# The synthesis, characterization and reactivity of metallacycloalkanes and their precursors

**Cecilia Rutendo Madzivire**

**BSc(Hons)**


**University of Cape Town**

**February, 2010**

A dissertation submitted to the

**University of Cape Town**

In fulfilment to the requirements for the degree of

**Master of Science**

**By**

**Cecilia Rutendo Madzivire**


Department of Chemistry
University of Cape Town
Rondebosch 7701, South Africa

DECLARATION

I declare that this dissertation, **The synthesis, characterization and reactivity of metallacycles and their precursors** is my original work and has not been presented for the award of any other degree at any university. All sources of information quoted and consulted have been acknowledged by means of a full reference.

Signed by candidate

Cecilia R. Madzivire

# Acknowledgements

I would like to take this opportunity to extend my sincere gratitude to the following people without whom I would not have made it this far.

Firstly, I thank my Saviour, Lord God Almighty for His never ending love, mercies and grace that are new every morning and for having given me the power, strength and courage to get this far.

My supervisors, Prof. John R. Moss and Prof. Alan Hutton for believing in me and giving me the opportunity to prove myself. I sincerely thank them for their valuable support, patience, input and motivation throughout my project.

The UCT Chemistry Department technical staff for their great contribution and help in the various analysis techniques of my compounds. They are, Noel Hendricks and Pete Roberts for recording all NMR spectra. Pierro Benincasa for all the elemental analyses.

To all the members of the UCT Transition Metal Chemistry Research Group especially Banothile, Tebello and Feng thank you for your input, support, encouragement and companionship. Thank you all for making the laboratory a great working environment

To the NRF-DST Centre of Excellence in Catalysis (C* Change) thank you for the funding and to Karen Badernhorst thank you for sorting out the finances.

To my immediate family: my parents (Whitmos and Simbisai Madzivire), my sisters (Mercy and Sandra), brothers (Collet, Defence and Huggins) and my brother in law Moises Simao thank you for your prayers, love and constant support throughout my life.

To my dear friends (Thembakazi, Pumeza, Rufaro and Kudzai) and all, thank you for being there.

# Abstract

A series of bis(alkenyl)platinum(II) complexes of the type $[PtL_2\{(CH_2)_nCH=CH_2\}_2]$ ($L_2$ = 1,3-bis(diphenylphosphino)propane and n = 3-6) have been successfully synthesized and characterized by $^1H$, $^{13}C$ and $^{31}P$ NMR spectroscopy, elemental analysis and mass spectrometry. $^{13}C$ NMR data for these complexes is herein presented for the first time.

The bis(alkenyl) complexes were used as precursors in the synthesis of platinacycloalkanes *via* ring-closing metathesis (RCM) and hydrogenation reactions. Even and odd numbered platinacyles were also prepared using the di-Grignard route, including the new even numbered platinacyclodecane $[(dppp)Pt(CH_2)_9]$.

Thermal decomposition studies were carried out on the bis(alkenyl) complexes, platinacyclononane and platinacyclodecane. Thermolysis of these complexes gave different organic products characteristic of the class each complex belonged to. Investigations on the effect of solvent system, nature of supporting ligand, ring size or alkenyl chain length and reaction time were investigated.

Insertion reactions with CO were done on the bis(heptenyl)platinum(II) complex and platinacyclopentane and propose the formation of di-acyl complexes in these reactions on the basis of IR, NMR and elemental analysis data obtained. Platinacylopentane was found to react at a slower rate when compared to the bis(alkenyl) complex.

A new route for the synthesis of dicarbonyldibromide rhenium complex $Cp^*Re(CO)_2Br_2$ affording the product in very high yields is herein reported. Attempts to synthesize the bis(alkenyl) rhenium complexes and rhenacycles *via* transmetallation and RCM respectively were not successful. This served as a further confirmation that the use of RLi or RMgX (R = alkenyl, X = halogen) reagents is not a reliable method for the synthesis of these complexes as has been reported for similar complexes where R = alkyl group.

# Abbreviations

| | |
|---|---|
| L | = Ligand |
| COD | = 1,5-cyclooctadiene |
| CO | = Carbon monoxide |
| Cp | = Cyclopentadienyl |
| Cp* | = Pentamethylcyclopentadienyl |
| Tpy* | = 4'-(4-tert-butylphenyl)-2,2':6',2"-terpyridine |
| $PPh_3$ | = triphenylphosphine |
| $PEt_3$ | = triethylphosphine |
| $PMePh_2$ | = methyldiphenylphosphine |
| $PEtPh_2$ | = ethyldiphenylphosphine |
| $P(OMe)_3$ | = trimethylphosphite |
| $P(OBu^t)_3$ | = tributylphosphite |
| $P(OPh)_3$ | = triphenylphosphite |
| dppe | = 1,2-bis(diphenylphosphino)ethane |
| dppp | = 1,3-bis(diphenylphosphino)propane |
| dppb | = 1,4-bis(diphenylphosphino)butane |
| dppd | = (2S, 4S)-2,4-bis(diphenylphosphino)pentane |
| Ph | = Phenyl, $-C_6H_5$ |
| Me | = Methyl, $-CH_3$ |
| Et | = Ethyl, $-CH_2CH_3$ |
| $Br_2$ | = Bromine |
| THF | = Tetrahydrofuran |
| TFA | = Triflouroacetic acid |
| $Et_2O$ | = Diethyl ether |
| DCM | = Dichloromethane |
| RCM | = Ring-closing metathesis |
| ROMP | = Ring-opening metathesis polymerization |
| Pd/C | = Palladium on activated carbon |
| GC | = gas chromatography |

| | |
|---|---|
| s | = singlet |
| d | = doublet |
| t | = triplet |
| dd | = doublet of doublets |
| q | = quartet |
| m | = multiplet |
| br m | = broad multiplet |
| J | = coupling constant |
| Hz | = Hertz |
| ppm | = parts per million |
| | |
| IR | = Infrared |
| ν | = stretching vibration |
| $cm^{-1}$ | = wave number |
| s | = strong |
| m | = medium |
| w | = weak |
| | |
| LRMS | = Low Resolution Mass Spectrometry |
| FAB | = Fast Atom Bombardment |
| $M^+$ | = parent molecular ion |
| m/z | = mass to charge ratio |

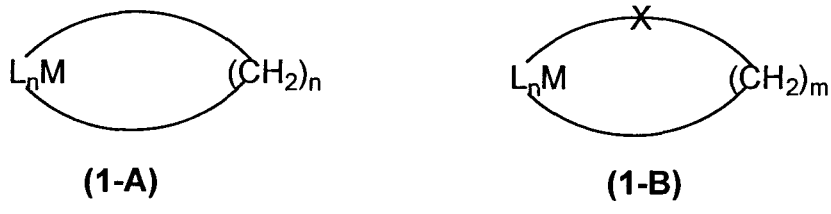
**Table of Contents**

As an introduction to this dissertation, two topics will be covered in depth in the form of review chapters. Chapter 1 will cover the literature behind metallacycles and Chapter 2 will cover bis(alkenyl) complexes of transition metals. Concluding remarks will be made for each chapter.

# Chapter 1: Metallacycles

## 1.1 General Introduction

Metallacycles form an important class of organometallic compounds. They can be defined as carbocylic systems in which one or more carbon atoms have been replaced by a transition metal as shown in Figure 1.1. A survey of the literature shows that metallacycles with saturated rings (1-A) and those of rings containing a heteroatom (1-B) have been synthesised and their reactivity covered in depth [1]. However there are only a few reports on metallacycles with saturated rings.




**(1-A)** **(1-B)**

**Figure 1.1:** Simplified representations of metallacycles. $L_nM$ = metal and associated ligands, X = heteroatom

This class of novel compounds has become a major field of research in both academic and industrial laboratories [2], mainly because it shows both interesting and useful chemistry. Metallacycles are important mainly because of two reasons:

Firstly they are generally more stable than their corresponding acyclic transition metal alkyl complexes [3], thus they are more useful as model compounds. Secondly they have been implicated as key intermediates in several transition metal catalysed reactions. Such reactions include metallacyclobutanes in alkene metathesis [4,5,6], ethylene oligomerization and polymerization [7] and Fischer Tropsch reaction [8].

Thus therefore, the synthesis, characterization and reactivity of these title compounds as model compounds for such important reactions might provide a better understanding and in depth knowledge of the mechanisms involved in catalytic reactions.

It has also been reported recently that platinacyclobutanes with attached biomolecules can been used as targeted *cis*platin prodrugs [9]. Thus with appropriate donor ligands metallaycles can be of significant use in the medical field.

Reported literature suggests that metallacycles have been reported for a large percentage of the transition metals [1,10,11]. A schematic representation of such metals is given in Figure 1.2.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
| Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd |
| Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg |

**Figure 1.2:** Known metallacycles (yellow area indicates that metallacycles are known for that particular transition metal). References: Ti [11], Zr [12], Hf [13], Nb [14], Ta [14,15], Cr [16], Mo [17], W [18], Mn [19], Re [20], Fe [21], Ru [22], Os [22], Co [23], Rh [24c], Ir [24], Ni [25a], Pd [25b], Pt [26] and Zr [25c].

In this review, the discussion on metallacycles has been restricted to complexes in which only one transition metal centre is bonded to two carbon atoms in either a saturated or unsaturated cyclic system. Thus, heterobimetallacycles and metallacyclic compounds containing heteroatoms have been excluded.

## 1.2 Synthesis, stability and chemical reactivity of metallacycles

### 1.2.1 Synthesis

Until recently the synthesis of metallacycles was found to be highly dependant on the ring size and on the nature of the ligand system associated with the complex. Thus, generally small metallacycles (with 4-6 membered rings) are easy to make and have been synthesized and intensively investigated, whilst medium to larger metallacycles (>6 membered rings) are more difficult to make and have not been investigated in depth [1].

One of the simplest synthetic routes reported in the literature for the synthesis of metallacycles is *via* an oxidative reaction in which the metal centre is reacted with two equivalents of ethylene (Figure 1.3a). Alternatively, for example a metallacyclopropane can be reacted with one equivalent of ethylene to generate a metallacyclopentane *via* a pericyclic migratory insertion reaction (Figure 1.3b) [27].

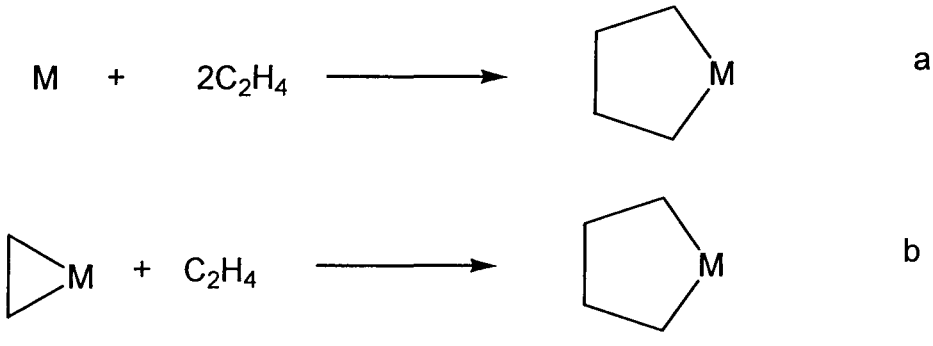
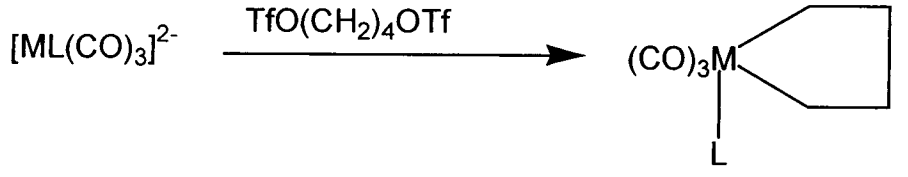



**Figure 1.3:** (a) oxidative addition, (b) pericyclic insertion reaction

However, the main methods of preparation of metallacycles are (i) the di-anion route (ii) transmetallation with di-Grignard or di-lithioalkane reagents and (iii) intramolecular coupling of alkenes and/ alkynes [11a,22,28]. It is also possible to synthesize metallacyloalkanes *via* two C-H activation steps from corresponding alkanes.

*Di-anion route*

The di-anion route has been used effectively by Lindner and co-workers in the synthesis of metallacylces particularly metallacyclopentanes of group 8 metals [22a,b]. In this method metal carbonylates are reacted with 1,5-di-triflates to yield metallacycles. Examples of reported metallacyclopentanes are given below (eq. 1.1)



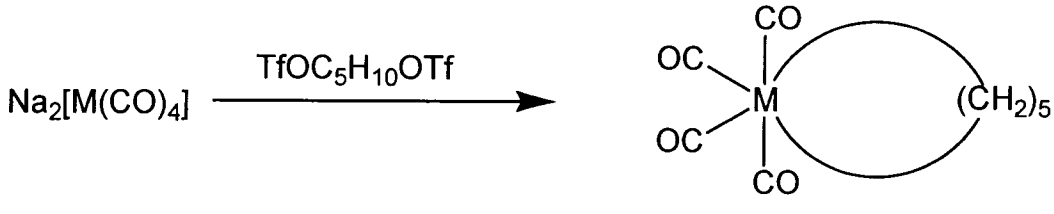

(eq. 1.1)

1: M = Fe; L = CO, $PPh_3$, $P(OMe)_3$

2: M = Ru; L = CO

3: M = OS; L = CO

The synthetic procedure described above has also been applied in the synthesis of metallacyclohexanes of Ru and Os. In this case metal carbonylates of the type $Na_2[M(CO)_4]$ (M = Ru and Os) were reacted with the di-triflates (eq. 1.2) [22c,d]. However, Fe derivates could not be obtained, as a result there are no known metallacyclohexanes of Fe [22b].




(eq. 1.2)

4: M = Ru

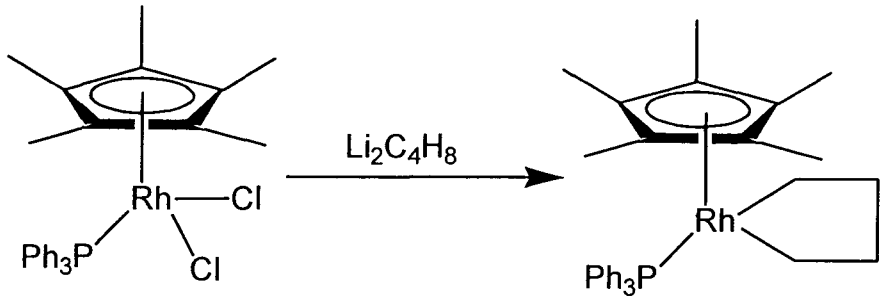
5: M = Os

These compounds have been fully characterized spectroscopically and analytically and a crystal structure has been reported for the metallacyclohexane of Os [22b]. However attempts to synthesize metallacycles with larger rings using this methodology were not successful. Thus, according to Lindner *et al.* synthesis of metallacycles using this route is largely dependant on the ring size [22a,b].

*Transmetallation*

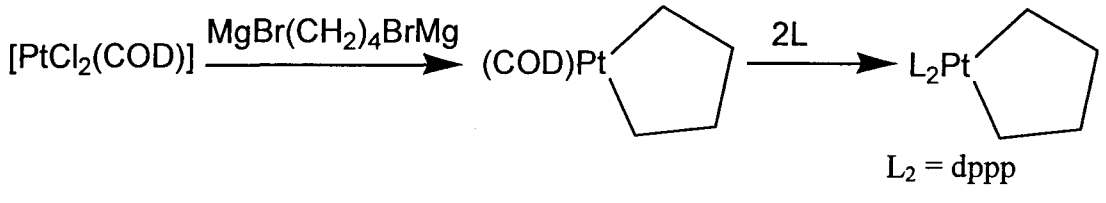
Perhaps the most widely used synthetic route in the preparation of metallacycles involves the reaction of metallocene dichlorides with 1, 4-dilithiobutane or a di-Grignard reagent. The major set back with this synthetic route arises in the synthesis of metallacyles with larger rings as these are either not obtained or obtained in low yields [1].

Literature survey shows that a number of metallacycles have been synthesized using this method, but only a few will be highlighted as examples in this review.
The rhodapentacycle, $Cp^*Rh(PPh_3)(C_4H_8)$ has been formed from the reaction of $Cp^*Rh(PPh_3)Cl_2$ with $Li(CH_2)_4Li$ in diethyl ether as shown below in eq. 1.3 [24a,c].




(eq. 1.3)

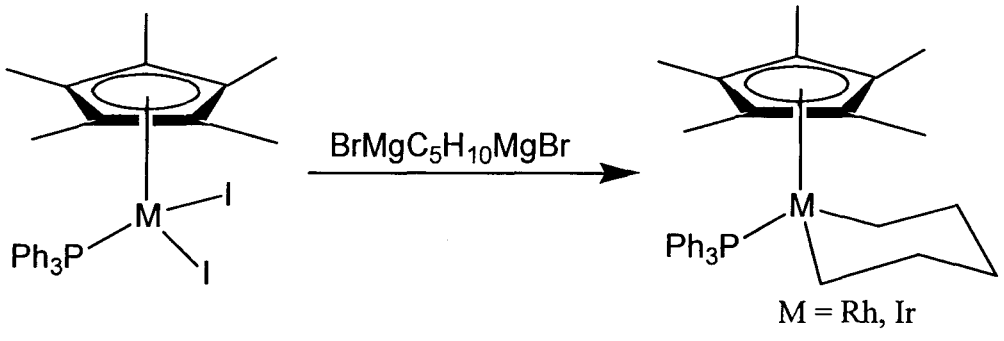
Platinacyclopentanes have also been prepared by the reaction of the di-Grignard reagent $BrMg(CH_2)_4MgBr$ with dichloro(1,5-cyclooctadiene)platinum(II) followed by the displacement of the labile COD ligand by tertiary phosphine ligands to give the product in about 25% yield (eq. 1.4). Alternatively, direct reaction of dichlorobis-(triphenylphosphine) platinum(II) with 1,4-dilithiobutane gives the respective product in yields of about 60% [29].




(eq. 1.4)

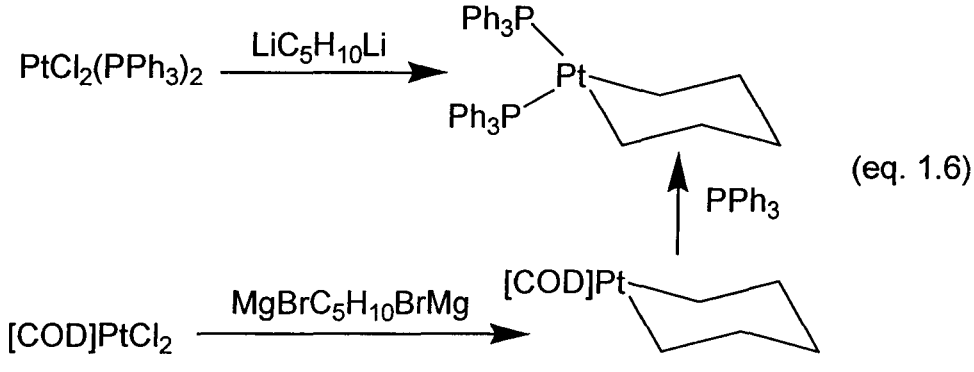
There are no reports of metallacyclohexane complexes for groups 5, 6 and 7 that have been synthesized using the transmetallation route [1]. Groups 9 and 10 metallacyclohexanes have however been synthesized using this method.

In group 9 the rhodacyclohexane $Cp^*Rh(PPh_3)(C_5H_{10})$ was prepared by the reaction of $Cp^*Rh(PPh_3)I_2$ in diethyl ether with $MgBr(CH_2)_5BrMg$ in THF at room temperature (eq. 1.5). The compound was obtained as orange crystals in 30% yield which melted with decomposition at 109°C. The iridium analogue was also synthesised in a similar way [24a,c].




(eq. 1.5)

In group 10 the platinacyclohexane $(PPh_3)_2Pt(C_5H_{10})$ was first reported in 1958 by Chatt and Shaw [30]. They synthesized this compound through the reaction of *cis*-$(PPh_3)PtCl_2$ with 1,5 dilithiopentane. The same compound was later synthesized using the di-Grignard route by Whitesides and co-workers in 1973. In their case they reacted $[(COD)PtCl_2]$ with the appropriate di-Grignard to yield the intermediate $[(COD)PtC_5H_{10}]$ which was then reacted with $PPh_3$ to give $[(PPh_3)_2Pt(C_5H_{10})]$ (eq. 1.6) [11a,31].




(eq. 1.6)

There are no reported metallacycloheptanes of groups 4 and 5 transition metals that have been synthesized using the transmetallation route. Emrich *et al.* have however reported the synthesis of a chromacycloheptane using the di-Grignard route (Figure 1.4 (a)). This chromacycloheptane has been structurally characterized by X-ray crystallography ]16].

In group 9, the rhodacycloheptane $Cp^*Rh(PPh_3)(C_6H_{12})$ (Figure 1.4 (b)) has been prepared by the reaction of $Cp^*Rh(PPh_3)I_2$ in diethyl ether with a solution of $MgBr(CH_2)_6BrMg$ at room temperature [24a,c]. In a similar fashion the group 10 platinacycloheptane (Figure 1.4(c)) was synthesized in very low yield [31].

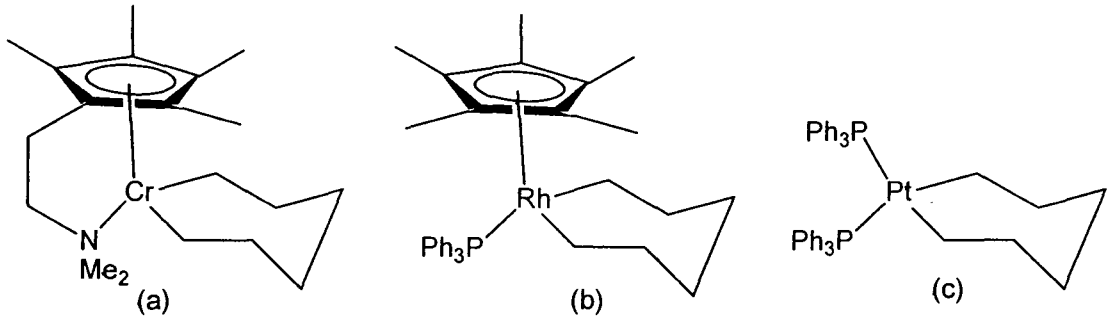
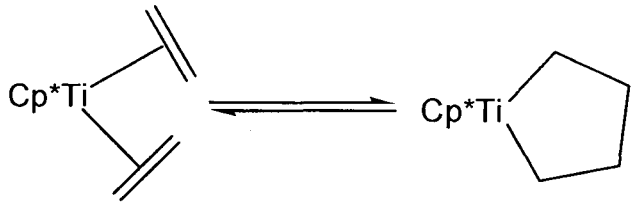



**Figure 1.4:** Examples of known metallacycoheptanes.

Thus looking at the examples shown above transmetallation has been widely applied in the synthesis of metallacycles particularly those of small ring sizes. The yields obtained vary according to the ring size, type of ligand and sometimes on the type of transition metal.

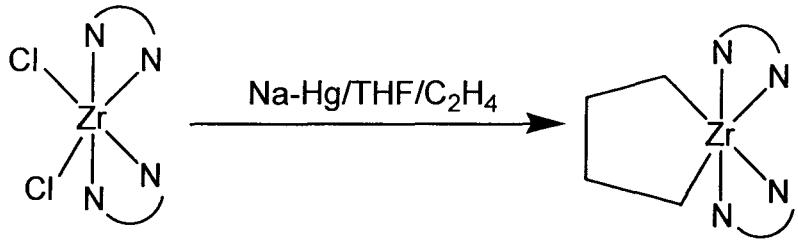
*Other methods*

Takaya and Mashima have reported on the synthesis of stable titanacyclopentanes *via* the coupling of two olefin ligands. In this reversible step, the oxidative coupling of two olefins on a metal gives back the metallacyclopentane (eq. 1.7) [11b,c]. In other instances a precursor complex is reacted with magnesium, sodium, butylithium or Na/Mg in the presence of an olefin to give a metallacycle [16,32,33].




(eq. 1.7)

In another example Zr amidates have also been shown to couple ethylene units in the presence of 1% Na-Hg, resulting in the formation of a zirconacyclopentane derivative (eq. 1.8) [33b].



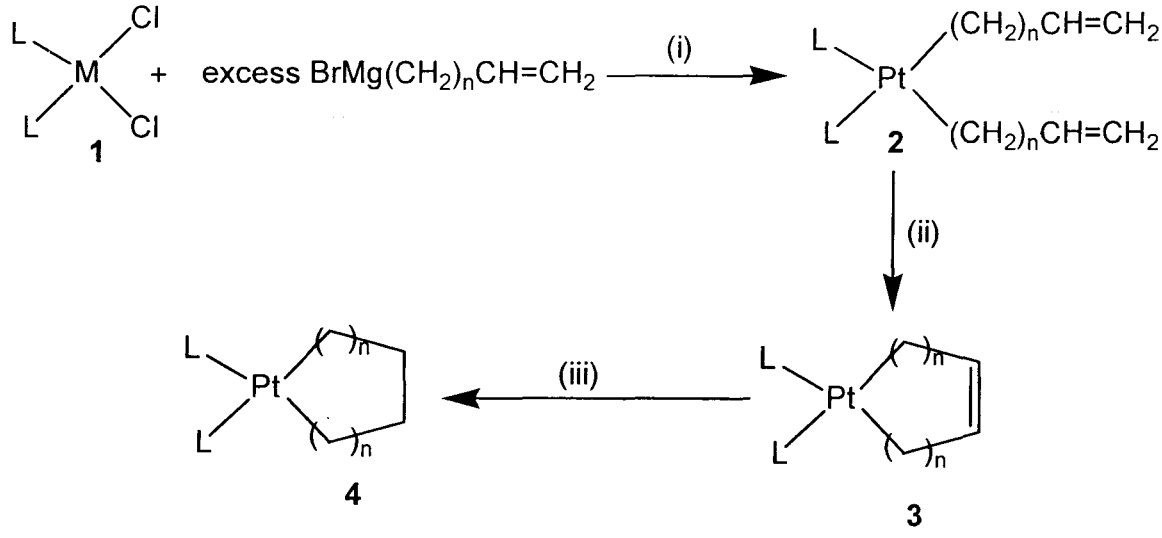

(eq. 1.8)

*New synthetic route for metallacycles*

The use of Grubbs' catalysts in the synthesis of medium to large ring size metallacycles has found wide applications in chemistry. It has lead to the efficient synthesis of organic ring complexes that are otherwise very difficult to make. Recently Moss *et al.* [34b] have reported a new synthetic route for medium to large ring size metallacycles that uses Grubbs' catalyst in a ring closing metathesis reaction to yield metallacycles in good yields (Scheme 1.1).

It has been reported that this new synthetic route allows the isolation of metallacycles in very good yields irrespective of the ring size. This route also allows the isolation of novel metallacycloalkene complexes whose chemistry has not yet been investigated in depth [34].

In this method the bis(1-alkenyl) precursor **2** was obtained from the reaction of 1-alkenyl Grignard reagents with the corresponding dichloro-metal precursor **1**.

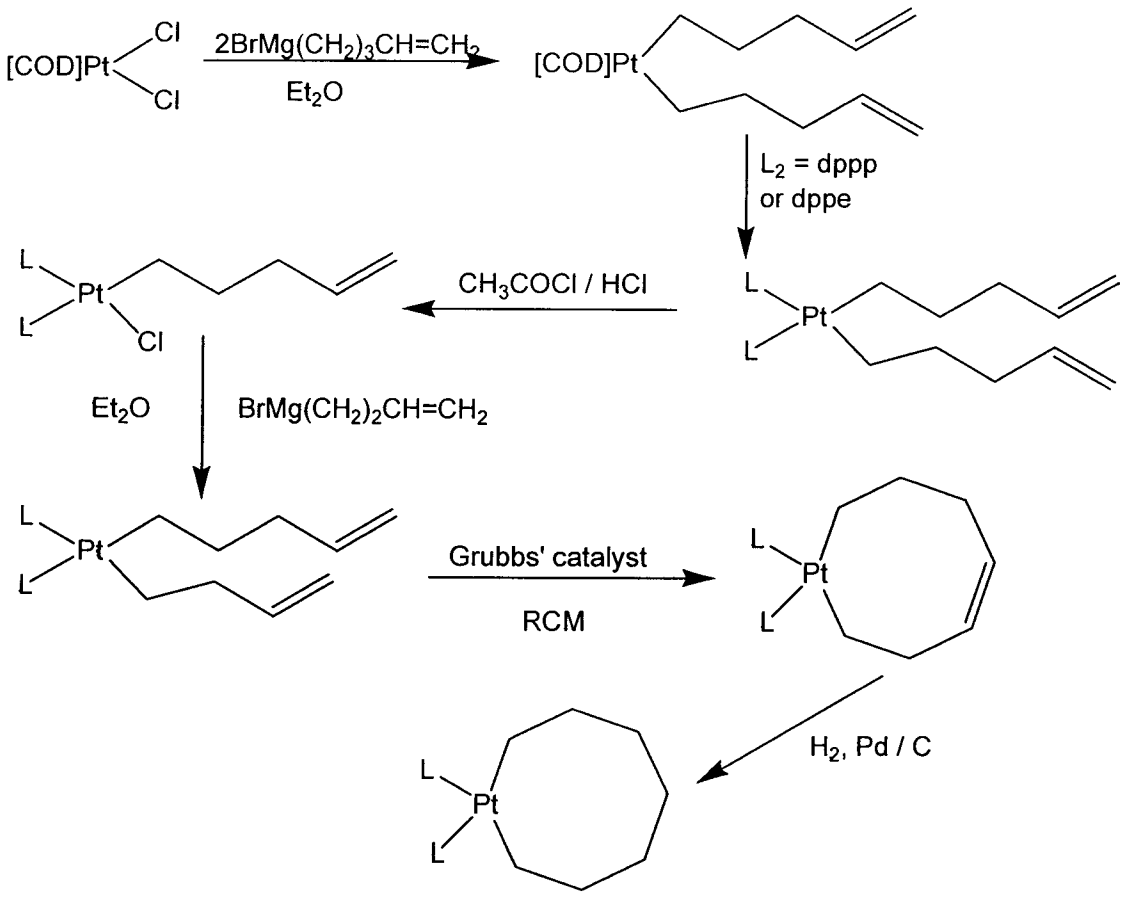



**Scheme 1.1:** New synthetic route for the synthesis of metallacycles; L = ligand, M = metal, n = 1, 2, ..., 6, 7. (i) THF/$Et_2O$, -78°C; (ii) Grubbs' 1st generation catalyst, $CH_2Cl_2$, reflux/50°C; (iii) $H_2$, Pd/C, toluene.

Reaction of **2** with Grubbs' 1st generation catalyst, $RuCl_2(PCy_3)_2(=CHPh)$, (5 mol%) results in ring closing metathesis of the bis(1-alkenyl) precursor **2** to yield the metallacycloalkene, **3**. Reaction of **3** with hydrogen in the presence of Pd/C results in the saturation of the C=C double bond to yield the metallacycloalkane **4** in quantitative yields. This method has been shown to work for the transition metals Pt, Pd, Rh and Ir [34d,f,35].

Slight modification of this synthetic route has resulted in the synthesis of even numbered ring metallacylces. In this instance, this has only been tested for Pt in the preparation of the first known platinacyclooctane (Scheme 1.2) [34c].

This new synthetic route therefore allows for the synthesis of various metallacycles of any ring size in quantitative yields for most of transition metals. It also allows for the synthesis of even numbered metallacycles that have not been covered in depth in the literature.




**Scheme 1.2:** Synthesis of the first platinacyclooctane.

### 1.2.2 Stability

Metallacycles can in some cases be unstable because of the presence of the reactive metal-carbon bonds. In such cases, decomposition of these compounds can give rise to interesting organic compounds [1,34,35]. It has been investigated and reported that the stability of metallacycles varies significantly and is highly dependant on factors such as the ring size, transition metal and also on the nature of the ligand [1,34,35,36]. These compounds therefore can decompose either at room temperature or at relatively high temperatures. Since decomposition to organic compounds is the termination step in the mechanism of every synthetically important and useful catalytic or stoichiometric reaction in which a metallacycle is involved [37], it is of fundamental importance to study and understand such reactions.

It is however interesting to note that metallacycles are generally more thermally stable than their acyclic analogues. For example, Whitesides and co-workers have studied the decomposition of platinacyclopentane (**a**) and its related diacyclic complex (**b**) in $CH_2Cl_2$ and have shown that the latter decomposes at 60°C whilst the former decomposes at 120°C (Figure 1.5) [11a,31].

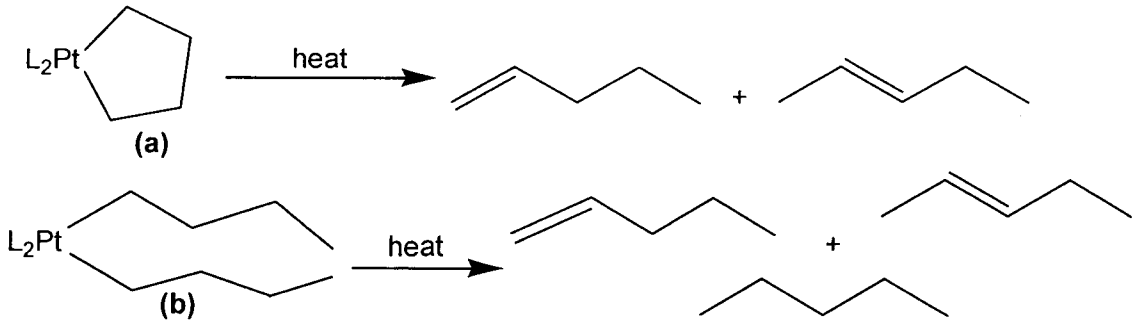
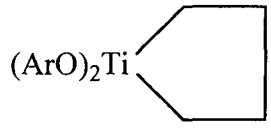
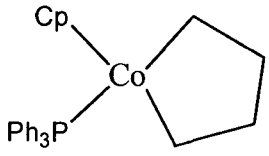
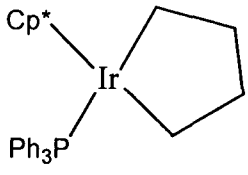
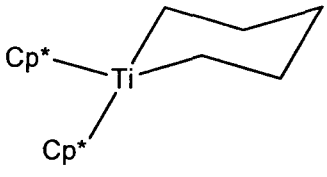
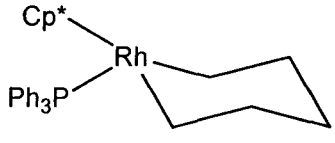
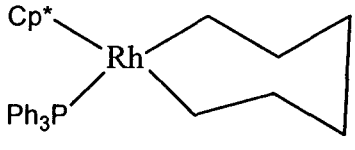
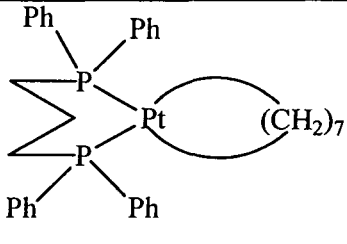



**Figure 1.5:** Decomposition pathways in $CH_2Cl_2$ for (a) platinacyclopentane at 120°C and (b) diacyclic complex at 60°C.

Table 1.1 shows some known metallacycles and their relative stability in solution or in their solid state.

**Table 1.1**: Relative stability of some metallacycles

| **Complex** | **Stability** | **Complex obtained as:** | **Reference** |
|---|---|---|---|
|  | Stable at room temperature and also in toluene solution up to 80°C | Orange crystalline solid | 38 |
|  | Stable at room temperature under $N_2$ atmosphere but decomposes in benzene at room temperature | Orange-red crystals | 24a,c |
|  | Melts with decomposition at 209°C | Yellow-green crystals | 24a |
|  | Air sensitive | Orange-red crystals | 39 |
|  | Melts with decomposition at 188°C | Pale yellow crystals | 24a,c |
|  | Melts with decomposition at 107°C | Orange crystals | 24a,c |
|  | Melts with decomposition between 134-136°C | Pale yellow oil | 34c |

### 1.2.3 Chemical reactivity

Metallacycles are generally reactive because of the presence of the reactive metal-carbon bonds [1,34]. As seen in the case of their stability, their reactivity is also largely dependant on factors such as the ring size, nature of the supporting ligand and sometimes on the type of metal. Some of the reactions that metallacycles undergo include oxidative addition, insertion reactions, thermal decomposition and cleavage of the metal-carbon bonds [1].

*Thermal decomposition*

The stability of metallacycles varies significantly with temperature and a range of interesting organic products are produced upon thermal decomposition. Since decomposition to organic products is the termination step in many important reactions, studies on the decomposition behaviour of metallacycles are important (i) for the development of organometallic chemistry and (ii) for enhancing our understanding on the role of metallacycles in organic synthesis and catalysis [10,34,35,40].

Factors influencing the decomposition pathways and products of matallacycles include ring size, metal type, nature of the ligand, solvent system, temperature and reaction time. Thermal decomposition may proceed *via* the following reaction pathways, reductive elimination, β-hydride elimination, carbon-carbon bond cleavage and α-hydride elimination [10,34,35,40].

Until recently thermal decomposition studies have been restricted to small and medium ring size metallacycles. They have however been extended to larger ring size metallacycles [34e]. A schematic representation of β-hydride elimination and α-hydride elimination is given below. 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.

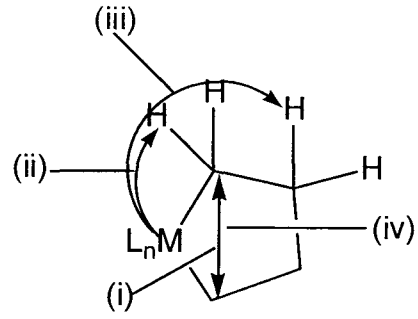
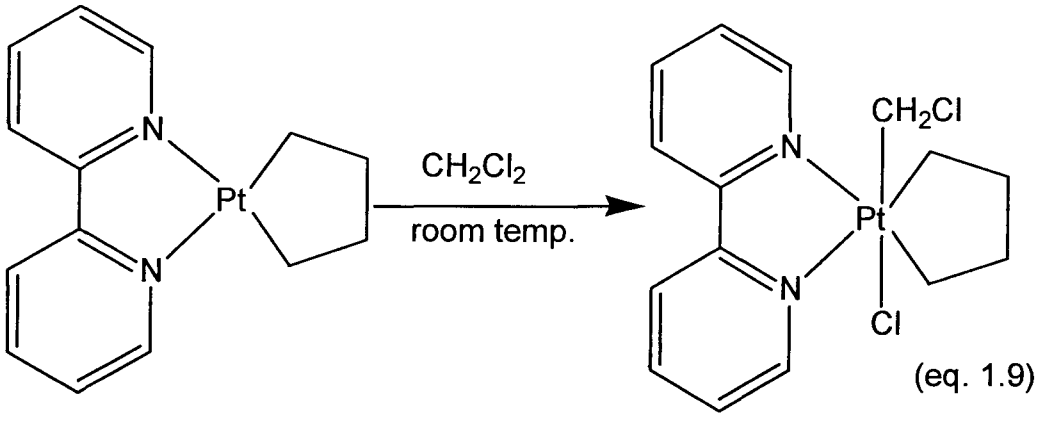


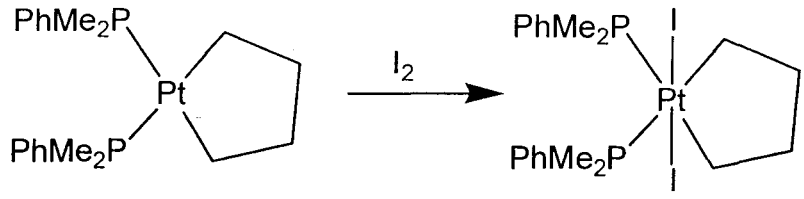

**Figure 1.6:** Decomposition pathways for metallacycloalkanes, ($L_nM$ = metal and associated ligand). (i) is reductive elimination, (ii) is α-hydride elimination, (iii) is β-hydride elimination and (iv) is β-C-C fission (retro-cycloaddition).

*Oxidative addition*

Oxidative addition is an important reaction which forms the initial step in palladium catalyzed coupling reactions. Young and Whitesides reported work on the oxidative addition of methylene chloride to platinum (II) complexes at room temperature to yield platinum (IV) complexes. A schematic representation of this reaction is given below (eq. 1.9). The dichloromethane solvent also influences the decomposition pathway of the hexacoordinate complex generated during thermal decomposition [41].



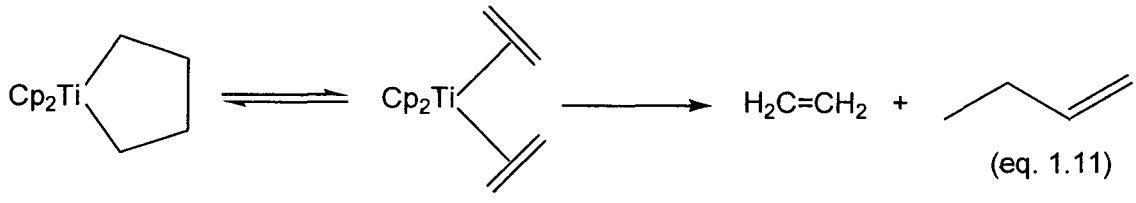

In another example, a Pt (IV) derivative has also been shown to undergo *trans*-oxidative addition with $I_2$ to yield the platinacyclic complex shown below (eq. 1.10) [42]. The crystal structure of the product has also been reported.




(eq. 1.10)

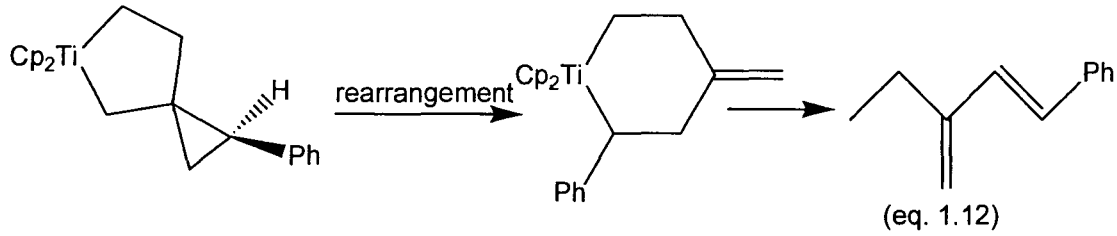
*Rearrangement*

Metallacycloalkanes have also been shown to undergo rearrangement in an attempt to increase their stability during or prior to thermal decomposition [1,13]. In such cases, thermal decomposition can occur *via* reversible rearrangement or carbon-carbon bond cleavage as reported by Grubbs and Miyashita [39]. Such processes give bis-ethylene complexes then ethylene as the major products (eq. 1.11) [11b,c].




(eq. 1.11)

Another example, shown below involves the rearrangement of a substituted titanacyclopentane to a six memembered ring metallacycle prior to decomposition. The main decomposition product is the diene [$CH_3CH_2C(=CH_2)CH_2=CHPh$] in 70% yield [11b,c].



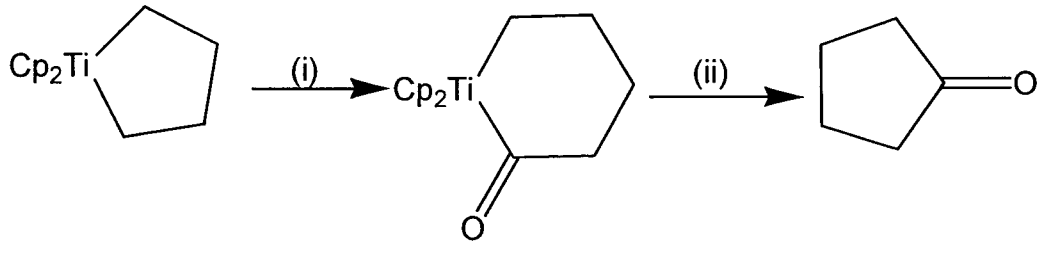

(eq. 1.12)

Thus in addition to the factors that influence thermal decomposition stated previously, prior rearrangement of metallacyclic complexes also affects thermal decomposition pathways and the products thereof.

*Insertion reactions*

Metallacycles undergo insertion reactions mainly because of the presence of the reactive metal-carbon bond. Molecules that can be inserted into the metal-carbon bond include CO, $SO_2$, $N_2$, $H_2C{=}CH_2$ and PhC≡CPh. The insertion of these groups usually results in the expansion of the ring and functionalisation of the alkyl moiety through mono, di-, or poly insertion. A few examples of such reactions are outlined below.

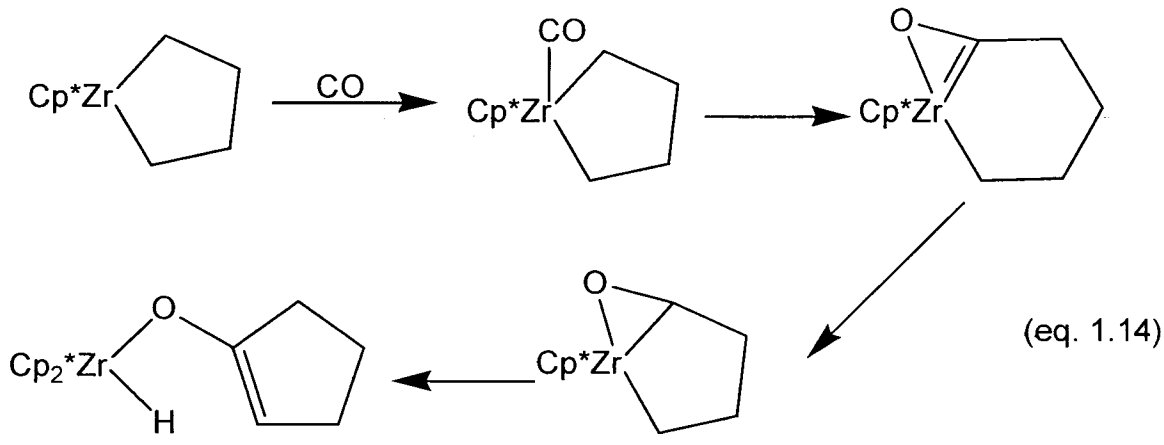
Mono-insertion of carbon monoxide into metallacyclic complexes is perhaps the most common of such reactions, and is usually followed by reductive elimination to form the corresponding cycloketone [11a,c,23b,43]. For example the titanium complex (eq. 1.13) reacts with CO at -55°C to yield an acyl species which rapidly converts to cyclopentanone at 0°C [11a].




(eq. 1.13)

CO insertion into a titanium complex: (i) CO/pentane/-55°C, (ii) Δ/CO

On the other hand, zirconacyclopentane has shown interesting reactivity towards carbon moxide. This compound was found to react instantaneously with CO at 25°C to form a white crystalline product which was shown to be an enolate hydride. A possible reaction pathway has since been proposed (eq. 1.14) [44].

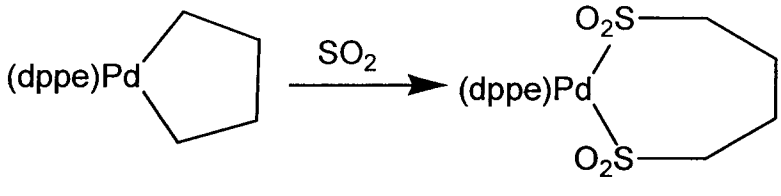



(eq. 1.14)

The reaction of palladacyclopentanes with small molecules has also been extensively studied. Diversi *et al.* have shown that insention reactions on the palladacycles are dependant on the nature of the supporting ligand(s). Palladacycles with dppe ligands do not react with CO at atmospheric pressure and room temperature and decomposition is observed at higher temperatures [10].

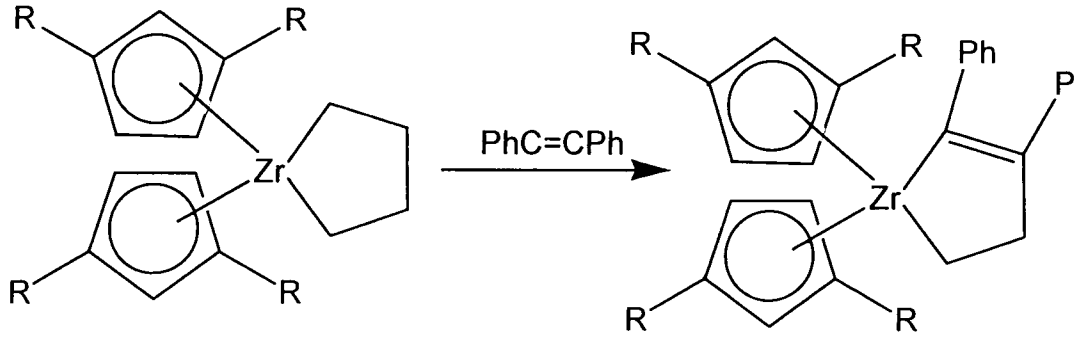
In contrast palladacycles with $PPh_3$ as the ligand react smoothly with CO to produce cyclopentanone, unindentified organic products and palladium black. Such different behaviour of these complexes due to the nature of the supporting ligand(s) has also been observed for nickelacyclopentanes and has been attributed to the reluctance of the dppe complex to form five-coordinated complexes with coordinated CO molecules [45].

The reaction of metallacycles with $SO_2$ has also been reported. Such reactions have been shown to be highly dependant on the nature of the supporting ligand(s) and also sensitive to experimental conditions. Palladacyclopentane reacts rapidly with $SO_2$ (no solvent) at low temperatures to yield an acyclic disulphinate compound (eq. 1.15) [45].




(eq. 1.15)

Zirconacyclopentane reacts with diphenylacetylene to yield a substituted zirconacyclopentene in a reaction that demonstrates the reversibility of metallacyclic formation (eq. 1.16). One equivalent of ethene and an alkyne is incorporated in this reaction [46].



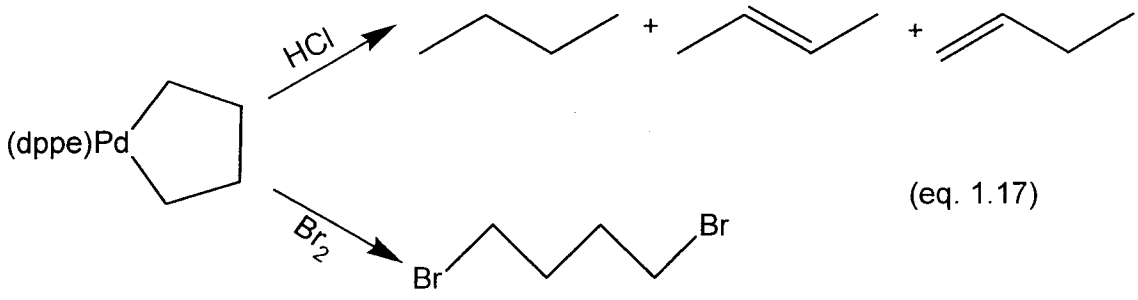

(eq. 1.16)

Ethylene insertion reactions have also been observed for metallacyclopropanes [47] and recently poly-insertion of ethylene into metal-carbon bonds of a platinacyclooctane to form larger ring platinacycloalkanes has also been reported. Mono- and di- insertion of other molecules such as benzaldehyde, isocyanide and sulphur have also been reported in the literature [48,49].

Thus metallacyclic compounds readily undergo insertion reactions and in some cases the supporting ligand determines the reactivity pathway and product(s) formed.

*Reaction with electrophilic reagents*

The interaction of metallacycles with electrophilic reagents such as acids and halogens usually results in the cleavage of the metal-carbon bond to give hydrocarbons and haloalkanes [10,11a]. Such reactions result in carbon-carbon and carbon-halogen bond formation which has wide applications in organic synthesis. An example is given below (eq. 1.17).




(eq. 1.17)

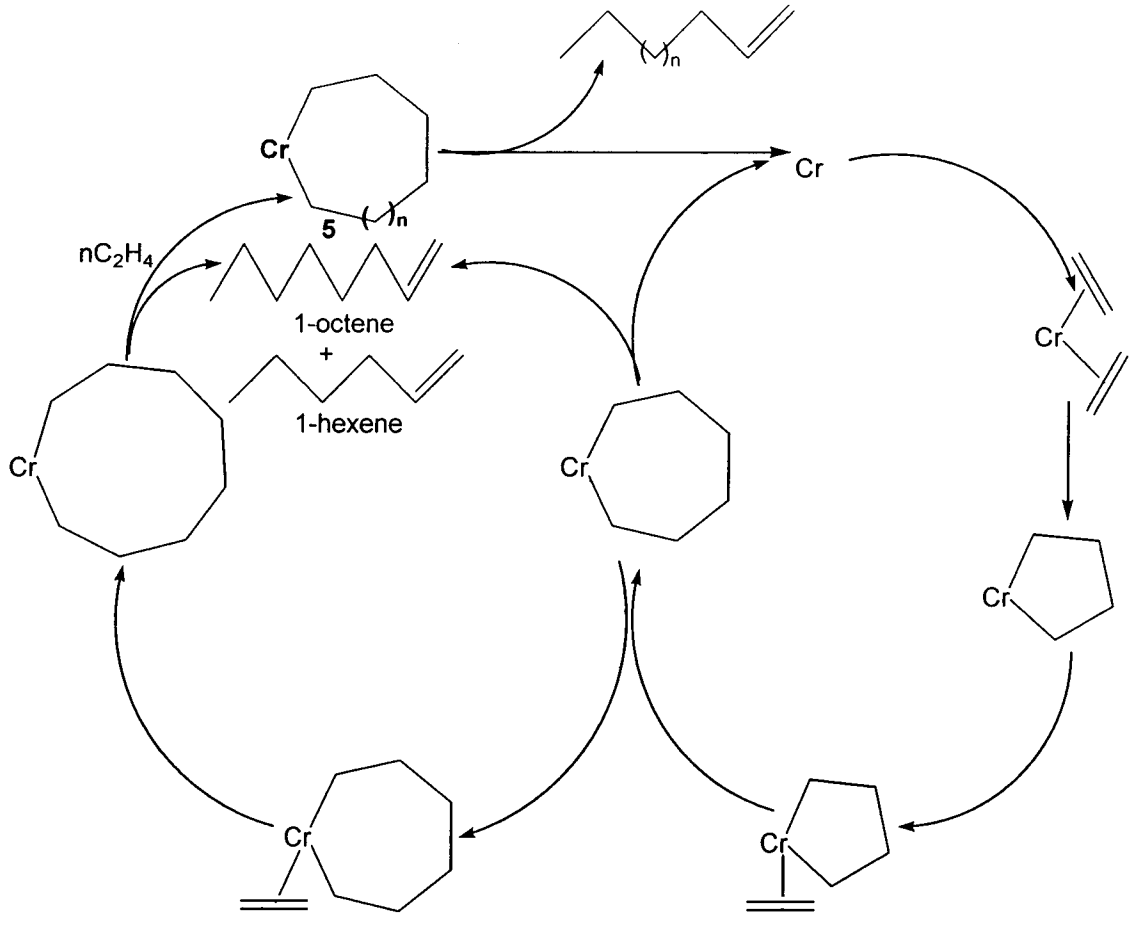
## 1.3 Implications and applications of metallacycloalkanes in catalysis

The principal steps in olefin metathesis according to the Chauvin mechanism involve a transition metal carbene which coordinates to an olefin to form a metallacyclobutane intermediate. A [2+2] cycloreversion and dissociation finally leads to the new olefin product and a new metal carbene complex [5].

Over the years the scope around olefin metathesis has broadened significantly, ranging from bulk chemistry to synthetic chemistry mainly due to the work of Grubbs and Shrock [5,6].

Olefin metathesis is a powerful method for the formation of carbon-carbon double bonds [4,50]. It has also found wide applications in organic synthesis, polymer chemistry, materials chemistry as well as in organometallic chemistry. Applications in organometallic chemistry include ring opening metathesis polymerization (ROMP), cross metathesis and ring closing metathesis (RCM) [4,34].

Metallacycles have been implicated as intermediates in some catalytic reactions and are also known to mediate ethylene oligomerization reactions. Their role as intermediates has been confirmed by ethylene labelling experiments. Some of the catalytic reactions in which they have been implicated as intermediates include, metallacycloheptanes in chromium catalyzed trimerization of ethylene to 1-hexene and more recently a metallacyclononane was implicated in the tetramerization of ethylene to 1-octene (Scheme 1.3) [7].

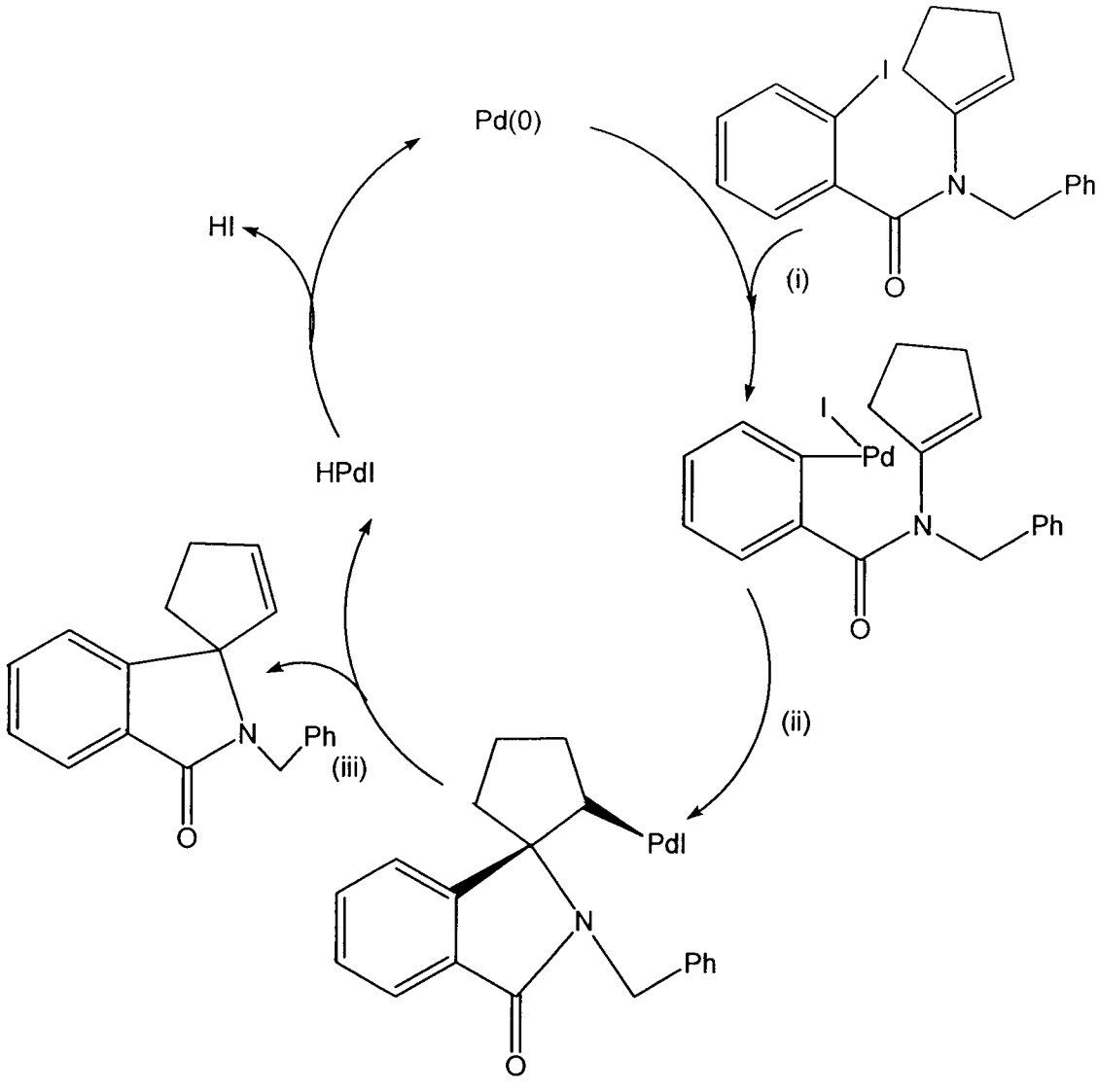



**Scheme 1.3:** Schematic representation oof chromium catalyzed ethylene oligomerization and polymerization reactions (ligands omitted for clarity).

It has also been reported that chain propagation in selected chromium catalyzed systems for ethylene oligomerization and polymerization occur mainly through mechanism involving the large metalllacycle **5**, (Scheme 1.3) [7b].

Linear α-olefins can be used industrially as co-monomers in the synthesis of low density polyethylene and also in the production of linear aldehydes *via* hydroformylation [7].

Palladacycloalkanes are known to mediate Heck type coupling reactions catalyzed by Pd(0) species [35]. The involvement of these compounds has been observed in both intra- [51] and inter-molecular Heck reactions (Scheme 1.3) [52].Such coupling reactions play an important role in drug synthesis.




**Scheme 1.4:** Mechanism for palladium catalyzed heck type coupling reaction, (ligands omitted for clarity. (i) Oxidative addition, (ii) carbopalladation, (iii) syn β-hydride elimination.

Other catalytic reactions in which metallacycles have been implicated as intermediates include Fischer-Tropsch, ethylene carbonylation [1] and catalytic dimerization of styrene [38b].

## 1.4 Concluding remarks

In conclusion, metallacycles can be synthesized using various methods in low to high yields. A number of factors, such as the nature of the supporting ligand influence the synthesis of these compounds. These compounds can be isolated and most of them are generally stable enough to carry out reactivity studies on. Metallacycles of most transition metals have been synthesized, with five- membered rings being by far the most prepared and studied.

Metallacycles show significantly different reactivity when compared to their acyclic analogues. Such reactivity includes insertion reactions, oxidative addition, thermolysis, rearrangement, cleavage of the metal-carbon bonds and β-hydride abstraction. It is due to this reactivity that these complexes are catalytic intermediates in many organic transformations.

Despite their important role in catalytic reactions, only a few investigations have been undertaken with medium and larger (>7-membered ring) ring size metallacycles due to the lack of efficient synthetic methods. It is interesting to note that only odd numbered metallacycles have been covered in depth as compared to even numbered metallacycles, though the latter have also been implicated as intermediates in catalytic reactions.

The new route for the preparation of metallacycles shown in this review, thus presents an opportunity to synthesize even and odd numbered medium to larger metallacycles, study their reactivity patterns and compare these with the small ring metallacycles. The knowledge obtained from such studies can be used in improving catalytic reactions and so enhance the advancement of organometallic chemistry and catalysis.

## 1.5 Aims and objectives of Project

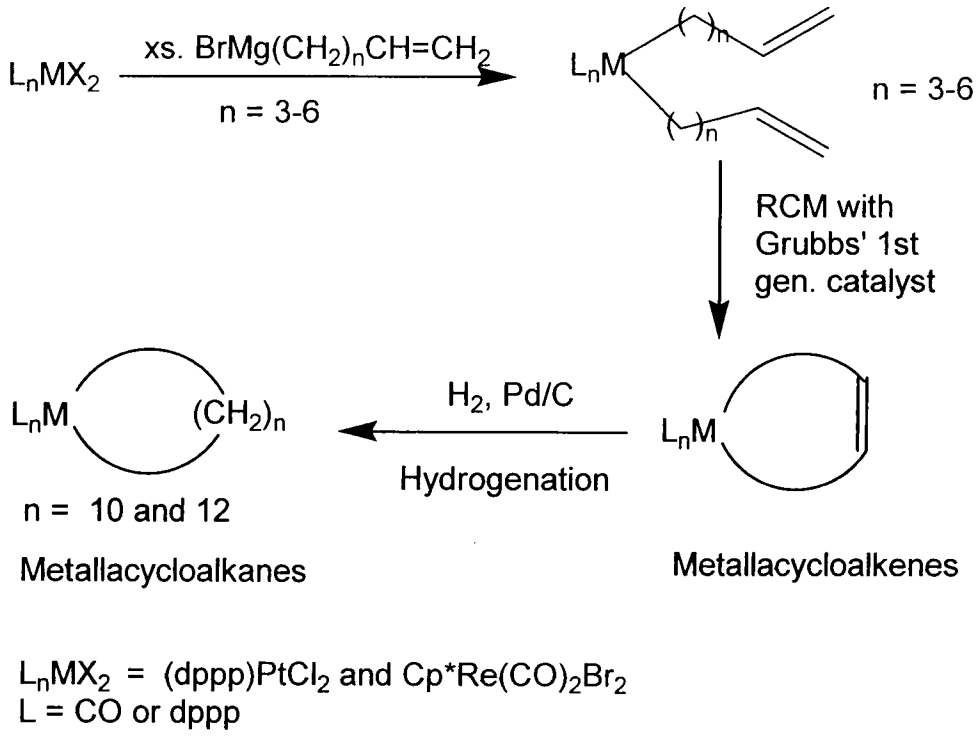
### 1.5.1 The main focus of this project

The main focus of this project was to synthesize platinacycles and their precursors. We hoped to apply the new route for the preparation of metallacycloalkanes in the synthesis of medium- and large-ring size metallacycles and to present new characterization data in the form of $^{13}C$ NMR for these compounds. We also sought to apply the new route in the synthesis of even numbered platinacycles *via* the synthesis of mono(alkenyl)precursors. Reactivity studies such as insertion reactions with CO were to be attempted on these compounds and their precursors. Thermal decomposition studies were also to be carried out.

We also intended to apply the new route in the synthesis of rhenium-containing metallacycles as there are only a few examples of such compounds in the literature [1]. This was so that we could observe and deduce the effect of the metal type on the synthesis of metallacycles.

### 1.5.2 Approach to the synthesis of metallacycles

The new synthetic route to be applied in the synthesis of the metallacycles is shown below (Scheme 1.5). In this route the bis(alkenyl) complexes undergo RCM using Grubbs' catalyst to yield metallacycloalkenes which are then hydrogenated allowing the isolation of metallacycles in relatively good yields.




**Scheme 1.5**: Method applied in the synthesis of metallacycles in this project

## 1.6 References


1. B. Blom, H. Clayton, M. Kilkenny and J.R. Moss, *Adv. Organomet. Chem.*, 2006, **54**, 150.
2. J.P. Collman, J.R. Norton, L.S Hegedus and R.G. Finke, *Principles and Applications of Organo-transition metal Chemistry,* University Science Books, Mill Valley California, 1976, 459.
3. J.X. McDermott, J.F. White and G.M. Whitesides, *J. Am. Chem. Soc.*, 1973, **95**, 4451.
4. R.H. Grubbs, *Handbook of Olefin Metathesis*, Wiley-VCH, Weinheim, *2003.*
5. Y. Chauvin and J.L. Herrison, *Makromol. Chem.*, 1971, **141**, 161.
6. R.H. Grubbs, *Tetrahedron*, 2004, **60**, 7117.
7. (a) T. Agapie, S.J. Schofer, J.A. Labinger and J.E. Bercaw, *J. Am. Chem. Soc.*, 2004, **126**, 1304. (b). A.K. Tomov, J.J. Chirinos, D.J. Jones, R.J. Long and V.C. Gibson, *J. Am. Chem. Soc.*, 2005, **127**, 10166. (c). A. Bollmann, K. Blann, J.T. Dixon, F.M. Hess, E. Killian, H. Maumela, D.S. McGuiness, D.H. Morgan, A. Neveling, S. Otto, M.overett, A.M.Z. Slawwin, P. Wasserscheid and S. Kuhlmann, *J. Am. Chem. Soc.*, 2004, **126**, 14712. (d). M.J. Overett, K. Blann, A. Bollmann, J.T. Dixon, D. Haasbroek, E. Killian, H. Maumala, D.S. McGuiness and D.H. Morgan, *J. Am. Chem. Soc.*, 2005, **127**, 10723.
8. M.E. Dry, *Appl. Catal.*, 1996, **138**, 319.
9. B.L Stocker and J.O. Hoberg, *Organometallics*, 2006, **25**, 4537.
10. P. Diversi, G. Lngrosso, A. Lucherini and S. Murtas, *J. Chem. Soc., Dalton Trans.*, 1980, **9**, 1633.
11. (a) J.X. McDermott, M.E. Wilson and G.M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6529. (b). K. Mashima and H. Takaya, *Organometallics*, 1985, **4**, 1464. (c). K. Mashima, N. Sakai and H. Takaya, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 2475.
12. L.W.M. Lee, W.E. Piers, M. Parves, S.J. Rettig and V.G. Young, *Organometallics*, 1999, **18**, 3904.
13. G. Erker, U. Dork and A.L. Rheingold, *Organometallics*, 1988, **7**, 138.
14. S.J. McLain, C.D. Wood, R.R. Schronk, *J. Am. Chem. Soc.*, 1977, **99**, 3519.
15. (a) M.R. Churchill and W.J. Young, *J. Am. Chem. Soc.*, 1979, **101**, 6462. (b). M.R. Churchill and W.J. Young, *Inorg. Chem.*, 1980, **19**, 3106.

16. R. Emrich, O. Heinemann, P.W. Jolly, C. Kruger and G.P. Verhonik, *Organometallics*, 1977, **16**, 1511.

17. P. Diversi, G. Ingrosso, A. Lucherini, W. Porzio and M. Zocchi, *J. Chem. Soc.*, Dalton Trans., 1983, **5**, 967.

18. S-Y. Wang, S.D. VanderLende, K.A. Abbound and J.M. Boncella, *Organometallics*, 1998, **17**, 2628.

19. K. Jonas, G. Brukart, C. Haselhoff, P. Betz and C. Kruger, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 322.

20. G.K. Young and R.G. Bergamn, *Organometallics*, 1985, **4**, 129.

21. E. Lindner, R-M. Jansen and H.A. Mayer, *Angew. Chem., Int. Ed.*, 1986, **25**, 1008.

22. (a). E.Lindner, E. Schaub, W. Hiller and R. Fawzi, *Chem. Ber.*, 1985, **118**, 3915. (b). E.Lindner, R-M. Jansen, W. Hiller and R. Fawzi, *Chem. Ber.*, 1989, **122**, 1403. (c). E. Lindner, T. Leibfritz, R. Fawzi and M. Steimann, *Chem. Ber.*, 1997, **130**, 347. (d). E.Lindner, R-M. Jansen and H.A. Mayer, *Angew. Chem., Int. Ed.*, 1986, **25**, 1008.

23. Y. Wakatsuki, T. Sakurai and H. Yamazaki, *J. Chem. Soc., Dalton Trans.*, 1982, **10**, 1923. (b). Y. Wakatsuki, O. Nomuro, H. Tone and H. Yamazaki, *J. Chem. Soc., Perkin II*, 1980, 1344.

24. (a). P. Diversi, G. Ingrosso, A. Lucherini, W. Porzio and M. Zocchi, *Inorg. Chem.*, 1980, **19**, 3590. (b). R. Bertani, P. Diversi, G. Ingrosso, A. Lucherini, F. Marchetti, V. Adovasio, M. Nardelli and S. Pucci, *J. Chem. Soc., Dalton Trans.*, 1988, **12**, 2983. (c). P. Diversi, G. Ingrosso, A. Lucherini and W. Porzio, *J. Chem. Soc., Chem. Commun.*, 1977, **22**, 811.

25. (a). R. Wyrwa, H-O. Frohlinch and H. Gorls, *J. Organomet. Chem.*, 1995, 491, 41. (b). R. Wyrwa, H-O. Frohlinch and H. Gorls, J. *Organomet. Chem.*, 1993, **110**, 8657. (c). H-O. Frohlinch, B. Kosan, B. Muller and W. Hiller, *J. Organomet. Chem.*, 1992, **441**, 177.

26. W.D. Neilson, R. D. Larson and P.W. Jennings, *J. Am. Chem. Soc.*, 1988, **110**, 8657.

27. M.L. Steigerwald, W.A. Goddard, *J. Am. Chem. Soc.*, 1985, **107**, 5027.

28. N.W. Alcock, K.H. Bryars and P.G. Pringle, *J. Organomet. Chem.*, 1990, **386**, 399.

29. C.G. Biefeld, H.A. Eide and R.H. Grubbs. *Inorg. Chem.*, 1973, **12**, 2166.

30. J. Chatt and B.L. Shaw, *J. Chem. Soc.*, 1959, 4020.

31. J.X. McDermott, J.F. White and G.M. Whitesides, *J. Am. Chem. Soc.*, 1973, **95**, 4451.

32. S. Mansel, D. Thomas, C. Lefeber, D. Heller, R. Kemper, W. Baumann and U. Rosenthal, *Organometallics*, 1977, **16**, 2886.

33. (a). T.W. Graham, J. Kickham, S. Courtenay, P. Wei and D.W. Stephan, *Organometallics*, 2004, **23**, 3309. (b). J.R. Hagadorn and J. Arnold, *J. Chem. Soc., Dalton Trans.*, 1997, 18, 3087.

34. (a). A. Sivaramakrishna, H. Su and J.R. Moss, *Angew. Chem., Int. Ed.*, 2007, **46**, 3541. (b). K. Dralle, N.L. Jaffa, T. le Roex, J.R. Moss, S. Travis, N.D. Watermeyer and A. Sivaramakrishna, *Chem. Commun.*, 2005, **30**, 3865. (c). A. Sivaramakrishna, H. Su and J.R. Moss, *Dalton Trans.*, 2008, **17**, 2228. (d). A. Sivaramakrishna, F. Zheng and J.R. Moss, *Polyhedron*, 2008, **27**, 1911. (e). F. Zheng, A. Sivaramakrishna and J.R.Moss, *Coord. Chem. Rev.*, 2007, **251**, 2056. (f). E.B. Hager, *MSc dissertation*, University of Cape Town, 2007.

35. T. Mahamo, F. Zheng, A. Sivaramakrishna, G.S. Smith and J.R. Moss, *J. Organomet. Chem.*, 2008, **693**, 103.

36. H. Nagashima, Y. Michino, K-I. Ara, F. Fukanori and K.J. Hoh, *J. Organomet. Chem.*, 1991, **406**, 189.

37. J. Campora, P. Palma and E. Carmona, *Coord. Chem. Rev.*, **1999**, **207**, 193.

38. (a). M.G. Thorn, S.A. Waratuke, E.S. Johnson, P.E. Fanwick and I.P. Rothwell, *Chem. Commun.*, 1996, **23**, 2617. (b). M.G. Thorn, J.H. Hill, S.A. Wataruke, E.S. Johnson, P.E. Fanwick and I.P. Rothwell, *J. Am. Chem. Soc.*, 1997, **119**, 8630.

39. R.H. Grubbs and A. Miyashita, *J. Am. Chem. Soc.*, 1978, **100**, 1300.

40. R.H Grubbs, A. Miyashita, M. Lui and P. Burk, *J. Am. Chem. Soc.*, 1977, **99**, 3863.

41. G.B. Young and G.M. Whitesides, *J. Am. Chem. Soc.*, 1978, **1100**(12), 5808.

42. D.K. Cheethan, R.J. puddephatt, A. Zalkin and D.H. Templeton, *Inorg. Chem.*, 1976, **15**, 12

43. W. Fischer, R.T. Hembre, D.R. Sidler and J.R. Norton, *Inorg. Chim. Acta.*, 1992, **57**, 198.

44. J.M. Manriquez, D.R. McAlister, R.D. Sanner and J.E. Bercaw, *J.Am. Chem. Soc.*, 1978, **100**, 2716.

45. R.H.Grubbs, A. Miyashita, M. Lui and P.Burk, *J. Am. Chem. Soc.*, 1978, **100**, 2418.

46. T. Takahosi, R. Fischer, Z. Xi and K. Nakajima, *Chem. Lett.*, 1996, 357.

47. M.L. Steigerwald and W.A. Goddard III, *J. Am. Chem, Soc.*, 1984, **106**(2), 308.

48. (a). C. Copert, E.I. Negishi, Z. Xi and T. Takahashi, *Tetrahedron Lett.*, 1994, **45**, 695. (b). P.X. Li, Z.F. Xiand T. Takahashi, *Chinese J. Chem.*, 2001, **19**, 45.

49. (a). K. Tsuchiya, H. Kondo and H. Nagashima, *Organometallics*, 2007, **26**, 1077. (b). P.T. Matsunaga, J.C. Mavropoulous and G.L. Hillhouse, *Polyhedron*, 1995, **14**, 175.

50. (a). A. Furstner, *Angew. Chem. Int. Ed.*, 2000, **39**, 3012. (b). C. Aldhart and P.J. Chen, *J. Am. Chem. Soc.*, 2004, **126**, 3496.

51. (a). B.M. Trost and M.K. Trost, Tetrahedron Lett., 1991, **30**, 3647. (b). G. Dyker, *Chem. Ber.*, 1997, **130**, 1567. (c). B.M. Trost, *Acc. Chem. Res.*, 1990, **23**, 34. (d). B.M.Trost and M.K Trost, *J. Am. Chem. Soc.*, 1991, **113**, 1850.

52. D. Masselot, J.P.H. Charmant and T. Gallagher, *J. Am. Chem. Soc.*, 2006, **128**, 694.

# Chapter 2: Metal(alkenyl) complexes

## 2.1 General Introduction

Metal(alkenyl) complexes can be defined as ligand supported metal carbon systems in which the metal is σ-bonded to an aliphatic group containing a least two methylene units ($m \geq 2$) and a pendant terminal $-CH_2=CH_2$ group, as shown in Figure 2.1 [1].

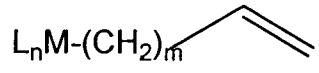



**Figure 2.1**: Structural representation of metal(alkenyl) complexes ($L_nM$ = transition metal and associated ligand and ($m \geq 2$)).

Transition metal(alkenyl) complexes are emerging as an important class of organometallic compounds and have found widespread use in organic synthesis. They have been implicated as key intermediates in important catalytic reactions such as in the Fischer-Tropsch process [2] and in ethylene oligomerization reactions [3].

Furthermore, these compounds exhibit interesting reactivity patterns and applications. For example, bis(alkenyl)platinum(II) complexes have an important application in generating thin platinum films [4] for micro-electronic and catalytic applications [5] using the chemical vapour deposition (CVD) method [6]. Recent publications show that this class of compounds shows novel reactivity patterns and are useful precursors for the preparation of other important classes of compounds particularly metallacycloalkanes [7,8].

Herein, we discuss the synthesis chemical reactivity and applications of these metal(alkenyl) complexes that are emerging as an important class of organometallic compounds. Complexes such as those illustrated in Figure 2.1 will be looked at as well as bis(alkenyl) complexes where two alkenyl chain groups are coordinated to a metal. Complexes containing heteroatoms within the alkenyl chain and heterobimetallic complexes are not discussed.

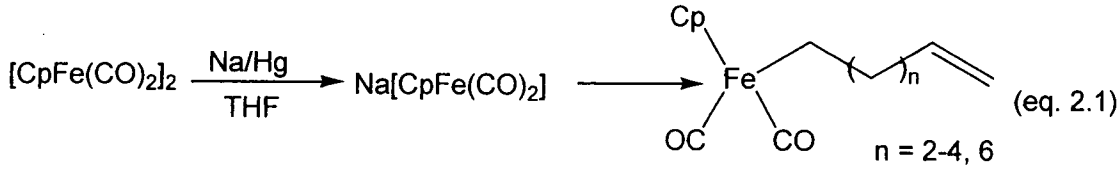
## 2.2 Synthesis of metal(alkenyl) complexes

### 2.2.1 Synthesis of mono(alkenyl) complexes

Literature survey shows that mono(alkenyl) complexes have been widely prepared and studied [1]. The main methods used in the synthesis of the complexes are (i) the anion route (ii) the transmetallation or Grignard route, with only a few reports on synthesis from (iii) dienes and (iv) oxidative addition of a haloalkene to a transition metal.

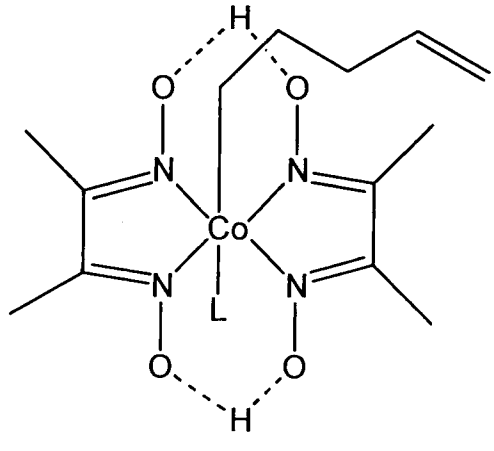
*Anion route*

The synthesis of a series of iron(alkenyl) complexes using the anion route has been reported by Roustan *et al.* [9], who have also reported on the reactivity of these complexes. Iron(alkenyl) complexes of this type have also been investigated by Mapolie and co-workers, who have prepared a series of these complexes with varying alkenyl chain lengths [10]. An example of such complexes is shown below (eq. 2.1).




(eq. 2.1)

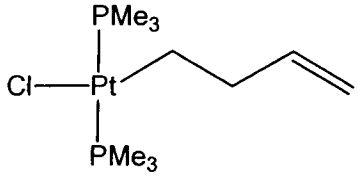
Furthermore, a number of cobaloxime bis(dimethylglyoximato)pyridine cobalt complexes of type **1** have also been prepared using this route [11,12].



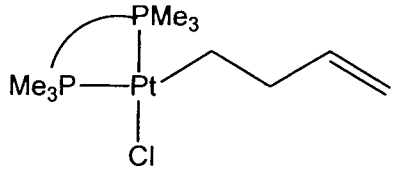

**1**

*Transmetallation*

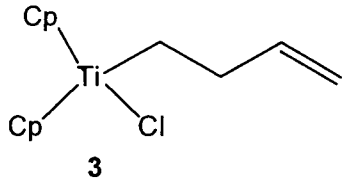
The Grignard route has so far been the most widely employed route in the preparation of metal(alkenyl) complexes [1]. Examples of transition metals whose mono(alkenyl) complexes have been prepared using this synthetic route include complexes of Pt (**2**) [8,13], Ti (**3**) [14], Ni (**4**) [15], Pd [16] and Ru [17].



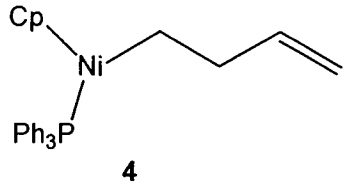

**2a**



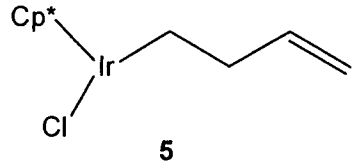

**2b**




**3**



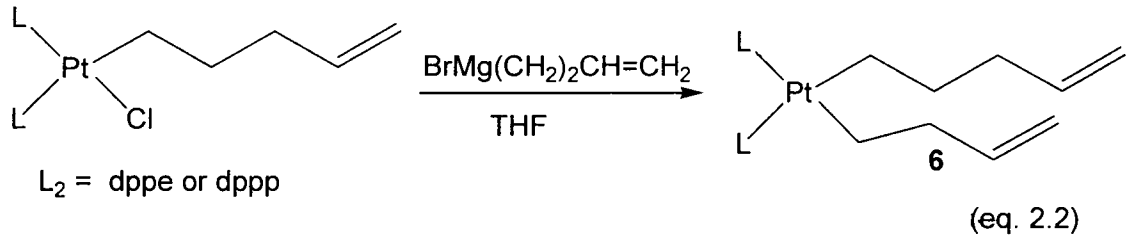

**4**




**5**

Synthesis of mono(alkenyl) complexes through transmetallation can be achieved by either (i) reacting a metal dihalide precursor with two molar equivalents of the appropriate alkenyl Grignard reagent to yield the bis(alkenyl) precursor, subsequent cleavage of one of the metal-carbon bonds with HCl affords the mono(alkenyl) compound or (ii) by alkylation of the metal precursor with 1 molar equivalent of the appropriate alkenyl Grignard reagent.

Synthesis through alkylation has also been applied in the synthesis of novel asymmetric bis(alkenyl)platinum(II) complexes of type **6** whose chemistry has not yet been extensively covered (eq. 2.2) [18].

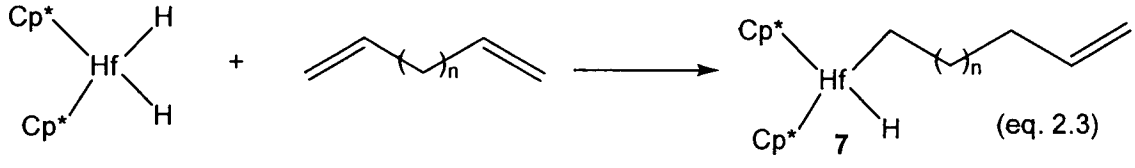



(eq. 2.2)

In some cases such as in the synthesis of the iridium mono(alkenyl) precursor **5**, the products are sensitive to light, heat and the solvent system [1].

*From dienes*

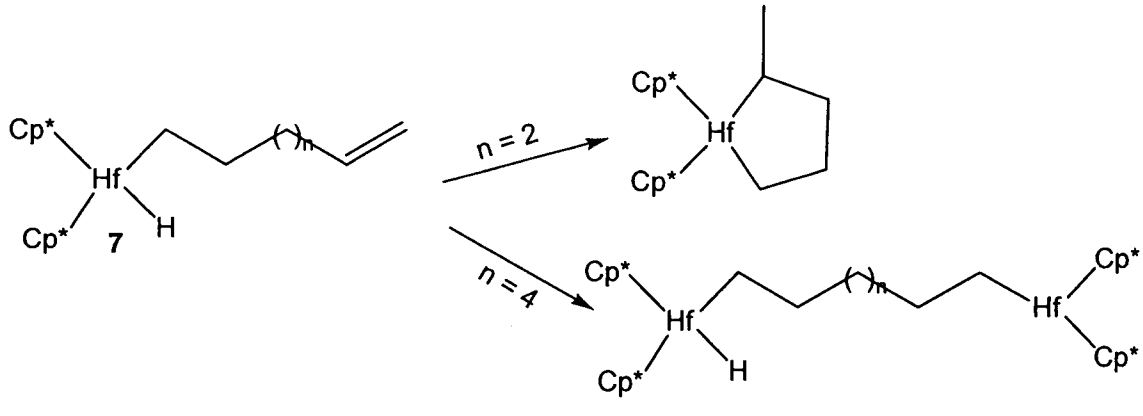
The hafnium(alkenyl) complex of type **7** was prepared by the reaction of $Cp^*_2HfH_2$ and the corresponding α, ω-diene (eq. 2.3) [19].




(eq. 2.3)

n = 3-5

The hafnium(alkenyl) hydride complex **7** was not isolated but was rather observed spectroscopically at low temperatures. On warming to 20°C the hafnium(alkenyl) hydride species converts to a mixture of the five membered hafnacycle and the binuclear alkanediyl derivate (Scheme 2.1).

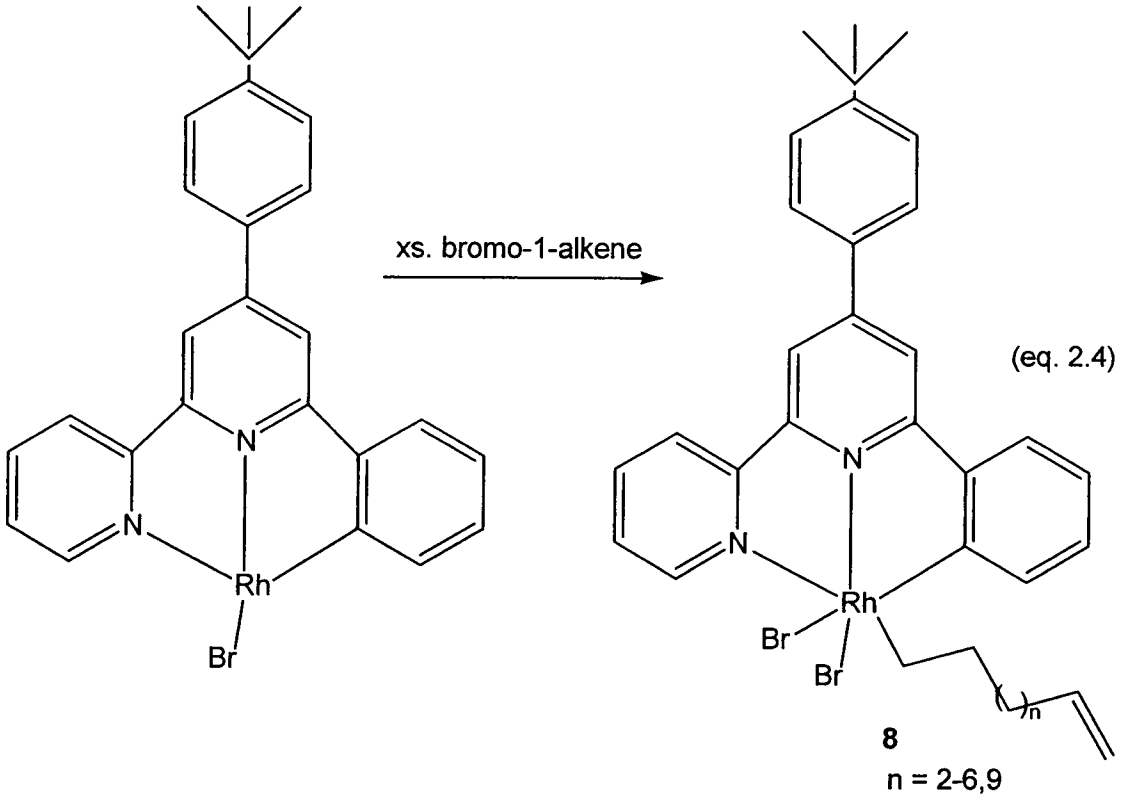



**Scheme 2.1**: Rearrangement of hafnium(alkenyl) complexes at 20°C.

In contrast, the hafnium(alkenyl) complex formed from the longer chain 1,6-heptadiene is stable and cyclization to the seven membered hafnacycle does not occur [19]. No other metal(alkenyl) complexes have been synthesized and reported using this route.

*Oxidative addition*

Frühauf and co-workers recently reported on the synthesis of a series of rhodium(alkenyl) complexes of type **8**, by the oxidative addition of the corresponding ω-bromo-1-alkene in excess to [RhBr(Tpy*)] to give a single product in quantitative yields [20], (Tpy* = 4'-(4-terpy-butylphenyl)-2,2':6',2"-tertpyridine) (eq. 2.4).



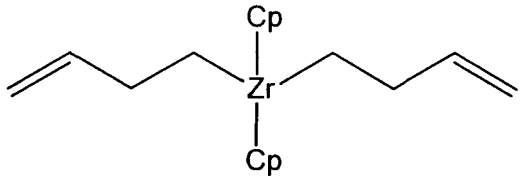

(eq. 2.4)

This method has also been applied in the synthesis of molybdenum(alkenyl) complexes [21].

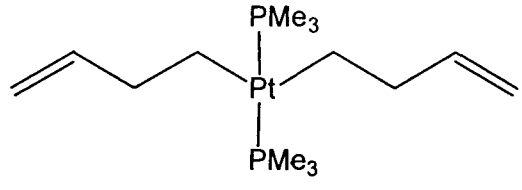
### 2.2.2 Synthesis of bis(alkenyl) complexes

While mono(alkenyl) complexes have been synthesized using various synthetic routes as discussed previously, the known bis(alkenyl) complexes have been prepared exclusively by the reaction of a metal di-halide with a Grignard reagent and are limited to platinum [22], molybdenum [21,23] and zirconium, **9**, [24]. No other synthetic routes are known for the synthesis of bis(alkenyl) complexes of these transition metals.

The bis(alkenyl)platinum(II) complex **10** was prepared by the alkylation of $[(COD)PtCl_2]$ with the corresponding Grignard reagent in the presence of $PMe_3$. Similar complexes with various ligand systems were also prepared by Benn *et al.* [24].

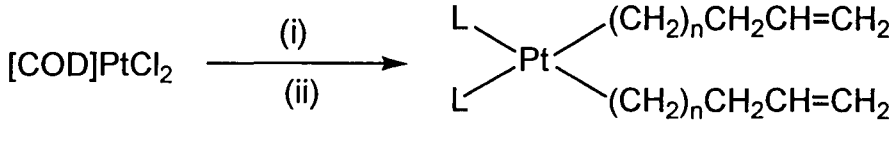



**9**




**10**

Thus bis(alkenyl) complexes can be prepared in relatively high yields using the reaction conditions shown in Scheme 2.2. X-ray crystal structures of some of these complexes have been obtained and reported [1]. These structures clearly show that the alkenyl groups are bonded in a $\eta^1$-mode with pendant alkene double bonds. Metal(alkenyl) complexes containing dppe and dppp ligands were obtained as crystalline solids and thermally stable up to about 100°C even though they have hydrogen atoms in the β-position.




**Scheme 2.2**: Synthesis of bis(alkenyl) complexes; (i) $BrMg(CH_2)_nCH_2CH{=}CH_2$, $Et_2O$, -78°C, (ii) L = $PPh_3$, dppe, dppp; n = 1-4 and 7.

## 2.3 Chemical Reactivity of metal(alkenyl) complexes

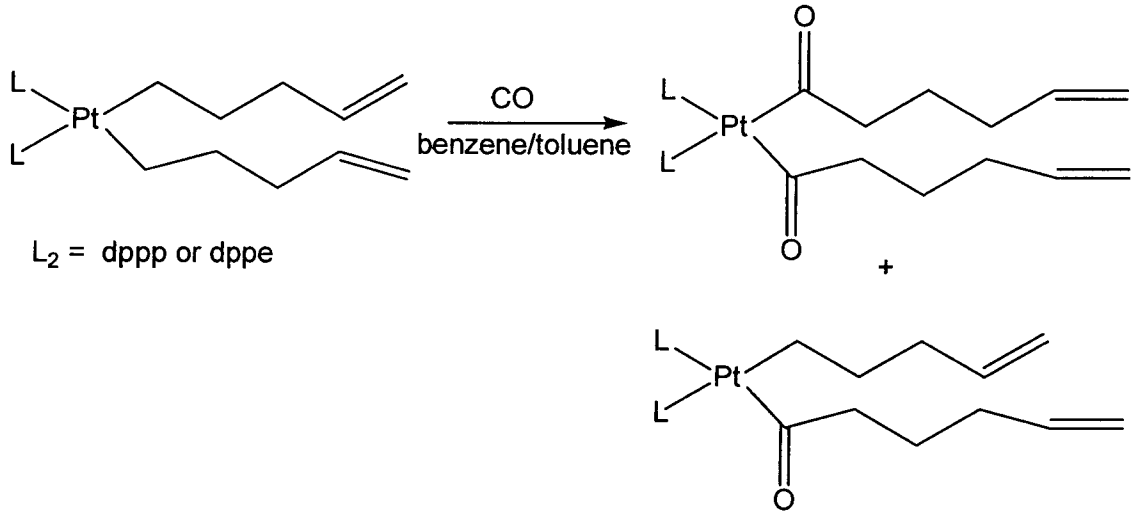
Metal(alkenyl) complexes show reactivity pathways that are not accessible to metal(alkyl) complexes because of the presence of the double bond. Metal(alkenyl) complexes can show three distinct reaction pathways (i) reaction at the metal-carbon bonds, (ii) reaction at the C=C bond and (iii) coordination of the pendant alkene. Some of these reactions may have potential use in organic synthesis since they lead to formation of new C-C bonds.

*Interaction with electrophilic reagents*

Like metallacycloalkanes, metal(alkenyl) complexes also undergo cleavage at the metal-carbon bond when they interact with electrophilic reagents such as acids and halogens. Such interactions give the corresponding hydrocarbons or 1-haloalkene as products [1].

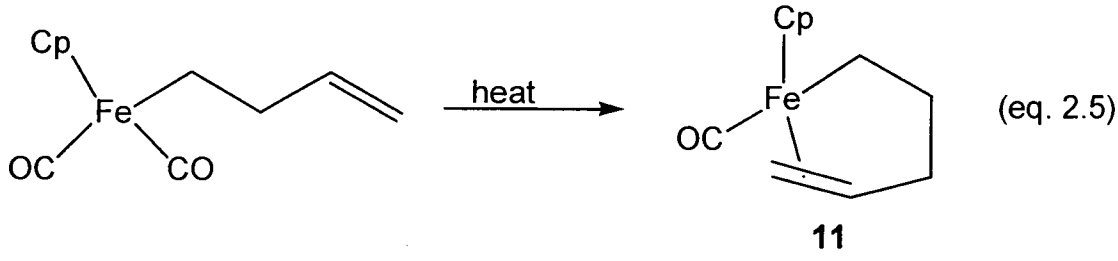
*Carbonylation*

Metal(alkenyl) complexes undergo insertion reactions with small molecules such as carbon monoxide through reactivity at the metal-carbon bond [1].The reaction of carbon monoxide with the bis(pentenyl)platinum(II) complex gave the expected mono(acyl) and di(acyl) products (Scheme 2.3).




**Scheme 2.3**: CO insertion reaction on the bis(pentenyl)platinum(II) complex.

It has also been reported that the iron(butenyl) complex reacts with $TiCl_4$ to form the acyl complex **11**, where the pendant alkene is coordinated to the iron in an $\eta^1$, $\eta^2$-fashion (eq. 2.5) [10b].




Complex **11** has also been reported to form when the iron(butenyl) complex is heated in $CH_3NO_2$. This sort of reactivity is however not observed with the longer chain iron(alkenyl) complexes.

*Rearrangement and formation of metal olefin bonds*

Formation of metal olefin complexes in which the pendant alkene is coordinated to the metal in an $\eta^1$, $\eta^2$-fashion has been observed for other metal(alkenyl) complexes (Figure 2.2). Such reactions occur when the metal(alkenyl) complex reacts with either a trityl salt [$Ph_3CBF_4$] [25], a silver salt [$AgBF_4$] [13] or a Lewis acid [$TiCl_4$] [10].

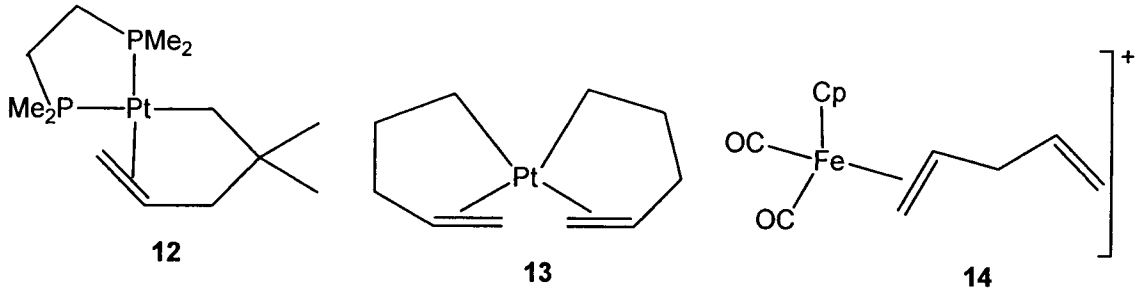
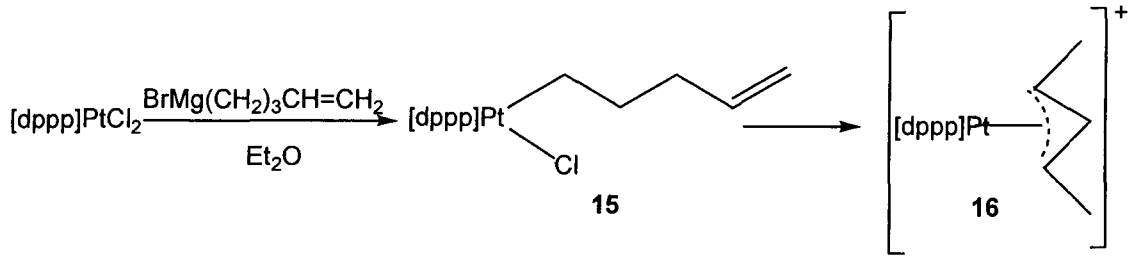



**Figure 2.2**: Examples of metal olefin complexes obtained from metal(alkenyl) complexes.

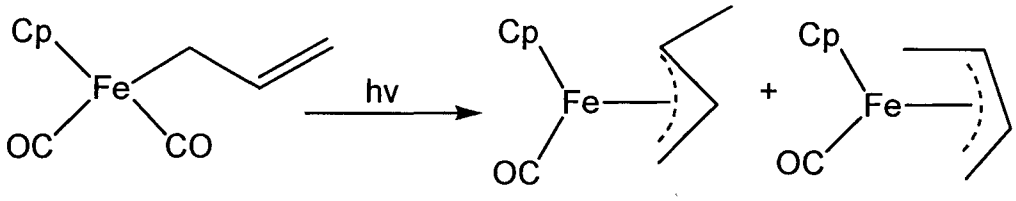
Metal bis(olefin) complexes of type **13** have been reported by Tagge *et al.* [22a]. These were obtained through the loss of [COD] from [Pt(COD){$(CH_2)_3CH=CH_2$}$_2$].

It has been reported that the [(dppp)PtCl{$(CH_2)_3CH=CH_2$}] complex **15**, undergoes an irreversible rearrangement to form the $\eta^3$-1,3-dimethylallyl cationic complex **16** (Scheme 2.4). Such reactions are highly dependant on experimental conditions and in this particular case the new mono(alkenyl) complex **15** is sensitive to solvent system, temperature and light [26]. Mono(alkenyl) complexes of Group 9 metals (M = Rh, Ir) readily rearrange to their allylic isomers in a similar fashion to that of the platinum analogues. The strong nucleophiles (halide ligands) in these complexes have been shown to accelerate the rate of rearrangement.




**Scheme 2.4**: Irreversible rearrangement of Pt mono(alkenyl) precursors.

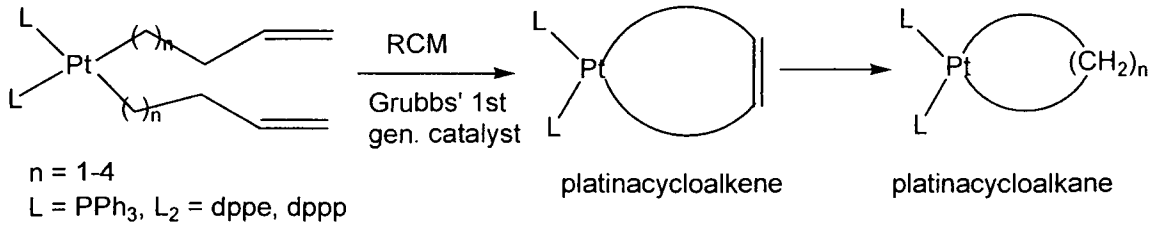
Rouston *et al.* [9] found that the photolysis or irradiation of the iron(butenyl) complexes resulted in the evolution of CO and formation of an isomeric mixture of two $\eta^3$-methylallyl complexes (eq. 2.6)




(eq. 2.6)

*Ring closing metathesis (RCM)*

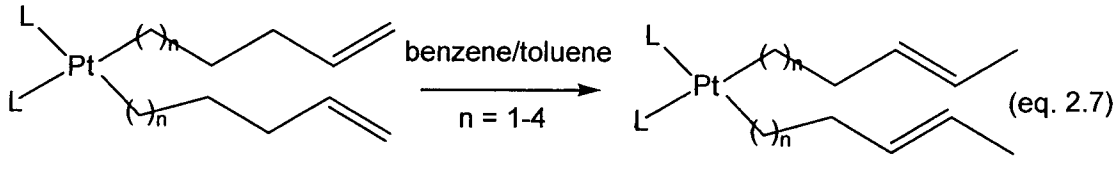
Moss *et al.* [8,18] have recently reported that some bis(alkenyl) metal complexes are able to undergo ring closing metathesis (RCM) reaction using Grubbs 1$^{st}$ generation catalyst to yield the corresponding metallacycloalkenes in quantitative yields. Using this synthetic route, a range of bis(alkenyl)platinum(II) complexes have been successfully converted to the corresponding platinacycloalkenes and further catalytic hydrogenation using palladium on carbon yielded the platinacycloalkanes (Scheme 2.5) [1,8,18]. This synthetic route has been extended to other metals such as Pd, Rh, Ir, Fe and Ru.




**Scheme 2.5**: Preparation of platinacyles from bis(alkenyl)platinum(II) complexes.

*Isomerization*

Bis(alkenyl) complexes also undergo quantitative isomerization to give the corresponding internal alkene complexes and their isomers (eq. 2.7) [27]. Such reactions are dependant on the nature of the supporting ligand and also on the length of the alkenyl chain. For example, in the case of (diphos)platinum(II) complexes the rate of isomerization increases with an increase in the alkenyl chain length. The mono(alkenyl) complexes of Pt, Ir and Rh also react and behave in a similar manner.



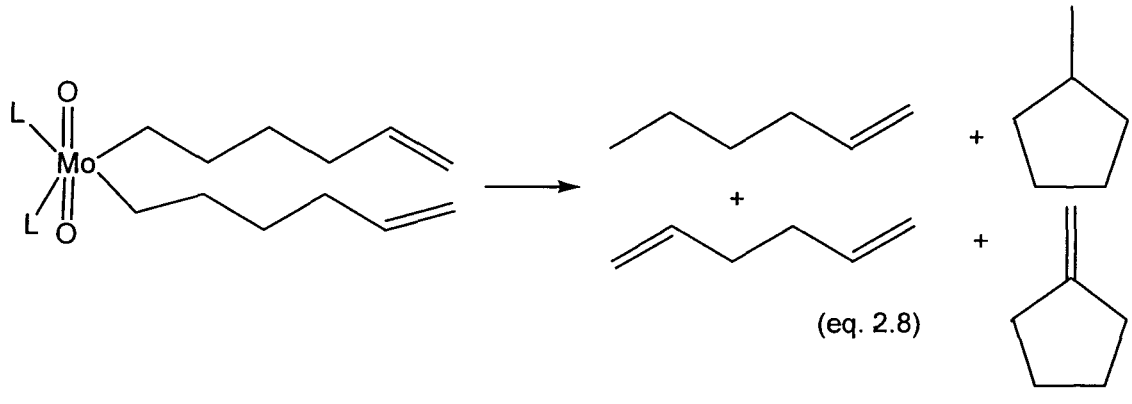

*Thermal decomposition*

The thermal stability of metal(alkenyl) complexes is highly dependant on the solvent system; thus halogenated solvents readily cleave the metal-carbon bond to form metal halides species irrespective of the associated ligand [1,27]. Although thermal decomposition pathways of metal(alkenyl) complexes may be similar to those of metallacycles or metal(alkyl) complexes, the products formed differ considerably because of the presence of the pendant alkene functionality.

Bis(alkenyl) metal complexes can give various products upon decomposition, these include (i) diene and 1-alkene through β-hydride elimination followed by reductive elimination, (ii) long chain dienes by reductive elimination and (iii) isomerization or rearrangement of the coordinated alkenyl ligand. It is also believed that metal(alkenyl) species may be important intermediates in the decomposition of metallacycloalkanes through β-hydride elimination [28].

The triphenylphosphine complex $[Pt(PPh_3)_2\{(CH_2)_nCH=CH_2\}_2]$ (n = 3 or 5) decomposes to yield an intense red colour which is believed to be due to $Pt_n(PPh_3)_m$ clusters. In contrast, similar complexes with diphosphine supporting ligands were found to be quite stable up to about 100°C without decomposition.
Thus, diphosphine ligands have been found to increase the thermal stability of these compounds significantly [29].

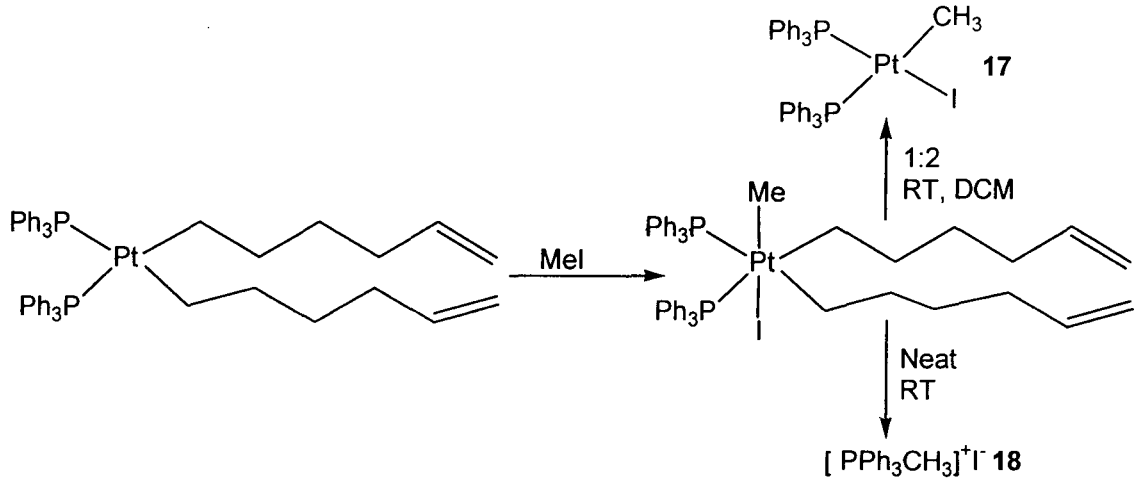
The anaerobic and aerobic decomposition of a molybdenum(VI)dioxo bis(alkenyl) complex has been investigated by Vetter and Sen (eq. 2.8) [23]. Under anaerobic conditions, thermal decomposition leads to formation of 1-hexene, 1,5-hexadiene, methylcyclopentane and methylenecyclopentane. On the other hand, the aerobic decomposition gave the same mixture of products but in addition, cyclopentylformaldehyde was also formed.




(eq. 2.8)

*Oxidative addition*

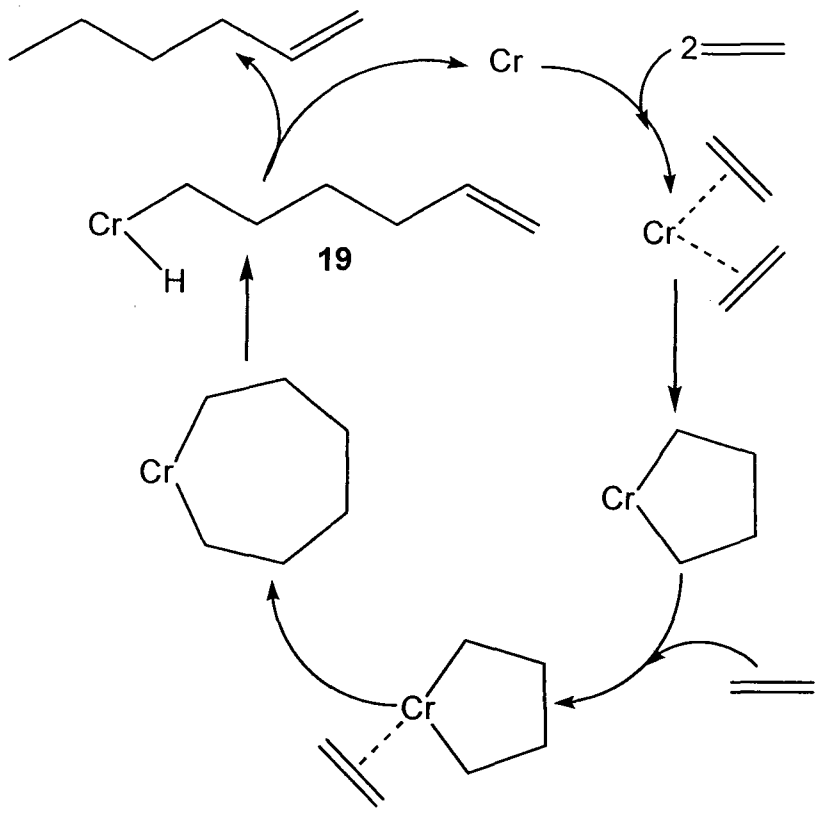
The bis(alkenyl)platinum(II) complexes have been shown to undergo oxidative addition reactions with methyl iodide to yield different products depending on the experimental conditions (Scheme 2.6) [26]. The reaction proceeds to give complexes **17** and **18** through the formation of hexacoordinate platinum(IV) species.




**Scheme 2.6**: Oxidative addition of MeI to a bis(hexenyl)platinum(II) complex.

## 2.4 Implications and applications of metal(alkenyl) complexes in catalysis

Mono(alkenyl) complexes have been shown to mediate chromium-catalyzed trimerization of ethylene to 1-hexene *via* the formation of a chromium seven membered metallacycle (Scheme 2.7) [27]. The mechanism proceeds by the insertion of ethylene into chromacyclopentane to form chromacycloheptane which undergoes ring opening β-hydride elimination to generate the chromium(hexenyl) hydride **19**. Reductive elimination of **19** gives the 1-hexene product and the active catalytic species [3,30 ].




**Scheme 2.7**: Schematic representation of chromium catalyzed ethylene trimerisation (Ligands omitted for clarity).

Recently, a new chromium catalyst has been developed for the selective trimerization and tetramerization of ethylene to 1-octene [3,31]. The reaction is believed to proceed *via* a metallacycle mechanism implicating the existence of a nine membered chromium metallacycle, which likely decomposes to the respective chromium-octenyl hydride intermediate [32].

Zirconocene mono- and bis-alkenyl complexes of the type $Cp_2ZrClR$ and $Cp_2ZrR_2$ (where R = alkenyl group) have been synthesized and reported to be precursors in alkene polymerization reactions [22b].

## 2.5 Concluding Remarks

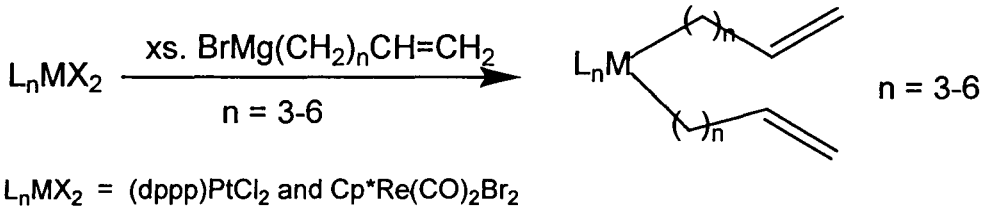
Metal(alkenyl) complexes form an important class of organo-transition metal compounds mainly because of their role as intermediates in ethylene oligomerization reactions. They are also useful precursors in the synthesis of metallacycles. A range of metal(alkenyl) complexes can be prepared using different synthetic procedures. However, as observed form this review mono(alkenyl) complexes have been more extensively synthesized and researched as compared to bis(alkenyl) complexes.

The active pendant alkene functionality in these complexes provides them with additional reaction opportunities such as isomerization and rearrangement which are not observed for metal(alkyl) complexes. Ring closing metathesis reaction on the bis(alkenyl) complexes has provided a new effective route towards the synthesis of larger ring-size metallacycloalkenes and metallacycloalkanes. This method has been shown to work for various transition metals such as Pd, Pt, Ir and Rh.

Reactivity studies on these complexes displays some interesting chemistry and could provide further knowledge on the nature and behaviour of these complexes. This information can be useful in improving and better understanding the mechanism of the catalytic reactions in which they are involved.

## 2.6 Approach in the preparation of bis(alkenyl) complexes

As stated earlier part of the aims and objectives of this project was to synthesize bis(alkenyl) complexes of platinum and rhenium using the transmetallation method (Scheme 2.8) and to carry out reactivity studies on these complexes as well as thermal decomposition studies.




$L_nMX_2$ = (dppp)$PtCl_2$ and Cp*$Re(CO)_2Br_2$
L = CO

**Scheme 2.8**: Method applied in the synthesis of bis(alkenyl) complexes in this project

## 2.7 References


1. A. Sivaramakrishna, H.S. Clayton, C. Kaschula and J.R. Moss, *Coord. Chem. Rev.*, 2007, **251**, 1294.
2. M.L. Turner, N. Marsih, B.E. Mann, R. Quyoum, H.C. Long and P.M. Maitlis, *J. Am. Chem. Soc.*, 2002, **124**, 10456.
3. J.R. Briggs, *J. Chem. Soc. Chem. Commun.*, 1989, **11**, 674.
4. S.M.A. Shibli and M. Noel, *J. Power Sources*, 1993, **45**, 139.
5. C. Dossi, R. Psaro, A. Bartsch, A. Fusi, L. Sordelli, R. Ugo, M. Bellatreccia, R. Zanoni and G. Vlaic, *J. Catal.*, 1994, **145**, 377.
6. (a). D.C. Bradley, *Polyhedron*, 1994, **13**, 1111. (b). R. J. Puddephatt, *Polyhedron*, 1994, **13**, 1233.
7. B. Blom, H. Clayton, M. Kilkenny and J.R. Moss, *Adv. Organomet. Chem.*, 2006, **54**, 155.
8. K. Dralle, N.L. Jaffa, T. le Roex, J.R. Moss, S. Travis, N.D. Watermeyer and A. Sivaramakrishna, *Chem. Commun.*, 2005, **30**, 3865.
9. J.L. Roustan, J.Y. Merour, C. Charrier, J. Benaim and P. Cadoit, *J. Organomet. Chem.*, 1979, **168**(1), 61.
10. (a). L. Hermans and S.F. Mapolie, *Polyhedron*, 1997, **16**, 869. (b). G. Joorst, R. Karlie and S.F. Mapolie, *S. Afr. J. Chem.*, 1998, **51**,132.
11. M.R. Ashcroft, A. Bury, C.J. Cooksey, A.G. Davies, B.D. Gupta, M.D. Johnson and H. Morns, *J. Organomet. Chem.*, 1980, **195**, 89.
12. T. Yamada and Y. Ohashi, *Bull. Chem. Soc. Jpn.*, 1998, **17**, 2527.
13. (a).T.C. Flood and J.A. Statler, *Organometallics*, 1984, **3**, 1795. (b). T.C. Flood and S.P. Bitler, *J. Am. Chem. Soc.*, 1984, **106**, 6067.
14. H. Lehmkuhl, Y.L. Tsien, E. Janssen and R. Mynott, *Chem. Ber.*, 1983, **116**, 2426.
15. J.M. Brown and K. Mertis, *J. Chem. Soc., Perkin Trans.*, 1973, 1993.
16. P. Barabotti, P. Diversi, G. Ingrosso, A. Lucherini and F. Nuti, *J. Chem. Soc., Dalton Trans.*, 1984, **11**, 2517.
17. H. Lehmkuhl, J. Grundke and R. Mynott, *Chem. Ber.*, 1983, **116**, 176.
18. A. Sivaramakrishna, H. Su and J.R. Moss, *Dalton Trans.*, 2008, **17**, 2228.
19. J.E. Bercaw and J.R. Moss, *Organometallics*, 1992, **11**, 639.

20. B.C. de Pater, E.J. Zijp, H.W. Frühauf, J.M. Ernsting, C.J. Elsevier and K. Vrieze, *Organometallics*, 2004, **23**, 269.

21. J.Y. Mérour, C. Charrier, J. Benaim, J.L. Rouston and D. Commereuc, *J. Organomet. Chem.*, 1972, **39**, 321.

22. (a).C.D. Tagge, R.D. Simpson, R.G. Bergman, M.J. Hostetler, G.S. Girolami and R.G. Nuzzo, *J. Am. Chem. Soc.*, 1996, **118**, 2634. (b). C.E. Denner and H.G. Alt, *J. Appl. Polym. Sci.*, 2003, **89**, 3379.

23. W.M. Vetter and A. Sen, *Organometallics*, 1991, **10**, 244.

24. R. Benn, R.D. Reinhardt and A. Rufińska, *J. Organomet. Chem.*, 1985, **282**, 291.

25. D.E. Laycock, J. Hartgerink and M.C. Baird, *J. Org. Chem.*, 1980, **45**, 291.

26. A. Sivaramakrishna, J.R. Moss, H.S. Clayton, E. Hager, T. Mahamo, M.M. Mogorosi, L.L.M. Mbatha and F. Zheng, unpublished work.

27. A. Sivaramakrishna, H. Su and J.R. Moss, *Organometallics*, 2007, **26**, 5786.

28. J.X. McDermott, J.F. White and G.M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521.

29. F. Zheng, *MSc dissertation* 2007.

30. J.T. Dixon, M.J. Green, F.M. Hess and D.H. Morgan, J. *Organomet. Chem.*, 2004, **689**, 3641.

31. L.A.MacAdams, G.P. Buffone, C.D. Incarvito, L.A. Golen, A.L. Rheingold and K.H. Theopold, *Chem. Commun.*, 2003, **10**, 1164.

32. A. Bollmann, K. Blann, J.T. Dixon, F.M. Hess. E. Killian, H. Maumela, D.S. McGuinness, D.H. Morgan, A. Neveling, S. Otto, M. Overett, A.M.Z. Slawin, P. Wasserscheid and S. Kuhlmann, *J. Am. Chem. Soc.*, 2004, **126**, 14712.

# Chapter 3: Synthesis, characterization and reactivity of platinacycles

## 3.1 Introduction

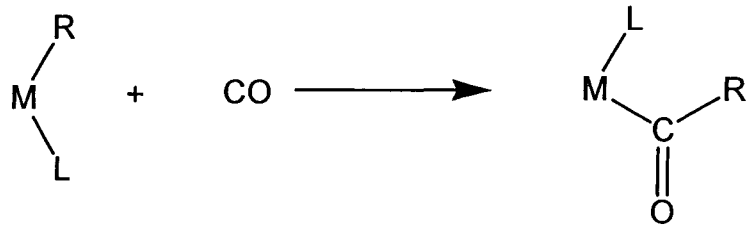
Literature review shows that a large number of platinacycles have been prepared and characterized (refer to Chapter 1). Stable large-ring size platinacycles have been prepared in quantitative yields from their bis(alkenyl)platinum(II) precursors through RCM reaction[1].

Thermal decomposition studies have also been done on large-ring size platinacyles and it has been shown that they decompose at high temperatures to give a mixture of organic products. Such products include 1-alkenes, 2-alkenes, *n*-alkenes, α, ω-dienes and cycloalkanes [2].

In this project, platinacycles and their precursors have been synthesized, insertion reactions with carbon monoxide (CO) have been attempted on these complexes. Thermal decomposition studies have also been carried out on the platinacycles and their precursors. A brief background on the reactivity of transition metal complexes with CO is given below.

### 3.1.1 CO insertion reactions

A schematic representation of carbon monoxide (CO) insertion reactions or carbonylation is given in equation 3.1, where [M(L)R)] is a reactant or intermediate, R = alkyl or related σ-bonded carbon group, L = other ligands and M = metal [3].




(eq. 3.1)

The first CO insertion reaction was observed in 1957 with methylmanganese pentacarbonyl [4]. Booth and Chatt [5] then discovered ten years later that Pd(II), Ni(II) and Co(II) alkyl and aryl derivates also undergo reversible CO insertion.

FT-IR and NMR spectroscopy are the most popular characterization techniques used in ascertaining the formation of metal acyl complexes. The molecular structures of some metal acyl complexes, such as $[MoCp(CO)_2(PPh_3)COMe]$ (**1**) [6] and $[Pd(P\sim N)(CH_2CH_2COMe)]OTf$ (**2**) [7] where P~N = phosphinomethyloxaline have been determined ( Figure 3.1).

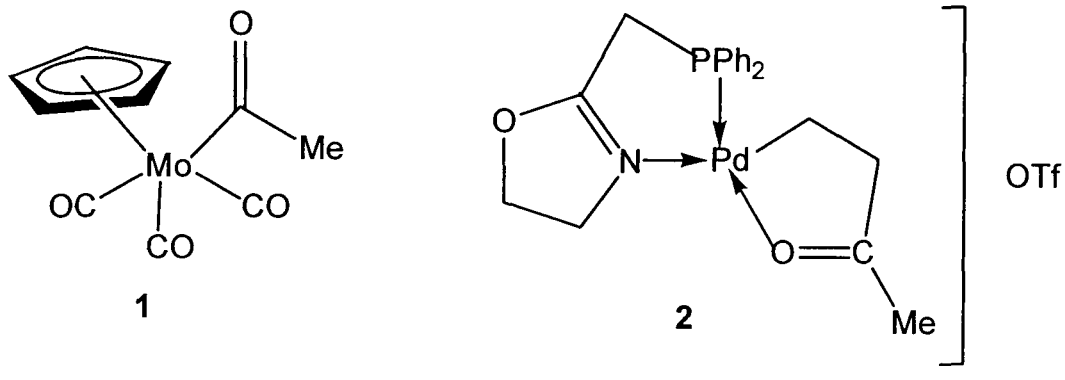
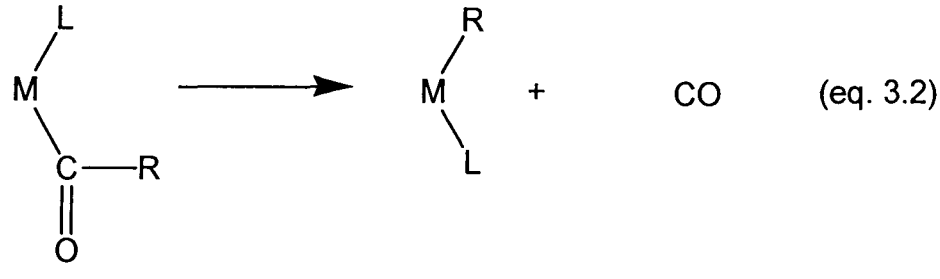



**Figure 3.1**: Some acyl complexes whose X-ray crystal structure has been determined.

Decarbonylation, which is the reverse of CO insertion, is also known (eq. 3.2) and has been studied [4,5]. This process is often promoted by heating or photolysis [4].




Decarbonylation, the elimination of CO accompanied by conversion of an acyl group to the corresponding alkyl moiety was initially shown by the formation of phenylmanganese pentacarbonyl from benzoylmanganese pentacarbonyl [5].

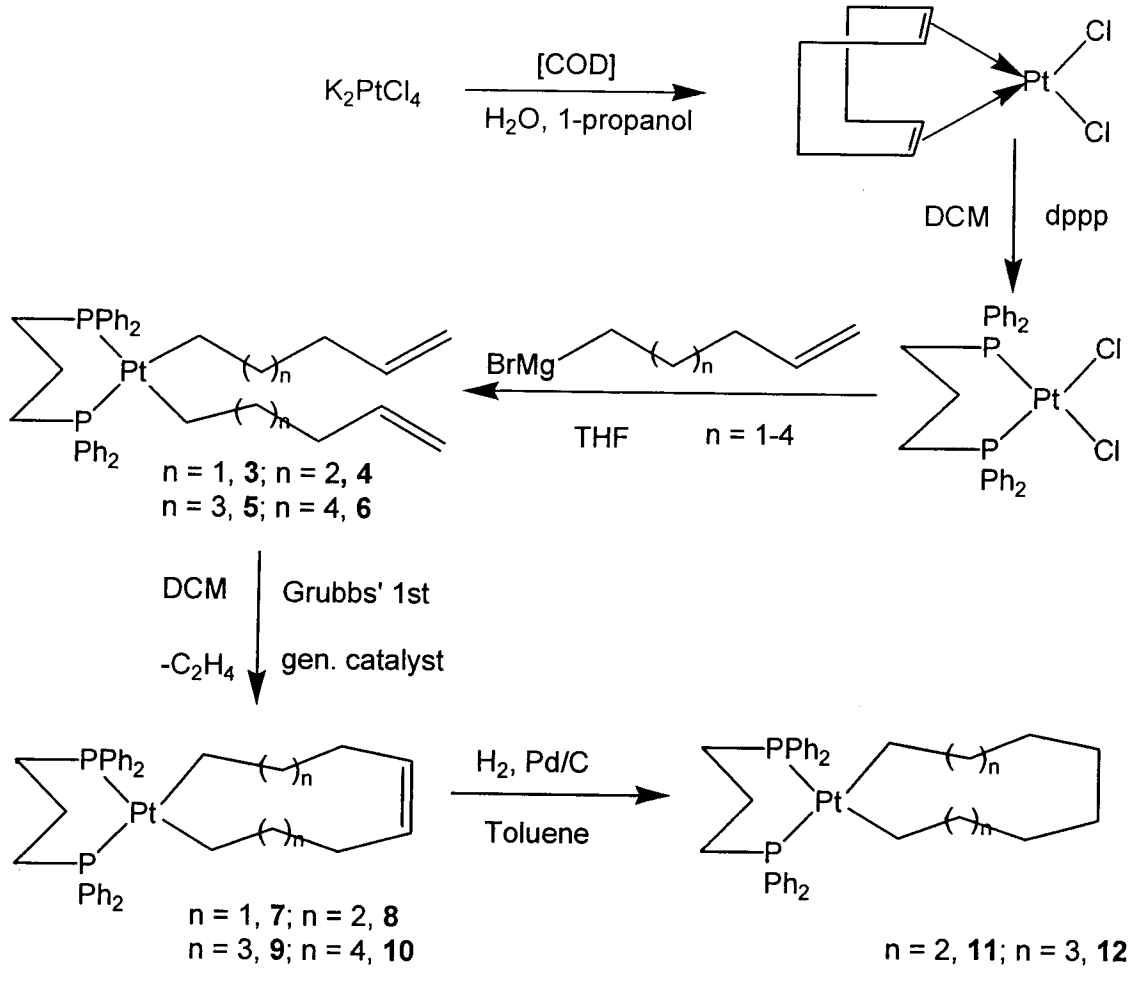
Over the years the kinetics and mechanism of CO insertion reactions has been intensively studied and a vast amount of information has been gathered on such reactions [8,9]. Metallacycloalkanes of Ti [10], Ru and Os [11], Co [12] and Pd [13] have been shown to undergo CO insertion, followed by reductive elimination to give the corresponding cyclic ketones. In all these reactions, insertion of a second molecule (double insertion) of CO into the other metal-carbon bond of the metallacyclic ring was observed and reported.

Our interest in CO insertion reactions resides in the fact that they offer for the functionalization of hydrocarbons to give valuable organic compounds such as cyclic ketones as well as the formation of interesting new acyl complexes.

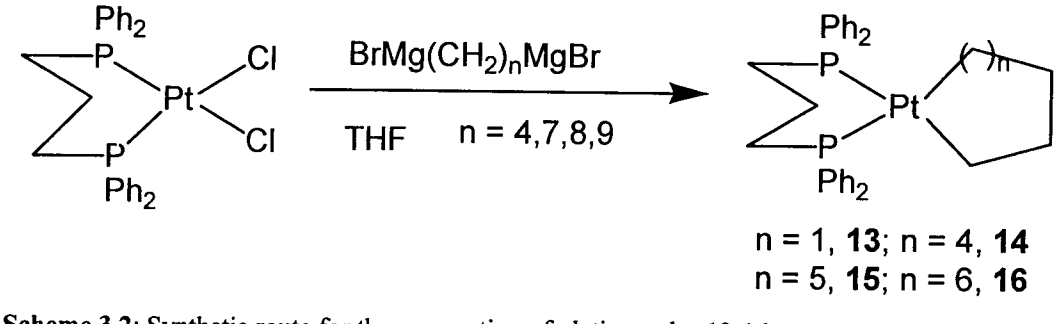
### 3.2 Synthesis and characterization of platinacycles and their precursors

Platinacycles were synthesized through a method that uses Grubbs' 1$^{st}$ generation catalyst. In this method the bis(alkenyl)platinum(II) complexes **3-6** were obtained from the transmetallation reaction of the dichloroplatinum(II) complex, [Pt(dppp)$Cl_2$], with the appropriate alkenyl Grignard reagent. Complexes **3-6** then underwent ring-closing metathesis (RCM) reaction to give the respective platinacycloalkenes, complexes **7-10**. These platinacycloalkenes were then hydrogenated to yield platinacycloalkanes **11** and **12** (Scheme 3.1) [1]. These complexes were obtained in relatively good yields irrespective of the ring size.

The di-Grignard route was applied in the synthesis of even and odd numbered platinacycles, complexes **13-16**. In this case [Pt(dppp)$Cl_2$] was treated with the appropriate di-Grignard reagent in dry diethyl ether or tetrahydrofuran (Scheme 3.2). The platinacyloalkanes were obtained as light brown or colourless oils.




**Scheme 3.1**: Synthetic route for the preparation of platinacycles **7-12**.




**Scheme 3.2**: Synthetic route for the preparation of platinacycles **13-16**

The bis(alkenyl)platinum(II) complexes **3-6** were obtained as white crystalline solids in relatively high yields. They have been characterized by melting point, $^{1}H$ and $^{31}P$ NMR spectroscopy, elemental analysis and mass spectroscopy. The data obtained for these complexes was in agreement with the literature [1]. $^{13}C$ NMR data has also been obtained for the first time for these complexes (see chapter 5 for data).

### 3.2.1 Characterization of bis(alkenyl)platinum(II) complexes

*NMR spectroscopy*

$^{1}H$ NMR spectra of complexes **3-6** showed similar patterns. Signals in the region of 0.84-1.25 ppm were observed for protons on the carbon atom directly bonded to the platinum centre. The remaining methylene protons of the alkenyl chains appeared as broad multiplets in the region of 0.95-2.35 ppm. The (CH=) protons appeared around 5.45-5.80 ppm with the terminal protons ($=CH_2$) appearing in the region of 4.72-4.90 ppm. Similar trends have been reported before for similar complexes [1].

$^{31}P$ NMR spectra of complexes **3-6** also showed similar trends, displaying singlets in the region of 3.44-4.10 ppm with satellites corresponding to $^{1}J(^{195}Pt\text{-}^{31}P)$ coupling constants in the range of 1605-1622 Hz. Similar patterns have also been reported for such complexes [1].

Similar trends in the $^{13}C$ NMR spectra were observed for complexes **3-5**. Therefore, only that of complex 5 will be discussed here. The singlet at 14.45 ppm was assigned to the carbon directly bonded to the platinum centre (C1) (Figure 3.2). The dppp ligand gave rise to singlets in the region of 24.37-27.76 ppm for its methylene carbons (C8-C10), as well as broad multiplets in the region of 127.75-133.49 ppm for the phenyl carbons.

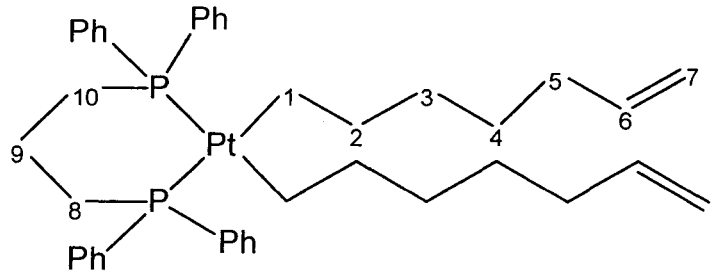



**Figure 3.2**: Representation of methylene and alkene carbons in bis(alkenyl)platinum(II) complex, **5**.

The carbons labelled as C2-C5 appeared as multiplets further upfield in the region of 27.73-35.60 ppm. The terminal alkene carbon C7 gave rise to a singlet at 113.30 ppm, whilst the alkene carbon C6 resonated at 140.07 ppm.

*Mass spectrometry*

The mass spectra for complex **4** is shown below (Figure 3.3), this compound showed a parent ion peak at *m/z* 773.8 $[M]^+$. It also displayed a fragmentation pattern involving the sequential loss of hexenyl chains, 689.7 $[M-(CH_2)_4CH=CH_2-H]^+$ and 601.1 $[M-2\{(CH_2)_4CH=CH_2\}]^+$.

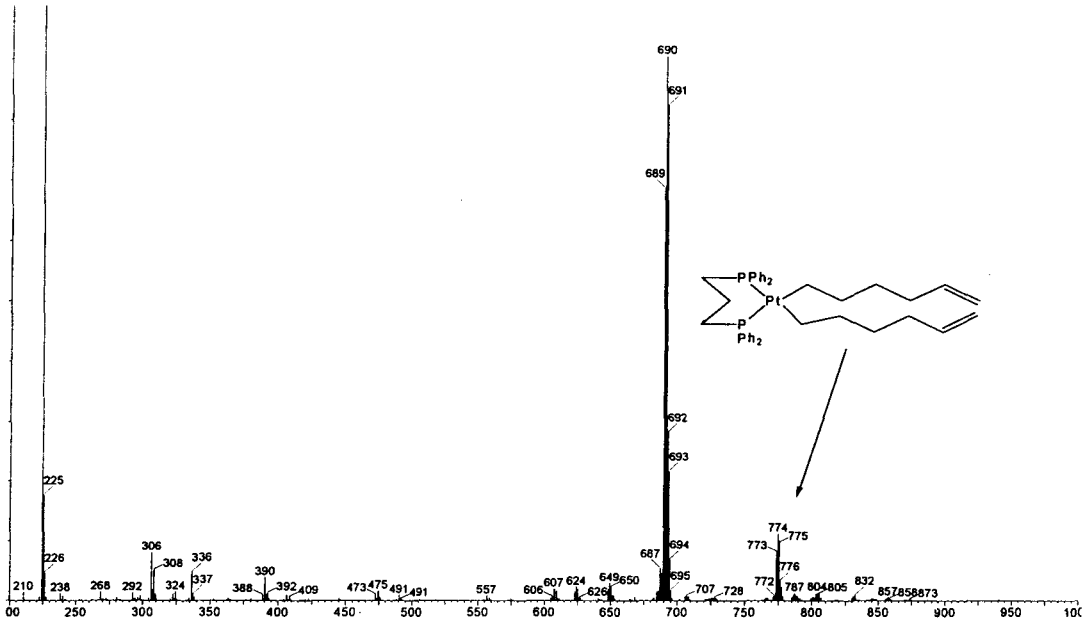



**Figure 3.3**: FAB mass spectrum for complex **4**.

### 3.2.2 Characterization of platinacycloalkenes

Platinacylcoalkenes were obtained in relatively high yields (for example 78% and 84% for complexes **8** and **9** respectively) from the ring-closing metathesis of their corresponding bis(alkenyl)platinum(II) precursors. These complexes were found to be thermally stable, melting within a range of 160-170°C to brown unidentified oils, for example complex **7** melted between 162-164°C.

These platinacycloalkenes were characterized using melting point, $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectroscopy, elemental analysis, as well as mass spectroscopy in the case of complex **8** and **9** (characterization data have been summarized in Tables 3.1-3.3). The data obtained for these complexes agreed with that reported in the literature for similar complexes [1].

*NMR spectroscopy*

The $^{1}H$ NMR spectra of these platinacycloalkenes displayed similar patterns to those displayed and observed for their precursors (the bis(alkenyl)platinum(II) complexes), except for the absence of the signal due to the terminal alkene protons. Since the progress of these reactions was monitored by $^{1}H$ NMR, one could clearly observe the merging of the two signals due to the CH= and $=CH_2$ protons into one broad peak representative of the internal alkene protons in the region 5.10-5.55 ppm.

$^{31}P$ NMR also displayed resonances similar to those displayed by the starting materials (complexes **3-6**) in the region of *ca.* 3.1 ppm. In the case of the 11- and 13-membered platinacycloalkenes **8** and **9**, two signals and their corresponding satellites were observed in the $^{31}P$ NMR spectrum (Figure 3.4). This could be due to the presence of cis and trans isomers around the C=C or it could also be due to the fluxional nature of the metallacyclic ring. A similar trend was reported by Gibson and co-workers when they observed an unprecedented α-olefin distribution in their study of a chromium-based homogeneous ethylene oligomerization precatalyst. They attributed this to the intermediate chromacycloalkene assuming different conformations [14].

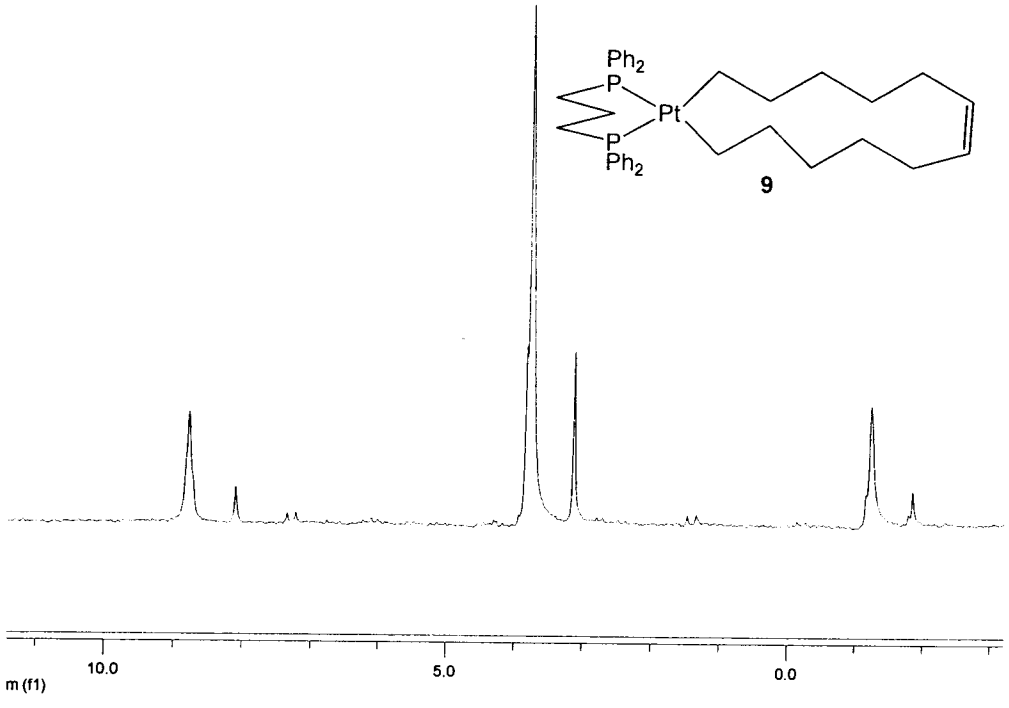



**Figure 3.4**: $^{31}P$ NMR spectra for complex **9**.

**Table 3.1**: $^{1}$H NMR data for complexes **3-12**

| Complex | $^{1}$H NMR (δ ppm)[a] |
|---|---|
| **3** | 0.95-1.05 (m, 4H) Pt{C**H**$_2$(CH$_2$)$_2$CH=CH$_2$}$_2$; 1.00-1.25 (m, 6H) Pt{CH$_2$C**H**$_2$CH$_2$CH=CH$_2$}$_2$ and PCH$_2$C**H**$_2$CH$_2$P; 1.55-1.62 (m, 4H) Pt{CH$_2$CH$_2$C**H**$_2$CH=CH$_2$}$_2$; 2.35-2.44 (m, 4H) PC**H**$_2$CH$_2$C**H**$_2$P; 4.85-4.92 (m, 4H) =C**H**$_2$; 5.45-5.56 (m, 2H) C**H**=; 7.32-7.46 (m, 20H) P**Ph**$_2$. |
| **4** | 0.85-1.13 (m, 4H) Pt{C**H**$_2$(CH$_2$)$_3$CH=CH$_2$}$_2$; 0.97-1.30 (m, 4H) Pt{CH$_2$C**H**$_2$(CH$_2$)$_2$CH=CH$_2$}$_2$; 1.62-1.75 (m, 6H) Pt{(CH$_2$)$_2$C**H**$_2$CH$_2$CH=CH$_2$}$_2$ and PCH$_2$C**H**$_2$CH$_2$P; 1.96-2.02 (m, 4H) Pt{(CH$_2$)$_3$C**H**$_2$CH=CH$_2$}$_2$; 2.45-2.52 (m , 4H) PC**H**$_2$CH$_2$C**H**$_2$P; 4.87-5.05 (m, 4H) =C**H**$_2$; 5.58-5.69 (m, 2H) C**H**=; 7.05-7.70 (m, 20H) P**Ph**$_2$. |
| **5** | 0.98-1.22 (m, 6H) Pt{C**H**$_2$(CH$_2$)$_4$CH=CH$_2$}$_2$ and PCH$_2$C**H**$_2$CH$_2$P; 1.62-1.78 (m, 12H) Pt{CH$_2$(C**H**$_2$)$_3$CH$_2$CH=CH$_2$}$_2$; 2.00-2.21 (m, 4H) Pt{(CH$_2$)$_4$C**H**$_2$CH=CH$_2$}$_2$; 2.28-2.35 (m, 4H) PC**H**$_2$CH$_2$C**H**$_2$P; 4.86 (td, 2H, J = 1.22 Hz) =C**H**$_2$; 5.03 (m, 2H) =C**H**$_2$; 5.75-5.93 (m, 2H) C**H**=; 7.31-7.77 (m, 20H) P**Ph**$_2$. |

[a]All spectra were recorded in $CDCl_3$ at room temperature, using tetramethylsilane as an internal standard unless otherwise stated, [b]Spectrum recorded in $C_6D_6$ at room temperature.

**Table 3.1**: $^{1}H$ NMR data for complexes **3-12**

| Complex | $^{1}H$ NMR (δ ppm)[a] |
|---|---|
| **6** | 0.88-0.96 (m, 4H) Pt{C**H**$_2$(CH$_2$)$_5$CH=CH$_2$}$_2$; 0.94-1.07 (m, 2H) PCH$_2$C**H**$_2$CH$_2$P; 1.15-1.26 (m, 12H) Pt{CH$_2$(C**H**$_2$)$_3$(CH$_2$)$_2$CH=CH$_2$}$_2$; 1.88-1.98 (m, 4H) Pt{ (CH$_2$)$_4$C**H**$_2$CH$_2$CH=CH$_2$}$_2$; 2.02-2.11 (m, 4H) Pt{ (CH$_2$)$_5$C**H**$_2$CH=CH$_2$}$_2$; 2.45-2.53 (m, 4H) PC**H**$_2$CH$_2$C**H**$_2$P; 4.85-5.03 (m, 4H) =C**H**$_2$; 5.64-5.88 (m , 2H) C**H**=; 7.25-7.80 (m , 20H) P**Ph**$_2$. |
| **7** | 0.85-1.08 (m , 4H), Pt-C**H**$_2$; 1.14-1.26 (m , 6H) Pt-CH$_2$C**H**$_2$ and PCH$_2$C**H**$_2$CH$_2$P; 1.72-2.08 (m , 4H) Pt-CH$_2$CH$_2$C**H**$_2$, 2.35-2.47 (m , 4H) PC**H**$_2$CH$_2$C**H**$_2$P; 5.38-5.50 (m , 2H) C**H**=; 7.04-7.80 (m , 20H) P**Ph**$_2$. |
| **8** | 0.95-1.02 (m, 4H) Pt-C**H**$_2$; 1.16-1.20 (m, 2H) PCH$_2$C**H**$_2$CH$_2$P; 1.24-1.78 (m, 8H) Pt-CH$_2$C**H**$_2$C**H**$_2$; 2.02-2.16 (m, 4H) Pt(CH$_2$)$_3$C**H**$_2$; 2.15-2.22 (m, 4H) PC**H**$_2$CH$_2$C**H**$_2$P, 5.38-5.48 (m, 2H) C**H**=; 7.02-7.78 (m, 20H) P**Ph**$_2$. |

[a]All spectra were recorded in $CDCl_3$ at room temperature, using tetramethylsilane as an internal standard unless otherwise stated, [b]Spectrum recorded in $C_6D_6$ at room temperature.

**Table 3.1**: $^{1}$H NMR data for complexes **3-12**

| Complex | $^{1}$H NMR (δ ppm)[a] |
|---|---|
| **9** | 0.82-0.98 (m, 4H) Pt-C**H**$_2$; 1.00-1.22 (m, 6H) Pt-CH$_2$C**H**$_2$ and PCH$_2$C**H**$_2$CH$_2$P; 1.24-1.36 (m, 4H) Pt(CH$_2$)$_2$C**H**$_2$; 1.62-1.81 (m, 4H) Pt(CH$_2$)$_3$C**H**$_2$; 1.88-2.02 (m, 4H) Pt(CH$_2$)$_4$C**H**$_2$; 2.41-2.62 (m, 4H) PC**H**$_2$CH$_2$C**H**$_2$P; 5.18-5.26 (m, 2H) C**H**=; 7.26-7.60 (m, 20H) P**Ph**$_2$. |
| **10** | 0.78-0.96 (m, 4H) Pt-C**H**$_2$; 0.98-1.12 (m, 2H) PCH$_2$C**H**$_2$CH$_2$P; 1.20-1.35 (m, 12H) PtCH$_2$(C**H**$_2$)$_3$; 1.45-1.55 (m, 4H) Pt(CH$_2$)$_4$C**H**$_2$; 1.76-8.02 (m, 4H) Pt(CH$_2$)$_4$CH$_2$C**H**$_2$; 2.35-2.58 (m, 4H) PC**H**$_2$CH$_2$C**H**$_2$P; 5.19-5.55 (m, 2H) C**H**=; 7.17-7.89 (m, 20H) P**Ph**$_2$. |
| **11** | 0.94-1.02 (m , 4H) Pt-C**H**$_2$; 1.06-1.42 (br m, 16H); 1.45-1.54 (m, 2H) PCH$_2$C**H**$_2$CH$_2$P; 2.02-2.24 (m, 4H) PC**H**$_2$CH$_2$C**H**$_2$P; 6.98-7.80 (m, 20H) P**Ph**$_2$. |
| **12** | 0.83-1.05 (m, 4H) Pt-C**H**$_2$; 1.08-1.16 (m, 2H) PCH$_2$C**H**$_2$CH$_2$P; 1.18-1.56 (br m, 16H); 1.60-1.64 (m, 4H); 2.38-2.44 (m, 4H) PC**H**$_2$CH$_2$C**H**$_2$P; 7.18-7.58 (m, 20H) P**Ph**$_2$. |

**Table 3.2**: $^{31}P$ NMR data for complexes **3-12**

| Complex | $^{31}P$ NMR ($\delta$ ppm)[a] |
|---|---|
| **3** | 3.46 {s, $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1623 Hz} |
| **4** | 3.36 {s, $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1612 Hz} |
| **5** | 3.38 {s, $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1606 Hz} |
| **6** | 4.10 {s, $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1612 Hz} |
| **7** | 3.78 {s, $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1618 Hz} |
| **8** | 3.78 {s, $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1619 Hz} |
| | 3.50 {s, $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1632 Hz} |
| **9** | 3.20 {s, $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1608 Hz} |
| | 4.30 {s, $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1620 Hz} |
| **10** | 3.79 {s, $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1600 Hz} |
| **11** | 3.20 {s, $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1632 Hz} |
| **12** | 3.27 {s, $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1644 Hz} |

[a]All spectra were recorded in $CDCl_3$ at room temperature, using tetramethylsilane as an internal standard unless otherwise stated, [b]Spectrum recorded in $C_6D_6$ at room temperature.

**Table 3.3**: Yields and melting points for complexes **3-12**

| Complex | Yield (%) | Melting Point (°C) |
|---|---|---|
| **3** | 87 | 114-116 |
| **4** | 85 | 107-110 |
| **5** | 79 | 98-101 |
| **6** | 64 | 88-91 |
| **7** | 66 | 162-164 |
| **8** | 78 | 155-157 |
| **9** | 84 | 158-162 |
| **10** | 80 | 161-163 |
| **11** | 68 | oil |
| **12** | 78 | oil |

### 3.2.3 Characterization of platinacycloalkanes

The platinacycloalkanes were obtained from hydrogenation of complexes **8** and **9** using 10 wt% Pd on activated carbon support over a period of 7-10 hours, and this allowed for the isolation of colourless oils of platinacycloalkanes **11** and **12** in yields of 68 and 78% respectively (Table 3.3).

Platinacycloalkanes **13-16** were synthesized using the di-Grignard route (Scheme 3.2) and were obtained as either fairly unstable yellow or light brown oils. These complexes were obtained in relatively low yields when compared to the yields of similar compounds (complexes **11** and **12**). This may be because of the different synthetic routes applied in the synthesis of these complexes. The di-Grignard route has been previously shown to give metallacycles in low yields, hence the conclusion that the synthetic route does have an effect on the yield of these complexes [15].

In addition, these complexes were found to be relatively much more stable when compared to their analogues with non chelating ligands [1]. This may be attributed to the positive chelating effect imposed by the diphosphine ligand, which plays a role in stabilizing these compounds. The 5- and 8-membered ring complexes are know, whilst the 9- and 10- membered platinacycles are new (Scheme 3.2).

The platinacycles were all characterized by $^{1}H$ and $^{31}P$ NMR. New data in the form of $^{13}C$ NMR for these complexes is presented herein. These data agree within reasonable range to the proposed formulations.

*NMR spectroscopy*

The platinacycles all displayed a similar pattern in the $^{1}H$ NMR spectra. For the platinacyclopentane, complex **13**, a broad multiplet was observed at 0.85-0.98 ppm for the protons of the carbon directly bonded to the platinum centre. A broad multiplet in the region of 1.25-1.39 ppm intergrating to twelve protons was assigned to the

remaining methylene protons of the metallacyclic ring. The remaining signals were assigned to the tertiary phosphine ligands.

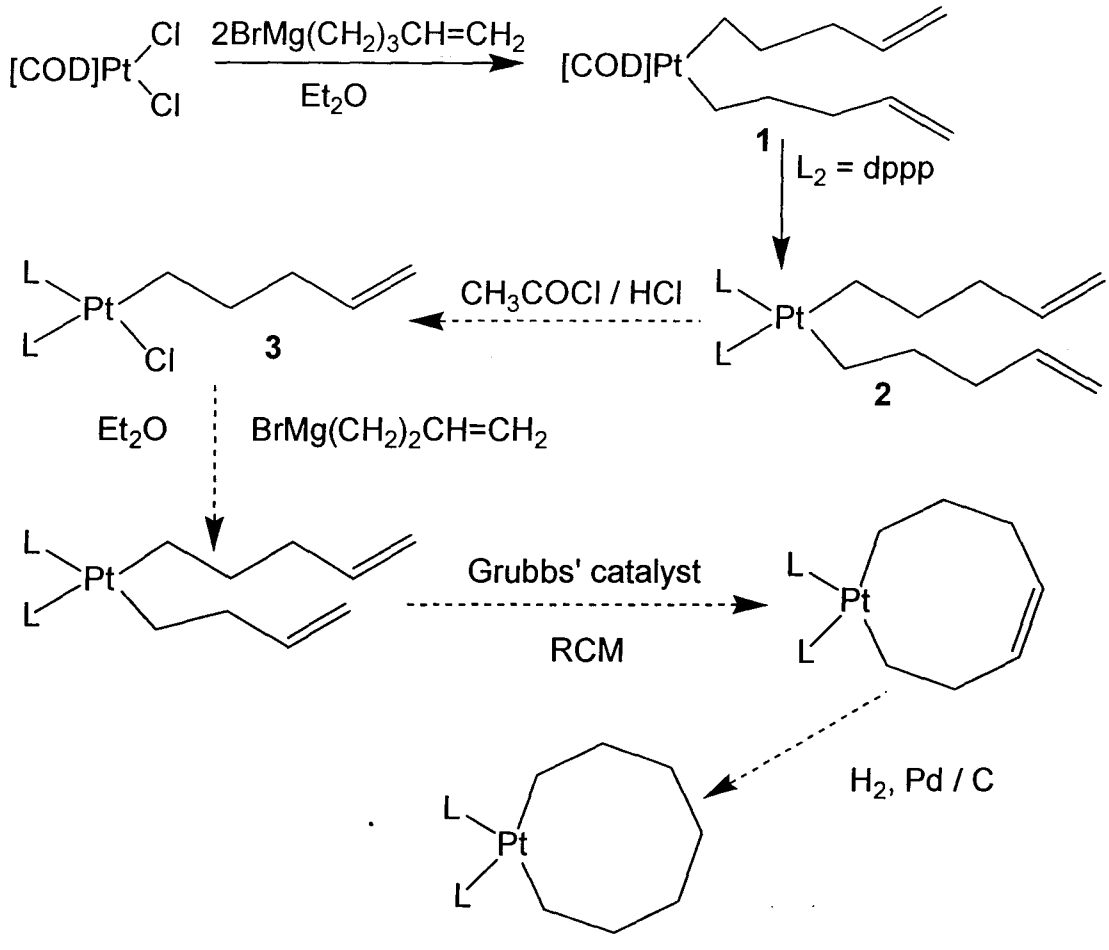
A similar pattern of broad signals has been observed and reported for related metallacycloalkane complexes containing other ligands such as $PPh_3$, dppe or dppp [1]. In a similar pattern, $^1H$ NMR for complexes **14-16** displayed expected signals in the downfield region for Pt-C$\underline{H}_2$, as well as broad multiplets corresponding to the methylene protons of the metallacyclic rings in the aliphatic region.

The $^{31}P$ NMR spectrum of platinacycloalkane **11** displayed a singlet at 3.2 ppm, which was accompanied by platinum satellites with a $^1J(^{195}Pt\text{-}^{31}P)$ coupling constant of 1632 Hz. A similar trend has been reported for similar complexes [1]. Other platinacycloalkanes complexes **12-16** all displayed similar shifts at *ca* 3.0 ppm in their $^{31}P$ NMR spectrum (Table 3.2) . These shifts are characteristic of $[L_2PtR_2]$ (L = dppp and R = alkyl, alkenyl or metallacyclic group) complexes [1].

$^{13}C$ NMR of complex **12** displayed a singlet at 14.33 ppm which was assigned to the carbons directly bonded to the platinum centre. The other carbons in the metallacyclic ring appeared as multiplets, slightly upfield in the region of *ca* 28.81-33.61 ppm. The remaining signals were assigned to the carbons of the diphosphine ligands. In the $^{13}C$ NMR spectra of platinacyles no coupling of $^{13}C$ to $^{31}P$ or $^{195}Pt$ was seen, this was attributed to the low abundance of $^{13}C$.

### 3.2.4 Synthesis of even numbered platinacyles

The synthetic methods discussed earlier (Chapter 1) have been applied in the synthesis of odd numbered metallacycles. Literature review shows that only one even numbered metallacycle, platinacyclooctane is known [16]. We therefore attempted to synthesize even numbered platinacycles using the ring-closing metathesis route, the results and products obtained are discussed herein. Scheme 3.3 shows the synthetic route attempted in the synthesis of the platinacyclodecane.

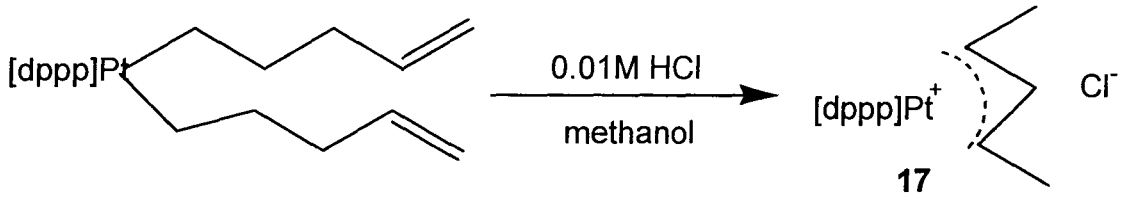



**Scheme 3.3**: Synthetic route for the synthesis of platinacyclodecane, (dashed arrows show reactions that did not work).

Attempts to synthesize the mono-alkenyl precursor (**3** in Scheme 3.3) were not successful; this was mainly attributed to the instability of the mono-alkenyl complex. Upon reaction of the bis(alkenyl)platinum(II) complex with HCl in equimolar ratio, characterization data showed that both alkenyl chains had been cleaved. This is because the rate of formation of the dichloro species, [Pt(dppp)$Cl_2$], was faster than the rate of formation of the mono-alkenyl species and even when the mono-alkenyl species was formed it quickly converted to the dichloro species. The [Pt(dppp)$Cl_2$] is generally much more stable than the mono-alkenyl complex thus its formation was preferred.

Coordination of the alkenyl moiety to the platinum centre was also observed in one of the reactions. In this instance, due to the nature of the double bond and its affinity for the platinum centre, an allyl species was obtained.

It is also interesting to note that this behaviour was only observed for bis(alkenyl) complexes with short chain lengths, in this case this was only observed for the bis(pentenyl)platinum(II) complex, **3**) (eq. 3.3) and not for the bis(hexenyl)platinum(II) complex, **4**. This suggests that in this case the mono-alkenyl complex was formed but quickly reverted to the much more stable allyl complex, **17**.




**17**

(eq. 3.3)

The di-Grignard route was then applied in the synthesis of even numbered platinacycles, platinaycloocta ne and platinacyclodecane and complexes **14** and **16** were successfully synthesized (Scheme 3.2). These complexes were characterized by melting point, $^{1}H$, $^{31}P$, $^{13}C$ NMR and elemental analysis (Table 4.4-4.5). $^{1}H$ and $^{31}P$ NMR is also given for complex **17**.

*NMR spectroscopy*

A similar trend to that observed for odd numbered platinacycles was observed in the $^{1}H$ NMR spectra of even numbered platinacycles. For the platinacyclodecane, complex **16**, a multiplet was displayed at 0.82-0.96 ppm for the protons on the carbon directly bonded to the platinum centre. A broad multiplet in the region of 1.20-1.38 ppm, integrating for fourteen protons was assigned to the methylene protons of the metallacyclic ring. Complex **17** displayed a broad multiplet at 3.45-3.78 ppm characteristic of allyl complexes [17].

The $^{31}P$ NMR spectrum of complex **17** displayed a singlet at -1.88 ppm accompanied by platinum satellites with a $^{1}J(^{195}Pt\text{-}^{31}P)$ coupling constant of 3862 Hz. Similar trends and coupling constants have been observed for similar complexes [17]. Complex **16** however gave a singlet at 3.33 ppm with corresponding platinum satellites and a $^{1}J(^{195}Pt\text{-}^{31}P)$ coupling constant of 1647 Hz.

$^{13}C$ NMR spectra for complex **16** displayed a singlet at 14.3 ppm which was assigned to C1 and C9 (Figure 3.5). The singlets at 23.1 and 26.0 ppm where assigned to C11 and C10 and C12 respectively. The remaining carbons in the metallacyclic ring appeared as multiplets slightly more upfield in the region of 28.2-33-6 ppm and these were assigned to carbons C2-C8. The aromatic carbons appeared as a multiplet in the region of 127.7-1.33.9 ppm. As previously observed for other platinacycloalkanes no coupling of $^{13}C$ to $^{31}P$ or $^{195}Pt$ was seen, possibly due to the low abundance of $^{13}C$.

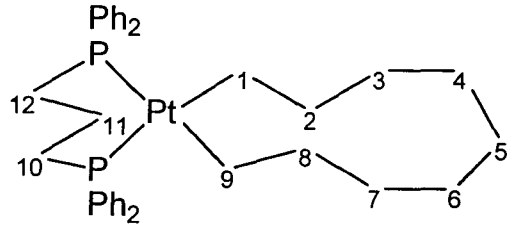



**Figure 3.5**: Schematic representation of the carbons of complex **16** for $^{13}C$ assignment.

**Table 3.4**: $^{1}$H NMR data of complexes **13-17**

| Complex | $^{1}$H NMR (δ ppm)[a] |
|---|---|
| **13** | 0.74-0.85 (m, 4H) Pt-C**H**$_2$; 0.91-1.05 (m, 2H) PCH$_2$C**H**$_2$CH$_2$P; 1.29-1.35 (br m, 4H); 2.05-2.34 (m, 4H) PC**H**$_2$CH$_2$C**H**$_2$P; 6.98-7.22 (m , 20H) P**Ph**$_2$. |
| **14** | 0.83-0.90 (m, 4H) Pt-C**H**$_2$; 1.27-1.36 (m, 10H); 1.40-1.42 (m, 2H) PCH$_2$C**H**$_2$CH$_2$P; 1.86-1.95 (m, 4H) PC**H**$_2$CH$_2$C**H**$_2$P; 7.21-7.83 (m, 20H) P**Ph**$_2$. |
| **15** | 0.84-0.87 (m, 4H) Pt-C**H**$_2$; 0.90-1.02 (m, 2H) PCH$_2$C**H**$_2$CH$_2$P; 1.05-1.24 (m, 12H); 1.28-1.62(m, 4H) PC**H**$_2$CH$_2$C**H**$_2$P; 7.21-7.83 (m, 20H) P**Ph**$_2$. |
| **16** | 0.82-0.96 (m, 4H) Pt-C**H**$_2$; 1.18-1.42 (br m, 16H); 2.08-2.18 (m, 4H) PC**H**$_2$CH$_2$C**H**$_2$P; 6.98-7.82 (m, 20H) P**P**h$_2$. |
| **17** | 1.08-1.37 (br m, 8H); 1.74-1.83 (m, 4H) PC**H**$_2$CH$_2$C**H**$_2$P; 3.45-3.78 (br m) allyl protons; 7.26-7.88 (m, 20H) P**P**h$_2$. |

[a]Spectrum recorded in $C_6D_6$ at room temperature.

**Table 3.5**: Yields, melting point and $^{31}$P NMR data of complexes **13-17**

| Complex | Yield (%) | Melting point (°C) | $^{31}$P NMR[a] |
|---|---|---|---|
| **13** | 52 | oil | 4.22 {s, $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1642 Hz} |
| **14** | 60 | oil | 3.46 {s, $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1619 Hz} |
| **15** | 57 | oil | 3.34 {s, $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1609 Hz} |
| **16** | 59 | oil | 3.33 {s, $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1647 Hz} |
| **17** | 84 | 92-94 | -1.88 {s, $^{1}J(^{195}Pt\text{-}^{31}P)$ = 3862 Hz} |

[a]Spectrum recorded in $C_6D_6$ at room temperature.

## 3.3 Reactivity of platinacyles

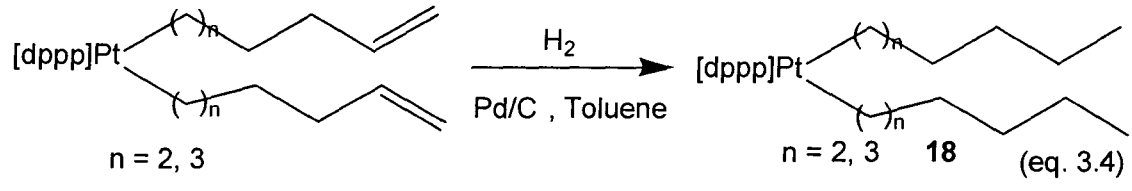
### 3.3.1 Reactivity studies on the bis(alkenyl)platinum(II) complexes

Preliminary reactivity studies on the bis(alkenyl)platinum(II) complexes were carried out. The reactivity studies done include hydrogenation, reaction with methyl iodide and insertion reactions using CO.

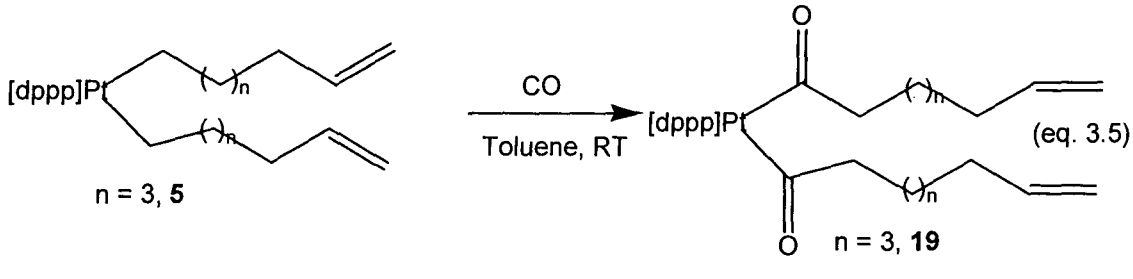
Simple hydrogenation of the bis(hexenyl)platinum(II) and bis(heptenyl)platinum(II) complexes (eq. 3.4) were carried in an attempt to compare the rate of hydrogenation of these complexes to the rate of hydrogenation of platinacycloalkenes to form platinacycloalkanes. This also provides another route for the synthesis of alkyl complexes. Bis(alkenyl) complexes **4** and **5** underwent hydrogenation using Pd/C within 2 hours as compared to complexes **8** and **9** which were completely hydrogenated after a period of 7-8 hours.

The bis(alkenyl) complexes reacted with hydrogen to give the corresponding alkyl complexes as solids in relatively good yields whilst the platinacycloalkenes reacted to give platinacycloalkanes as light brown oils in lower yields. In both cases the progress and completion of the reaction was monitored by $^1$H NMR.

It was also observed that the use of halogenated solvents lead to the cleavage of the metal-carbon bonds therefore these reactions were carried out using dry toluene as the solvent (eq. 3.4).




Insertion reaction with CO on the bis(heptenyl)platinum(II) complex **5** were carried out at atmospheric pressure and room temperature. It was observed that the reaction proceeded through the insertion of CO into one metal-carbon bond first within 48 hours, followed by complete insertion (double insertion) into both metal-carbon bonds after a period of 5 days. This later was supported by the appearance of a strong carbonyl band at 1732 cm$^{-1}$ in the IR spectrum (eq. 3.5) (Figure 3.7 (a) and (b)) [18].




Pt-acyl complexes of the type *cis*-[Pt(COR)X(P~P)] where R = Me, Cy or Ph, X = Cl or $SnCl_3$ and P~P = dppe, dppp, bdpp or dppb have been reported and they display similar bands at *ca* 1700 cm$^{-1}$ [18]. The new complexes were obtained as light brown oils in relatively good yields and were further characterized by $^1$H NMR, mass spectroscopy and elemental analysis.

*NMR spectroscopy*

The $^1$H NMR spectrum of complex **19** showed a broad multiplet in the region of 0.93-2.15 ppm, integrating for the 18 methylene protons in the alkenyl chain, as well as the methylene protons of the dppp ligand.

The protons on the carbon atoms α to the carbonyl carbons and the protons of the dppp ligand, P-C$\underline{\mathbf{H}}_2$, gave rise to a multiplet at 2.12-2.48 ppm. The alkene protons appeared as multiplets in the region of 4.87-5.05 ppm and 5.54-5.78 ppm for the =C$\underline{\mathbf{H}}_2$ and C$\underline{\mathbf{H}}$= protons respectively. The phenyl rings of the dppp ligand gave rise to multiplets in the region of 6.97-7.98 ppm. Similar shifts have been observed for related complexes [16].

*Mass spectroscopy*

Complex **19** showed a parent ion peak at *m/z* 857.2 $[M]^+$ (Figure 3.6), this compound displayed a fragmentation pattern involving the sequential loss of octenyl chains, 731.2 $[M-(CO)(CH_2)_5CH=CH_2-H]^+$ and 607.1 $[M-2((CO)(CH_2)_5CH=CH_2]^+$.

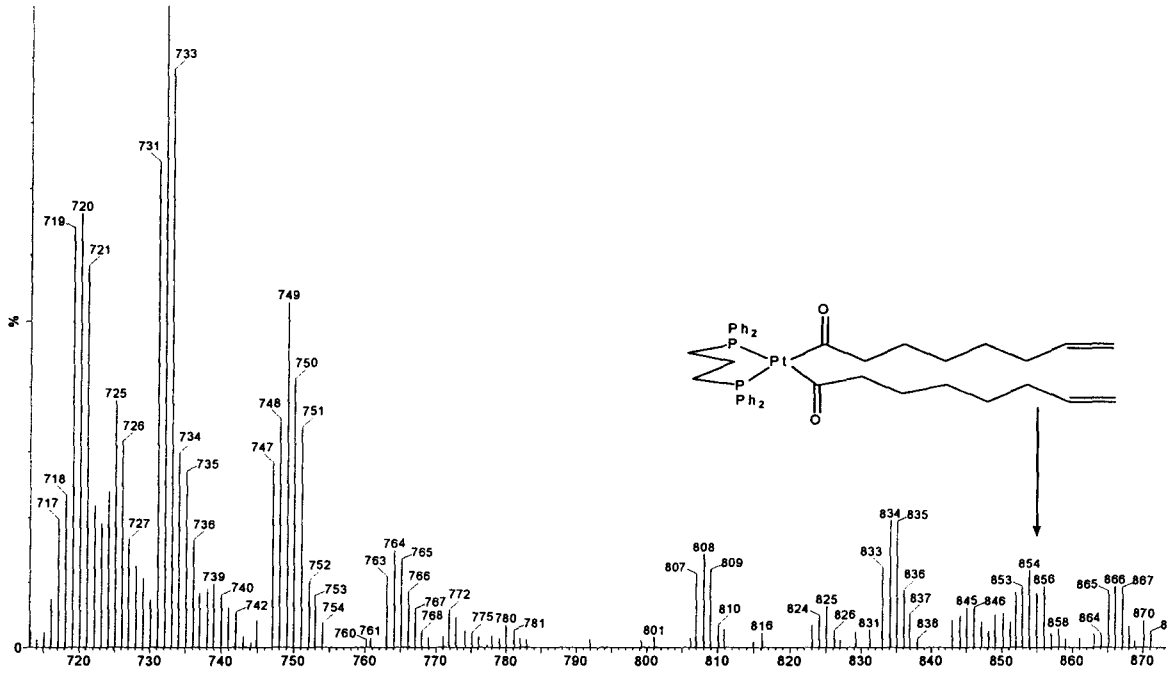
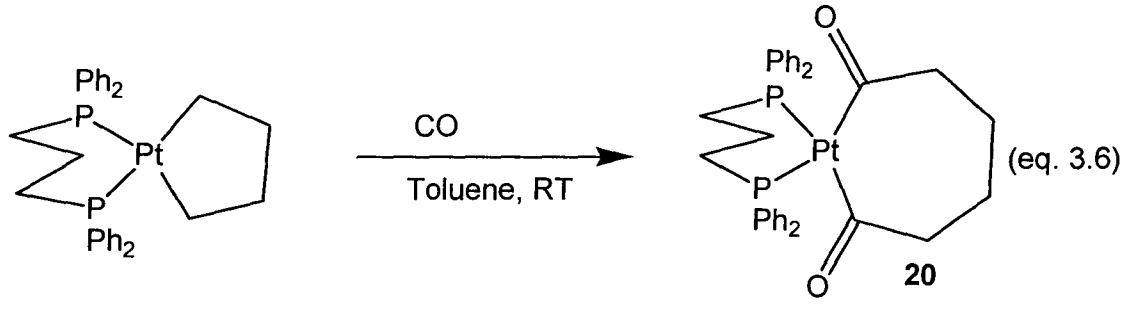



**Figure 3.6**: FAB mass spectrum of complex **19**.

### 3.3.2 CO insertion reactions on metallacycles

Insertion reaction using CO was also done on complex **13**. A solution of this complex in dry toluene was subjected to an atmosphere of CO contained in a balloon at room temperature with constant stirring (eq. 3.6). Complete insertion of CO into both metal-carbon bonds was relatively slow; this could be attributed to the strong metal-carbon bond observed in most 5d transition metal complexes [18].

The progress of this reaction was monitored by IR spectroscopy. Complete insertion was observed after a period of 3 weeks. IR spectroscopy displayed strong bands in the acyl carbonyl region together with vibrations in the region of *ca* 1600 $cm^{-1}$ corresponding to the carbons on the phenyl ring of the dppp ligand. Complex **20** was obtained as light brown oil in relatively low yields (55%). Further characterization of this complex was done by $^{1}H$ and $^{31}P$ NMR. Although we have tentatively suggested the formation of complex **20**, molecular structures by X-ray crystallography would be essential in further confirming the proposed structure.



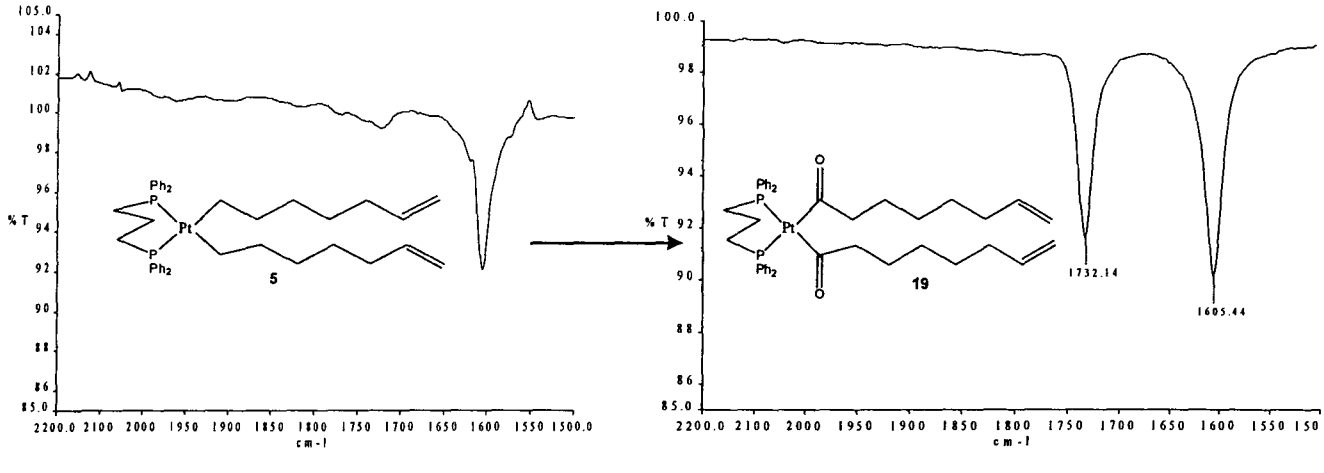

*IR spectroscopy*

As mentioned, the formation of the di-acyl product was monitored by IR spectroscopy. In addition to the $\nu$(C=C) band at 1590 $cm^{-1}$ for the phenyl carbons, a new strong band was observed in the acyl carbonyl region at 1681 $cm^{-1}$, suggesting the formation of complex **20** from the insertion of two CO molecules into the metal-carbon bond of the platinacyclopentane (Figure 3.7 (c) and (d)).

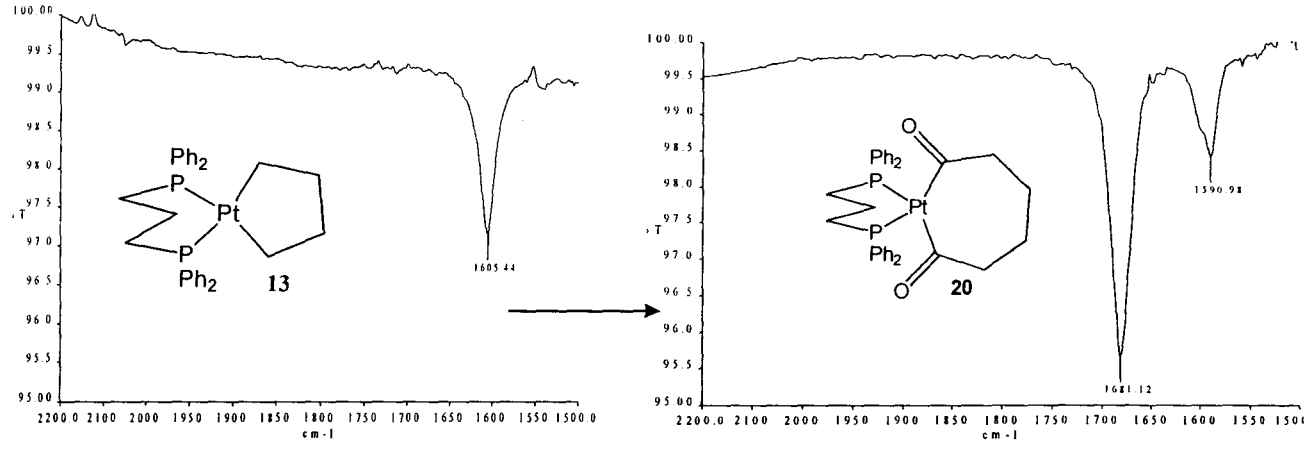
*NMR spectroscopy*

$^{31}P$ of complex **20** showed deshielding as it displayed a new singlet at *ca* 14.0 ppm as compared to *ca* 3 ppm in the starting material with corresponding satellites for the two phosphorus atoms in the same environment. The shifts were accompanied by a decrease in the $^{1}J(^{195}Pt\text{-}^{31}P)$ coupling constant from *ca* 1600 Hz to *ca* 1400 Hz. Such lower coupling constants are characteristic of Pt-acyl complexes reported in the literature, in which the phosphorus donor ligand experiences the trans influence of an acyl ligand [18b,c].

The $^{1}H$ NMR spectrum of complex **20** showed a broad multiplet at 0.80-1.83 ppm which was assigned to the 6 methylene protons of the metallacyclic ring as well as the methylene protons of the dppp ligand. The protons on the carbon atoms α to the carbonyl carbons together with the P-C$\underline{H}_2$ protons of the dppp ligand were represented by a multiplet at 1.97-2.33 ppm which integrated for 8 protons. The phenyl rings of the dppp ligand gave rise to a multiplet in the region of 7.03-7.98 ppm.




(a) (b)




(c) (d)

**Figure 3.7**: (a) IR spectrum of bis(heptenyl)platinum(II) complex **5** before carbonylation. (b) IR spectrum of complex **19**. (c) IR spectrum of platinacyclopentane **13** before carbonylation. (d) IR spectrum of complex **20**.

### 3.3.3 Possible intermediates in the CO insertion reactions

During the carbonylation reactions with bis(heptenyl)platinum(II) complex **5**, vibrational bands characteristic of terminal carbonyls were observed in the region of *ca* 2037 $cm^{-1}$ in the IR spectra after 24 hours of reaction (Figure 3.8). These observations suggested that these reactions may proceed *via* four- or five-coordinate platinum species as intermediates, in which one of the phosphorus donor atoms of the dppp ligand initially dissociates prior to insertion or coordination of the first CO molecule to the platinum centre (Figure 3.9 (a) or (b)).

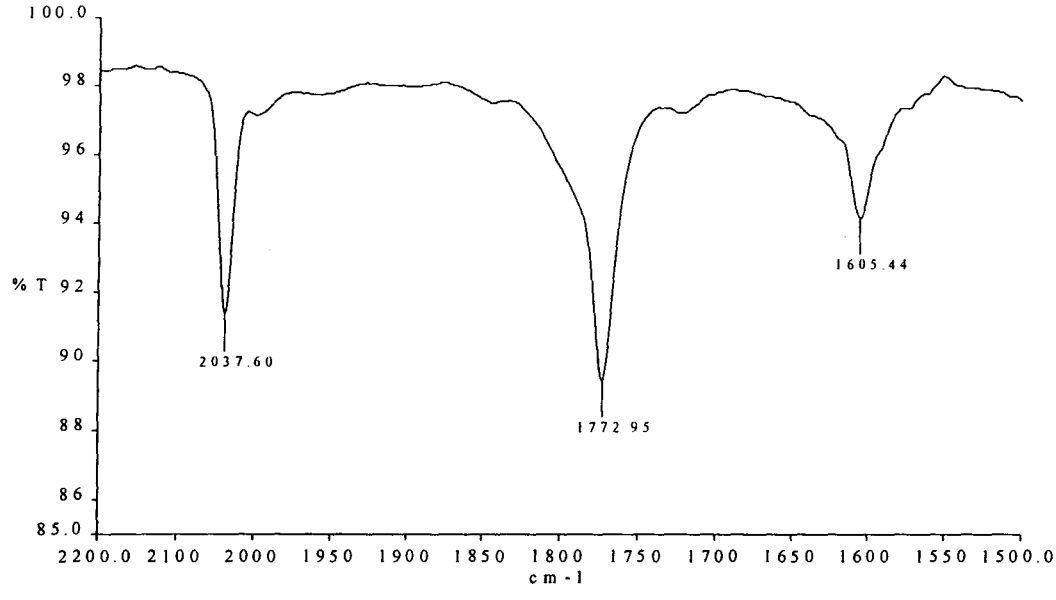



**Figure 3.8**: IR spectrum of possible intermediates formed during CO insertion (complex **5**).

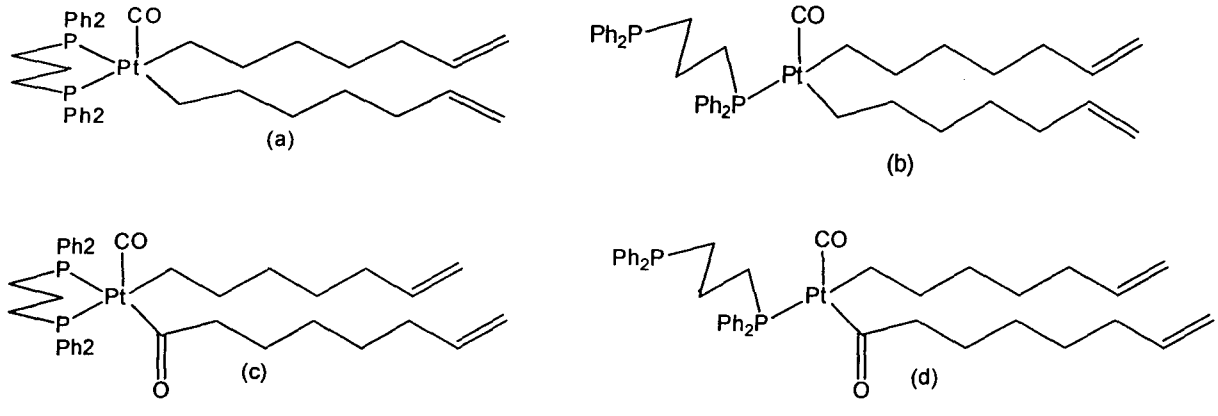



**Figure 3.9**: (a) or (b) possible intermediates during insertion of the first CO molecule, (c) or (d) possible intermediates during insertion of the second CO molecule.

After 48 hours of reaction additional carbonyl bands $\nu$(C≡O) appeared together with the terminal carbonyl bands $\nu$(C≡O) in the IR spectra of the reaction mixture of complex **5**. The new band at 1772 $cm^{-1}$ suggests the formation of either a four- or five-coordinate second intermediate species in which one of the CO molecules has already been inserted into the metal-carbon bond (Figure 3.9 (c) or (d)).

A similar trend was observed for the reaction of CO with platinacyclopentane **13** (Figure 3.10). The four- or five- coordinate species that have been proposed as intermediates are represented in Figure 3.11, (a) and (b) represent the first possible intermediates while (c) and (d) represent the second possible intermediate.


**Figure 3.10**: IR spectrum of possible intermediates formed during CO insertion (complex **13**).

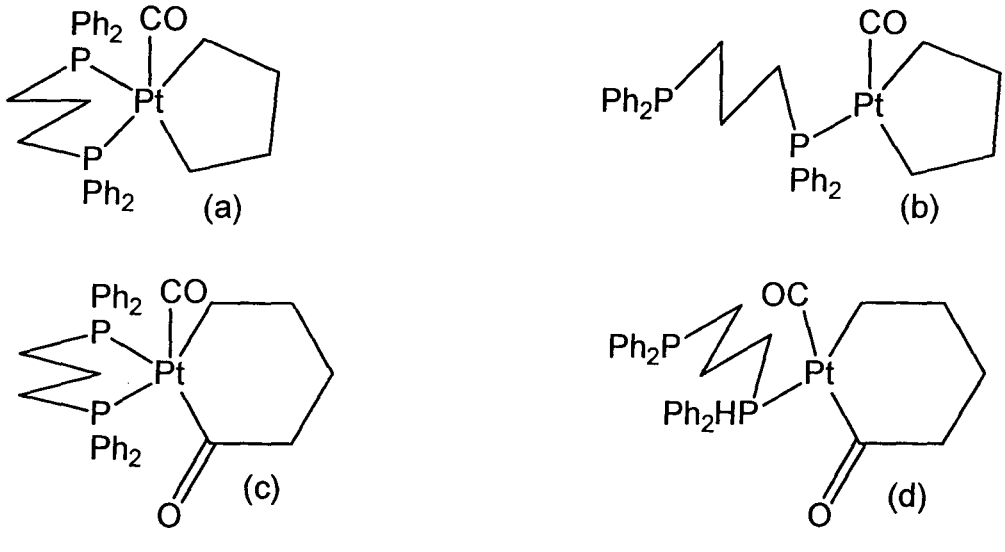



**Figure 3.11**: (a) or (b) possible intermediates during insertion of the first CO molecule, (c) or (d) possible intermediates during insertion of the second CO molecule.

Further characterization of these intermediates by $^{31}P$ NMR spectroscopy in order to establish whether they were four- or five-coordinate species was unsuccessful as these complexes were unstable once the solvent was removed and thus difficult to isolate and purify. In the literature, a five-coordinate platinum species has been proposed as the intermediate through which CO insertion proceeds in Pt(II) diphosphine complexes [18a-c].

## 3.4 Thermal decomposition studies

### 3.4.1 Thermal decomposition studies on bis(alkenyl)platinum(II) complexes

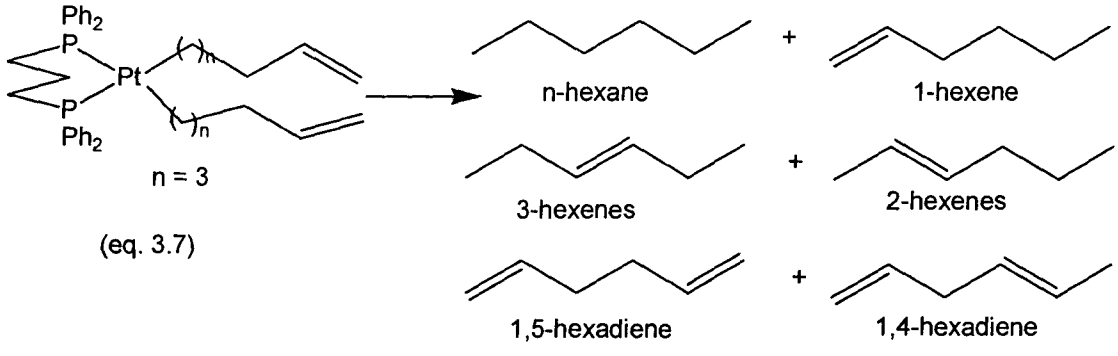
Thermal decomposition of bis(alkenyl) complexes of various metals affords various products [19] including (i) long chain dienes by reductive elimination, (ii) dienes and 1-alkenes by β-hydride elimination followed by reductive elimination. However the products formed can differ considerably due to the pendant alkene functionality which can undergo other decomposition pathways such as isomerization or rearrangement of the coordinated alkenyl moiety [1a]. It has also been shown that thermolysis products are highly dependent on various factors such the metal centre, nature of supporting ligand and solvent system [20].

Thermal decomposition studies of bis(hexenyl)platinum(II) **4** and bis(heptenyl)platinum(II) **5** complexes were carried out in sealed evacuated tubes which were immersed in a thermostated oil bath. The solvent system used to dissolve the complexes was dichloromethane. The thermolysis of the dried complexes was carried out at 150°C for 2 hours. There was significant colour change from the original pale yellow to a dark brown colour after the 2 hours. The organic products obtained were analyzed by GC.

In this section, we report the products afforded and hence thermal decomposition pathways of complexes **4** and **5** and compare the results obtained with literature findings.

*Thermal decomposition of bis(hexenyl)platinum(II) complex **4***

Complex **4** decomposed for 2 hours in DCM to give a mixture of organic products (eq. 3.7). The major organic products were identified by comparison of their retention times with those of known ($C_6$) standards [2]. From the chromatogram (Figure 3.12) one can observe the presence of 2-hexenes as the major product. The shoulders observed on the chromatogram for example for the peak due to the 2-hexenes are due to the presence of cis and trans isomers.




(eq. 3.7)

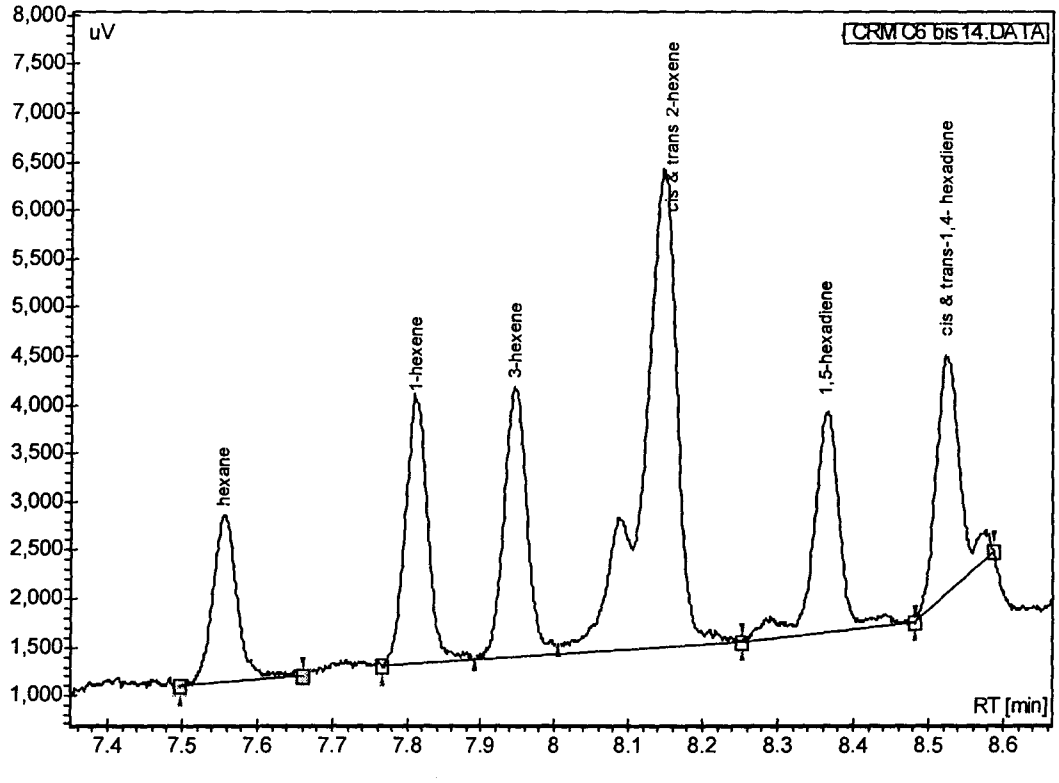



**Figure 3.12**: Chromatogram for the products formed from the thermal decomposition of complex **4**.

Table 3.6 shows the products obtained from thermolysis of complex **4** as percentages and these have been compared with literature values when the same compound was decomposed with no solvent system for 2 hours [2].

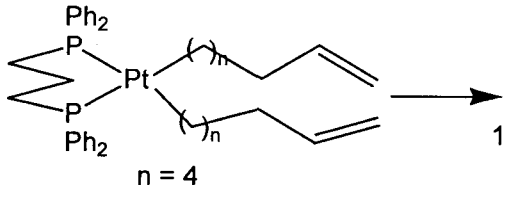
**Table 3.6**: Products of thermal decomposition of complex **4** in DCM and solvent free

| Medium | Observed products (%) | | | | | | Ref. |
|---|---|---|---|---|---|---|---|
| | n-hexane | 1-hexene | 2-hexenes | 3-hexenes | 1,5-hexadiene | 1,4-hexadiene | |
| $CH_2Cl_2$ | 9 | 13 | 38 | 14 | 13 | 13 | this work |
| Solid | 2 | 5 | 43 | 0 | 12 | 13 | 2 |

Thermolysis in a solvent free environment resulted in a slight increase in the percentage of 2-hexenes formed. Also no 3-hexenes were observed in the solvent free medium.

*Thermal decomposition of bis(heptenyl)platinum(II) complex 5*

Complex **5** decomposed for 2 hours in DCM to give a mixture of organic products (eq. 3.8). The major organic products were identified by comparison of their retention times with those of known ($C_7$) standards [2].




1-heptene + 2-heptenes + 3-heptenes +
5% 24% 14%

1,6-heptadiene + 1,5-heptadienes +1,4-heptadienes
25% 17% 5%

(eq. 3.8)

A similar trend to that for the thermolysis of complex **4** was observed. In this case however there was a very small difference between the percentages of the 2-heptenes and 1, 6-heptadiene as compared to the 2-hexenes and 1, 6-hexadiene. Table 3.7 shows the tabulated results.

**Table 3.7**: Products of thermal decomposition of complex **5** in DCM

| Medium | Observed products (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | heptane | 1-heptene | 2-heptenes | 3-heptenes | 1,6-heptadiene | 1,5-heptadiene | 1,4-heptadiene |
| $CH_2Cl_2$ | 5 | 10 | 24 | 14 | 25 | 17 | 5 |

### 3.4.2 Thermal decomposition studies on platinacycles

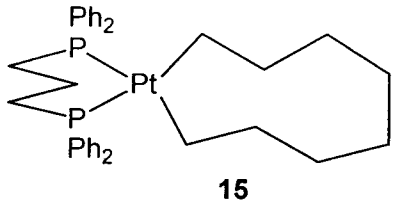
Manyik *et al.* [21] in 1977 suggested for the first time the involvement of metallacycles as key intermediates in the catalytic trimerization of ethylene. Since then the chemistry of metallacycloalkane complexes has developed significantly [22], with thermal decomposition studies being an important area of investigation [20].

Due to the difficulty in making medium and larger ring size metallacycles, much of the early work on thermal decomposition studies has been restricted to the decomposition of small ring size metallacycles (4- to 6- membered rings). It is only recently that our research group has managed to synthesize medium and larger ring size metallacycles and hence carry out thermal decomposition studies on them [1,2].

In this section, we report the products formed and hence thermal decomposition pathways of platinacyclononane complex **15** and platinacyclodecane complex **16**.

*Thermal decomposition of platinacyclononane **15***

Thermolysis studies were carried out in a sealed evacuated tube which was immersed in a thermostated oil bath. The solvent system used was dichloromethane. The thermolysis of this complex was carried out at 150°C for 2 hours. Complex **15** decomposed to give a mixture of organic products (eq. 3.9). The major organic products obtained were identified by comparison with known $C_8$ standards [2].




15

n-octane + 1-octene +
22% 48%

2-octenes + 1,7-octadiene
26% 5%

(eq. 3.9)

*Formation of organic products*

Platinacyclononane **15** decomposed to give 1-octene as the major product (48%) Figure 3.13. A possible mechanism for the formation of this product is the β-hydride elimination followed by reductive elimination (Scheme 3.4). Small amounts of 1,7-octadiene (5%) could be due to the second β-hydride elimination reaction (Scheme 3.4) [2,20]. Formation of 2-octenes may be by the isomerization of the 1-octene that was formed initially. Finally *n*-octane could be a result of intermolecular hydrogenation reactions, with the hydrogen source coming from either the metal hydride species or the coordinated ligand [2].

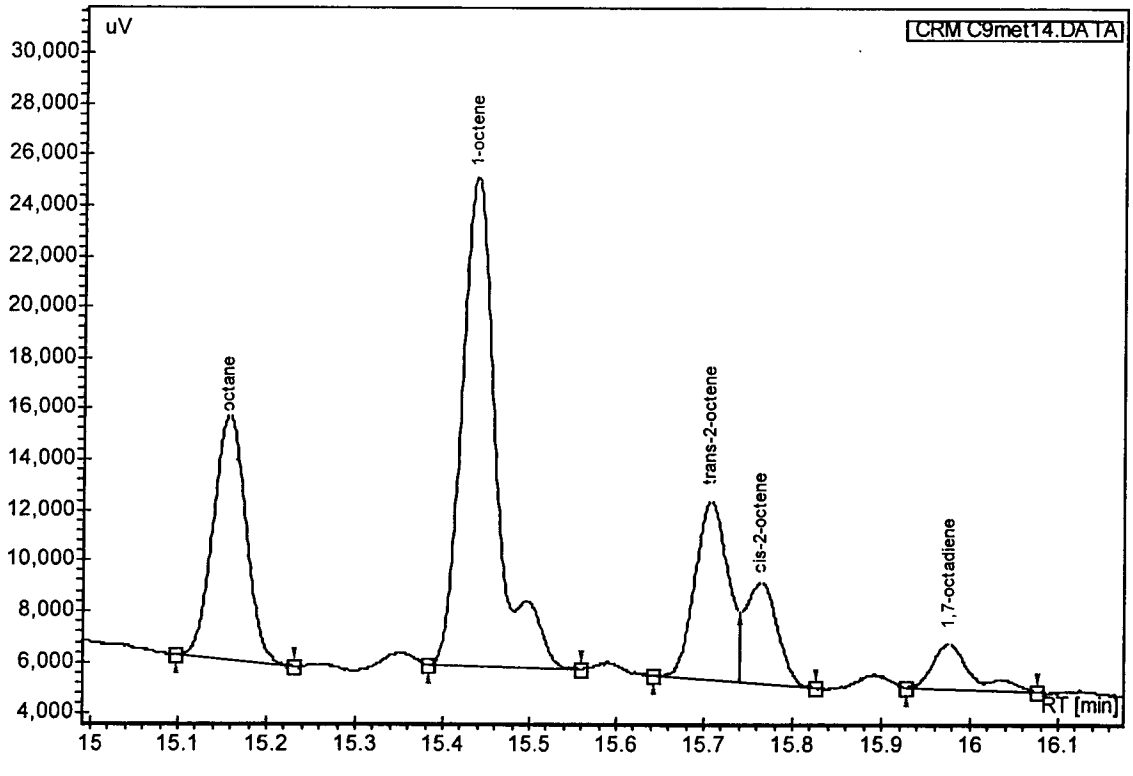
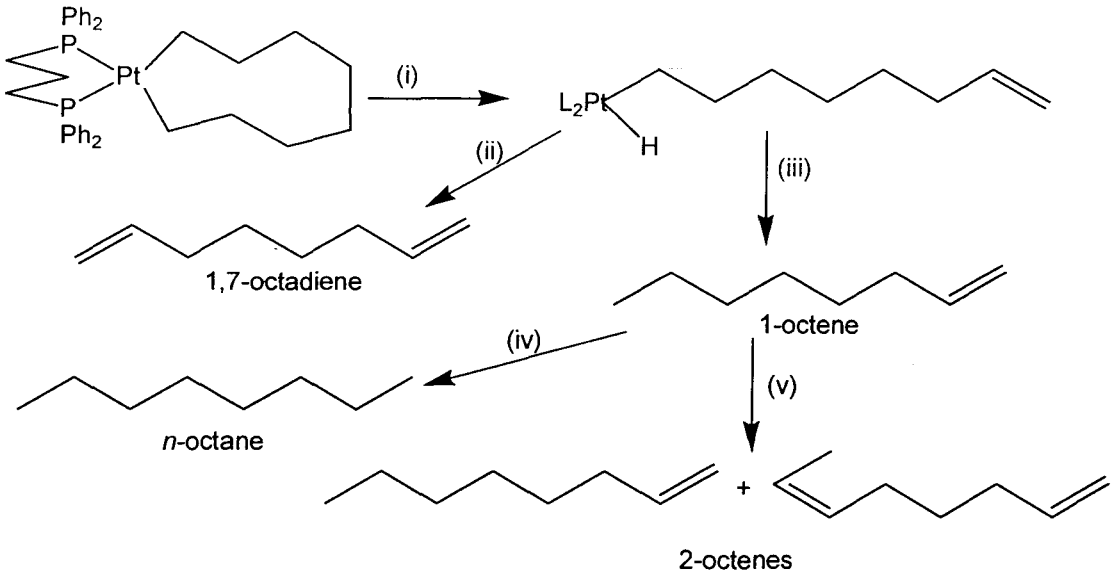



**Figure 3.13**: Chromatogram for the products formed from the thermal decomposition of complex **15**.

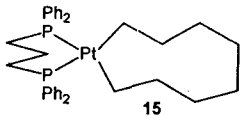
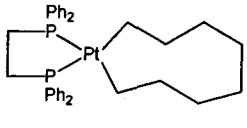
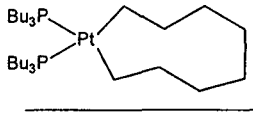



**Scheme 3.4**: Mechanism for the formation of organic products. (i) β-elimination, (ii) β-elimination, (iii) reductive elimination, (iv) hydrogenation and (v) isomerization.

*Comparison of products formed with similar platinacyclononanes*

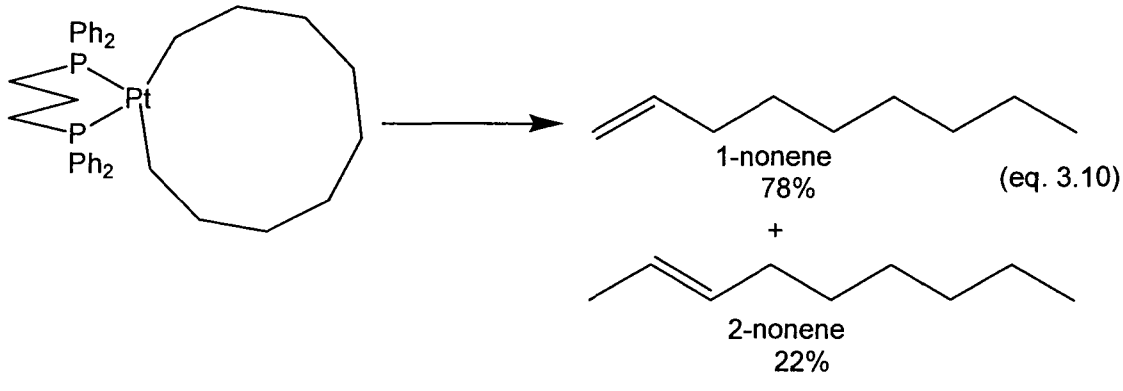
Comparison of the results obtained in this study with those of analogous 9-membered-ring platinum complexes containing dppe or $PBu_3^t$ donor ligands [2], shows that the same decomposition routes occur although less 1-octenes were formed (Table 3.8).

**Table 3.8**: Comparison of thermolysis products for platinacyclononanes

| Complex | Ref. | Products (%) | | | |
|---|---|---|---|---|---|
| | | n-octane | 1-octene | 2-octenes | 1,7-octadiene |
|  15 | this work | 22 | 48 | 26 | 5 |
|  | 2 | 23 | 41 | 21 | 13 |
|  | 2 | 28 | 32 | 26 | 6 |

*Thermal decomposition of platinacyclodecane **16***

Thermal decomposition studies were carried out in a sealed evacuated tube which was immersed in a thermostated oil bath. The solvent system used was dichloromethane. The thermolysis of this complex was carried out at 150°C for 45 minutes. Complex **16** decomposed within the 45 minutes to give 1-nonene as the major product (78%). A small amount of 2-nonene (22%) was also produced suggesting the start of isomerization (eq. 3.10). The major organic products obtained were identified by comparison with known $C_9$ standards [2].




(eq. 3.10)

When compared to the thermolysis of platinacyclononane **15** there was less isomerization during thermolysis of platinacyclodecane **16** because the reaction was carried out for a shorter period.

### 3.4.3 Relationship between the thermal decomposition of bis(alkenyl) complexes and platinacycles

Thermal decomposition pathways of bis(alkenyl) complexes may be similar to those of platinacycles but the products formed differ considerably because of the presence of the pendant alkene moiety. From the preliminary studies done, the following can be observed about these two classes of compounds, (i) both classes of compounds could decompose to give useful organic products such as 1-alkene, 2-alkenes and dienes, (ii) β-hydride elimination and reductive elimination are the key steps in the decomposition mechanisms for both classes of compounds and (iii) the nature of the

supporting ligand, reaction time and pendant functionality size (i.e ring size and the length of the alkenyl chains) influence the decomposition patterns and product distribution for both platinacycles and bis(alkenyl) complexes. Another observation was that isomerization dominated in the thermolysis of bis(alkenyl) complexes to give 2-alkenes and 1,(n-2)-dienes, however it remained a minor decomposition pathway for platinacycles.

## 3.5 Conclusions

Some bis(alkenyl)platinum(II) complexes, platinacycloalkenes and platinacycloalkanes were successfully synthesized using the ring-closing metathesis and the di-Grignard routes. Failure to synthesize the even numbered platinacycles using the RCM route was attributed to the instability of the mono(alkenyl)platinum(II) intermediate. Thus, the even membered platinacycles were successfully synthesized using the di-Grignard route and are herein represented for the first time.

The products were isolated in high to low yields depending on the synthetic route as reasonably stable solids or oils. The complexes were characterized spectroscopically and analytically using melting points (for the known solid complexes), NMR spectroscopy, mass spectroscopy and elemental analysis. $^{13}C$ NMR data has been obtained for the bis(alkenyl)platinum(II) complexes and the platinacycles for the first time. In the $^{13}C$ NMR spectra no $^{1}J(^{195}Pt\text{-}^{13}C)$ was observed, this may possibly be due to the low abundance of $^{13}C$ and $^{195}Pt$.

Reactivity studies were attempted on the bis(alkenyl)platinum(II) complexes and platinacyclopentane. IR evidence from these studies shows that the insertion reaction with CO proceeds to give di-acyl compounds. The products were characterized using NMR and IR spectroscopy. These studies have shown that the bis(alkenyl)platinum(II) complexes undergo complete di-insertion reactions at the same rate irrespective of the chain length (4-5 days).

The platinacyclopentane however, reacts with CO at a slower rate, with complete di-insertion being observed only after a period of 3 weeks.
Possible four- or five-coordinate species have been proposed as intermediates in these reactions, and have been detected using IR spectroscopy. However, these intermediates were found to be highly unstable therefore they could not be isolated for further characterization.

Thermal decomposition studies on the bis(alkenyl) complexes **4** and **5** gave 2-alkenes as the major products. The total percentage of isomerization products increased with increase in chain length, 26% for the bis(hexenyl) complex **4** and 46% for the bis(heptenyl) complex **5**. Thermolysis studies on platinacycles gave 1-alkenes as the major product. Shorter reaction times lead to a significant decrease in the percentage of isomerization products, for example platinacyclodecane gave 78% of 1-nonene and 22% of 2-nonene as the major products. These thermolysis studies show that β-hydride elimination and reductive elimination are the key steps pathways in decomposition pathways as previously reported in the literature.

### 3.6 References

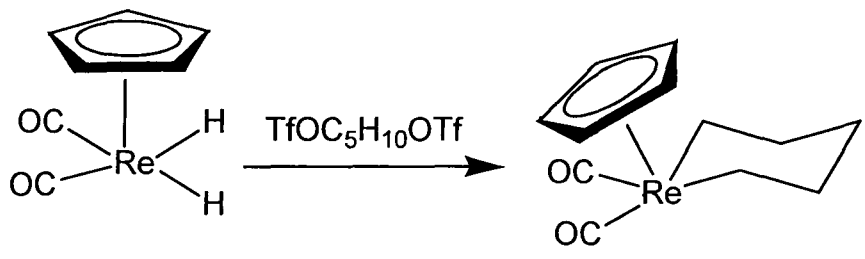

1. (a) A. Sivaramakrishna, H. Su and J.R. Moss, *Angew. Chem., Int. Ed.*, 2007, **46**, 3541. (b). K. Dralle, N.L. Jaffa, T. le Roex, J.R. Moss, S. Travis, N.D. Watermeyer and A. Sivaramakrishna, *Chem. Commun.*, 2005, **30**, 3865.
2. F. Zheng, *MSc dissertation, University of Cape Town*, (2007).
3. (a) A. Wojcicki, *Adv. Organomet. Chem.* 1973, 87, (b) F. Calderazzo and F.A. Cotton, *Inorg. Chem.*, 1962, **1**, 30.
4. T.H. Coffield, R.D. Closson and J. Kozikowski, *J. Org. Chem.*, 1957, **22**, 598.
5. G. Booth and J. Chatt, *Proc. Chem. Soc.*, 1967, **67**.
6. M.R. Churchill and J.P. Fennessy, *Inorg. Chem.*, 1968, **7**, 953.
7. M. Agostinho and P. Braustiein, *Chem. Commun.*, 2007, **1**, 58.
8. (a) R.W. Glyde and R.J. Mawby, *Inorg. Chem.*, 1971, **10**, 854. (b) P. Uguagliati, A. Palazzi, G. Deganello and U. Belluco, *Inorg. Chem.*, 1970, **9**, 724. (c) P.J. Craig and M. Green, *J. Chem. Soc A.*, 1969, **157**. (d) M. Green and D.J. Westlake, *J. Chem. Soc A.*, 1971, 367. (e) B.L. Booth, R.N. Haszeldine and N.P. Woofenden, *J. Chem. Soc A.*, 1970, 1979. (f) F. Calderazzo and K. Noack, *Coord. Chem. Rev.*, 1966, **1**, 118. (g) M. Green and R.I. Hancock and D.C. Wood, *J. Chem. Soc A.*, 1968, 2718.
9. F. De Angelis, S. Fantacci, A. Sdamellotti and N. Re, *Theo. Chem. Acc.*, 2003, **110**(3), 196.
10. J.X. McDermott, M.E. Wilson and G.M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6529.
11. E. Lindner, R-M. Jansen, W. Hiller and R. Fawzi, *Chem. Ber.*, 1989, **122**, 1403.
12. Y. Wakatsuki, O. Nomura, H. Tone and H. Yamazaki, *J. Chem. Soc., Perkin. II*, 1980, 1344.
13. P. Diversi, G. Ingrosso, A. Lucherini and S. Murtas, *J. Chem. Soc., Dalton Trans.*, 1980, **9**, 1633.
14. A.K. Tomov, J.J. Chirinos, R.J. Long, V.C. Gibson and M.R.J. Elsegood, *J. Am. Chem. Soc.*, 2006, **128**, 7704.

15. (a) T. Mahamo, F. Zheng, A. Sivaramakrishna, G.S. Smith and J.R. Moss, *J. Organomet. Chem.*, 2008, **693**, 103. (b) E.B. Hager, *MSc dissertation, University of Cape Town,* 2007. (c) J.X. McDermott, J.F. White and G.M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521.
16. A. Sivaramakrishna, H. Su and J.R. Moss, *Dalton Trans.*, 2008, **17**, 2228.
17. P. Barabotti, P. Diversi, G. Ingrosso, A. Lucherini and F. Nuti, *J, Chem. Soc. Dalton Trans.*, 1984, **11**, 2517.
18. (a) I. Tóth, T. K□gl, C.J. Elsevier and L. Kollar, *Inorg. Chem.*, 1994, **33**, 5708. (b) M. Gerisch, F.W. Heinemann, C. Bruhn, J. Scholz and D. Steinborn, *Organometallics,* 1999, **18**, 564. (c) G.K. Anderson and G.J. Lumetta, *Organometallics,* 1985, **4**, 1542. (d) A. Scrivanti, C. Bottenhi, L. Toniolo and A. Berton, *J. Organomet. Chem.*, 1988, **344**, 261. (e) G.K. Anderson, H.C. Clark and J.A. Davies. *Inorg. Chem.*, 1981, **20**, 1636. (f) M. Gómez, G. Muller, D. Sainz, J. Sales and X. Solans, *Organometallics,* 1991, **10**, 4036.
19. A. Sivaramakrishna, H.S. Clayton, C. Kaschula and J.R. Moss, *Coord. Chem. Rev.*, 2007, **251**, 1294.
20. F. Zheng, A. Sivaramakrishna and J.R.Moss, *Coord. Chem. Rev.*, 2007, **251**, 2056.
21. R.M. Manyik, W.E. Walker and T.P. Wilson, J. Catal., 1977, **47**, 197.
22. B. Blom, H. Clayton, M. Kilkenny and J.R. Moss, *Adv. Organomet. Chem.*, 2006, **54**, 150.

# Chapter 4: Synthesis and characterization of rhenium dibromide precursors, rhenium bis(alkenyl) complexes and rhenacycles

## 4.1 Introduction

A survey of the literature shows that only a small number of rhenacycles are known [1]. The earliest report of a rhenacyclopentane was that by Yang and Bergman in 1983 [2]. In this report the rhenacyclopentane was prepared by cationic alkylation of the system $CpRe(CO)_2H_2$/DBU (Cp = $\eta^5$-$C_5H_5$) with diiodobutane. Later on in 1991, Lindner and Wassing reported on the synthesis of both rhenacyclopentane and rhenacyclohexane [3]. Similar to the report by Yang and Bergman this route exploits the acidity of the hydride $CpRe(CO)_2H_2$ complex, but instead of using diiodobutane as the alkylating agent a bis(triflate) was used (eq. 4.1).




(eq. 4.1)

Thus, not much work has been done on the synthesis of metallacycles containing the metal rhenium and the di-Grignard route although a common method in the synthesis of metallacycles of many metals has not been applied in the synthesis of rhenacycles. It is mainly for this reason that we attempted to synthesize rhenacycles and their precursors.

No bis(alkenyl)dicarbonyl rhenium complexes are known, although their analogues such as bis(alkyl)dicarbonyl rhenium complexes are known and have been reported in the literature [4]. These complexes were prepared by substitution reactions involving rhenium dicarbonyldihalide complexes.

These substitution reactions were first reported by Nesmeyanov *et al.* for the reaction of $CpRe(CO)_2Br_2$ with Grignard reagents to yield $CpRe(CO)_2Me_2$ [5a]. However, this synthetic method could not be reproduced [5b].
In the (pentamethylcyclopentadienyl)dicarbonyl rhenium series, Richmond and co-workers [5b] reported on the reactions of the dibromo rhenium species $Cp^*Re(CO)_2Br_2$ ($Cp^* = \eta^5$-$C_5Me_5$) with different Grignard and organolithium reagents but none of the reactions resulted in the incorporation of the organo ligand.

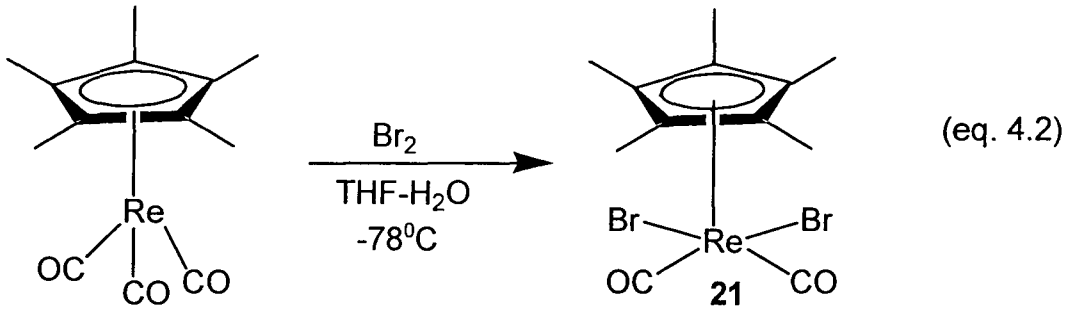
In this project, we therefore sought to attempt the synthesis of bis(alkenyl)rhenium(III) precursors using the transmetallation method and to use these precursors in the synthesis of rhenacycles *via* the new RCM route.

## 4.2 Synthesis of rhenium precursors

(Pentamethylcyclopentadienyl)dicarbonylrhenium dihalide complexes $Cp^*Re(CO)_2X_2$ have been known for a number of years. The most common method of preparation of these complexes is *via* oxidative addition of halogens to the dinitrogen rhenium complex $Cp^*Re(CO)_2(N_2)$. This method was found to be selective towards the formation of the *cis*-isomer when $X = Br_2$ or $I_2$ [6, 7]. Due to the multi-steps involved in this method final products were afforded in relatively low yields.

It was because of this reason that Diaz and co-workers reported on an improved one-step synthesis of the dicarbonylrhenium dihalide complexes from the tricarbonyl complex $Cp^*Re(CO)_3$ [8]. Using their method, products were obtained in yields ranging from 50-55%. In 1990, Nunn *et al.* [9] also reported on the synthesis of dicarbonylrhenium dibromide complexes from the tricarbonyl complex. Using their method shorter reaction times (< 1 hour) afforded the *cis*-isomer in 30-40% yield whilst longer reaction times gave both isomers in lowered yields. In addition to the formation of the desired product was the formation of a green material which was believed to be the tetrabromide complex $Cp^*Re(Br)_4$.

It is because of these reasons that we sought to find a better and more effective one-step synthetic route for the synthesis of $Cp^*Re(CO)_2Br_2$ from the tricarbonyl complex. Using our method (eq. 4.2) shorter reaction times (< 2 hours) gave the *trans-* isomer as the main product in yields ranging from 85-90% (Figure 4.1(a)). Using this method no side products such as tetrabromide were observed (refer to Chapter 5 for detailed method).

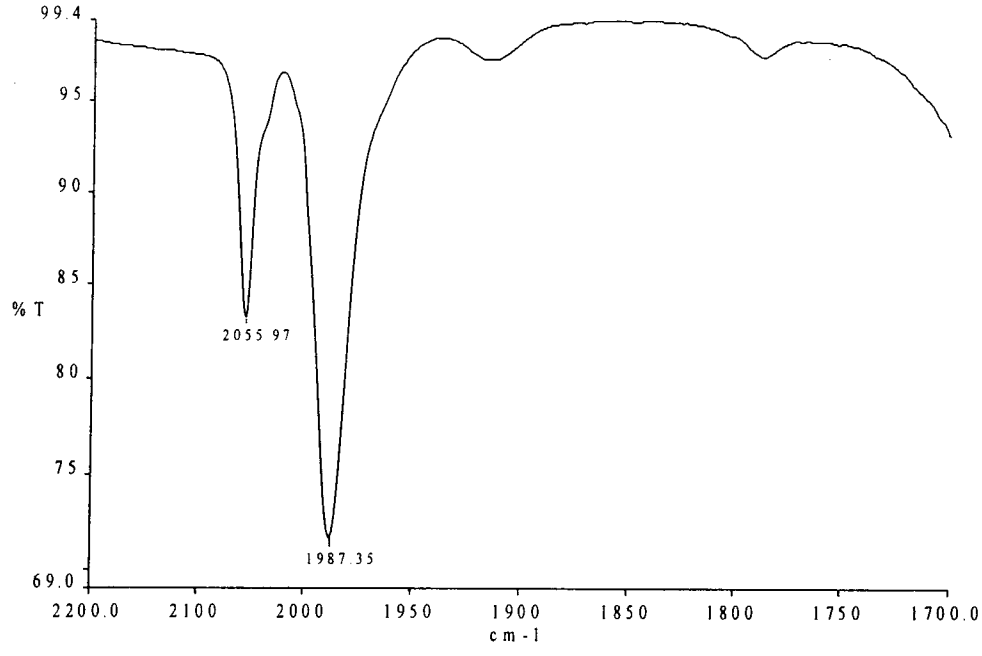



(eq. 4.2)

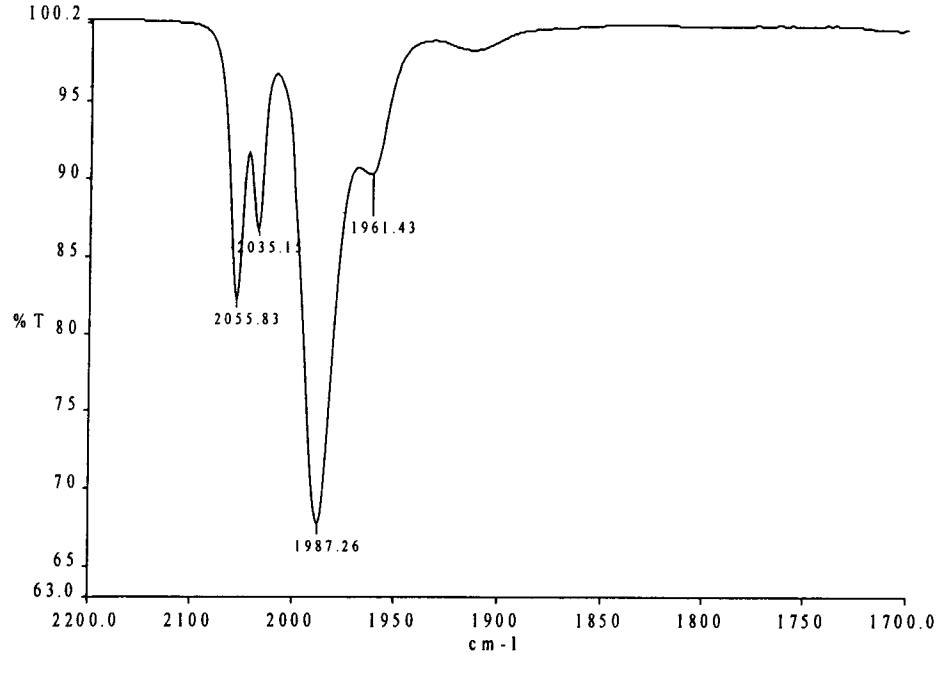
trans isomer (major product)

During our attempts in finding a more effective route some observations were drawn on the conditions necessary for synthesis of these complexes in high yields, (i) the reaction proceeded to give the best yields at -78°C whilst reaction at room temperature gave both isomers in low yields and the tricarbonyl complex as a by product, (ii) addition of $Br_2$ into the reaction mixture without dissolving it in any solvent system led to the formation of the green material that we believe to be $Cp^*ReBr_4$ that resisted purification *via* column chromatography, (iii) the THF-$H_2O$ mixture is the more effective solvent system since preparation in TFA lead to low product formation, this was attributed to the fact that in TFA, reaction of $Cp^*Re(CO)_3$ with $Br_2$ stopped when the cationic complex $[Cp^*Re(CO)_3Br]^+$ was formed [8] and (iv) longer reaction times and addition of more $Br_2$ did not increase the percentage yield but only resulted in the conversion of the *trans*-isomer to the *cis*-isomer (Figure 4.1(b)).

The products obtained were characterized by $^1H$, $^{13}C$ NMR, IR, elemental analysis and mass spectrometry.




(a)




(b)

**Figure 4.1**: (a) IR spectra for reactions times < 2 hours. (b) IR spectra for reaction times > 2 hours.

### 4.3 Synthesis of bis(alkenyl)rhenium complexes and rhenacycles

The use of freshly made alkenyl Grignard and di-Grignard reagents with the dibromide complex $Cp^*Re(CO)_2Br_2$ in THF at -78°C did not yield the desired products. Immediate decomposition was observed upon slow addition of the Grignard reagents. This observation agrees with results found by Richmond and co-workers [5a] for alkyl complexes of rhenium. Thus, we concluded that as in case of alkyl complexes the use of alkenyl and di-Grignard reagents is not realiable for the direct alkenyl-halide exchange in cyclopentadienyl rhenium dihalide complexes.

Attempts to improve the stability of the dibromide precursor $Cp^*Re(CO)_2Br_2$ prior to these reactions through substitution of one of the CO with $PPh_3$ [10] were not successful as the major product obtained was the triphenylphosphine oxide.

We then turned to the use of organocopper reagents which have been shown to be useful and efficient alkylating agents for the synthesis of alkylrhenium(I) complexes [4,11,12]. These are attempts did not yield the desired products but rather rapid decomposition was observed as in the case of Grignard reagents.

### 4.4 Conclusions

Thus herein we report that the new route for the synthesis of metallacycles could not be extended to the metal rhenium, hence bis(alkenyl) complexes of rhenium could not be synthesized. We tentatively suggest that alkenyl and di-Grignards can not be used as efficient alkylating agents for the synthesis of rhenacycles and their precursors.

## 4.5 References


1. B. Blom, H. Clayton, M. Kilkenny and J.R. Moss, *Adv. Organomet. Chem.*, 2006, **54**, 150.
2. G. Yang and R.G. Bergman, *J. Am. Chem. Soc.*, 1983, **105**, 6500.
3. E. Lindner and W. Wassing, *Organometallics*, 1991, **10**, 1640.
4. A.H. Klahn, C. Manzur, A. Toro and M. Moore, *J. Organomet. Chem.*, 1996, **516**, 51.
5. (a) A.N. Nesmeyanov, N.E. Kolobova. Y.V. Makarov and K.N. Anisimov, *J. Gen. Chem.*, 1974, **44**, 2179. (b) C.M. Nunn, A.H. Cowley, S.W. Lee amd M.G. Richmond, *Inorg. Chem.*, 1990, **29**, 2105.
6. F.W.B. Einstein, A.H. Klahn-Oliva, D. Sutton and K.G. Tyers, *Organometallics*, 1986, **5**, 53.
7. A.H. Klahn-Oliva, R.D. Singer, J.M. Aramini and D. Sutton, *Inorg. Chem.*, 1989, **28**, 4217.
8. G. Diaz, A.H. Klahn and C. Manzur, *Polyhedron*, 1988, **7**, 2743.
9. C.M. Nunn, A.H. Cowley, S.W. Lee and M.G. Richmond, *Inorg. Chem.*, 1990, **29**, 2105.
10. L. Cheng and N.J. Coville, *J. Organomet. Chem.*, 1998, **556**, 111.
11. J.R. Sweet and W.A.G. Graham, *J. Organomet. Chem.*, 1983, **241**, 45.
12. J.A. Ramsden, T-S. Peng and J.A. Gladysz, *Bull. Soc. Chim. Fr.*, 1992, **129**, 625.

# Chapter 5: Experimental procedures

## 5.1 Experimental Details

### 5.1.1 General Experimental Procedures

All reactions were carried out under inert nitrogen atmosphere using a dual vacuum/nitrogen line and standard Schlenk line techniques unless otherwise stated. All solvents were commercially obtained and freshly distilled under $N_2$ prior to use. Dichloromethane, chloroform and hexane were dried over calcium hydride, whereas toluene, tetrahydrofuran and diethyl ether were dried over sodium wire with benzophenone.

1,3-bis(diphenylphosphinopropane), Grubbs' 1$^{st}$ generation catalyst, 10 wt% palladium on activated carbon, bromine liquid and all deuterated solvents were obtained from Aldrich and were used as received. $Re_2CO_{10}$ was obtained from Strem Chemicals. $K_2PtCl_4$ was obtained from Johnson Matthey and Anglo Platinum. [Pt(COD)$Cl_2$] [1], [Pt(dppp)$Cl_2$ [2] and Cp*Re$(CO)_3$ [3], were prepared according to methods reported in the literature.

### 5.2.1 Instrumentation

$^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded on a Varian XR300 MHz or XR400 MHz spectrometers. Tetramethylsilane (TMS) was used as the internal standard for $^1$H and $^{13}$C, and $H_3PO_4$ as the external standard for $^{31}$P NMR. FTIR spectra were recorded on a Perkin Elmer Spectrum One FT-IR Spectrometer using solution cells with NaCl windows and the solutions were either dissolved in dichloromethane or benzene.

Melting points were recorded by a Kolfer hot stage microscope (Riechert Thermovar). Mass spectra were recorded at Stellenbosch University using a Waters API Quattro Micro with 3.5kV acceleration and a Iontech Saddlefield FAB gun. Microanalyses were conducted with a Thermo Flash 1112 Series CHNS-O Analyzer instrument. GC analyses were carried out 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 used was oxygen at 5.0 psi. The oven was programmed to hold at 32°C for 4 min and then ramp to 200°C at 10°C/min and hold for 5 minutes.

### 5.2 Preparation of Grignard reagents

Alkenyl Grignard reagents were prepared by treatment of the appropriate alkenyl bromide with excess magnesium turnings in freshly distilled tetrahydrofuran (THF) or diethyl ether ($Et_2O$) [4].

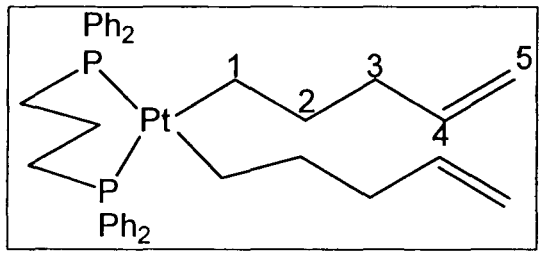
To an excess of magnesium turnings, freshly distilled THF or $Et_2O$ was added in a two-neck round bottom flask fitted with a reflux condenser under $N_2$. The flask together with the contents was then placed in an ice bath and to this the appropriate bromoalkene was slowly added. The flask was left to reach room temperature and the reaction refluxed for 4-5 hours until the solution turned to a pale grey colour. To determine the concentration of the Grignard reagent 1 ml of the Grignard reagent was hydrolyzed with 2 ml of distilled water. HCl (0.1 M, 20 ml) together with 2-3 drops of phenolphthalein indicator was added to the hydrolyzed Grignard and this was then back titrated with 0.1 M NaOH.

The same procedure was followed for the preparation of even and odd numbered di-Grignard reagents using α, ω-dichloroalkanes and freshly distilled THF. To avoid polymerization these reactions were carried out in very dilute solutions with a large excess of magnesium turnings.

### 5.3 Preparation of bis(alkenyl)platinum(II) complexes

Bis(alkenyl)platinum(II) complexes **3-6** were synthesized using the transmetallation method. Using this method [Pt(dppp)$Cl_2$] in diethyl ether or tetrahydrofuran was reacted with the appropriate alkenyl Grignard, for example for complex **3** [Pt(dppp)$Cl_2$] was reacted with a 5-pentenyl Grignard reagent. These compounds were obtained as stable white or pale yellow crystalline solids in relatively good yields and have been characterized by melting point, elemental analysis, mass spectroscopy and $^1H$, $^{31}P$ and $^{13}C$ NMR spectroscopy. Characterization data is in agreement with that reported in the literature [5]. Atom numbering applies to the carbons.

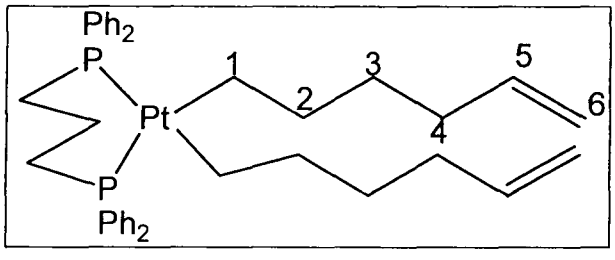
*Synthesis of [(dppp)Pt{$(CH_2)_3CH=CH_2$}$_2$]* **3** [5]




[Pt(dppp)$Cl_2$] (612 mg, 0.899 mmol) was weighed into a Schlenk tube and dried under vacuum for 15 min. 50 ml of dry diethylether was then added, the tube was then cooled to -78°C and 5-pentenyl Grignard reagent (0.46 M, 7 ml, 3.15 mmol) was slowly added to the reaction vessel. The solution was stirred at room temperature under $N_2$ for 14 hours, during which time the solution turned from cloudy to transparent. The Schlenk tube was again cooled to -78°C and 20 ml of saturated $NH_4Cl$ solution was added to the solution. The tube was allowed to reach room temperature and 20 ml of dichloromethane was added to the solution. The organic layer was separated, dried over anhydrous magnesium sulphate and filtered. The volatiles were removed using a rotary evaporator to give a white crystalline solid product, which was further dried under vacuum for 3 hours. Yield (533 mg, 87%); m.p. 114-116°C; $^1H$ NMR (300 MHz, $CDCl_3$) δ ppm: 0.95-1.05 (m, 4H) Pt{C**H**$_2$$(CH_2)_2CH=CH_2$}$_2$, 1.00-1.25 (m, 6H) Pt{$CH_2$C**H**$_2$$CH_2CH=CH_2$}$_2$ and P$CH_2$C**H**$_2$$CH_2$P, 1.55-1.62 (m, 4H) Pt{$CH_2CH_2$C**H**$_2$$CH=CH_2$}$_2$, 2.35-2.44 (m, 4H) PC**H**$_2$$CH_2$C**H**$_2$P, 4.85-4.92 (m, 4H) =C**H**$_2$, 5.45-5.56 (m, 2H) C**H**=, 7.32-7.46 (m,

20H) P**Ph**$_2$; $^{31}$P NMR (121 MHz, $CDCl_3$) δ ppm: 3.43 (s), $^1J(^{195}Pt\text{-}^{31}P)$ = 1623 Hz; Elemental analysis calculated for $C_{37}H_{44}P_2Pt$: C, 59.59; H, 5.95, Found: C, 60.41; H, 6.10 %; lRMS (FAB) $C_{37}H_{44}P_2Pt$: m/z = 745.2 $[M]^+$, 676.2 $[M\text{-}(CH_2)_3CH{=}CH_2]^+$ and 601.1 $[M\text{-}2\{(CH_2)_3CH{=}CH_2\}]^+$.

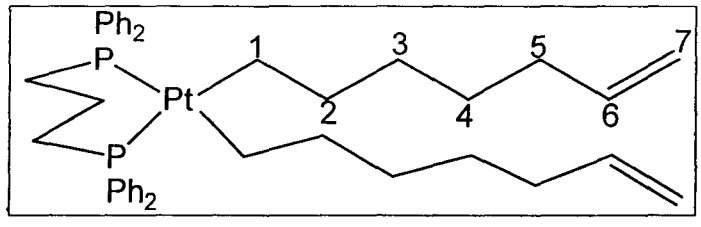
*Synthesis of [(dppp)Pt{$(CH_2)_4CH{=}CH_2$}$_2$]* **4** [5]




$[Pt(dppp)Cl_2]$ (1.432 g, 2.104 mmol) was transferred into a Schlenk tube and dried under vacuum for 15 minutes. 50 ml of dry diethylether was then added and the tube cooled to -78°C, after which 6-hexenyl Grignard reagent (0.56 M, 15 ml, 8.41 mmol) was slowly added to the contents of the Schlenk tube. The solution was then stirred at room temperature under $N_2$ for 16 hours during which time the solution turned from cloudy to transparent. The Schlenk tube was again cooled to -78°C and 25 ml of saturated $NH_4Cl$ solution was added to the solution. After reaching room temperature 25 ml of dichloromethane was added to the solution. The organic layer was separated, dried over anhydrous magnesium sulphate and filtered. The volatiles were removed using a rotary evaporator to give a white crystalline solid product, which was further dried under vacuum for 3 hours. Yield (1.26 g, 88%); m.p. 98-101°C; $^1$H NMR (300 MHz, $CDCl_3$) δ ppm: 0.85-1.13 (m, 4H) Pt{C**H**$_2$$(CH_2)_3CH{=}CH_2\}_2$, 0.97-1.30 (m, 4H) Pt{$CH_2$C**H**$_2$$(CH_2)_2CH{=}CH_2\}_2$, 1.62-1.75 (m, 6H) Pt{$(CH_2)_2$C**H**$_2$$CH_2CH{=}CH_2\}_2$ and $PCH_2$C**H**$_2$$CH_2P$, 1.96-2.02 (m, 4H) Pt{$(CH_2)_3$C**H**$_2$$CH{=}CH_2\}_2$, 2.45-2.52 (m, 4H) PC**H**$_2$$CH_2$C**H**$_2$P, 4.87-5.05 (m, 4H) =C**H**$_2$, 5.58-5.69 (m, 2H) C**H**=, 7.05-7.70 (m, 20H) P**Ph**$_2$; $^{13}$C NMR (100 MHz, $CDCl_3$) δ ppm: 14.28 (s, 2C) C1, 23.42 (s, 1C) $PCH_2$C**H**$_2$$CH_2P$, 25.34 (s, 2C) PC**H**$_2$$CH_2$C**H**$_2$P, 27.25-28.64 (m, 4C) C2-C3, 30.53 (s, 2C) C4, 112.31 (s, 2C) C6, 126.98-133.88 (m, 24C) P**Ph**$_2$, 140.56 (s, 2C) C5; $^{31}$P NMR (121 MHz, $CDCl_3$) δ ppm: 3.36 (s), $^1J(^{195}Pt\text{-}^{31}P)$ = 1612 Hz. Elemental analysis calculated for $C_{39}H_{48}P_2Pt$: C, 60.53; H, 6.25, Found: C, 61.47; H, 6.31 %; lRMS

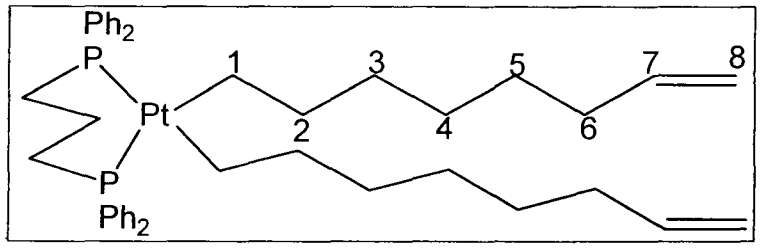
(FAB) $C_{39}H_{48}P_2Pt$: m/z = 773.2 $[M]^+$, 690.2 $[M-(CH_2)_4CH=CH_2]^+$ and 601.1 $[M-2\{(CH_2)_4CH=CH_2\}]^+$.

*Synthesis of [(dppp)Pt{$(CH_2)_5CH=CH_2$}$_2$]* **5** [5]




To a Schlenk tube, [Pt(dppp)$Cl_2$] (857 mg, 1.263 mmol) was weighed in and dried under vacuum for 15 minutes. 40 ml of dry tetrahydrofuran was then added. The Schlenk tube was then cooled to -78°C and 7-heptenyl Grignard reagent (0.50 M, 11 ml, 5.05 mmol) was added dropwise to the reaction vessel. The solution was then stirred at room temperature under $N_2$ for 16 hours, during which time the solution turned from cloudy to transparent. The Schlenk tube was again cooled to -78°C and 20 ml of saturated $NH_4Cl$ solution was added to the solution. After reaching room temperature, 20 ml of dichloromethane was then added to the solution. The organic layer was separated using a separating funnel, dried over anhydrous magnesium sulphate for 30 minutes and filtered. All the volatiles were removed using a rotary evaporator to give a yellow solid. The crude product was recrystallised from dichloromethane/hexane solution to give a pale yellow crystalline solid product, which was further dried under vacuum for 2.5 hours. Yield (677 mg, 79%); m.p. 98-101°C; $^1H$ NMR (300 MHz, $CDCl_3$) δ ppm: 0.98-1.22 (m, 6H) Pt{C**H**$_2$$(CH_2)_4CH=CH_2$}$_2$ and $PCH_2C$**H**$_2CH_2P$, 1.62-1.78 (m, 12H) Pt{$CH_2$(C**H**$_2$$)_3CH_2CH=CH_2$}$_2$, 2.00-2.21 (m, 4H) Pt{$(CH_2)_4$C**H**$_2CH=CH_2$}$_2$, 2.28-2.35 (m, 4H) PC**H**$_2CH_2$C**H**$_2$P, 4.86 (td, 2H, J = 1.22 Hz) =C**H**$_2$, 5.03 (m, 2H) =C**H**$_2$, 5.75-5.93 (m, 2H) C**H**=, 7.31-7.77 (m, 20H) P**Ph**$_2$; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ ppm: 14.45 (s, 2C) C1, 23.37 (s, 1C) $PCH_2$**C**$H_2CH_2P$, 26.74 (s, 2C) P**C**$H_2CH_2$**C**$H_2P$, 27.73-35.60 (m, 6C) C2-C4, 30.53 (s, 2C) C5, 112.31 (s, 2C) C7, 126.98-133.88 (m, 24C) P**Ph**$_2$, 140.56 (s, 2C) C6; $^{31}P$ NMR (121 MHz, $CDCl_3$) δ ppm: 3.38 (s), $^1J(^{195}Pt-^{31}P)$ = 1612 Hz; Elemental analysis calculated for $C_{39}H_{48}P_2Pt$ + 1 mole $H_2O$: C, 58.98; H, 6.40; Found: C, 58.63; H, 6.43 %; lRMS (FAB) $C_{41}H_{52}P_2Pt$: m/z = 801.3 $[M]^+$, 704.2 $[M-(CH_2)_5CH=CH_2]^+$ and 601.1 $[M-2\{(CH_2)_5CH=CH_2\}]^+$.

*Synthesis of [(dppp)Pt{$(CH_2)_6CH=CH_2$}$_2$]* **6** [5]

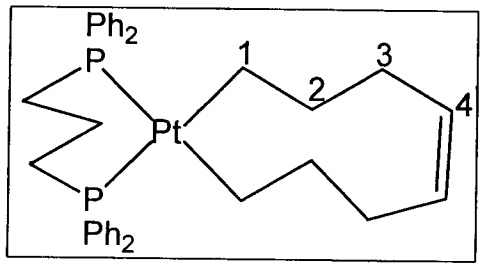



To a Schlenk tube, [Pt(dppp)$Cl_2$] (605 mg, 0.8918 mmol) was weighed in and dried under vacuum for 15 minutes. 40 ml of dry tetrahydrofuran was then added. The Schlenk tube was then cooled to -78°C and 8-octenyl Grignard reagent (0.38 M, 10 ml, 3.57 mmol) was slowly added to the reaction vessel and a pale white precipitate immediately resulted. The mixture was then stirred at room temperature under $N_2$ for 15 hours, during which time the precipitate disappeared. The Schlenk tube was again cooled to -78°C and 20 ml of saturated $NH_4Cl$ solution was added to the solution. After reaching room temperature, 20 ml of dichloromethane was then added to the solution. The organic layer was separated using a separating funnel, dried over anhydrous magnesium sulphate for 45 minutes and filtered. All the volatiles were removed using a rotary evaporator to give a yellow oil as the crude product. The crude product was recrystallized from dichloromethane/hexane solution to give a pale yellow crystalline solid, which was further dried under vacuum for 2 hours. Yield (387 mg, 64 %); m.p. 88-91°C; $^1$H NMR (300 MHz, $CDCl_3$) δ ppm: 0.88-0.96 (m, 4H) Pt{C**H**$_2$$(CH_2)_5CH=CH_2$}$_2$, 0.94-1.07 (m, 2H) $PCH_2C$**H**$_2$$CH_2P$, 1.15-1.26 (m, 12H) Pt{$CH_2$(C**H**$_2$$)_3$$(CH_2)_2CH=CH_2$}$_2$, 1.88-1.98 (m, 4H) Pt{ $(CH_2)_4$C**H**$_2$$CH_2CH=CH_2$}$_2$, 2.02-2.11 (m, 4H) Pt{ $(CH_2)_5$C**H**$_2$$CH=CH_2$}$_2$, 2.45-2.53 (m, 4H) PC**H**$_2$$CH_2$C**H**$_2$P, 4.85-5.03 (m, 4H) =C**H**$_2$, 5.64-5.88 (m , 2H) C**H**=, 7.25-7.80 (m , 20H) P**Ph**$_2$; $^{13}$C NMR (100 MHz, $CDCl_3$) δ ppm: 14.45 (s, 2C) C1, 23.37 (s, 1C) $PCH_2$**C**$H_2CH_2P$, 26.74 (s, 2C) P**C**$H_2CH_2$**C**$H_2P$, 27.73-35.60 (m, 8C) C2-C5, 30.53 (s, 2C) C6, 112.31 (s, 2C) C8, 126.98-133.88 (m, 24C) P**Ph**$_2$, 140.56 (s, 2C) C7; $^{31}$P NMR (121 MHz, $CDCl_3$) δ ppm: 4.10 (s), $^1J(^{195}Pt\text{-}^{31}P)$ = 1612 Hz.

## 5.4 Preparation of platinacycles

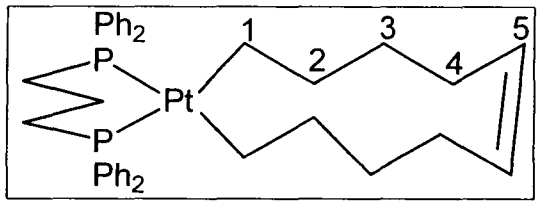
Platinacycles **7-12** were prepared by the RCM of bis(alkenyl)platinum(II) precursors complexes **3-6** at 55°C using Grubbs' 1st generation catalyst in dry dichloromethane, followed by hydrogenation with 10 wt% Pd/C in toluene. These compounds have been characterized by elemental analysis, $^{1}H$, $^{13}C$ and $^{31}P$ spectroscopy. Platinacycloalkanes **13-17** were synthesized by the di-Grignard route and these complexes were obtained in relatively low yields. These compounds have been characterized by elemental analysis, $^{1}H$, $^{13}C$ and $^{31}P$ spectroscopy. Atom numbering applies to both hydrogens and carbons.

*Synthesis of [(dppp)Pt{$CH_2$)$_3$CH=CH(CH)$_2$$CH_2$}] 7 [6]*



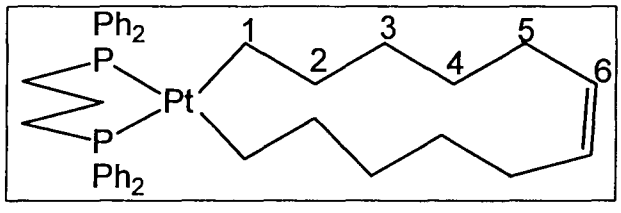

In a Schlenk tube [Pt(dppp)($(CH_2)_3CH=CH_2)_2$] (408 mg, 0.547 mmol) was dissolved in 20 ml of dry dichloromethane. To this Grubbs' 1st generation catalyst (11.2 mg, 5 mol%) was added and the reaction refluxed at 55°C. After 8 hours the solvent was removed using a rotary evaporator to give a black oil as the crude product. The product was then extracted with diethyl ether (5 ml), filtered and dried under vacuum for 1 hour to give a white crystalline solid. Yield (269 mg, 66%); m.p. 162-164°C; $^{1}H$ NMR (300 MHz, $CDCl_3$) δ ppm: 0.85-1.08 (m , 4H), H1, 1.14-1.26 (m , 6H) H2 and $PCH_2C\underline{H}_2CH_2P$, 1.72-2.08 (m, 4H) H3, 2.35-2.47 (m, 4H) $PC\underline{H}_2CH_2C\underline{H}_2P$, 5.38-5.50 (m, 2H) H4, 7.04-7.80 (m, 20H) $P\underline{Ph}_2$; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ ppm: 14.60 (s, 2C) C1, 20.63 (s, 1C) $PCH_2\underline{C}H_2CH_2P$, 26.12-26.78 (s, 2C) $P\underline{C}H_2CH_2\underline{C}H_2P$, 27.11-28.52 (m, 2C) C2, 29.77-30.13 (s, 2C) C3, 127.68-133.85 (m, 24C) $P\underline{Ph}_2$, 139.56 (s, 2C) C4; $^{31}P$ NMR (121 MHz, $CDCl_3$) δ ppm: 3.78 (s), $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1618 Hz.

*Synthesis of [(dppp)Pt{$CH_2$)$_4$CH=CH(CH)$_3$$CH_2$}] 8 [6]*




[Pt(dppp)($(CH_2)_4CH=CH_2)_2$] (1.07 g, 1.383 mmol) and Grubbs' 1st generation catalyst (0.0283 g, 5 mol%) were transferred into a Schlenk tube under nitrogen. To this dry dichloromethane (30 ml) was added. The solution was refluxed at 55°C for 7 hours. All the volatiles were removed using a rotary evaporator to give a black oil as the crude product. The product was then extracted with diethyl ether (5ml), filtered and dried under vacuum for 1 hour to give a pale yellow solid. Yield (834.5 mg, 78%); m.p. 155-157°C; $^1$H NMR (300 MHz, $C_6D_6$) δ ppm: 0.95-1.02 (m, 4H) H1, 1.16-1.20 (m, 2H) $PCH_2C\underline{H}_2CH_2P$, 1.24-1.78 (m, 8H) H2-H3, 2.02-2.16 (m, 4H) H4, 2.15-2.22 (m, 4H) $PC\underline{H}_2CH_2C\underline{H}_2P$, 5.38-5.48 (m, 2H) H5, 7.02-7.78 (m, 20H) $P\underline{Ph}_2$; $^{13}$C NMR (100 MHz, $C_6D_6$) δ ppm: 20.98 (s, 2C) C1, 26.07 (s, 1C) $PCH_2\underline{C}H_2CH_2P$, 27.13 (s, 2C) $P\underline{C}H_2CH_2\underline{C}H_2P$, 27.50-28.32 (m, 4C) C2-C3, 29.05-31.50 (s, 2C) C4, 126.98-133.88 (m, 24C) $P\underline{Ph}_2$, 141.19 (s, 2C) C5; $^{31}$P NMR (121 MHz, $C_6D_6$) δ ppm: 3.78 (s), $^1J(^{195}Pt\text{-}^{31}P)$ = 1619 Hz. Elemental analysis calculated for $C_{39}H_{48}P_2Pt$ + 2 mol DCM: C, 53.15; H, 5.81; Found: C, 52.51; H, 6.14 %.

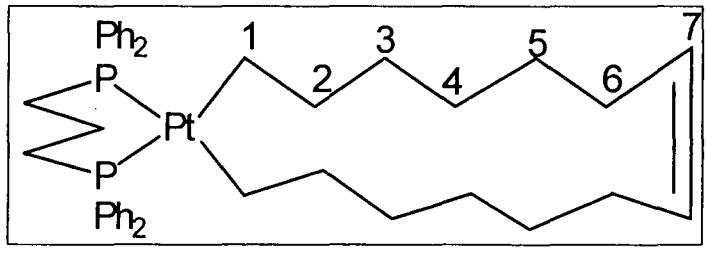
*Synthesis of [(dppp)Pt{$CH_2$)$_5$CH=CH(CH)$_4$$CH_2$}] 9 [6]*




This complex was prepared in a similar method to complexes **7** and **8**. To a solution of [Pt(dppp)($(CH_2)_5CH=CH_2)_2$] (456 mg, 0.569 mmol) and dichloromethane (25 ml), Grubbs' 1st generation catalyst (12 mg, 5 mol%) was added. After refluxing for 8 hours at 55°C, the volatiles were removed using a rotary evaporator to afford a black

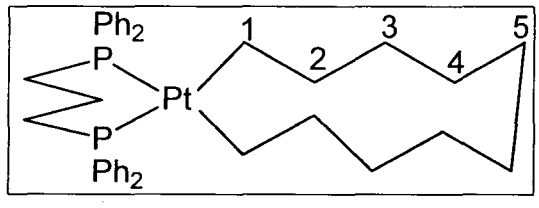
oil. The oil was dissolved in dichloromethane (15 ml) and the solution was filtered, the solvent was once again removed using a rotary evaporator to yield a residual pale yellow oil. The oil was then dried under vacuum for 2 hours to afford a pale yellow solid. Yield (383 mg, 84%); m.p. 158-162°C; $^{1}$H NMR (300 MHz, $CDCl_3$) δ ppm: 0.82-0.98 (m, 4H) H1, 1.00-1.22 (m, 6H) H2 and $PCH_2C\underline{H}_2CH_2P$, 1.24-1.36 (m, 4H) H3, 1.62-1.81 (m, 4H) H4, 1.88-2.02 (m, 4H) H5, 2.41-2.62 (m, 4H) $PC\underline{H}_2CH_2C\underline{H}_2P$, 5.18-5.26 (m, 2H) H6, 7.26-7.60 (m, 20H) $P\underline{Ph}_2$; $^{13}$C NMR (100 MHz, $CDCl_3$) δ ppm: 14.10 (s, 2C) C1, 22.68 (s, 1C) $PCH_2\underline{C}H_2CH_2P$, 25.65 (s, 2C) $P\underline{C}H_2CH_2\underline{C}H_2P$, 27.70-29.65 (m, 6C) C2-C4, 31.92-32.83 (s, 2C) C5, 127.78-133.47 (m, 24C) $P\underline{Ph}_2$, 140.56 (s, 2C) C6; $^{31}$P NMR (121 MHz, $CDCl_3$) δ ppm: 3.00 (s), $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1608 Hz.

*Synthesis of [(dppp)Pt{$CH_2$)$_6$CH=CH(CH)$_5$$CH_2$}] **10** [6]*



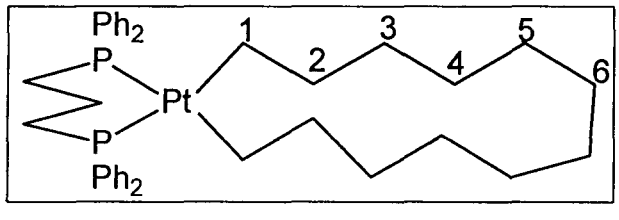

[Pt(dppp)($(CH_2)_6CH=CH_2)_2$] (256 mg, 0.3085 mmol) and Grubbs' 1$^{st}$ generation catalyst (6.5 mg, 5 mol%) were transferred into a Schlenk tube under nitrogen. To this dry dichloromethane (20 ml) was added. The solution was refluxed at 55°C for 8.5 hours. All the volatiles were then removed using a rotary evaporator to give a black oil as the crude product, which was further dried under vacuum for 1 hour. The product was then recrystallized from dichloromethane/hexane solution, filtered and dried under vacuum for 2 hours to give a pale yellow solid. Yield (204 mg, 80%); m.p. 161-163°C; $^{1}$H NMR (300 MHz, $CDCl_3$) δ ppm: 0.78-0.96 (m, 4H) H1, 0.98-1.12 (m, 2H) $PCH_2C\underline{H}_2CH_2P$, 1.20-1.35 (m, 12H) H2-H4, 1.45-1.55 (m, 4H) H5, 1.76-8.02 (m, 4H) H6, 2.35-2.58 (m, 4H) $PC\underline{H}_2CH_2C\underline{H}_2P$, 5.19-5.55 (m, 2H) H7, 7.17-7.89 (m, 20H) $P\underline{Ph}_2$. $^{31}$P NMR (121 MHz, $CDCl_3$) δ ppm: 3.79 (s), $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1600 Hz. Elemental analysis calculated for $C_{41}H_{52}P_2Pt$: C, 61.24; H, 6.63; Found: C, 60.06; H, 6.51 %.

*Synthesis of [(dppp)Pt{$CH_2$)$_9$$CH_2$}] **11** [6]*




Complex **9** (400 mg, 0.5335 mmol) was transferred into a 100 ml round bottom flask and dissolved in dry toluene (40 ml). 10 wt% Pd/C (8 mg) was added to the flask. The flask was then closed with a tap which was equipped with a $H_2$ gas filled balloon. The tap was opened thereby allowing the $H_2$ to flow and enter the flask. The reaction mixture was left to stir at room temperature. After 7 hours the solution was filtered and the solvent removed using a rotary evaporator to afford a colourless oil, which was dried under vacuum for 2.5 hours. Yield (272 mg, 68%); $^1$H NMR (300 MHz, $C_6D_6$) δ ppm: 0.94-1.02 (m, 4H) H1, 1.06-1.42 (br m, 16H) H2-H5, 1.45-1.54 (m, 2H) $PCH_2C\underline{H}_2CH_2P$, 2.02-2.24 (m, 4H) $PC\underline{H}_2CH_2C\underline{H}_2P$, 6.98-7.80 (m, 20H) ) $P\underline{Ph}_2$; $^{13}$C NMR (100 MHz, $C_6D_6$) δ ppm: 18.80 (m, 2C) C1, 24.02-24.80 (m, 1C) $PCH_2\underline{C}H_2CH_2P$, 26.50-26.48 (m, 2C) $P\underline{C}H_2CH_2\underline{C}H_2P$, 29.30-30.20 (m, 2C)C2, 31.88-33.00 (m, 4C) C3-C4, 37.10-38.20 (m, 2C) C5, 127.78-133.47 (m, 24C) $P\underline{Ph}_2$; $^{31}$P NMR (121 MHz, $C_6D_6$) δ ppm: 3.20 (s), $^1J(^{195}Pt\text{-}^{31}P)$ = 1632 Hz.

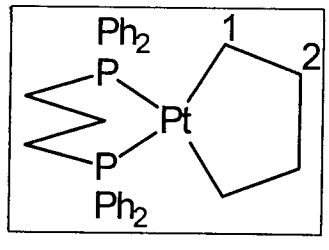
*Synthesis of [(dppp)Pt{$CH_2$)$_{11}$$CH_2$}] **12** [6]*




This complex was prepared in a similar method as complex **11**, starting with compound **9** (150 mg, 0.1933 mmol) in a 100 ml Schlenk round bottom flask which was dried under vacuum for 10 minutes. Dry toluene (35 ml) was added to the flask followed by Pd/C (5 mg). The flask was then fitted with a stopper equipped with a balloon filled with hydrogen gas. The tap was then opened to allow hydrogen gas to

flow into the flask. The solution was left to stir at room temperature for 10 hours. After 10 hours the solution was filtered and all volatiles removed using a rotary evaporator to give a colourless oil. The oil was washed with *n*-hexane (15 ml) and then dried under vacuum for 3 hours affording complex **12** as a colourless oil. Yield ( 117 mg, 78%); $^{1}$H NMR (300 MHz, $CDCl_3$) δ ppm: 0.83-1.05 (m, 4H) H1, 1.08-1.16 (m, 2H) $PCH_2C\underline{H}_2CH_2P$, 1.18-1.56 (br m, 16H) H2-H5, 1.60-1.64 (m, 4H) H6, 2.38-2.44 (m, 4H) $PC\underline{H}_2CH_2C\underline{H}_2P$, 7.18-7.58 (m, 20H) $P\underline{Ph}_2$. $^{13}$C NMR (100 MHz, $CDCl_3$) δ ppm: 14.33 (s, 2C) C1, 23.07 (s, 1C) $PCH_2\underline{C}H_2CH_2P$, 28.24 (s, 2C) $P\underline{C}H_2CH_2\underline{C}H_2P$, 28.81-33.61 ( br m, 10C) C2-C6, 127.68-133.81 (m, 24C) $P\underline{Ph}_2$; $^{31}$P NMR (121 MHz, $CDCl_3$) δ ppm: 3.27 (s), $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1644 Hz.

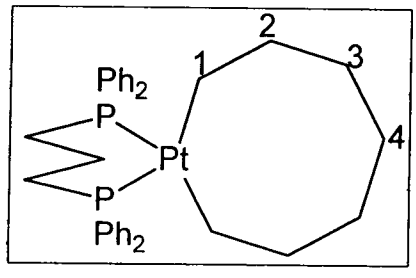
*Synthesis of [(dppp)Pt{$CH_2$)$_3$$CH_2$}] **13** [7]*




[Pt(dppp)$Cl_2$] (400 mg, 0.5896 mmol) was transferred into a Schlenk tube. To this diethyl ether (30 ml) was added under nitrogen. The tube was brought to -78°C and $MgBr(CH_2)_4BrMg$ (0.20 M, 11.80 ml, 2.353 mmol) was slowly added to the solution. The solution was left to stir at room temperature, during which time it turned colourless. The Schlenk tube was again cooled to -78°C and 20 ml of saturated $NH_4Cl$ solution was added to the solution. After reaching room temperature, 20 ml of dichloromethane was then added to the solution. The organic layer was separated using a separating funnel, dried over anhydrous magnesium sulphate for 45 minutes and filtered. All the volatiles were removed using a rotary evaporator to give a yellow oil as the crude product. The crude product was recrystallized from dichloromethane/hexane solution to give a colourless oil as the final product, which was further dried under vacuum for 2 hours. Yield ( 208 mg, 52%); $^{1}$H NMR (300 MHz, $CDCl_3$) δ ppm: 0.74-0.85 (m, 4H) H1, 0.91-1.05 (m, 2H) $PCH_2C\underline{H}_2CH_2P$, 1.29-1.35 (m, 4H) H2, 2.05-2.34 (m, 4H) $PC\underline{H}_2CH_2C\underline{H}_2P$, 6.98-7.22 (m , 20H) $P\underline{Ph}_2$; $^{13}$C NMR (100 MHz, $CDCl_3$) δ ppm: 14.10 (s, 2C) C1, 20.08-20.27 (s, 1C)

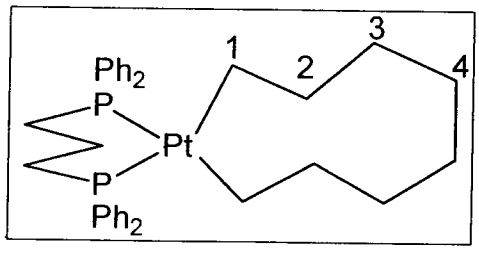
$PCH_2\underline{C}H_2CH_2P$, 24.82-24.95 (s, 2C) $P\underline{C}H_2CH_2\underline{C}H_2P$, 27.02-29.26 (m, 2C) C2, 127.77-133.46 (m, 24C) $P\underline{Ph}_2$; $^{31}P$ NMR (121 MHz, $CDCl_3$) δ ppm: 4.22 (s), $^1J(^{195}Pt\text{-}^{31}P)$ = 1642 Hz; Elemental analysis calculated for $C_{31}H_{34}P_2Pt$ + 1 mole DCM: C, 52.58; H, 5.19; Found: C, 53.60; H, 5.00 %.

*Synthesis of [(dppp)Pt{$CH_2$)$_6$$CH_2$}] **14** [7]*



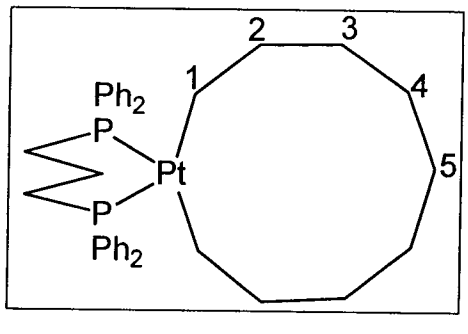

[Pt(dppp)$Cl_2$] (500 mg, 0.7085 mmol) and dry tetrahydrofuran (30 ml) was transferred into a Schlenk tube under nitrogen. The tube was brought to -78°C and $MgBr(CH_2)_7BrMg$ (0.35 M, 8.00 ml, 2.834 mmol) was slowly added to the solution. The solution was left to stir at room temperature, during which time it turned colourless. After 15 hours the same work-up procedure as that described for the synthesis of compound **13** was followed. A colourless oil was isolated and dried under vacuum for 3 hours. Yield ( 300 mg, 60%); $^1H$ NMR (300 MHz, $CDCl_3$) δ ppm: 0.83-0.90 (m, 4H) H1, 1.27-1.36 (m, 10H) H2-H4, 1.40-1.42 (m, 2H) $PCH_2C\underline{H}_2CH_2P$, 1.86-1.95 (m, 4H) $PC\underline{H}_2CH_2C\underline{H}_2P$, 7.21-7.83 (m, 20H) $P\underline{Ph}_2$; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ ppm: 14.34 (s, 2C) C1, 18.07 (s, 1C) $PCH_2\underline{C}H_2CH_2P$, 23.03-23.09 (s, 2C) $P\underline{C}H_2CH_2\underline{C}H_2P$, 28.26-30.17 (m, 4C) C2-C3, 32.18-33.59 (m, 1C) C4, 127.68-131.95 (m, 24C) $P\underline{Ph}_2$; $^{31}P$ NMR (121 MHz, $CDCl_3$) δ ppm: 3.46 (s), $^1J(^{195}Pt\text{-}^{31}P)$ = 1619 Hz.

*Synthesis of [(dppp)Pt{$CH_2$)$_7$$CH_2$}] **15** [7]*




[Pt(dppp)$Cl_2$] (300 mg, 0.4168 mmol) and dry tetrahydrofuran (30 ml) was transferred into a Schlenk tube under nitrogen. The tube was brought to -78°C and $MgBr(CH_2)_8BrMg$ (0.33 M, 5.05 ml, 1.6673 mmol) was slowly added to the solution. The solution was left to stir at room temperature, during which time it turned colourless. After 16 hours the same work-up procedure as that described for the synthesis of compound **13** was followed. A colourless oil was isolated and dried under vacuum for 3 hours. Yield ( 171 mg, 57%); $^1$H NMR (300 MHz, $CDCl_3$) δ ppm: 0.84-0.87 (m, 4H) H1, 0.90-1.02 (m, 2H) $PCH_2C\underline{H_2}CH_2P$, 1.05-1.24 (m, 12H) H2-H4, 1.28-1.62(m, 4H) $PC\underline{H_2}CH_2C\underline{H_2}P$, 7.21-7.83 (m, 20H) $P\underline{Ph_2}$; $^{31}$P NMR (121 MHz, $CDCl_3$) δ ppm: 3.34 (s), $^1J(^{195}Pt\text{-}^{31}P)$ = 1609 Hz; Elemental analysis calculated for $C_{35}H_{42}P_2Pt$ + 1 mole DCM: C, 54.81; H, 5.81; Found: C, 54.40; H, 5.06 %.

*Synthesis of [(dppp)Pt{$CH_2$)$_8$$CH_2$}] **16** [7]*



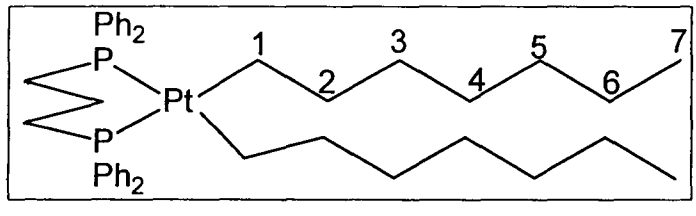

[Pt(dppp)$Cl_2$] (600 mg, 0.8177 mmol) was transferred into a Schlenk tube. To this diethyl ether (30 ml) was added under nitrogen. The tube was brought to -78°C and $MgBr(CH_2)_4BrMg$ (0.42 M, 7.80 ml, 3.2708 mmol) was slowly added to the solution. The solution was left to stir at room temperature for 16 hours, during which time it turned colourless. After 16 hours the same work-up procedure as that described for

the synthesis of compound **13** was followed. A colourless oil was isolated and dried under vacuum for 3 hours. Yield ( 354 mg, 59%); $^{1}$H NMR (300 MHz, $CDCl_3$) δ ppm: 0.82-0.96 (m, 4H) H1, 0.98-1.08 (m, 2H) $PCH_2C\underline{H}_2CH_2P$, 1.18-1.42 (br m, 16H) H2-H5, 2.08-2.18 (m, 4H) $PC\underline{H}_2CH_2C\underline{H}_2P$, 6.98-7.82 (m, 20H) $P\underline{P}h_2$; $^{13}$C NMR (100 MHz, $CDCl_3$) δ ppm: 14.30 (s, 2C) C1, 23.07 (s, 1C) $PCH_2\underline{C}H_2CH_2P$, 26.05 (s, 2C) $P\underline{C}H_2CH_2\underline{C}H_2P$, 28.22-30.35 (m, 6C) C2-C4, 32.29-33.58 (m, 1C) C5, 127.67-133.89 (m, 24C) $P\underline{P}h_2$; $^{31}$P NMR (121 MHz, $CDCl_3$) δ ppm: 3.33 (s), $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1647 Hz.

## 5.5 Reactivity of platinacycles

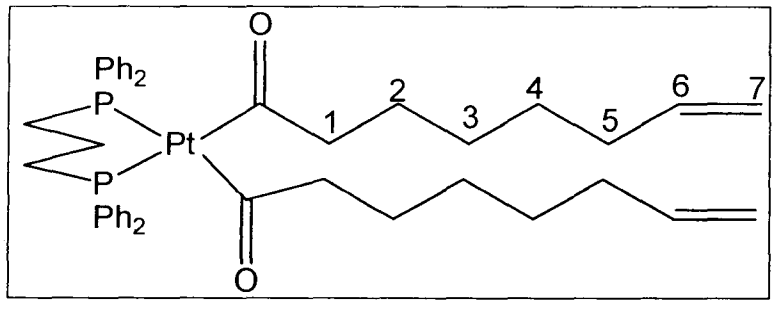
The same atom numbering applies for both carbons and hydrogens.

*Synthesis of [(dppp)Pt{$(CH_2)_6CH_3$}$_2$]* ***18***



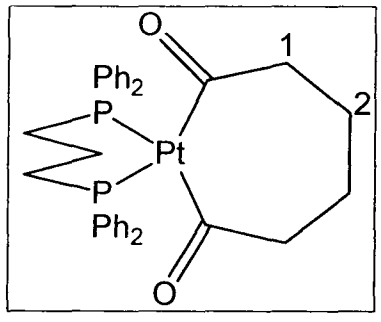

[Pt(dppp)($(CH_2)_5CH{=}CH_2)_2$] (170 mg, 0.2120 mmol) was transferred into a 100 ml Schlenk round bottom flask and dried under vacuum for 15 minutes. Dry toluene (25 ml) was added to the flask followed by Pd/C (5 mg). The flask was then fitted with a stopper equipped with a balloon filled with hydrogen gas. The tap was then opened to allow hydrogen gas to flow into the flask. The solution was left to stir at room temperature for 2 hours. After 2 hours the solution was filtered and all volatiles removed using a rotary evaporator to give a colourless oil. The oil was washed with *n*-hexane (15 ml) and then dried under vacuum for 3 hours affording complex **18** as a white solid. Yield ( 136 mg, 80%); $^{1}$H NMR (300 MHz, $CDCl_3$) δ ppm: 0.76-0.94 (m, 4H) H1, 0.95-1.07 (m, 6H) H7, 1.11-1.23 (m, 2H) $PCH_2C\underline{H}_2CH_2P$, 1.24-1.30 (m, 16H) H2-H5, 1.80-1.96 (m, 4H) H6, 2.00-2.38 (m, 4H) $PC\underline{H}_2CH_2C\underline{H}_2P$, 6.7.32-7.80 (m, 20H) $P\underline{P}h_2$; $^{31}$P NMR (121 MHz, $CDCl_3$) δ ppm: 3.39 (s), $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1600 Hz.

*Synthesis of complex **19***




Complex **5** (300 mg, 0.3741 mmol) was transferred into a 100 ml round bottom flask and dissolved in dry toluene (30 ml). The flask was then fitted with a stopper containing a tap, which was in turn equipped with a balloon fitted with CO gas. The tap was then opened allowing the gas to enter the flask while stirring at room temperature for 5 days. The progress of the reaction was monitored by IR spectroscopy. After 5 days the solvent was removed using a rotary evaporator, to afford a light brown oil that was further dried under vacuum for 2 hours. Yield( 234 mg, 78%); $^{1}$H NMR (300 MHz, $CDCl_3$) δ ppm: 0.93-2.15 (br m, 18H) H2-H5 and $PCH_2C\underline{H}_2CH_2P$, 2.12-2.48 (m, 8H) H1 and $PC\underline{H}_2CH_2C\underline{H}_2P$, 4.87-5.05 (m, 4H) H7, 5.54-5.78 (m, 2H) H6, 6.97-7.98 (m, 20H) $P\underline{Ph}_2$; $^{31}$P NMR (121 MHz, $CDCl_3$) δ ppm: 13.05 (s), $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1420 Hz. Elemental analysis calculated for $C_{43}H_{52}O_2P_2Pt$: C, 60.20; H, 6.11; Found: C, 59.45; H, 6.19 %; FTIR ($\nu_{max}/cm^{-1}$, DCM): 1732 s (C=O), 1605 s (C=C); lRMS (FAB) $C_{43}H_{52}O_2P_2Pt$: m/z = 857.2 $[M]^+$, 731.2 $[M\text{-}(CO)(CH_2)_5CH{=}CH_2]^+$ and 607.1 $[M\text{-}2((CO)(CH_2)_5CH{=}CH_2]^+$.

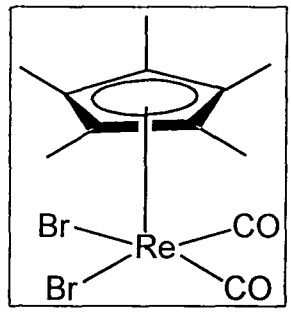
*Synthesis of complex* ***20***




Complex **20** was prepared in a similar method as compound **19** using (250 mg, 0.3767 mmol) of compound **13**. The product was isolated as a light brown oil. Yield(162.5 mg, 65%); $^{1}$H NMR (300 MHz, $CDCl_3$) δ ppm: 0.83-1.83 (m, 6H) H2 and $PCH_2C\underline{H}_2CH_2P$, 1.97-2.33 (m, 8H) H1 and $PC\underline{H}_2CH_2C\underline{H}_2P$, 6.97-7.98 (m, 20H) $P\underline{Ph}_2$; $^{31}$P NMR (121 MHz, $CDCl_3$) δ ppm: 13.20 (s), $^{1}J(^{195}Pt\text{-}^{31}P)$ = 1408 Hz. FTIR ($\nu_{max}/cm^{-1}$, DCM): 1681 s (C=O), 1590 s (C=C).

## 5.6 Synthesis of rhenium precursors

*Synthesis of* $Cp^*Re(CO)_2Br_2$ ***21***




The complex $Cp^*Re(CO)_3$ (1 g, 2.46 mmol) was dissolved in 75 ml of THF in a two-neck Schlenk flask. The flask was then cooled to -78°C and an excess of $Br_2$ dissolved in 15 ml THF was slowly added under stirring to immediately give a dark red solution. The flask was then allowed to reach room temperature and 15 ml of $H_2O$ was added and the mixture stirred for a further 2 hours at room temperature. THF was removed using a rotary evaporator and the residual water pipetted out. The product was then flitered using a Buchner funnel to afford the trans-isomer as a brick red solid which was further dried under vacuum for 45 minutes. Yield(1.2 g, 91%, decomposed without melting above 118°C); $^{1}$H NMR (300 MHz, $CDCl_3$) δ ppm: 2.00 (s, 15H)

$C_5(C\underline{H}_3)_5$; $^{13}C$ NMR (100 MHz, $CDCl_3$) δ ppm:10.42 $C_5(\underline{C}H_3)_5$, 106.8 $\underline{C}_5(CH_3)_5$, 201.6 CO; Elemental analysis calculated for $C_{12}H_{15}Br_2O_2Re$: C, 26.83; H, 2.81; Found: C, 26.56; H, 2.19 %; FTIR ($\nu_{max}/cm^{-1}$, DCM): 2046 (s), 1981 (vs); IRMS (FAB) $C_{12}H_{15}Br_2O_2Re$: m/z = 537.2 $[M]^+$, 509.2 $[M\text{-}CO]^+$, 481.2 $[M\text{-}2CO]^+$, 401.3 $[M\text{-}Br]^+$.

## 5.7 Thermal Decomposition

### 5.7.1 General procedure for the thermal decomposition experiments

Thermolysis reactions were carried out in clean, dry, sealed evacuated vertical Schlenk tubes. Decomposition was accomplished by immersion in a thermostated oil bath for 2 hours for complexes **4**, **5** and **15** and 45 minutes for complex **16**. The oil bath was maintained at 150±5°C.

For all complexes approximately 10 mg of the sample was added to the tube directly then dried under vacuum for at least 1 hour before thermolysis. The samples were then immersed in the thermostated oil bath. After 2 hours or 45 minutes the tubes wer removed and quenched by immersion in liquid nitrogen. The decomposition products were then extracted by adding 20 μl of chlorobenzene (internal standard) and 480 μl of the appropriate solvent (nonane for complexes **4** and **5** and pentane for complexes **15** and **16**).

Decomposition products were analyzed by GC through injection of 1 μl portion of sample. Products were identified by comparison of retention times to those of known samples used as internal standards.

## 5.8 References


1. H.C. Clark and L.E. Manzer, *J. Organomet. Chem.*, 1973, **59**, 411.
2. D.A. Slack and M.C. Baird, *Inorg. Chim. Acta*, 1977, **59**, 277.
3. A.T. Patton, C.E. Strouse, C.B. Knobier and J.A. Gladysz, *J. Am. Chem. Soc.*, 1983, **105**, 5807.
4. G.S. Silverman and P.E. Rakita, (Eds), *Handbook of Grignard Reagents*, 1996, Marcel Dekker, Inc, New York.
5. (a) H.S. Clayton, 2007, University of Cape Town, unpublished work. (b) W.A. Kiel, R.G. Ball and W.A.G. Graham, *J. Organomet. Chem.*, 1990, **383**, 481.
6. (a). A. Sivaramakrishna, H. Su and J.R. Moss, *Angew. Chem., Int. Ed.*, 2007, **46**, 3541. (b). K. Dralle, N.L. Jaffa, T. le Roex, J.R. Moss, S. Travis, N.D. Watermeyer and A. Sivaramakrishna, *Chem. Commun.*, 2005, **30**, 3865.
7. J.X. McDermott, J.F. White and G.M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521.

# Chapter 6: General Conclusions and Future work

In this project, a series of bis(alkenyl)platinum(II) precursors with the same alkenyl chain length were synthesized using the transmetallation method. Platinacycloalkene complexes were then prepared using RCM and subsequent hydrogenation methods to yield platinacycloalkanes in relatively good yields. New characterization data in the form of $^{13}C$ NMR was obtained for these complexes. The synthesis of even numbered platinacycles using the new route was not successful because of the instability of the mono(alkenyl)precursor. This led us to the conclusion that this route although theoretically valid is practically not a definite route for the synthesis of even numbered metallacycles.

The di-Grignard route was then applied in the synthesis of both even and odd numbered platinacycles, complexes **13-16**. Complexes **13** and **14** are known [1], however complexes **15** (odd numbered) and **16** (even numbered) are new. These complexes were obtained in relatively low yields. Thus when comparing the two methods, the di-Grignard route although affording products in a much lower yield is a more realiable route for the synthesis of even numbered metallacycles.

Thermal decomposition studies were done on the bis(alkenyl) complexes and the even and odd numbered platinacycles and a number of conclusions can be drawn from these reactions (refer to section 3.4). For both classes of compounds, β-hydride elimination and reductive elimination were the key steps in the decomposition mechanisms. Certain factors such as the nature of the supporting ligand, the solvent system, reaction time and type of functional group greatly influence the nature and amounts of products formed. Thus one can modify and select the final products formed by fine tunings such parameters.

The total percentage of isomerization products increased with an increase in chain length for bis(alkenyl) complexes, whilst shorter reaction times decreased the product percentage of isomerization products for platinacylces. Both even and odd numbered metallacycles decomposed *via* the same mechanism.

Reaction of bis(alkenyl)platinum complex **5** and platinacyloalkane complex **13** with CO yielded products that correspond to the formation of di-acyl complexes **20** and **21** respectively as evidenced by the characterization data obtained. IR spectroscopy also suggests the formation of first and second four- and five-coordinate platinum species as intermediates. The rate of double CO insertion is faster for the bis(alkenyl) complexes as compared to the platinacyles. Complex **20** was obtained as a light brown solid whilst complex **21** was obtained as an oil, both complexes were relatively stable at room temperature and pressure.

Rhenacycles could not be successfully synthesized using the new route (RCM) and the di-Grignard route; this was attributed to the nature of these complexes and their instability. However, a new synthetic route for the synthesis of $Cp^*Re(CO)_2Br_2$ which affords the product in good yields and as one isomer has been found and is herein reported for the first time.

Future work in this study could include:

- Attempt to obtain good crystals for the characterization of the products obtained form the CO insertion reactions through X-ray crystallography.
- Thermal decomposition studies on the CO inserted products to establish what organic products will be given upon thermolysis.
- Further attempts to try and stabilize the rhenium bis(alkenyl) complexes (by choosing a different ligand system) in order to carry out RCM reactions and obtain rhenacycles *via* this route.
- Further reactivity studies on the platinacycles and their precursor with other small molecules such as $CO_2$, $O_2$ and $S_8$.

## References

1. (a) K. Dralle, N.L. Jaffa, T. le Roex, J.R. Moss, S. Travis, N.D. Watermeyer and A. Sivaramakrishna, *Chem. Commun.*, (**2005**), **30**, 3865. (b) A. Sivaramakrishna, H. Su and J.R. Moss, *Angew. Chem., Int. Ed.*, 2007, **46**, 3541. (c) J.X. McDermott, J.F. White and G.M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521