Thermal Decomposition studies on Metallacycloalkanes and Their Precursors

by

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DECLARATION

I declare that **Thermal Decomposition studies on Metallacycloalkanes and Their Precursors** is my own work and has not been presented for the award of any other degree at any university. All the sources I have used or quoted have been indicated and acknowledged by means of complete references.

signature removed

Feng Zheng

16 November 2007

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ABBREVIATIONS

DCM	Dichloromethane
THF	Tetrahydrofuran
Et_2O	Diethyl ether
Ph	Phenyl
Me	Methyl
Et	Ethyl
COD	1,5-Cyclooctadiene
NBD	Norbornadiene
bipy	Bipyridyl
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
Cy	Cyclohexyl
Cyp	Cyclopentyl
dba	Dibenzylideneacetone
dpe	(Diphenylphosphino)ethane
dppe	1,2-Bis(diphenylphosphino)ethane
dppp	1,3-Bis(diphenylphosphino)propane
dmpe	1,2-Bis(dimethylphosphino)ethane
dcpe	1,2-Bis(dicyclohexylphosphino)ethane
decp	Diethylphenylphosphine
^{i}Pr	Isopropyl
^{t}Bu	Tert-butyl
Pde	Phosphodiesterase
tmen	Tetramethylethylenediamine
TMEDA	N,N,N'N'-tetramethylenediamine

L	Ligand
R	Alkyl
Ar	Aryl
RCM	Ring closing metathesis
o	ortho
NMR	Nuclear magnetic resonance
s	singlet
d	doublet
t	triplet
m	multiplet
j	coupling constant
FAB	Fast atom bombardment
M^+	parent molecular ion
m/z	mass to charge ration
^oC	degrees Celsius
mM	millimoles
mg	milligrams
hr	hours
min	minutes
sec	seconds
ca.	approximately

PUBLICATIONS

Journal Articles

Feng Zheng, Akella Sivaramakrishna and John R. Moss

Thermal studies on metallacycloalkanes

Coordination Chemistry Reviews, 251 (2007) 2056 – 2071.

Tebello Mahamo, Feng Zheng, Akella Sivaramakrishna and John R. Moss

New synthesis and thermal studies of palladacycloalkanes and their Precursors

Journal of Organometallic Chemistry, 693 (2008) 103 – 108.

Akella Sivaramakrishna, Emma Hager, Feng Zheng, Hong Su, Gregory S. Smith and John R. Moss

Synthesis and structural aspects of M-allyl (M = Ir, Rh) complexes

Journal of Organometallic Chemistry, 692 (2007) 5125 – 5132.

Akella Sivaramakrishna, Banothile C.E. Makhubela, Feng Zheng, Hong Su, Gregory S. Smith and John R. Moss

Synthesis, Structure and Reactivity of *cis*-[PtL2(1-alkenyl)2] complexes

Polyhedron, 27 (2008) 44 – 52.

Conference contributions

F. Zheng, J. R. Moss and A. Sivaramakrishna

Thermal decomposition of metallacycloalkanes and their precursors

4th Cape Organometallic Symposium, Organometallics and Their Applications, Cape Town, South Africa, August 2006.

Poster presentation.

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Thermal decomposition of metallacycloalkanes and their precursors

15th International Symposium on Homogenous Catalysis, Sun City, South Africa, August 2006.

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Poster presentation.

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Poster presentation.

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Poster presentation.

ABSTRACT

Metallacycloalkanes are important intermediates in organic transformations involving transition metals. These transformations include olefin metathesis, ethylene oligomerization etc. The studying of thermal decomposition behavior of these compounds can help us to understand the termination step in the mechanism of these transformations. This thesis describes the thermal decomposition studies on some new metallacycloalkanes with medium to large ring size and their precursor compounds.

Chapter 1 presents an overview of the thermal studies on metallacycloalkanes based on the reported literature, with particular attention to the general factors which affect thermal decomposition. This review includes the various types of decomposition pathways involved in metallacycloalkanes and different decomposition conditions as well as the interesting decomposition products.

There are two main routes to prepare metallacycloalkanes. Chapter 2 describes the synthesis of four palladacycloalkanes of the type $L_2Pd(CH_2)_n$ (L = PPh_3, L_2 = dppe and n = 6, 8). These complexes were prepared using ring closing metathesis (RCM) reactions of the precursor, bis(1-alkenyl) palladium complexes, followed by hydrogenation reactions. The complexes with dppe ligand were also prepared by transmetallation reactions with appropriate di-Grignard reagents.

In Chapter 3, thermal decomposition of the novel metallacycloalkanes with various metal centres and ring sizes is described. The kinetics of decomposition of some metallacycloalkanes with and without additional ligands has been studied. The effects of decomposition conditions, supporting ligands, metal centres and ring size have been investigated. The possible decomposition mechanisms have been proposed and are discussed.

Thermal decomposition of some bis(1-alkenyl) metal complexes is described in Chapter 4. The effects of various factors on the decomposition of these compounds have been observed; possible decomposition mechanisms have been proposed and are discussed.

General experimental details are described in Chapter 5.

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Chapter 1

Review on thermal studies on metallacycloalkanes

1.1. Introduction

Organometallic compounds are in some cases unstable because of the presence of reactive metal-carbon bonds and on thermolysis, give interesting organic products.[1,2] Also, attention has been recently focussed on the pyrolysis studies of organometallic precursors, which have potential applications in the preparation of multi-walled as well as single-walled carbon nanotubes[3,4] and a wide range of inorganic materials as thin films on a variety of substances.[5,6] Metallacycloalkane compounds are an important class of organometallic compounds, which are known to be key intermediates in olefin metathesis, hydrocarbon cracking and isomerization, epoxidation, de-epoxidation and oligomerisation of alkenes.[7,8] The chemistry of metallacycloalkane compounds is a growing area of organometallic chemistry.[8] These compounds also play an important role in many catalytic transformations. Thus, metallacyclopentanes appear to be key intermediates in a number of olefin dimerisation reactions.[7,9] Ethylene trimerisation, tetramerisation and oligomerisation to high linear α-olefins proceed by the intermediacy of metallacycloheptanes, metallacyclononanes and larger size rings.[10] Recently, certain platinacyclobutanes with attached biomolecules have been used as targeted, cisplatin prodrugs.[11]

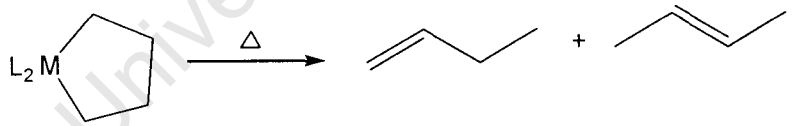
There are only a few review articles on metallacycloalkanes reported in the literature and in these, thermal decomposition studies are restricted to small and medium ring size metallacycloalkanes.[8,12-14] The most recent review published in 1999 includes decomposition studies of group 10 metallacycles.[12]

The purpose of this review is to assess the stability of the wide range of known metallacycloalkanes at various temperatures and to discuss the range of interesting organic products produced upon their decomposition. Herein we bring

together the results of extensive research on the thermolysis reactions of metallacycloalkanes, particularly focusing on the organic product formation.

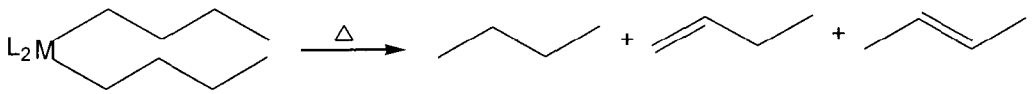
Decomposition to organic products is the termination step in the mechanism of every synthetically useful catalytic or stoichiometric reaction in which a metallacycle is involved.[12] Therefore, studies on the decomposition behaviour of organometallic compounds are fundamental to the development of organometallic chemistry and provide a better understanding of the role of organometallic complexes in organic synthesis and catalysis.[13]

Metallacycloalkanes have two metal-carbon single bonds and can formally be regarded as metal complexes with two alkyl ligands; however, their chemistry can be quite different from that of acyclic dialkyl complexes.[13] Based on the thermal decomposition studies, metallacyclobutanes, –pentanes and –hexanes which have quite rigid rings are found to be much more thermally stable than their acyclic analogues. For instance, Whitesides *et al*[15,16] studied the decomposition of five-membered platinum metallacycles **1-1a** and **1-1b** in CH_2Cl_2 at 120°C while the related acyclic dialkyl complexes (**1-2a**, **1-2b**) decomposed at 60°C in the same solvent. Similarly, the palladacyclopentane **1-1c**[17] decomposes slowly in toluene at 95°C (ca. 12 hours) while the dibutyl palladium complex **1-2c** requires only 1 hour for complete decomposition at the same temperature (Eqs. 1-1 & 1-2).



(Eq. 1-1)

1-1a, M = Pt, L = PPh_3
1-1b, M = Pt, L_2 = dppe
1-1c, M = Pd, L_2 = dppe



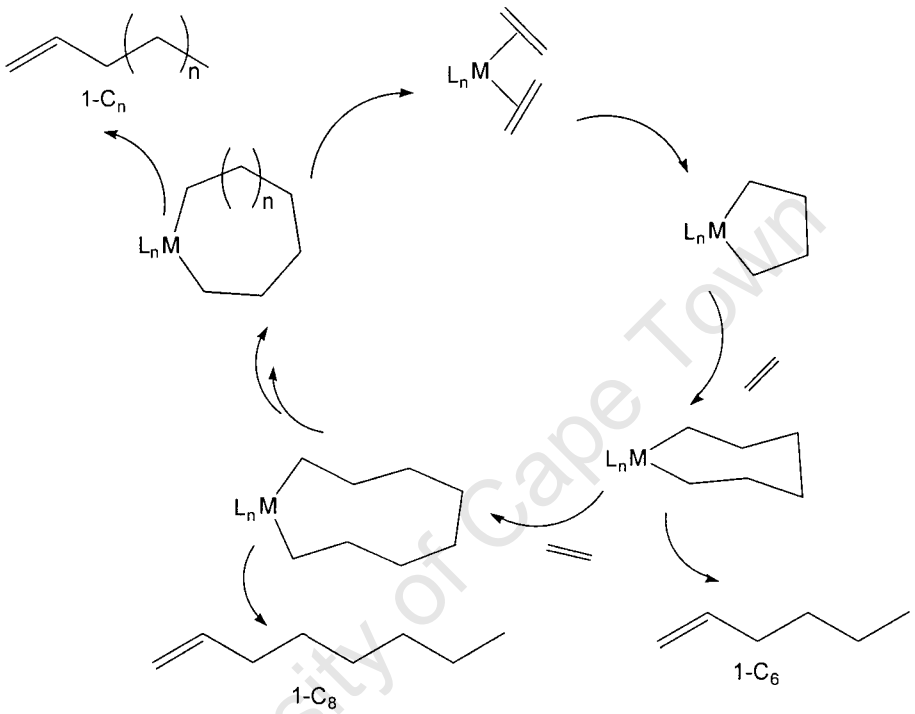
(Eq. 1-2)

1-2a, M = Pt, L = PPh_3
1-2b, M = Pt, L_2 = dppe
1-2c, M = Pd, L_2 = dppe

In contrast, and from limited studies, it appears that the conformationally flexible larger size rings have lower thermal stability[15,16,18] and the chemistry of these

compounds has been said to become increasingly indistinguishable from that of dialkyl compounds.[13]

The most important application of metallacycloalkanes is in affording linear α-olefins by decomposition of catalytic intermediates in ethylene oligomerisation. Linear α-olefins are useful and widely used in the chemical industry.[19]



Scheme 1-1. Catalytic cycle for ethylene trimerisation, tetramerisation and polymerisation

According to the reported literature, selective catalytic ethylene trimerisations to 1-hexene were based on chromium, tantalum, titanium, zirconium and vanadium catalyst precusors.[19] Tetramerisation of ethylene involves the insertion of an ethylene molecule into a metallacycloheptane to form a metallacyclononane, which then decomposes to give 1-octene. The first catalyst capable of ethylene tetramerisation with selectivities of up to 70% for 1-octene was reported recently.[20,21] In addition, Gibson et al. provided experimental evidence for the presence of large ring metallacyclic intermediates in catalytic reactions that give higher ethylene oligomers using homogeneous chromium catalysts.[10] Various theoretical studies on titanium-,[22,23] tantalum-[24], zirconium- and hafnium–based[25] selective ethylene oligomerisation catalysts have also been reported recently. The

catalytic cycle and proposed mechanistic pathway based on chromium is shown in Scheme 1.

1.2. Decomposition pathways for metallacycloalkanes

The decomposition pathways of metallacycloalkanes may be the termination step in several important catalytic processes.[7] The thermal chemistry of metallacycloalkanes involves several known processes including β-hydride elimination, reductive elimination, α-hydride elimination and carbon-carbon bond cleavage (Fig. 1-1),[12] as well as certain specific processes which have only been proposed in metallacyclic systems.

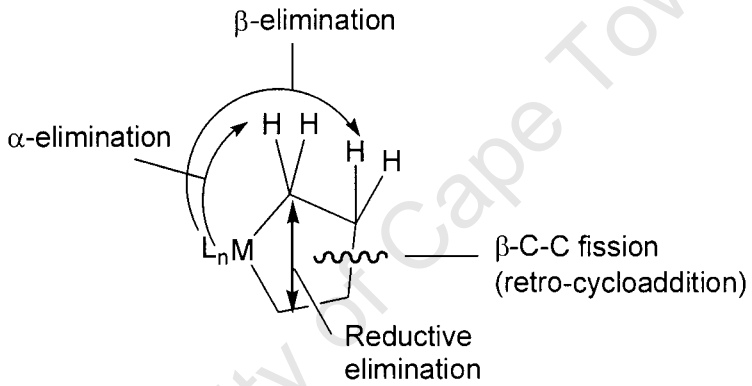
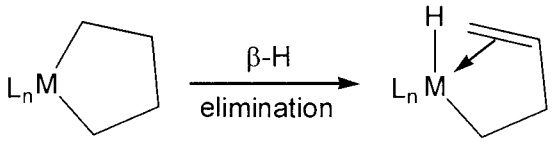


Fig.1-1. The conventional decomposition pathways for metallacycloalkanes

1.2.1. β-Hydride elimination

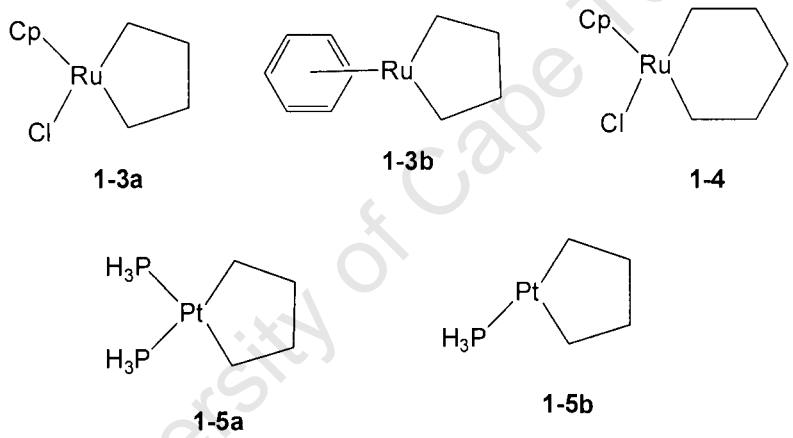
β-Hydride elimination probably occurs most readily from conformations of the organometallic compounds in which M-C-C-H dihedral angles are 0°.[15] This is the most common decomposition pathway for acylic transition metal alkyls. However, it is more hindered in six-, five-, four-, (and three-) membered metallacycles since their M-C-C-H dihedral angles would be greater than 90°.[15,16]

In fact, no metallacyclobutane has ever been directly observed to form an allyl hydride complex by β-hydride elimination.[13] However, β-hydride elimination reactions of five-membered metallacyclic complexes, to give hydridometal alkene complexes (Eq. 1-3), are thought to be possible according to recent evidence.[23-25]



(Eq. 1-3)

To explore this possibility, Huang et al.[26] carried out systematic theoretical calculations to study the β-hydride elimination in several metallacyclic complexes of ruthenium and platinum shown in Scheme 1-2. It was found that favourable structural arrangements, in which the transferring β-hydrogen is in close proximity to the metal center, for β-hydride elimination exist in 16-electron ruthenacyclopentanes (**1-3a**, **1-3b**) and –hexanes (**1-4**). In contrast, the corresponding reactions of platinum complexes (**1-5a**, **1-5b**) appeared more difficult.



Scheme 1-2. Metallacyclic species of ruthenium and platinum

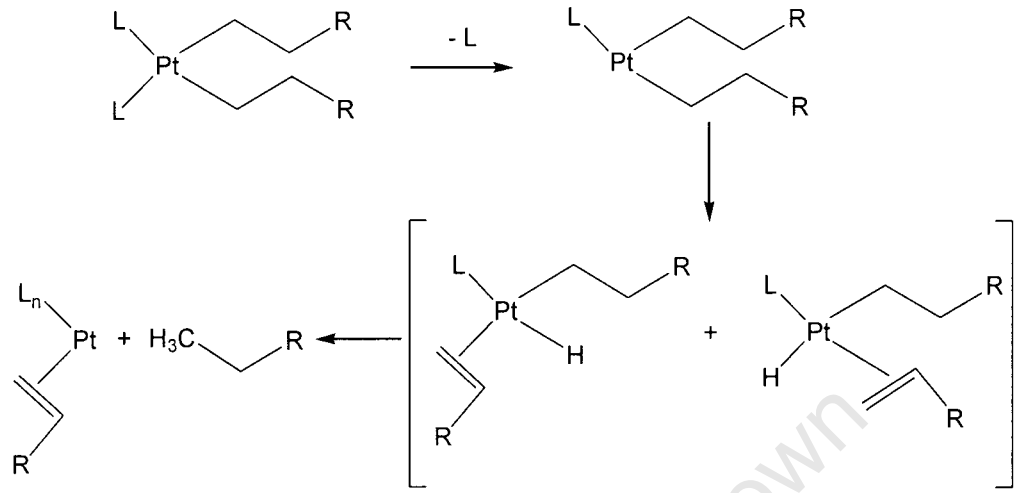
In seven-membered and larger metallacycloalkanes, β-hydride elimination is expected to be less hindered.[16]

1.2.2. Reductive elimination

Carbon-carbon bond formation by reductive elimination from transition metal alkyls is an important product-forming reaction in organometallic synthesis and catalysis.[27]

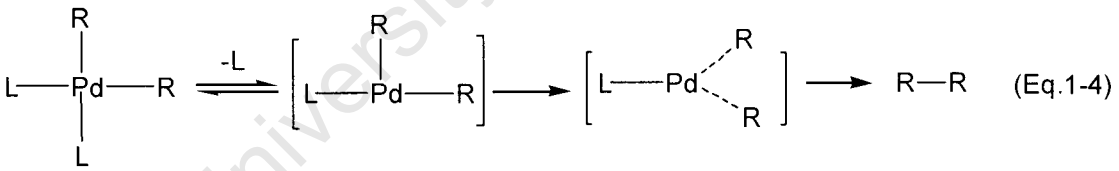
This process is frequently observed in dialkyls. Thus in complexes such as PtR_2L_2 (L = PPh_3, R = alkyl), reductive elimination of a C-H bond to form alkane from an

intermediate hydridoalkylplatinum(II) is the major step during decomposition (Scheme 1-3).[16]



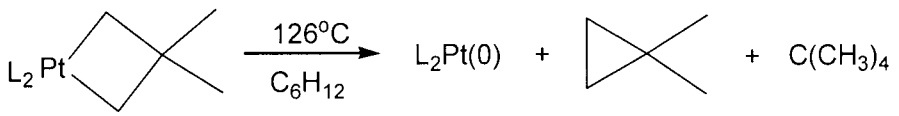
Scheme 1-3

In contrast, *cis*-PdR_2L_2 compounds afford C-C bond reductive elimination products exclusively (Eq. 1-4), while the *trans*- isomers give β-hydride elimination products.[28]



(Eq.1-4)

Reductive elimination of a C-C bond to form cycloalkanes is also an important decomposition pathway for metallacycloalkanes. A typical example of such a process is seen in the decomposition of bis(trialkylphosphane)-3,3-dimethyplatinacyclobutanes **1-6a** and **1-6b**, for which β-elimination is not possible; this was demonstrated some years ago by Whitesides and DiCosimo (Eq. 1-5).[29]

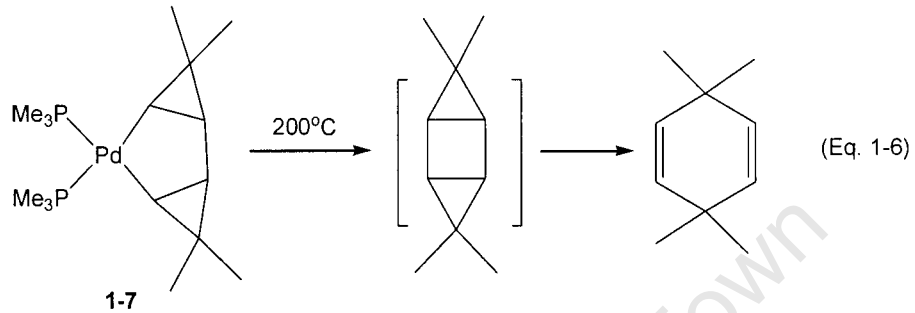


(Eq. 1-5)

1-6aL = P^iPr_3 98% 2%

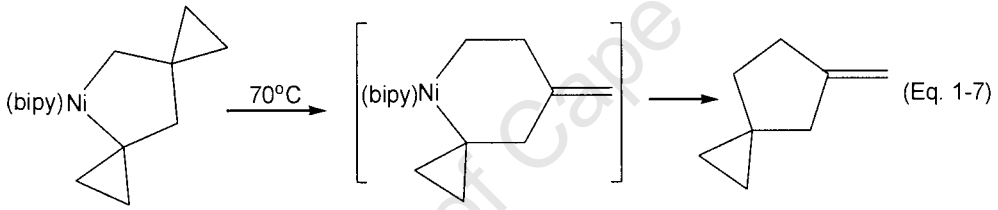
1-6bL = PCy_3 94% 7%

In some metallacycles which have a rigid carbon skeleton, the most common decomposition pathway is reductive elimination accompanied by some type of rearrangement. As an example, the palladacyclopentane **1-7** with the extremely rigid ring decomposes by reductive elimination followed by rearrangement (Eq. 1-6),[30] while the nickelacyclopentane **1-8** experiences rearrangement and a ring expansion, prior to reductive elimination (Eq. 1-7).[31]



(Eq. 1-6)

1-7

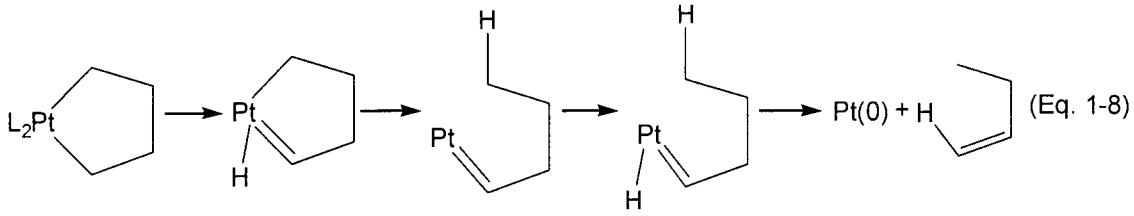


(Eq. 1-7)

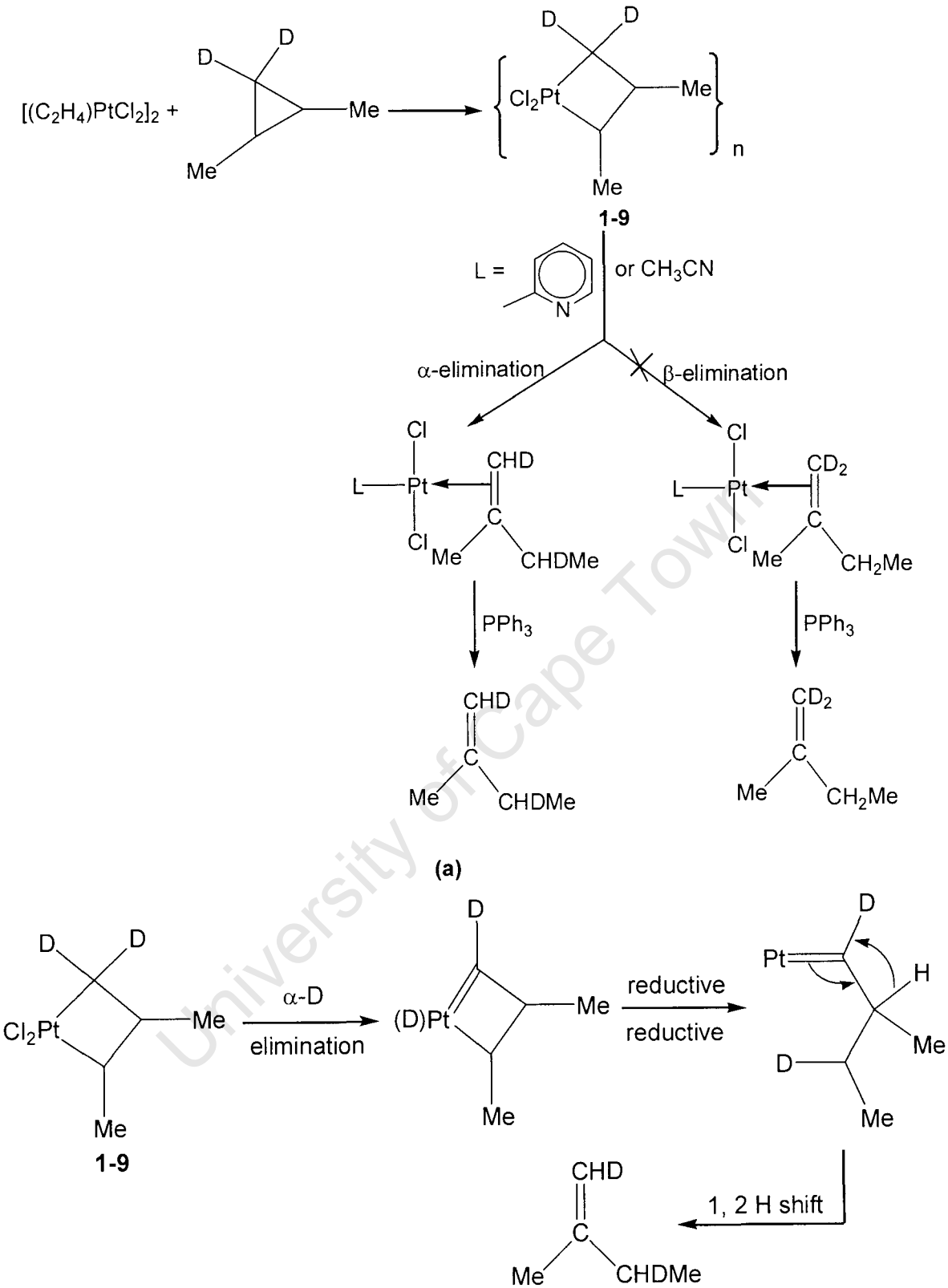
1-8

1.2.3. α-Hydride elimination

Hydride elimination from the α-position, that is, from the carbon directly bonded to the metal, is much less favourable than that from the β carbon. The possibility of an olefin extrusion step starting with α-hydride elimination (Eq. 1-8) was suggested in the decomposition mechanisms of the platinacyclopentane compound **1-1a** by Whitesides and co-workers.[16]



(Eq. 1-8)

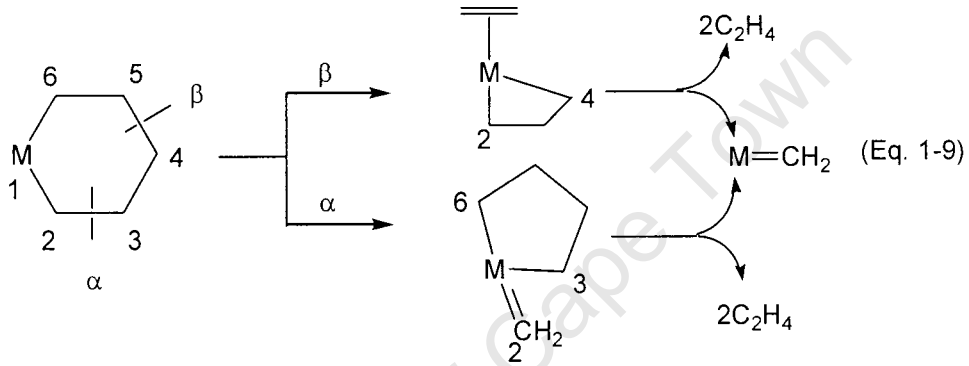


Scheme 1-4

The rearrangement of platinacyclobutane **1-9** was initially studied by Burton and Puddephatt (Scheme 1-4-a),[32] and the reaction mechanism was later reported by Fischer *et al*, who provided evidence for the α-hydride elimination step (Scheme 1-4-b).[33]

1.2.4. Carbon-carbon bond cleavage

α- or β- Carbon-carbon bond cleavage (retro-cycloaddition) can be a facile process in simple organometallic complexes (Eq. 1-9).[9]



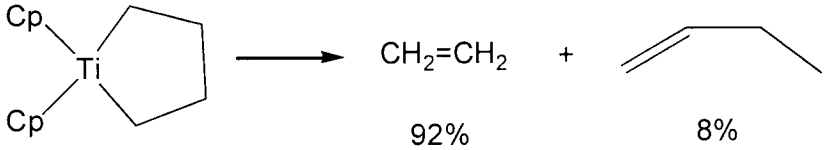
(Eq. 1-9)

β-Carbon-carbon bond cleavage, expected to be the major pathway of decomposition of metal alkyls, always takes place in metallacyclopentane systems that have symmetrical, β, β-carbons. Decomposition of the five-coordinate nickelacyclopentane **1-10**[34] and titanacyclopentane **1-11**[35] to produce ethylene are typical examples (Eqs. 1-10, 1-11).

1-10

90% 10%

(Eq. 1-10)

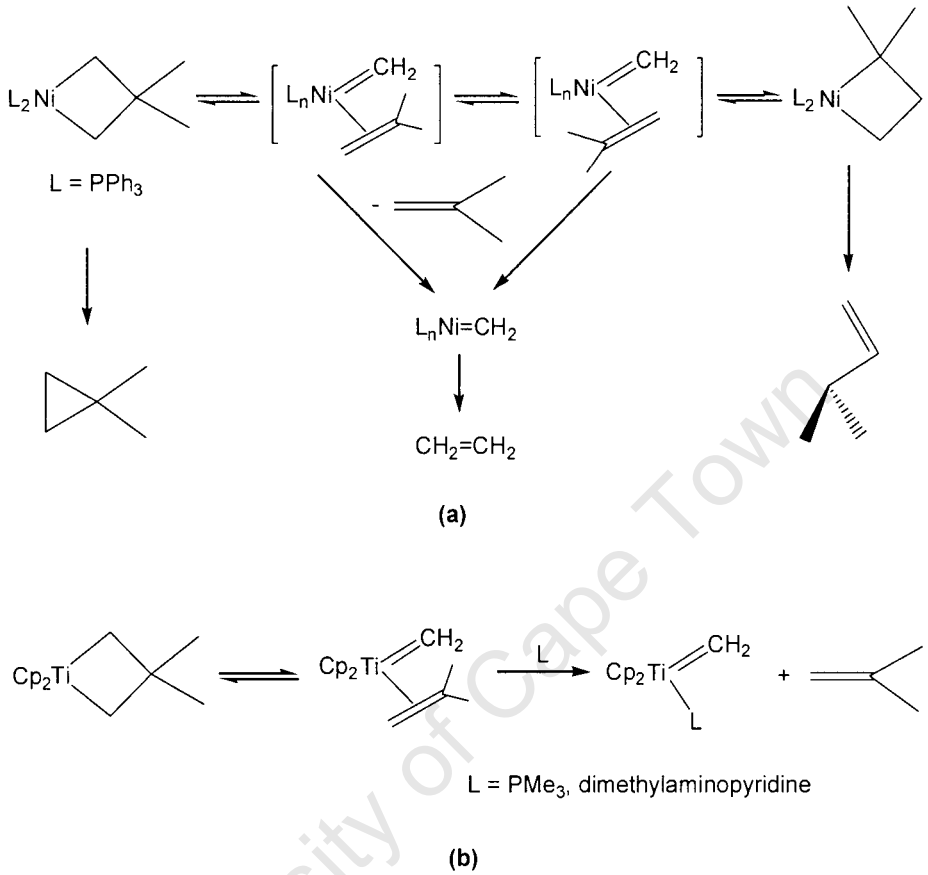


1-11

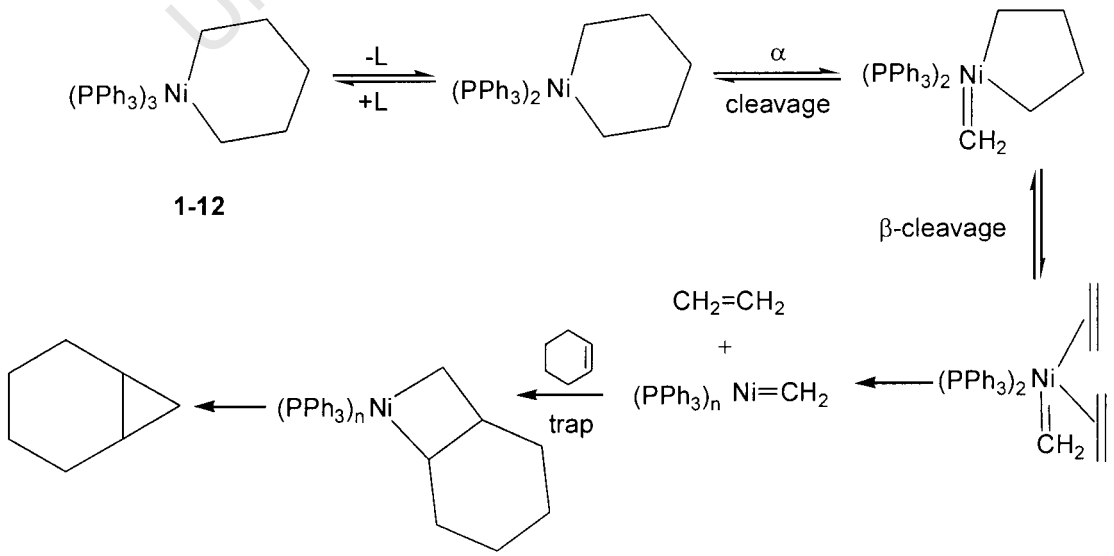
92% 8%

(Eq. 1-11)

However, the evidence for the formation of a metal carbene intermediate by α-carbon-carbon bond cleavage is very strong in Ni[36] and Ti[37,38] systems (Scheme 1-5).

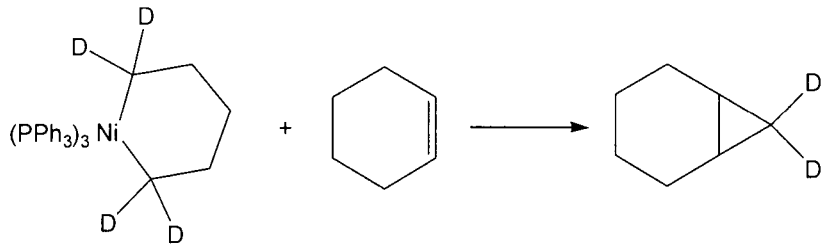


Scheme 1-5



Scheme 1-6

The α-cleavage seems to be the major route in decomposition of nickelacyclohexane **1-12** in the presence of cyclohexene (Scheme 1-6), which was also demonstrated by partially deuterated metallacyclic complex **1-13** (Eq. 1-12).[9, 14(a)]



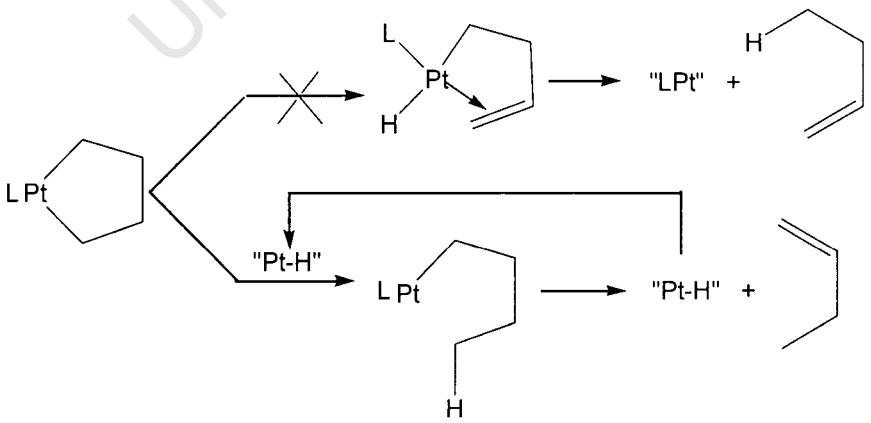
1-13

(Eq. 1-12)

1.2.5. Other pathways

1.2.5.1. Intermolecular chain reaction

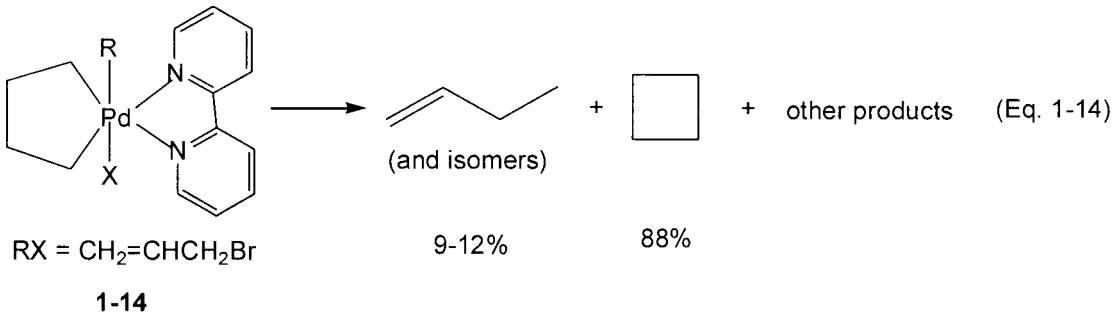
An intermolecular chain reaction was first proposed in a study on the mechanism of the thermal decomposition of bis(tricyclopentylphosphine)platinacyclopentane.[39] In this work, the authors suggested that the decomposition pathway is an intermolecular hydride chain transfer process, and not the simple β-hydride elimination/reductive elimination pathway, due to the high thermal stability of the platinacyclopentane ring (Eq. 1-13).



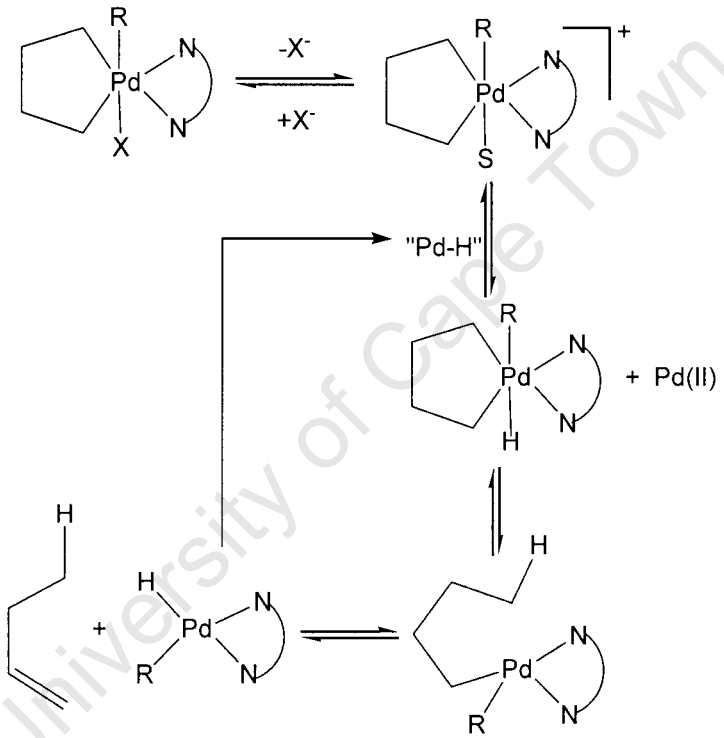
(Eq.1-13)

This process was also observed in the decomposition of the pallada(IV)cyclopentane complex **1-14** forming 1-butene (Eq. 1-14), which was

then proved by a deuteration study.[40] The proposed mechanism for the formation of butenes is shown in Scheme 1-7.



1-14

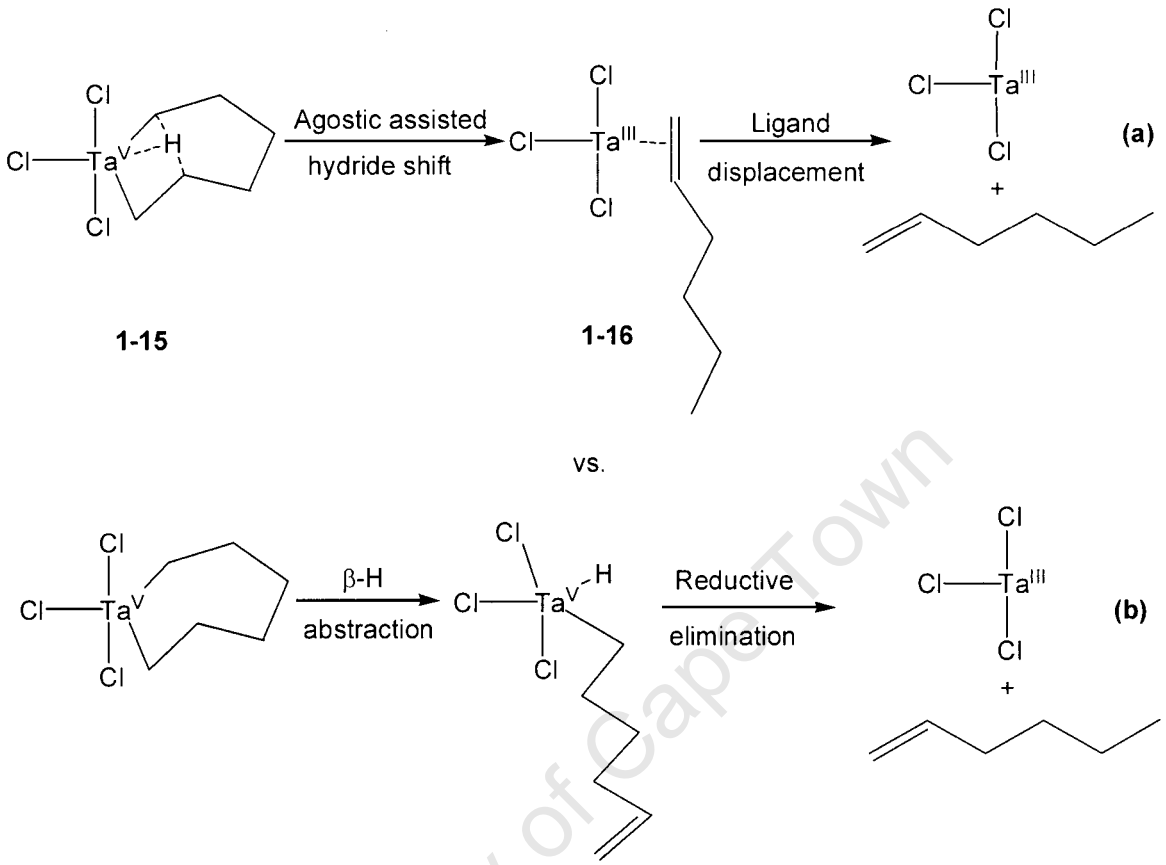


Scheme 1-7

1.2.5.2. Concerted transition-metal-assisted β-hydride transfer

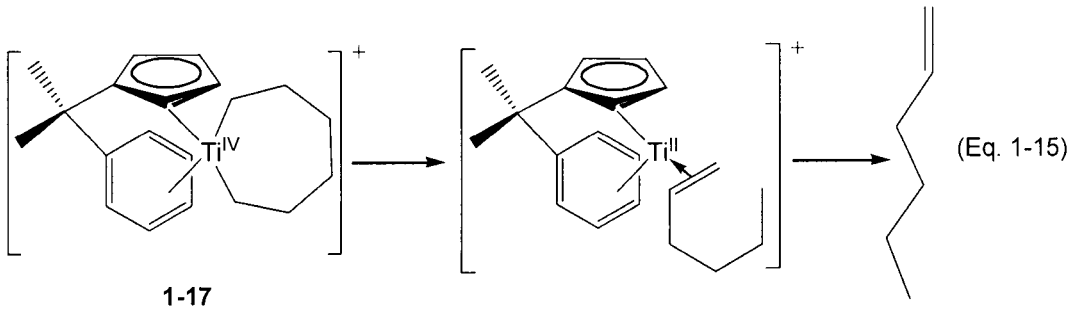
Yu and Houk[24] recently considered such a mechanism, on which MP2 and B3LYP calculations were carried out, as an alternative to the conventional two-step metallacycle decomposition mechanism postulated by Whitesides and co-workers.[15,16] The theoretical results suggested that the conversion of tantalacycloheptane **1-15** to a tantalum-(1-hexene) complex **1-16** could go via a novel concerted process (**a**) described in Scheme 1-8.[19] The authors found that

the concerted route was favoured over the conventional two-step route (**b**), in which the reductive elimination step is particularly unfavourable.[24]



Scheme 1-8

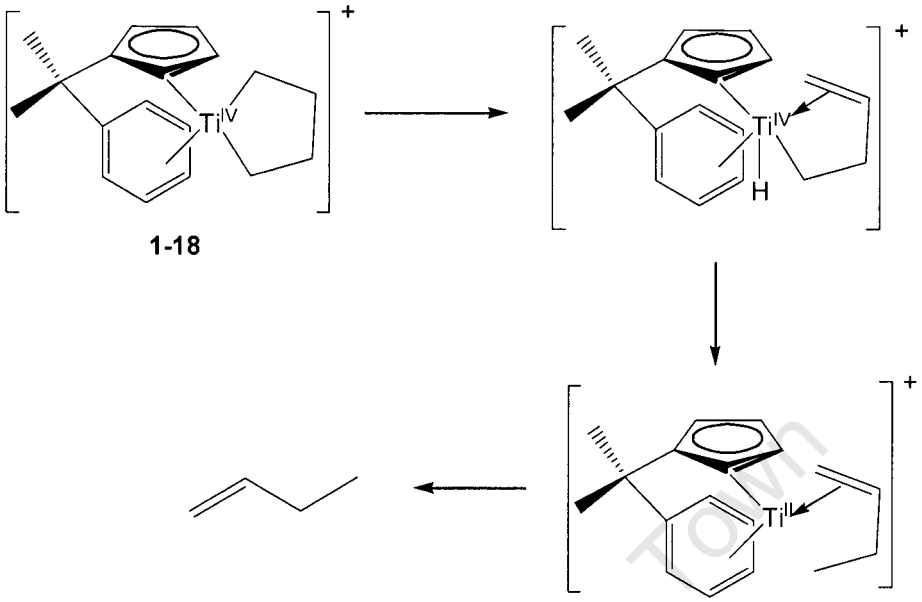
Decomposition of the conformationally flexible seven-membered titana(IV)cycloheptane **1-17**, to yield 1-hexene, takes place via the concerted transition metal-assisted β-hydrogen transfer (Eq. 1-15).[22,25]



1-17

The decomposition of **1-18**, the rigid five-membered titana(IV)cyclopentane to 1-butene was proposed to occur from computational studies in a stepwise route

which involves β-hydrogen abstraction and subsequent reductive C-H elimination (Scheme 1-9).



1-18

Scheme 1-9

1.3. Decomposition conditions and products

Most of the decomposition studies on metallacycloalkanes reported so far were carried out in a solvent in which decomposition reactions can easily take place and temperatures were generally low. On the other hand, decomposition in solid and gas phases will be interesting since no solvent molecules are present to interfere with the decomposition pathways. However, these experiments are largely unexplored, due to instrumental and other limitations.[7] The experimental conditions such as temperature, solvent, and mode of heating will play a significant role in the formation of a variety of products and in different compositions.

1.3.1 Decomposition in solvent

Thermal decomposition studies in a solvent are usually carried out in the following way: the metallacycloalkane complexes are dissolved in the appropriate solvent and the resulting solutions are heated in sealed tubes in a thermostable oil bath

for a specific time. The resulting decomposition products can then be analyzed by gas chromatograph equipped with a flame ionization detector (GC-FID) or with a mass spectrometer detector (GC-MS). These decomposition reactions are carried out under anhydrous, oxygen-free conditions. Experimental conditions and decomposition products of metallacycloalkanes are given in Table 1-1.

1.3.1.1. General decomposition conditions

Table 1-1 summarises the products obtained from the thermal decomposition of metallacycloalkanes under the given experimental conditions.

In Table 1-1, platinacyclopentanes (**1-A**) and platinacyclohexanes (**1-B**) were decomposed in methylene chloride at 120°C, while platinacycloheptanes (**1-C**) were decomposed at 60°C to give in each case the corresponding alkenes.[15,16] Thermal decomposition in cyclohexane of bis(trialkylphosphine)-3,3-dimethylplatinacyclobutanes (**1-D**) produced 1,1-dimethylcyclopropane at 126°C;[29] whereas bis(tricyclopentylphosphine)-platinacyclopentane (**1-E**) yielded 1-butene as the major product at 99°C.[39] At 177°C, bis(trialkylphosphine)-3,3,4,4-tetramethylplatinacyclopentane (**1-F**) yielded two major products: namely 2,2,3,3,-tetramethylbutane and 1-methyl-1-*tert*-butylcyclopropane.[41]

Toluene is the solvent in which most thermal decompositions of nickel and palladium metallacycloalkanes have been carried out. Bis(phosphine)-3,3-dimethylinickela-cyclobutane (**1-G**) decomposed when heated, undergoing competitive carbon-carbon bond cleavage to give isobutene and ethylene, with reductive elimination affording 1,1-dimethylcyclopropane and skeletal isomerization of the metallacyclic ring yielding 3-methyl-1-butene, whereas the palladium analog (**1-H**) gave no significant amount of carbon-carbon bond cleavage products.[36] Thermolysis (9°C) of phosphine nickel metallacyclopentanes (**1-I**, **1-J**, **1-K**) produced ethylene, cyclobutane or butenes depending on the coordination number.[34] Thermal decomposition of palladacyclopentane derivatives of the type of $Pd(CH_2)_4L_2$ (**1-L**) gave butenes as the major products, whereas cyclobutane (for L = PPh_3) and ethylene (for L_2 = dppe or dcpe) are formed as minor products.[42]

Thermal decomposition of the rhenacyclopentane $(CO)_2CpRe(CH_2)_4$ (**1-M**)[43] in benzene-d_6 solution at 100°C was rapid and gave methylcyclopropane (67%). In contrast, the cobaltacyclopentane compound $CpCo(PPh_3)(CH_2)_4$ (**1-N**) decomposed in benzene solution at room temperature giving a mixture of 1-butene (11%), *trans* 2- butene (64%) and *cis* 2-butene (25%).[44]

Table1-1. General experimental conditions[a] and products of decomposition of metallacycloalkanes

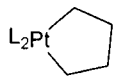
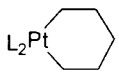
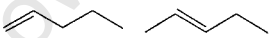
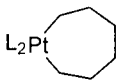
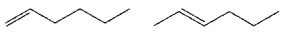
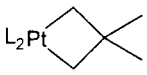
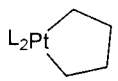
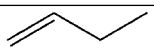
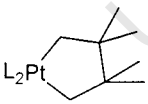
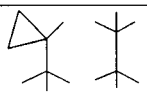
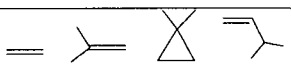
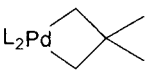
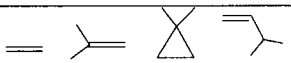
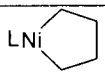
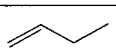
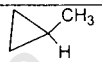
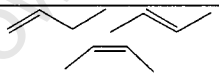
Type of compound		Ligand	Solvent[b]	Temp. (°C)	Products (%)	Ref.
1-A		L: PPh_3 L_2: dppe	Methylene chloride	120	 (78) (20)	15, 16
1-B		L: PPh_3 L_2: dppe	Methylene chloride	120	 (75) (17)	15, 16
1-C		L: PPh_3 L_2: dppe	Methylene chloride	60	 (83) (17)	15, 16
1-D		L: PEt_3, P^iPr_3, PCy_3	Cyclohexane	126	 (94 – 98)	29
1-E		L: $PCyp_3$	Cyclohexane	99	 & isomers (60 – 93)	39
1-F		L: PEt_3	Cyclohexane	177	 (12) (88)	41
1-G		L: PPh_3 L_2: dpe	Toluene	24	 (15) (26) (47) (6)	36
1-H		L: PPh_3	Toluene	60 & 85	 (5) (12) (74) (4)	36
1-I		L: PPh_3	Toluene	9	 (major)	34

Table 1-1. (Continued)

1-J	L_2Ni	L: PPh_3, PCy_3 L_2: dppe	Toluene	9	 (major)	34
1-K	L_3Ni	L: PPh_3	Toluene	9	(major)	34
1-L	L_2Pd	L: PPh_3 L_2: dppe, tmen, bipy, dcpe	Toluene	60	Butenes (major)	42
1-M	$L_2L'Re$	L: CO L': Cp	Benzene-d_6	100	 (67)	43
1-N	LL'Co	L: Cp L': PPh_3	Benzene	Room temp.	 (11) (64) (25)	44

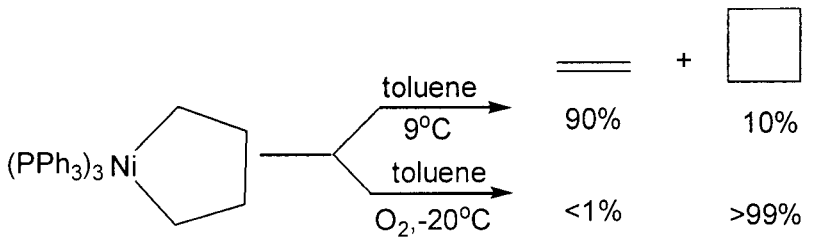
[a] General decomposition conditions here are compared to induced decomposition conditions described in **section 3.1.2**, which means the metallacycloalkane complexes decomposed in solvent at various temperatures in the absence of air.

[b] The solvents mentioned in the table were used in most cases, for others see Eqs. (1-22), (1-23) and (1-24)

1.3.1.2. Induced decomposition conditions

Under certain conditions, thermal decompositions can be induced to give more selective products than those obtained under normal conditions.

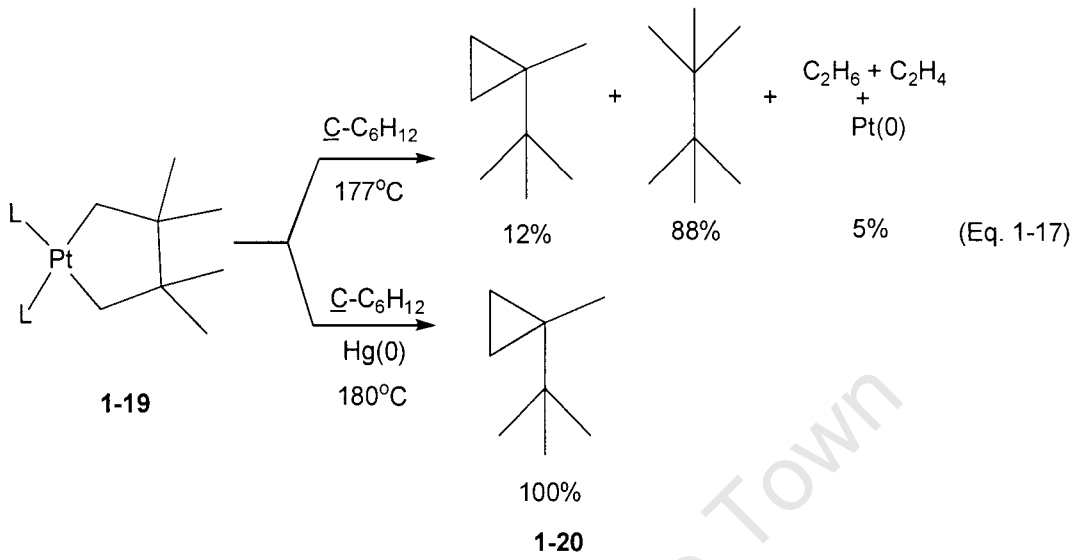
Oxidation induced rapid decomposition of the phosphine nickelacyclopentane complexes to cyclobutane (eg. Eq. 1-16).[34]



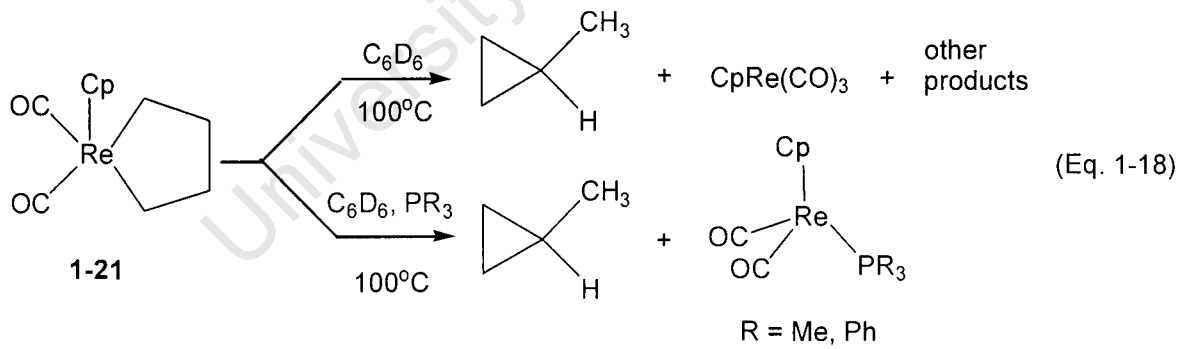
(Eq. 1-16)

1-10

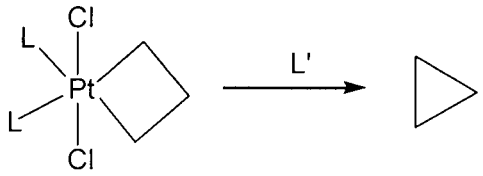
By poisoning with mercury, the thermal decomposition of bis(triethylphosphine)-3,3,4,4-tetramethylplatinacyclopentane **1-19** was induced to generate 1-methyl-1-*tert*-butylcyclopropane **1-20**, the product of a homogeneous reaction sequence (Eq. 1-17).[41]



In comparison to decomposition in benzene-d_6 as mentioned above, the decomposition products of the rhenacyclopentane $(CO)_2CpRe(CH_2)_4$ **1-21** were methylcyclopropane and $CpRe(CO)_2PR_3$ in the presence of PR_3 (Eq. 1-18).[43]



The presence of π-acceptor ligands, or ligands with a strong *trans* effect, favours the reductive elimination of metallacycles.[11,45] Thus, the addition of phosphines, arsine, stibines or anionic ligands (I^-, SCN^-, CN^-) to otherwise stable platina(IV)cyclobutane complexes **1-22** can induce their decomposition by reductive elimination (Eq. 1-19).



(Eq. 1-19)

1-22

L' = PR_3, AsR_3, SbR_3, I-, CN-,
SCN-, olefins, H_2O, CO etc.
L = nitrogen donor ligand, THF

The decomposition of palladacyclopentanes is induced by $Bu^n{}_2O.BF_3$ to give an increased amount of n-butane and extensive isomerization to 2-butenes (**Table 1-2**).[42]

Table 1-2. Decomposition of the palladacyclopentanes of type of $Pd(CH_2)_4L_2$ induced by $Bu^n{}_2O.BF_3$.

Ligand (L)	n-C_4 Distribution (%)			
	1-Butene	n-Butane	2-Butene (*cis*)	2-Butene (*trans*)
dppe	1.6	47.9	11.2	39.0
tmen	1.7	50.0	12.1	36.0
bipy	3.2	20.9	15.4	58.1
PPh_3	4.7	4.2	20.9	70.2

1.3.1.3. General Factors Affecting Thermal Stability

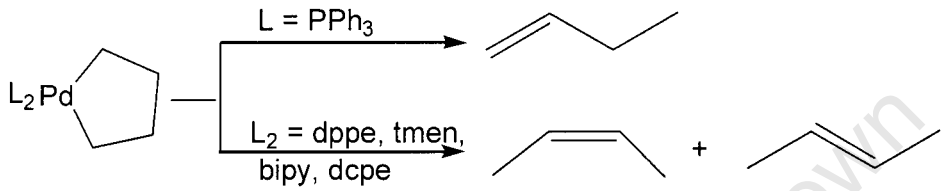
As the stability of the metallacycles is quite dependent on the nature of metal, size of the ring, solvent and supporting ligands, the following factors also have their significance in thermal studies of various metallacycles.

A. Effect of Ligand

The nature of the ligands with chromium catalysts affects the activity and selectivity of ethylene oligomerisation reactions. For example, PNP ligands having bulky ortho alkyl-phenyl groups favour 1-hexene formation, whereas in the absence of ortho-substitution of the phenyl rings, 1-octene formation is

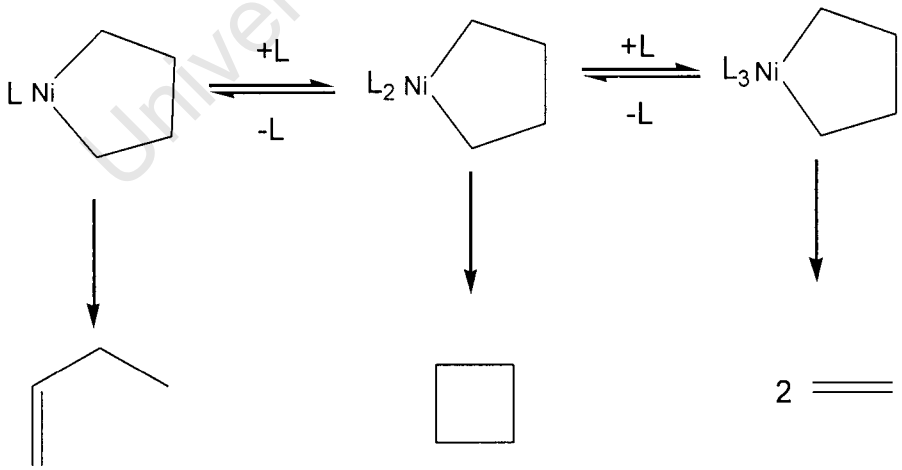
favoured.[20,46] The effect of ligands also plays an important role in the decomposition pathway in metallacyclic systems. Palladacyclopentanes of the type of $L_2Pd(CH_2)_4$,[42] which have been mentioned above, with different ligands give different products when they decompose in toluene.

It was found that butenes were the major products in all cases when heating at 60°C, but 1-butene predominated when the ancillary ligand was a phosphine, while 2-butenes were the major products in the other cases (Eq. 1-20).



(Eq.1-20)

Besides the nature of the ligands, coordination number of the metal has an effect on the decomposition. It is well known that the mechanism of decomposition of nickelacyclopentanes in solvent is strongly dependent on the coordination number of the nickel, leading to the formation of n-butenes, cyclobutane or ethylene, for 3-, 4- or 5- coordinate nickel respectively (Scheme 1-10).[34,35,47]

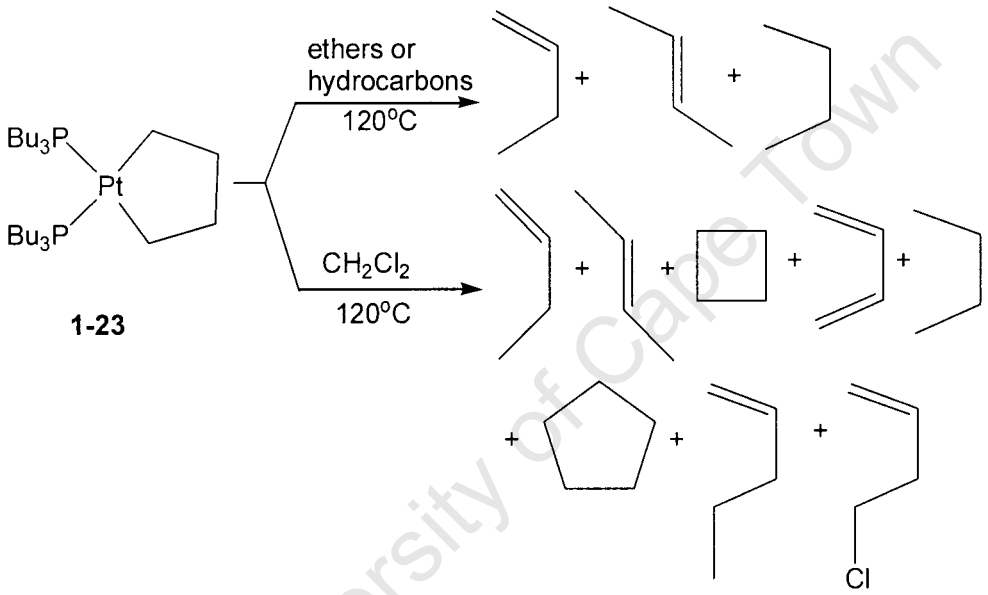


L = trialkyl or aryl phosphine

Scheme 1-10

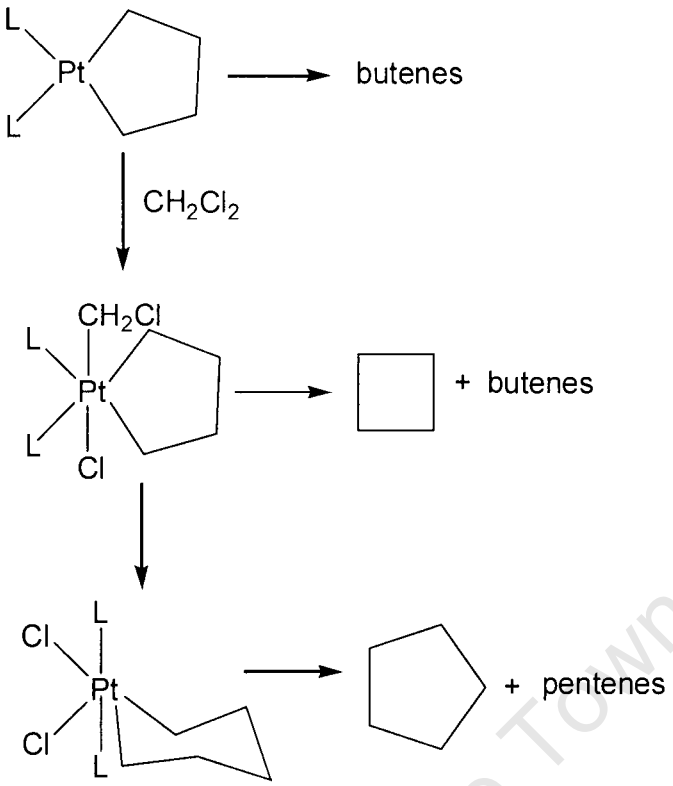
B. Effect of Solvent

In the case of platinacyclopentanes,[27] thermal decomposition of 1,4-tetramethylenebis(tri-n-butylphosphine)platinum(II) **1-23** at 120°C in non-halogenated solvents (diethyl ether, tetrahydrofuran, *n*-hexane, cyclohexane) yielded only butenes and butane. However, decomposition of this compound in methylene chloride solution proceeded more rapidly and yielded significant quantities of cyclobutane, cyclopentane, 1-pentene and 5-chloro-1-pentene (Eq. 1-21).



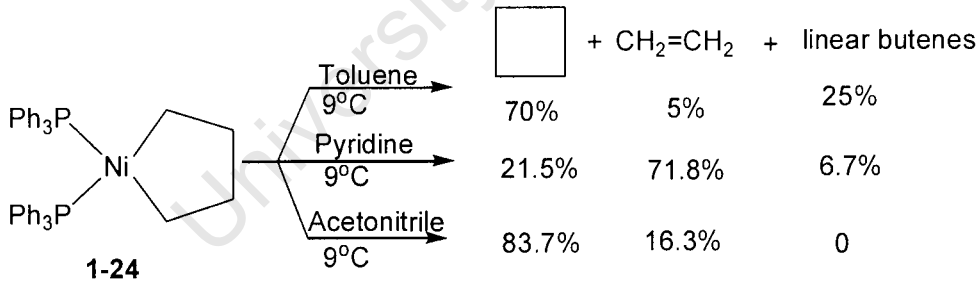
(Eq. 1-21)

The decomposition pathway leading to cyclobutane can be explained by the oxidative addition of a solvent molecule (methylene chloride) to platinum(II) to give a platinum(IV) intermediate, which can then form cyclobutane by reductive elimination, while it undergoes the normal decomposition pathway in non-halogenated solvents (Scheme 1-11).[27]

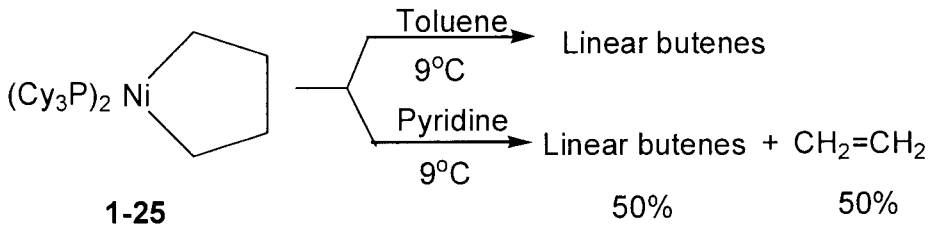


Scheme 1-11

The decomposition pathway for nickelacyclopentanes with different phosphine ligands, as a function of solvent, is shown in Eqs. 1-22 and 1-23.[34]



(Eq. 1-22)

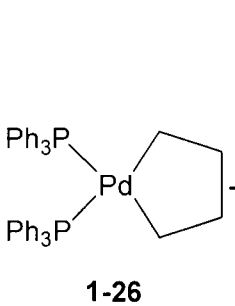


(Eq. 1-23)

Ethylene became the major product when the bis(triphenylphosphine) complex **1-24** was decomposed in pyridine. The tricyclohexyl phosphine complex **1-25**, which

produced only linear butenes on decomposition in toluene, gave a 50% yield of ethylene in pyridine.

The effect of solvent upon the decomposition products of the palladium analogue **1-26,** of complex **1-24** has also been investigated.[42] Decomposition reactions in each solvent were carried out by heating the compound at 60°C for five hours, with an initial concentration of 8 x 10^{-3} mol dm^{-3}. 1-Butene and 2-butene were the major constituents of the product mixture in all cases, but the cyclobutane content was significant when poorly coordinating solvents such as toluene and dimethylformamide were used, and dropped to low levels when highly co-ordinating solvents such as pyridine, acetonitrile and dimethyl sulfoxide were used (Eq. 1-24).



1-26

	Ethylene +	Cyclo-butane +	1-Butene +	2-Butenes +	Buta-diene
Toluene		17%	79.5%		3.5%
Pyridine			92.0%		8.0%
Dimethyl-formamide		10.8%	68.9%	2.5%	16.9%
Acetonitrile	0.4%	0.6%	95.5%	0.8%	2.7%
Dimethyl sulfoxide		2.8%	91.2%	3.0%	3.0%

(Eq. 1-24)

C. Effect of Changes of Metal and Its Oxidation State

The thermal stability of M-C bonds of organometallic compounds generally increases on descending a triad, eg. for Group 8, 9 and10 which is in contrast to the situation for the main group metals where M-C bond strengths significantly decrease.[48] It is clearly observed that thermal stability of 3d transition metal-containing metallacycles are relatively unstable in comparison with their 4d and 5d analogues. For example, t_{dec} = 9°C for bis(triphenylphosphine)nickelacyclopentane **1-24**,[34] 60°C for its palladium analogue **1-26**[42] and 120°C for the platinum analogue **1-1a**.[15,16] Different decomposition products were also formed with different oxidation states, eg.

compare Pd(II) and Pd(IV) compounds, 2-butenes were obtained as major thermal decomposition products for Pd(II)cyclopentane[42] with bipy ligand, while reductive elimination to form cyclobutane was favoured for the Pd(IV) analogue **1-14**.[40]

D. Effect of the Size of the Ring

Medium ring compounds with seven to eleven members and larger ring compounds are more difficult to make[8] and this can in part be due to their decreased thermal stability. For example, Whitesides et al. found that five- and six- membered ring metallacycles are much more stable than the seven-membered metallacycles.[15,16] Despite this, we have prepared a variety of medium to large metallacycloalkanes with various ligand systems by an alternative route[49] to study the effect of the ring size on the organic product distribution on thermolysis, which will be discussed in detail in **chapter 3**.

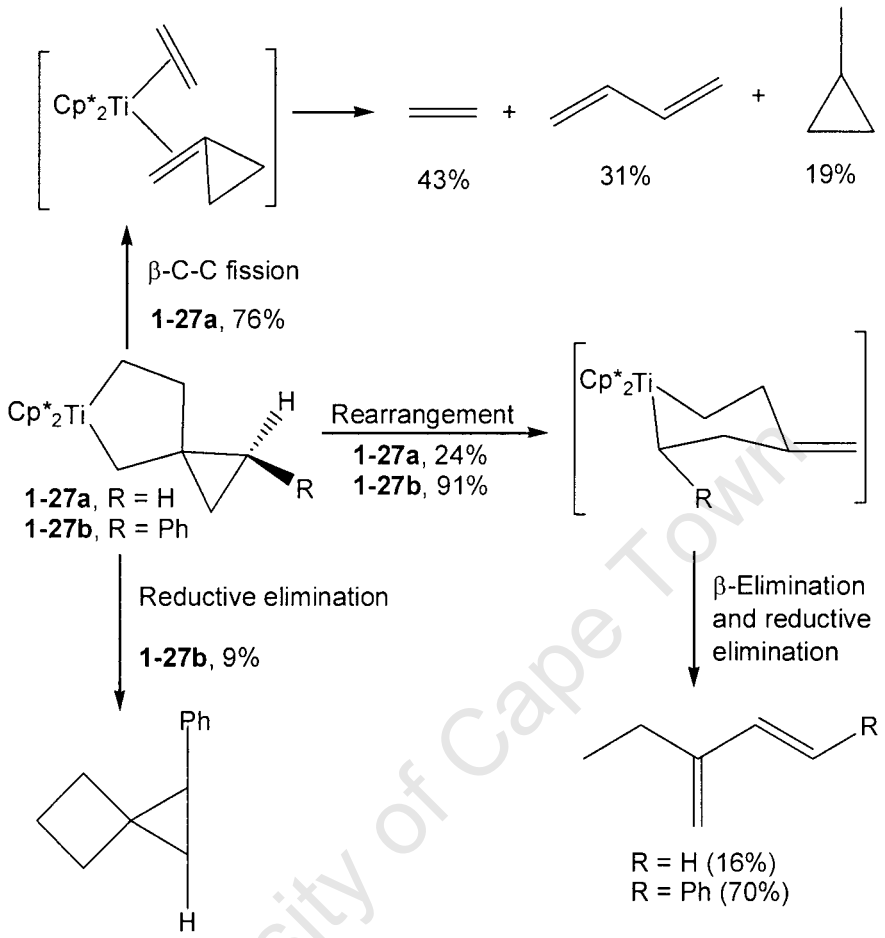
1.3.2. Decomposition in the solid and gas phase

Although few decomposition studies have been carried out in the solid and gas phases, there is an obvious advantage that metallacycloalkanes may be studied in the absence of solvent interactions of various kinds.

Decomposition of metallacycloalkane compounds as a solid can be carried out in two ways. One is direct heating of the solid sample under vacuum and the other is using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

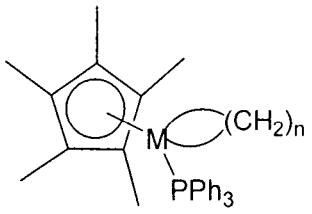
Mashima and Takaya studied the decomposition of compounds **1-27a** and **1-27b**.[50] Solid **1-27a** decomposed when heated rapidly to 200 °C under vacuum to give ethylene, 1,3-butadiene, and methylcyclopropane by β-carbon-carbon bond cleavage. The 1,3-diene $CH_3CH_2C(=CH_2)CH_2=CH_2$, which is derived from the decomposition of a six membered metallacycle, was also formed.[51] In contrast,

the main decomposition product of **1-27b** was the diene, $CH_3CH_2C(=CH_2)CH_2=CHPh$ (Scheme 1-12).



Scheme 1-12

The thermal decomposition of rhodium(III) and iridium(III) metallacycloalkane complexes (Fig. 1-2) was studied by DSC and TGA.[52]

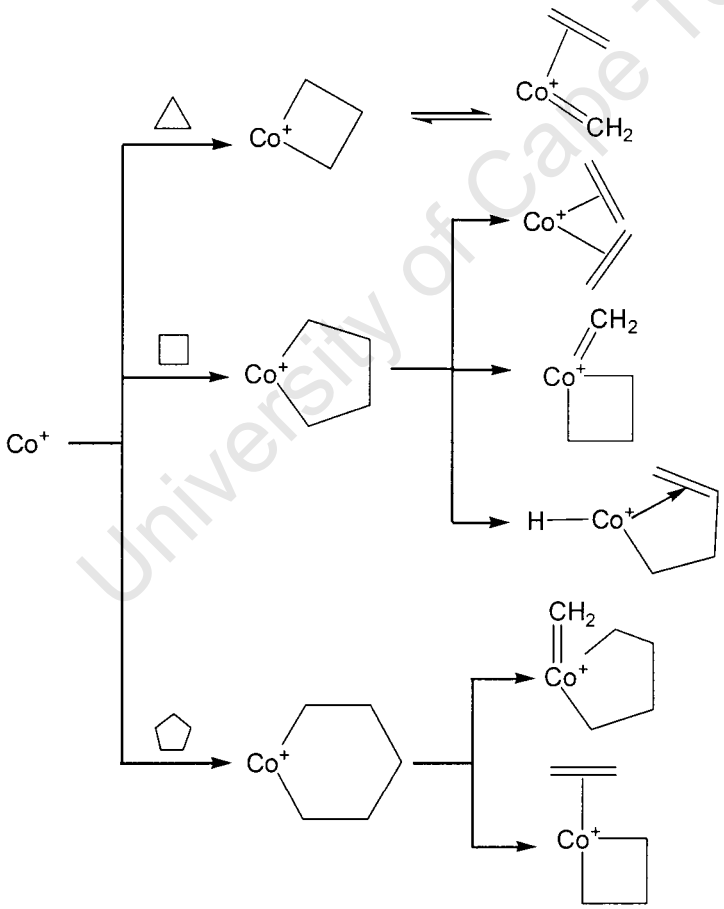


M = Rh, n = 4, 5, 6;
M = Ir, n = 4, 5

Fig. 1-2. Rhodium(III) and iridium(III) metallacycloalkane complexes

In all cases three decomposition steps were identified, the first being the release of the C_nH_{2n} moiety giving the corresponding n-alkenes as the major product, which was confirmed by GLC analysis of the gases leaving the thermobalance during this step; the second, the release of a C_5Me_5 group followed by the third with the release of PPh_3.

Decomposition of naked gas-phase metallacyclic ions is believed to provide some fundamental information.[7] Beauchamp et al. using both an ion cyclotron resonance (ICR) spectrometer and an ion beam instrument, studied the formation and decomposition of cobalt metallacycles.[53] This study showed the ring cleavage reactions in all cases (Eq. 1-25) and suggested that symmetric or nearly symmetric C-C bond cleavage was preferred.

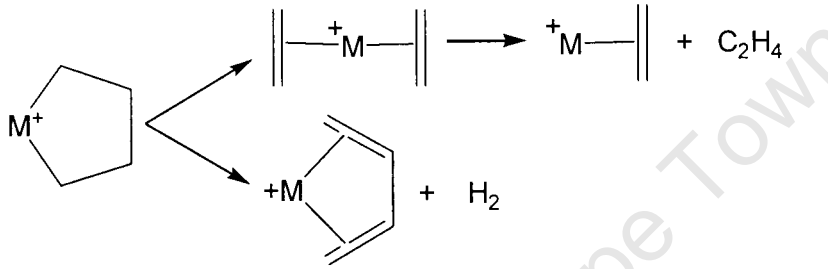


(Eq. 1-25)

Jacobson and Freiser reported a study on the generation and decomposition processes for gas-phase group 8 metal (Fe, Co, Ni) metallacyclic ions using Fourier transform mass spectrometry (FTMS).[7]

In this study, Fe^+ decarbonylated cyclobutanone to generate a stable metallacyclobutane ion, which decomposed by the low energy pathway (either β-hydride transfer or reductive elimination of cyclopropane) competing with the high energy pathway (initial rearrangement to a carbene ethene complex, followed by elimination of ethene). However, both Ni^+ and Co^+ generated unstable metallacyclobutane intermediates.

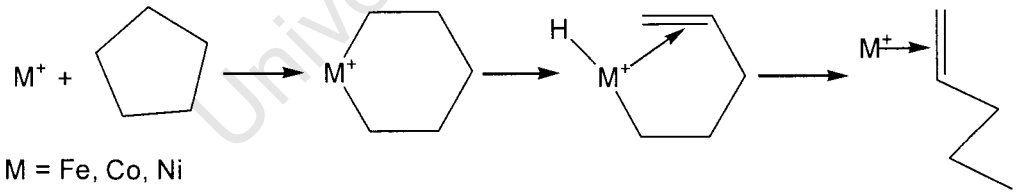
Metallacyclopentane ions decomposed by both symmetric ring cleavage and dehydrogenation processes (Eq. 1-26).



(Eq. 1-26)

M= Fe, Co, Ni

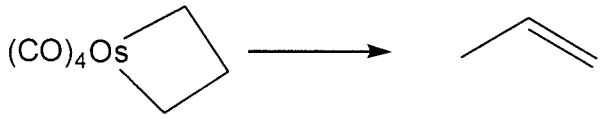
In contrast, the metallacyclohexane ions appeared to decompose by an initial 1,4-hydrogen atom shift generating an activated (1-pentene) metal ion complex (Eq. 1-27).



(Eq. 1-27)

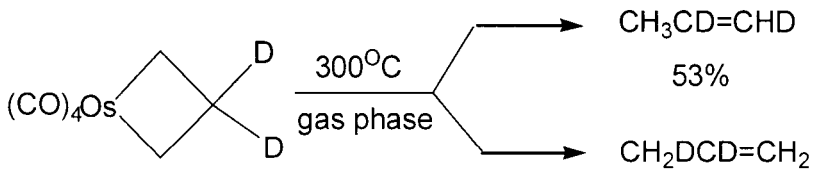
M = Fe, Co, Ni

Thermal decomposition of the osmacyclobutane compound **1-28a** gives propylene under all conditions.[33] However, the authors found that intermolecular products and secondary reactions occurred when the osmacyclobutane compound **1-28b** was decomposed in C_6D_6 solution. In order to preclude secondary reactions, the thermal decomposition of **1-28a** was carried out in gas phase (Eqs. 1-28 and 1-29), and results indicated that both α- and β-hydride elimination mechanisms are operative (Scheme 1-13).



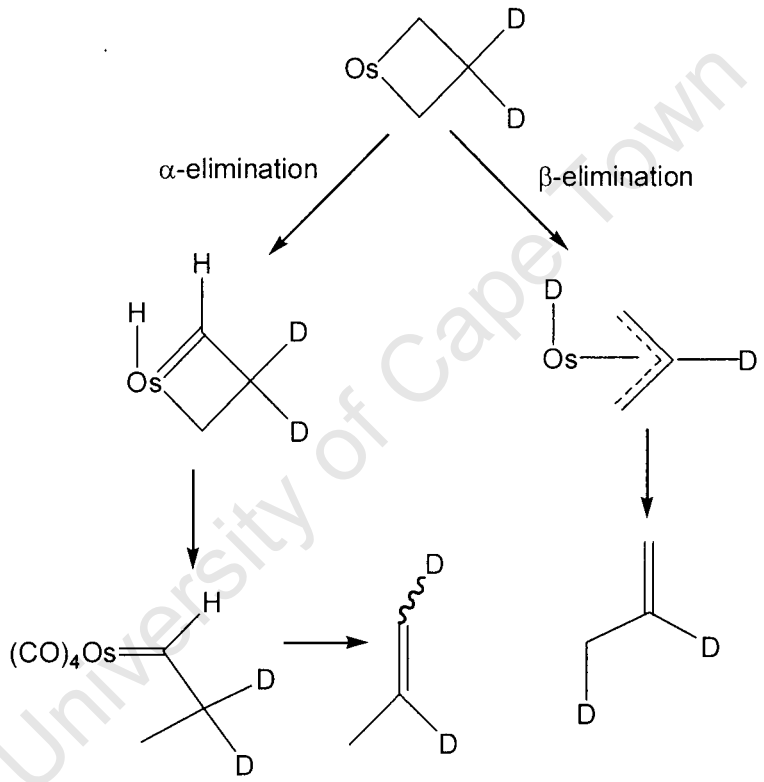
(Eq. 1-28)

1-28a



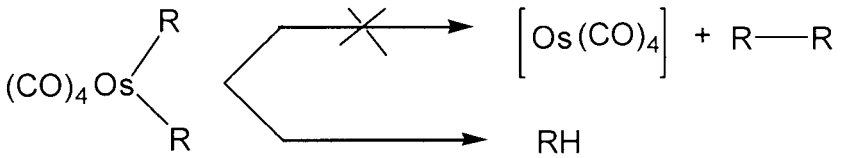
(Eq. 1-29)

1-28b



Scheme 1-13

No reductive elimination products were reported to be found in this study. Interestingly, this finding is consistent with a study on the decomposition of dialkyl osmium, $Os(CO)_4R_2$, in which the most significant result is the absence of simple intramolecular reductive elimination and products are RH (Eq. 1-30).[54]



(Eq. 1-30)

1.4. Conclusions

A large number of small metallacycloalkanes with a variety of metals have been reported, particularly since the 1970s. Recently, there has been considerable interest in the preparation of medium to large metallacycloalkanes, partly because they are key intermediates in various catalytic transformations. The thermal decomposition patterns of these compounds can give new information on the formation of a variety of organic products. Because of their high reactivity, these compounds can yield unexpected products in the presence of reactive substrates, which may be difficult to produce by conventional routes, eg. formation of *n*-alkanes, cycloalkanes, 1-alkene, 2-alkene and dienes from dihaloalkanes through metal mediation. To yield the organic products, metallacycles can go through conventional decomposition pathways such as β-hydride elimination etc. or certain pathways only proposed in metallacyclic systems. Thermal decomposition products strongly depend on the nature of the metal, ligand systems, ring size, as well as the decomposition conditions.

1.5. Scope of thesis

From the literature review in **Chapter 1**, the information obtained on the thermal decomposition patterns and mechanisms is based on results of numerous studies of small metallacycloalkanes in which the maximum ring size is seven. We therefore carried out the thermolysis studies on some novel medium and large ring size metallacyclolakanes in order to expand the understanding on the decomposition mechanisms of metallacycloalkanes.

A new route to metallacycloalkanes, using ring closing metathesis on bis(1-alkenyl) precursors and subsequent hydrogenation of the metallacycloalkene products, has been reported in platinum systems recently.[49] The aim of the work in **Chapter 2** was to apply this route to make some novel palladacycloalkanes according to the previous work done by Mahamo.[55] The same complexes were also prepared by the conventional di-Grignard route for comparison. Characterisation of the complexes was carried out using spectroscopic and analytical techniques such as ^{1}H, ^{31}P NMR spectroscopy and mass spectrometry.

Chapter 3 is concerned with the details on the thermal decomposition of various medium to large metallacycloalkanes. The organic products formed from decomposition were analysed by GC and GC-MS. The kinetics of the decomposition were examined on platinacyclononanes and the effects of additional ligand, decomposition medium, ring size as well as supporting ligands and metal centres were investigated. According to the results obtained, possible decomposition mechanisms are proposed.

The thermal decomposition of some bis(1-alkenyl) complexes, the precursors of metallacycloalkanes, were also studied and described in **Chapter 4**. All the experimental details are reported in **Chapter 5**.

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Chapter 2

The synthesis and characterization of some palladacycloalkane compounds

2.1 Introduction

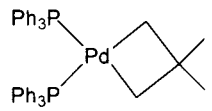
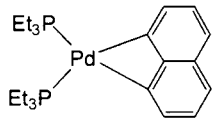
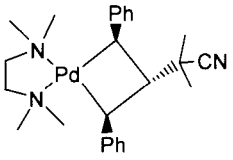
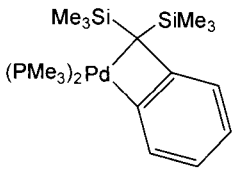
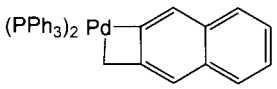
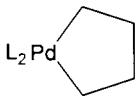
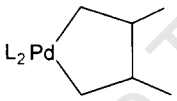
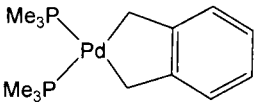
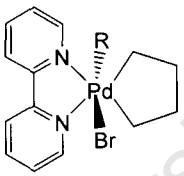
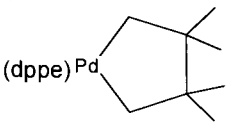
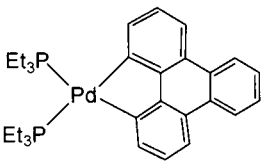
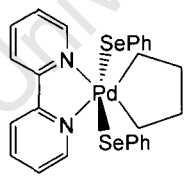
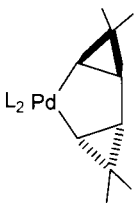
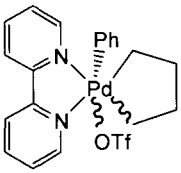
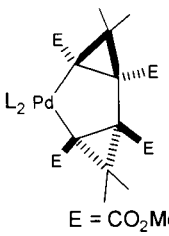
2.1.1 General

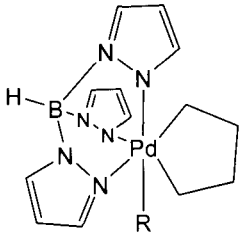
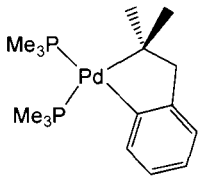
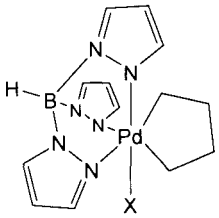
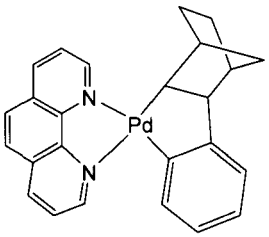
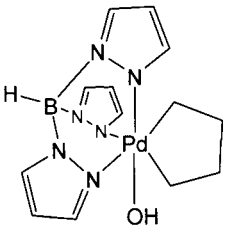
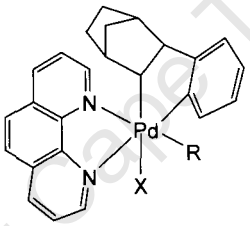
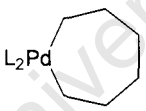
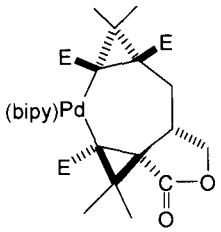
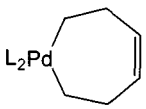
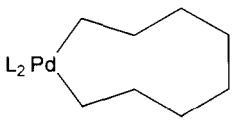
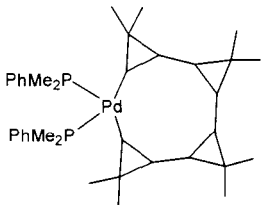
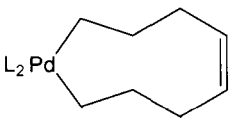
Palladium is an extensively studied transition-metal in organometallic chemistry, partly due to the significant role of palladium complexes in organic synthesis and catalysis.[1] Palladium-catalyzed transformations, which can open up short and efficient pathways from simple starting materials to complex target molecules,[2] have seen a fascinating development in recent years, such as Pd-catalyzed olefin oligomerisation[3] and polymerisation,[4] C-C and C-heteroatom bond formations.[5] In many Pd-catalyzed processes, palladacycles have been reported as alternative catalysts[6] or key intermediates.[7,8] Such species can have both carbon atom and heteroatoms as ring members, but in this brief overview we will focus on the ones exclusively containing carbon atoms.

2.1.2. Types of palladacycles

The general types of palladacycles can be divided into three as shown in Table 2-1. Type I is the simplest palladacycloalkane such as palladacyclopentanes. Extensions to the simplest palladacycloalkanes, i.e., type II, can be obtained by placing functional groups such as alkyl, ester groups as substituents on the ring. More fundamental changes can be made by introducing unsaturation in the ring as well as substiutents on the ring, which can be described as type III. These are the examples of palladacycles reported so far according to these three types in Table 2-1.

Table 2-1. The types of carbopalladacycles

n[a]	I[b]	II[c]	III[d]
n = 3		 **2-A-1**	 **2-B-1**
		 **2-A-2**	 **2-B-2**
		 **2-A-3**	
n = 4	 L2 = dppe **2-C-1** tmen **2-C-2** bipy **2-C-3** decp **2-C-4** L = PPh_3 **2-C-5** PMe_2Ph **2-C-6**	 L = dppe **2-E-1** tmen **2-E-2** bipy **2-E-3**	 **2-L-1**
	 R = CH_2Ph **2-D-1** CH_2COPh **2-D-2** $CH_2CHCHPh$ **2-D-3**	 **2-F-1**	 **2-M-1**
	 **2-D-4**	 L = PMe_3 **2-G-1** PMe_2Ph **2-G-2**	
	 *cis*- and *trans*-**2-D-5**	 E = CO_2Me L_2 = NBD **2-H-1** COD **2-H-2** E = $CO_2CH_2CHCH_2$ L_2 = bipy **2-H-3**	

n = 4	 R = Me **2-D-6** Et **2-D-7** CH_2Ph **2-D-8** CH_2CHCH_2 **2-D-9**	 **2-I-1**
	 X = Cl **2-D-10** Br **2-D-11** I **2-D-12**	 **2-J-1**
	 **2-D-13**	 RX = MeI **2-K-1** CH_2=$CHCH_2Br$ **2-K-2** $NO_2C_6H_4CH_2Br$ **2-K-3**
n = 6	 L = PPh_3 **2-9** L_2 = dppe **2-10**	 E = $CO_2CH_2CHCH_2$ **2-N-1**
		 L = PPh_3 **2-5** L_2 = dppe **2-6**
n = 8	 L = PPh_3 **2-11** L_2 = dppe **2-12**	 **2-O-1**
		 L = PPh_3 **2-7** L_2 = dppe **2-8**

[a] Number of carbon atoms in the ring; [b] The simplest palladacycloalkanes;

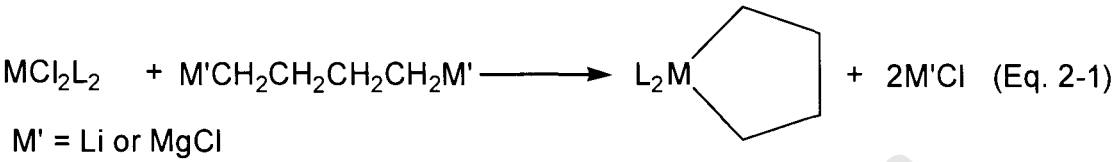
[c] Palladacycloalkanes with substituents on the ring;

[d] Palladyacycles with unsaturation in the ring and substituents on the ring.

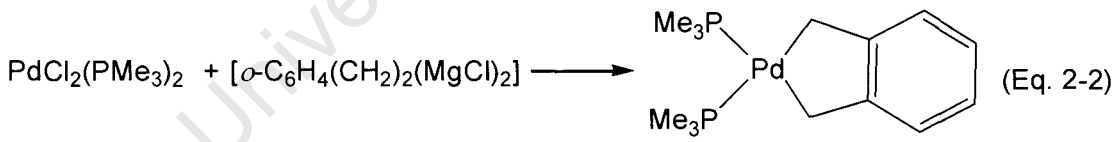
2.1.3. Methods of preparation of palladacycles

2.1.3.1. Transmetallation reactions

The transmetallation reaction, one of the classical methods for the preparation of open-chain metal alkyls, has often applied to the synthesis of metallacycles fromα,ω-dilithium or dimagnesium Grignard reagents, e.g. Eq. 2-1.

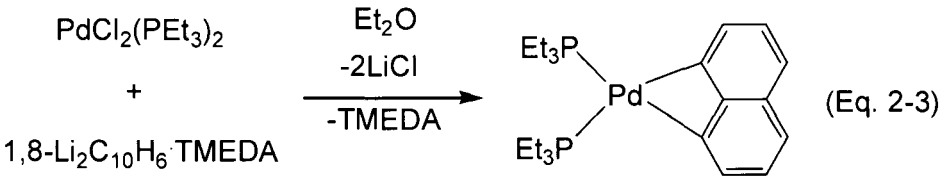


The first palladacyclopetane complex **2-C-1**[9] as well as some early palladacyclopentane derivatives such as **2-C-2** – **2-C-5**[10] and **2-C-6**[11] were obtained by treating the corresponding palladium dihalides with 1,4-dilithiobutane. The palladacyclopentanes containing methyl or dimethyl substituents at the β positions of the metallacycle **2-E**[12] and **2-F-1**[10] were made from the corresponding di-Grignard or dilithium reagents. A palladium xylylene complex **2-L-1** was also synthesized from the α,α-xylyl di-Grignard reagent by Cámpora et al (Eq. 2-2).[13]



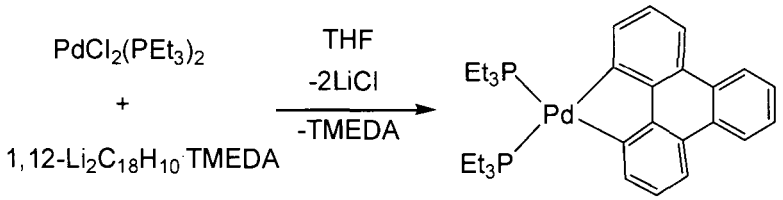
2-L-1

More recently, the four-membered and five-membered palladacycles **2-B-1** and **2-M-1** were prepared from $(PEt_3)_2PdCl_2$ and the appropriate dilithio reagents (Eq. 2-3 & 2-4).[14]



(Eq. 2-3)

2-B-1

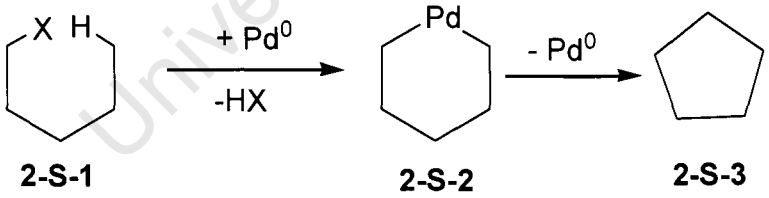


(Eq. 2-4)

2-M-1

2.1.3.2. Cyclometallation reactions

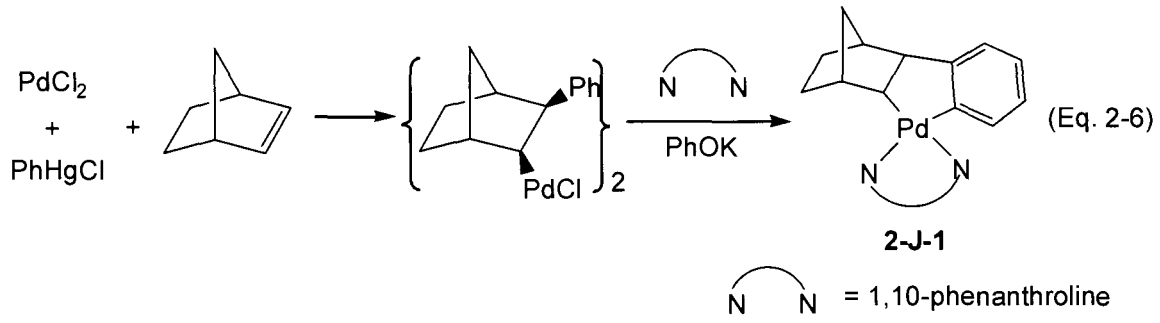
Cyclometallation is regarded as an intramelocular C-H activation reaction. In palladium-catalyzed cyclizations, a six-membered palladacyclic intermediate **2-S-2** can be formed via the cyclopalladation reaction of a substrate **2-S-1** with a reactive halogen atom X and a hydrogen atom in a suitable distance, and **2-S-2** rapidly transfer to a five-membered ring **2-S-3** (Eq. 2-5).[7]



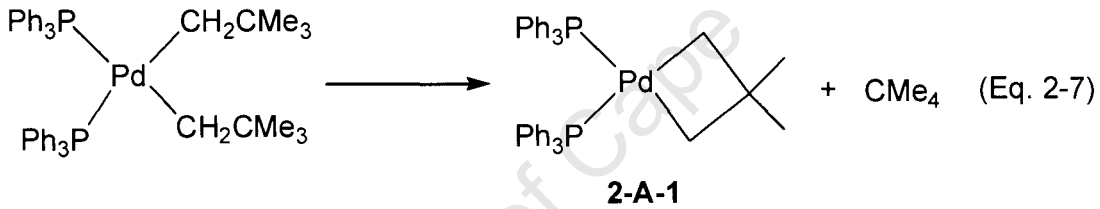
(Eq. 2-5)

2-S-1 **2-S-2** **2-S-3**

The isolation of stable palladacycles such as **2-S-2** has been pursued by several research groups. The formation of these compounds involves the treatment haloalkyl palladium complexes with bases, a method used in the cyclopalladation reaction.[15] The formation of complex **2-J-1** is shown in Eq. 2-6, palladium exchanges with arylmercury halides followed by insertion of norbornene into the palladium aryl bond and cyclization in the presence of phenantroline as stabilizing ligands, using PhOK as a base.[16]



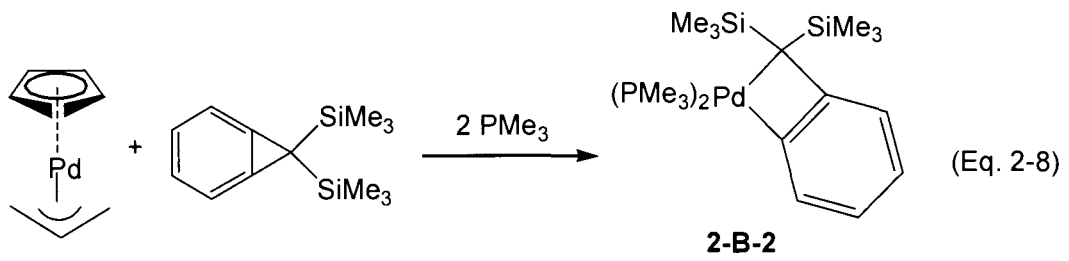
Whitesides group have investigated a mechanism of thermal cyclometallation in dineopentylbis(triethylphosphine)platinum(II).[15,17] The similar example in palladium case is the formation of bis(phosphine)-3,3-dimethylpalladacyclobutane **2-A-1** via intramolecular C-H insertion reaction of the corresponding dineopentyl metal complex (Eq. 2-7).[18]



2.1.3.3. Oxidative addition of C-C bonds

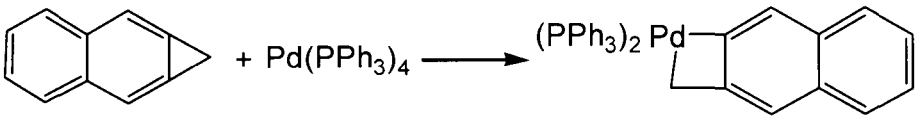
Carbocyclic compounds can oxidatively add to transition metal centers to form metallacycles.[13] Tipper reported the first metallacycle of the Ni group by the treatment of cyclopropane with hexachloroplatinic acid in 1955.[19] This method has also been applied to prepare some palladacycles.

The reaction of 7,7-bis(trimethylsilyl)cycloprapabenzene with Pd(0) afforded bis(trimethylsilyl)benzocyclobutane of palladium **2-B-2** (Eq. 2-8).[20] Stang has reported that cyclopropa[*b*]naphthalene reacts with Pd(0) with oxidative C-C cleavage and formation of the corresponding palladacycle **2-A-3** (Eq. 2-9).[21]



(Eq. 2-8)

2-B-2

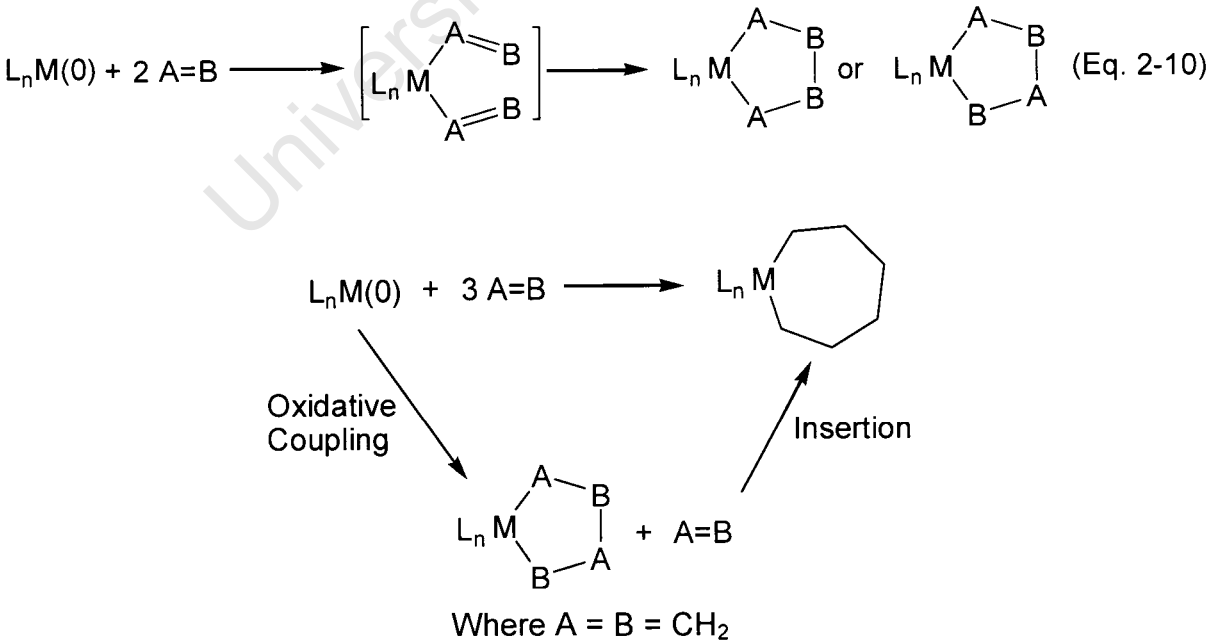


(Eq. 2-9)

2-A-3

2.1.3.4. Oxidative coupling (cycloaddition) of unsaturated molecules

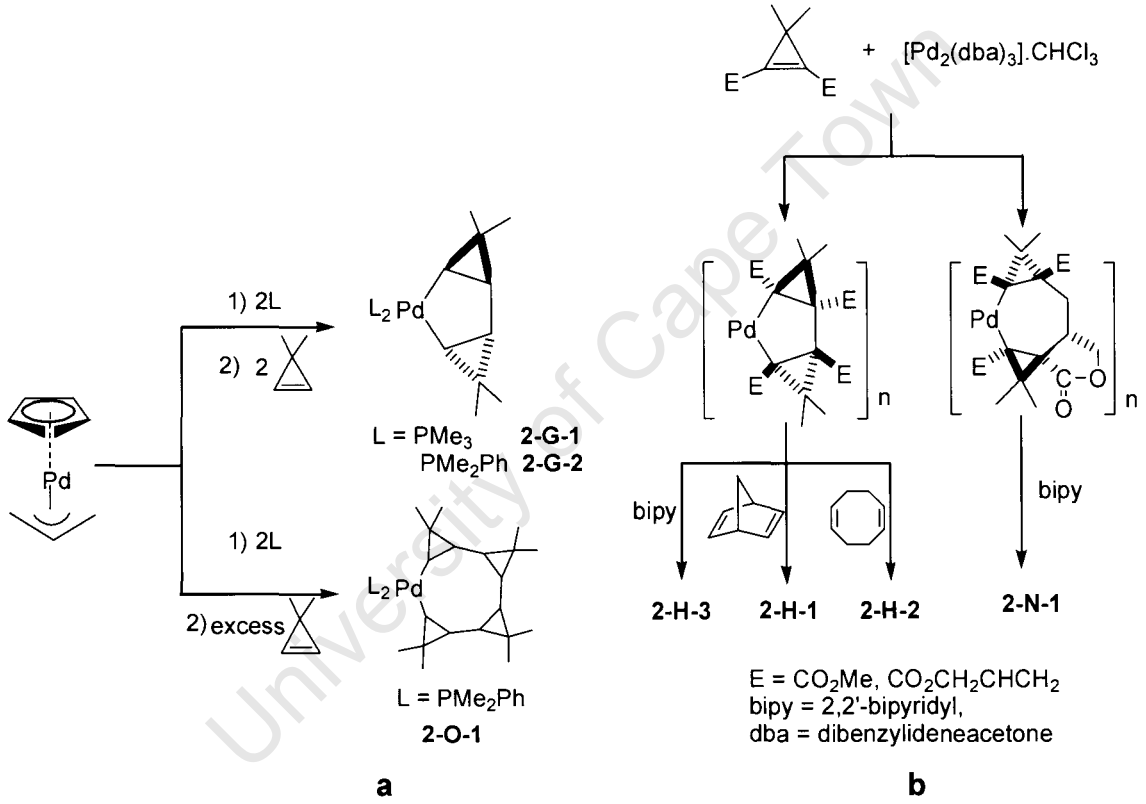
Oxidative coupling or cycloaddition is one of the most useful methods of metallacycle synthesis. The cycloaddition of two unsaturated fragments to a metal unit leads to metallacycle species (Eq. 2-10), while the formal cycloaddition of more than two fragments involves a true cycloaddition process followed by an insertion reaction (Scheme 2-1).[13]



(Eq. 2-10)

Scheme 2-1

Typical examples for oxidative coupling are the preparation of 5-palladatricyclo[4.1.0.$0^{2,4}$]heptanes (PTHs) and their analogues with larger ring sizes. Binger et al isolated the first PTHs derivatives **2-G** and a nine-member palladacycloalkane **2-O-1** by oxidative coupling of 3,3-dimethylcyclopropene with latent palladium(0) complexes (Scheme 2-2-a).[22] Substituted 3,3-dimethylcyclopropenes behave similarly to 3,3-dimethylcyclopropene itself, affording PTHs[23] and palladacycloheptane[7] derivatives by oxidative coupling with Pd(0) complexes (Scheme 2-2-b).

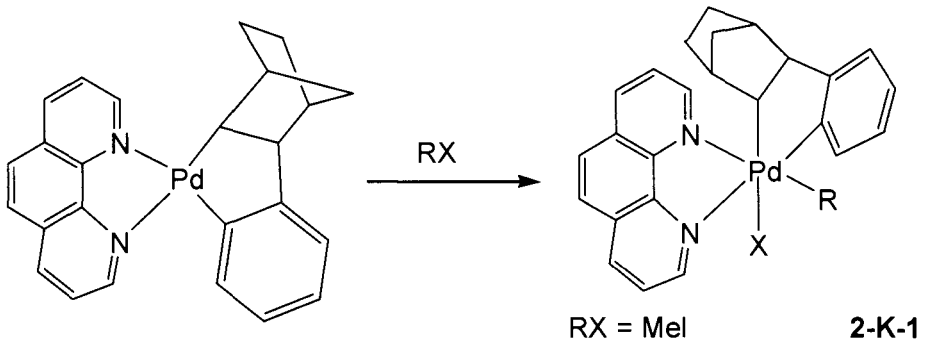


Scheme 2-2

2.1.3.5. Oxidation of Pd(II) metallacycles to Pd(IV) metallacycles

Some of the first Pd(IV) metallacycles which are stable enough to be isolated and characterized were obtained from Pd(II) metallacycles supported by rigid nitrogen ligands such as bipy or phen by oxidation addition of alkyl halides etc.[13] Compounds **2-K** were prepared by Catellani from Pd(II) metallacycle **2-J-1** and

different alkyl halides (Eq. 2-11).[16]

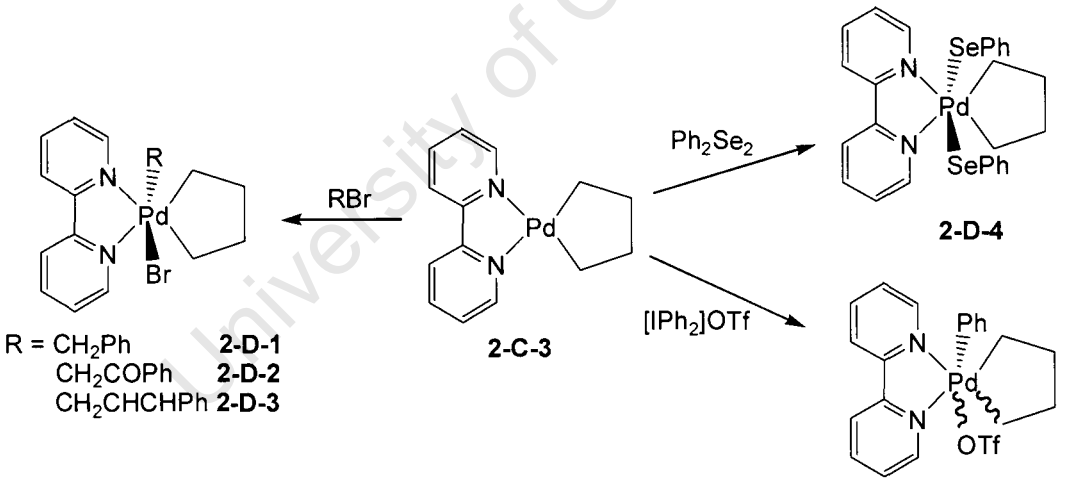


2-J-1

RX = MeI **2-K-1**
CH_2=$CHCH_2Br$ **2-K-2**
$NO_2C_6H_4CH_2Br$ **2-K-3**

(Eq. 2-11)

Canty has shown that Ph_2Se_2 and primary alkyl bromides undergo *trans* oxidation of [Pd(C_4H_8)(bipy)] **2-C-3** to provide Pd(IV) derivatives **2-D-1** to **2-D-4**.[24] The oxidation addition of phenyl and triflato groups (delivered as [IPh_2]OTf) resulted in both *cis* and *trans* isomers of **2-D-5** (Scheme 2-3).[25]



R = CH_2Ph **2-D-1**
CH_2COPh **2-D-2**
$CH_2CHCHPh$ **2-D-3**

2-C-3

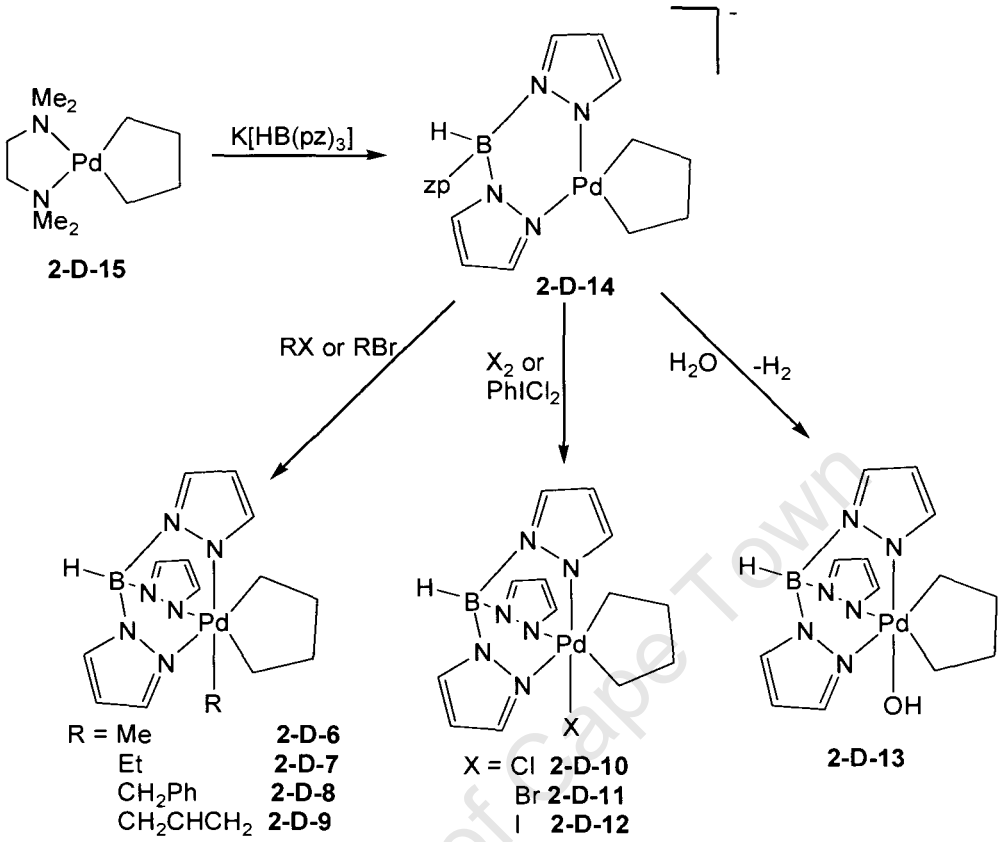
2-D-4

cis- and *trans*-**2-D-5**

Scheme 2-3

The use of rigid, tripodal ligands such as tris(pyrazolyl)borate (Tp) allows the preparation of very stable Pd(IV) metallacyclopentanes **2-D-6** to **2-D-13**, by oxidative addition of alkyl halides,[26] halogen or halogen sources or water (Scheme 2-4),[27] from K[Pd(C_4H_8){HB($pz)_3$}] **2-D-14** which is readily accessible via reaction of

[Pd(C_4H_8)(TMEDA)] **2-D-15** with K[HB($pz)_3$].



Scheme 2-4

2.1.3.6. New route to palladacycloalkanes

Recently, a novel route to the synthesis of medium to large platinacycloalkanes from their bis(1-alkenyl) precursors by ring closing metathesis reaction using Grubbs' catalysts was reported.[28] This route has now been applied to make some novel palladacycloalkanes (see Scheme 2-5-a).[29,30]

The palladacycloalkanes **2-3**, **2-4** and **2-7**, **2-8** were prepared by ring-closing metathesis (RCM) of bis(1-alkenyl)palladium(II) with Grubbs catalyst. The bis(1-alkenyl) complexes were prepared by the transmetalation reaction of 1-alkenyl Grignard reagents with corresponding dichloropalladium(II) complexes, and then converted into palladacycloalkenes **2-1**, **2-2**, **2-5** and **2-6** using RCM

reaction. These complexes were then hydrogenated to yield the corresponding palladacycloalkanes.

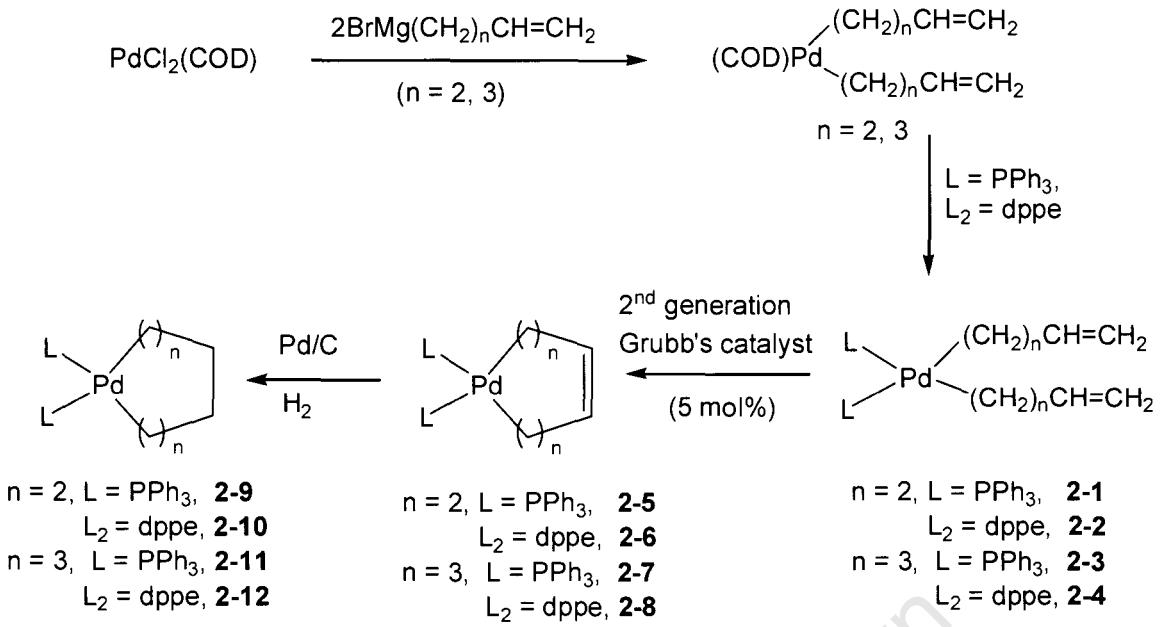
2.1.4. Outlines of the Chapter

Even though there are many ways to make palladacycles as described above, the method for preparation of the simplest palladacycloalkanes seems to be very limited. Mahamo has applied the new route to make some novel palladacycloalkanes in her MSc project. These palladacycloalkane complexes were, however, unstable at room temperature after keeping for 1 – 2 days even under inert atmosphere.[29] The aim of the work in this chapter was to prepare and characterize the palladacycloalkanes **2-9 – 2-12** according to the previous work done by Mahamo,[29] and to carry out thermal decomposition studies on these freshly prepared complexes. For comparison, the complexes with dppe ligand **2-10** and **2-12** were also prepared by the conventional transmetallation reaction of (dppe)$PdCl_2$ and the appropriate di-Grignard reagents. Characterisation of the complexes was carried out using spectroscopic and analytical techniques such as ^{1}H, ^{31}P NMR spectroscopy and mass spectrometry. These results together with Mahamo's work have now been reported in the literature.[30]

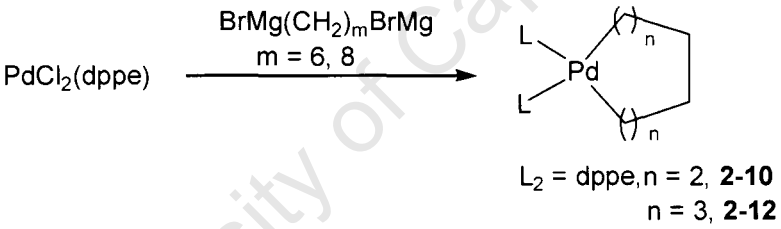
Due to the fact that Mahamo has reported very detailed results on the complexes made through the new route, this chapter only gives a brief description of this route. More detailed results for the complexes prepared using di-Grignard route have been reported in this chapter and the decomposition studies on these complexes have been reported in **Chapter 3**.

2.2. Synthesis of the pallacycloalkane compounds

The preparation of the new pallacycloalkane complexes (**2-9 – 2-12**) employed two reaction routes which are shown in Scheme 2-5.



(**a**). Route 1



(**b**). Route 2

Scheme 2-5: Preparation of palladacycloalkanes

In route 1, the bis(alkenyl)palladium(II) intermediates with COD ligand were obtained by the transmetalation reaction of 1-alkenyl Grignard reagents with [$PdCl_2$(COD)] (COD = 1,5-cyclooctadiene) in diethyl ether at -78°C. Formation of the products was signaled by dissolution of the palladium species.[31] The COD ligand is easily displaced from the intermediates by a number of ligands. Therefore, treatment of pentane solutions of *cis*-bis(alkenyl)palladium(II)(COD) complexes with PPh_3 or dppe gave almost immediately the complexes **2-1** – **2-4**. These complexes were found to be relatively stable at -4 to 0°C for 3 – 5 days.

Treatment of these bis(alkenyl) complexes with Grubbs 2nd generation catalyst (5 mol%) in benzene readily gave the palladacycloalkenes **2-4** – **2-8** via the RCM reaction. The Grubbs' 1st generation catalyst was firstly tried in the RCM reactions, but the reaction times were long which resulted in both the precursors and the products decomposing before the reactions completed. The palladacycloalkene complexes were obtained as brown oils in moderate yields using the second generation catalyst. Reaction of palladacycloalkene complexes with hydrogen in presence of Pd/C (10%) results in saturation of the C=C double bond to yield palladacycloalkane complexes **2-9** – **2-12** as off-white or pale yellow solids quantitatively.

In the conventional route 2, the palladacycloalkane complexes with dppe ligand **2-10** and **2-12** were also prepared by the reaction of di-Grignard reagents using the method reported by Whitesides *et al* for the synthesis of a series of platinacyclopentanes and a platinacycloheptane.[32] In the current study, di-Grignard reagents were used as alkylating reagents because these reagents are easier to handle than dilithio- or di-mercury reagents.

By treating a solution of [$PdCl_2$(dppe)] in diethyl ether with the di-Grignard reagents ($BrMg(CH_2)_6MgBr$ for **2-10** and $BrMg(CH_2)_8MgBr$ for **2-12**) at -78°C, followed by ligand displacement to give complexes **2-10** and **2-12**. The reaction was stable at room temperature for more than 5 hours and resulted in *ca.* 50% yields.

The palladacycloalkane complexes **2-9** – **2-12** are soluble in THF, DCM and aromatic solvents. They were found to be unstable in air. Exposure of the complexes to air at room temperature for a few hours resulted in complex decomposition to give an intense red product initially, and then gradually turns to black residue after longer hours (*ca.* 20 hours).

2.3. Characterization of the pallacycloalkane compounds

The complexes were characterized by ^{1}H and ^{31}P NMR spectroscopy as well as mass spectrometry. The product formation was indicated by the NMR spectrum, however, these compounds are quite unstable. Although we submitted the sample many times for element analysis, the results obtained suggested that the products were partially decomposed. The mass spectra showed product molecular ions as well as the other fragments. All spectroscopic data agrees with the proposed structures for the products obtained and are consistent with Mahamo's report.[29]

2.3.1. ^{1}H and ^{31}P NMR spectroscopy

For the complexes prepared by the new route, the RCM reaction and hydrogenation process were monitored by ^{1}H NMR spectroscopy. This proved to be a very useful tool as these complexes have certain characteristics that are common to all the palladium complexes in this study.

The ^{1}H NMR spectra of the bis(1-alkenyl) complexes, **2-1** – **2-4**, show their characteristic signals for the protons in the alkenyl chains. The furthest upfield signals appeared as triplets at 1.4 – 1.8 ppm assigned to four methylene protons on the carbons next to the metal centre. The signals for the terminal alkene protons appeared at 4.5 – 4.9 ppm and 5.3 – 5.8 ppm. The products yielded from the RCM reactions, **2-5** – **2-8**, were indicated by the disappearance of the terminal alkene protons in alkenyl chains and the appearance of the new broad multiplet at between 5 and 6 ppm, which is due to the alkene protons in the palladacycloalkenes, similar to their platinum analogs.[28] The signal appears as multiplet might be due to the *E* and *Z* isomers of the palladacycloalkenes. The palladacycloalkanes, **2-9** – **2-12**, were obtained by the hydrogenation reaction of the palladacycloalkenes. Reaction progress was monitored by ^{1}H NMR. Product formation was indicated by the reduction and eventual disappearance of the peak

for alkene protons in palladacycloalkenes.

Palladacycloalkanes with dppe ligand **2-12** and **2-10** were also prepared by transmetallation reaction using di-Grignard reagents. The ^{1}H and ^{31}P NMR spectra for both complexes obtained are shown in Fig. 2-1 and Fig. 2-2. Compare to palladacycloheptane **2-10**, palladacyclononane **2-12** has much broader signals in the aliphatic region due to the fact that **2-12** has more methylene protons in the metallacyclic moiety and may have more conformations. This observation is consistent with the report by Mahamo.[29]

As shown in Fig. 2-1, the multiplets between 7.0 and 8.0 ppm are due to the phenyl protons in dppe ligand in complex **2-12**, which integrate for twenty protons. The signals in the aliphatic region integrate for sixteen protons. Other small signals in the spectrum could be due to the impurities. Attempts to purify the product resulted in the decomposition to a black complex.

The spectrum for complex **2-10** (Fig. 2-2) shows a similar pattern as that for **2-12**. The phenyl protons in dppe ligand appear between 7.0 and 8.0 ppm, and the signals in the aliphatic region integrate for twelve protons. The smaller amount of impurities could not be removed.

The ^{31}P NMR spectra obtained in this study are consistent with the observation by Mahamo. The signals in ^{31}P NMR appeared in the region 25.5 to 29.7 ppm for the PPh_3 complexes and 30.1 to 33.5 ppm for the dppe complexes.[29] As shown in Fig. 2-1 and Fig. 2-2, the signals for the phosphorus atoms in complexes **2-12** and **2-10** appear at 32.85 ppm and 30.78 ppm respectively.

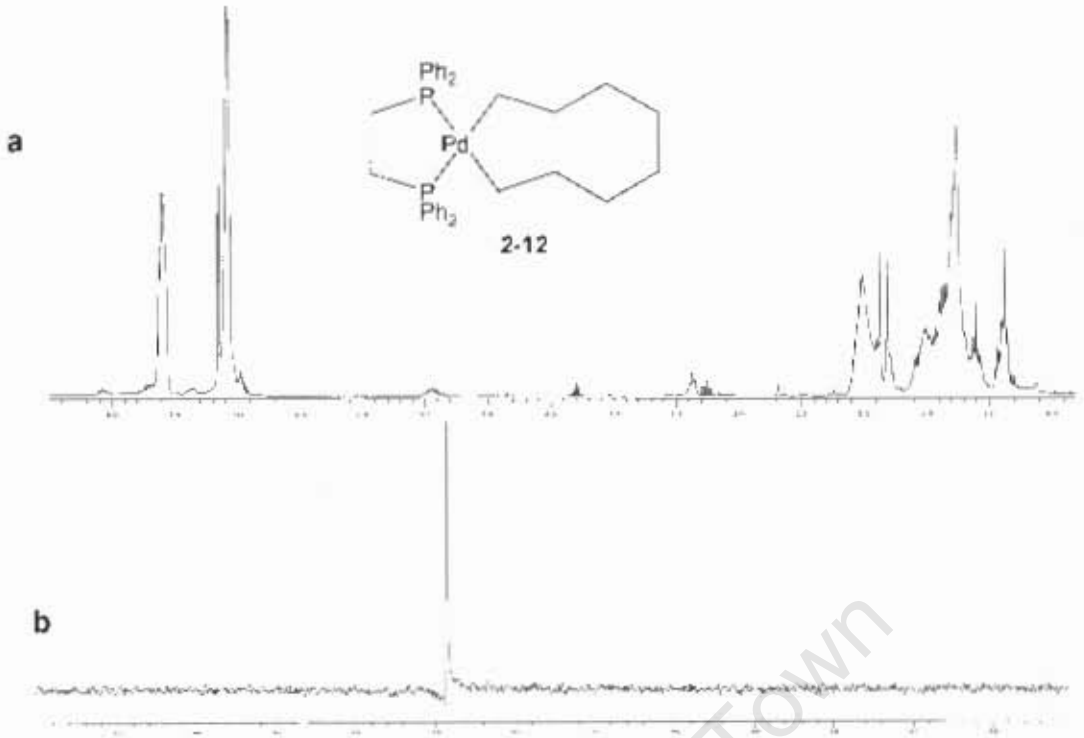


Fig. 2-1. (a) ^{1}H and (b) ^{31}P NMR spectrum of **2-12** recorded in C_6D_6.

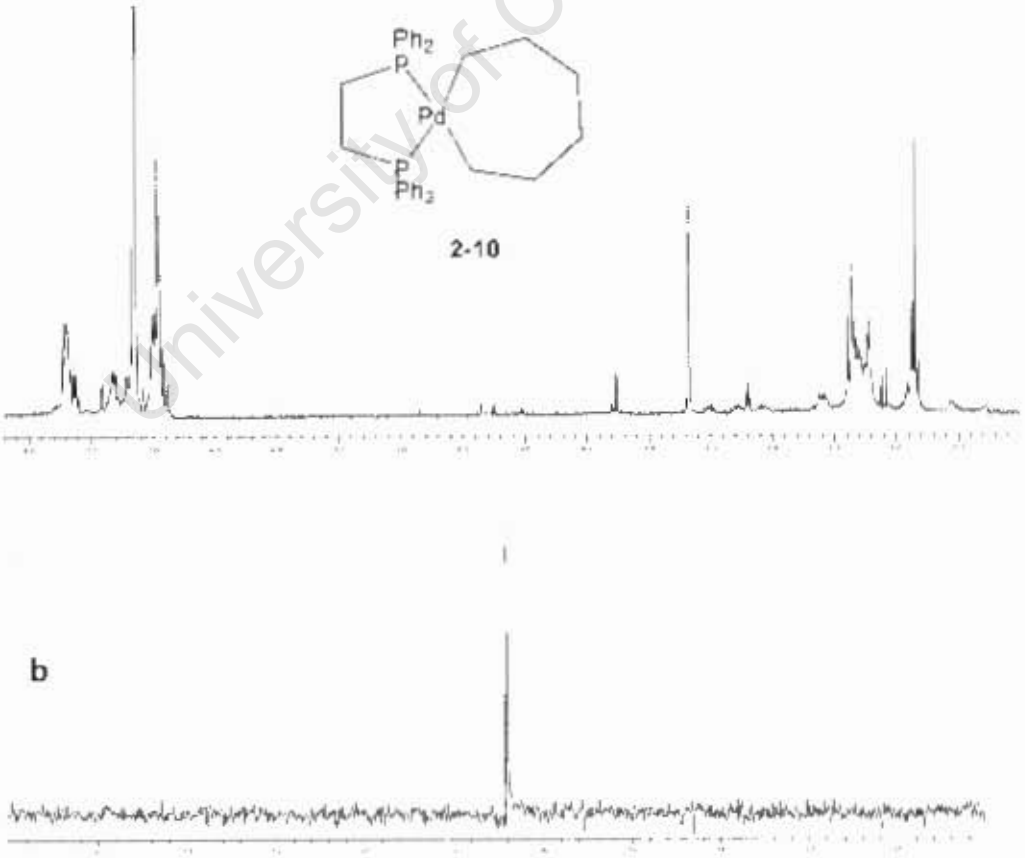


Fig. 2-2. (a) ^{1}H and (b) ^{31}P NMR spectrum of **2-10** recorded in C_6D_6.

2.3.2. Mass spectra

The mass spectra (FAB) of the palladacycloalkane complexes prepared via di-Grignard route **2-12** (Fig. 2-3) and **2-10** (Fig. 2-4) show parent molecular ions and characteristic isotope patterns in the fragmentation pathways. A breakdown of the various ions for **2-12** and **2-10** is presented in Table 2-2. It was found in both mass spectra that there is a peak at m/e 430 without the isotopic pattern for palladium, which could be due to phosphine oxide.

Table 2-2. Assignment of fragment ions from the mass spectrum of **2-12** and **2-10**.

2-12 M = [(dppe)Pd$(CH_2)_8$]			**2-10** M = [(dppe)Pd$(CH_2)_6$]		
Ion[a]	m/e	Relative peak intensities[b]	Ion[a]	m/e	Relative peak intensities[c]
$[M]^+$	617	74	$[M]^+$	589	76
$[M\text{-}CH_2]^+$	603	15	$[M\text{-}CH_2]^+$	575	22
$[M\text{-}(CH_2)_3]^+$	575	14	$[M\text{-}(CH_2)_5]^+$	519	8
$[M\text{-}(CH_2)_7]^+$	519	12	$[M\text{-}(CH_2)_2\text{-}Ph]^+$	484	10
$[M\text{-}(CH_2)_4\text{-}Ph]^+$	484	24	$[dppe(O_2)]^+$	430	100
$[dppe(O_2)]^+$	430	86	$[M\text{-}(CH_2)_5\text{-}(Ph)_2]^+$	365	14
$[M\text{-}(CH_2)_7\text{-}(Ph)_2]^+$	365	20	$[M\text{-}(C_6H_{16})\text{-}(Ph)_2]^+$	347	60
$[M\text{-}(C_8H_{20})\text{-}(Ph)_2]^+$	347	100	$[M\text{-}(CH_2)_7\text{-}P(Ph)_2]^+$	306	11
$[M\text{-}(CH_2)_9\text{-}P(Ph)_2]^+$	306	16	$[M+CH_2]^+$	603	38
$[M+CH_2]^+$	631	38	$[M+(CH_2)_2]^+$	617	15
$[M+(CH_2)_2]^+$	645	16	$[M+(CH_2)_3]^+$	631	28

[a] ion refers to proposed assignment;

[b] peak intensities relative to m/e 347;

[c] peak intensities relative to m/e 430.

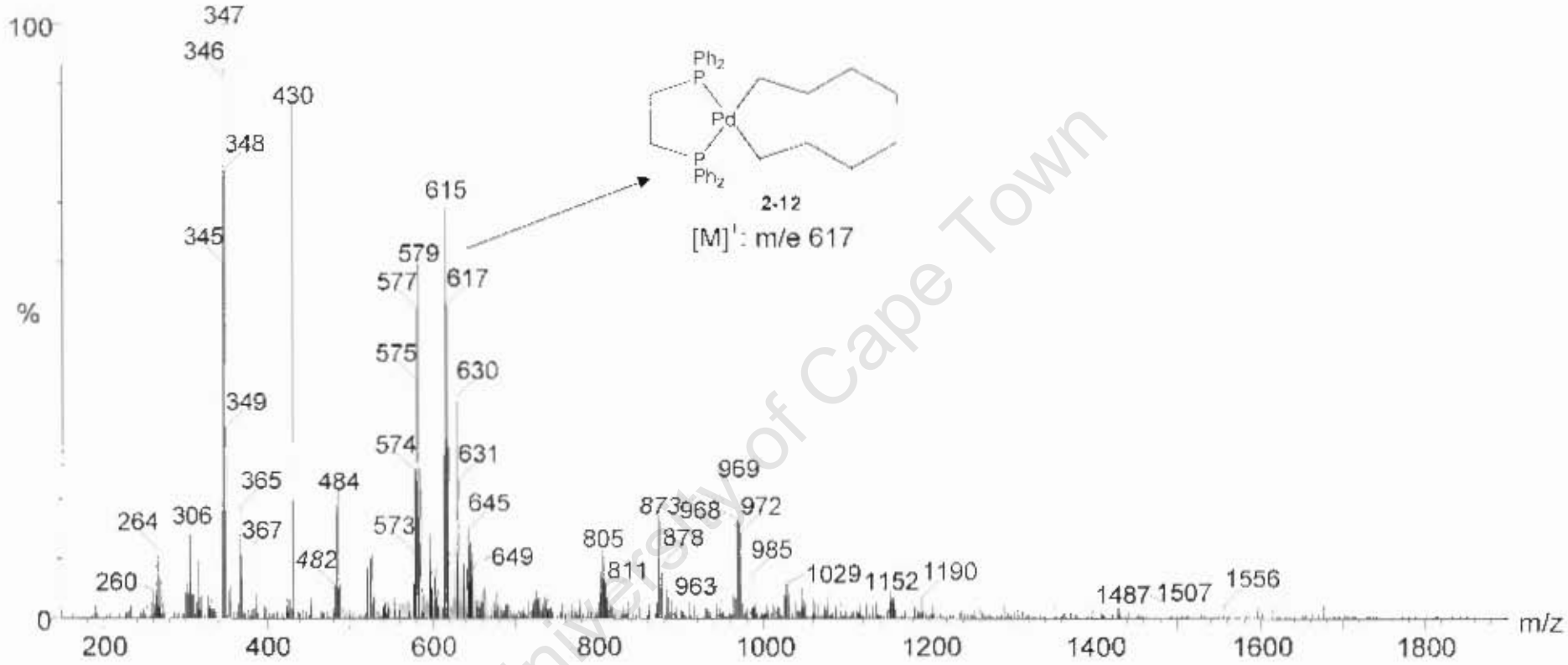


Fig. 2-3. Mass spectra (FAB) of **2-12**

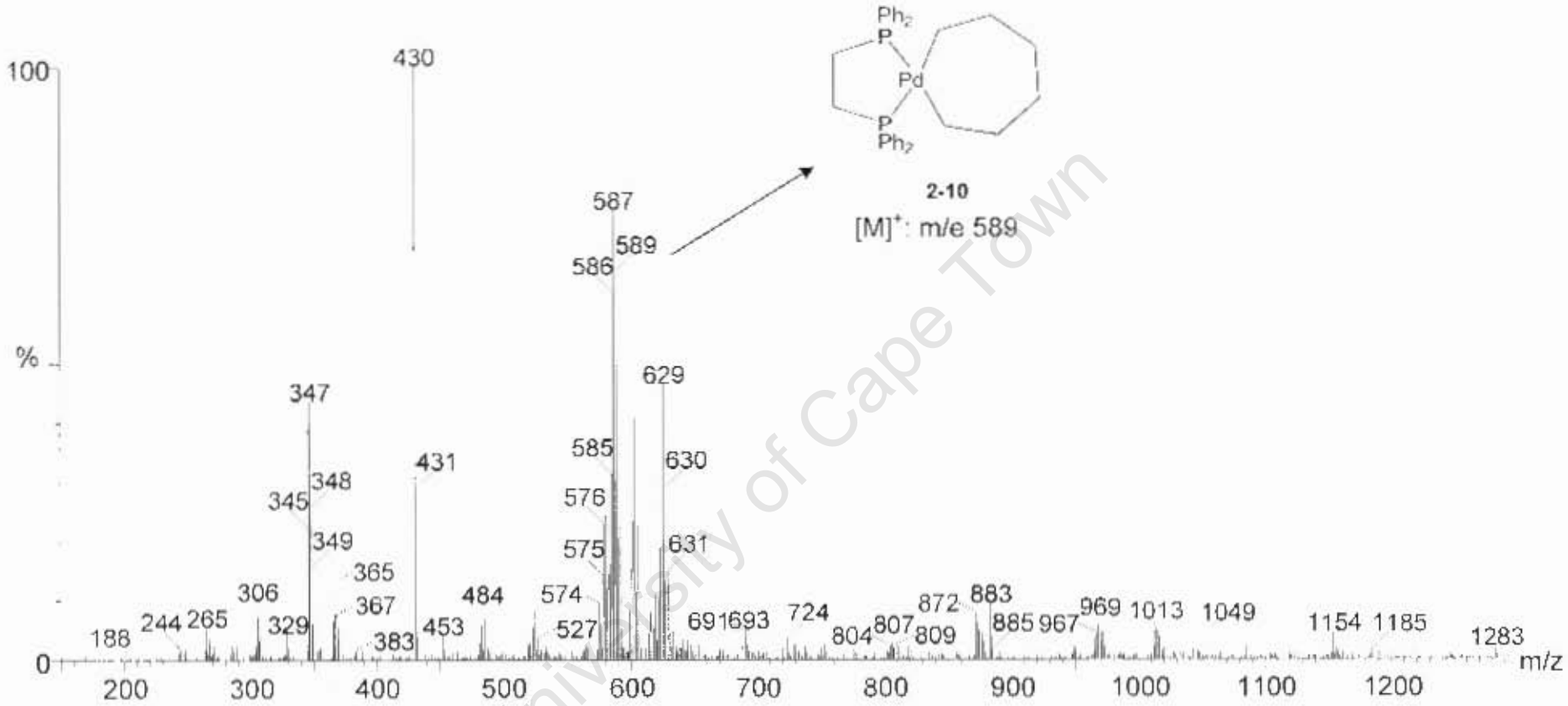
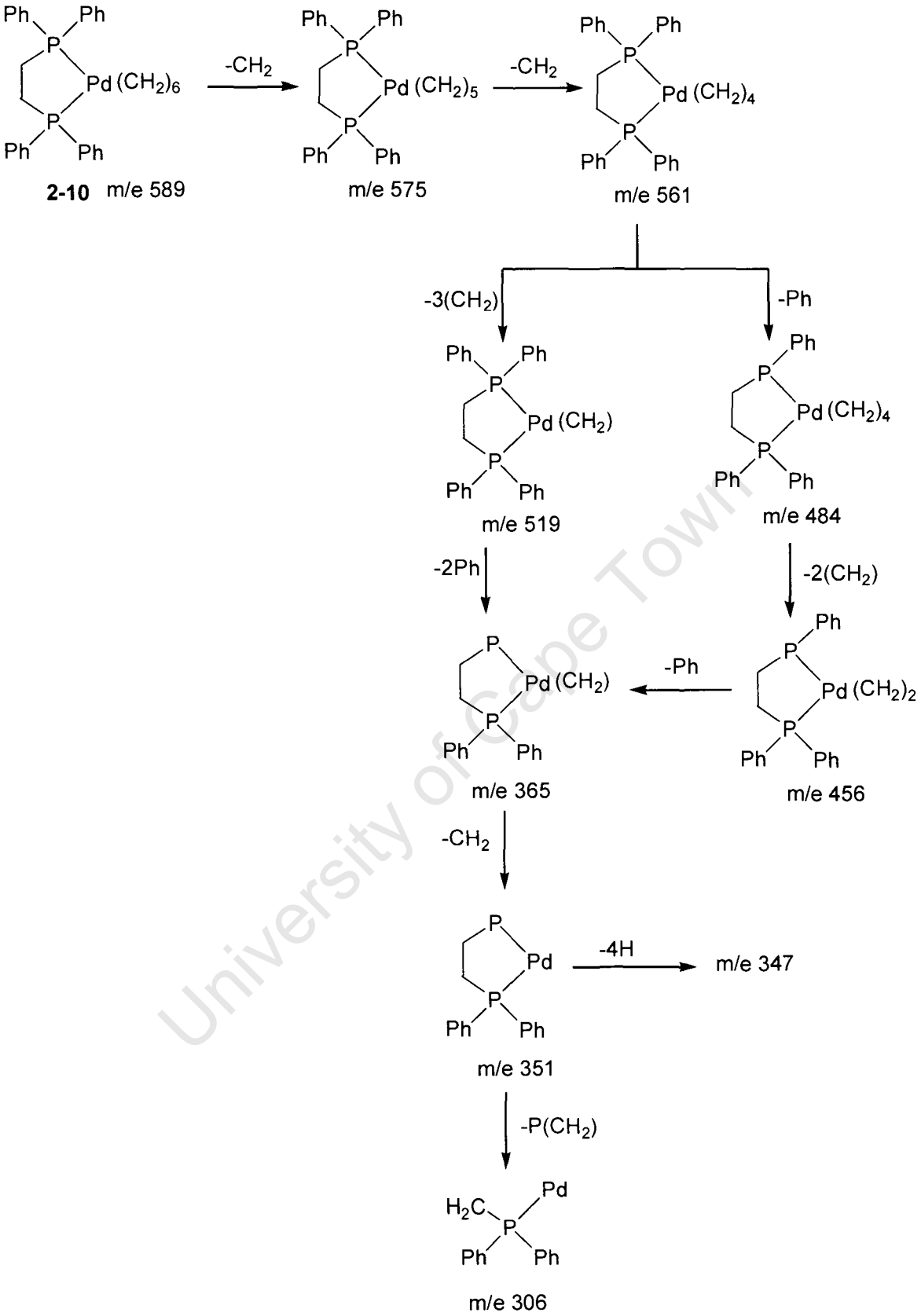


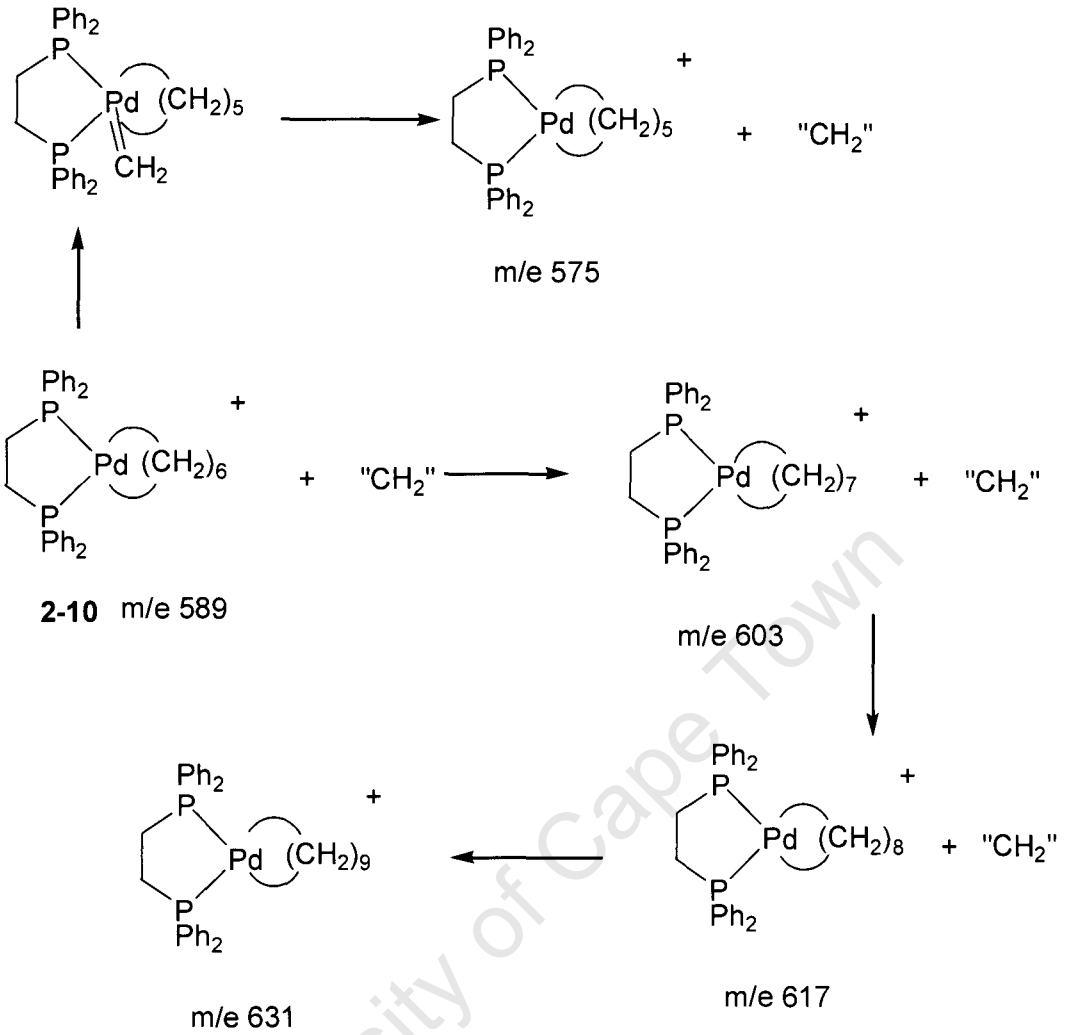
Fig. 2-4. Mass spectra (FAB) of **2-10**

The fragmentation pathways for the palladacycloheptane **2-10** could be either sequential loss of methylene fragments followed by loss of phenyl groups in the ligand (Scheme. 2-6). **2-12** shows similar fragmentation pathways from the mass spectrum.

It is interesting to note that the mass spectra for both complexes show fragments at higher mass than the parent molecular ion. The high mass peaks presented in Table 2-2 could be assigned for the fragment of the parent molecular with one methylene group or more. This could be due to gas-phase ion-molecule reactions which occurred in the mass spectrometry during the measurement. This behaviour is also seen in some platinacycloalkanes.[33] For complex **2-10**, the sequential insertion of methylene groups to the palladacycloheptane ion (m/e 589) resulted in the formation of palladacyclooctane ion (m/e 603), palladacyclononane ion (m/e 617) and palladacyclodecane ion (m/e 631) (see Scheme 2-7). The same phenomenon was observed from the mass spectra of **2-12**. Some of the peaks at much higher mass could be due to the presence of traces of dimeric species in the product.



Scheme 2-6. Fragmentation pathways of **2-10**



Scheme 2-7. The formation of the fragments higher than the parent molecular ion via gas-phase ion-molecule reactions

2.4. Conclusion

In this study, the palladacycloalkanes **2-9** to **2-12** were successfully prepared by ring closing metathesis reactions of the bis(alkeny)l complexes according to the work done by Mahamo.[29] The complexes with dppe **2-10** and **2-12** were also synthesized by transmetallation reactions using appropriate di-Grignard reagents.

The complexes were characterized by ^{1}H and ^{31}P NMR spectroscopy as well as mass spectrometry. All spectral data obtained agree with what is expected for the proposed structures of the products. The details of characterization of the palladacycloalkanes made by di-Grignard route are also reported.

Thermal decomposition studies were carried out on these freshly prepared complexes, the results are reported in **Chapter 3**.

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Chapter 3

Thermal decomposition studies on metallacycloalkane complexes

3.1. Introduction

In the 1970s, there was an upsurge of interest in the decomposition modes of orgaotransition-metal complexes.[1] Since 1977 when Manyik et al. proposed the involvement of metallacycles for the first time as key intermediates in the catalytic ethylene trimerisation reaction,[2] the chemistry of metallacycloalkane compounds has been growing[3] and more studies of decomposition of these compounds have been carried out.[4,5] The understanding of these decomposition processes can be exploited in the design of stable organotransition-metal complexes, including metallacycloalkanes and in the interpretation of synthetic and catalytic reactions involving such complexes.

Much of the early information available on this topic is restricted to the decomposition of small metallacycloalkanes (with four- to six-membered rings) largely due to the difficulty of making medium and lager metallacycloalkanes. It is only recently that thermal decomposition studies were able to be carried out on medium and large metallacycloalkanes, which were prepared using a new route developed in our research group.[6,7]

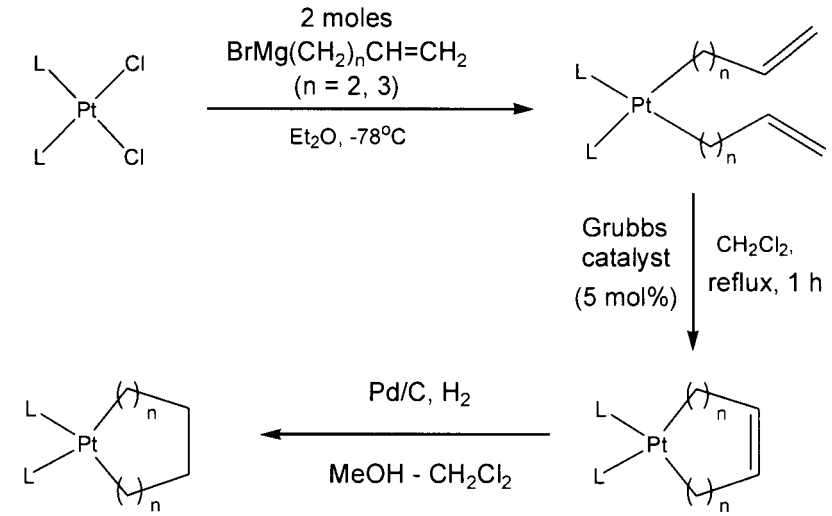
Thermal decomposition of metallacycloalkanes often affords a complex mixture of products. Our first objective was to identify the decomposition pathways although it was not always possible to ascertain all the product-forming reactions, and to assess their relative importance within various combinations of metal, ligand and ring size. The second objective was to establish decomposition rates for an

analysis of the comparative thermal stability and to understand the effect of additional neutral ligands on decomposition pathways. However, not many kinetic studies have been carried out due to the limitation of the amount and stability of metallacycloalkane complexes available. This chapter describes an attempt to understand the decomposition pathways of medium to large metallacycloalkanes.

3.2. Results

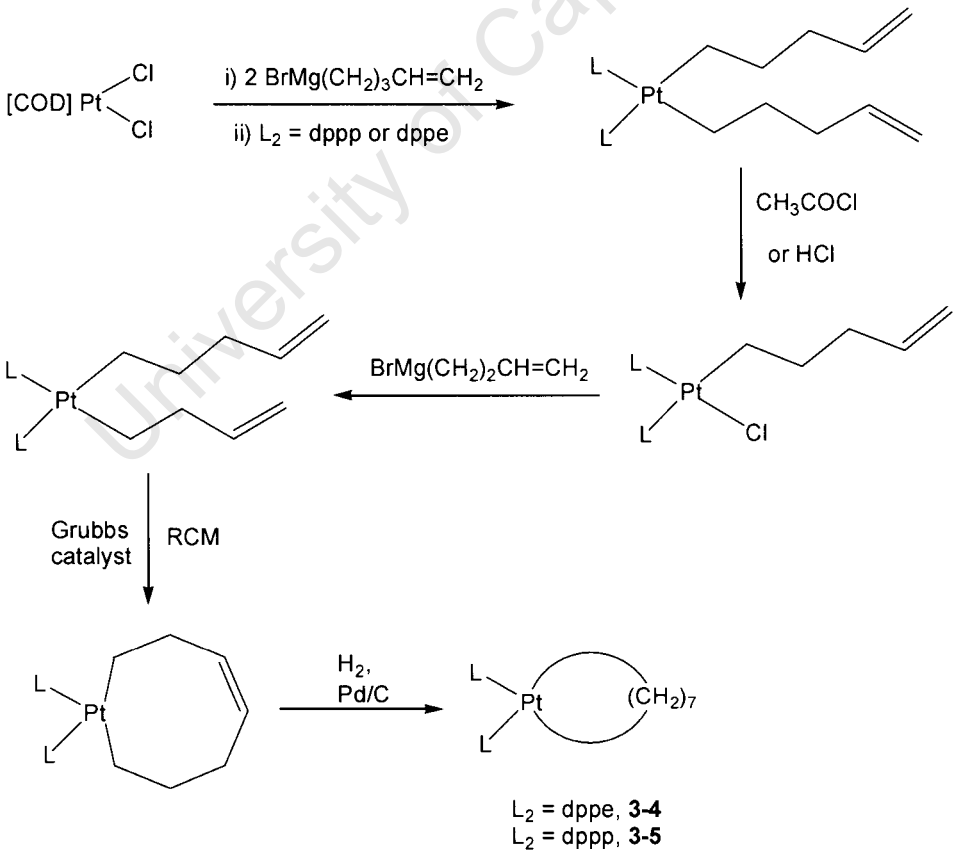
3.2.1. Thermal decomposition of platinacycloalkanes

Two different synthetic strategies are required for the preparation of metallacycloalkanes with odd-membered and even-membered ring size. The platinacycloalkanes with odd membered ring size **3-1**– **3-3**, and **3-6** – **3-8** were prepared by ring-closing metathesis (RCM) of bis(1-alkenyl)platinum(II) with symmetrical alkenyl ligands with Grubbs catalyst. The bis(1-alkenyl)platinum(II) complexes were prepared by the transmetallation reaction of 1-alkenyl Grignard reagents with corresponding dichloroplatinum(II) complexes, and then converted into platinacycloalkenes using ring-closing metathesis reaction. These complexes were then hydrogenated to yield the corresponding platinacycloalkanes (Scheme 3-1-a).[6,7] Complexes with even member ring size complexes **3-4**, **3-5** were prepared using RCM reaction of the precursor complexes with unsymmetrical alkenyl groups, *i.e.*, 1-butenyl and 1-pentenyl group, and followed by hydrogenation (Scheme 3-1-b).[8]



n = 3, L_2 = dppp, **3-1**
L_2 = dppe, **3-2**
L = Bu_3^tP, **3-3**
n = 2, L = PPh_3, **3-6**
L_2 = dppe, **3-7**
n = 4, L_2 = dppp, **3-8**

a



L_2 = dppe, **3-4**
L_2 = dppp, **3-5**

b

Scheme 3-1. Preparation of platinacycloalkanes.

3.2.1.1. Temperature and time effects on thermolysis of 3-1 and 3-2

The data for the examination of temperature and time effects on the thermal decomposition of **3-1** and **3-2**, using cyclohexane as solvent, was obtained by monitoring the appearance of 1-octene. The studies of temperature effects were carried out by heating **3-1** and **3-2** at various temperatures for the same period (2 hours), and then cooling to -196°C. The organic products obtained were analysed by injecting the solution phase, once warmed to room temperature into a GC. The amount of 1-octene (mol %*) was relative to the internal standard.

Thermal decomposition of **3-1** at 80°C for 2 hours only afforded 1-octene (65%†) and octane (35%). When the temperature was increased to above 120°C, 2-octenes and 1,7-octadiene were formed. The amount of 1-octene as well as the total amount of hydrocarbon products increased with the temperature when heating for the same period. In contrast, decomposition of **3-2** proceeded much more rapidly, it gave 1-octene (34%), octane (19%), 2-octenes (28%) as well as 1,7-octadiene (16%) and a small amount of cyclooctane (3%) when the thermolysis was carried out at 80°C for 2 hours. The product distribution of **3-2** at different temperatures varied slightly, but the formation of products remained unchanged. The amount of 1-octene formed was also found to increase with temperature. As shown in Fig. 3-1-a, high decomposition temperature is necessary for the thermal decomposition of platinacycle complexes with stable chelating ligands, *e.g.* dppe and dppp.

The time effect on the thermal decomposition of **3-1** and **3-2** was investigated at 170°C. The reasons for carrying out the experiment at this temperature are twofold: 1), according to the above results, decomposition at the higher temperature gave a

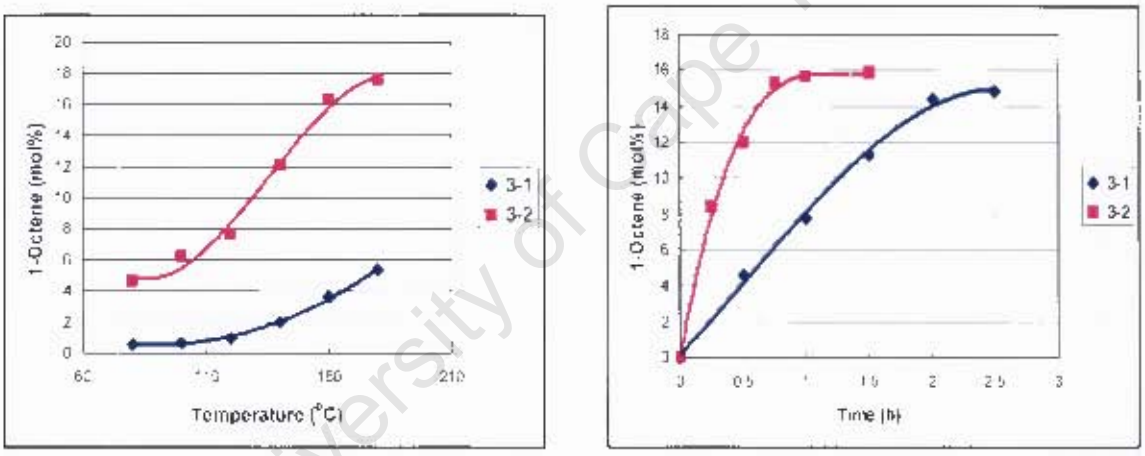
---

* mol % = (mol of 1-octene / mol of Pt) x 100%.

† Relative percentage in the total products detected (the same for the other products).

higher yield of 1-octene, and 2), by using a thermolstated hot plate, this temperature is relatively high and easily achieved using an oil bath.

The amount of 1-octene from thermal decomposition of **3-1** increased with decomposition time. A similar result was obtained in the thermal decomposition of **3-2**. Complex **3-1** decomposed at a much slower rate than **3-2**, which is shown in Fig. 3-1-b. Formation of 1-octene was complete after 2.5 hours for **3-1**, while for **3-2**, after 1 hour no further formation of 1-octene could be detected. The organic products obtained after decomposition in both cases consisted of a mixture of alkenes, with 1-octene as the major product, while 2-octenes, 1,7-octadiene and octane were present as minor products.



a b

Fig. 3-1. (a) Temperature effect (decomposition time = 2hr) and (b) time effect (decomposition temperature = 170°C) on the thermal decomposition of **3-1**(◆)and **3-2** (■) followed by the appearance of 1-octene (mol%).

According to the above studies, we used 170±5°C and 2 hours as the standard decomposition conditions for the thermolysis of platinacycloalkanes. These conditions were also applied to the metallacycloalkanes with other metal centres. Therefore, the results obtained under the same decomposition conditions can be compared.

3.2.1.2. Kinetic studies

Kinetic studies were carried out on the thermal decomposition of the platinacycloalkanes using a similar procedure reported by Whitesides and co-workers.[9,10,11] The principal reason for choosing these complexes was that they are easily purified, well-characterized and experimentally convenient because of stability to air and have a high decomposition temperature. Error analysis for the kinetic studies was not carried out due to the insufficient amount of the complexes.

*A. Kinetics of thermal decomposition of **3-1** and **3-2***

The rates of thermal decomposition of platinacyclononanes $L_2Pt(CH_2)_8$ (**3-1**, L_2 = dppp; **3-2**, L_2 = dppe) in cyclohexane were examined by GC following the appearance of the total hydrocarbon products from decomposition, which include 1-octene, octane, 2-octenes, 1,7-octadiene and cyclooctane. Results were obtained by following the total concentration of the products relative to that of an added internal standard (chlorobenzene).

The rate constants of decomposition were calculated according to Eq. 3-1.

$$\ln[a_0/(a_0 - x)] = kt \qquad \text{(Eq. 3-1)}$$

Where, a_0 = [Pt compound]$_0$, x = [total hydrocarbon products]$_t$

The examination of rate constants for the thermal decomposition of complexes **3-1** and **3-2** was carried out at different conditions and different concentrations in cyclohexane. The results obtained have been summarized in Table 3-1.

Table 3-1. Rate constants of the thermal decomposition of **3-2** and **3-2** in cyclohexane

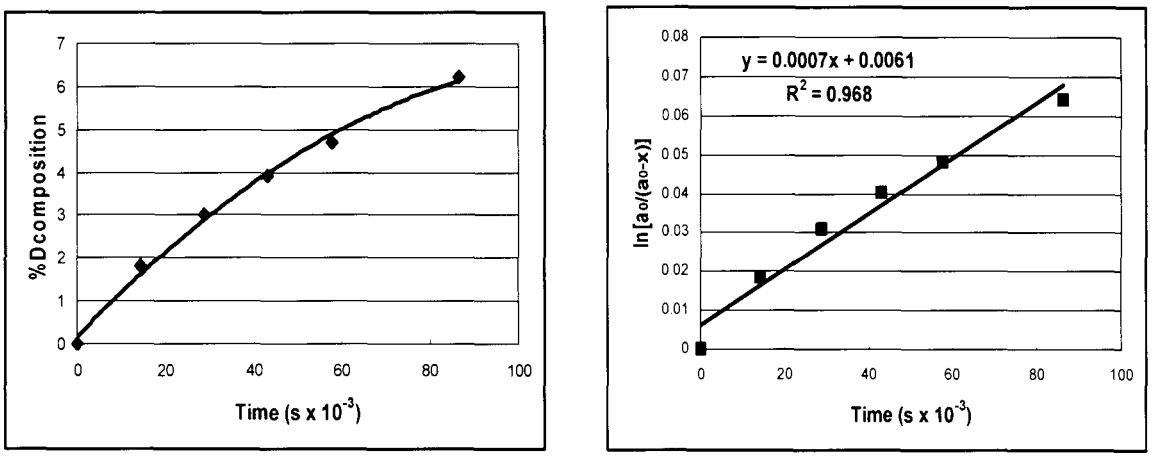
Compound	Concentration	Rate constant	
	(mM)	80°C (s^{-1})	170°C (k x 10^4 s^{-1})
3-1	23.2	7.00 x 10^{-7}	
3-1	23.2		0.471
3-1	2.32		0.485
3-2	5.74		2.01

Thermolysis of a 23.2mM sample of **3-1** at 80°C for 24 hours in cyclohexane gave the following results. The decomposition was found to be first order with a rate constant of 7.0 x 10^{-7} sec^{-1} during this period (Fig 3-2-a). The extent of decomposition‡ of **3-1** was, however, ca. 6% even after 24 hours (Fig 3-2-b), which indicates complex **3-1** is quite stable at 80°C. Compared with decomposition for 2 hours from which only 1-octene and octane was formed, after decomposition for 4 hours at 80°C, 2-octene was also found. This suggests that the formation of 2-octene might follow an isomerisation pathway, which was not only dependent on decomposition temperature but also on the heating time.

‡ % decomposition = $[\text{total hydrocarbon products}]_t$ / $[\text{Pt compound}]_0$ × 100%

= (total amount of hydrocarbon products) / (theoretical amount of hydrocarbon products) ×100%

(If 100% decomposition, the theoretical concentration of the total decomposition products = the initial concentration of Pt compound)

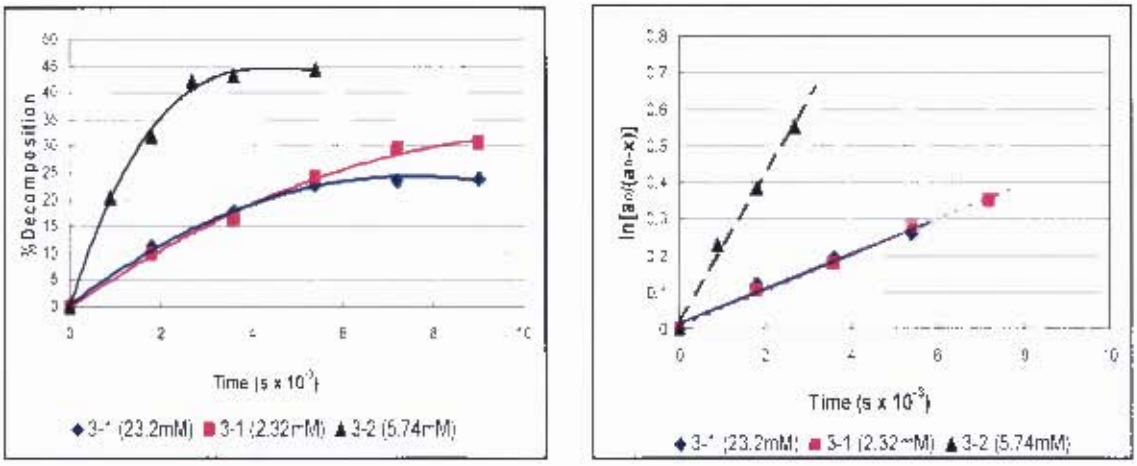


a b

Fig. 3-2. Representative speciation (**a**) and first order (**b**) plots for the thermal decomposition of **3-1** (23.2mM) at 80°C.

The rate of thermolysis of **3-1** at 170 °C was studied at two concentration levels, *i.e.* 23.2mM and 2.32mM in cyclohexane. The decomposition of **3-1** was first order only over approximately the first 30%[§] of decomposition for the low concentration sample, and over ca.20% for the higher concentration one (Fig. 3-3-a). In the kinetic studies, the decomposition only goes to 40% within the heating period. Rate constants in the linear region were independent of the initial concentration of the platinum complex (Fig. 3-3-b). The thermolysis of a 5.74mM sample of **3-2** in cyclohexane showed first-order kinetic behaviour over ca. 40% of the decomposition (Fig. 3-3-a). The observed rate constant for **3-2** was 4 times greater than that for **3-1** (Table 3-1), which again showed that the thermal stability of platinacyclononane with dppe ligand is lower than that with dppp ligand. The products formed from thermal decomposition of **3-1** at both concentration levels were found to be the same with similar distributions of organic products. Not surprising, the product formation and distribution obtained from decomposition of **3-2** was different. This could be due to the stability and the ancillary ligand.

[§] The extent of decomposition.



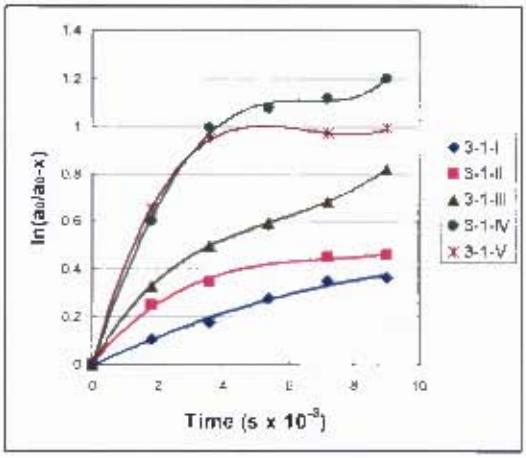
a **b**

Fig. 3-3. Representative speciation[‡] (**a**) and first order (**b**) plots for the thermal decomposition of **3-1** (23.2mM ♦ & 2.32mM ■) and **3-2** (5.74mM ▲) at 170°C.

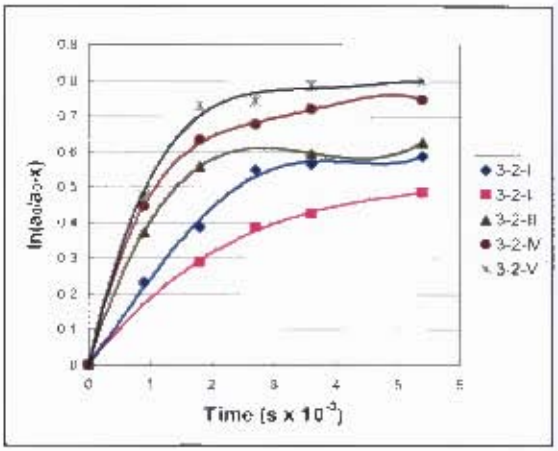
*B. Kinetics of thermal decomposition of **3-1** and **3-2** with added ligands*

The rates of thermal decomposition of platinacyclononanes $L_2Pt(CH_2)_8$ (**3-1**, L_2 = dppp; **3-2**, L_2 = dppe) in cyclohexane with added ligand were examined by GC following the appearance of the total hydrocarbon products from decomposition. By using the same phosphine as that already present in the complexes to be the additional ligand avoids complications of ligand exchange.

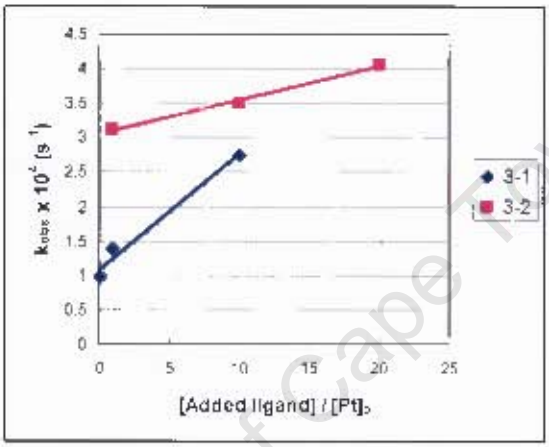
The decomposition of **3-1** in the presence of added bis(diphenylphosphino)propane (dppp) ligand was carried out on a 2.32mM sample solution in cyclohexane and the concentrations of added dppp in cyclohexane was varied from 0.224mM to 44.8mM, *i.e.*, the ratios of added dppp to **3-1** were from 0.1 to 20. The kinetic behaviour in all cases was first order only over approximately the first 30% of decomposition (Fig. 3-4-a). Rate constants in this region (see experimental section **5.3.3-B**) were dependent on the concentration of added dppp and the linear region increased when the concentration of dppp increased from 0.224mM to 22.4mM (Fig. 3-4-c).



a



b



c

Fig. 3-4.

a: The rate of thermal decomposition of **3-1** depends on the concentration of dppp in solution at 170°C. Data are for runs in cyclohexane, having $[\mathbf{3\text{-}1}]_0$ = 2.32mM and these values for [dppp] (mM): 3-1-I, 0.0; 3-1-II, 0.224; 3-1-III, 2.24; 3-1-IV, 22.4; 3-1-V, 44.8.

b: The rate of thermal decomposition of **3-2** depends on the concentration of dppp in solution at 170°C. Data are for runs in cyclohexane, having $[\mathbf{3\text{-}2}]_0$ = 5.74mM and these values for [dppp] (mM): 3-2-I, 0.0; 3-2-II, 0.594; 3-2-III, 5.94; 3-2-IV, 59.4; 3-2-V, 118.8.

c: Observed rate constants (k_{obs}) for the thermal decomposition of **3-1** (♦) and **3-2** (■) as a function of the ratio of added ligand to Pt complex. These curves are derived from the data of **a** and **b**.

The influence of added dppp ligand on the rate constant for decomposition of **3-1** is linear from 0.224 to 22.4mM, *i.e.*, the ratio of added ligand to **3-1** is from 0.1 to 10. The overall rate in this region can be expressed by a two-term rate expression (Eq. 3-2):[9]

$$-\frac{d[3-1]}{dt} = (k_a + k_b[dppp])[3-1] \qquad \text{(Eq. 3-2)}$$

Where k_a = 4.85x10^{-5} s^{-1} and k_b = 1.69x10^{-5} s^{-1} at 170°C, [dppp] (mM): (0.224, 22.4).

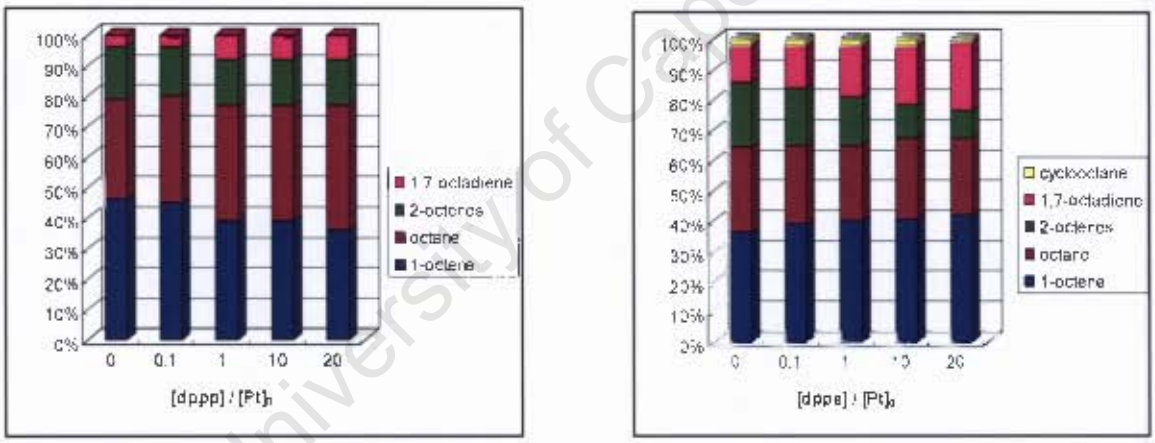
The thermal decomposition of **3-2** with added bis(diphenylphosphino)ethane (dppe) was studied in the same way, and showed the same general kinetic features (Fig. 3-4-b). The decomposition of **3-2** was first order only over ca. the first 30% except run 3-2-I (without added ligand). It was noticed that the decomposition was inhibited when the concentration of added dppe was lower than that of **3-2** (*e.g.* [dppe] = 0.594mM, *i.e.* [dppe]/[pt]$_0$ = 0.1). However when the concentration of dppe increased from 5.94 to 118.8mM, *i.e.*, [dppe]/[pt]$_0$ from 1 to 20, the rate increased in a not entirely reproducible manner. This is in contrast to the behaviour of **3-1** under similar conditions when the extent of decomposition passed *ca.* 30% (rate constants see experimental section **5.3.3.-B**). Added dppe ligand also accelerated the reaction; the overall rate in the linear region can be expressed by the similar rate expression as Eq.3-2.

$$-\frac{d[3-2]}{dt} = (k_c + k_d[dppe])[3-2] \qquad \text{(Eq.3-3)}$$

Where k_c = 2.01x10^{-4} s^{-1} and k_d = 4.96x10^{-6} s^{-1} at 170°C, [dppe] (mM): (5.94, 118.8).

The hydrocarbon products formed from the decomposition of **3-1** and **3-2** are shown in Fig.3-5. An experimentally significant shift in product composition accompanies an increase in added ligand concentration: the C_8-derived products consist of a mixture of 1-octene, octane, 2-octenes and 1,7-octandiene for the

decomposition of **3-1**, while a mixture of the products as well as cyclohexane were obtained for the thermolysis of **3-2**. However, the product distributions are not the same during the course of decomposition for each complex. For the decomposition of **3-1**, the percentage of 1-octene decreased with the increase of the concentration of added dppp, whilst, the percentage of octane increased clearly (Fig. 3-5-a). In contrast, the decomposition of **3-2** with added dppe showed a different trend, the percentage of 1-octene increased slightly while the percentage of octane remained constant (Fig. 3-5-b). This difference might be caused by the effects of the different ligands present in the complexes and the property of the additional ligand involved in the thermolysis. The different thermal stability of the complexes could also be a possible reason for the different product distributions obtained on decomposition.



a **b**

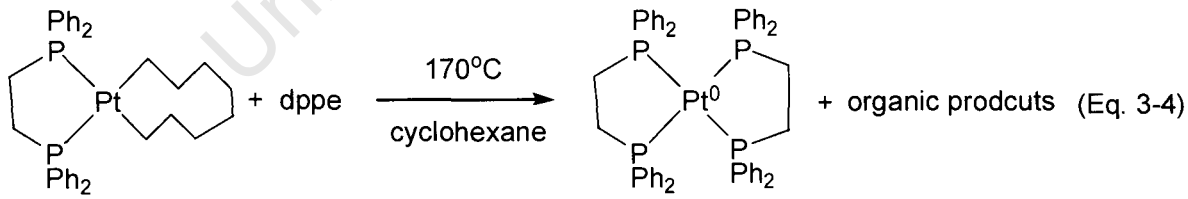
Fig. 3-5. Product composition (%†) for the thermal decomposition of **3-1** (**a**) and **3-2** (**b**) as a function of the concentration of added ligand. Errors in product determination are ±3% for 1-octene, +2% for octane and 1,7-octandiene, ±1% for 2-octenes and cyclooctane.

The added phosphine ligands influence the formation not only of the major products (1-octene & octane), but also on the minor products (2-octenes & 1,7-octadiene), particularly for the decomposition of **3-2**. As shown in Fig. 3-5-b,

when the ratio of added dppe to **3-2** varied from 0 to 20, suppressing of the formation of 2-octenes was observed along with an acceleration of the formation of 1,7-octadiene

The same phenomenon was observed in the thermal decomposition of bis(phosphine)platinum(II) metallacyclopentanes.[9] The authors suggested that it could be useful to carry out deuterium labelling studies to understand the mechanisms for the product composition shift. Unfortunately, these investigations were not able to be done in the current study.

The decomposition of **3-2** with added dppe ligand in cyclohexane gave a clear golden yellow solution. The organic products from the reaction of **3-2** with one equivalent of dppp at 170°C are shown in Fig. 3-5-a and the metal-containing product was identified as $[Pt^0(dppe)_2]$ (Eq. 3-4) by ^1H and ^{31}P NMR. The major singlet at δ 4.49 in ^{31}P NMR spectrum shifted to δ 32.35 after 2 hours, and agreed with the literature report; no sign of Pt-H bonds or hydridic hydrogen were observed.[12] In addition, the similar metal-containing product was obtained from the reaction of dppe and $[PtPh_2(dppe)]$ (Eq. 3-5),[13] as well as the reaction of dppe and $(dppe)Pd(CH_2)_4$ (Eq. 3-6).[14]



3-2

$$[PtPh_2(dppe)] + dppe \xrightarrow{217^\circ C} [Pt(dppe)_2] + Ph_2 \quad \text{(Eq. 3-5)}$$

$$(dppe)Pd(CH_2)_4 + dppe \longrightarrow (dppe)_2Pd + n\text{-}C_4H_8 \quad \text{(Eq. 3-6)}$$

In contrast, an intense red residue was formed when complex **3-1** decomposed without added dppp, which was insoluble in cyclohexane and we believe to be due to $Pt_n(L)_m$ clusters.[15]

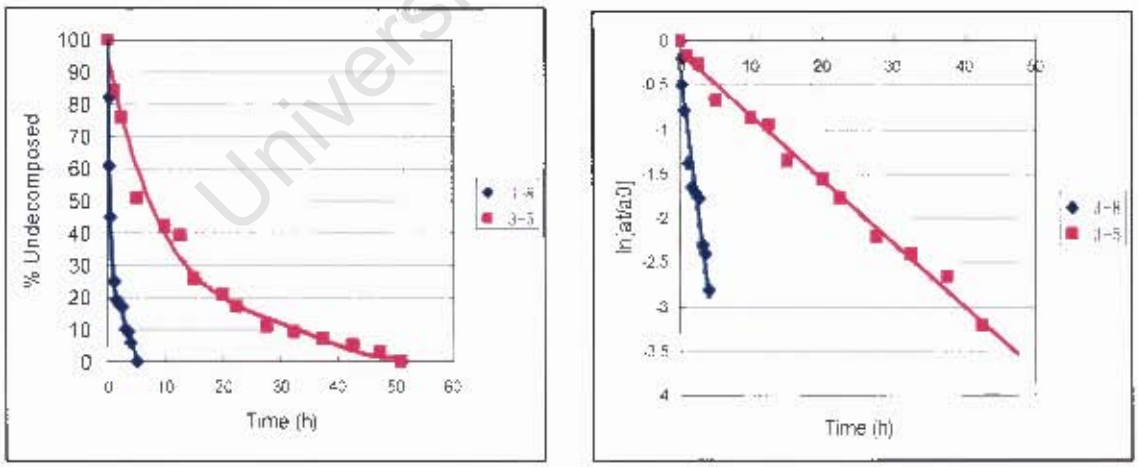
*C. Kinetics of thermal decomposition of **3-5** and **3-8***

Kinetic studies were carried out on the thermal decomposition of the complexes of the type (dppp)$Pt(CH_2)_n$ (**3-5**, n = 7; **3-8**, n = 10) in order to examine the effects of different ring sizes on the thermal stability of platinacycloalkanes. The rates of decomposition of **3-5** and **3-8** in tolouene-d_8 at 90°C were determined by following the disappearance ^{31}P peak of the starting platinacycloalkanes by $^{31}P\{^1H\}$ NMR spectroscopy.[16,17]

The rate constants of decomposition were calculated according to Eq. 3-7.

$$\ln[a_t/a_0] = -kt \qquad \text{(Eq. 3-7)}$$

Where, a_0 = [Pt compound]$_0$, a_t = [Pt compound]$_t$



a **b**

Fig. 3-6. Representative speciation** (**a**) and first order (**b**) plots for the thermal decomposition of **3-5** (■) and **3-8** (♦) in toluene-d_8 at 90°C.

** % undecomposed = ([Pt compound]$_t$ / [Pt compound]$_0$) × 100%

Thermal decomposition of **3-5** at 90°C was much slower than **3-8**. The decomposition of **3-8** completed after heating for 5 hours which was indicated by the totally disappearance of the starting material peak in ^{31}P NMR spectrum. However, the decomposition of **3-5** completed after 50 hours (see Fig. 3-6-a). Fig. 3-6-b shows plots of representative kinetic data obtained of **3-5** and **3-8**. Decomposition of both complexes followed first-order kinetics, the rate of decomposition of the eleven-membered ring **3-8** was greater than that of the eight-membered ring **3-5** ($k_{3\text{-}5}$ = 0.071 h^{-1}, $k_{3\text{-}8}$ = 0.63 h^{-1}).

Whitesides and co-workers have found that five- and six-membered platinacycloalkanes are markedly more stable than platinacycloheptane.[9] In this study, we found that the eight-membered platinacycloalkane **3-5** is significantly more stable than the larger and conformationally more mobile eleven-membered ring **3-8**.

3.2.1.3. Products of decomposition of platinacycloalkanes

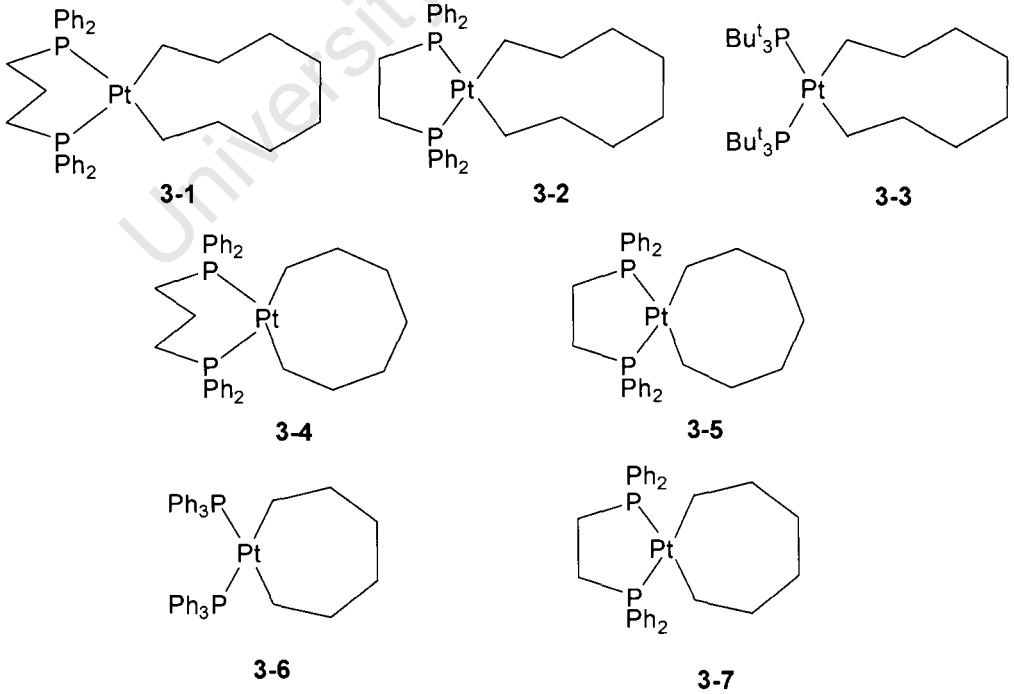


Chart 3-1. Platinacycloalkane complexes **3-1** – **3-7**.

The non-kinetic decomposition studies of platinacycloalkanes **3-1** – **3-7** (Chart 3-1) were carried out both in solvent and solvent free under the standard conditions. Heating a ca. 10mg solid sample or a 0.02M sample solution in cyclohexane or toluene at 170°C for two hours resulted in formation of a mixture of alkene and n-alkane products (see Table 3-2) accompanied by transformation of the solid, or solution, from its original pale yellow colour to an intense red colour.

Table 3-2. Products for the thermal decomposition of the platinacycloalkanes **3-1** – **3-7** at 170°C for 2 hours.

	Medium	Products observed (%)*				
		1-alkene	2-alkenes	1,n-diene	n-alkane	cycloalkane
3-1	Solid	49	21	4	26	
	Cyclohexane	46	17	4	33	
	CH_2Cl_2	27	21	4	44	4
3-2	Solid	41	21	13	23	2
	Cyclohexane	37	21	12	28	2
3-3	Solid	54	20	9	17	
	Cyclohexane	51	24	5	20	
	CH_2Cl_2	32	26	6	28	8
3-4	Solid	45	14	9	32	
	Toluene	43	22	<1	35	
3-5	Solid	50	20	2	28	
	Toluene	43	13	3	40	
3-6	solid	41	27	13	20	
3-7	solid	44	23	9	24	

* Products were analysed by GC and GC-MS.

Two methods for product extraction were used on the solvent free thermal decomposition of complex **3-1** in order to draw comparisons. The first method was

to collect the volatile products using trap-to-trap distillation. and the second one was addition of appropriate solvent to extract the products. The products obtained were found to be the same using either method, however, the relative amount of individual product that could be recovered by the former method was clearly less than the later one (Fig. 3-7).

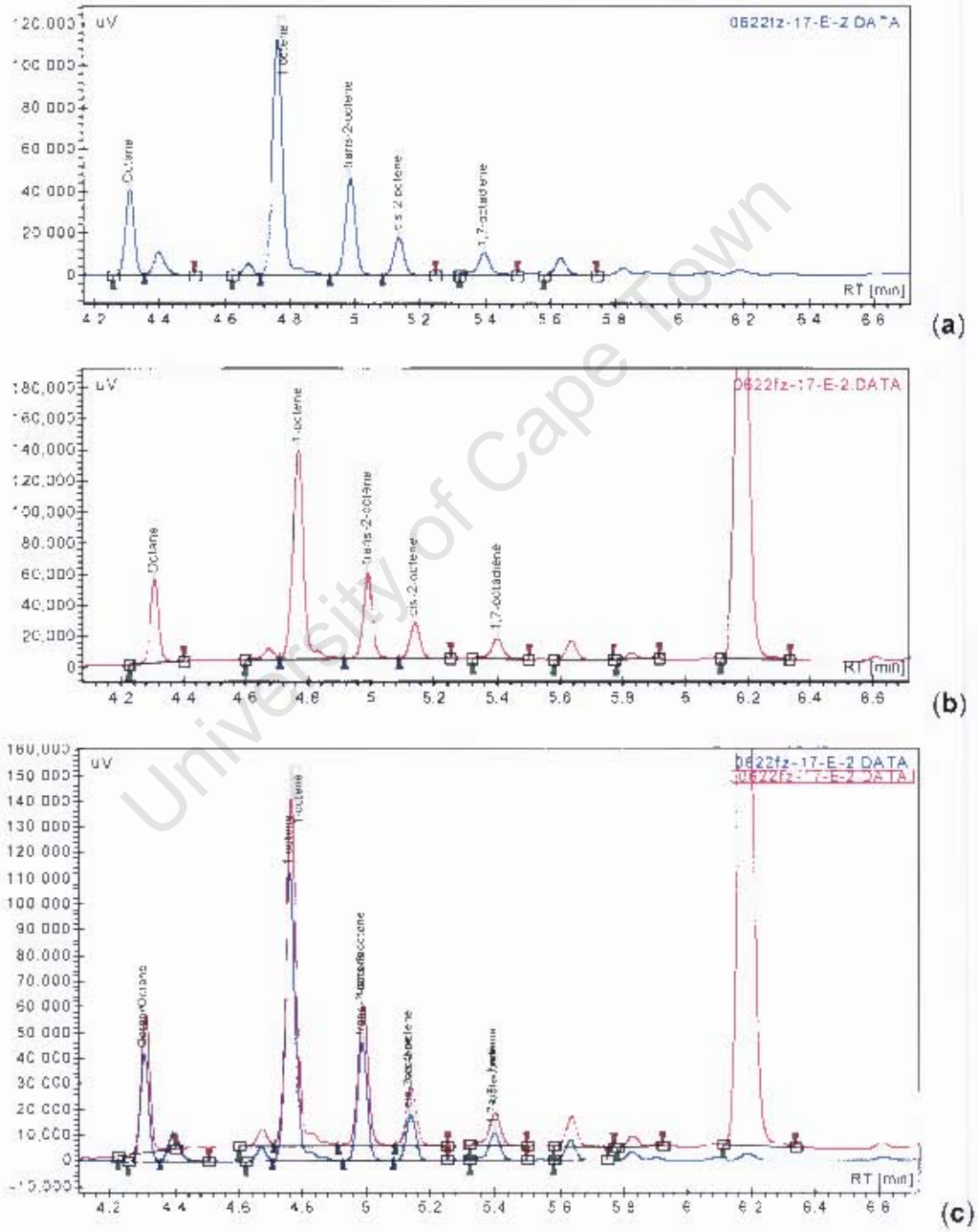


Fig. 3-7. Sample gas chromatogram for the volatile products formed from the

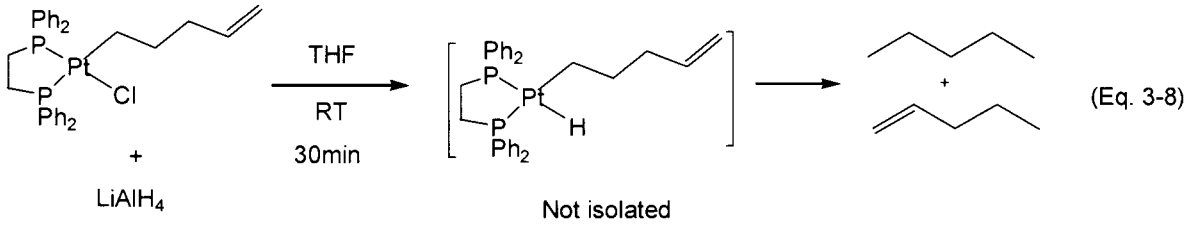
thermal decomposition of **3-1**.

a: products distilled by trap-to-trap distillation; **b**: products extracted by adding dichloromethane; **c**: the comparison of these two methods.

Besides this, it was practically difficult to handle a trap-to-trap distillation when the amount of metallacycle complex was small so that it could only result in trace volatile products. For the results reported here, we used the method of adding an appropriate solvent to extract the volatile products when the thermal decomposition was carried out under solvent free conditions.

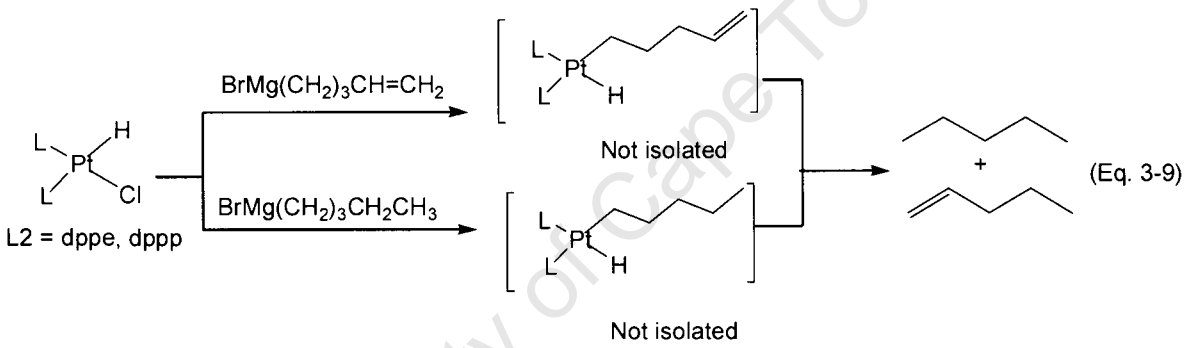
The results presented in Table 3-2 show that the overall decomposition patterns for the platinacycloalkanes are independent on the ring size. These complexes can decompose thermally in several ways to give a range of organic products, including 1-alkenes, 2-alkenes, n-alkanes and dienes (only complex **3-2** decomposed in dichloromethane gave cycloalkane)

The formation of 1-alkenes and 2-alkenes is known from the decomposition of metallacyclopentanes[18], -hexanes and –heptanes,[9] which was in agreement with our observations of the decomposition of these larger ring-size metallacycloalkanes. Assuming that the reaction pathway to form 1-alkene takes place via the β-hydride elimination, the hydridoalkenylplatinum(II) complex should be a key intermediate. Attempts here made to isolate this compound and we carried out a reaction of (dppe)PtCl(1-pentyl) with $LiAlH_4$ in THF at room temperature. The reaction was monitored by ^1H NMR, and no hydride signal could be observed. The solution was then injected into GC, n-pentane (24%) and 1-pentene (76%) were identified (Eq 3-8).



(Eq. 3-8)

Sivaramakrisha also tried to isolate the hydridoalkenylplatinum(II) complex by reacting a chloride hydridoplatinum(II) complex with Grignard reagent at -78°C. However, no hydride signal was obtained from ^{1}H NMR after reaction. The products formed were 1-alkene and n-alkane which were analyzed by GC (Eq. 3-9).[19]

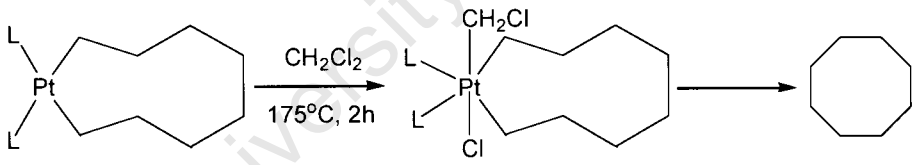


(Eq. 3-9)

Due to the absence of any direct evidence, it is suggested that formation of the alkenyl hydride intermediate might take place rapidly and perhaps reversibly, or the formation of 1-alkene may not involve such an intermediate. An alternative pathway might be via a concerted metal-assisted hydride transfer route.[20] The formation of 2-alkenes could probably be caused by the occurrence of isomerization either during or after decomposition. In addition, the corresponding n-alkane was also obtained as one of the major products (>20%) in all cases.

The thermolysis products of **3-1** – **3-5** obtained in solvent and solvent free conditions were compared to determine the influence of solvent on the decomposition pathways. The product formation patterns were similar although the relative yields of the products were different in the different decomposition media.

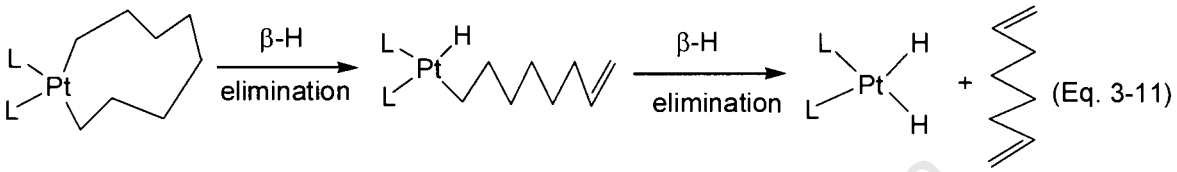
The decomposition of **3-1** and **3-3** were carried out in three media, *i.e.* solvent free, in cyclohexane and in dichloromethane. Under both solvent free condition and in non-halogenated solvent, only linear C_8 products were formed. In contrast, small amounts of cyclooctane were also obtained when decomposition of these two complexes was carried out in dichloromethane. In a solvent capable of oxidative addition, like dichloromethane, formation of cyclobutane and C_5 materials from the decomposition of platinacyclopentanes was reported by Whitesides and co-workers.[11] We propose that cyclooctane could be formed in the same way as reported for the formation of cyclobutane.[11] Platinum(IV) intermediates were produced by oxidative addition of dichloromethane to platinum(II) metallacycles, which then generated cyclooctane by reductive elimination (Eq. 3-10). The products with one more carbon than the metallacyclic group were not observed in this study. In addition, it was observed that the decomposition residue in dichloromethane for complex **3-1** formed white needle crystals with a melting point at 155 – 160°C. This residue was identified by ^{1}H and ^{31}P NMR, as the starting material dichloride platinum(II), L_2PtCl_2.



(Eq. 3-10)

A trend of increasing formation of n-alkane was observed when complexes **3-1** and **3-3** decomposed in different media: solvent free < in solvent (cyclohexane < dichloromethane). The same phenomenon was found from the decomposition of complexes **3-2**, **3-4** and **3-5**, whereas the relative yield of n-alkane is slightly under solvent free conditions than in solvent. The chosen solvents were cyclohexane, dichloromethane and toluene, which can donate hydrogen to effect the formation of n-alkane. In addition, the specific hydrogen-atom donor ability of dichloromethane is slightly stronger than cyclohexane, which could be the reason why decomposition in dichloromethane formed more n-alkane.

Nevertheless, n-alkane formed under solve free conditions indicates the hydrogen-atom responsible for producing the saturated alkane is not only from the solvent but also from other sources. The most likely sources are considered to involve two components: 1) platinum hydride species produced by releasing diene from platinacycles (Eq. 3-11)[17], and 2) hydrogen transferred from coordinated ligand, e.g. *ortho* activation of the phenyl group of PPh_2.[21]



(Eq. 3-11)

The thermal decomposition of platinacycloheptanes **3-6** and 3-**7** was firstly reported by Whitesides and co-workers: decomposition of platinacycloheptanes in dichloromethane at 60°C afforded 1-alkene and 2-alkenes only.[9] In contrast, many more products formed when these complexes decomposed at higher temperature (170°C) in this study. Higher thermolysis temperature is required for the stable platinacycle complexes, especially for those with chelating ligands, might make available additional reaction pathways.

3.2.2. Thermal decomposition of metallacycloalkanes with other metal centres

The metallacycloalkanes with other metal centres are either thermally or air unstable, therefore the thermolysis of these complexes was studied in less detail than that of platinacycloalkanes. Some showed the same general decomposition patterns, while others showed quite different trends involving new decomposition pathways. We believe such difference might be caused by the effect of different metal centres on the thermal decomposition.

3.2.2.1. Thermal decomposition of palladacycloalkanes

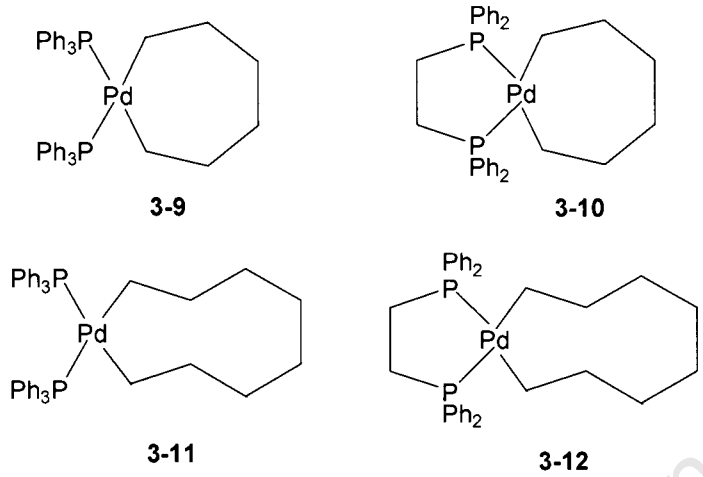


Chart 3-2. Palladacycloalkane complexes **3-9** – **3-12**.

The preparation of the palladacycloalkane complexes **3-9** – **3-12** (Chart 3-2) has been described in **Chapter 2**. Thermal decomposition studies were carried out directly on freshly prepared complexes without any solvent.

Table 3-3. Products for the solvent free thermal decomposition of the palladacycloalkanes **3-9** – **3-12** at 170°C for 2 hours.

Complex	Products observed (%)				
	1-alkene	2-alkenes	1,n-diene	n-alkane	cycloalkane
3-9	43	17	6	18	16
3-10	52	24	11	6	7
3-11	33	32	17	15	3
3-12	17	71	2	10	<1

The thermal decomposition of palladacycloalkanes at 170°C under solvent free conditions gave alkenes, n-alkane, diene and cycloalkane (Table 3-3) accompanied by the formation of a black residue. The decomposition patterns of palladacycloalkanes show more reductive elimination to give cycloalkane than

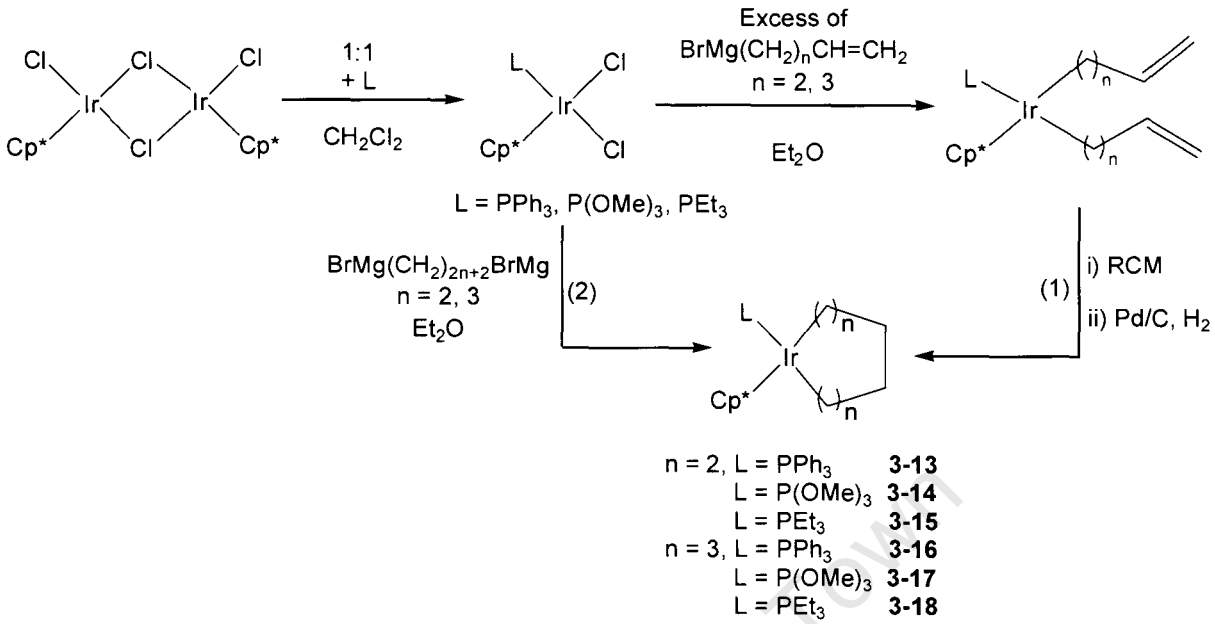
those of their platinum(II) analogues.

1-alkene and 2-alkenes are the major products in all cases whereas 1-alkene predominates except for complex **3-12**. The formation of 1-alkene might go through the β-hydride transfer and the occurrence of isomerization gives 2-alkenes. Palladium mirror was seen to form as a black mirror for some palladacyclopentanes, which could perhaps catalyze the isomerization of 1-alkene to 2-alkenes.[14] Furthermore, in our group, $Ru_3(CO)_{12}$ has been found to efficiently isomerizes 1-alkene, possibly via the $16e^-$ species $Ru(CO)_4$.[22] These also could be the reasonable ways for the formation of 2-alkenes in the current study.

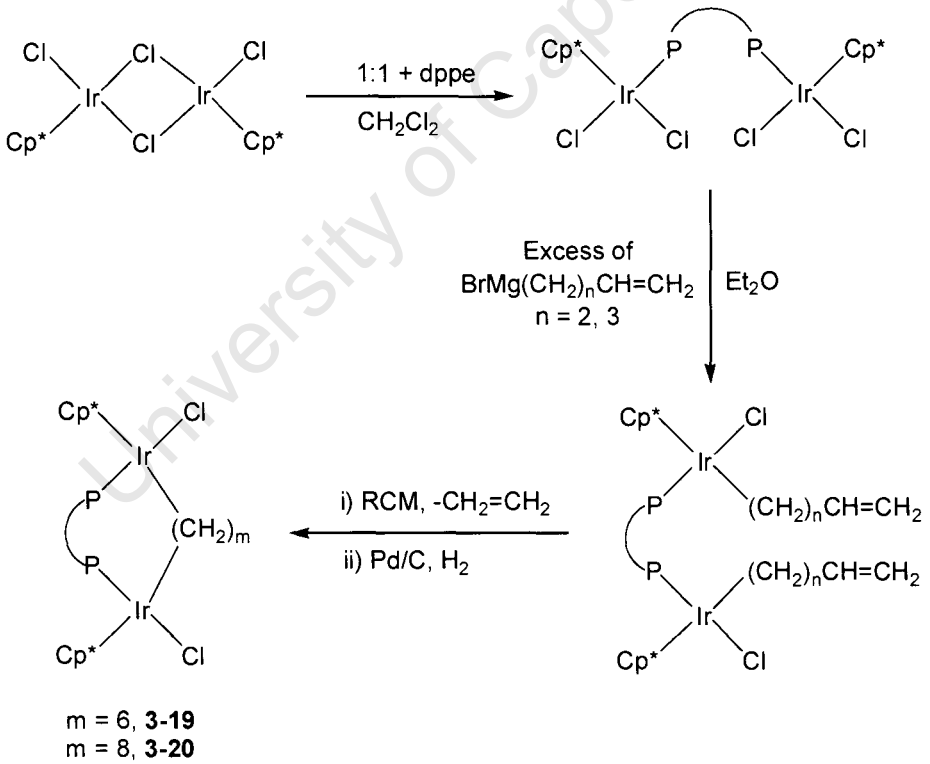
For complex **3-12**, the degree of isomersization of the organic fragment to 2-alkenes is much larger than that for the other complexes. There might be two factors that influence the decomposition pathway. One is the effect of ring size. It appears that the conformationally flexible larger size rings have lower thermal stability,[9,23] which could make the decomposition via β-hydride elimination/isomerization easier for the nine-membered ring than that for the smaller ring complexes. Another factor is the effect of the ancillary ligand. Compared to their analogues, the complexes with the chelating ligand dppe formed higher yield of 2-alkenes (24% for **3-10** and 71% for **3-12**).

The observation of cycloalkanes as the minor decomposition products is consistent with the palladacyclopentan system.[14] It was suggested that the production of cycloalkane via reductive elimination is favored only when the ancillary ligand dissociates easily. For instance, complexes **3-9** (16%) and **3-11** (3%) gave higher yield than their analogues with dppe ligand. In addition, n-alkane was also found as the minor product, which could formed by intermolecular reactions involving a hydridopalladium(II) species[24], or intramolecular hydrogen abstraction from the ancillary ligand.[21(b)]

3.2.2.2. Thermal decomposition of iridacycloalkanes



a



b

Scheme 3-2. Preparation of iridacycloalkanes.

The preparation of iridacycloalkanes, outlined in scheme 3-2, can either go

through the ring closing metathesis (RCM) using Grubbs' 1st generation catalyst from their bis(1-alkeny)iridium precursors or the well-known di-Grignard route. Some dppe bridging ligand containing dimeric iridium metallacycles were also synthesized via the RCM reaction. The iridacycloalkane derivates were isolated as yellow oily products.[25]

The thermal decomposition of iridacycloalkanes **3-13** – **3-18** without solvent under standard conditions (170°C, 2 hr) gave organic products and a brown to black residue. Compared to the thermolysis of group 10 metallacycloalkanes, these complexes decomposed to produce predominately 2-alkenes. This was consistent the results obtained for the decomposition of smaller ring size iridium(III) metallacycles in solid phase by DSC and TGA technique reported by Diversi et al.[26] Additional hydrocarbon products included varying amounts of 1-alkene, diene, n-alkane and cycloalkane (see Table 3-4).

Table 3-4. Products for the solvent free thermal decomposition of the iridacycloalkanes **3-13** – **3-20** at 170°C for 2 hours.

Complex	Products observed (%)				
	1-alkene	2-alkenes	1,n-diene	n-alkane	cycloalkane
3-13	21	62		17	
3-14	2	55	4	34	5
3-15	19	33	3	42	3
3-16	29	41	9	21	
3-17	30	47		23	
3-18	34	44		22	
3-19[a]	42	8	11	18	20
3-20[a]	60	15	13	12	

[a] Decomposed at 210°C for 32 hours.

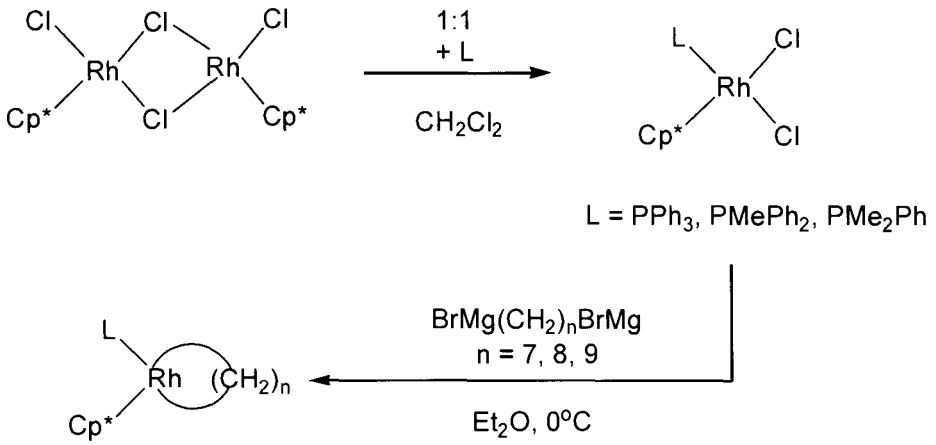
As shown in Table 3-4, there is a clear decreasing trend of the formation of 2-alkenes with the increase of electron-donating ability of the ligands coordinated to the iridocyclohexanes **3-13** – **3-15**, *i.e.*, (PPh_3 < $P(OMe)_3$ < PEt_3), which could probably effect the regioselectivity of hydrogen migration for the production of 2-alkanes. The thermal stability of these complexes might be another reason for the decreasing amounts of 2-alkenes. Due to the influence of the nature of ligands, the stability of complexes **3-13** – **3-15** can be seen in the following order: PPh_3 < $P(OMe)_3$ < PEt_3.[25] On the other hand, n-alkane was found to form in the opposite way: the relative yield of n-alkane increased while 2-alkenes decreased.

The same trend, however, was not found in the iridacyclooctane systems. The distribution of the products did not change much for the decomposition of complexes **3-16** – **3-18** and the formation of 2-alkene was consistently found to be the major pathway. The different decomposition trends between iridocyclohexanes and iridacyclooctanes might be caused by the effect of the ring size.

The solvent free thermolysis of the dimeric iridium metallacycles **3-19** and **3-20** was carried out at 210°C for 32 hours due to their being remarkably thermal stable. In contrast, the decomposition of these complexes gave a deep yellow residue instead of the brown to black colour, and 1-alkene was obtained as the major product. Dienes and cycloalkane was also found to be the minor products.

3.2.2.3. Thermal decomposition of rhodacycloalkanes

Rhodacycloalkane complexes **3-21** – **3-25** were prepared in the conventional di-Grignard route. The reaction between Cp^*RhCl_2L (L = PPh_3, $PMePh_2$, PMe_2Ph) and the alkylating reagents, $BrMg(CH_2)_nMgBr$ (n = 7, 8, 9), in diethyl ether at 0°C gives the rhodacyloalkane derivatives as yellow-orange oils.[27]



n = 7, L = PPh_3 **3-21**
L = $PMePh_2$ **3-22**
L = PMe_2Ph **3-23**
n = 8, L = PPh_3 **3-24**
n = 9, L = PPh_3 **3-25**

Scheme 3-3. Preparation of rhodacycloalkanes.

The solvent free thermal decomposition of rhodacycloalkanes under standard conditions gave various organic products shown in Table 3-5 as well as intense red decomposition residues.

Table 3-5. Products for the solvent free thermal decomposition of the rhodacycloalkanes **3-21** – **3-25** at 170°C for 2 hours

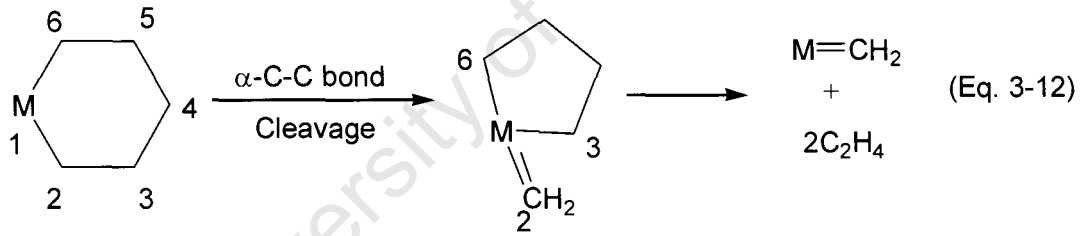
Complex	Products observed (%)				
	1-alkene	2-alkenes	1,n-diene	n-alkane	cycloalkane[b]
3-21	20			19	61
3-22	26	24	2	48	
3-23	27	24	1	48	
3-24	30	24	21	19	6
3-25	71	23			6
3-25[a]	60	26			14

[a] decomposed in cyclohexane, [b] cycloalkane with (n-1) carbon

For the rhodacycloalkanes with the monodentate PPh_3 ligand, a new

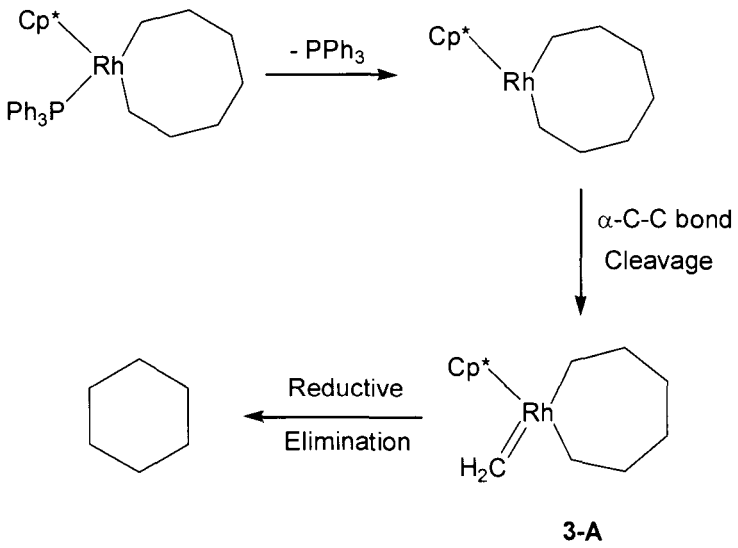
decomposition pathway appears to be responsible for the formation of organic fragments. Cyclohexane was formed as major decomposition products of rhodacyclooctane **3-21**, while cycloheptane and cyclooctane was obtained as minor product of the decomposition of rhodacyclononane **3-22** and rhodacyclodecane **3-23** (in both solid phase and cyclohexane) respectively. It seems that the new pathway happened more easily for the smaller ring size complex **3-21**, which could probably be due to the effect of ring size.

Grubbs and Miyashita[28] reported a α-C-C bond cleavage reaction pathway in the study on the decomposition of nickelacyclohexanes and titanacyclohexanes (Eq. 3-12), which was also proposed by Jacobson and Freiser[29] from the decomposition of gas-phase metallacyclhexane and metallacycloheptane. This is presumably because the smaller five-membered ring complex formed is more stable.



(Eq. 3-12)

Although there have not been many reports on α-C-C bond cleavage, it could be nicely explained assuming that the occurrence of a phosphine ligand dissociation give the vacant site (*e.g.* for rhdocyclooctane **3-21**), the intermediate (**3-A**) could be generated by the α-C-C bond cleavage, which could easily form cyclohexane by reductive elimination (Scheme 3-4).



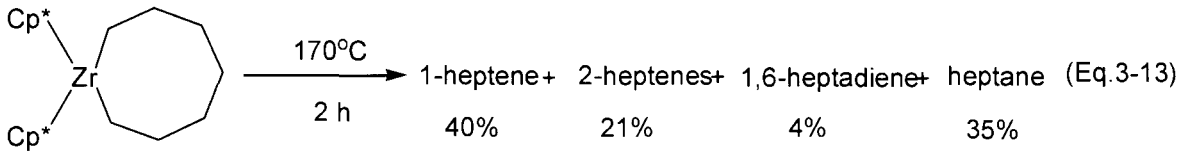
3-A

Scheme 3-4. Proposed mechanism for the formation of cyclohexane from the decomposition of rhodacyclooctane **3-21**

In contrast, the α-C-C bond cleavage reaction pathway was not observed in the rhodacyclooctanes with $PMePh_2$ and PMe_2Ph ligand, **3-22** and **3-23**, which decomposed in the general patterns to form 1- and 2-alkenes, diene, n-alkane. The formation of n-alkane as major product is perhaps due to the ancillary ligands which could be the source of hydrogen-atom.

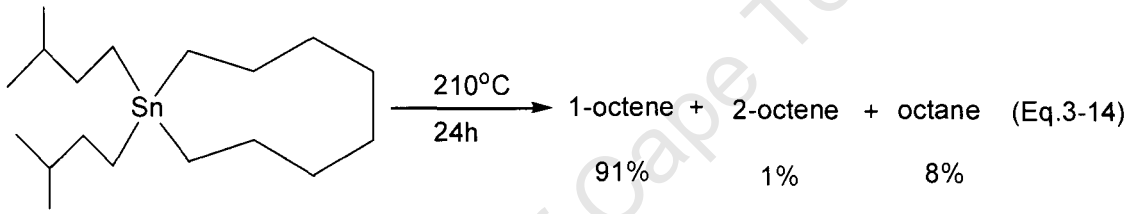
3.2.2.4. Thermal decomposition of other metallacycloalkanes

The thermal decomposition studies were mainly concerned with group 9 and 10 metallacycloalkanes, with a little work was carried out on the thermal decomposition of other group metallacycles. One example is the thermolysis of a group 4 complex, zirconacyclooctane **3-26**,[30] affording 1-heptene 2-heptenes, heptane and very small amount of 1,6-heptadiene (Eq. 3-13). There were not any differences in decomposition patterns between **3-26** and the group 9 and 10 metallacycloalkanes.



3-26

Another example that we investigated is the main group metallacyclooctane **3-27**,[30] which is much more thermally stable than the transition-metal contained metallacycles. The decomposition of **3-27** at 210°C for 24 hours produced 1-octene in very high selectivity (91%), and minor products including 2-octene and octane (Eq. 3-14). Similar decomposition pathways as that for transition metal ring complexes could be responsible for the formation of the organic products.



3-27

3.3. Discussion

We have previously reported a survey on the thermal studies of metallacycloalkanes restricted to small and medium ring compounds, in which the maximum size is a seven-membered ring. The decomposition pathways and general factors affecting thermal stability of those compounds have been pointed out.[5] We now account for the current results of the thermal decomposition of the medium to lager ring size metallacycloalkanes based on this information.

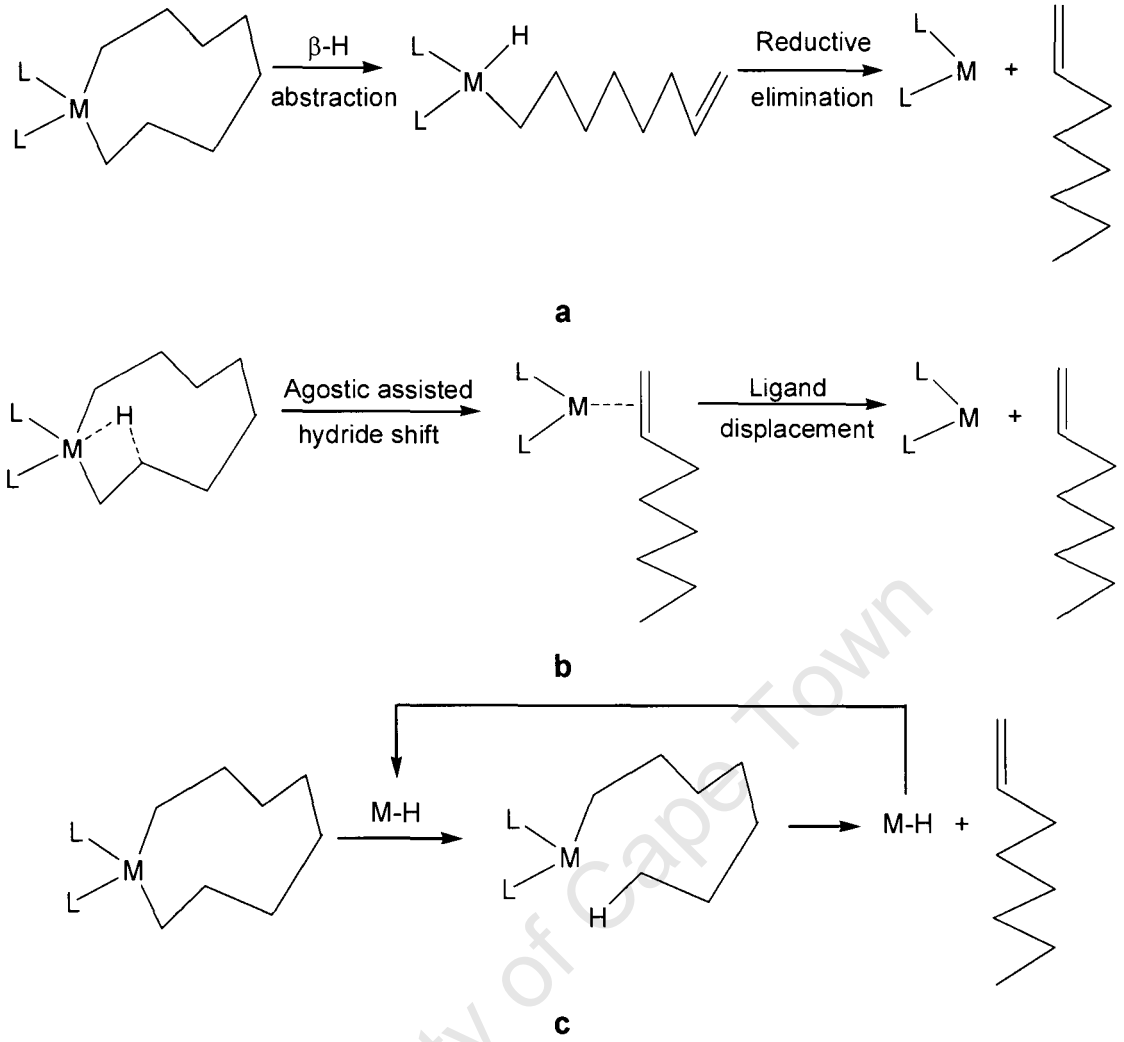
3.3.1. The mechanisms of the thermal decomposition of metallacycloalkanes

Since metallacycloalkanes have two metal-carbon single bonds, it is first necessary to consider the decomposition pathways of transition-metal alkyl

complexes which have been discussed frequently,[21(b),31] α- and β-hydride elimination, ligand-hydrogen abstraction, reductive elimination and homolytic M-C bond cleavage have been observed. Due to the relationship of stereochemistry, structure, bonding and thermal stability between these two classes of complexes, the decomposition pathways of metallacycloalkanes documented so far are not only relative to those of alkyl complexes but also involve the new modes.[5] We try to draw a detailed mechanism based on these decomposition pathways to interpret the formation of various products mentioned above. Some of the discussion on the mechanism that follows is based on the literature, and the rest is a consequence of our recent studies.

3.3.1.1. The formation of 1-alkene

The best documented reaction pathway to produce 1-alkene is via β-hydride elimination from metal-alkyl complexes. This could also be the possible decomposition mechanism for the formation of 1-alkene from metallacycloalkanes with flexible medium to lager ring size, even though this pathway is reported to be hindered in the small metallacycloalkanes. β-hydride elimination is formally meant as β-hydride abstraction by the metal, followed by reductive elimination of the resultant alkenyl hydride species (Scheme 3-5-a).[32] The alternative mechanism for generation of 1-alkene is via concerted metal-assisted hydride transfer from C_2 to C_n of the metallacycloalkane which was supported by the calculations for Ti and Cr trimerisation systems (Scheme 3-5-b).[20] Nowadays, these two mechanisms are called as "β-hydride transfer" due to the difficult to distinguish them in various metallacycle systems. Furthermore, Miller and Whitesides[17] demonstrated an intermolecular chain reaction pathway for the formation of 1-alkene, in which a hydridoplatinum intermediate was involved (Scheme 3-5-c).

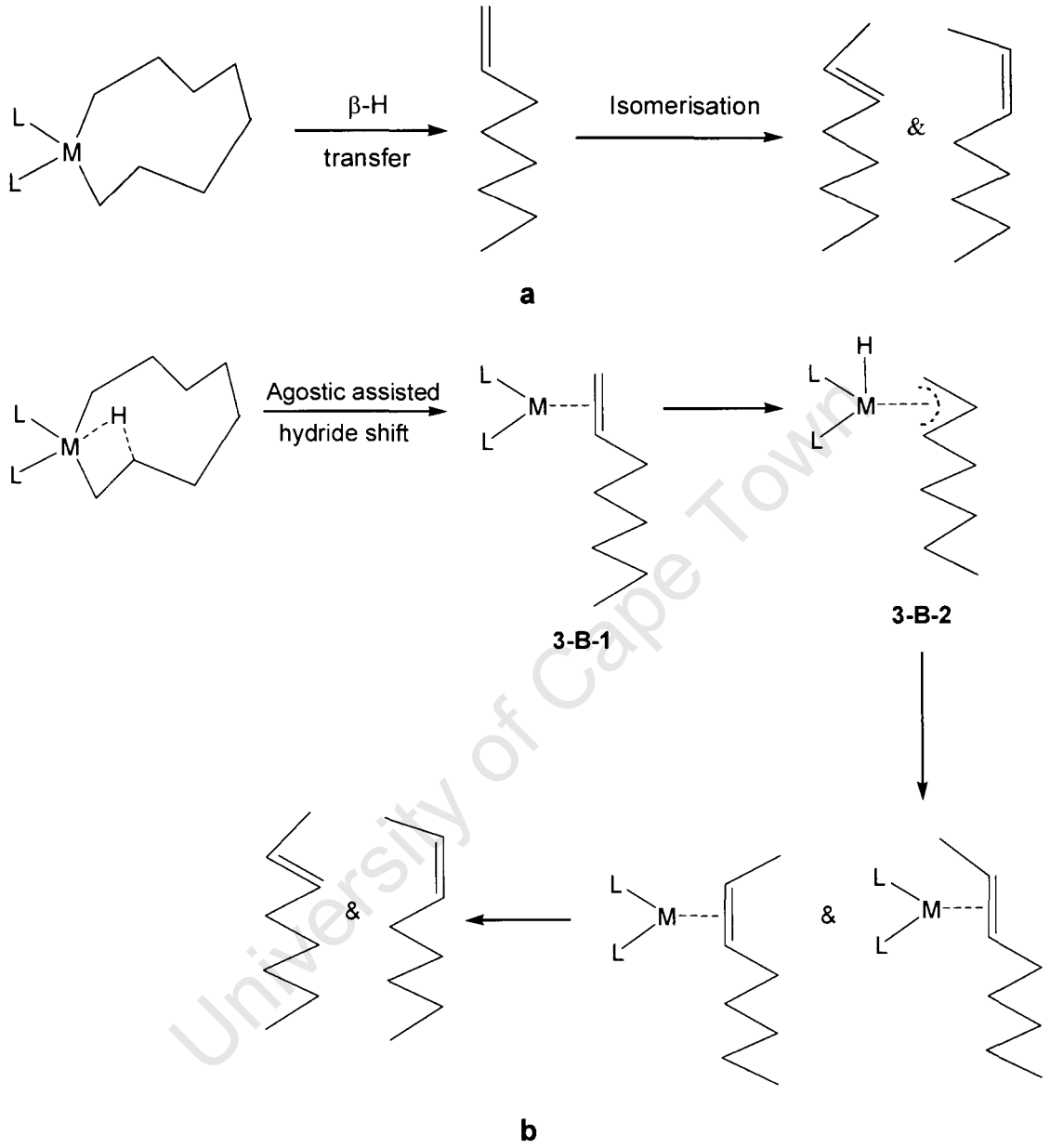


Scheme 3-5. The possible mechanisms of the formation of 1-alkene from metallacyclononane.

3.3.1.2. The formation of 2-alkenes

While a reaction pathway such as that shown in scheme 3-5 accounts well for the formation of 1-alkenes, R-CH=CH_2, some authors pointed out that the appearance of an internal alkene, R-CH=CH-R', could result from the isomerisation of the initially formed 1-alkene (Scheme 3-6–a).[33] And some reported that it could be presumably explained by a metal hydride-catalyzed intramolecular isomerisation before the olefin is released into solution.[9] The proposed mechanism is outlined in Scheme 3-6-b according to the literature[22],[34]: Agnostic assisted hydride shift of the metallacycloalkane could form the intermediate species **3-B-1**. Hydrogen migration

from C_3 of **3-B-1** to metal centre could rise for the η^3-allyl metal hydride intermediate **3-B-2** which could then decompose to give *cis*- and *trans*-2-alkene.

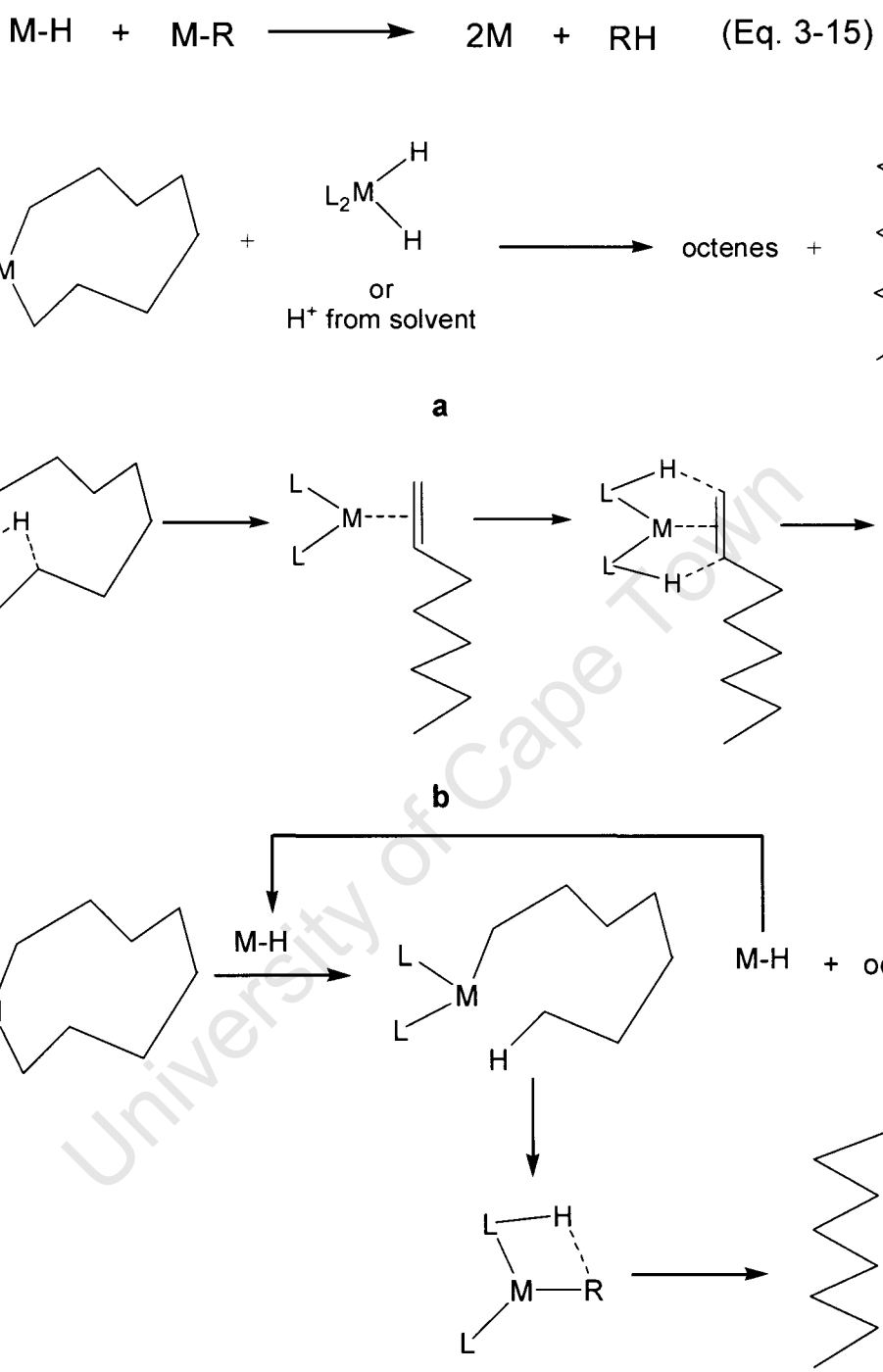


Scheme 3-6. The possible mechanisms of the formation of 2-alkenes from metallacyclononane.

3.3.1.3. The formation of n-alkane

For the thermal decomposition of metal-alkyl complexes, one suggests that with only a single alkyl ligand, alkanes should not form unless an intermolecular

reaction (Eq. 3-15) occurs.[21(b)]

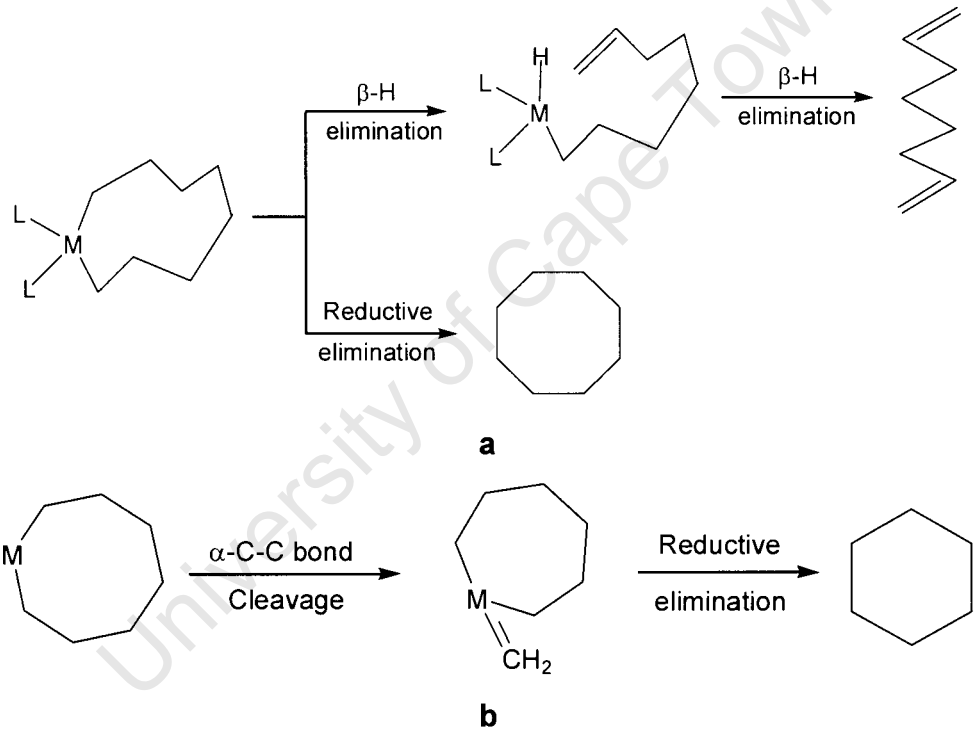


Scheme 3-7. The possible mechanisms of the formation of n-alkane from metallacyclononane.

Similarly, the formation of alkane from the decomposition of metallacycloalkane

complexes should only occur with an extra hydrogen source other than the metallacyclic moieties such as solvent, metal hydride species and hydrogen transferred from coordinated ligand. Therefore, the mechanism of the formation of n-alkane could be proposed in three ways: intermolecular hydrogen abstraction (Scheme 3-7-a), intramolecular hydrogen abstraction (Scheme 3-7-b) and the combination of intermolecular and intramolecular hydrogen abstraction (Scheme 3-7-c).

3.3.1.4. The formation of diene, cycloalkane



Scheme 3-8.

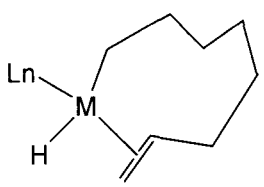
a: The possible mechanisms of the formation of dienes and cycloalkane from metallacyclononane.

b: The possible mechanisms of the formation of cycloalkane from rhodacyclooctane.

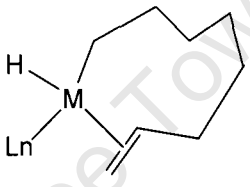
The smaller amount of dienes and cycloalkane were also produced from certain metallacycles. Dienes might be formed via β-hydride elimination from an alkenyl

hydride species and a reductive elimination pathway could result in C-C bond formation to give cycloalkane (Scheme 3-8-a). In contrast, cycloalkane formed from rhodacycle complexes might involve the α-C-C cleavage followed by reductive elimination route (Scheme 3-8-b).

For the metallacycles with mono-dentate ligands, some authors suggest that the formation of dienes might involve an intermediate structure in which a hydride and an alkyl group are coordinated *trans* (**3-C-1**) and reductive elimination of alkene from this structure should be slower than from a *cis* isomer (**3-C-2**).[9]



3-C-1



3-C-2

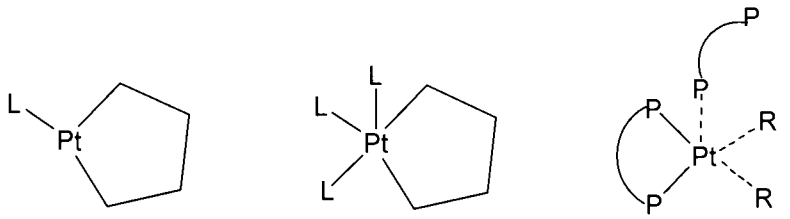
3.3.2. Effect of General factors on thermal decomposition of metallacycloalkanes

Information from the thermal decomposition of small metallacycles have shown that the thermal stability of these complexes is quite dependent on the nature of metal, size of the ring, solvent and supporting ligands.[5] These factors also played a significant role in the current thermal studies on various medium to large metallacycles.

3.3.2.1. Additional neutral ligands

The notable effect of the presence of free phosphine ligands (dppp and dppe) on the thermolytic behaviour of complexes **3-1** and **3-2** is the facilitation of decomposition in every case. This effect is indeed found in the decomposition of some bis(phosphine)platinacyclopentanes with added ligand.[9]

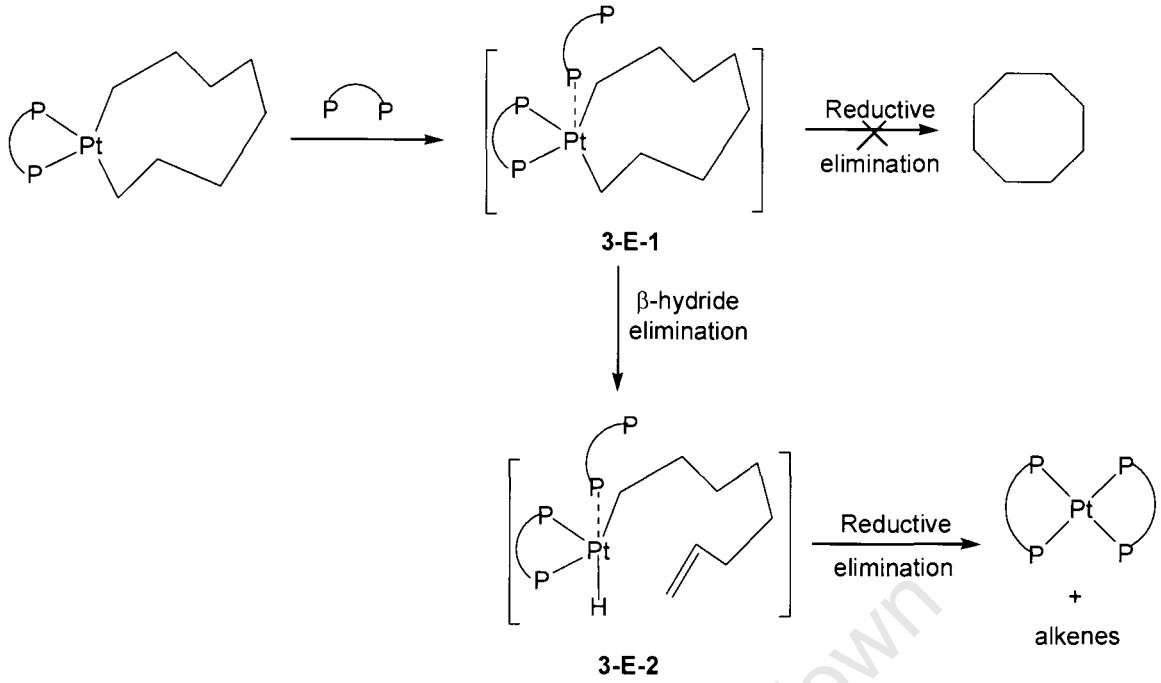
There is no clear mechanism on such reactions so far. According to Whitesides and co-workers,[9] this acceleration by added ligand might due either to inhibition of the formation of a three-coordinate intermediate **3-D-1**, or to promotion of the formation of a five-coordinate intermediate **3-D-2**.



3-D-1 **3-D-2** **3-D-3**

Braterman and co-workers also reported that reductive elimination of biaryl was enhanced by added phosphines in the thermolysis reactions due to their electrodonor capability.[1,13,21(c),35] Again, a five-coordinate intermediate **3-D-3** was proposed according to their evidence from the DSC results.

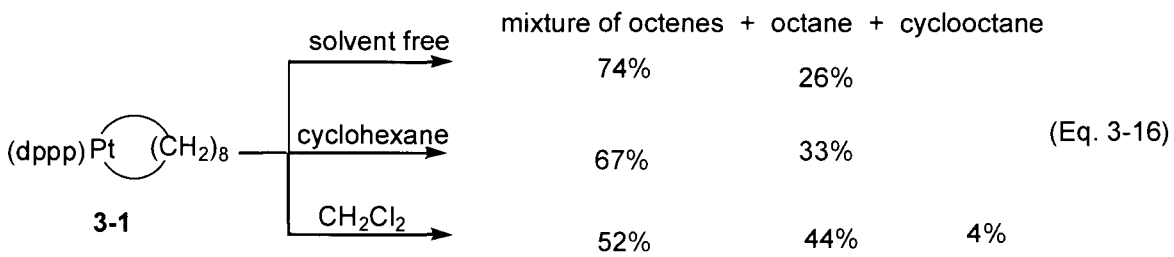
The complexes **3-1** and **3-2** with the chelating ligands dppp and dppe, however, do not involve a three-coordinate intermediate during the thermal decomposition as they ensure retention of the configuration. The mechanism of the decomposition of **3-1** (or **3-2**) with additional ligand is easily rationalized using the hypothesis that a five-coordinated intermediate **3-E-1** could be formed initially followed by β-hydride elimination to form a metal-hydride intermediate **3-E-2**, and the reductive elimination of alkenes could be then facilitated by the added phosphine ligand (Scheme 3-9). The five-coordinated metal-hydride species **3-E-2** is presumably the favoured intermediate due to the fact that no (or no more) cyclooctane was formed with added ligand, which indicated reductive elimination from the initial intermediate **3-E-1** to form cyclooctane might be blocked.



Scheme 3-9. The proposed mechanism of the decomposition of platinacyclononane with additional ligand.

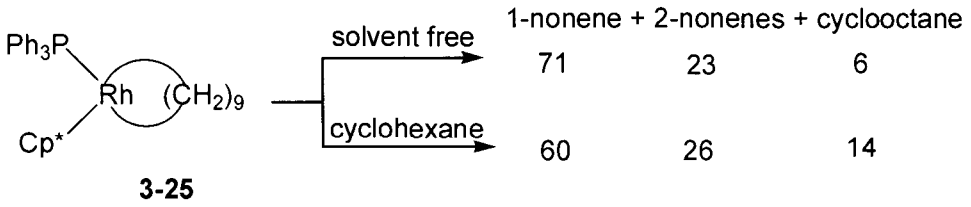
3.3.2.2. Changes of decomposition medium

The effect of decomposition medium on the hydrocarbon products of the platinacyclononane **3-1** was observed (Eq. 3-16). The relative amount of the mixture of octenes including 1-octene, 2-octenes and 1,7-octadiene is significantly higher for the solvent free decomposition than those decomposed in solvent. Decomposition in the halogenated, highly co-ordinating and polar solvent, dichloromethane, was found to favour formation of n-octane and cyclooctane. On the other hand, the formation of octane showed contrary trends compared to octenes.



(Eq. 3-16)

This effect was also found for the other platinacycle complexes as well as the group 9 metallacycloalkane **3-25**, which yielded 1-nonene much higher from solvent free decomposition (Eq. 3-17).

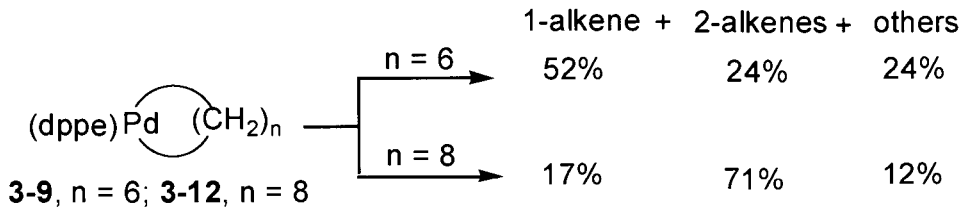


3-25 (Eq. 3-17)

3.3.2.3. Changes of ring size

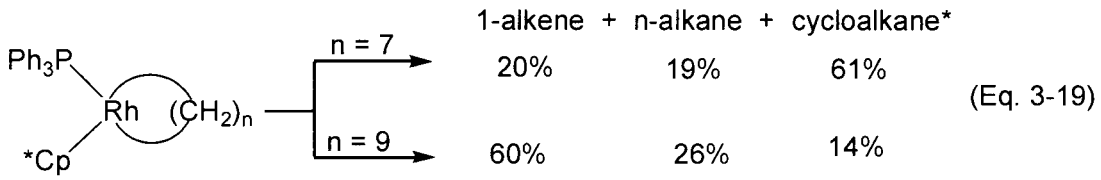
Whitesides and co-workers[9] found ring size of metallacycloalkanes affected the activation energy in the thermal decomposition. In this study, the ring size was also found to affect the thermal stability of platinacycles and the distribution of the hydrocarbon products upon decomposition of various metallacycloalkanes. The typical examples in our study could be palladacyclic and rhodacyclic systems.

Alkenes were the major products in all case for the solvent free decomposition of palladacycle complexes of the type (dppe)Pd$(CH_2)_n$ 170°C, 1-alkene predominated for palladacycloheptane **3-6** whereas 2-alkene was the major product for the larger ring complex **3-12** (Eq. 3-18).



3-9, n = 6; **3-12**, n = 8 (Eq. 3-18)

In the case of rhodacycloalkanes, the formation of 1-alkenes is favoured for the ten-membered ring compound **3-25**, while the α-C-C bond cleavage followed by reductive elimination route to form cycloalkane was favoured in the eight-membered ring **3-21** (Eq. 3-19).



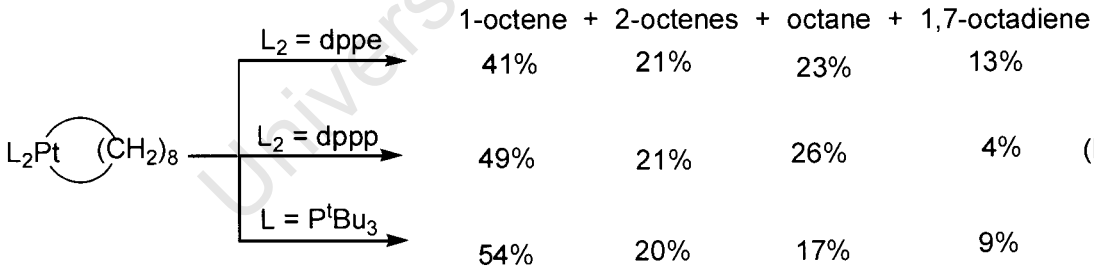
(Eq. 3-19)

3-21, n = 7; **3-25**, n = 9

* cycloalkane with one carbon less than metallacyclic moieties

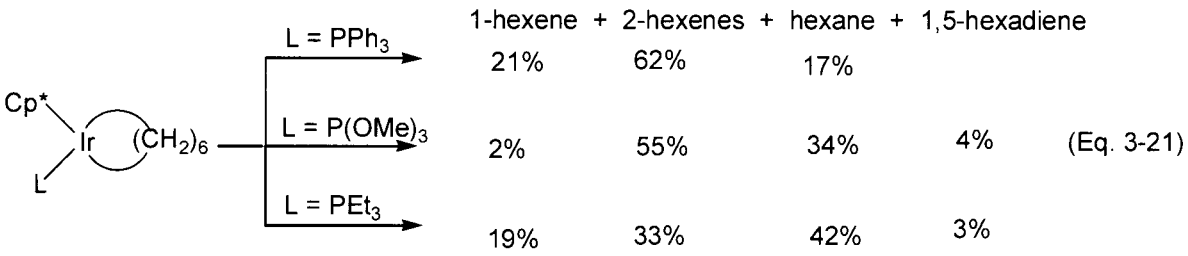
3.3.2.4. Changes of supporting ligands

The thermal stability of metallacycles is dependent on the ligand systems. The order of stability for Pd and Pt complexes is as follows: PPh_3 < P^tBu_3 < diphos (diphos = dppe, dppp, dmpe, dcpe), while for Ir complexes: PPh_3 < $P(OMe)_3$ < PEt_3. The role of the supporting ligands seems to hold the balance in the decomposition pathways of certain metallacycle systems. For instance, all platinacyclononane complexes (**3-1**, L_2 = dppp; **3-2**, L_2 = dppe; **3-3**, L = P^tBu_3) produced 1-octene as major products upon solvent free decomposition, whereas the relative amount of 1-octene was increasing with the order of the ligands: dppe < dppp < P^tBu_3 (Eq. 3-20).



(Eq. 3-20)

The same effect was also observed in iridacyclohexanes (**3-13**, L = PPh_3; **3-14**, L = $P(OMe)_3$; **3-15**, L = PEt_3), the major product 2-hexenes decreased according to the ligand: PPh_3 < $P(OMe)_3$ < PEt_3 (Eq. 3-21). This effect might be due to the different cone angle and electronic properties of the ligands.

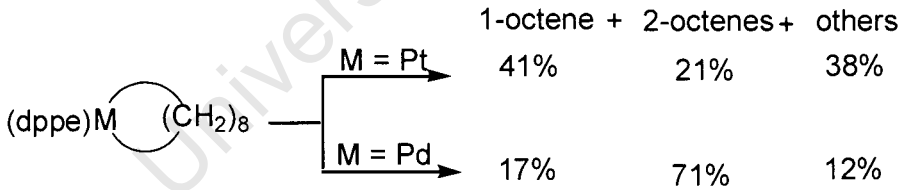


(Eq. 3-21)

3.3.2.5. Changes of metal centre

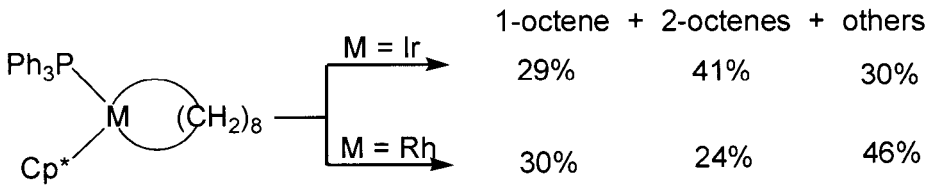
It is clearly observed that not only the thermal stability but also the distribution of decomposition products are quite different among 3d, 4d and 5d transition metal containing metallacycles.

According to the current observation, platina- and palladacyclononanes with dppe ligand, **3-2** and **3-12**, decomposed to give 1-octene and 2-octenes as the major product respectively (Eq. 3-22). For the group 9 metallacycles, a significant trend of the relative yield on the decomposition products was also observed. Irida- and rhodacyclononanes, **3-16** and **3-24**, both gave the same amount of 1-octene, while 2-octenes formed easily on the decomposition of complex **3-26** (Eq. 3-23).



(Eq. 3-22)

3-2, M = Pt; **3-12**, M = Pd



(Eq. 3-23)

3-16, M = Ir; **3-24**, M = Rh

Due to the observation from Eqs 3-22 and 3-23, the thermal decomposition of the metallacycloalkanes with different metal centres in different groups gave the same

major products, *i.e.*, 1- and 2-octenes, in spite the involvement of different ligand systems.

3.4. Conclusions

Due to the fact that we could now prepare a series of novel medium to large ring size metallacyaloalkanes by the new route: ring closing metathesis followed by hydrogenation of their bis(1-alkenyl) precursors, we were able to carry out the thermal decomposition studies discussed in this thesis.

Some useful evidence pertinent to the thermal decomposition of metallacycloalkanes emerges from the current study:

(1) The kinetic studies have been carried out the thermal decomposition of platinacycloalkanes. The rate of decomposition of **3-1** and **3-2** in cyclohexane is increased by adding dppp and dppe ligands respectively. The effect of the additional ligands could be that of facilitating the reductive elimination of alkenes from a five-coordinated metal-hydride intermediate.

(2) The relative amount of 1-octene formed from the thermal decomposition of platinacyclononanes **3-1** and **3-2** is dependent on the decomposition temperature and time. The formation of the total products including 1-octene, 2-octenes, n-octane, 1,7-octadiene and cyclooctane is first-order for about the first 30% of the decomposition.

(3) The rate of decomposition of eleven-membered platinacycle **3-8** at 90°C has been found to be greater than that of the eight-membered platinacycle **3-5**. The different ring sizes have a significant effect on the thermal stability of metallacycloalkanes.

(4) The products of the thermal decomposition of various medium to large metallacycloalkanes are the mixture of alkenes and n-alkane, in which 1- and 2-alkenes are produced predominately.

(5) These results taken together demonstrate that changes of decomposition medium, ring size, supporting ligands and metal centres have significant effects on the decomposition pathways; moreover, these factors seem to have a cooperative effect in the decomposition of certain metallacycloalkanes.

(6) The isolation of the hydridoalkenylplatinum(II) complex which is believed to be the key intermediate to form 1-alkene via β-hydride elimination was not successful. The products from these reactions were 1-alkene and n-alkane, which suggested that the hydridoalkenylplatinum(II) complex are too unstable to be determined.

(7) The possible decomposition pathways involved in the thermolysis of these metallacycloalkanes could be: β-hydride transfer or an intermolecular chain reaction to form 1-alkene; intermolecular or intramolecular isomerisation for 2-alkenes; the formation of n-alkane by an intermolecular hydrogen abstraction, or alternatively an intramolecular hydrogen abstraction from supporting ligands. In addition, an α-C-C bond cleavage followed by reductive elimination reaction pathway was proposed in rhodacycle systems.

The thermolysis data in this study suggest that medium to large metallacycloalkanes can be useful model for the intermediates in selective catalytic oligomerisation reactions, particularly ethylene trimerisation and tetramerisation.

3.5. References

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Chapter 4

Thermal decomposition studies on precursor compounds of metallacycloalkanes

4.1. Introduction

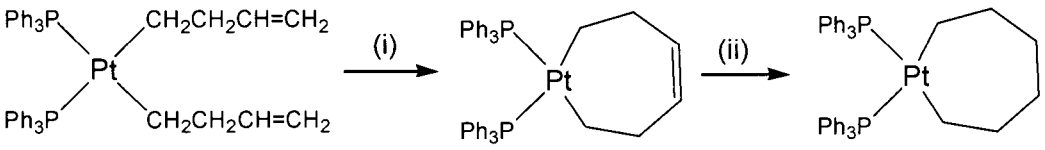
Medium to larger metallacycles (ring size ≥ 7) are difficult to make although smaller ones (with four- to six-membered rings) can be prepared relatively easily by two routes (Eqs 4-1, 4-2).[1,2]

$$LM^{2-} + Y(CH_2)_nY \longrightarrow LM(CH_2)_n + 2Y^- \text{ (Y = triflate)} \quad \text{(Eq. 4-1)}$$

$$LMX_2 + M^1(CH_2)_nM^1 \longrightarrow LM(CH_2)_n + 2M^1X \quad \text{(Eq. 4-2)}$$

(M1 = Li or MgBr, X = halogen, L = other ligands)

The first structurally characterized metallacycloheptane was only reported very recently, and this was prepared by a new route: reaction of the bis(1-alkenyl) complex **4-A** with Grubbs 1st generation catalyst to give the metallacycloalkene **4-B** which was then hydrogenated to the metallacycloalkane **4-C** (*eg.* Eq. 4-3).[2] Thus, metal bis(1-alkenyl) complexes are indeed useful precursors for the preparation of metallacycloalkanes.



(Eq. 4-3)

4-A **4-B** **4-C**

(i) Grubbs catalyst generation 1, CH_2Cl_2 reflux 1h; (ii) H_2, Pd/C, CH_2Cl_2

Transition metal–alkenyl complexes find widespread use in organic synthesis and have been implicated as intermediates in a number of catalytic reactions.[3] Generally, both mono- and bis(1-alkenyl) complexes can show three distinct reaction pathways: (i) reaction at the M-C bond, (ii) reaction at the C=C bond and (iii) coordination of the pendant alkene. In addition, bis(1-alkenyl) complexes can undergo further reaction pathways including ring closing metathesis (RCM) reaction,[2,4,5] selective and quantitative isomerization to yield corresponding bis(2-alkenyl) complexes[6] and some other reactions such as transmetalation, intermolecular alkenyl migrations, oxidative addition of methyl iodide etc.[7]

The known bis(1-alkenyl) complexes are $L_2Pt(alkenyl)_2$, $MoL_2(O)_2(alkenyl)_2$ and $Cp_2Zr(alkenyl)_2$ reported a decade ago, as well as some novel complexes (M = Pt, Pd, Rh, Ir, Cr, Zr, Fe, Ru, Os and others) recently prepared in our research group.[8] They are regarded as an important class of compounds with potential useful applications. Some have been shown to be useful for generating thin platinum films[9] for micro-electronic and catalytic applications[10] using the chemical vapour deposition (CVD) method.[11] Others can be used as precursors for preparation of other important classes of compounds including metallacycloalkanes.[2,4,5]

Thermal decomposition of metal-bis(alkenyl) complexes could give various products (Fig. 4-1)[8] including (i) long chain dienes by reductive elimination, (ii) diene and 1-alkene by β-hydride elimination followed by reductive elimination. Nevertheless, the products formed can differ considerably due to the pendant alkene functionality,[4] which can undergo other pathways such as isomerization[6] or rearrangement[12] of the coordinated alkenyl ligand. It is believed that decomposition to give organic products is a particularly important and final step in the mechanism of a catalytic or stoichiometric reaction, involving a metal-alkenyl species.[8] Fundamental understanding of the decomposition process may lead to the design of better catalytic reactions with intermediates that undergo cleaner thermolysis reactions to produce for example higher quality metal films or useful

organic products.[9]

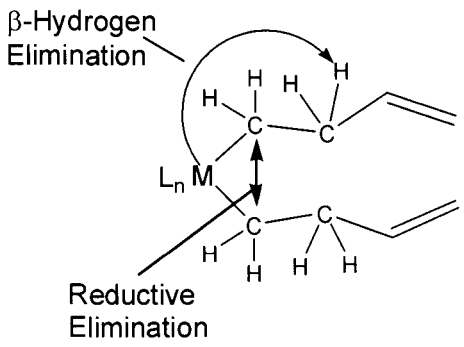
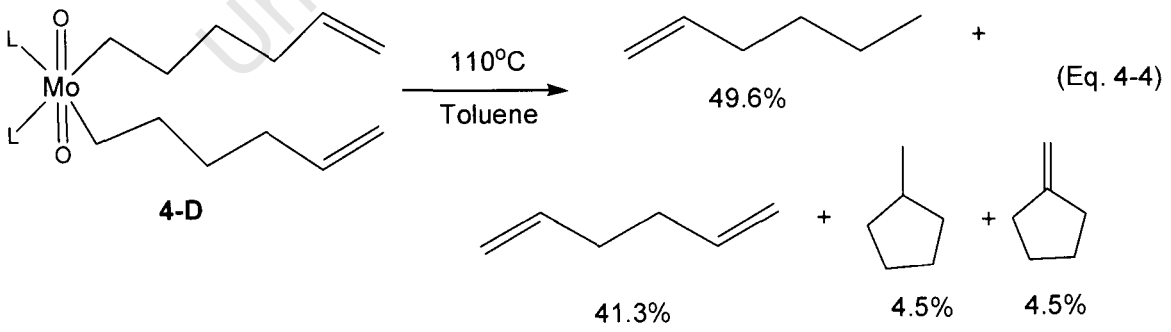


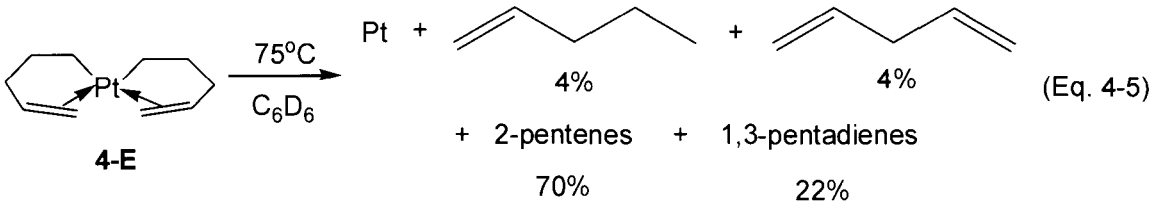
Fig. 4-1. Possible decomposition pathways for metal bis(alkenyl) compounds

There are only a few examples of thermal decomposition of metal-bis(alkenyl) complexes reported thus far. The anaerobic and aerobic decomposition of $L_2Mo(O)_2\{(CH_2)_4CH=CH_2\}_2$ (**4-D**) was studied by Vetter and Sen.[13] As shown in Eq.4-4, equal amounts of alkene and diene were formed through a β-hydrogen abstraction pathway, as well as a small amount of methylcyclopentane and methylenecyclopentane which were formed by a rearrangement of the 5-hexenyl free radical. In addition, cyclopentylformaldehyde was found under aerobic decomposition condition, which was formed through cyclization of the 1-hexenyl free radical prior to its reaction with oxygen.



Tagge *et al.* investigated the thermal decomposition studies on *cis*-bis(η^1,η^2-pent-4-ene-1-yl)platinum(II) (**4-E**).[9] Under CVD conditions (220°C), the decomposition products, 1-pentene, 2-pentene, 1,3-pentadiene and

1,4-pentadiene, were formed in approximately equal amounts. The same products were formed during thermolysis of **4-E** in aromatic solvents at 75°C, although the product ratios were significantly different (Eq. 4-5). At 75°C, the isomerization seemed to occur prior to the β-hydrogen elimination reactions.



(Eq. 4-5)

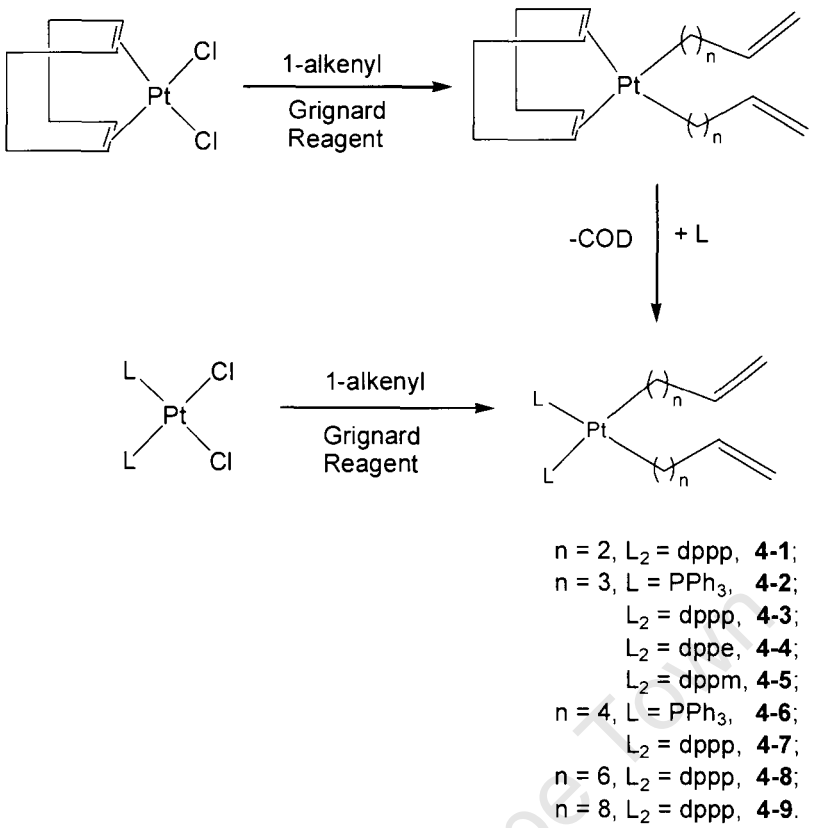
Obviously, there is not enough evidence based on the reported literature to reveal the similarities and differences of decomposition pathways of metal-bis(alkenyl) complexes compared to metallacycloalkane complexes. To fill this gap in the understanding of decomposition on bis(alkenyl) complexes, this chapter describes more results and we discuss thermal decomposition studies of a series of novel metal-bis(alkenyl) complexes, which have seen used as precursors for the preparation of metallacycloalkanes, as discussed above.

4.2. Results

4.2.1. Thermal decomposition of group 10 bis(1-alkenyl) complexes of the type $L_2M(1\text{-alkenyl})_2$ (M = Pt, Pd)

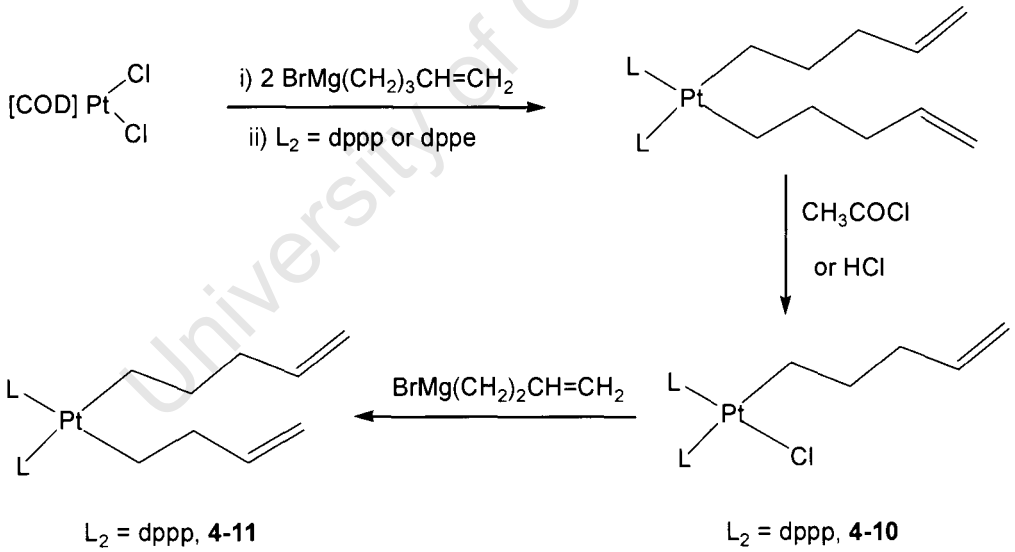
4.2.1.1. Thermal decomposition of bis(1-alkenyl)platinum(II) complexes

The bis(1-alkenyl)platinum(II) complexes $L_2Pt(1\text{-alkenyl})_2$ with two equal length chains were prepared in high yields by reacting the appropriate Grignard reagents with L_2PtCl_2 (L = PPh_3, L_2 = dppm, dppe, dppp)[4] or $Pt(COD)Cl_2$ followed by displacement using various ligand systems[7] (Scheme 4-1-a). The complex with two different length chains and its mono(1-alkenyl) precursor were prepared using the route outlined in Scheme 4-1-b.[5]



n = 2, L_2 = dppp, **4-1**;
n = 3, L = PPh_3, **4-2**;
L_2 = dppp, **4-3**;
L_2 = dppe, **4-4**;
L_2 = dppm, **4-5**;
n = 4, L = PPh_3, **4-6**;
L_2 = dppp, **4-7**;
n = 6, L_2 = dppp, **4-8**;
n = 8, L_2 = dppp, **4-9**.

a



L_2 = dppp, **4-11**

L_2 = dppp, **4-10**

b

Scheme 4-1. The preparation of bis(1-alkenyl)platinum(II) complexes

Thermal decomposition studies of bis(1-alkenyl)platinum(II) complexes were carried out in a sealed evacuated tube which was immersed in a thermostated oil bath. The thermolysis of these complexes which was carried out at 170°C for two

hours without solvent resulted in a mixture of olefins and was accompanied by a color change from their original pale yellow to an intense red. The organic products obtained on decomposition were analyzed by GC or GC-MS. The analysis errors were ±3% for 1-alkene, ±1% for 2-alkenes, ±4% for dienes and ±1% for cycloalkane (the same for the other complexes).

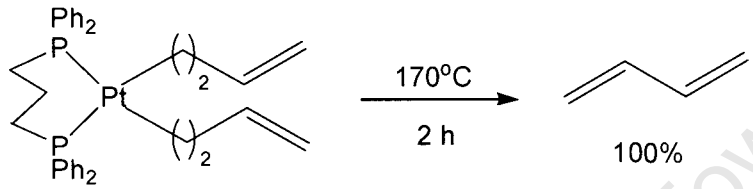
A. The thermolysis of bis(1-pentenyl)platinum(II) and shorter-chain complexes

Table 4-1 summarized the products of the thermal decomposition on bis(1-pentenyl)platinum(II) complexes, **4-2** – **4-5**, and the complexes with shorter length alkenyl chains, **4-1** and **4-11**, as well as the (η'-pentenyl)chloroplatinum(II) complex **4-10**.

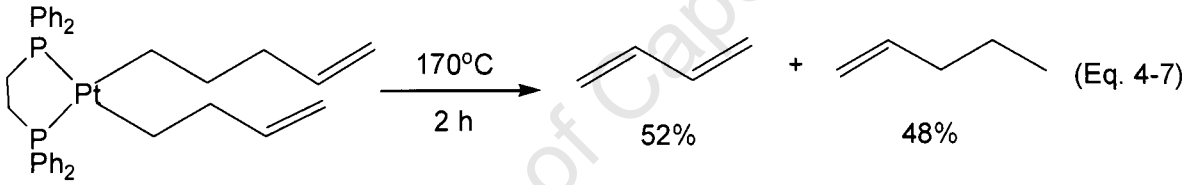
Table 4-1. Products of thermal decomposition of bis(1-pentenyl)platinum(II) complexes of the type $L_2Pt(1\text{-alkenyl})_2$ and comparison with others having shorter chains

Complex	Observed products %			
4-1	1,3-Butadiene 100			
4-11	1,3-Butadiene 52		1-Pentene 48	
	1-Pentene	2-Pentenes	1,4-Pentadiene	1,3-Pentadiene
4-2	14	12	64	10
4-3	6	25	52	17
4-4	27	33	26	13
4-5	31	35	24	10
4-10	4	15	63	17

Only one product, 1,3-butadiene, was obtained from the thermal decomposition of bis(1-butenyl)(dppp)platinum **4-1** (Eq. 4-6). In this case, β-elimination seems to be the only decomposition pathway. For the thermolysis of the complex with different length alkenyl chains **4-11**, 1,3-butadiene and 1-pentene were formed in approximately equivalent amounts, where β-hydride elimination seemed to occur on the shorter butenyl chain and the pentenyl chain underwent a reductive elimination subsequently (Eq. 4-7) (for further discussion see section **4.3.2.1**).

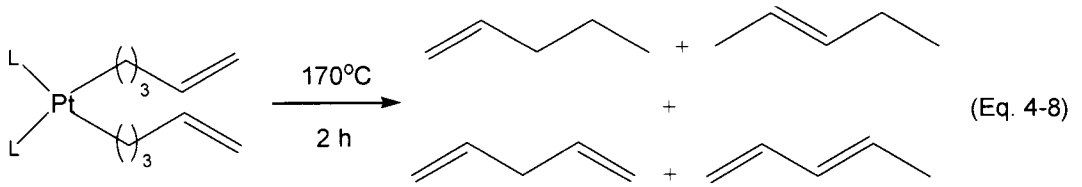


4-1 (Eq. 4-6)



4-11 (Eq. 4-7)

In contrast, complexes **4-2** – **4-5** gave various products on thermolysis, leading to the formation of 1-pentene, 2-pentenes and dienes (Eq. 4-8), which were also obtained from the decomposition of **4-10**. No higher alkenes, which could result from the coupling of two alkenyl ligands through reductive elimination, were detected.



L = PPh_3 **4-2**;
L_2 = dppp **4-3**,
dppe **4-4**,
dppm **4-5**.

(Eq. 4-8)

The results of the decomposition of bis(1-pentenyl) complexes presented in Table 4-1 show that the nature of the phosphine ligands did not affect the type of products but resulted in the different product distributions. The relative yields of 1,4-pentadiene followed the order: PPh_3 > dppp > dppe > dppm, and the formation of 2-pentenes behaved in the opposite way. In addition, the reductive elimination to form 1- and 2-pentenes predominated in the decomposition of the complexes with the chelating ligands, especially with dppe and dppm ligands.

B. The thermolysis of bis(1-hexenyl)platinum(II) complexes

The thermal decomposition of bis(1-hexenyl)(dppp)platinum **4-7** was previously reported according to earlier studies.[7] The product analysis, however, was limited by the instrument and available authentic samples. Due to the fact that the bis(1-alkenyl)platinum(II) complexes undergo an isomerization in solution at 100°C to yield the corresponding bis(2-alkenyl)platinum(II) complexes[6] and the observation of the formation of some isomers from mass spectra, we then obtained the appropriate authentic samples and carried out further product analysis, and the results are presented in Table 4-2.

Several interesting points were noted in the products isolated from the thermolysis of bis(1-hexenyl)(dppp)platinum(II) **4-7**. First, all the decomposition reactions showed the presence of 2-hexenes as major components, especially for the decomposition in dichloromethane. Second, the organic product distributions are quite dependent on the time of heating as well as the medium of decomposition, whether in the solid state or in solution (Table 4-2). It can be seen that there is a significant decrease in the quantities of 1-hexene with increasing time of heating. In contrast, for the thermolysis of PPh_3 containing complex **4-6**, the decomposition products which formed prior to isomerization, *ie*., 1-hexene and 1,5-hexadiene, were the main components.

The present observations are in agreement with the early reports,[6,7] the organic products depend on the nature of the ligands due to the fact that the chelating effect of diphosphine ligands reduces the amount of decomposition of the 1-alkenyl compounds and isomerization occurs preferentially, while the PPh_3 containing metal alkenyl complexes decompose rapidly at a relative low temperature which make the isomerization hard to be detected.

Table 4-2: Products of thermal decomposition of bis(1-hexenyl)platinum(II) complex **4-6** and **4-7**

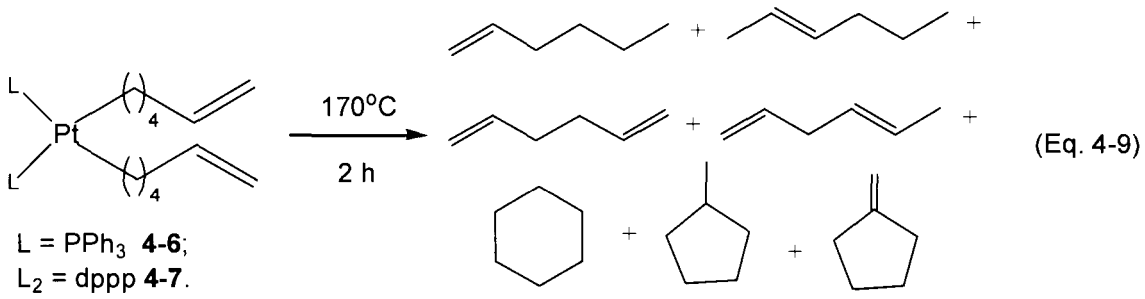
	Medium and time	Observed products (%)[a]						
		n-Hexane	1-Hexene	2-Hexenes	Cyclo-hexane	1,5-Hexadiene	1,4-Hexadiene	Others[b]
4-7	Solid 1h	21	7	34	12	9	8	9
	2h	2	5	43	19	12	13	8
	3h	2	0	47	16	9	13	13
	10h	1	0	47	13	6	22	11
	24h	0	0	54	16	6	16	8
	CH_2Cl_2 4 days	14	0	83	3	1	0	0
4-6	Solid 2h	0	34	18	6	30	10	3

[a] by GC-MS analysis.

[b] methylcyclopentane and methylenecyclopentane were obtained in ratio of 1:1.

Some cyclic products such as cyclohexane, methylcyclopentane and methylenecyclopentane were also obtained from the thermolysis reactions (Eq. 4-9). The formation of the latter two products could presumably occur via a free

1-hexenyl radical[13] which is known to rearrange rapidly to the corresponding cyclopentylmethyl radical.[14]



L = PPh_3 **4-6**;
L_2 = dppp **4-7**.

(Eq. 4-9)

C. The thermolysis of bis(1-octenyl)platinum(II) and bis(1-decenyl)platinum(II) complexes

The thermolysis of the complexes with the longer alkenyl chains **4-8** and **4-9** was carried out without solvent at 170°C for 2 hours and gave a mixture of alkenes: 1- and 2-alkenes, dienes, 3-alkene due to the further isomerization and some cyclic products (see Table 4-3).

Table 4-3. Products of thermal decomposition of bis(1-octenyl)(dppp)platinum(II) **4-8** and bis(1-decenyl)(dppp)platinum(II) **4-9**.

	Observed products %					
	1-Octene	2-Octenes	3-Octenes	1,7-Octadiene	1,6-Octadiene	Others
4-8	15	27	6	16	34	2[c]
	1-decene	2-decenes	3-decene	1,9-Decadiene	1,8-Decadiene	others
4-9	16	34	4	5	31	10[d]

[c] methylcycloheptane and methylenecycloheptane in ratio of 1:1.

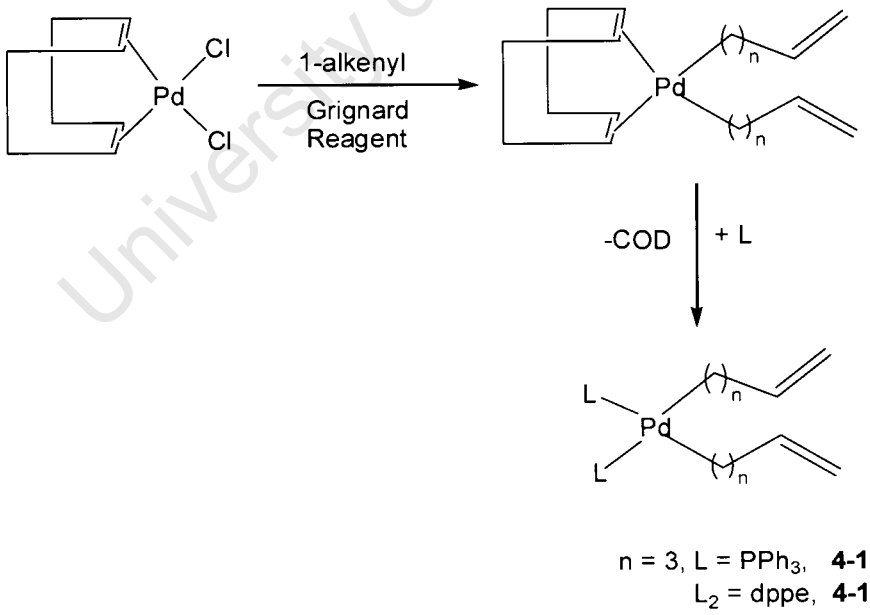
[d] methylcyclononane and methylenecyclononane in ratio of 1:1.

As for the complexes with shorter alkenyl chains, the decomposition pathway of **4-8** and **4-9** favoured isomerization prior to the occurrence of β-hydride elimination or reductive elimination, which led to the formation of 2-octenes and 1,6-octadiene for complex **4-8**, 2-decenes and 1,8-decadiene for complex **4-9** as the major products.

It was found that the decomposition pathways are quite different to platinum bis(1-hexenyl) complexes because no alkane and cycloalkane were detected. This could be due to the effect of the length of alkenyl chains.

4.2.1.2. Thermal decomposition of bis(1-alkenyl)palladium(II) complexes

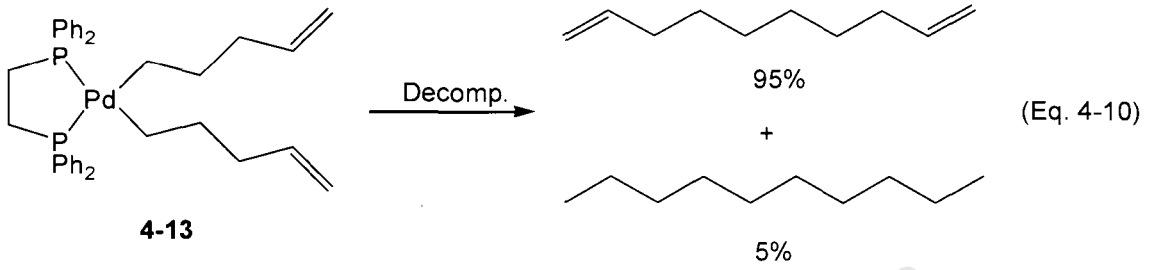
The bis(1-alkenyl)palladium(II) complexes **4-12** and **4-13** were prepared by treating a solution of $[Pd(COD)Cl_2]$ in diethyl ether with the corresponding Grignard reagents at -78°C, followed by ligand displacement.[15]



Scheme 4-2. The preparation of bis(1-alkenyl)palladium(II) complexes

The bis(1-pentenyl)palladium(II) complex, **4-13**, partially decomposed at room temperature during the synthesis[16] but the decomposition was also carried out at

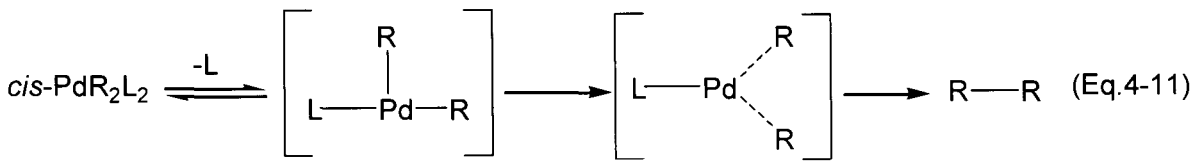
170°C in solid phase to give 1,9-decadiene as the major product (95%) in both the cases via the reductive elimination reaction. These organic products were confirmed by NMR spectra and GC-MS. n-Decane was also found as the minor product (Eq. 4-10).



4-13

(Eq. 4-10)

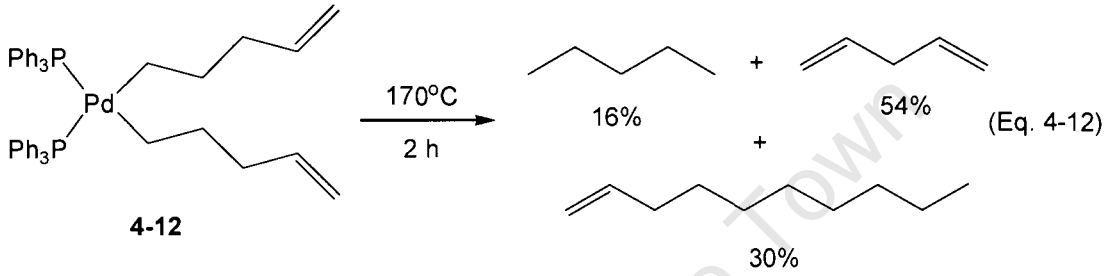
Even though no decomposition studies have previously been reported on bis(1-alkenyl)palladium(II) complexes, the possible decomposition pathways of this class of complexes have been summarized in a review, in which the long chain diene products are formed due to reductive elimination.[8] The formation of 1,9-decadiene in the thermolysis of **4-13** is consistent with the reductive elimination pathway and also agrees with the findings by Ozawa and Yamamoto.[17] They observed that thermal decomposition of *cis*-L_2PdEt_2 complexes afforded reductive elimination products exclusively (Eq. 4-11). The small amount of n-decane in the decomposition of **4-13** could be the result of reductive elimination followed by hydrogenation.



(Eq.4-11)

In contrast to the reductive elimination reaction that occurred for **4-13**, the solvent free thermolysis of bis(1-pentenyl)palladium(II) complex with PPh_3 ligand **4-12** indicated the formation of a mixture of products through the β-hydride elimination as well as reductive elimination reactions: n-pentane (16%), 1,4-pentadiene (54%)

and 1-decane (30%) (Eq. 4-13), which is presumably due to the effect of the nature of the ligands. PPh_3-containing complexes are usually thermally unstable compare to those with chelating diphosphine ligands and PPh_3 can dissociate creating a vacant site on the metal for β-hydride elimination. The formation of n-pentane and 1-decane could presumably involve an intermolecular or intramolecular hydrogen abstraction pathway, hydrogen atoms could come from metal-hydride species or *o*-position on PPh_3 (for more discussion see Section **4.3.1.2**).

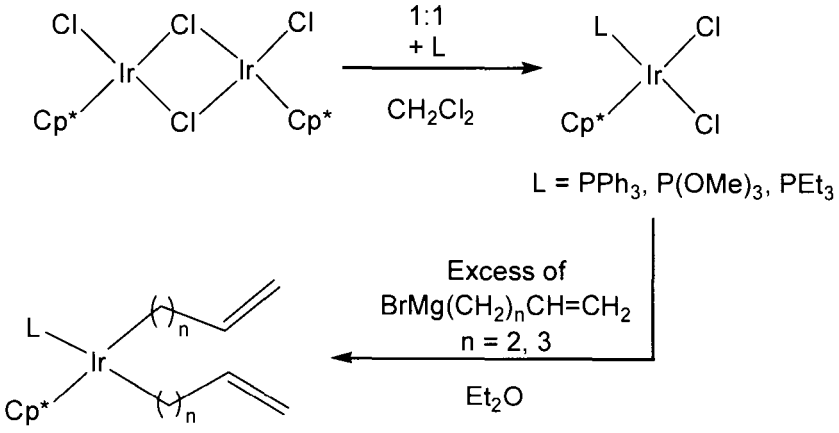


4-12 (Eq. 4-12)

4.2.2. Thermal decomposition of group 9 bis(1-alkenyl) complexes

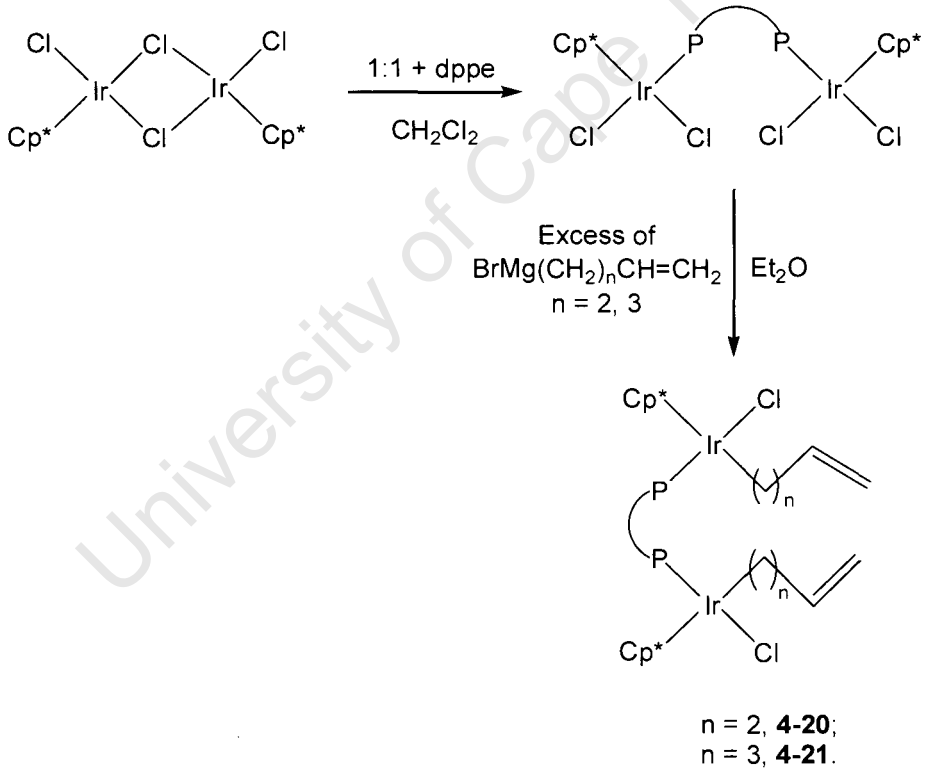
The bis(1-alkenyl) complexes of iridium were prepared by the transmetalation reaction of 1-alkenyl Grignard reagents with the corresponding dihaloiridium(III) precursors, as shown in Scheme 4-3.[18]

The solvent free thermal decomposition of bis(1-alkenyl)iridium(III)complexes **4-14** – **4-19** at 170°C for two hours gave various organic products (shown in Table 4-4) and brown residues.



n = 2, L = PPh_3 **4-14**;
L = $P(OMe)_3$ **4-15**;
L = PEt_3 **4-16**;
n = 3, L = PPh_3 **4-17**;
L = $P(OMe)_3$ **4-18**;
L = PEt_3 **4-19**.

a



n = 2, **4-20**;
n = 3, **4-21**.

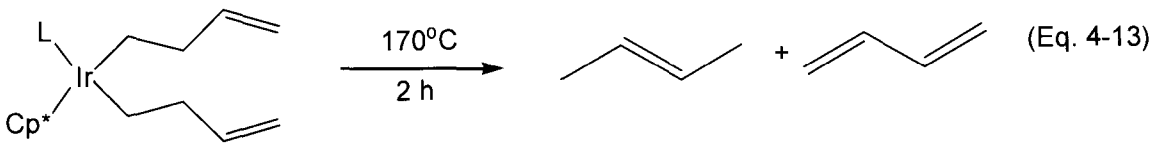
b

Scheme 4-3. The preparation of bis(1-alkenyl)iridium(III) complexes

Table 4-4. Products of thermal decomposition of bis(1-alkenyl)iridium(III) complexes.

Complex	Observed products %				
	2-Butene			1,3-Butadiene	
4-14	37			63	
4-15	67			33	
4-16	62			38	
4-20	30			70	
	n-Pentane	1-Pentene	2-Pentenes	1,4-Pentadiene	1,3-Pentadiene
4-17	5	14	33	42	6
4-18	3	8	72	9	8
4-19	0	18	29	48	5
4-21	0	28	37	28	7

The thermolysis of bis(1-butenyl)iridium(III) complexes yielded 2-butene and 1,3-butadiene as their decomposition products; 1-butene was not detected (Eq. 4-13). The product distribution on decomposition was strongly dependent on the nature of phosphine ligands. The complex with PPh_3 ligand, **4-14**, decomposed giving 1,3-butadiene as the major product. As with Pd, PPh_3 can dissociate to create a vacant site for β-hydride elimination to take place. However, 2-pentene predominated from the decomposition of **4-15** and **4-16**.

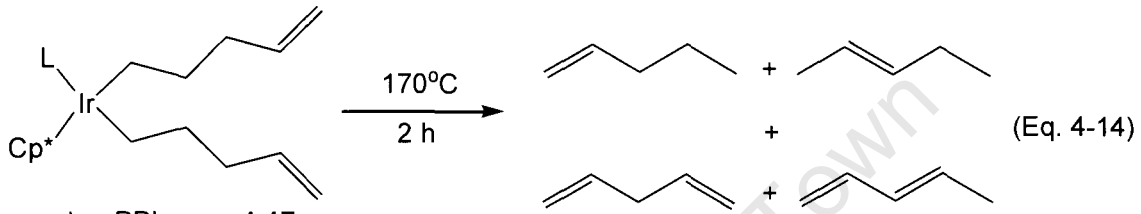


(Eq. 4-13)

L = PPh_3, **4-14**;
$P(OMe)_3$, **4-15**;
PEt_3, **4-16**.

It is interesting to note that the length of alkenyl chain has a significant effect on the

product formation from the decomposition of bis(1-alkenyl)iridium(III) complexes. As shown in Table 4-4, the bis(1-pentenyl) complexes gave a greater variety of products than their analogues with butenyl chain, *i*.e., 1-pentene, 2-pentenes and dienes (Eq. 4-14). The effect of phosphine ligands is also obvious, with $P(OMe)_3$ ligand, complex **4-18** preferred to undergo isomerization prior to β-hydride elimination forming 2-pentenes as major products, while 1,4-pentadiene was mainly obtained in the other cases.



L = PPh_3, **4-17**;
$P(OMe)_3$, **4-18**;
PEt_3, **4-19**.

(Eq. 4-14)

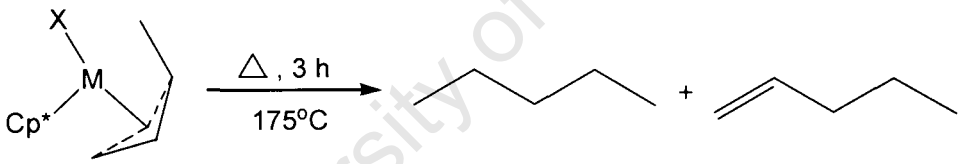
The dppe bridging ligand containing dimeric iridium complexes **4-20** and **4-21** were found to be much more thermally stable, so that their decomposition reactions were carried out at 210°C for 20 hours. 1,3-butadiene was the major product for the thermolysis of complex **4-20**, while complex **4-21** decomposed to form mainly 1- and 2-pentenes, according to which the effect of the length of alkenyl chain was observed as well.

In addition, when we tried to prepare a series of iridium and rhodium alkenyl complexes with an M-C σ-bond and a pendant alkene group, some metal allyl complexes were obtained.[19] Thermal decomposition of these allyl complexes gave a range of organic products (Table 4-5).

Table 4-5. Products of thermal decomposition of metal allyl complexes (M = Ir and Rh).

Complex	Observed products %			
	n-Pentane		1-Pentene	
4-22	70		30	
4-23	59		41	
	1-Pentene	2-Pentene	2-Hexene	1,5-Hexadiene
4-24	23	25	40	12
4-25	27	18	46	9

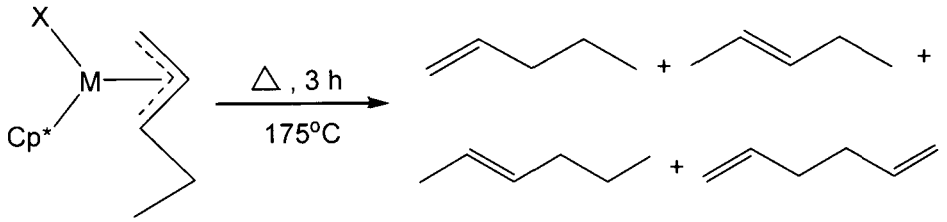
Unexpectedly, complex **4-22** gave n-pentane (70%) and 1-pentene (30%) on decomposition instead of the corresponding C_4-hydrocarbon products (Eq. 4-15). Similar trends were observed with the compound **4-23** on decomposition.



(Eq. 4-15)

M = Ir, X = Cl, **4-22**;
M = Rh; X = Br, **4-23**.

Complex **4-24**, however, yielded 1-pentene (23%) and 2-pentene (25%), 2-hexene (40%) and 1,5-hexadiene (12%), which were analyzed by GC (Eq. 4-16). Similar decomposition products were observed with the rhodium analog, **4-25**.



(Eq. 4-16)

M = Ir, X = Cl, **4-24**;
M = Rh, X = Br, **4-25**.

The methyl groups on pentamethylcyclopentadiene or tetramethylcyclopentadiene ligand may be the source for the extra carbon atom in the organic products after the decomposition. It is interesting to note that the organic product distribution on thermal decomposition depends on the length of the allyl chains, whether it is iridium or rhodium.

4.3. Discussion

4.3.1. The mechanisms of the thermal decomposition of metal bis(1-alkenyl) complexes

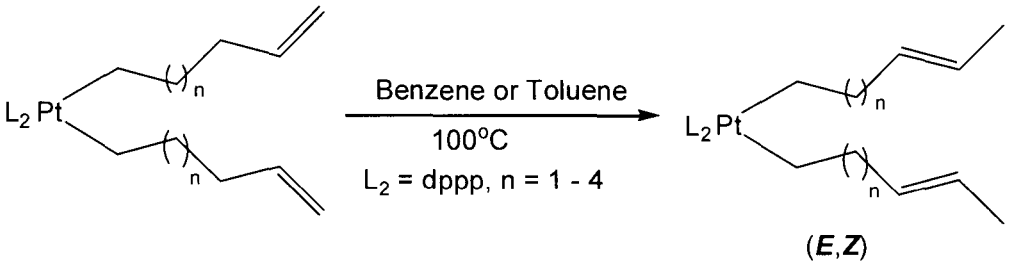
4.3.1.1. The major decomposition pathways

According to our latest results, the thermolysis reactions of the metal bis(1-alkenyl) complexes usually give 1-alkene, 2-alkenes and dienes as the major decomposition products. The possible decomposition pathways responsible for the formation of these major products could be described as following:

(1) Initial β-hydride elimination gives 1,(n-1)-alkadiene, which was especially observed in the complexes with short alkenyl chains (for more discussion see section **4.3.2.1**) and the complexes with PPh_3 ligands (for more discussion see section **4.3.2.2**). This is followed by a reductive elimination to form 1-alkene.
(2) Alternatively, the complexes could isomerise to their corresponding bis(2-alkenyl) complexes followed by β-hydride elimination/reductive elimination forming 2-alkenes and 1,(n-2)-alkadiene. For most bis(1-alkenyl) complexes, these pathways merged on the thermal decomposition.

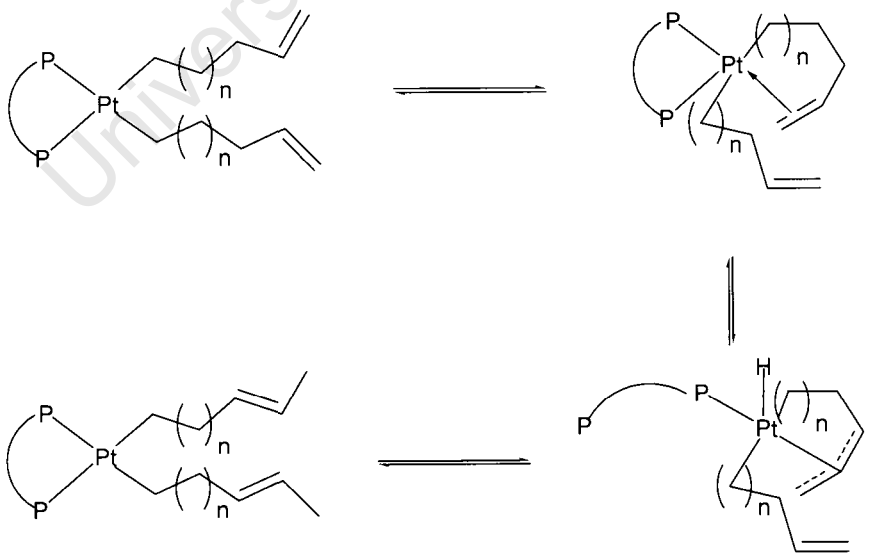
Moss et al. have recently reported the first example of the irreversible and quantitative isomerization for the bis(1-alkenyl)platinum(II) complexes.[6] Heating these complexes in benzene or toluene at 100°C resulted in the corresponding bis(2-alkenyl)platinum(II) complexes, without prior decomposition (Eq. 4-17). They also found that a rise in temperature (>150°C) of benzene solutions of these

complexes led to the cleavage of the Pt-C bonds, yielding 1-alkene, 2-alkenes and dienes etc.



(Eq. 4-17)

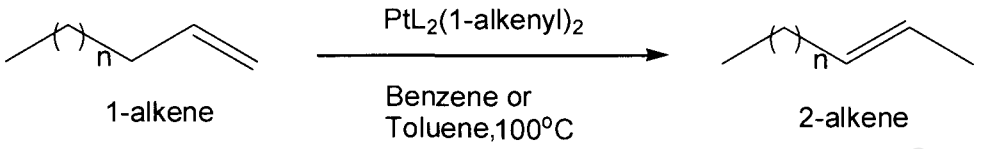
Our present thermal decomposition reactions were carried out at 170±5°C for two hours under solvent-free conditions, which gave isomeric products in most cases. Isomerization reactions are reported as the most studied solvent-free intramolecular transformations of organometallic compounds.[20] A possible intramolecular mechanism for these isomerizations has been proposed by Moss et al., involving a coordination of the pendant alkene followed by a ligand dissociation, a rearrangement to an allyl hydride intermediate then isomerization to give the 2-alkenyl complexes (Scheme 4-4),[6] which could decompose subsequently.



Scheme 4-4. The possible mechanism of intramolecular isomerization.

1-alkenes such as 1-pentene, 1-hexene and 1-octene were found to undergo

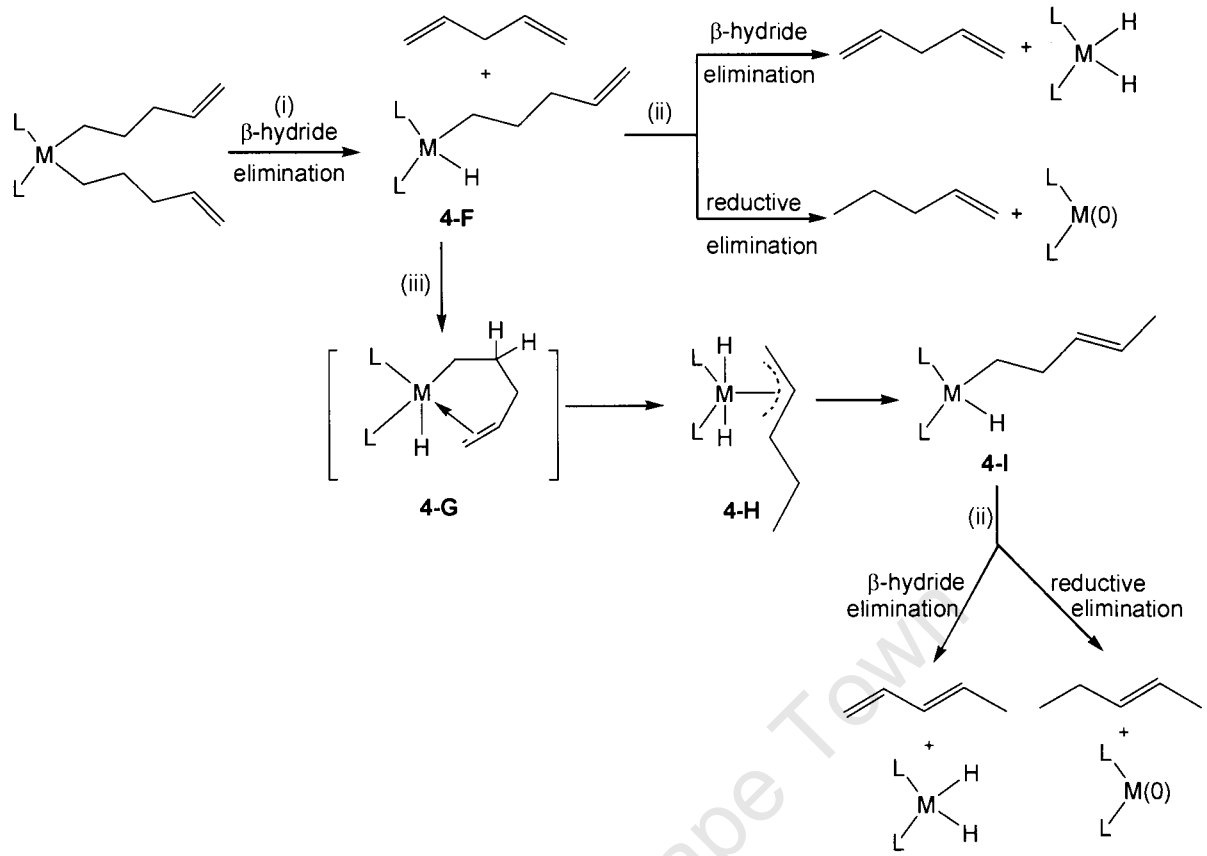
selective isomerization to their corresponding 2-alkenes in the presence of bis(1-alkenyl)platinum(II) complexes (Eq. 4-18).[6] Due to the fact that the authors showed the incoming 1-alkene ends up as the alkyl group in L_2PtR_2,[6] the most possible catalytic species is not bis(1-alkenyl)platinum(II) itself, instead a metal-dihydride species formed *in situ* seems to be more likely as the catalyst for the isomerizations.



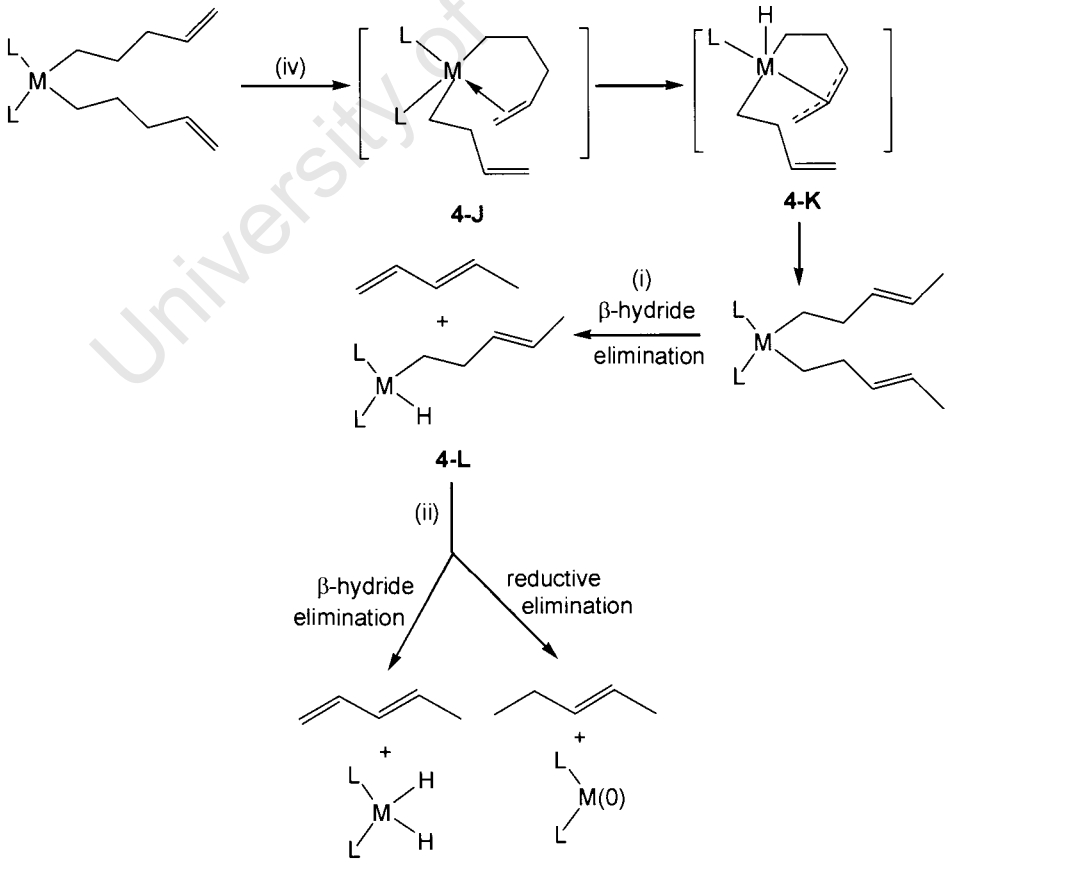
(Eq. 4-18)

The formation of 2-alkenes and 1,(n-2)-alkadienes on decomposition could also be accounted in the involvement of the species with catalytic activity. Presumably, the initially formed 1-alkene and 1,(n-1)-diene could be isomerized to the corresponding 2-alkenes and 1,(n-2)-diene by the metal-dihydride species.

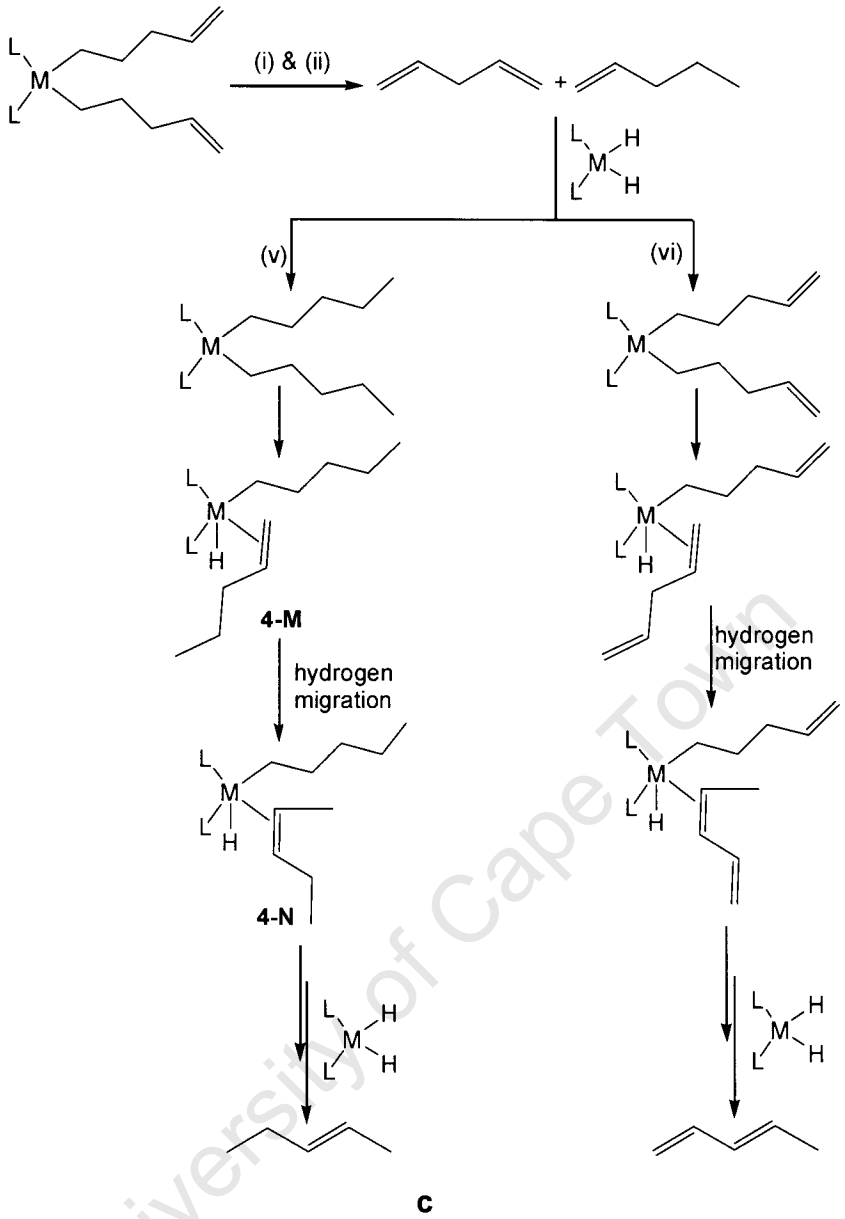
The results summarized above for the decomposition of the metal bis(1-alkenyl) complexes to give 1-alkene, 2-alkenes and dienes can be rationalized by the mechanism shown in Scheme 4-5 (bis(1-pentenyl) is used as model). Bis(1-pentenyl) complexes could initially undergo β-hydride elimination (i) to give 1,4-pentadiene and a metal hydridoalkenyl species **4-F**, which is followed by either β-hydride elimination or reductive elimination forming 1,4-pentadiene or 1-pentene (ii). The metal hydrido(1-alkenyl) **4-F** could occur via olefin coordination to form the intermediate **4-G** (iii). The conversation of **4-G** to **4-H**, a metal hydridoallyl species, could involve predominant [1,4] hydrogen migration. The corresponding metal hydrido(2-alkenyl) **4-I** could then be formed which could produce 2-pentenes and 1,3-pentadiene via route (ii) (see Scheme 4-5-a).



a



b



Scheme 4-5 The proposed mechanisms (**a**, **b** and **c**) for the formation of the major products on the decomposition of bis(1-pentenyl) complexes

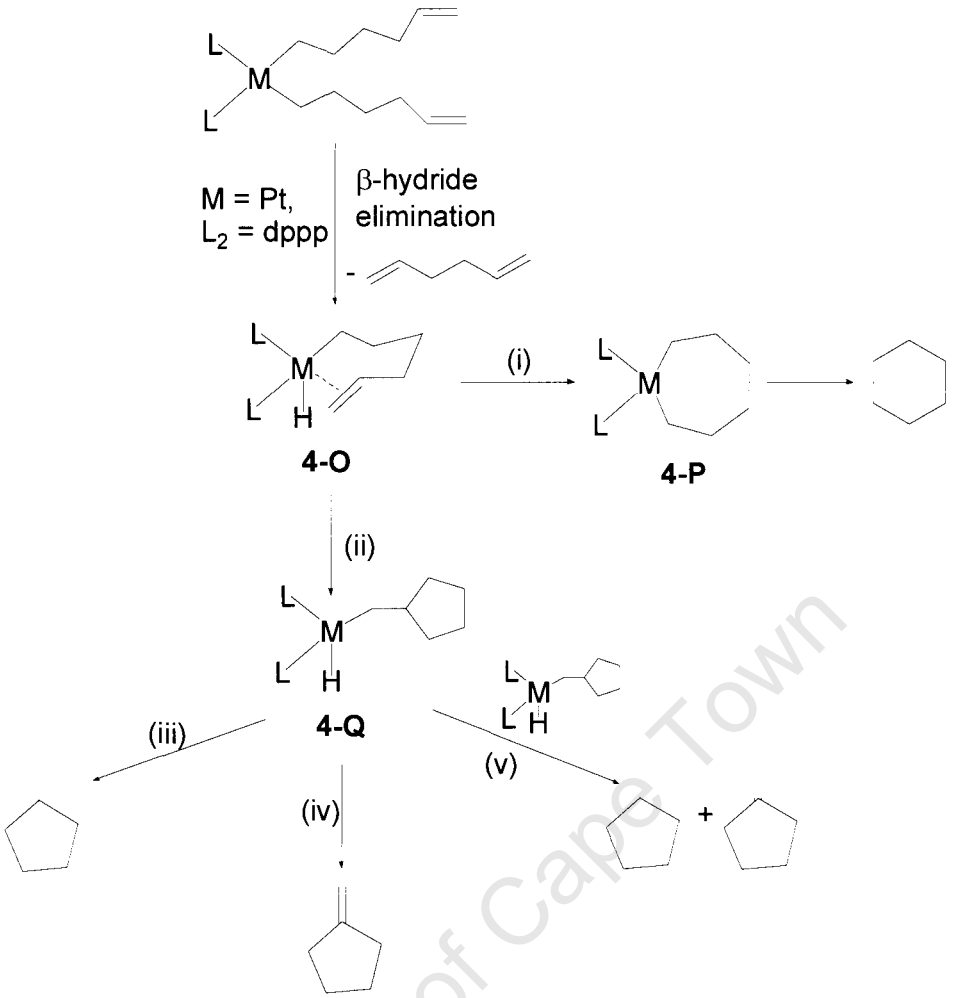
Scheme 4-5-b shows an alternative possible mechanism. Bis(1-pentenyl) complexes could firstly undergo the isomerization which involves the pendant alkene coordination forming **4-J** (iv). An allyl hydride intermediate **4-K** could be rearranged from **4-J** and then isomerization occurs to give the corresponding bis(2-pentenyl) complexes. The decomposition of bis(2-pentenyl)s could occur via route (i) and (ii) to give 2-pentenes and 1,3-pentadiene.

According to the observations by Moss *et al.* (see Eq. 4-18),[6] 2-pentenes and 1,3-pentadiene could also be produced probably by the selective isomerization of the corresponding 1-pentene and 1,4-pentadiene initially formed from bis(1-pentenyl) complexes in the presence of the catalytically active metal-dihydride species (v) and (vi). For the catalytic isomerization of 1-pentene, L_2MR_2 species could be formed by olefin coordination and followed by a β-hydrogen elimination step giving **4-M**. This species could be converted to **4-N** via hydrogen migration through an intermediate similar to **4-H**. The final step for this reaction is to release the catalytically active metal-dihydride species and give the isomerised product 2-pentene. The formation of 1,3-pentadiene could follow a similar route as described in route (vi) (see Scheme 4-5-c).

4.3.1.2. The minor decomposition pathways

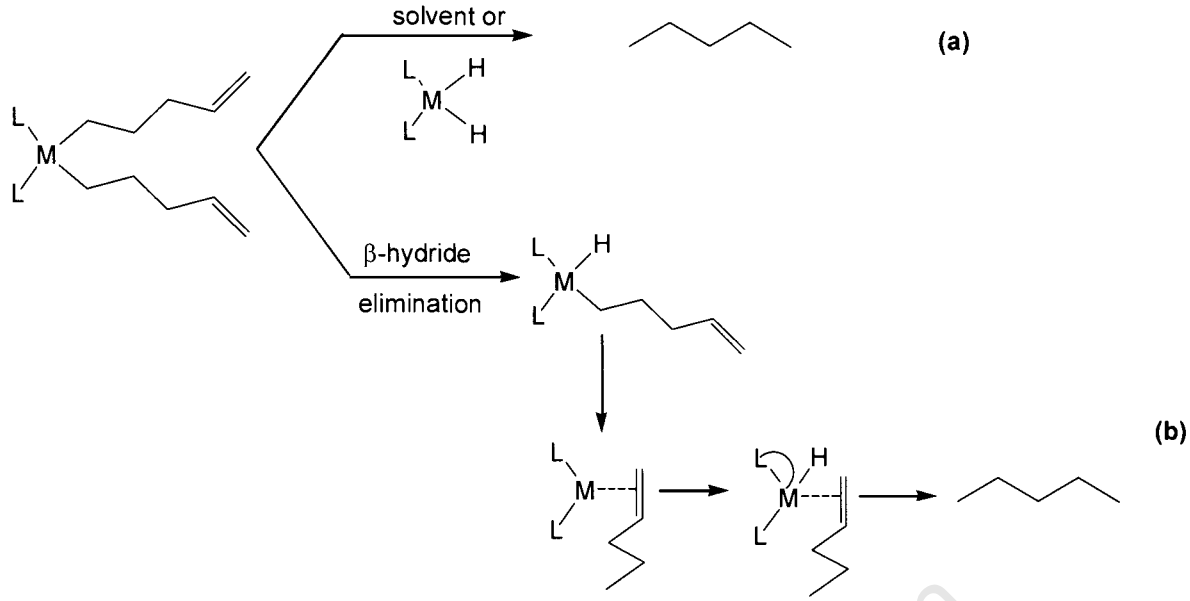
The thermal decomposition of bis(1-hexenyl)platinum(II) complexes **4-6**, **4-7** and the complexes with longer alkenyl chains **4-8**, **4-9** gave some cyclic products in small amounts, which suggests an additional thermolysis pathway. The possible mechanism of the formation of these cyclic products according to complex **4-7** is shown in Scheme 4-6, which is similar to the one reported by Overett and co-workers.[21]

This may take place via a formal β-hydride elimination releasing 1,5-hexadiene from complex **4-7** to form the 1-hexenyl moiety **4-O**, which could undergo a subsequent cyclization to form either a metallacycle intermediate **4-P** followed by reductive elimination giving cyclohexane (i), or a cyclopentylmethyl hydride species **4-Q** (ii). The intermediate **4-Q** undergoes reductive elimination to give methylcyclopentane (iii) and β-hydride elimination to give methylenecyclopentane(iv). Alternatively, **4-Q** undergoes a disproportionation process to yield methylcyclopentane and methylenecyclopentane (v).[21]



Scheme 4-6. Postulated mechanisms for the formation of cyclohexane, methylcyclopentane and methylenecyclopentane from bis(1-hexenyl)(dppp)platinum(II) 7.

The formation of n-alkane was also found in the decomposition of several bis(1-alkenyl) metal complexes: the thermolysis of bis(1-pentenyl)palladium(II) complex with PPh_3 **4-12** gave n-pentane and 1-decane; n-hexane was formed from the decomposition of bis(1-hexenyl)platinum(II) complex **4-7**, and the decomposition of bis(1-pentenyl)iridium complexes **4-17** as well **4-18** produced very small amounts of n-pentane. There are two possible pathways for the formation of n-alkane as described in scheme 4-7. The bis(1-alkenyl) metal complex could abstract the extra hydrogen atom from a metal-hydride species or solvent via an intermolecular hydrogen transfer (a), or a reaction that transfers hydrogen intramolecularly from the *o*-position on phosphine ligands (b).



Scheme 4-7. Proposed mechanism for the formation of n-alkane.

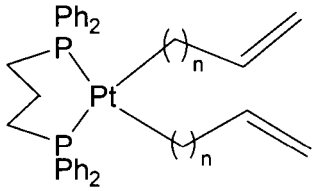
4.3.2. General factors affecting the thermal decomposition of metal bis(1-alkenyl) complexes

Taking all the decomposition results together, there are three main factors that affect the thermolysis patterns of the metal bis(1-alkenyl) complexes: the length of the alkenyl chains, the nature of supporting ligands and the nature of metal centres.

4.3.2.1. Changes in the length of the alkenyl chains

Andersen and Moss investigated the carbonylation and decarbonylation reactions of an extensive series of manganese pentacarbonyl alkyl and acyl compounds and they found that the length of the alkyl chains has a combination of steric and electronic effects on the rates of both reactions.[22] More recently, the length of the alkenyl chains was found to strongly affect the isomerizations of (dppp)bis(1-alkenyl)platinum(II) complexes to their corresponding bis(2-alkenyl) complexes, *i.e.*, the longest chain investigated is the fastest to undergo isomerization.[6] The reduction in melting points of these complexes by the longer

alkenyl chains is another manifestation of this effect (Fig. 4-2).[4] In this study, changing of the length of the alkenyl chains had a significant effect on the pathways of thermolysis of bis(1-alkenyl) complexes.



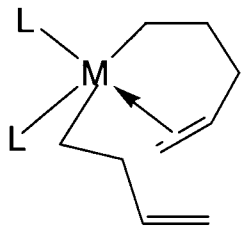
4-1, n = 2 oil;
4-3, n = 3, 120 - 122 °C (m.p.);
4-7, n = 4, 108 - 110 °C (m.p.);
4-8, n = 6, 80 - 82 °C (m.p.);
4-9, n = 8 oil.

Fig. 4-2. Melting points for (dppp)bis(1-alkenyl)platinum(II) complexes

Changing the length of the alkenyl chains generally effects a change in decomposition patterns. On the decomposition of (dppp) bis(1-alkenyl)platinum(II) complexes, the formation of the products expected to occur via the isomerizations, *i.e.*, 2-alkenes and 1,(n-2)-diene, increased on going from butenyl chain to higher alkenyl chain, as shown in Table 4-6.

On the other hand, the β-hydride elimination pathway appeared to be more and more predominant when the pendant alkene is smaller. Thus chain length 4 gives 100% 1,(n-1)-diene and chain length 10 only gives 5% (see Table 4-6). The typical cases are the (dppp)bis(1-butenyl)platinum(II) **4-1** and the complex with unsymmetrical alkenyl groups **4-11**. β-hydride elimination was the only one pathway on the decomposition of **4-1** (see Eq. 4-6). And for **4-11**, the butenyl chain released was also via β-hydride elimination (see Eq. 4-7). As far as we are aware, this sort of behaviour has not been observed previously. As discussed in the proposed mechanisms (see section **4.3.1.1**), β-hydride elimination and isomerization could be two competitive steps on the decomposition of bis(1-alkenyl) complexes. The isomerizations probably involve an intermediate like **4-J**. It is

much more likely for the long alkenyl chains to coordinate to the metal centre to achieve this intermediate, while it seems not to occur for the very short butenyl chain due to the strain in the small rings. Thus, for complexes **4-1** and **4-11**, β-hydride elimination predominated to form 1,3-butadiene when the isomerization was unlikely.



4-J

Table 4-6. The effect of the length of alkenyl chains of the decomposition patterns of (dppp)bis(1-alkenyl)platinum(II) complexes.

Complex	Chain length[a]	2-Alkenes and 1,(n-2)-diene[b] (%)	1-(n-1)-Diene[c] (%)
4-1	4	0	100
4-3	5	42	53
4-7	6	56	12
4-8	8	61	16
4-9	10	65	5

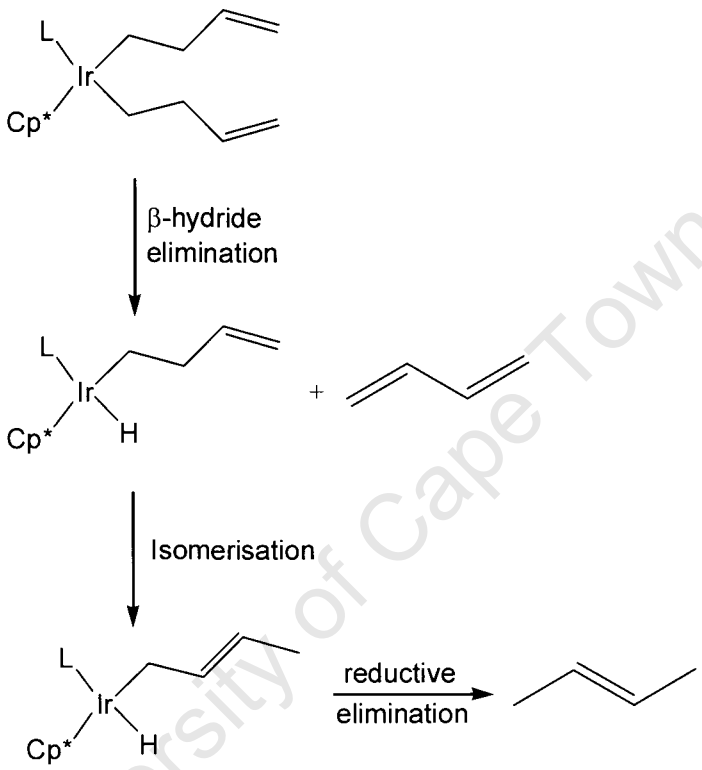
[a] The number of carbon atoms in the alkenyl chain

[b] Expected to be formed via isomerization.

[c] Expected to be formed via β-hydride elimination.

Only two different alkenyl chains were involved in the bis(1-alkenyl)iridium(III) complexes, however, their decomposition results showed a similar effect of the chain length on the decomposition pathways. For the bis(1-butenyl) complexes (see Eq. 4-13), the decomposition occurred via initial β-hydride elimination to

release 1,3-butadiene from one butenyl group and to form a metal hydrido(1-butenyl) species. This was followed by the isomerization to the corresponding metal hydrido(2-butenyl) species and gave 2-butene by reductive elimination (Scheme 4-8). In contrast, the decomposition pathways for bis(1-pentenyl)iridium(III) complexes are similar to described in Scheme 4-5.



Scheme 4-8. The possible decomposition pathways for bis(1-butenyl)iridium(III) complexes.

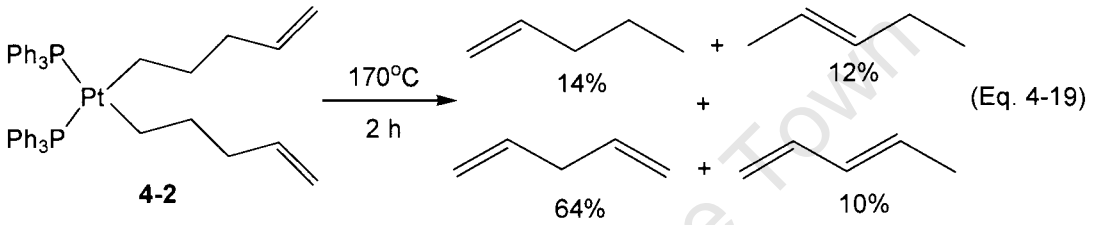
Changing the length of the alkenyl chains has a significant effect on the thermal decomposition of bis(1-alkenyl) complexes according to our present results. This affects not only the decomposition patterns but also the product distributions of the title complexes.

4.3.2.2. Changes of supporting ligands

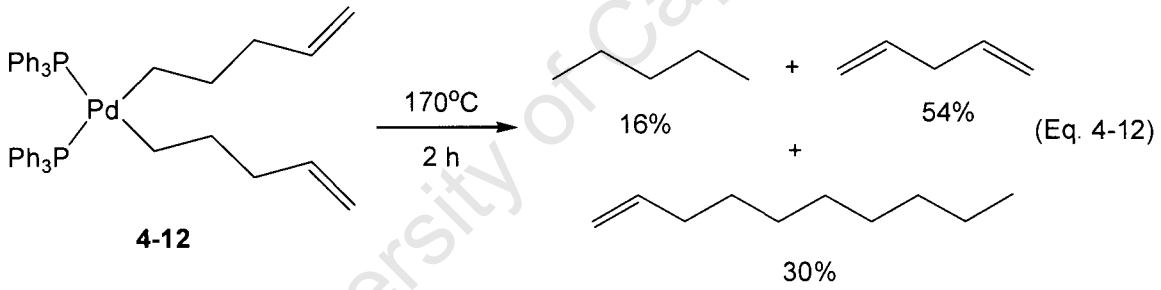
The nature of supporting ligands was found to affect the thermal stability[6] and

reactivity[7] of metal bis(1-alkenyl) complexes. This also has an important effect on the decomposition pathway and product distribution of the bis(1-alkenyl) complexes according to this study.

It was found that the decomposition of bis(1-alkenyl) complexes with PPh_3 ligands mainly occurred via β-hydride elimination (see Eqs. 4-19 & 4-12). This could be due to the phosphine dissociation to give a three-coordinated intermediate, which is favourable for β-hydride elimination.

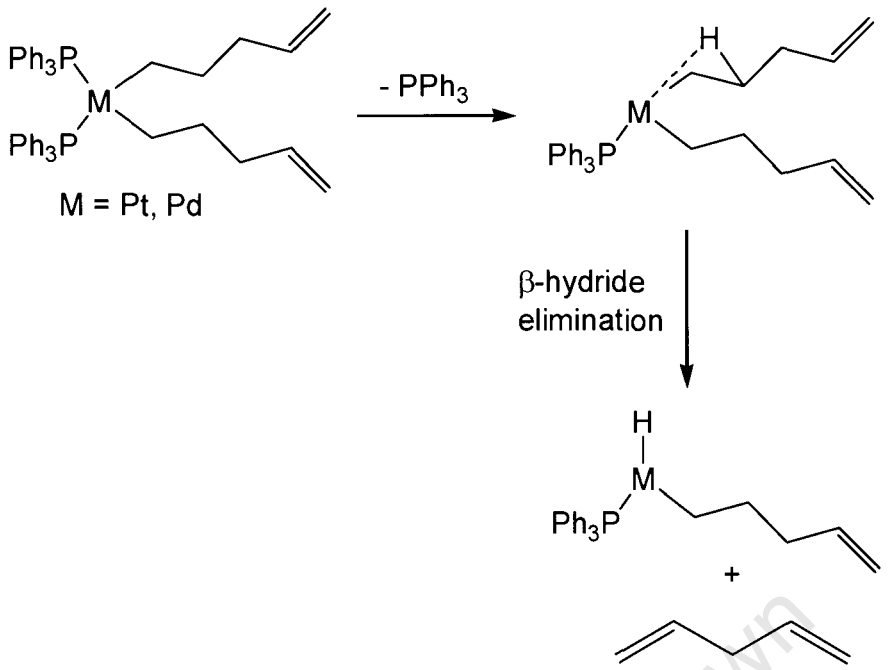


(Eq. 4-19)



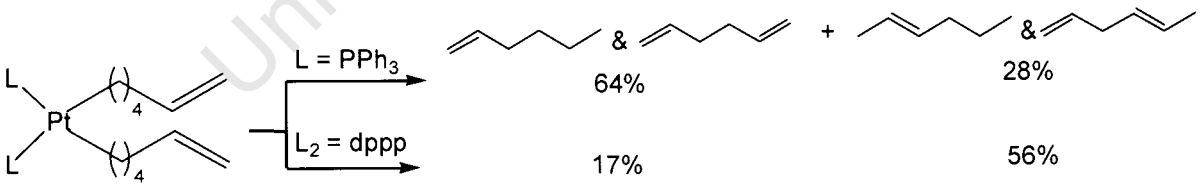
(Eq. 4-12)

Thorn and Hoffmann concluded from a theoretical investigation that β-hydride elimination proceeds much more readily from a three-coordinate d^8 intermediate.[23] Furthermore, Whitesides and co-workers extensively studied the decomposition of L_2PtR_2 (L = phosphine; R = alkyl) and found that the lowest energy β-hydride eliminations occur in systems where a phosphine dissociates to give a three-coordinate $LPtR_2$ intermediate.[24] Our results are consistent with these previous reports (Scheme 4-9).



Scheme 4-9

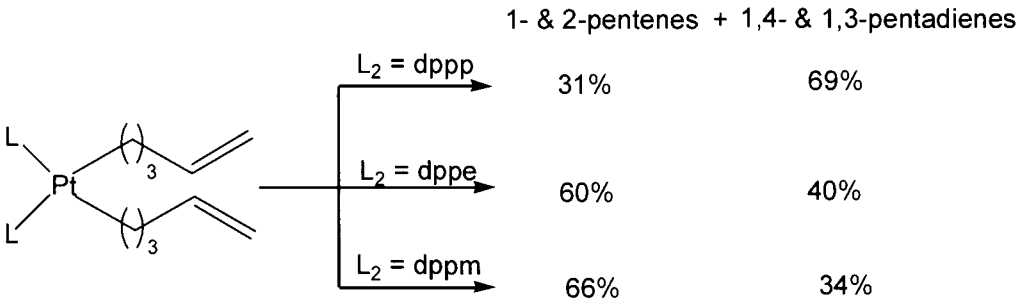
When phosphine dissociation is inhibited by using a chelating phosphine, β-hydride elimination is severely retarded, while the isomerizations become the major decomposition pathways for the bis(1-alkenyl) complexes. As shown in Eq 4-20, the products due to isomerization, 2-hexene and 1,4-hexadiene are much more prevalent for the complex with dppp ligand than that for the complex with PPh_3 ligands. This could be due to the chelating effect of the diphosphines.



(Eq. 4-20)

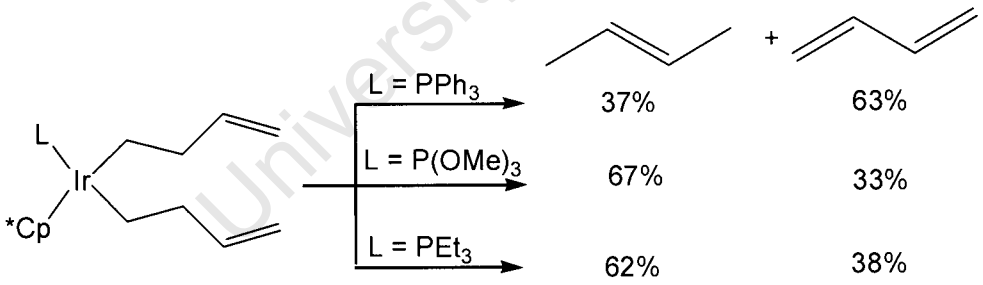
The nature of the bite angle of diphosphine ligands plays an important role in certain reaction such as metal-catalyzed C-C bond formation,[25] and also affects the decomposition patterns of bis(1-pentenyl)platinum(II) complexes, leading to the different product distributions (Eq. 4-21). The formation of 1- and 2-pentenes is

typically accelerated by the presence of ancillary diphosphine ligands with decreased bite angles (bite angle for dppp: 91°, dppe: 85°, dppm: 72°),[26] while the formation of dienes behaves in the opposite way.



(Eq. 4-21)

In contrast, for the bis(1-alkenyl)iridium(III) complexes, the steric effect exerted by the monophosphines becomes eased and the electronic effects predominate. The electron-donating ability of these monophosphine ligands is as follows: PEt_3 > $P(OMe)_3$ > PPh_3, which influences the stability of the bis(1-alkenyl)iridium to follow the same order.[18] Thus, the most unstable PPh_3-coordinated complexes underwent β-hydride elimination more readily than other complexes (Eq. 22).

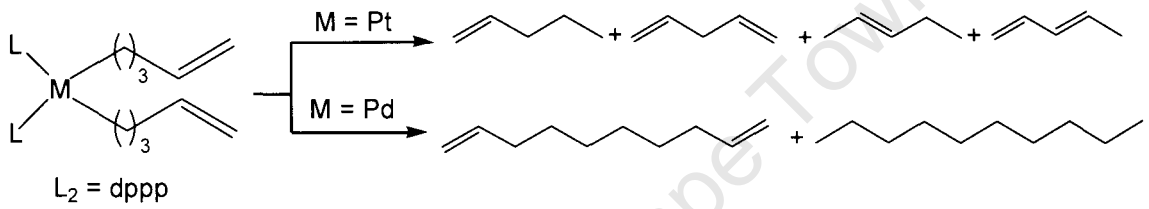


(Eq. 4-22)

It is found from the above investigations that the decomposition pathways and product distributions on the thermolysis of bis(1-alkenyl) complexes is strongly dependent on the nature of the supporting ligands which may be due to differences in steric, electronic and chelating effects in the ligands.

4.3.2.3. Changes of metal centre

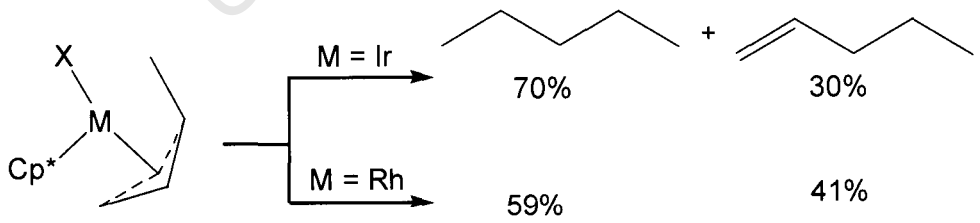
Comparisons are only made within an isostructural series, *i.e.*, the complexes with the same ligand systems and same alkenyl chains. We draw attention to the bis(1-pentenyl)platinum(II) complex **4-13** (where L_2 = dppe) and relatively unstable palladium analogs **4-4**. In contrast to the occurrence of reductive elimination of two pentenyl groups from complex **4-13**, the thermolysis of complex **4-4** liberated pentenes and pentadienes, indicating β-hydride elimination/reductive elimination and isomerization pathways are operative (Eq. 4-23).



L_2 = dppp

(Eq. 4-23)

For the group 9 bis(1-alkenyl) complexes, only the iridium ones were successfully prepared. Nevertheless, the effect of the metal centre was also observed in their allyl complexes, which did not affect the decomposition patterns but did change the product distributions (*eg.* Eq. 4-24).

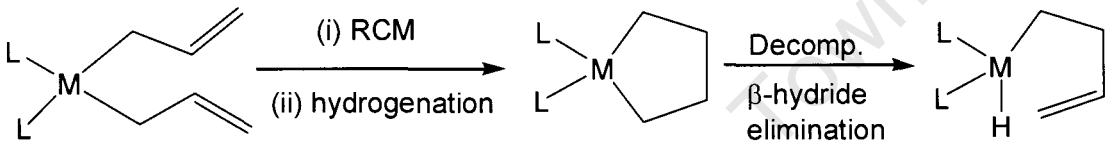


(Eq. 4-24)

Therefore, the metal centre plays an important role in the decomposition of the bis(1-alkenyl) complexes.

4.3.2.4. Relationship between the thermal decomposition of metal bis(1-alkenyl) complexes and metallacycloalkanes

Bis(1-alkenyl) metal complexes have been shown to be novel precursors for the preparation of a range of metallacycloalkenes through the ring closing metathesis (RCM) reaction.[2,4] On the other hand, it is also believed that metal alkenyl species may be important intermediates in the decomposition of metallacycloalkanes through β-hydride elimination.[27] The relationship between metal alkenyls and metallacycloalkanes could be described in Eq. 4-25.



(Eq. 4-25)

Thermal decomposition pathways of metal-bis(alkenyl) complexes may be similar to those of metallcycles, while the products formed can differ considerably because of the pendant alkene functionality. From our preliminary thermal decomposition studies, some interesting relationships have been observed between these two classes of complexes.

We found their similarities on decomposition: (i) both of these two classes of complexes could decompose to give useful organic products such as 1-alkene, 2-alkenes and dienes, indicating β-hydride elimination and reductive elimination are the key steps in the decomposition mechanisms for both; (ii) the combination effects of metal, supporting ligand and pendant functionality size (*i.e.*, ring size and the length of the alkenyl chains) influence the decomposition patters and product distributions for both metallacycloalkanes and bis(1-alkenyl) complexes. One may get the desired organic product from the decomposition of the complexes by adjusting these factors.

On the other hand, the differences on decomposition exerted by the different pendant functionality were also concluded: (i) the formation of n-alkane was observed in the decomposition of most metallacycloalkanes, which could be due to the hydrogenation by the metal hydride species or the ortho phosphines (see **Chapter 3**, section **3.3.1.3**), while this decomposition pathway emerges rarely in the thermolysis of bis(1-alkenyl) complexes; (ii) isomerization predominates in the thermal decomposition of bis(1-alkenyl) complexes to give 2-alkenes and 1,(n-2)-dienes; however, for metallacycloalkanes this remains a minor decomposition pathway.

4.4. Conclusions

Thermal decomposition studies have been carried out on an extensive series of bis(1-alkenyl) metal complexes, which are important precursors for preparing metallacycloalkanes. Taking all our results into account, we can make the following general conclusions based on the evidences obtained:

1. We find that the formation of products and product distributions depend on the length of the alkenyl chains, the nature of the supporting ligands and the metal centres. This may be a consequence of different decomposition pathways. Thus we can change decomposition products by changing the ligand, the metal or the length of the alkenyl chains.
2. We believe that the major decomposition pathways for the title complexes involve β-hydride elimination and/or reductive elimination as well as isomerization. Mechanisms for the major and minor decomposition pathways have been proposed.
3. According to the decomposition products obtained, we find that the bis(1-alkenyl) complexes with shortest chain, *i.e.*, C_4, favor β-hydride elimination, while those with longer chains ($\geq C_5$) undergo β-hydride elimination and/or reductive elimination as well as isomerization pathways.

The formation of the isomeric products, 2-alkenes and 1,(n-2)-diene, increases with increasing chain length.

4. The relationship between the decomposition of metallacycloalkanes and bis(1-alkenyl) complexes has been briefly summarized as a result of the present studies.

These results may pertain to bis(1-alkenyl) complexes acting as intermediates in catalytic reactions.

4.5. References

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Chapter 5

Experimental

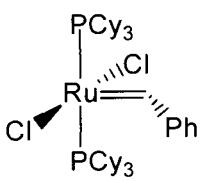
5.1 General and Instrumental

5.1.1 General methods

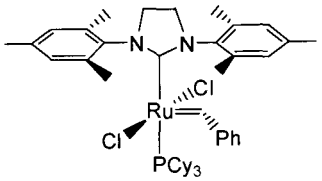
Preparation of organometallic materials was carried out under argon or nitrogen using a dual vacuum/nitrogen line and standard Schlenk line techniques unless otherwise stated. Solvents for organometallics were purified by distillation under an inert atmosphere over a suitable drying agent. Diethyl ether and tetrahydrofuran were distilled from sodium wire and benzophenone. Dichloromethane was dried over calcium hydride (CaH_2). Hexane and pentane were distilled from ^tBuLi and 2,2'-bipyridine. Benzene was distilled from sodium melt. All solvents were freshly distilled before use. Organometallic complexes were stored in the dark at ambient temperature in glass-stoppered vessels initially filled with argon or nitrogen. Prior to analyses or thermolytic studies, each was dried in vacuo for at least 3 hours at ambient temperature. Thermal decompositions and kinetics[1] were carried out under anhydrous, oxygen-free conditions.

$PdCl_2$ was obtained from Johnson Matthey. Grubbs' 1st generation catalyst[a] and 2nd generation catalyst[b] were purchased from Aldrich Chemical Co. The alkane and alkene standards were purchased from Aldrich, purity shown in parentheses: pentane (99%), 1-pentene (99%), 2-pentenes (95%), hexane (95%), 1-hexene

a



b



(97%), 2-hexenes (85%), 1,5-hexadiene (97%), cyclohexane (99%), heptane (97%), 1-heptene (97%), octane (98%), 1-octene (98%), trans-2-octene (97%), trans-3-octene (98%), 1,7-octadiene (99%), cyclooctane (99%), nonane (99%), 1-nonene (98%), decane (99%), 1-decene (94%), undecane (99%), 1-undecene (97%), dodecane (99%), 1-dodecene (95%), chlorobenzene (99%). All other reagents were obtained commercially from Aldrich and, unless otherwise stated, were used as received without further purification.

$(COD)PdCl_2$[2], $(dppe)PdCl_2$[3] were prepared by literature methods. All compounds of platinacycloalkane and their bis(alkenyl) precursors were prepared as previously reported.[4] The rhodium complexes were prepared by E. Hager.[5] Some of the palladium complexes were synthesized by T. Mahamo.[6]

5.1.2 Instrumental

Melting points were determined using a Kofler hot stage microscope (Riechert Thermovar). ^1H NMR was obtained using chloroform-d1, benzene-d6 with Varian XR300 MHz and XR400 MHz spectrometers. All ^1H chemical shifts are reported relative to the residual proton resonance in the deuterated solvents. ^{31}P NMR spectra were recorded on Varian XR400. Elemental analysis was carried out at the University of Cape Town using a Fisons EA 1108 CHNS Elemental Analysis apparatus at the University of Cape Town. Mass spectra were recorded at the University of Witwatersrand. Gas chromatographic analyses were performed on a Varian 3900 instrument and GC-MS analyses were carried out with an Agilent 5973 instrument (columns see later).

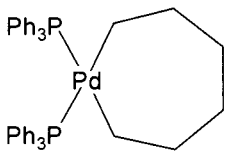
5.2 Experimental details pertaining to Chapter 2

5.2.1 Preparation of Grignard Reagents

Alkenyl Grignard reagents were prepared by reaction of the appropriate alkenyl bromide and excess magnesium turnings in dry diethyl ether.[7] A three-necked round-bottomed flask fitted with a dropping funnel and a reflux condenser was charged with the appropriate amount of magnesium turnings. The system was evacuated under vacuum and then flushed with nitrogen or argon three times. Dry diethyl ether was then added to the flask with stirring. A solution of the alkyl bromide in dry diethyl ether was placed in the dropping funnel and this solution was added drop-wise to the round-bottomed flask. When the reaction mixture started refluxing the flask was placed in an ice bath at 0 °C and was kept in the cold bath until the reaction was complete (*ca.* 5 hours). When the reaction was complete the Grignard reagents were transferred into Teflon-valve storage bottles under an inert atmosphere and were then stored under vacuum at 0°C. The same procedure was followed for the preparation of di-Grignard reagents except that terminal di-bromoalkyls were used and dry tetrahydrofuran was used as a solvent instead of diethyl ether. The reaction conditions were monitored more closely in the preparation of di-Grignard reagents as these reactions occur more vigorously than those of Grignard reagents. The reactions were also carried out in highly dilute solutions with a large excess of magnesium turnings to avoid polymerization. Concentration determination was done by taking the Grignard reagent (1 ml) and hydrolyzing it with water (2 ml). An indicator (phenolphthalein, 2 or 3 drops) was added and HCl (0.1 M, 20 ml) was added. The solution was then back-titrated with NaOH (0.1 M) and the concentration of the Grignard was calculated.

5.2.2. Synthesis of palladacycloalkanes and their precursors

Palladacycloheptane (L = PPh_3) (**2-9**)



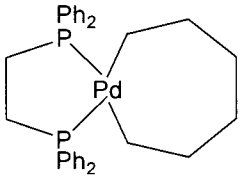
A Schlenk flask was charged with (COD)$PdCl_2$ (0.43 g, 1.51 mmol) and diethyl ether (15 ml). The mixture was cooled to -78°C and a solution of $BrMg(CH_2)_2CH=CH_2$ (1.69 M, 2.7 ml, 4.52 mmol) in diethyl ether solution was slowly added. The solution was stirred for 40 minutes, then warmed to room temperature and stirred for another 20 minutes. The reaction was quenched by adding a saturated aqueous solution of NH_4Cl (5 ml). The product was extracted with hexane and the organic layer was collected and dried over anhydrous $MgSO_4$. Excess solvent was removed under reduced pressure and the product was obtained as bright yellow oil, which was then dried under vacuum. The yellow oil obtained was dissolved in Et_2O and PPh_3 (0.40 g, 1.51 mmol) was added. The solution was stirred for 1 hour at room temperature, after which the solvent was removed and the product was obtained as bright yellow oil **2-1** (0.59 g, 52%). ^{1}H-NMR (C_6D_6): 7.32 – 7.64 (30H, m, Ph), 5.68 (2H, m, =CH), 4.87 – 4.96 (4H, m, $=CH_2$), 1.32 – 2.29 (8H, m, CH_2). ^{31}P-NMR: 28.7 (PPh_3).

To a solution of **2-1** (0.36 g, 0.50 mmol) in benzene (30 ml), Grubbs' second generation catalyst was added. The mixture was refluxed with stirring at 50°C for 18 hrs, and then cooled to room temperature. The solvent was removed under reduced pressure gave a maroon residue which was extracted with hexane (4 x 5 ml). The product was obtained as brown oil **2-5** (0.25 g, 71%). ^{1}H-NMR: 7.34 – 7.69 (30H, m, Ph), 5.36 (2H, m, =CH), 2.27 (4H, m, CH_2), 1.48 (4H, m, Pd-CH_2). ^{31}P-NMR: 27.9 (PPh_3).

To the solution of **2-5** (0.22 g, 0.30 mmol) in Et_2O (20 ml), 10% Pd/C (22 mg) was

added. The solution was stirred under hydrogen (a take-off fitted with a tap was attached to a balloon and this balloon was filled with hydrogen gas) for 46 hrs. The mixture was then filtered and excess solvent was removed under reduced pressure and the product was obtained as a brownish yellow solid **2-9** (0.20 g, 91%), melting point: 52 - 58°C (with decomposition). ^{1}H-NMR: 7.21 – 7.68 (30H, m, Ph), 2.09 – 2.32 (8H, m, CH_2), 1.93 (4H, m, Pd-CH_2). ^{31}P-NMR: 27.8 (PPh_3).

*Palladacycloheptane (L_2 = dppe) (**2-10**):*



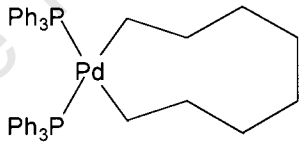
A solution of $BrMg(CH_2)_2CH=CH_2$ (1.69 M, 2.6 ml, 4.50 mmol) in Et_2O was slowly added to a suspension of (COD)$PdCl_2$ (0.42 g, 1.50 mmol) in Et_2O (15 ml) at -78°C. The suspension was stirred for 40 minutes, then warmed to room temperature and stirred for another 20 minutes. The reaction was quenched by adding a saturated aqueous solution of NH_4Cl (5 ml). The product was extracted with hexane and the organic layer was collected and dried over anhydrous $MgSO_4$. Excess solvent was removed under reduced pressure and the product was obtained as bright yellow oil, which was then dried under vacuum. The yellow oil obtained was dissolved in Et_2O and dppe (0.38 g, 1.50 mmol) was added. The solution was stirred for 1 hour at room temperature, after which the solvent was removed and the product was obtained as bright yellow oil ***2-2*** (0.52 g, 46%). ^{1}H-NMR: 7.48 – 7.83 (20H, m, Ph), 5.87 (2H, m, =CH), 4.84 – 5.07 (4H, m, $=CH_2$), 2.78 (4H, d, P-CH_2), 1.57 – 2.29 (8H, m, CH_2),. ^{31}P-NMR: 31.6 (-PPh_2).

To a solution of **2-2** (0.36 g, 0.50 mmol) in benzene (30 ml), Grubbs' second generation catalyst was added. The mixture was refluxed with stirring at 50°C for 18 hrs, and then cooled to room temperature. The solvent was removed under reduced pressure to give a maroon residue which was extracted with hexane (4 x 5 ml). The product was obtained as brown oil **2-6** (0.285 g, 82%). ^{1}H-NMR: 7.26 –

7.81 (20H, m, Ph), 5.36 (2H, m, =CH), 2.54 (4H, d, P-CH_2), 1.63 – 2.05 (8H, m, CH_2). ^{31}P-NMR: 32.6 (-PPh_2).

10% Pd/C (20 mg) was added to the solution of **2-6** (0.21 g, 0.29 mmol) in Et_2O (20 ml). The solution was stirred under hydrogen (a take-off fitted with a tap was attached to a balloon and this balloon was filled with hydrogen gas) for 46 hrs. The mixture was then filtered and excess solvent was removed under reduced pressure and the product was obtained as a brownish yellow solid **2-10** (0.16 g, 78%), Melting point: 62 - 75°C (with decomposition). ^{1}H-NMR: 7.08 – 7.79 (20H, m, Ph), 2.74 (4H, d, P-CH_2), 1.69 – 2.13 (m, 8H, CH_2), 1.43 (4H, m, Pd-CH_2). ^{31}P-NMR: 31.3 (-PPh_2).

*Palladacyclononane (L = PPh_3) (**2-11**):*

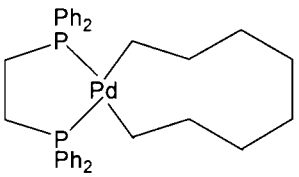


A solution of $BrMg(CH_2)_3CH=CH_2$ (2.39 M, 2.0 ml, 4.78 mmol) in Et_2O was slowly added to a suspension of (COD)$PdCl_2$ (0.42 g, 1.50 mmol) in Et_2O (15 ml) at -78°C. The suspension was stirred for 40 minutes, then warmed to room temperature and stirred for another 20 minutes. The reaction was quenched by adding a saturated aqueous solution of NH_4Cl (5 ml). The product was extracted with hexane and the organic layer was collected and dried over anhydrous $MgSO_4$. Excess solvent was removed under reduced pressure and the product was obtained as bright yellow oil, which was then dried under vacuum. The yellow oil obtained was dissolved in Et_2O and PPh_3 (0.40 g, 1.50 mmol) was added. The solution was stirred for 1 hour at room temperature, after which the solvent was removed and the product was obtained as bright yellow oil **2-3** (0.56 g, 50%). ^{1}H-NMR (C_6D_6): 7.02 – 7.38 (30H, m, Ph), 5.80 (2H, m, =CH), 5.02 (4H, m, =CH_2), 1.98 (4H, m, CH_2), 1.19 – 1.41 (8H, m, Pd-CH_2-CH_2). ^{31}P-NMR: 26.3 (PPh_3).

To a solution of **2-3** (0.36 g, 0.50 mmol) in benzene (30 ml), Grubbs' second generation catalyst was added. The mixture was refluxed with stirring at 50°C for 18 hrs, and then cooled to room temperature. The solvent was removed under reduced pressure to give a maroon residue which was extracted with hexane (4 x 5 ml). The product was obtained as brown oil **2-7** (0.29 g, 83%). ^{1}H-NMR (C_6D_6): 7.37 – 7.85 (30H, m, Ph), 5.52 (2H, m, =CH), 1.61 – 2.23 (8H, m, CH_2), 1.38 (4H, m, Pd-CH_2). ^{31}P-NMR: 27.5 (PPh_3).

10% Pd/C (22 mg) was added to the solution of **2-7** (0.22 g, 0.30 mmol) in Et_2O (20 ml). The solution was stirred under hydrogen (a take-off fitted with a tap was attached to a balloon and this balloon was filled with hydrogen gas) for 46 hours. The mixture was then filtered and excess solvent was removed under reduced pressure and the product was obtained as a brownish yellow solid **2-11** (0.16 g, 76%), melting point: 42 - 49°C (with decomposition). ^{1}H-NMR: 7.52 – 7.86 (30H, m, Ph), 1.08 – 1.53 (12H, m, CH_2), 0.79 (4H, m, Pd-CH_2). ^{31}P-NMR: 25.8 (PPh_3).

*Palladacyclononene (L_2 = dppe) (**2-12**):*



A solution of $BrMg(CH_2)_3CH{=}CH_2$ (2.39 M, 2.0 ml, 4.78 mmol) in Et_2O was slowly added to a suspension of (COD)$PdCl_2$ (0.42 g, 1.50 mmol) in Et_2O (15 ml) at -78°C. The suspension was stirred for 40 minutes, then warmed to room temperature and stirred for another 20 minutes. The reaction was quenched by adding a saturated aqueous solution of NH_4Cl (5 ml). The product was extracted with hexane and the organic layer was collected and dried over anhydrous $MgSO_4$. Excess solvent was removed under reduced pressure and the product was obtained as bright yellow oil, which was then dried under vacuum. The yellow oil obtained was dissolved in Et_2O and dppe (0.38 g, 1.50 mmol) was added. The solution was stirred for 1 hour at room temperature, after which the solvent was

removed and the product was obtained as bright yellow oil **2-4** (0.59 g, 52%). ^{1}H-NMR (C_6D_6): 7.33 – 7.68 (20H, m, Ph), 5.74 (2H, m, =CH), 4.82 – 4.97 (4H, m, $=CH_2$), 2.49 (4H, d, P-CH_2), 2.18 (4H, m, CH_2), 1.25 – 1.82 (8H, m, Pd-CH_2-CH_2). ^{31}P-NMR: 29.3 (-PPh_2).

To a solution of **2-4** (0.36 g, 0.50 mmol) in benzene (30 ml), Grubbs' second generation catalyst was added. The mixture was refluxed with stirring at 50°C for 18 hrs, and then cooled to room temperature. The solvent was removed under reduced pressure to give a maroon residue which was extracted with hexane (4 x 5 ml). The product was obtained as brown oil **2-8** (0.27 g, 79%). ^{1}H-NMR (C_6D_6): 7.40 – 7.65 (20H, m, Ph), 5.46 (2H, m, =CH), 2.49 (4H, t, P-CH_2), 1.89 – 2.29 (8H, m, CH_2), 1.73 (4H, m, Pd-CH_2). ^{31}P-NMR: 31.9

10% Pd/C (20 mg) was added to the solution of **2-8** (0.19 g, 0.30 mmol) in Et_2O (20 ml). The solution was stirred under hydrogen (a take-off fitted with a tap was attached to a balloon and this balloon was filled with hydrogen gas) for 46 hrs. The mixture was then filtered and excess solvent was removed under reduced pressure and the product was obtained as a brownish yellow solid **2-12** (0.19 g, 90%), melting piont: 55 - 67°C (with decomposition). ^{1}H-NMR (C_6D_6): 7.03 – 7.65 (20H, m, Ph), 2.06 (4H, t, P-CH_2), 1.48 (8H, m, CH_2), 0.90 – 1.28 (8H, m, Pd-CH_2-CH_2). ^{31}P-NMR: 32.6 (-PPh_2).

5.2.3. Synthesis of palladacycloalkanes by di-Grignard route

*Palladacycloheptane (L_2 = dppe) (**2-10**):*

An excess of a solution of $BrMg(CH_2)_6MgBr$ (0.78 M, 1 ml, 0.78 mmol) in anhydrous THF was slowly added to a suspension of (dppe)$PdCl_2$ (0.29 g, 0.5

mmol) in dry Et_2O in a Schlenk tube. The mixture was cooled to -78°C and stirred for 30 minutes, then warmed to room temperature. The mixture was stirred for another 5 hours. The reaction was quenched by adding a saturated solution of NH_4Cl (5 ml). The product was extracted with hexane and the organic layer was collected and dried over anhydrous $MgSO_4$. Excess solvent was removed under reduced pressure and the product was obtained as brown yellow solid (yield: 0.12 g, 42%). Melting point: 58 - 72°C (with decomposition). ^{1}H-NMR (C_6D_6): 6.94 – 7.00 (10H, m, Ph), 7.62 – 7.73 (10H, m, Ph), 2.67 (4H, d, P-CH_2), 1.23 – 1.32 (m, 8H, CH_2), 0.87 (m, 4H, Pd-CH_2). ^{31}P-NMR: 30.8 (-PPh_2). Mass spec. (FAB): m/z 589.0 $[M]^+$, 575 $[M\text{-}CH_2]^+$, 484 $[M\text{-}(CH_2)_2\text{-}Ph]^+$, 347 $[M\text{-}(C_6H_{16})\ \text{-}(Ph)_2]^+$, 603 $[M+CH_2]^+$, 631 $[M+(CH_2)_3]^+$.

*Palladacyclononane (L_2 = dppe) (**2-12**):*

An excess of a solution of $BrMg(CH_2)_8MgBr$ (0.37 M, 2.0 ml, 0.74 mmol) in anhydrous THF was slowly added to a suspension of (dppe)$PdCl_2$ (0.29 g, 0.5 mmol) in dry Et_2O in a Schlenk tube. The mixture was cooled to -78°C and stirred for 30 minutes, then warmed to room temperature. The mixture was stirred for another 5 hours. The reaction was quenched by adding a saturated solution of NH_4Cl (5 ml). The product was extracted with hexane and the organic layer was collected and dried over anhydrous $MgSO_4$. Excess solvent was removed under reduced pressure and the product was obtained as brown yellow solid (yield: 0.17 g, 54%). Melting point: 58 - 72°C (with decomposition). ^{1}H-NMR (C_6D_6): 7.08 (10H, m, Ph), 7.63 (10H, m, Ph), 1.81 – 2.01 (4H, t, P-CH_2), 0.87 – 1.52 (16H, m, CH_2). ^{31}P-NMR: 32.9 (-PPh_2). Mass spec. (FAB): m/z 617 $[M]^+$, 603 $[M\text{-}CH_2]^+$, 484 $[M\text{-}(CH_2)_4\text{-}Ph]^+$, 347 $[M\text{-}(C_8H_{20})\ \text{-}(Ph)_2]^+$, 631 $[M+CH_2]^+$, 645 $[M+(CH_2)_2]^+$.

5.3 Experimental details pertaining to Chapters 3 and 4

5.3.1 General procure for the thermal decomposition experiments

Thermolysis reactions were carried out in clean, dry, sealed evacuated vertical Schlenk tubes of 1-cm o.d. and 10-cm lengths. Unless otherwise specified in the text, decomposition was accomplished by immersion for 2 h in stirred oil whose temperature was 170 ± 5°C. Before use, the tubes were washed with acetone and distilled water, and dried in an oven at 120°C for at least 24h, then cooled under dry nitrogen.

Two procedures were used when the thermal decomposition experiments were carried out under solvent free conditions. For solid complexes, about 10mg sample was added to the tube directly, then dried under vacuum for at least 3 hours before themolysis and the tube was sealed. For oil complexes, about 10mg sample was dissolved in dichloromethane and transferred into the tube, the solvent was removed under vacuum, then dried for at least 3 hours before themolysis and the tube was sealed. In the case of thermal decomposition in solvent, the sample solutions (*ca.* 0.02M) were prepared in toluene or cyclohexane. About 0.5 ml of the solution to be thermolyzed was added to each tube by syringe. The tubes were connected to a vacuum line and degassed through three freeze-thaw cycles. The sample was refrozen and the tube sealed under vacuum. The samples were then immersed in a thermostated oil bath constant at 170 ± 5°C. The tubes were removed at intervals (2 h) and quenched by immersion in liquid nitrogen. For the thermolysis under solvent free conditions, the decomposition products were extracted by adding 0.5 ml pentane or other appropriate solvents containing 20 μl of chlorobenzene as internal standard. For the thermolysis in solvent, the decomposition solutions were transferred to a sample vial which was marked as 0.5 ml and containing 20 μl of internal standard.

Decomposition products were analyzed by GC or GC-MS. Products were identified by comparison of retention times to those of authentic samples. Product yields were determined by response relative to an internal standard (chlorobenzene). Response factors were obtained from authentic samples.

GC analyses were performed using a Varian 3900 gas chromatograph equipped with an FID and a 30 m x 0.32 mm CP-Wax 52 CB column (0.25 μm film thickness). The carrier gas was helium at 5.0 psi. The oven was programmed to hold at 32°C for 4 min and then to ramp to 200°C at 10 deg/min and hold 5 min.

GC-MS analyses for peak identification were performed using an Agilent 5973 gas chromatograph equipped with MSD and a 60m x 0.25 mm Rtx-1 column (0.5 μm film thicknesses). The carrier gas was helium at 0.9 ml/min. The oven was programmed to hold at 50 °C for 2 min and then ramp to 250 °C at 10deg/min and hold 8 min.

5.3.2. Temperature and time effects on thermolysis of 3-1 and 3-2

Solutions of compound **3-1** and **3-2** used for the study of temperature and time effects were prepared by weighing the platinacycle compounds into volumetric flasks and dissolving in DCM. (The reason for using DCM here was that **3-1** and **3-2** are soluble in it while only slightly soluble in cyclohexane, thus to make sure the amount for every reaction is same, DCM is a better solvent).

All the solvents used were HPLC grade in order to avoid involving traces impurity and obtain fully reproducible rates. Great caution was taken in sealing evacuated sample tubes to avoid sample pyrolysis.

*A. Thermal decomposition of **3-1** and **3-2** at various temperatures*

Aliquots (0.5 ml) of sample solutions of **3-1** (2.32 mM) and **3-2** (5.74 mM) in DCM were transferred to decomposition tube. DCM was removed under vacuum and dried for at least 3 hours. Cyclohexane (0.5ml) was added in the tube as the solvent before thermolysis. The tubes were degassed through three freeze-thaw cycles and the samples were thermally decomposed at 0, 100,120, 140, 160 and 180 °C for 2 hours respectively. All samples were stored at -20 °C before GC analysis. The concentration of total products (for **3-1**: total products = 1-octene + octane + 2-octenes; for **3-2**, total products = 1-octene + octane + 2-octenes + 1,7-octadiene + cyclooctane) increased with temperature.

*B. Thermal decomposition of **3-1** and **3-2** at various times*

Aliquots (0.5 ml) of sample solutions of **3-1** (2.32 mM) and **3-2** (5.74 mM) in DCM were transferred to decomposition tube. DCM was removed under vacuum and dried for at least 3 hours. Cyclohexane (0.5ml) was added in the tube as the solvent before themolysis. The tubes were degassed through three freeze-thaw cycles and the samples were thermally decomposed at 170 °C for 0, 0.5, 1.0, 1.5, 2.0 and 2.5 hours respectively. All samples were stored at -20 °C before GC analysis. The concentration of total products increased with time.

5.3.3. Kinetic studies

*A. Kinetics of thermal decomposition of **3-1** and **3-2***

Solutions of compound **3-1** (2.32 mM & 23.2 mM) and **3-2** (5.74 mM) used for kinetics studies were prepared in the similar manner as mentioned in section 5.3.2.

Aliquots (0.5ml) of sample solution were transferred to decomposition tube. DCM was removed under vacuum and dried for at least 3 hours. Cyclohexane (0.5ml) was added in the tube as the solvent before themolysis. The tubes were degassed through three freeze-thaw cycles and the samples were thermally decomposed at 170°C for 0, 0.5, 1.0, 1.5, 2.0 and 2.5 hours respectively. All samples were stored at -20°C before GC analysis. As a control, one tube in each set was not heated but was otherwise treated in the same manner as the thermolyzed sample.

For 23.2 mM **3-1** solution, the rate of decomposition was also studied at 80°C.

*B. Kinetics of thermal decomposition of **3-1** and **3-2** with added ligands*

Ligand solutions with different concentrations were prepared in DCM. Aliquots (0.5ml) of sample solution and ligand solution were transferred to decomposition tube and the same procure as section A was used.

*Thermal decomposition of **3-1** in the presence of added bis(diphenylphoshineo)propane (dppp)* The concentration of solution of **3-1** was held constant at 2.32mM while the concentration of dppp solution (mM) was varied over 3-1-I, 0.0; 3-1-II, 0.224; 3-1-III, 2.24; 3-1-IV, 22.4; 3-1-V, 44.8. First-order rate constants derived from Fig. 3-4-a are: 3-1-I, 0.485; 3-1-II, 0.969; 3-1-III, 1.38; 3-1-IV, 2.75; 3-1-V, 2.63 ($k \times 10^4$, s^{-1}).

*Thermal decomposition of **3-2** in the presence of added bis(diphenylphoshineo)ethane (dppe)* The concentration of solution of **3-2** was held constant at 5.74mM while the concentration of dppe (mM) was varied over 3-2-I, 0.0; 3-2-II, 0.594; 3-2-III, 5.94; 3-2-IV, 59.4; 3-2-V, 118.8. First-order rate constants derived from Fig. 3-4-b are: 3-2-I, 2.01; 3-2-II, 1.22; 3-2-III, 3.11; 3-1-IV,

3.51; 3-1-V, 4.05 (k x 10^4, s^{-1}).

*C. Kinetics of thermal decomposition of **3-5** and **3-8***[8]

This process was monitored by ^{31}P NMR. Into each of two oven-dried and nitrogen-filled NMR tubes were weighed 25.0 mg of **3-5** and 22.0 mg of **3-8** respectively. The NMR tubes were capped with rubber septa and flushed with nitrogen. To the tubes was added by syringe 0.50 ml of toluene-d_8. The tubes were then immersed in a thermostated oil bath constant to $90 \pm 5^{o}C$. The tubes were removed at intervals and the decomposition reactions were followed by the disappearance of starting material indicated by $^{31}P\{^{1}H\}$ NMR spectroscopy.

5.4. Reference

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