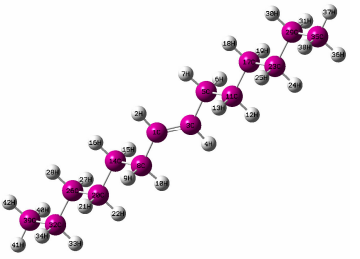
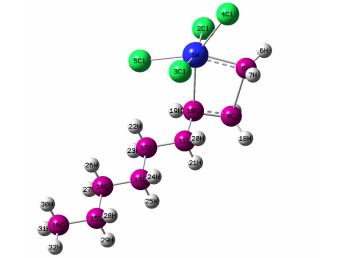
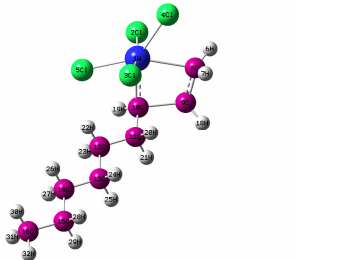
Molecule		Bond Length (Å)	Mulliken Charges	E (RB+HF-LYP) (a.u.)	ZPE (kcal/mol)	Total Energy (a.u.)	Total Energy (kcal/mol)
ts6a		$W_1 - C_6 : 1.90$ $W_1 - C_{13} : 3.34$ $C_6 - C_{14} : 3.38$ $C_{13} - C_{14} : 1.36$ $C_6 - C_7 : 1.53$ $C_{14} - C_{15} : 1.55$	$W_1 : 0.277$ $C_6 : -0.566$ $C_7 : -0.378$ $C_{13} : -0.379$ $C_{14} : -0.008$ $C_{15} : -0.420$	-717.29228	0.426154	-716.866128	-449840.31
ts6b		$W_1 - C_6 : 2.01$ $W_1 - C_{14} : 2.17$ $C_6 - C_{13} : 2.01$ $C_{14} - C_{13} : 1.49$ $C_6 - C_7 : 1.51$ $C_{14} - C_{15} : 1.54$	$W_1 : 0.042$ $C_6 : -0.355$ $C_7 : -0.456$ $C_{13} : -0.518$ $C_{14} : -0.258$ $C_{15} : -0.380$	-717.290700	0.427878	-716.862823	-449838.23
9a		$W_1 - C_6 : 2.19$ $W_1 - C_{13} : 2.17$ $C_6 - C_{14} : 1.55$ $C_{13} - C_{14} : 1.53$ $C_6 - C_7 : 1.53$ $C_{14} - C_{15} : 1.55$	$W_1 : 0.026$ $C_6 : -0.368$ $C_7 : -0.389$ $C_{13} : -0.840$ $C_{14} : -0.650$ $C_{15} : -0.431$	-717.308676	0.429848	-716.878828	-449848.28



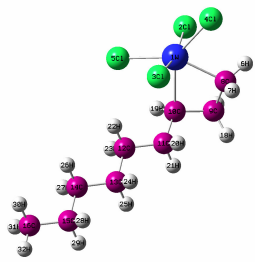
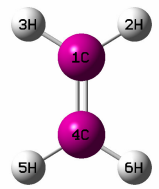
Appendix : Selected geometric parameters continued

Molecule		Bond Length (Å)	Mulliken Charges	E (RB+HF-LYP) (a.u.)	ZPE (kcal/mol)	Total Energy (a.u.)	Total Energy (kcal/mol)
9b		$W_1 - C_6 : 2.17$ $W_1 - C_{14} : 1.53$ $C_6 - C_{13} : 1.53$ $C_{14} - C_{13} : 2.17$ $C_6 - C_7 : 1.53$ $C_{14} - C_{15} : 1.53$	$W_1 : -0.067$ $C_6 : -0.196$ $C_7 : -0.420$ $C_{13} : -0.509$ $C_{14} : -0.196$ $C_{15} : -0.420$	-717.302234	0.428991	-716.873243	-449844.77
ts7a		$W_1 - C_6 : 3.05$ $W_1 - C_{13} : 2.09$ $C_6 - C_{14} : 1.51$ $C_{13} - C_{14} : 2.54$ $C_6 - C_7 : 1.57$ $C_{14} - C_{15} : 1.49$	$W_1 : 0.195$ $C_6 : -0.015$ $C_7 : -0.451$ $C_{13} : -0.776$ $C_{14} : 0.018$ $C_{15} : -0.461$	-717.287205	0.427747	-716.859458	-449836.12
ts7b		$W_1 - C_6 : 2.01$ $W_1 - C_{14} : 2.17$ $C_6 - C_{13} : 2.01$ $C_{14} - C_{13} : 1.49$ $C_6 - C_7 : 1.51$ $C_{14} - C_{15} : 1.54$	$W_1 : 0.042$ $C_6 : -0.355$ $C_7 : -0.456$ $C_{13} : -0.518$ $C_{14} : -0.258$ $C_{15} : -0.380$	-717.290700	0.427878	-716.862823	-449838.23

Appendix : Selected geometric parameters continued

Molecule		Bond Length (Å)	Mulliken Charges	E (RB+HF-LYP) (a.u.)	ZPE (kcal/mol)	Total Energy (a.u.)	Total Energy (kcal/mol)
<b>C<sub>14</sub></b>		C <sub>1</sub> – C <sub>3</sub> : 1.35 C <sub>1</sub> – C <sub>8</sub> : 1.51 C <sub>3</sub> – C <sub>5</sub> : 1.51	C <sub>1</sub> : -0.202 C <sub>3</sub> : -0.203 C <sub>5</sub> : -0.413 C <sub>8</sub> : -0.413	-550.270605	0.394495	-549.876150	-345052.51
<b>ts8a</b>		W <sub>1</sub> – C <sub>8</sub> : 2.17 W <sub>1</sub> – C <sub>10</sub> : 2.23 C <sub>8</sub> – C <sub>9</sub> : 1.53 C <sub>9</sub> – C <sub>10</sub> : 1.55 C <sub>10</sub> – C <sub>11</sub> : 1.55 C <sub>11</sub> – C <sub>12</sub> : 1.55	W <sub>1</sub> : -0.039 C <sub>8</sub> : -0.549 C <sub>9</sub> : -0.380 C <sub>10</sub> : -0.243 C <sub>11</sub> : -0.350 C <sub>12</sub> : -0.353	-481.461536	0.258984	-481.202552	-301959.17
<b>ts8b</b>		W <sub>1</sub> – C <sub>8</sub> : 2.09 W <sub>1</sub> – C <sub>10</sub> : 2.06 C <sub>8</sub> – C <sub>9</sub> : 1.57 C <sub>9</sub> – C <sub>10</sub> : 1.64 C <sub>10</sub> – C <sub>11</sub> : 1.53 C <sub>11</sub> – C <sub>12</sub> : 1.54	W <sub>1</sub> : 0.105 C <sub>8</sub> : -0.583 C <sub>9</sub> : -0.442 C <sub>10</sub> : -0.379 C <sub>11</sub> : -0.410 C <sub>12</sub> : -0.326	-481.446300	0.257597	-481.188703	-301950.48

Appendix : Selected geometric parameters continued

	Molecule	Bond Length (Å)	Mulliken Charges	E (RB+HF-LYP) (a.u.)	ZPE (kcal/mol)	Total Energy (a.u.)	Total Energy (kcal/mol)
10		$W_1 - C_8 : 2.17$ $W_1 - C_{10} : 2.24$ $C_8 - C_9 : 1.52$ $C_9 - C_{10} : 1.54$ $C_{10} - C_{11} : 1.54$ $C_{11} - C_{12} : 1.54$	$W_1 : -0.054$ $C_8 : -0.518$ $C_9 : -0.398$ $C_{10} : -0.188$ $C_{11} : -0.395$ $C_{12} : -0.337$	-481.462620	0.258565	-481.204055	-301960.12
C <sub>2</sub>		$C_1 - C_4 : 1.35$ $C_1 - H_2 : 1.09$ $C_1 - H_3 : 1.09$ $C_4 - H_5 : 1.09$ $C_4 - H_6 : 1.09$	$C_1 : -0.408$ $C_4 : -0.408$ $H_2 : 0.204$ $H_3 : 0.204$ $H_5 : 0.204$ $H_6 : 0.204$	-78.578209	0.051324	-78.526885	-49276.37

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