The synthesis, characterization and reactivity of metallacycloalkanes and their precursors

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Master of Science

By

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DECLARATION

I declare that this dissertation. **The synthesis, characterization and reactivity of metallacycloalkanes 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 consulted and quoted have been acknowledged by means of a full reference.

Signed by candidate

Banothile C. E. Makhubela

19 January 2009

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Conference Outputs and Publications

1. South African Chemical Institute (SACI), Inorganic Chemistry Conference (INORG 007), Club Mykonos (Western Cape) 2007.

   Poster Title and number : Synthesis Characterization and Reactivity of novel osmacycloalkanes.
   Poster No. 69

   Authors: : Banothile.C.E.Makhubela, A. Sivaramakrishna, G.S. Smith, and J.R. Moss.

2. Catalysis Society of South Africa Conference (CATSA), Richards Bay (Kwa-Zulu Natal) 2007.

   Poster Title and number : Metallacycloalkanes, key intermediates in catalytic oligomerization and polymerization reactions.
   Poster No. 71

   Authors : Banothile. C.E. Makhubela, A. Sivaramakrishna, G.S. Smith, and J.R. Moss.

3. Journal and Reference : *Journal of Organometallic Chemistry*, **693**(16), 2008, 2700- 2702.

   Title : C–H activation of benzene with $Cp^*Ru(CO)_2CH_3$

   Authors : John R. Moss, Siyabonga Ngubane, Akella Sivaramakrishna, Banothile C.E. Makhubela, John E. Bercaw, Jay A. Labinger, Michael W. Day, Lawrence M. Henling, Hong Su.

4. Journal and Reference : *Coordination Chemistry Reviews*, **252**, (12-14), 2008, 1460-1485.

   Title : Platinum based mixed-metal clusters ($Pt_nM_m(CO)_xL_y$, M = Ru or Os; $n + m = 2$ to10 and L_y = other ligands) Synthesis, structure, reactivity and application.

Authors : A. Sivaramakrishna, H. S. Clayton, B. C.E. Makhubela, J.R. Moss.

5. Journal and Reference : *Polyhedron*, **27**(1), 2008, 44-52.
   Title : Synthesis, structure and reactivity of *cis*-[PtL_2(1-alkenyl)$_2$] complexes
   Authors : A. Sivaramakrishna, B. C.E. Makhubela, F. Zheng, H. Su, G. S. Smith, John R. Moss.

Abstract

The synthesis and characterization of a series of new osmium(II)dibromido complexes of the type $[(\eta^6\text{-Ar})OsLBr_2]$ (Ar = *p*-cymene and C_6Me_6, L = phosphines, phosphites and CO) have been carried out successfully. The complexes were obtained in good yields and characterized by ^1H and ^{31}P NMR spectroscopy and elemental analysis.

The dibromido complexes were then used in the preparation of osmium bis(alkenyl) and osmacycloalkane complexes. These complexes were found to be very unstable, both in solution and in the solid state. They were obtained in moderate yields and characterized by ^1H and ^{31}P NMR spectroscopy, IR spectroscopy, and mass spectrometry for one of the complexes. Further characterization of these complexes was difficult due to their unstable nature.

Platinum bis(alkenyl) complexes of the type $[PtL_2\{(CH_2)_nCH{=}CH_2\}_2]$ (L_2 = 1,3-bis(diphenylphosphino)propane, L = ethyldiphenylphosphine and n = 3 and 6) have been synthesized and characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy, elemental analysis and mass spectrometry. The molecular structure of the bis(alkenyl) complex $[Pt(dppp)\{(CH_2)_6CH{=}CH_2\}_2]$ was determined for the first time, by X-ray crystallography.

The bis(alkenyl) complexes were further employed in the synthesis of platinacycles *via* ring-closing metathesis (RCM). Some platinacycloalkanes were also prepared using the di-Grignard methodology, including a new platinacyclononane $[Pt(PEtPh_2)_2(CH_2)_8]$. Thermal decomposition of this complex yielded similar organic products to those previously reported for related platinacyclononane complexes.

The platinacycles reacted slowly with CO and we have tentatively suggested the formation of di-acyl complexes in these reactions on the basis of IR, NMR and elemental analysis results.

Reaction of the platinacyclononane $[Pt(dppp)(CH_2)_8]$ with S_8 gave the platinaheptasulphide complex $[Pt(dppp)S_6]$ which was characterized using ^{31}P NMR spectroscopy, mass spectrometry and elemental analysis.

Abbreviations

L = Ligand
Bipy = bipyridine
COD = 1,5-cyclooctadiene
CO = Carbon monoxide
S_8 = Elemental sulfur
C_6Me_6 = Hexamethylbenzene
Cym = *p*-Cymene
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
bdpp = (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane
Bu^n = *n*-Butyl, $–CH_3(CH_2)_2CH_3$
Bu^t = Tertiary butyl, $–C(CH_3)_3$
Ph = Phenyl, $–C_6H_5$
Cy = Cyclohexyl, $–C_6H_{11}$
Me = Methyl, $-CH_3$
Et = Ethyl, $-CH_2CH_3$
THF = Tetrahydrofuran
Et_2O = Diethyl ether
DCM = Dichloromethane
RCM = Ring-closing metathesis

ROMP = Ring-opening metathesis polymerization
Pd/C = Palladium on activated carbon
GC = gas chromatography

NMR = Nuclear Magnetic Resonance
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

1.1 Introduction

Metallacycles have become a major field of research in both academic and industrial laboratories [1], owing to the fact that metallacyclic compounds are key intermediates in catalytic reactions. These compounds have been implicated in catalytic alkene metathesis [2,3], ethylene oligomerization and polymerization [4] and palladium coupling reactions [5]. Studies of the synthesis, properties and reactivities as well as possible peculiarities of this fascinating class of compounds should, therefore provide rich and prolific knowledge which is key to advancing organo-transition metal chemistry and catalysis.

Generally metallacycles can be defined as carbocyclic systems in which one of the carbon atoms have been substituted by a transition metal, as shown in Figure 1.1.

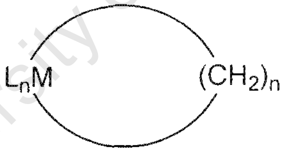


Figure 1.1 Structural representation of a metallacycle (L_nM = metal and associated ligands)

In this review, the definition is restricted to complexes in which one transition metal centre is bonded to two carbon atoms, in a saturated and unsaturated cyclic system, and therefore excludes heterobimetallacycles and metallacyclic compounds containing heteroatoms.

A survey of the literature reveals that metallacycles have been reported for nearly all the transition metals. The shaded areas in Figure 1.2 represent those transition metals for which metallacycles are known (generally speaking a metallacycle is known when it has been fully characterized) [6,7]

▨ 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 (shaded areas mean that metallacycles are known for the transition metal concerned), References: Ti [8], Zr [9], Hf [10], Nb [11], Ta [11, 12a,b] Cr [13], Mo [14], W [15], Mn [16], Re [17], Fe [18], Ru [18], Os [18], Co [19], Rh [20a], Ir [20], Ni [21a], Pd [21b], Pt [22] and Zn [21c].

1.2 Synthesis, stability and chemical reactivity of metallacycles

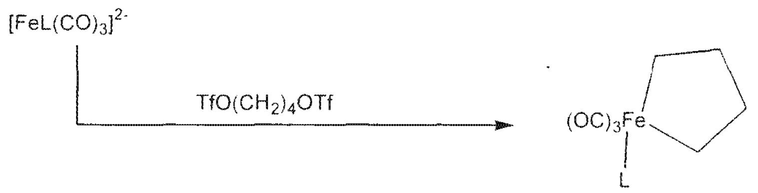
1.2.1 Synthesis

Despite their significance and importance in organo-transition metal chemistry and catalysis, metallacycloalkanes have proved remarkably difficult to isolate and characterize completely [7]. However, introducing certain ligand systems can provide more stable complexes which can be subsequently characterized analytically and spectroscopically.

The main methods used for the synthesis of these complexes are (i) the di-anion route, (ii) transmetallation with di-Grignard or di-lithioalkane reagents and intramolecular coupling of alkenes and/or alkynes [7]. It is also possible that metallacycloalkanes could be derived from alkanes *via* two C-H activation steps.

Di-anion route

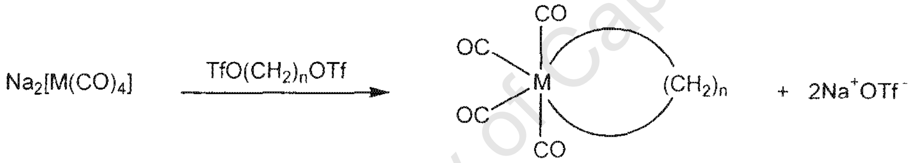
The synthesis of a series of metallacycloalkanes of the group 8 triad, using the di-anion method was reported by Lindner *et al.* [18a-c]. This approach has been employed to provide the iron derivatives $[FeL(CO)_3(CH_2)_4]$ **1**, **2** and **3** from the reaction of $TfO(CH_2)_4OTf$ with the di-anion $[FeL(CO)_3]^{2-}$ (L = CO, PPh_3 or $P(OMe)_3$) (eq. 1.1) [18b].



(eq. 1.1)

1 L = CO
2 L = PPh_3
3 L = $P(OMe)_3$

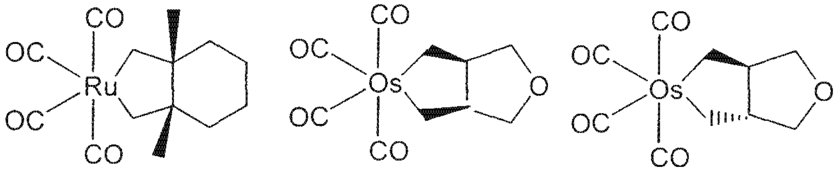
Similarly, metallacyclohexanes **4** and **5** as well as the metallacycloheptane **6** were prepared *via* the reaction of metal carbonylates of the type $Na_2[M(CO)_4]$ with bis(triflates), $TfO(CH_2)_nOTf$, (M = Ru and Os, n = 5 and 6) (eq. 1.2) [18c,d]. These compounds were fully characterized by elemental analysis, mass spectrometry as well as IR, ^1H and ^{13}C NMR spectroscopy. In general, the osmium compounds were found to be much more stable than their ruthenium analogues, and thus the X-ray crystal structure of compound **5** could be obtained [18c].



(eq. 1.2)

4 n = 5; M = Ru
5 n = 5; M = Os
6 n = 6; M = Os

This route has also been used to prepare substituted metallacyclopentanes **7** and **8** (Figure 1.3), the *cis* isomer having been structurally characterized [23b].



7

8
cis and *trans*

Figure 1.3 Substituted metallacycles prepared by the di-anion method

Transmetallation

The di-Grignard and di-lithioalkane method has so far been the most widely employed route in preparing metallacycloalkane complexes of Ti [8] **9**, Hf [10] **10**, Cr [13] **11**, **12**, Mo [14] **13**, W [15] **14**, Ru [24] **15**, Co [20a] **16**, Rh [20a,b] **17**, **18**, **19** Ir [20a] **20**, **21**, Ni [25] **22**, Pd [26, 27] **23**, **24** **25** and Pt [28,29] **26**, **27**, **28**, **29**, **30** (Figure 1.4).

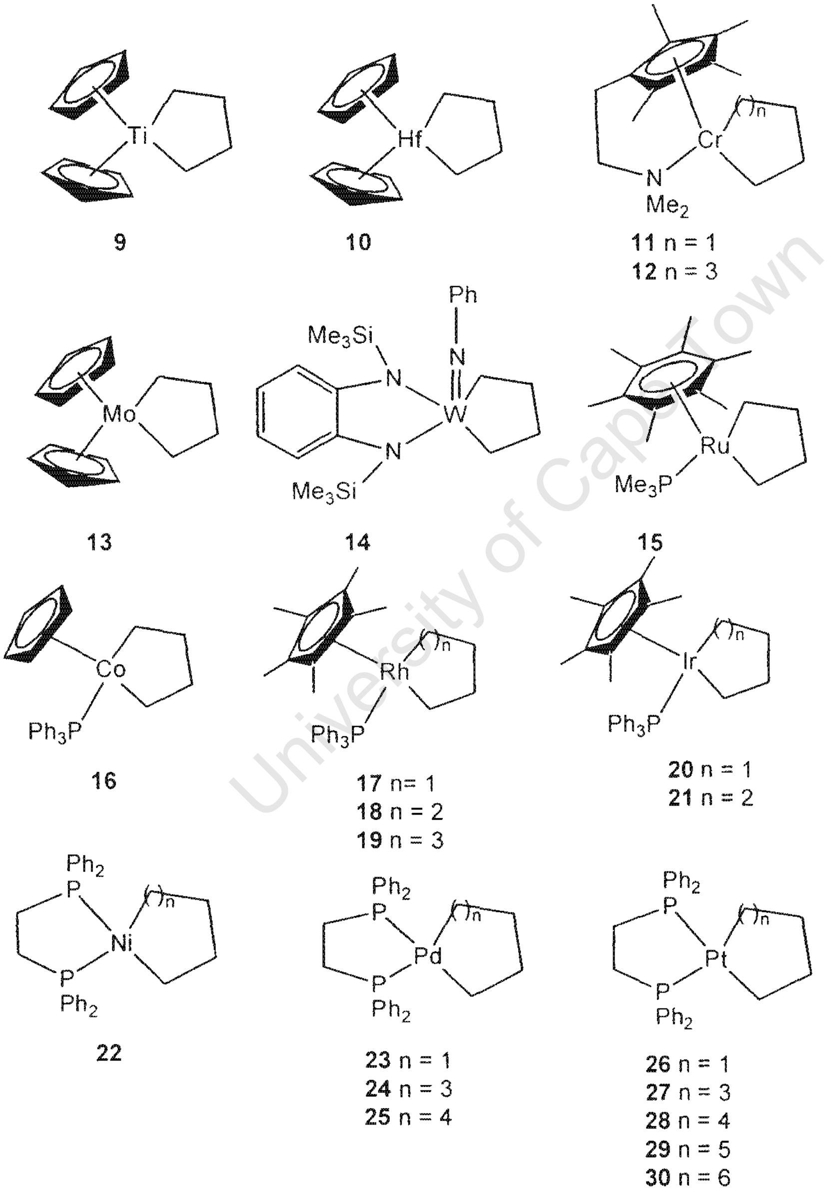


Figure 1.4 Metallacycles prepared by transmetallation

Titanacyclopentane **9** has been synthesized from [Cp_2TiCl_2] and 1,4-dilithiobutane in diethyl ether at -78°C, and was isolated as an orange crystalline solid in 20 % yield. This compound was said to be unstable in solution, even at -30°C, and was thus characterized by its reactions, including thermal decomposition [8].

Similarly, hafnacyclopentane **10** and molybdenacyclopentane **13** were obtained from the reaction of [Cp_2HfCl_2] and [Cp_2MoI_2] with $Li(CH_2)_4Li$ [10,14]. In contrast to the related titanacycle **9**, compound **10** was sufficiently stable to be handled at ambient temperature. Compound **13** was also found to be thermally stable and has been structurally characterized.

Iridacycloalkane complexes of types **20** and **21**, cobaltacyclopentane **16** and rhodacycloalkanes **17**, **18** and **19** have been reported by Diversi *et al.* [20].

The iridacycles can be prepared by reaction of [$Cp^*Ir(PPh_3)Cl_2$] with either $BrMg(CH_2)_4MgBr$ or magnesiacyclopentane in THF. No reaction took place when diethyl ether was used as the solvent. Products were obtained as stable yellow-green crystals [20a].

Similarly, cobaltacyclopentane **16** was isolated as orange-red crystals (15-20 % yield) by the reaction of $BrMg(CH_2)_4MgBr$ or magnesiacyclopentane with [$CpCo(PPh_3)I_2$] in diethyl ether. Compound **16** was found to be stable at room temperature under N_2 atmosphere and can be stored for months at -30°C [20c].

Chromacycloalkanes of the types **11** and **12** as well as ruthenacyclopentane **15** have been reported, from the di-lithioalkane route [13,24]. High to good yields ranging from (70-90%) were obtained for the chromacycloalkanes [13]. Yellow crystals of ruthenacyclopentane **16** were isolated and structurally characterized [24].

Group 10 metallacycloalkanes, with a range of tertiary phosphine and diphosphine ligands have been prepared and studied extensively. These complexes have been prepared by the treatment of the corresponding metal dihalide with di-Grignard or di-lithium alkylating reagents [25-29].

Grubbs *et al.* [25], reported a series of nickelacyclopentane complexes with a range of tertiary phosphines and diphosphines, including compound **22**, which was obtained as yellow crystals in 40 % yield.
Similarly, Diversi and co-workers prepared and characterized a range of palladacycles containing tertiary phosphines, diphosphines and nitrogen donor ligands [26].

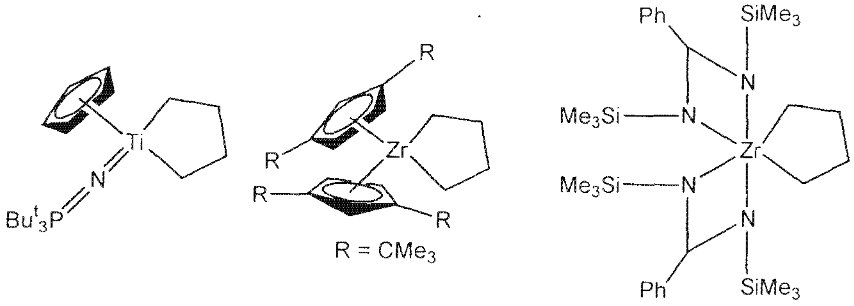
Platinacyclopentane **26** can be prepared by the reaction of $BrMg(CH_2)_4MgBr$ with $[Pt(COD)\ Cl_2]$ followed by displacement of the labile COD ligand (COD = 1,5-cyclooctadiene) with dppe or alternatively, direct treatment of $[Pt(dppe)Cl_2]$ with $Li(CH_2)_4Li$. The former procedure allowed 25 % yield while the latter gave a yield of 60 % [28].

The transmetallation method has until recently been the most effective and convenient way of preparing metallacyclic complexes containing various transition metals. This methodology, however suffers a drawback (very low yields obtained) when it comes to the preparation of medium to large metallacycles (with 8-membered rings and above) [7].

Coupling of olefins

Metallacycles can also be prepared by the so-called reductive coupling of olefins route. In this method, a precursor complex is treated with magnesium, sodium, butyllithium or sodium amalgam in the presence of an olefin (ethylene being the widely used olefin) to give a metallacycle [9a,13,30a,c,d].

In this manner, metallacycloalkanes **31**, **32** and **33** have been successfully isolated and characterized (Figure 1.5) [30a,c,d].

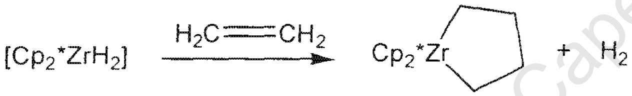


31 **32** **33**

Figure 1.5 Metallacycles prepared by reductive coupling of olefins

Some instances where only ethylene and the corresponding metal precursor are reacted at moderate temperatures are also known [11,30b,31].

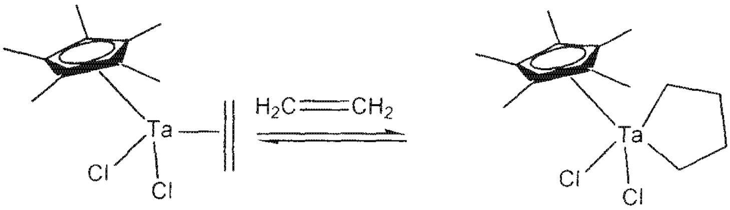
For example, zirconacyclopentane **34** was isolated by reacting [Cp*ZrH$_2$] with ethylene at 25°C (eq. 1.3) [30b].



34

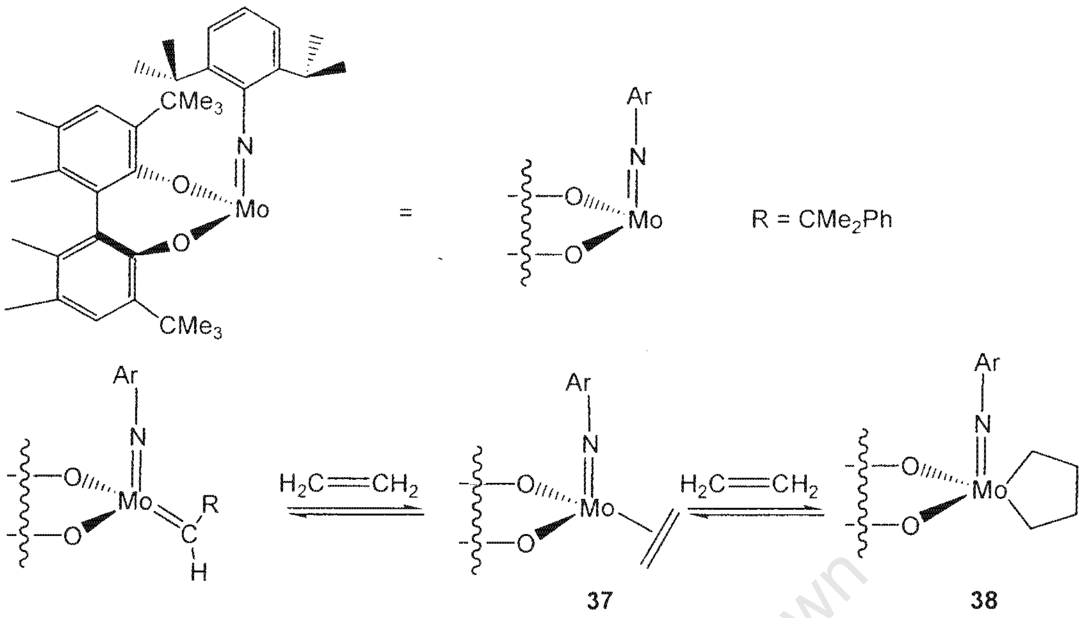
(eq. 1.3)

The treatment of olefin complexes **35** and **37** with ethylene at room temperature affords metallacycles **36** and **38** in almost quantitative yields (eq. 1.4 and Scheme 1.1) [11,31].



35 **36**

(eq. 1.4)

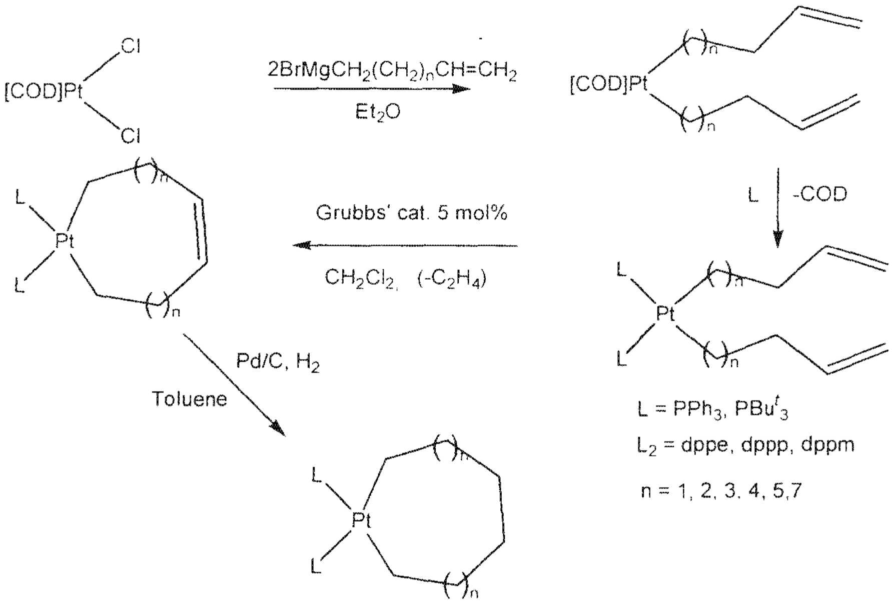


Scheme 1.1 Molybdenacyclopentane prepared from ethylene at room temperature

Other olefins such as propene [30a], norbornadiene [9a] as well as pendant alkene groups to ancillary ligands [32] have also been employed in this methodology for preparing metallacycles. The use of alkynes instead of alkenes is also known, in this case metallacycloalkenes are afforded [33].

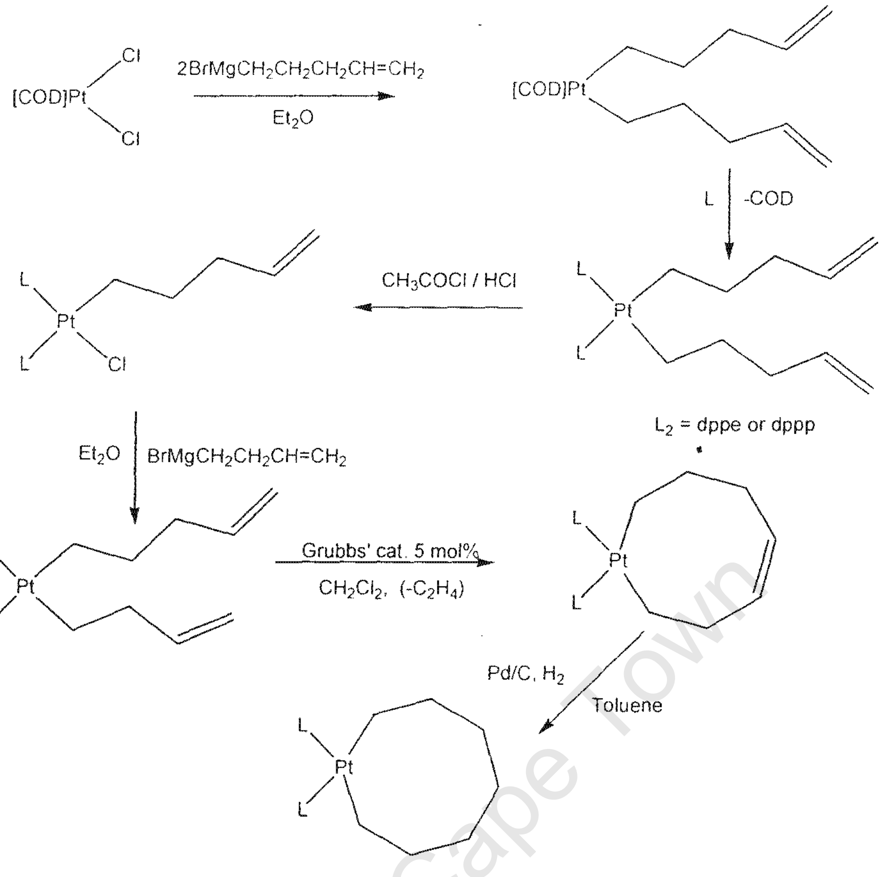
New route to metallacycloalkanes

A new route to metallacycloalkanes was introduced in 2005 by Moss and co-workers [29b], from the ring-closing metathesis reaction (RCM) of bis(1-alkenyl) complexes with Grubbs' 1st generation catalyst (Scheme 1.2). This method not only allows isolation of medium to large ring compounds (with more than 8 members), but also allows isolation of novel metallacycloalkene complexes [29].



Scheme 1.2 New route for the preparation of metallacyloalkanes

Using this route, a range of stable medium to large ring platinacycloalkanes have been prepared and characterized, including the largest (i.e. 15-membered ring) platinacycloalkene to ever be structurally characterized [29a]. In addition, slight modification of this methodology resulted in even-membered ring platinacycles **39a** and **39b** (Scheme 1.3). These compounds are the first ever reported platinacyclooctanes [29c].



39a L_2 = dppe
39b L_2 = dppp

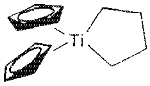
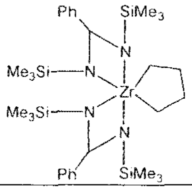
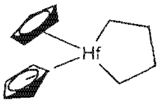
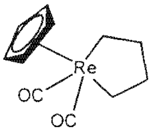
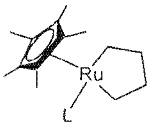
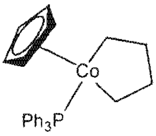
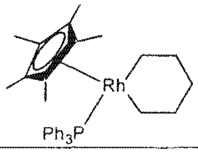
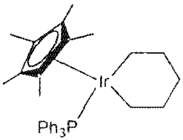
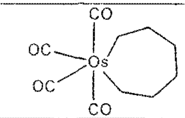
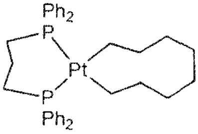
Scheme 1.3 Preparation of even-membered metallacycloalkanes by the new route

This method has since been extended to other transition metals including Pd, Rh and Ir [27, 29d,e].

1.2.3 Stability

The stability of metallacycloalkanes can vary, depending on the ring size and transition metal involved [7,29]. However, the choice of supporting ligands can have a marked effect on their stability [7,27,29,34]. These compounds often decompose at room temperature or at high temperatures and in solution to give interesting organic products [7,27,29].The decomposition pathways often observed are reductive elimination and α- or β-hydride elimination. Some metallacycles such as those of Ru and Co have been found to be air sensitive [20,24]. Examples of some metallacycloalkanes and their relative stability in the solid state or in solution are shown in Table 1.1.

Table 1.1 Metallacycloalkanes and their thermal stability in solution and in the solid state

Examples	**Stability**	**Some Physical properties**	**Reference**
	Decomposes at 250°C. Unstable in solution, even at -30°C	Orange crystalline solid	8c
	Remarkably stable. No decomposition after 1 year in a florescent-lit dry box at room temperature.	Orange crystalline solid	30d
	Melts with decomposition at 126°C.Stable in toluene up to 90°C	Yellow crystalline solid	10
	Decomposes in benzene at 100°C.	Yellow crystalline solid	17
 L = PPh_3, $PMePh_2$, PMe_2Ph	Compounds are stable at room temperature and in most organic solvents, under inert atmosphere.	Yellow crystalline solids	24
	Stable at room temperature under N_2 atmosphere and can be stored for months in benzene at -30°C.	Red-orange crystals	20a
	Melts with decomposition at 188°C.	Pale-yellow crystalline solid	20a,b
	Melts with decomposition at 109°C.	Orange crystalline solid	20a
	Decomposes at 3°C.	Colourless crystals	18e
	Decomposes at 120°C. Stable in non-halogenated solvents at room temperature	Colourless oil	29a,g

1.2.4 Chemical reactivity

The presence of reactive metal-carbon bonds in metallacycloalkanes is key in them participating in chemical reactions [7,29]. It is known that chemical reactivity, in some cases, depends on ring size [7]. Some reactions that have been observed for metallacycloalkanes are shown in Figure 1.6 below.

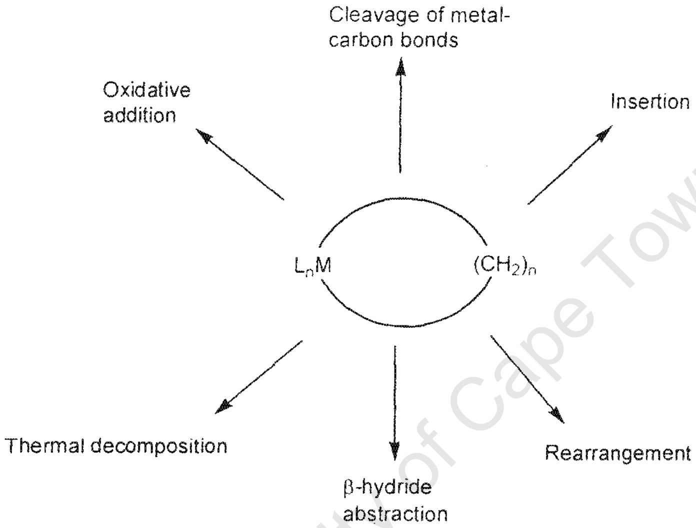


Figure 1.6 Reactivity pathways observed for metallacycloalkanes (L_nM = metal and associated ligands)

Thermal decomposition

The thermal decomposition of metallacycloalkane complexes has been extensively studied mostly for the following reasons: (i) to determine the organic products which can be the last stage in the mechanism of catalytic reactions involving metallacyclic intermediates, and (ii) understanding these decomposition processes can be of great importance in the design of new catalyst systems as well as stable metallacycloalkanes [25-27,29].

Various factors such as ring size, metal and supporting ligands, solvent and temperature can influence the decomposition modes in metallacycloalkanes, while product distribution depends on heating time. Decomposition pathways frequently observed include: α or β-hydride elimination, reductive elimination and carbon-carbon bond cleavage (Figure 1.7) [25-27,29].

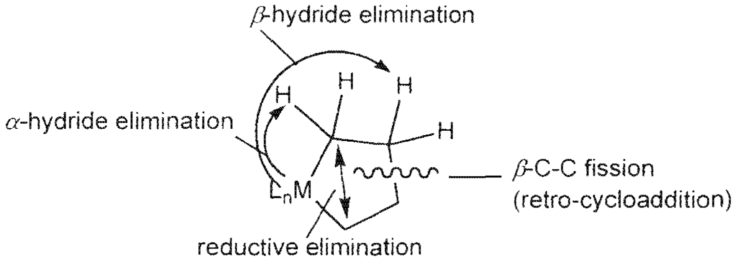


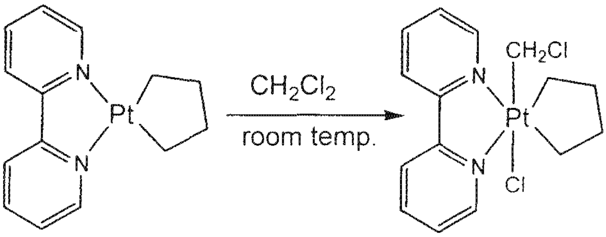
Figure 1.7 The conventional decomposition pathways for metallacycloalkanes (L_nM = metal and associated ligands)

The thermal decomposition of small metallacycloalkanes with a variety of transition metals has been reported. On the other hand there has been considerable interest in medium to large metallacycloalkanes partly because they are key intermediates in various catalytic transformations. The thermal decomposition patterns of these novel compounds can give new information on the formation of a variety of organic products [29].

Oxidative addition

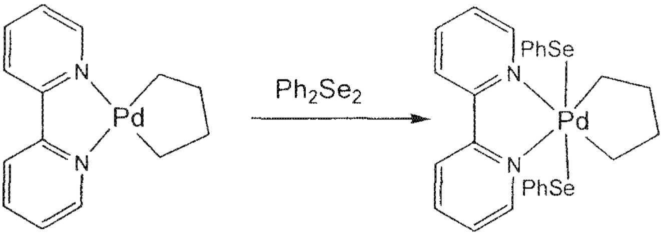
Oxidative addition is an important reaction which forms the initial step in palladium catalyzed coupling reactions [29e].

The oxidative addition reaction of chlorinated solvents to platinacyclopentanes during thermolysis and at room temperature has been reported in the literature. These complexes undergo oxidation with dichloromethane at room temperature (eq. 1.5) [35]. The dichloromethane solvent also influences the decomposition pathway of the hexacoordinate complex generated during thermal decomposition [35].



(eq. 1.5)

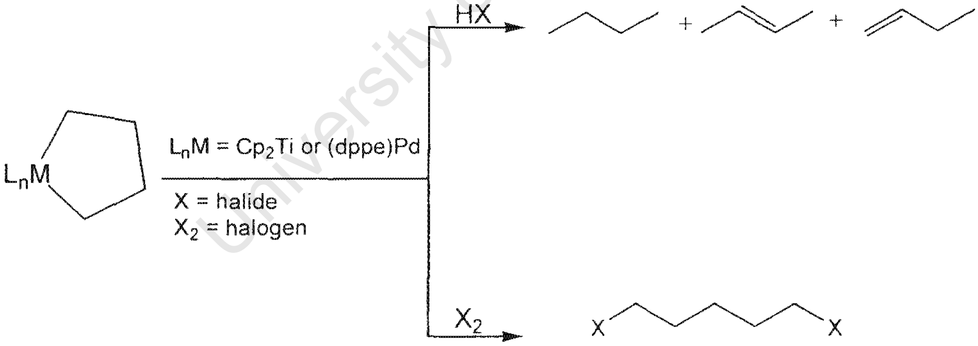
Similarly, the palladium analogue undergoes oxidation by diphenyl diselenide to give a Pd^{IV} compound (eq. 1.6) [36].



(eq. 1.6)

Reaction with electrophilic reagents

The interaction of metallacycloalkanes with electrophilic reagents such as acids and halogens to give the corresponding hydrocarbons or haloalkanes, by metal-carbon bond cleavage has also been documented (Scheme 1.4) [6,8a]. These reactions present opportunities for applications in organic synthesis *via* formation of C-C and C-X bonds.



Scheme 1.4 Cleavage of metal-carbon bonds by electrophillic reagents

Insertion

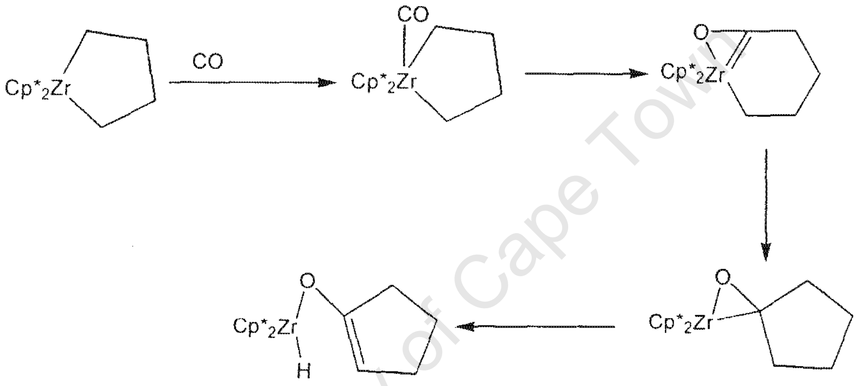
The insertion of molecules (such as those shown in Table 1.2 page 20) into the metal-carbon bonds of metallacycloalkanes is also known. The result of insertion of these groups is often expansion of the metallacyclic ring and subsequent functionalization of the alkyl moiety, *via* mono-, di- or poly-insertion [8a,18,19,30c,37-40]. The resulting products of insertion can act as models for transition metal-catalyzed hydrocarbon transformation processes.

Table 1.2 Experimentally detected insertion reactions in metallacycloalkanes.

Transition metal	**Ring size**	**Inserted group**	**Observed insertion**	**Reference**
Ti	5	CO	mono-insertion then, reductive elimination	8c
Ru & Os	6	CO	mono-insertion then, reductive elimination	18c
Co	5	CO	mono-insertion then, reductive elimination	19b
Pd	5	CO	mono-insertion then, reductive elimination	6
Fe	5	SO_2	mono-insertion	18a
Pd	5	SO_2	di-insertion	6
Ni	5	N_2O	mono insertion	41a
Ti	3	$H_2C{=}CH_2$	mono-insertion	38a,b
Pt	8	$H_2C{=}CH_2$	poly-insertion	39
Zr	5	$PhC{\equiv}CPh$	mono insertion	30c
Hf	5	$PhC{\equiv}CPh$	di-insertion	10
Zr	5	O=CHPh	mono-insertion	40b
Co	3	RNC (R = Cy, C_6H_2-2,4,6-Me_3 or C_6H_3-2,6-Me_2)	mono-insertion	41b
Pt	3	CNR (R = Cy, C_6H_2-2,4,6-Me_3 or C_6H_3-2,6-Me_2)	di-insertion	41a

Mono-insertion of carbon monoxide into metallacycles is the most common and is almost always followed by reductive elimination to form the corresponding cycloketone [8a,18c,19b,37]. Nowhere in these reports, has the CO inserted product been isolated. An unusual reaction of CO with [Cp*$_2$Zr(CH$_2$)$_4$] to form the enolate hydride complex **40** was reported by Bercaw and co-workers [30b]. Scheme 1.5 represents the proposed mechanism for the formation of this complex.

CO insertion into metal-carbon bonds is also known to occur in catalytic transformations such as hydroformylation and ethylene CO copolymerization (The topic of CO insertion will be reviewed further in Chapter 4).

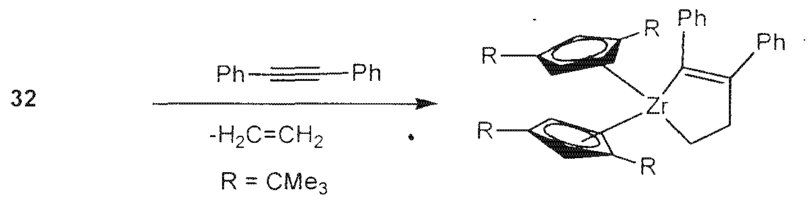


40

Scheme 1.5 Mechanism for the formation of enolate hydride complex **40**

Ethylene insertion reactions have been observed for metallacyclopropanes [38], and recently poly-insertion of ethylene into the metal-carbon bonds of a platinacyclooctane to form larger ring platinacycloalkanes of up to 42-members as evidenced by mass spectral data has been reported [39]. These studies further support the intermediacy of metallacycloalkanes in catalytic ethylene oligomerisation and polymerization reactions [4].

Diphenylacetylene reacts with zirconacyclopentane **32** to demonstrate the reversibility of metallacycle formation through the incorporation of the alkyne and one equivalent of ethylene (eq. 1.7) [30c]. Subsequent incorporation of a second molecule of diphenylacetylene has also been observed [10].



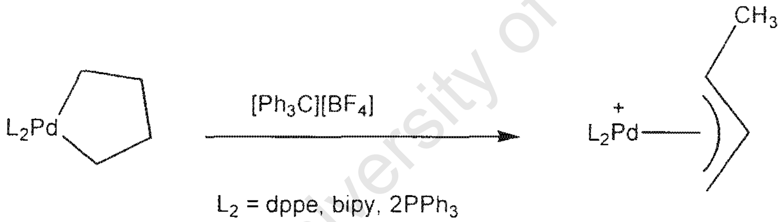
(eq. 1.7)

Mono- and di-insertion of other molecules including benzaldehyde, isocyanide and sulfur dioxide have been documented [6,18,40,41].

β-hydride abstraction

Metallacycloalkanes were found to undergo facile β-hydride abstraction to give cationic π-allylic complexes [6,20].

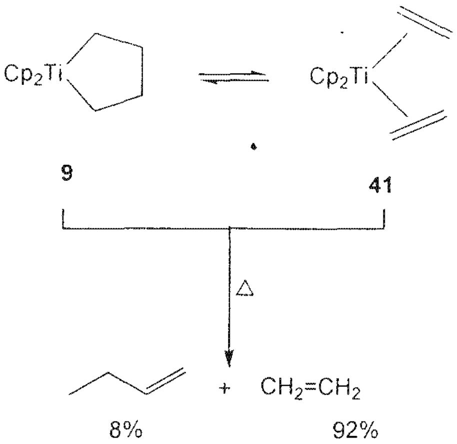
Diversi and co-workers reported formation of cationic π-allylic Pd(II) complexes, upon treatment of several palladacyclopentanes with the trityl salt $[CPh_3][BF_4]$ at room temperature (eq. 1.8) [6]. They then later on showed that rhodacycles **17-19** as well as iridacycles **20** and **21** (in Figure 1.4) undergo similar reactions under the same conditions [20].



(eq. 1.8)

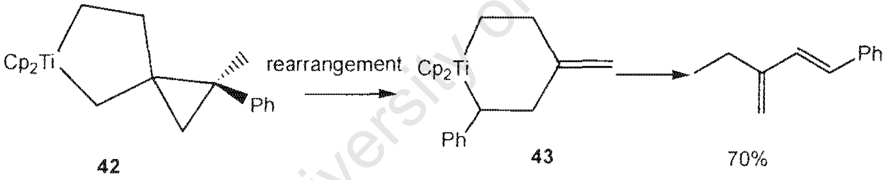
Rearrangement

Rearrangement of metallacycloalkanes in order to increase stability during or before thermal decomposition has been reported [7,10,34]. Studies have shown that decomposition by reversible rearrangement or carbon-carbon bond cleavage can occur to produce bis-ethylene complexes then ethylene as the major decomposition product [8b,c,42]. Such was the case in the decomposition of $[Cp_2Ti(CH_2)_4]$ **9** (Scheme 1.6) [8].



Scheme 1.6 Rearrangement of a titanacyclopentane to form a titanium bis(ethylene) complex

On the other hand the substituted titanacyclopentane **42** rearranges to the 6-membered ring **43**, prior to decomposition to give mainly the diene [$CH_3CH_2C(=CH_2)CHCHPh$] as the decomposition product (eq. 1.9) [8b,c]. This suggests that in addition to the reported factors that influence thermal decomposition pathways [29f], prior rearrangement of the metallacycle also affects the thermal decomposition pathway and organic products formed.



(eq. 1.9)

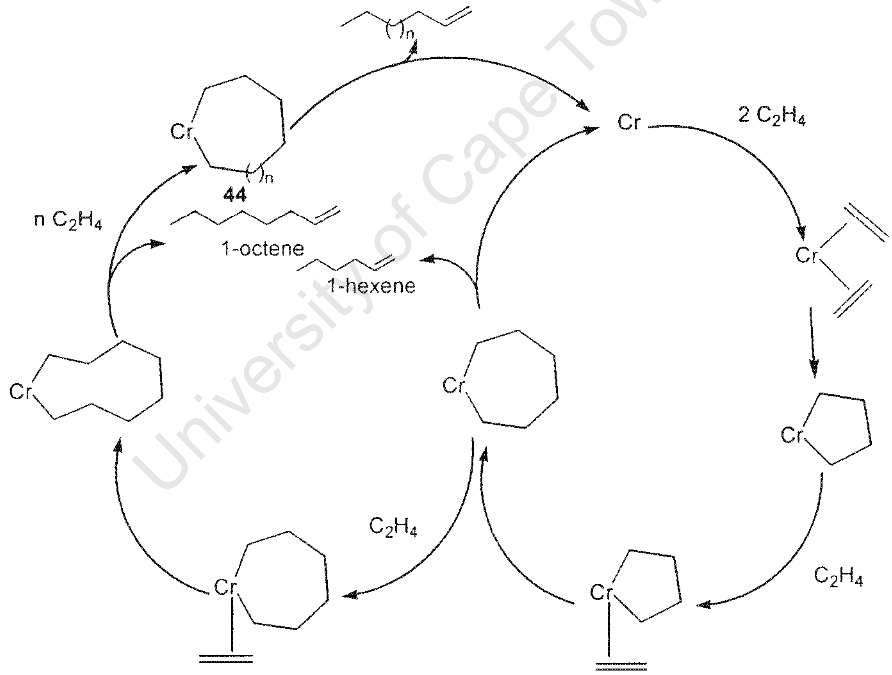
Rearrangement promoted by irradiation to give a tungsten butylidene complex has also been reported [43].

1.3 Implications and applications of metallacycloalkanes in catalysis

In 1971 Yves Chauvin and Jean-Louis Hérrisson suggested that olefin metathesis is initiated by a metal carbene which reacts with an olefin to form a metallacyclobutane intermediate that breaks apart to form a new olefin and a new metal carbene [2]. This reaction has gained great importance in recent years through the work of Grubbs and Schrock [3,44]. Olefin metathesis has found applications in organic synthesis, polymers, materials chemistry as well as organometallic chemistry in ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM), cross metathesis etc. [29,44].

Metallacycloalkanes are known to mediate ethylene oligomerization reactions. For example, metallacycloheptanes have been shown to be involved in chromium-catalyzed trimerization of ethylene to 1-hexene and more recently a metallacyclononane was implicated in the tetramerization of ethylene to 1-octene [4]. The intermediacy of metallacycloalkanes in these reactions has been confirmed by ethylene labeling experiments (Scheme 1.7).

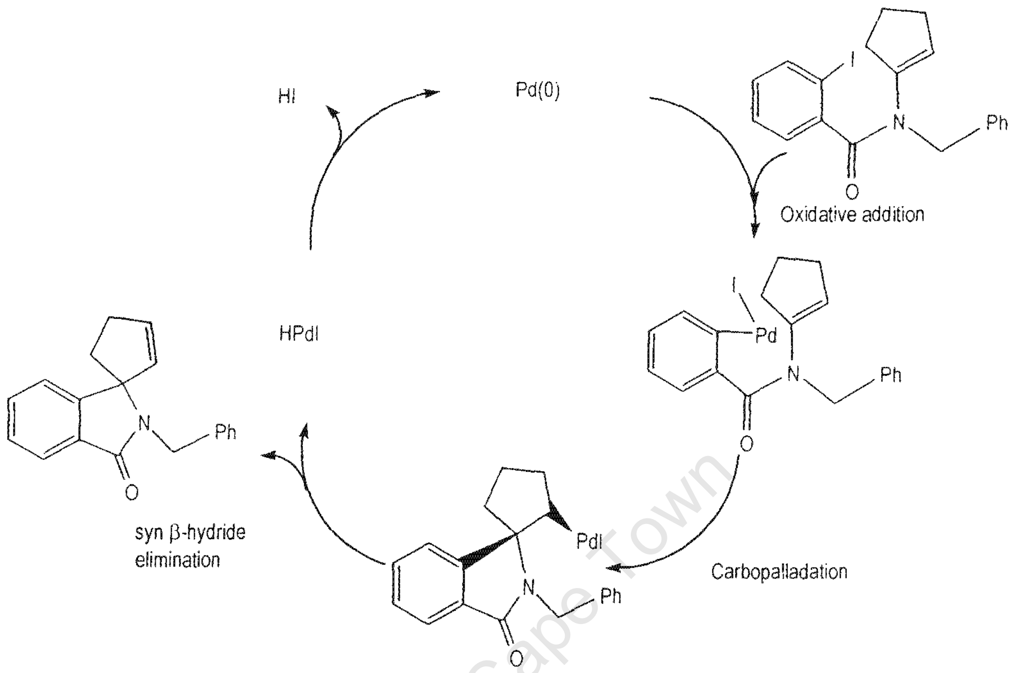
Furthermore, studies have shown that chain propagation in selected chromium catalyst systems for ethylene oligomerization and polymerization occurs predominantly *via* the mechanism involving the large ring metallacycle **44** (Scheme 1.7) [4b].



Scheme 1.7 Mechanism for chromium catalyzed ethylene oligomerization and polymerization reactions
(Ligands omitted for clarity)

Linear α-olefins are used industrially as co-monomers in the production of low density polyethylene and in the production of linear aldehydes *via* hydroformylation [4].

Palladacycloalkanes are known to mediate "Heck type" coupling reactions catalyzed by Pd(0) species [27]. The involvement of these compounds has been observed in both intra- [5] and intermolecular [45] (Scheme 1.8) Heck reactions. Such coupling reactions play an important role in drug synthesis.



Scheme 1.8 Mechanism for palladium catalyzed "Heck type" coupling reactions (Ligands omitted for clarity)

Other catalytic reactions in which metallacycles have been proposed as intermediates include ethylene carbonylation and Fischer-Tropsch [7].

Titanacyclopentanes have been implicated in the catalytic dimerization of styrene [46].

1.4 Concluding remarks

Metallacycloalkanes can be synthesized using various methods. These compounds are sometimes isolated and are stable enough to carry out reactivity studies on.

Five-membered rings are by far the most widely prepared and studied metallacycles, indeed they have been reported for most transition metals (Figure 1.2) [7,8-22].

This review has revealed that metallacycles exhibit significantly different reactivity than the acyclic analogues, displaying interesting reactions such as insertion, 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. Though the transient species are difficult or impossible to isolate, numerous examples of stable metallacyclic complexes which can serve as models in these catalytic reactions have been discussed in the present review.

It is interesting to note that, despite their importance in catalytic reactions, few investigations have been undertaken with medium and large (> 7-membered ring) metallacycles due to the lack of efficient synthetic methods. The new route for the preparation of these novel medium to large ring complexes presents the opportunity to prepare and study their stability as well as reactivity patterns and compare these with the small ring metallacycles. The knowledge gained from these studies can be useful in improving the catalytic reactions in which they are involved and so aid the advancement of organometallic chemistry and catalysis.

1.5 Aims and Objectives of this Project

1.5.1 The main focus of this project

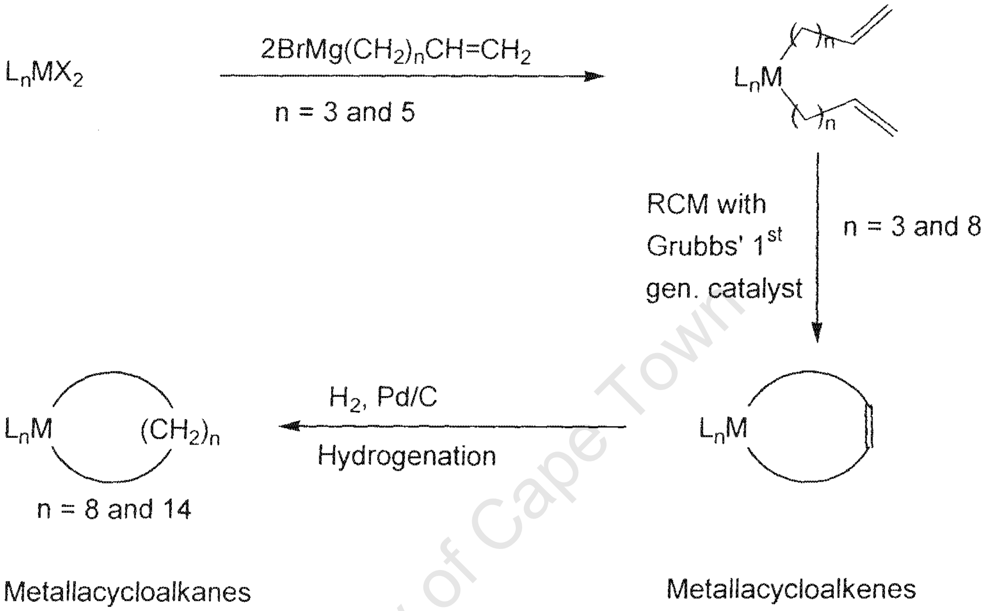
The first aim of this project was to synthesize osmium-containing metallacycles. There are a few examples of such compounds in the literature [18], and we hoped to expand on this area of chemistry through applying the new route for the preparation of metallacycles to preparing novel medium and large ring osmacycloalkanes.

The second aim of this project was to synthesize platinacycloalkanes and platinacycloalkenes and study their reactivity patterns.

Reactions with carbon monoxide (CO), elemental sulfur (S_8) and oxygen (O_2) were to be investigated.

1.5.2. Approach to the synthesis of metallacycles

The new route, involving the preparation of bis(alkenyl) complexes which were then subjected to RCM to yield metallacycloalkenes was employed. Finally, hydrogenation of the metallacycloalkenes allowed isolation of the metallacycloalkanes in this project (Scheme 1.9).



L_nMX_2 = (dppp)$PtCl_2$, Cym(L)$OsBr_2$ and (C_6Me_6)L$OsBr_2$
L = CO, $P(OMe)_3$, $P(OBu)_3$, $P(OPh)_3$, PEt_3 $PMePh_2$, PPh_3, and $PEtPh_2$
Cym = p-cymene

Scheme 1.9 Method used for preparation of matallacycles in this project

1.6 References

1. 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 Carlifornia*, (**1976**), pp 459-522.
2. Y. Chauvin, and J-L. Hérrisson, *Makromol. Chem.*, (**1971**), 141, 161.
3. R.H. Grubbs, Tetrahedron, (**2004**), 60, 7117.
4. (a) T. Agapie, S.J. Schofer, J.A. Labinger, and J.E. Bercaw, *J. Am. Cherm. 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) M.J. Overett, K. Blann, A. Bollmann, J.T. Dixon, D. Haasbroek, E. Killian, H. Maumela, D.S. McGuinness, and D.H. Morgan, *J. Am. Chem. Soc.*, (**2005**), 127, 10723. (d) 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.
5. (a) G. Dyker, *Chem. Ber.*, (**1997**), 130, 1567. (b) B.M. Trost, *Acc. Chem. Res.*, (**1990**), 23, 34. (c) B.M. Trost, and M.K. Trost, *J. Am. Chem. Soc.*, (**1991**), 113, 1850. (d) B.M. Trost, and M.K. Trost, *Tetrahedron Lett.*, (**1991**), 30, 3647.
6. P. Diversi, G. Ingrosso, A. Lucherini, and S. Murtas, *J. Chem. Soc. Dalton Trans.*, (**1980**), 1633.
7. B. Blom, H.S. Clayton, M. Kilkenny, and J.R. Moss, *Adv. Organomet. Chem.*, (**2006**), 54, 149.
8. (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.
9. (a) S. Mansel, D. Thomas, C. Lefeber, D. Heller, R. Kempe, W. Baumann, and U. Rosenthal, *Organometallics*, (**1997**), 16, 2886. (b) L.W.M. Lee, W.E. Piers, M. Parves, S.J. Rettig, and V.G. Young, *Organometallics*, (**1999**), 18, 3904.

10. G. Erker, U. Dork, and A.L. Rheingold, *Organometallics*, (**1988**), 7, 138.

11. S.J. McLain, C.D. Wood, R.R. Schrock, *J. Am. Chem. Soc.*, (**1977**), 99, 3519.

12. (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.

13. R. Emrich, O. Heinemann, P.W. Jolly, C. Krüger, and G.P. Verhonik, *Organometallics* (**1997**), 16, 1511.

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

15. S-Y. Wang, S.D. VanderLende, K.A. Abboud, and J.M. Boncella, *Organometallics* (**1998**), 17, 2628.

16. (a) K. Jonas, C. Häselhoff, R. Goddard, and C. Krüger, *Inorg. Chim. Acta*, (**1992**), 198, 533. (b) K. Jonas, G. Brukart, C. Häselhoff, P. Betz, and C. Krüger, Angew. *Chem., Int. Ed. Engl.*, (**1990**), 29, 322.

17. G.K. Young, and R.G. Bergamn, *Organometallics*, (**1985**), 4, 129.

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

19. (a)Y. Wakatsuki, T. Sakurai, and H. Yamazaki, *J. Chem. Soc., Dalton Trans.*, (**1982**), 1926. (b) Y. Wakatsuki, O. Nomura, H. Tone, and H. Yamazaki, *J. Chem. Soc., Perkin. II,* (**1980**), 1344.

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

21. (a) R. Wyrwa, H-O. Fröhlich, and H. Görls, *J. Organomet. Chem.*, (**1995**), 491, 41. (b) H-O. Fröhlich, R. Wyrwa, and H. Görls, *J.*

Organomet. Chem., (**1993**), 110, 8657. (c) H-O. Fröhlich, B. Kosan, B. Müller, and W. Hiller. *J. Organomet. Chem.*, (**1992**), 441, 177.

22. W.D. Neilsen, R.D. Larson, and P.W. Jennings, *J. Am. Chem. Soc.*, (**1988**), 110, 8657.
23. (a) J. Krausse, and G. Schödl, *J. Organomet. Chem.*, (**1971**), 27, 59.(b) E. Lindner, R. Pabel, R. Fawzi, M. Steimann, *J. Organomet. Chem.*, (**1992**), 441, 63.
24. P. Barabotti, P. Diversi, G. Ingrosso, A. Lucherini, F. Marchetti, L. Sagramora, V. Adovasio, and M. Nardelli, *J. Chem. Soc., Dalton Trans.*, (**1990**), 179.
25. R.H. Grubbs, A. Miyashita, M. Lui, and P. Burk, *J. Am. Chem. Soc.*, (**1977**), 99, 3863.
26. P. Diversi, G. Ingrosso, A. Lucherini, and S. Murtas, *J. Chem. Soc., Dalton Trans.*, (**1980**), 1633.
27. T. Mahamo, F. Zheng, A. Sivaramakrishna, G.S. Smith, and J.R. Moss, *J. Organomet. Chem.*, (**2008**), 693, 103.
28. C.G. Biefeld, H.A. Eick, and R.H. Grubbs, *Inorg. Chem.*, (**1973**), 12, 2166.
29. (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**), 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**), submitted. (e) E.B. Hager, *MSc dissertation, University of Cape Town,* (**2007**), (f)T. Mahamo, *MSc dissertation, University of Cape Town,* (**2007**). (g) F. Zheng, A. Sivaramakrishna, and J.R. Moss, *Coord. Chem. Rev.*, (**2007**), 251, 2056.
30. (a) T.W. Graham, J. Kickham, S. Courtenay, P. Wei, and D.W Stephan, *Oragnometallics,* (**2004**), 23, 3309. (b) J.M. Manriquez, D.R. McAlister, R.D. Sanner, and J.E. Bercaw, *J. Am. Chem. Soc.*, (**1978**), 100, 2716. (c) T. Takahasi, R. Fischer, Z. Xi, K. Nakajima, *Chem. Lett.*, (**1996**), 357. (d) J.R. Hagadorn, and J. Arnold, *J. Chem. Soc., Dalton Trans.*, (**1997**), 3087.

31. W.C.P. Tsang, J.Y. Jamieson, S.L. Aeilts, K.C. Hultzsch, R.R. Schrock, and A.H. Hoveyda, *Organometallics* (**2004**), 23, 1997.

32. T.H. Warren, G. Erker, R. Fröhlic, and B. Wibbeling, *Organometallics* (**2000**), 19, 127.

33. A. Dohring, R. Emrich, R. Goddard, P.W. Jolly, and C. Kruger, *Polyhedron*, (**1993**), 12, 2671.

34. H. Nagashima., Y. Michino, K-I. Ara, T. Fukanori, and K.J. Itoh, *J. Organomet. Chem.*, (**1991**), 406, 189.

35. G.B. Young, and G.M. Whitesides, *J. Am. Chem. Soc.,* (**1978**), 1100(18), 5808.

36. A.J. Canty, H. Jin, B.W. Skelton, and A.H. White, *Inorg Chem.,* (**1998**), 37, 3975.

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

38. M.L. Steigerwald, and W.A. Goddard III, *J. Am. Chem. Soc.,* (**1985**), 107, 5027. (b) M.L. Steigerwald, and W.A. Goddard III, *J. Am. Chem. Soc.,* (**1984**), 106, 308.

39. A. Sivaramakrishna, and J.R. Moss, (**2008**), *manuscript submitted.*

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

41. (a) K. Tsuchiya, H. Kondo, and H. Nagashima, *Organometallics,* (**2007**), 26, 1044. (b) P.T. Matsunaga, J.C. Mavropoulos, and G.L. Hillhouse, *Polyhedron*, (**1995**), 14, 175.

42. R.H. Grubbs, and A. Mayashita, *J. Am. Chem. Soc.,* (**1978**), 100, 1300.

43. (a) L. Giannini, E. Solari, C. Floriani, A. Chiesi-Villa, and C, Rizzoli, *J. Am. Chem. Soc.,* (**1998**), 120, 823. (b) L. Giannini, G. Guillmot, E. Solari, C. Floriani, N. Re, A. Chiesi-Villa, and C. Rizzoli, *J. Am. Chem. Soc.,* (**1999**), 121, 2797.

44. (a) R.R. Schrock, *J. Mol. Cat. A Chem.,* (**2004**), 213, 21. (b) R.H. Grubbs, *Handbook of olefin metathesis*, Wiley-VCH, Weinheim, Germany, (**2003**).

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

46. M.G. Thorn, J.E. Hill, S.A. Waratuke, E.S. Johnson, P.E. Fanwick, and I.P. Rothwell, *J. Am. Chem. Soc.*, (**1997**), 119, 8630

2.1 Introduction

Metal alkenyl complexes can be defined as a ligand-supported metal carbon system in which the metal is σ-bonded to an alkyl group containing at least ($m \geq 2$) two methylene units and an alkene group [1]. In this review we discuss only those complexes containing a pendant alkene group as shown in Figure 2.1

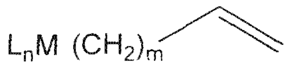


Figure 2.1 Structural representation of metal alkenyl complexes (L_nM = metal and associated ligands)

Metal alkenyl complexes are emerging as an important class of organo-transition metal complexes and have found use in organic synthesis. They have been implicated as key intermediates in Fischer-Tropsch synthesis [2], and ethylene oligomerization reactions [3].

In recent reports bis(alkenyl)-platinum, -palladium and -rhodium complexes have been employed as precursors in the synthesis of novel medium and large metallacycloalkanes [4]. Furthermore, these compounds have showed interesting reactivity patterns [5]. Our interest in this class of compounds lies chiefly in the former application as well as in exploring the chemical reactivity and properties that these previously less-studied complexes have to offer.

Herein we discuss the synthesis, chemical reactivity and applications of metal alkenyl complexes such as those in Figure 2.1, including bis(alkenyl) complexes. Compounds containing heteroatoms within the alkenyl chain and heterobimetallic complexes are not discussed.

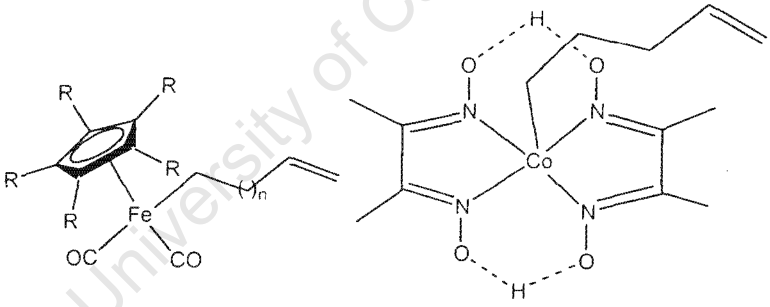
2.2 Synthesis and chemical reactivity of metal(alkenyl) complexes

2.2.1 Synthesis of mono(alkenyl) complexes

In contrast to their bis(alkenyl) analogues, the mono(alkenyl) complexes have indeed been widely prepared and studied [1]. The key synthetic routes that have been followed in preparing metal alkenyl complexes include the anion [6-8] and transmetallation [9-10] routes. Other methods such as the oxidative addition route [11,12] and preparation from dienes [13] are also known.

Anion route

Iron alkenyl complexes of type **45** (Figure 2.2) with varying alkenyl chain lengths were reported by Roustan *et al.* in 1979 and later by Mapolie and co-workers by the anion route [7,8].



45

46

n = 1,2,3, &5
R = H or Me

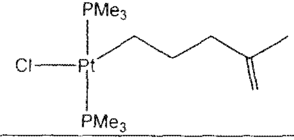
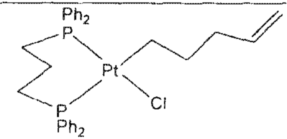
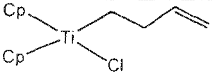
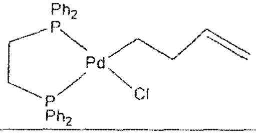
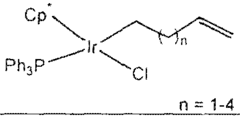
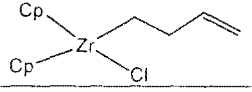
Figure 2.2 Metal(alkenyl) complexes prepared by the anion method

Furthermore, cobaloxime complexes of the type **46** (Figure 2.2) with a pentenyl ligand have also been prepared using this route [14].

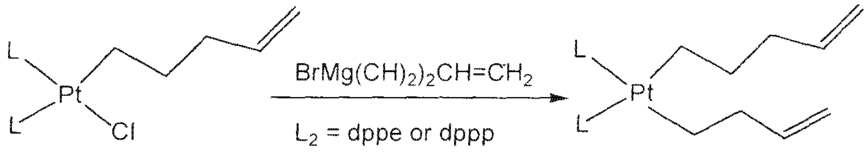
Transmetallation

As with metallacyclic complexes, the transmetallation methodology has been the most widely used route in the preparation of metal alkenyl complexes [1]. The preparation of mono(alkenyl) metal complexes in particular, has been achieved by either treating a metal dihalide with 2 molar equivalents of the appropriate alkenyl Grignard reagent to give the bis(alkenyl) compound, and subsequent cleavage of one of the metal-carbon bonds with HCl to afford the mono(alkenyl) compound, or by simple alkylation of the metal precursor with 1 molar equivalent of the alkenyl Grignard reagent (Table 2.1) [9,10,15].

Table 2.1 Examples of mono(alkenyl) complexes prepared using different methods.

Examples	Method of preparation	Reference
	Alkylation with 2 molar equivalents, then cleavage of one alkenyl chain	9
	Alkylation with 2 molar equivalents, then cleavage of one alkenyl chain or alkylation with 1 molar equivalent	1,15a
	Alkylation with 2 molar equivalents, then cleavage of one alkenyl chain	10
	Alkylation with 1 molar equivalent	15
	Alkylation with 1 molar equivalent	1
	Alkylation with 1 molar equivalent	16

The latter method has been used in the preparation of novel asymmetric bis(alkenyl)platinum(II) complexes of type **47**, which can be obtained by alkylation of platinum mono(alkenyl) compounds (eq. 2.1) [15a].

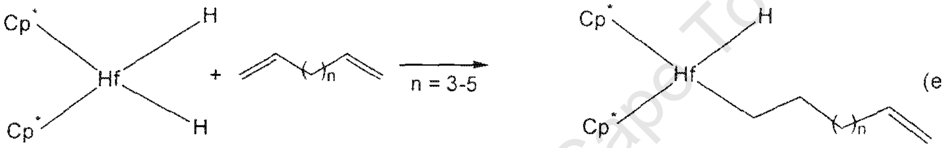


(eq. 2.1)

47

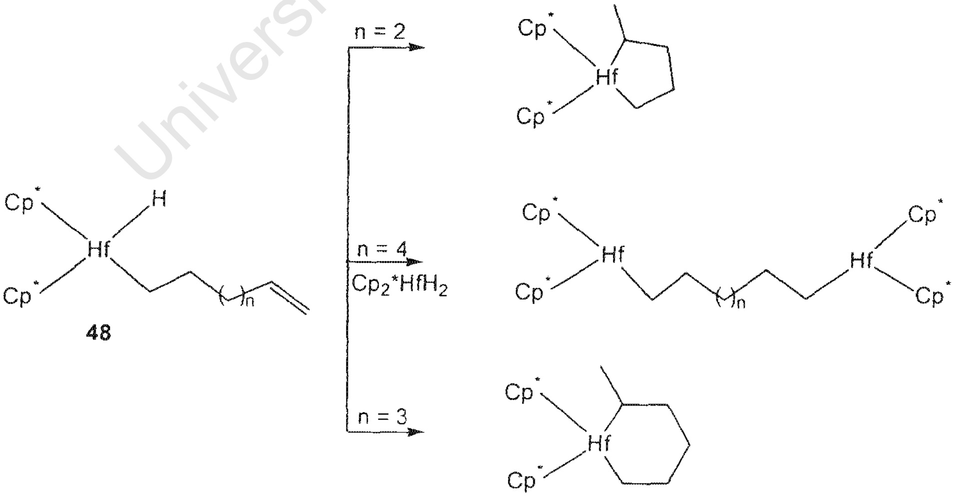
Other methods

Synthesis of hafnium alkenyl hydride complexes **48** (eq. 2.2) was achieved by the reaction of $[Cp_2{}^*HfH_2]$ with α,ω-dienes. These complexes were observed spectroscopically at low temperatures but were not isolated. Upon warming to 20°C the hafnium alkenyl hydrides form a mixture of hafnacycles and binuclear alkanediyl complexes (Scheme 2.1) [13].



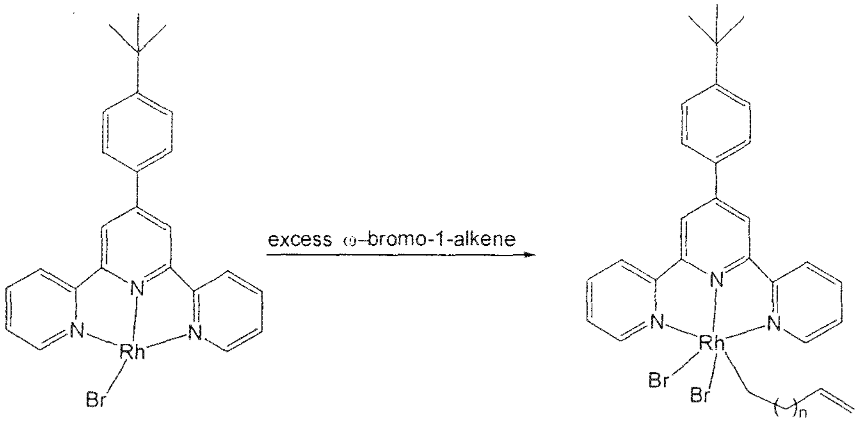
(eq. 2.2)

48



Scheme 2.1 Rearrangement of hafnium(alkenyl) complexes at 20°C and room temp. over 4 days

Frühauf and co-workers have recently reported the synthesis of rhodium alkenyl complexes **49**-**53** in quantitative yields, by the oxidative addition of the corresponding ω-bromo-1-alkene to [RhBr(Tpy*)] (Tpy* = 4'-(4-tert-butylphenyl)-2,2':6',2"-terpyridine) (eq. 2.3) [17].



(eq. 2.3)

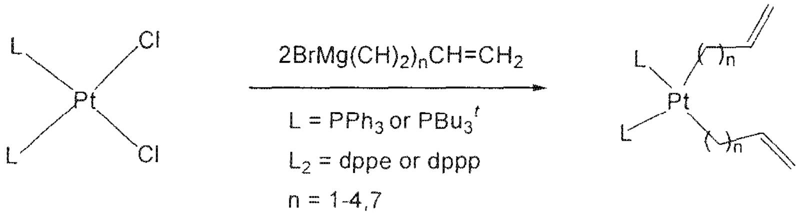
49, n = 2
50, n = 3
51, n = 4
52, n = 6
53, n = 9

2.2.2 Synthesis of bis(alkenyl) complexes

Bis(alkenyl) complexes have been prepared exclusively by the transmetallation method [1]. Using this methodology, Mo [11,12], Pt [18] and Zr [16] bis(alkenyl) complexes have been obtained.

In addition, various bis(alkenyl) platinum(II) complexes with tertiary phosphine and diphosphine ligands have been synthesized using this protocol (eq. 2.4) [4].

The dppe and dppp containing bis(alkenyl) complexes were obtained as stable crystalline solids. X-ray crystal structures of some of these complexes have been determined [4a,b].



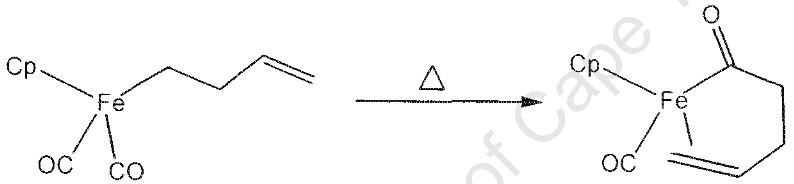
(eq. 2.4)

2.2.3 Chemical reactivity of metal(alkenyl) complexes

As well as reaction at the metal-carbon bond, which can occur for metal alkyl complexes, metal alkenyl complexes also have the added possibility of reaction at the pendant alkene functionality. For example, the hydrogenation and hydroformylation of the pendant C=C bond of [Cp*Fe(CO)$_2${(CH$_2$)$_n$CH=CH$_2$}] (n = 2-4) has been reported [8].

Carbonylation

Metal alkenyl complexes have shown reactivity at the metal-carbon bond by CO insertion [1]. The iron butenyl complex **54** has been observed to react with [TiCl$_4$] to undergo carbonyl insertion to afford the acyl complex **55** (eq. 2.5) [8].



54 **55**

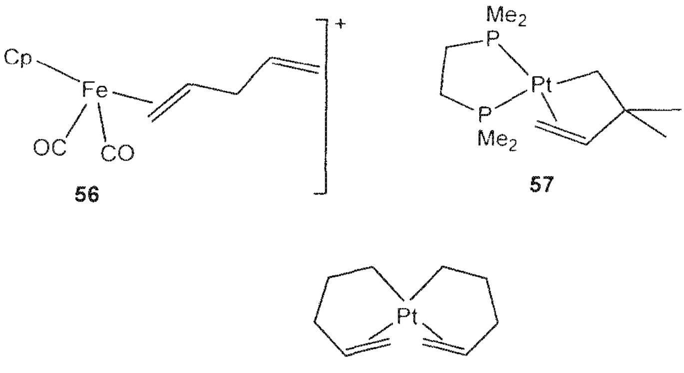
(eq. 2.5)

Interaction with electrophilic reagents

Like the metallacycloalkanes, metal alkenyl complexes also undergo cleavage by electrophilic reagents such as acids (e.g HCl) and halogens (e.g Br$_2$) to give the corresponding hydrocarbons or haloalkanes *via* cleavage of metal-carbon bonds [1].

Formation of metal olefin bonds and rearrangement

Formation of metal olefin complexes in which the olefin is coordinated to the metal in a η^1,η^2-fashion has been achieved using metal alkenyl complexes of Fe (**55** and **56**) and Pt (**57**) (Figure 2.3), through reaction with either trityl salt [Ph$_3$CBF$_4$] [19], silver salt [AgBF$_4$] [9] or Lewis acid [TiCl$_4$] [8]. In addition metal bis(olefin) complexes of type **58** have been reported by Tagge *et al.* [18a], by the loss of (COD) from [Pt(COD){$(CH_2)_3CH=CH_2$}$_2$].

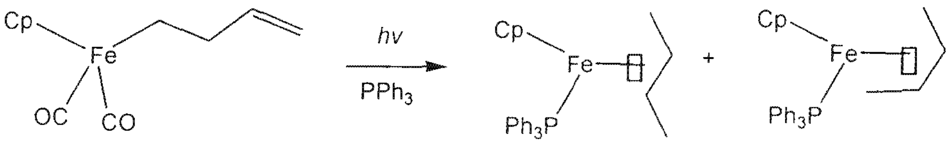


58

Figure 2.3 Experimentally observed metal olefin complexes obtained from metal alkenyl complexes

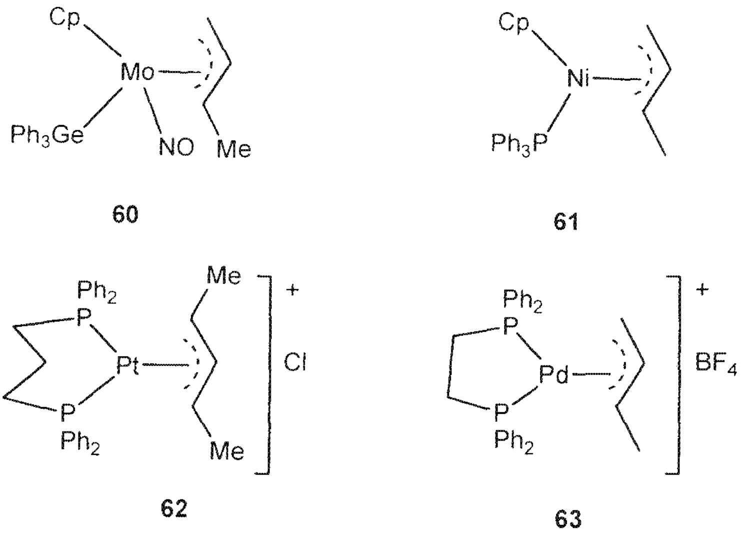
The rearrangement of metal(alkenyl) complexes to form π-allyl complexes is known for Fe [8], Pd [9], Pt [4], Ni [20], Mo [11], Ir and Rh [4] (Figure 2.4). Rearrangement in these complexes is often promoted by irradiation or heat [8,11,20]. However, experimental conditions may also induce the formation of η^3-allylic complexes [1,4]. For example, iron complexes **59a** and **59b** were obtained from irradiation of iron butenyl complexes in the presence of PPh_3 **54** (eq. 2.6) [8].

Similarly, molybdenum and nickel complexes **60** and **61** can be formed by simply irradiating or heating the corresponding metal butenyl complexes [11,20].



(eq. 2.6)

54 **59a** **59b**



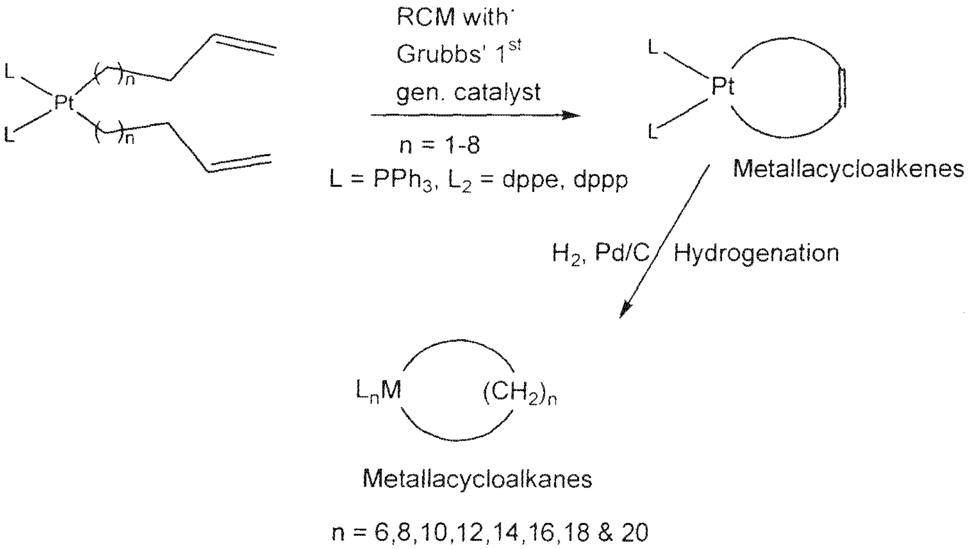
60 **61** **62** **63**

Figure 2.4 π-Allylic complexes obtained from metal alkenyl complexes

On the other hand, complex **62** was prepared by treatment of [Pt(dppp)Cl_2] with 1 molar equivalent of the 5-pentenyl Grignard reagent in diethyl ether. The subsequent mono(alkenyl) platinum complex undergoes irreversible rearrangement to give the η^3-1,3-dimethylallyl cationic complex **62** [1,4]. Reagents such as [$AgBF_4$] have also been employed in the preparation of cationic η^3-1-methylallyl complex **63** [9].

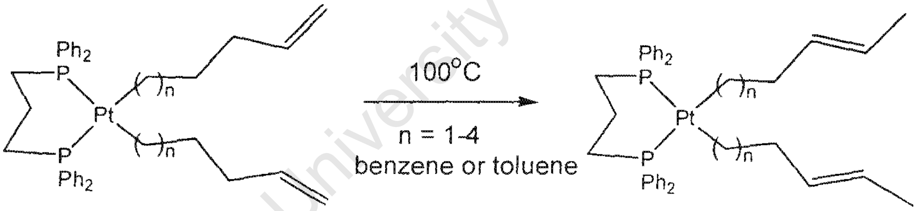
Ring-closing metathesis and isomerization

Our research group has shown that bis(alkenyl) platinum complexes undergo ring-closing metathesis (RCM) with Grubbs' 1st generation catalyst to yield platinacycloalkenes in good yields. Using this synthetic procedure we have successfully converted a range of bis(alkenyl)platinum(II) complexes to the corresponding platinacycloalkenes and further hydrogenated them to form platinacycloalkanes (Scheme 2.2) [4]. Other metals such as Pd, Rh and Ir have also been investigated in this regard [4].



Scheme 2.2 Platinacycles prepared from bis(alkenyl)platinum(II) complexes

More recently, quantitative isomerization of these bis(alkenyl) complexes to give a mixture of isomers of the corresponding internal alkene complexes was reported (eq. 2.7) [5a]. In these reactions no organic products of β-hydride elimination or reductive elimination were observed.



(eq. 2.7)

Oxidative addition reactions with methyl iodide to these bis(alkenyl)platinum(II) complexes have also been documented [1].

Thermal decomposition

The thermal stability of metal alkenyl complexes depends largely on the solvent system; thus halogenated solvents readily cleave the metal-carbon bond to form metal halides [5].

Though their thermal decomposition pathways may be similar to those of metallacycles and metal alkyl complexes (Figure 2.5), the products formed in the case of metal alkenyl complexes differ considerably due to the pendant alkene functionality [16,18,21].

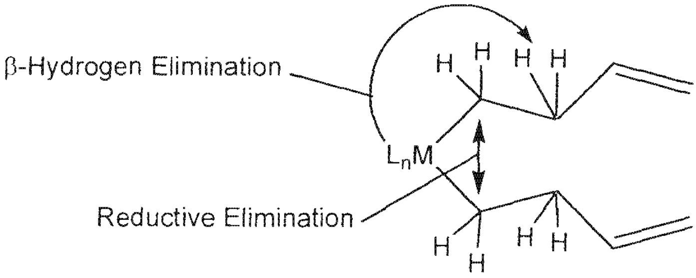


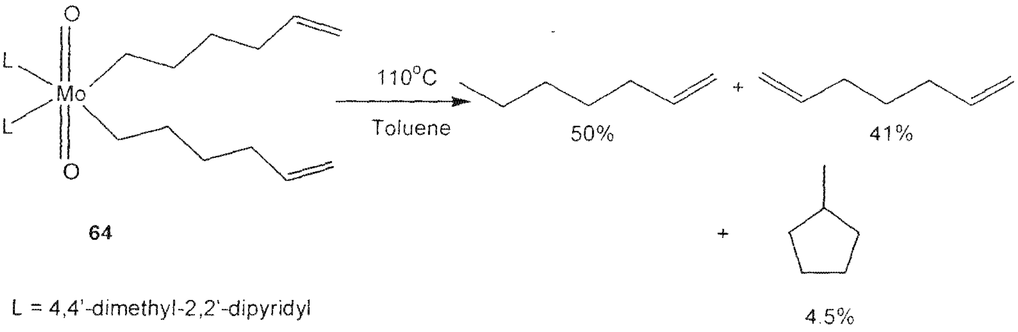
Figure 2.5 Possible decomposition pathways for metal alkenyl complexes (L_nM = metal and associated ligands)

Experiments have shown that the organic products formed upon thermolysis of bis(alkenyl)platinum(II) complexes at 150 to 250°C depend on the supporting ligands. Certainly, this relates to the stability and reactivity of these compounds in solution.

The triphenylphosphine complexes $[Pt(PPh_3)_2\{(CH_2)_nCH{=}CH_2\}_2]$ (n = 3 or 5) give an intense red colour upon decomposition; this is believed to be due to $Pt_n(PPh_3)_m$ clusters. In contrast, the compounds with diphosphine supporting ligands were stable up to 100°C [21].

The majority of products obtained contained mixtures of 1- and 2-alkenes, dienes and cycloalkanes. Product distributions depended on heating time and the medium in which the thermolysis reaction was carried out, whether in solid state or in solution [21].

The anaerobic thermal decomposition of molybdenum(IV) dioxo bis(alkenyl) complex **64** (eq. 2.8) also gave a mixture of 1-alkenes, dienes and cycloalkanes as products [16], while *cis*-bis(η^1,η^2-pent-4-ene-1-yl)platinum(II) **58** (in Figure 2.3) gave C_5 products by β-hydride elimination exclusively [18].



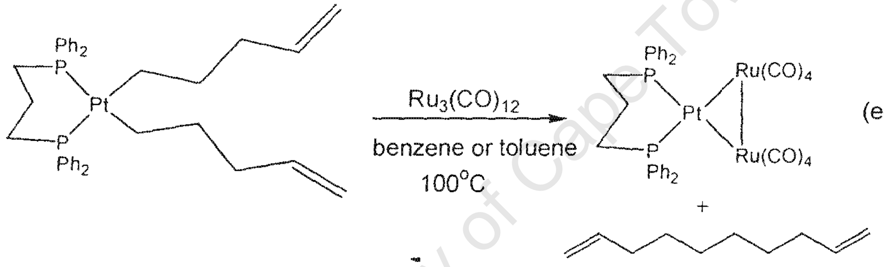
64

L = 4,4'-dimethyl-2,2'-dipyridyl

(eq. 2.8)

Other reactions

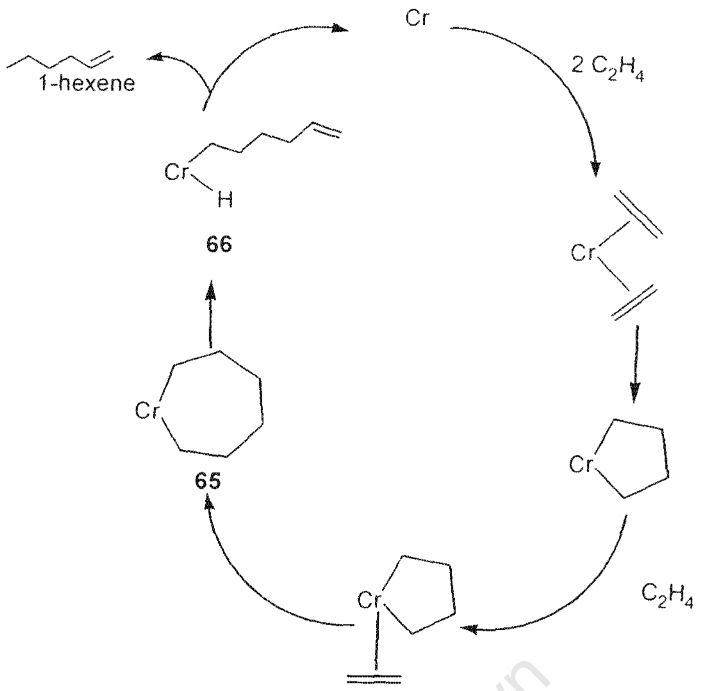
A high yielding synthetic route for the trinuclear cluster [Pt(dppp){$Ru_2(CO)_8$}] from the reaction of bis(pentenyl)platinum(II) with [$Ru_3(CO)_{12}$] has been developed (eq. 2.9). The mechanism through which this reaction proceeds is currently being investigated [5b].



(eq. 2.9)

2.3 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 chromacycloheptane **65** (Scheme 2.3), which undergoes β-hydride elimination to generate the chromium-hexenyl hydride **66**. Reductive elimination of intermediate **66** produces 1-hexene as well as the active catalytic species [22].



Scheme 2.3 Mechanism for chromium-catalyzed ethylene trimerization
Ligands omitted for clarity

Recently a chromium catalyst for selective tetramerization of ethylene to 1-octene was developed. The authors proposed that an intermediate chromacyclononane was involved in this reaction. This chromacyclononane decomposes to the respective chromium-octenyl hydride intermediate prior to reductive elimination to give 1-octene [22c].

Zirconocene mono- and bis(alkenyl) complexes have been applied as catalyst precursors in alkene polymerization [16]. Furthermore, bis(alkenyl) complexes have been used as precursors for the preparation of thin metal films [18,23] by the chemical vapour deposition method (CVD) [24].

2.4 Concluding Remarks

Metal alkenyl complexes are clearly an important class of organo-transition metal compounds because they can model intermediates in ethylene oligomerization reactions and are useful precursors in the preparation of metallacycles.

These complexes can be prepared using several methods including the anion and transmetallation routes.

The pendant alkene functionality in these compounds provides additional reaction opportunities such as isomerization and rearrangement, which are not seen in metal alkyl complexes.

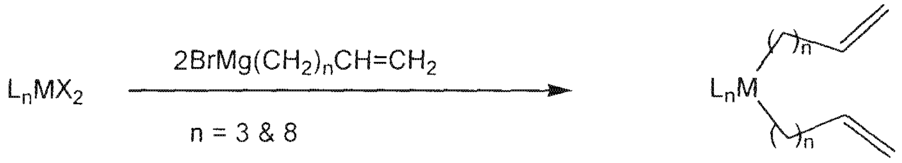
Much of the work on metal alkenyl complexes has been dominated by the mono(alkenyl) complexes and thus less was known about their related bis(alkenyl) complexes until recently.

The use of bis(alkenyl) complexes in the preparation of large ring-size metallacycloalkenes and metallacycloalkanes has presented the opportunity to prepare these complexes with various metals, including Pt, Pd, Rh and Ir. Investigations into their reactivity patterns should display some interesting chemistry and provide information regarding the nature and behaviour of these compounds. This information can be useful in improving the catalytic reactions in which they are involved.

In this project, novel osmium and platinum bis(alkenyl) complexes were prepared and employed as precursors for the preparation of metallacycles.

2.5 Approach for the preparation of bis(alkenyl) complexes

A series of bis(alkenyl)osmium(II) complexes with various ligand systems and some bis(alkenyl)platinum(II) complexes will be prepared by the transmetallation method (Scheme 2.4) (Chapter 3 and 4).



L_nMX_2 = (dppp)$PtCl_2$, Cym(L)$OsBr_2$ and (C_6Me_6)L$OsBr_2$
L = CO, $P(OPh)_3$, $PMePh_2$, $P(OMe)_3$, $P(OBu)_3$, PEt_3 and PPh_3
Cym = *p*-cymene

Scheme 2.4 Method used for preparation of bis(alkenyl) complexes in this project

2.6 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. (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**), 3865. (c) T. Mahamo, F. Zheng, A. Sivaramakrishna, G.S. Smith, and J.R. Moss, *J. Organomet. Chem.*, (**2008**), 693, 103. (d) E.B. Hager *MSc dissertation*, *University of Cape Town*, (**2007**).
5. (a) A. Sivaramkrishna, H. Su, and J.R. Moss, *Organometallics*, (**2007**), 26, 5786. (b) A. Sivaramkrishna, H.S. Clayton, B.C.E. Makhubela, and J.R. Moss, *Coord. Chem. Rev.*, (**2008**), 252, 1460.
6. M.L.H. Green, and M.J. Smith *J. Chem. Soc. A*, (**1971**), 3220.
7. J.L. Roustan, J.Y. Mérour, C. Charrier, J. Benaim, and P. Cadoit, *J. Organomet. Chem.*, (**1979**), 168, 61.
8. (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.
9. (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, 6076.
10. (a) H. Lehmkuhl, Y.L. Tsien, E. Janssen, and R. Mynott, *Chem. Ber.*, (**1983**), 116, 2426. (b) H. Lehmkhul. J. Grundke, R. Mynott, *Chem. Ber.*, (**1983**), 116, 176.
11. F. Carré, E. Colomer, R.J.P. Corriu, and A. Vioux, *Organometallics*, (**1984**), 3, 970.
12. J.Y. Mérour, C. Charrier, J. Benaim, J.L. Roustan, and D. Commereue, *J. Organomet. Chem.*, (**1979**), 39, 321.
13. J.E. Bercaw, and J.R. Moss, *Organometallics*, (**1992**), 11, 639.

14. (a) M.R. Ashcroft, A. Bury, C.J. Cooksey, A.G. Davies, B.D. Gupta, M.D. Johnson, and H. Morris, *J. Organomet. Chem.*, (**1980**), 195, 89. (b) T. Yamada, and Y. Ohashi, *Bull. Chem. Soc. Jpn.*, (**1998**), 71, 2527.

15. (a) A. Sivaramakrishna, H. Su, and J.R. Moss, *Dalton Trans.*, (**2008**) 17, 2228. (b) P. Barabotti, P. Diversi, G. Ingrosso, A. Lucherini, and F. Nutti, *J. Chem. Soc. Dalton Trans.*, (1984), 2517.

16. (a) W.M. Vetter, and A. Sen, *Organometallics*, (**1991**), 10, 244. (b) C.E. Denner, and H.G. Alt, *J. Appl. Polym. Sci.*, (**2003**), 89, 3379.

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

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

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

20. J.M. Brown, and K. Mertis, *J. Chem. Soc. Perkin Trans.*, (**1973**), 1993.

21. F. Zheng, *MSc dissertation*, (**2007**).

22. (a) T. Agapie, S.J. Schofer, J.A. Labinger, and J.E. Bercaw, *J. Am. Cherm. 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) M.J. Overett, K. Blann, A. Bollmann, J.T. Dixon, D. Haasbroek, E. Killian, H. Maumela, D.S. McGuinness, and D.H. Morgan, *J. Am. Chem. Soc.*, (**2005**), 127, 10723. (d) 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.

23. S.M.A. Shibli, and M.J. Noel, *J. Power Sources*, (**1993**), 45, 139.

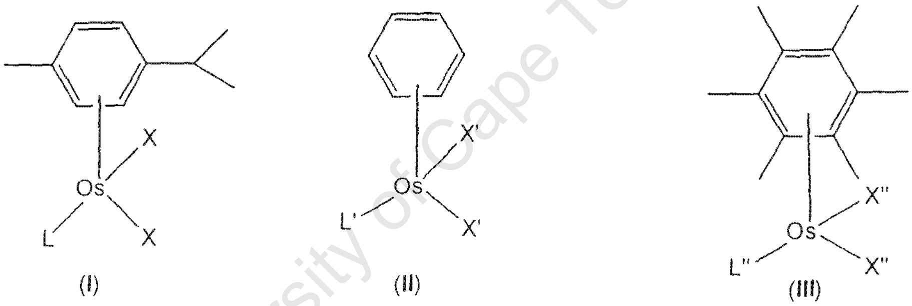
24. (a) D.C. Bradley, *Polyhedron*, (**1994**), 13, 1111. (b) R.J. Puddephatt, *Polyhedron*, (**1994**), 13, 1233.

Chapter 3: Synthesis and Characterization of Osmium dibromide precursors, Osmium bis(alkenyl) complexes and Osmacycloalkanes

3.1 Introduction

Osmium arene complexes of the type $[(\eta^6\text{-Ar})OsX_2]_2$ (Ar = *p*-cymene, C_6Me_6, C_6H_6, X = Cl^- and I^-) are well known and have been synthesized mainly from OsO_4 and $OsCl_3.3H_2O$ starting materials [1].

These dinuclear halide-bridging complexes have been employed in the preparation of mononuclear dihalide complexes of the series (**I**)-(**III**) (Figure 3.1), by cleavage of the two halide bridges with nitrogen, phosphorus and even carbon donor ligands, such as benzonitrile, pyridine, triphenylphosphine trimethylphosphite and carbon monoxide [1,2].



(I)

(II)

(III)

L = C_5H_5N, PMe_3, P^nBu_3, PCy_3, P^iPr_3, $PMePh_2$, $P(m\text{-tolyl})_3$, $P(OMe)_3$, $P(OEt)_3$, $P(OBu^n)_3$, $P(OPh)_3$
X = Cl^-, Br^- and I^-

L' = C_5H_5N, NCPh, PCy_3, PPh_3
X' = Cl^- and I^-

L'' = CO, PMe_3
X'' = Cl^-

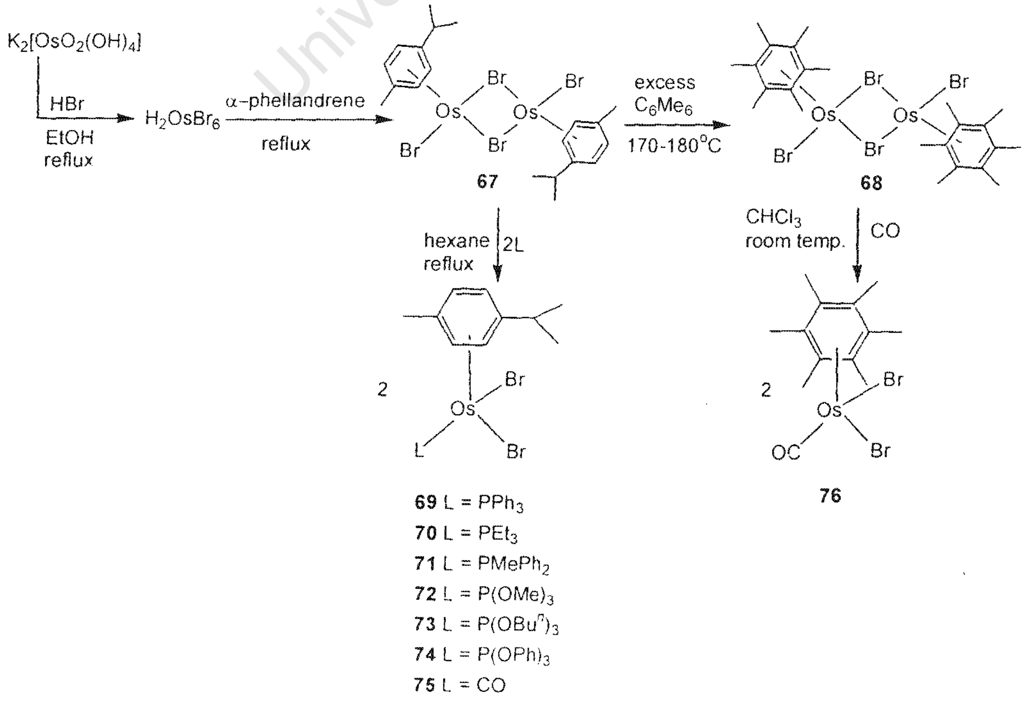
Figure 3.1 Series of known osmium arene complexes

Early work on the synthesis and properties of osmium complexes of the type $[(\eta^6\text{-Ar})OsLX_2]$ (Ar = *p*-cymene, C_6Me_6, C_6H_6, X = Cl^- and I^- and L = P or N donor ligands) was carried out by Taube [1a], Stephenson [2a] and later Maitlis [1c], as well as Werner and Zenkert. [1d]. These osmium dihalide systems have displayed interesting alkane activation behaviour [1]. It has also been demonstrated that these complexes can act as active precatalysts for organic transformations such as cyclopropanation of olefins and ring-opening metathesis polymerization [2b-d].

Osmium dihalide complexes of this type also have the potential to act as precursors in the synthesis of osmium di-alkyl complexes [1,3].
We have exploited the latter property of some osmium dibromide complexes in the preparation of osmium bis(alkenyl) complexes and osmacycloalkanes (Sections 3.4 and 3.5).

3.2 Synthesis of osmium arene precursors

The dimer $[(Cym)OsBr_2]_2$ **67** (Cym = *p*-cymene) was obtained by refluxing potassium osmate, $K_2[OsO_2(OH)_4]$, in aqueous ethanol and concentrated HBr for 18 hours followed by addition of the *p*-cymene ligand and refluxing for another 18 hours, as outlined in Scheme 3.1 [1g]. The complex was isolated in 27% yield as a red-brown stable solid which was also found to be stable in solution, including chlorinated solvents. Syntheses of the chloride and iodide analogues of this complex have been reported in good yields of 97% and 85% using OsO_4 and $OsCl_3.3H_2O$ as starting materials respectively [1a-f]. Attempts to improve the yields in our synthesis by using a large excess of the *p*-cymene ligand or by refluxing for longer periods were not successful as this lead to decomposition of the product.



Scheme 3.1 Outline for the synthesis of osmium dihalide complexes and their precursors

A series of osmium arene dibromide complexes **69**-**74** with tertiary phosphine and phosphite ligands was prepared by refluxing a suspension of the dimeric compound **67** in *n*-hexane with 2 equivalents of the appropriate ligand over 4 hours (Scheme 3.1). These complexes were obtained as stable red-orange to orange and bright orange solids in good yields ranging from 73-92%. Furthermore, complexes **69**-**74** were found to be stable in solution including chlorinated solvents, with compound **69** showing remarkable stability in chloroform on bench top for 2 weeks and thereafter decomposing to a brown unidentified species.

Complexes of the type [(Cym)OsLX_2] (where L = CO, P or N donor ligands and X = Cl and I) are well known in the literature [1-4]. Only one example of the complex containing Br was found, i.e. [(Cym)Os(PMe_3)Br_2], which was prepared by metathesis of the chlorides in [(Cym)Os(PMe_3)Cl_2] with NaBr [4a]. All other reports found described dichloride and di-iodide complexes [1,2,4]. Thus, to the best of our knowledge complexes **69**-**76** and their precursors are all new.

Preparation of complex **68** was achieved following the protocol reported by Graham and co-workers [3b] for the chloride analogue, which involves heating compound **67** and excess of hexamethylbenzene at 170-180°C in a sealed and evacuated tube for 24 hours (Scheme 3.1). The product was isolated as a brownish air-stable solid which decomposes without melting at 280°C. A similar decomposition temperature is also found for the analogous chloride complex [3b].

Complexes **75** and **76** were formed by bubbling CO gas through a suspension of compound **67** in *n*-hexane or a solution of compound **68** in chloroform at room temperature for 45 min. Reddish-orange, highly thermally stable solids of complexes **75** and **76** were afforded in good yields of 91% and 62% respectively.

3.3 Characterization of osmium arene precursors

The dimers $[(Cym)OsBr_2]_2$ **67** and $[(\eta^6\text{-}C_6Me_6)OsBr_2]_2$ **68** were characterized by ^1H NMR and elemental analysis (Table 3.1).
These complexes were found to be highly thermally stable with complex **67** having a melting range of 246-249°C and complex **68** decomposing without melting at 280°C.

The ^1H NMR spectrum of complex **67** displayed characteristic *p*-cymene ligand chemical shifts, while a singlet at 2.25 ppm corresponding to the methyl groups of hexamethylbenzene was seen in the ^1H NMR spectrum of complex **68** (Table 3.1). The methyl signal in complex **68** was at a slightly higher field than that of the chloride analogue (1.92 ppm) [3b]. This is evidence of less electronic interaction between the large highly electronegative bromide ion and the osmium centre as opposed to when a smaller chloride ion is present.

Table 3.1 ^1H NMR data, elemental analyses and melting points of complex **67** and **68**

Complex	δ(ppm)[a] J(Hz)	assignment	C[b] %	H[b] %	m.p. (°C)
67	1.12-1.30 (m)	$CH(C\underline{H}_3)_2$	24.01(24.78)	2.82(2.89)	246-249
	2.17 (d)	$C(C\underline{H}_3)$			
	2.78 (m)	$C\underline{H}(CH_3)_2$			
	6.02 (d) J = 5.65	$C_6\underline{H}_4$			
	6.15 (d) J = 5.64	$C_6\underline{H}_4$			
68	2.25 (s)	$C(C\underline{H}_3)_6$	28.49(28.13)	3.57(3.54)	decomp. without melting at 280

[a] spectra recorded in $CDCl_3$, internal standard is tetramethylsilane (TMS)
[b] calculated values in parentheses.

The osmium dibromide complexes **69**-**76** were characterized by melting point, ^1H and ^{31}P NMR spectroscopy, elemental analysis and IR spectroscopy.

3.3.1 Melting ranges

Generally, all the complexes were found to be perfectly stable in air, and either decomposed without melting, or melted to brown unidentified species, when exposed to high temperatures.

Those complexes bearing CO ligands (**75** and **76**) were remarkably thermally stable, only decomposing to black unidentified species at and above 200°C respectively. The complexes with tertiary phosphine ligands (**60**-**71**) all showed high melting points of between 196 and 225°C. The triphenylphosphine derivative displayed the highest melting point of 223-225°C.

Phosphite containing complexes **72**-**75** proved to be the least thermally stable of the entire series, exhibiting melting points of between 85 and 177°C. Within this series, the tributylphosphite derivative had the lowest melting range of 85-87°C, while the triphenylphosphite complex had the highest melting range of 175-177°C. These differences in melting points could be due to differences in inter- molecular interactions.

In short, the melting points of this series of complexes were found to decreases in the order CO ≈ $PR_3 > P(OR)_3$.

3.3.2 NMR Spectroscopy

The ^1H NMR spectra of complexes **69**-**75** all exhibited signals characteristic of *p*-cymene ligands (^1H NMR data have been summarized in Table 3.2, pages 55-56). These signals are similar to those reported for the related dichloride and di-iodide compounds [4a], with slight shifts as a result of the different halides present. Figure 3.2 shows the ^1H NMR spectrum of complex **69** which is a typical example of the *p*-cymene ligand chemical shifts in this series of complexes.

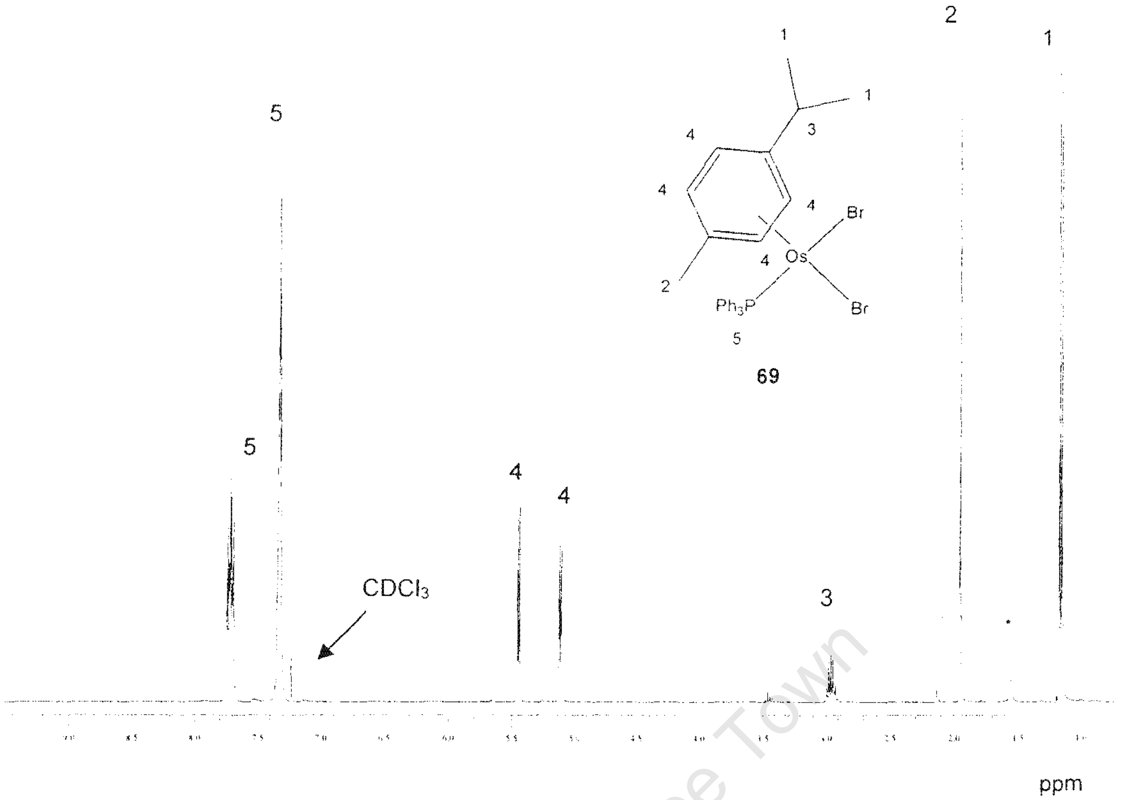


Figure 3.2 ^{1}H NMR spectrum of complex **69**. (* = H_2O impurity in $CDCl_3$)

Complex **76** showed a singlet corresponding to the methyl groups on the hexamethylbenzene in the region of 1.98 ppm, slightly more downfield than the chloride derivative (1.96 ppm). This may be due to similar reasons (i.e. different halides present) as in the dimeric starting materials [3b].

The phosphine-containing complexes **69-71** showed downfield ^{31}P NMR peaks which are characteristic of tertiary phosphine ligands coordinated to a metal center containing halide ligands [1,4]. In addition to these singlets, coupling of ^{187}Os (with 1.96% abundance)and ^{31}P was observed in the spectra resulting in the observation of satellites (Table 3.3 page 57 and Figure 3.3(a)). Similar coupling of ^{187}Os and ^{31}P has been reported for related (η^6-Arene)osmium(II) complexes (Table 3.3) [4a].

These satellite peaks were also seen in the phosphite-bearing complexes **72-74** (Table 3.3 and Figure 3.3(b)). Furthermore, the ^{31}P NMR peaks of these complexes proved to be more deshielded when compared to their phosphine counterparts (^{31}P NMR chemical shifts are summarized in Table 3.3).

This halide dependence is also observed in the $^{1}J(^{187}Os-^{31}P)$ coupling constants (Table 3.3), which increase slightly in the order I > Br > Cl.

In addition to the size and electronegativity of halides, the magnitude of coupling constants also depend on the electronegativity of the substituents on the phosphorus donor ligand [4a]. Thus when the phosphorus is attached to a electron withdrawing oxygen atom in the phosphites ($P(OR)_3$), larger $^{1}J(^{187}Os-^{31}P)$ coupling constants were seen (complexes **72-74**), as opposed to the tertiary phosphine complexes (PR_3) (Table 3.3).

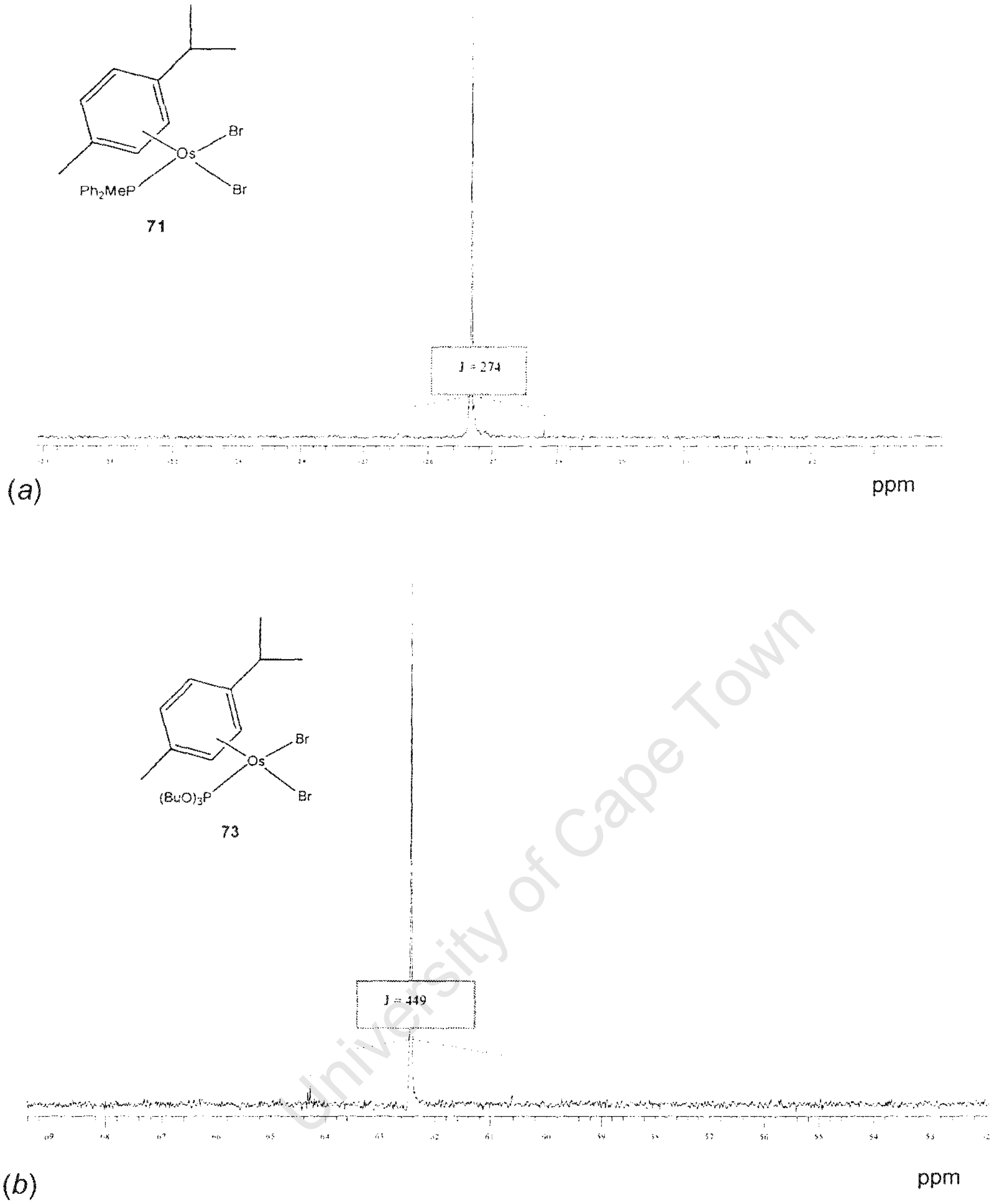


Figure 3.3 (a) ^{31}P NMR spectrum showing, $^1J(^{187}Os-^{31}P)$ coupling, of complex **71**. (b) ^{31}P NMR spectrum showing, $^1J(^{187}Os-^{31}P)$ coupling, of complex **73**.

Apart from the type of phosphorus donor ligand, the position of the ^{31}P NMR chemical shifts in complexes of the type [(Cym)OsLX$_2$] also depends on the halide present. It was observed that the complexes exhibit halide dependence, with deshielding in the order of Cl < Br< I. Thus replacement of the bromide ligands of complexes **69**-**74** with chlorides results in deshielding of the ^{31}P NMR signal. The opposite effect can be seen when the bromide ligands are replaced by iodide ligands (Table 3.3) [4a].

Table 3.2 ^{1}H NMR data for complexes **69-75**

Complex	$\delta^a\{CH(C\underline{H}_3)_2\}$	$\delta^a\{C(C\underline{H}_3)\}$	$\delta^a\{C\underline{H}(CH_3)_2\}$	$\delta^a(C_6\underline{H}_4)$	P donor ligands
69[c]	1.19(d) J^b(HH) = 6.93	1.97(s)	2.99(q) J^b(HH) = 7.04, 7.23, 7.23	5.13(d) J^b(HH) = 5.82 5.47(d) J^b(HH) = 6.93	7.30-7.82(m) PR$_3$[d]
70[c]	1.27(d) J^b(HH) = 6.86	2.28(s)	2.88(q) J^b(HH) = 7.04, 7.23, 7.23	5.55(d) J^b(HH) = 4.98 5.61(d) J^b(HH) = 5.71	1.04-1.22(m) 2.05-2.18(m) PR$_3$[e]
71[c]	1.22(d) J^b(HH) = 6.97	2.18(d) J^b(HH) = 10.68	2.89(q) J^b(HH) = 7.04, 7.23, 7.23	5.40(d) J^b(HH) = 5.75 5.49(d) J^b(HH) = 5.71	2.02-2.15(m) 7.39-7.76(m) PR$_3$[f]
72[c]	1.25(d) J^b(HH) = 6.95	2.33(d) J^b(HH) = 1.71	2.99(q) J^b(HH) = 7.04, 7.23, 7.23	5.49(d) J^b(HH) = 5.88 5.64(d) J^b(HH) = 5.93	3.58(d) J = 10.90 P(OR)$_3$[g]
73[c]	1.21(d) J^b(HH) = 6.95	2.28(s)	2.87-2.92(m)	5.43(d) J^b(HH) = 5.76	0.83-0.95(m)

[a] δ in ppm, [b] *J* in Hz, [c] Spectra recorded in CDCl$_3$ at room temp., internal standard was tetramethylsilane (TMS), [d] R = Ph, [e] R = Et, [f] R = MePh$_2$, [g] R = Me

Table 3.2 continued

Complex	$\delta^{a}\{CH(C\underline{H}_3)_2\}$	$\delta^{a}\{C(C\underline{H}_3)\}$	$\delta^{a}\{C\underline{H}(CH_3)_2\}$	$\delta^{a}(C_6\underline{H}_4)$	P donor ligands
				5.57(d) $J^{b}(HH) = 5.72$	1.36(qd) $J^{b} = 7.24, 7.24, 7.15$ 1.52-1.69(m), 3.76(dd) $J^{b} = 6.90, 13.90$ $P(OR)_3$[h]
74[c]	1.20(d) $J^{b}(HH) = 6.99$	2.23(s)	2.55-2.78(m)	5.16(d) $J^{b}(HH) = 5.92$ 5.48(d) $J^{b}(HH) = 5.92$	7.09-7.36(m) $P(OR)_3$[d]
75[c]	1.20(d) $J^{b}(HH) = 6.99$	2.13(s)	2.77(q) $J^{b}(HH) = 7.04, 7.23, 7.23$	5.14(d) $J^{b}(HH) = 5.82$ 5.47(d) $J^{b}(HH) = 5.90$	

[a] δ in ppm, [b] *J* in Hz, [c] Spectra recorded in $CDCl_3$ at room temp., internal standard was tetramethylsilane (TMS), [d] R = Ph, [h] R = Bu

Table 3.3 ^{31}P NMR data for complexes **69-75** and previously reported related complexes

Complex	$\delta^a(^{31}P)$	$^1J^b(^{187}Os-^{31}P)$
69^c	-17.57(s)	283
70^c	-28.35(s)	269
71^c	-26.68(s)	274
72^c	68.06(s)	455
73^c	62.43(s)	449
74^c	52.28(s)	476
[(*p*-Cym)Os(PPh$_3$)Cl$_2$]^d	-13.1	282
[(*p*-Cym)Os(PMePh$_2$)Cl$_2$]^d	-20.3	275
[(*p*-Cym)Os(PPh$_3$)I$_2$]^d	-23.7	285
[(*p*-Cym)Os(PMePh$_2$)I$_2$]^d	-37.6	275
[(*p*-Cym)Os{P(OMe)$_3$}Cl$_2$]^d	73.6	453
[(*p*-Cym)Os{P(OBu^n)$_3$}Cl$_2$]^d	68.0	447
[(*p*-Cym)Os{P(OPh)$_3$}Cl$_2$]^d	58.4	477

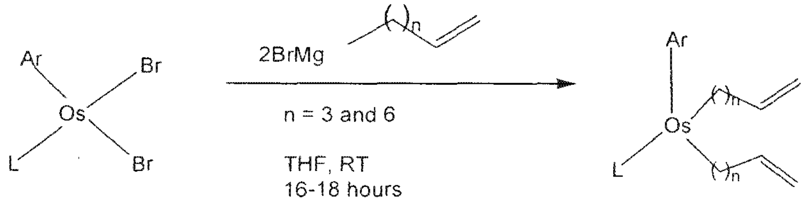
[a] δ in ppm, [b] *J* in Hz, [c] Spectra recorded in CDCl$_3$ at room temperature relative to H$_3$PO$_4$. [d] Reference = [4a].

3.3.3 IR Spectroscopy

The IR spectra of complexes **75** and **76** showed the expected band due to the terminal carbonyl ligand, ν(C≡O) at 2022 cm^{-1} and 2005 cm^{-1}, respectively.

3.4 Synthesis and Characterization of Osmium bis(alkenyl) complexes

Reactions of [(η^6-Ar)OsLBr$_2$] with alkenyl Grignard reagents in freshly dried THF at room temperature (Scheme 3.2) were carried out, with the aim of preparing bis(alkenyl) complexes of the type [(η^6-Ar)OsL{(CH$_2$)$_n$CH=CH$_2$}$_2$] (Ar = *p*-cymene or C$_6$Me$_6$, L = CO, phosphines or phosphites and n = 3 or 6).



77 L = PPh_3, n = 3 Ar = *p*-cymene
78 L = PEt_3, n = 3 Ar = *p*-cymene
79 L = $PMePh_2$, n = 3 Ar = *p*-cymene
80 L = $P(OMe)_3$, n = 3 Ar = *p*-cymene
81 L = $P(OMe)_3$, n = 6 Ar = *p*-cymene
82 L = $P(OBu^n)_3$, n = 3 Ar = *p*-cymene
83 L = $P(OPh)_3$, n = 3 Ar = *p*-cymene
84 L = CO, n = 3 Ar = *p*-cymene
85 L = CO, n = 3 Ar = C_6Me_6

Scheme 3.2 Outline of the synthesis of osmium bis(alkenyl) complexes **77**-**85**

These complexes were isolated as yellow to brown or dark brown oils. All these oils proved to be extremely unstable, even at low temperature and under an N_2 atmosphere, decomposing rapidly to black species within minutes of isolation. These bis(alkenyl) complexes were found to be even more unstable in solution.

Complexes **77**-**85** were characterized by ^1H and ^{31}P NMR spectroscopy, and IR spectroscopy only in the case of complexes **84** and **85**.
Further characterization by elemental analysis and mass spectrometry proved difficult, and was hampered by the instability of the complexes.

3.4.1 NMR Spectroscopy

In addition to the shifts corresponding to the protons of the respective tertiary phosphine or phosphite ligands, the ^1H NMR spectra of complexes **77**-**84** all displayed expected signals for the *p*-cymene ligand. Complex **85** showed a signal for the methyl groups of the hexamethylbenzene at 2.03 ppm.

The alkenyl chains of the complexes showed patterns in their ^1H NMR spectra which are common to all complexes **77**-**85**. Thus, they will be discussed collectively.

The methylene protons on the carbon atoms directly bonded to the osmium centre appeared furthest downfield as multiplets in the region of *ca.* 0.80-0.90 ppm. These multiplets integrated for four protons.

The signals corresponding to the remaining methylene protons of the alkenyl chains appeared as broad multiplets in the region of 1.00 and 2.11 ppm. These signals integrated for eight protons, except for complex **81** (where they integrated for eighteen protons) and complexes **78** and **82** (where they overlapped with PEt_3 and $P(OBu)_3$ signals, respectively).

Osmium has a shielding effect on the methylene protons α to it, therefore they resonate further downfield. This shielding effect has also been observed in similar Pt and Pd bis(alkenyl) complexes [6].

The pendant alkenyl functionality in all the complexes gave rise to distinct multiplets in the region of *ca.* 4.48 and 5.21 ppm for the protons labelled H_b and between 5.55 and 5.98 ppm for the protons labelled H_a (Figure 3.4).

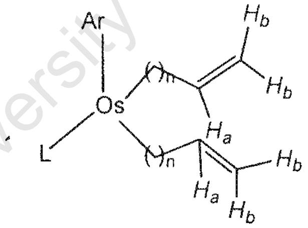


Figure 3.4 Labelling of the alkenyl protons in bis(alkenyl) complexes **77-85**.

The ^{31}P NMR spectra of the complexes bearing tertiary phosphine ligands (**77-79**) and those bearing tertiary phosphite ligands (**80-83**) all showed deshielding of the ^{31}P NMR singlets when compared to the initial precursor dibromide complexes to the bis(alkenyl) complexes. This may be a result of alkenyl ligands being weaker donor ligands than bromide ligands.

The PPh_3 derivative **77** experienced deshielding of its ^{31}P NMR signal from -17.57 ppm in complex **69** to 12.61 ppm. No $^1J(^{187}Os-^{31}P)$ coupling constants were observed in the ^{31}P NMR spectrum of complex **77**, as well as PEt_3 and

$PMePh_2$ containing complexes **78** and **79**, possibly a result of their rapid decomposition in solution.

Along with shifts to higher frequencies, bis(alkenyl) complexes **80-83** displayed an increase in $^1J(^{187}Os\text{-}^{31}P)$ coupling constants when compared to their precursor complexes (see Chapter 5). Figure 3.5 (*a*) and (*b*) below illustrates the changes in the ^{31}P NMR signal and coupling constant in complex **83**, compared to the precursor dibromide complex **74**.

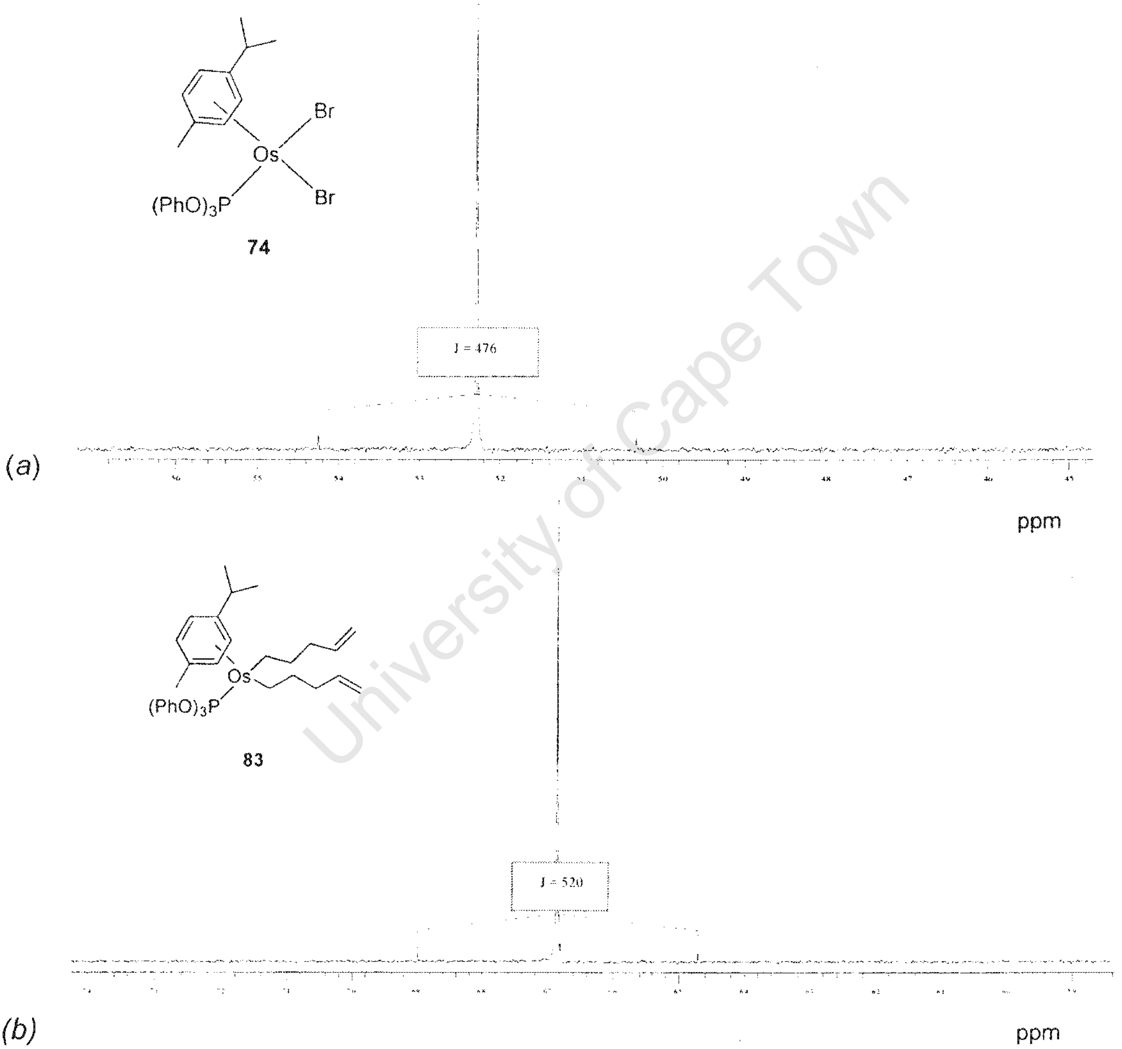


Figure 3.5 (*a*) ^{31}P NMR spectrum, showing $^1J(^{187}Os\text{-}^{31}P)$ of complex **74**. (*b*) ^{31}P NMR spectrum, showing $^1J(^{187}Os\text{-}^{31}P)$ of complex **83**.

The observation that the tertiary phosphine complexes **77-79** did not exhibit $^1J(^{187}Os\text{-}^{31}P)$ coupling constants may be a result of these complexes decomposing more rapidly in solution than their tertiary phosphite analogues.

3.4.2 IR Spectroscopy

Complexes **84** and **85** displayed strong ν(C≡O) bands at 1965 cm^{-1} and 1897 cm^{-1}, respectively, which are lower IR frequencies than those found for complexes **75** and **76**, their precursors (ν(C≡O) = 2022 cm^{-1} and 2005 cm^{-1} , respectively).

A similar ν(C≡O) band was seen for the related osmium dichlorido complex $[(C_6Me_6)Os(CO)Cl_2]$ (ν(C≡O) = 1998 cm^{-1}) and a new lower frequency band (1929 cm^{-1}) was also observed upon alkylation of this complex to form $[(C_6Me_6)Os(CO)Cy_2]$ [3a].

3.4.3 Mass Spectrometry

Complex **85** showed a peak corresponding to the parent ion (*m/z* = 519.3 $[M]^+$) in its mass spectrum (Figure 3.6). This was the only complex for which we managed to identify a parent ion in mass spectrometry results. Thus, it appears that replacing the *p*-cymene ligand in complex **84** with hexamethylbenzene does contribute to stabilization of this bis(pentenyl) complex to some extent. Complex **85** fragments by sequential loss of the pentenyl moieties (*m/z* = 451.2 $[M-C_5H_9]^+$) and (*m/z* = 383.1 $[M-(C_5H_9)_2]^+$). The spectrum also shows small amounts of impurities with higher molecular mass.

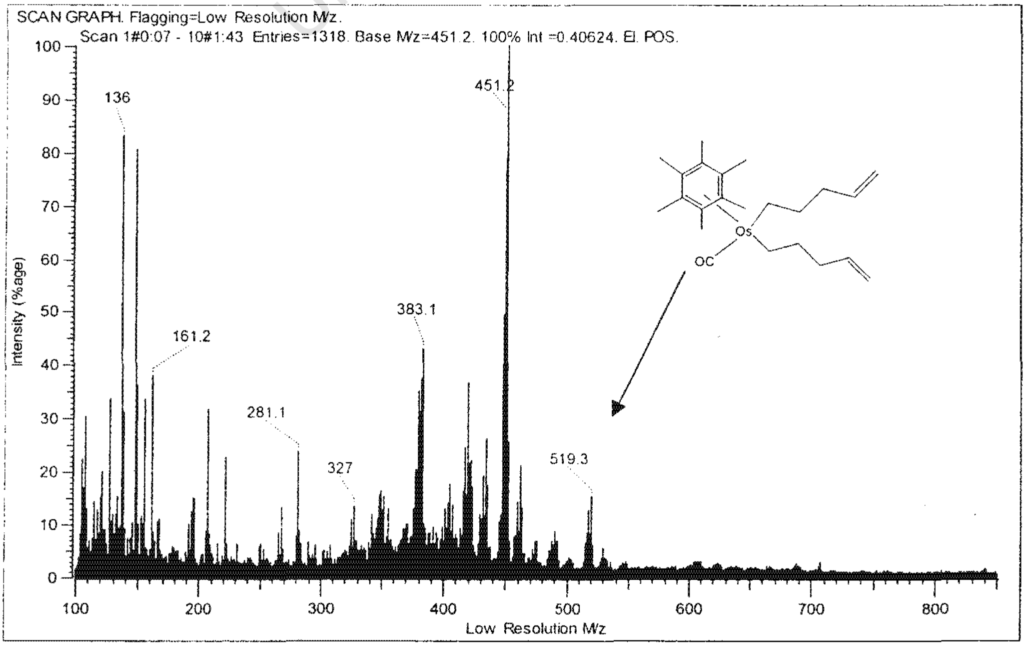


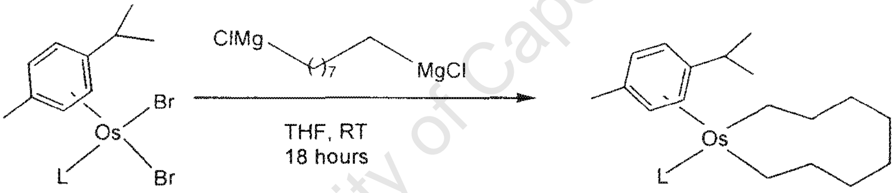
Figure 3.6 FAB mass spectrum of bis(pentenyl) complex **85**.

The bis(pentenyl) complexes **77**, **82** and **84** all decomposed at room temperature to black species and when the residues were extracted and analysed by GC, the results showed that the complexes decompose to yield 1,4-pentadiene and 1-pentene exclusively as the organic products.

Similar decomposition pathways have been reported in the thermal decomposition studies of platinum bis(alkenyl) complexes containing mono- and diphosphine ligands [7].

3.5 Synthesis and Characterization of Osmacycloalkanes

Osmacyclononanes **86-88** were prepared by transmetallation of the appropriate dibromido complexes with $ClMg(CH_2)_8MgCl$ in THF, at room temperature over 18 hours.



86 L = PEt_3
87 L = $P(OBu)_3$
88 L = CO

Scheme 3.3 Synthetic route for the preparation of osmacyclononanes **86-88**

The products **86-88** were isolated as dark yellow and brown oils or semi-solids. Similar to the bis(alkenyl) complexes, the osmacyclononanes were also extremely unstable, even at low temperature and under a N_2 atmosphere.

These complexes were characterized using only ^1H and ^{31}P NMR spectroscopy and IR spectroscopy in the case of CO-containing complex **88** and are thus not fully characterized complexes.

3.5.1 NMR Spectroscopy

^{1}H NMR spectra for the osmacyclononanes **86**-**88** displayed the expected signals due to the *p*-cymene ligand.

The protons for the methylene groups directly bonded to osmium resonated as multiplets furthest downfield. The signals ranged from 0.78 to 0.91 ppm and integrated for four protons.

The remaining methylene protons in the metallacyclic rings appeared as broad multiplets in the region of *ca.* 1.02 and 2.19 ppm and overlapped with signals due to the PEt_3 and $P(OBu)_3$ ligands in the spectra for complexes **86** and **87** respectively. The signal for the latter methylene protons in complex **88** integrated for twelve protons.

Peaks at higher frequencies (compared to the precursor dibromide complexes) in the ^{31}P NMR spectra of osmacyclononane complexes **86** and **87** were also observed, as for the bis(pentenyl) complexes **77** and **78**. This may be attributed to similar reasons mentioned in section 3.4.

Osmacyclononane complex **86** experienced a deshielding of its ^{31}P NMR signal from -28.35 ppm (in its precursor complex **70**) to -2.80 ppm and the $P(OBu)_3$ derivative **87** displayed a similar shift from 62.43 ppm (in its precursor complex **73**) to 79.59 ppm. Thus the ^{31}P NMR signals of the bis(alkenyl) **82** and the osmacyclononane **87** are virtually identical due to both complexes having Os-C bonds.

In addition to the shift to higher frequency, the osmacyclononane **87** also showed an increase in $^{1}J(^{187}Os-^{31}P)$ coupling constant from 449 to 476 Hz.

3.5.2 IR Spectroscopy

Similar to bis(pentenyl) complex **84**, a new ν(C≡O) band at lower frequency was seen in the IR spectrum of complex **88** (Figure 3.7) when compared to the dibromide complex **75**.

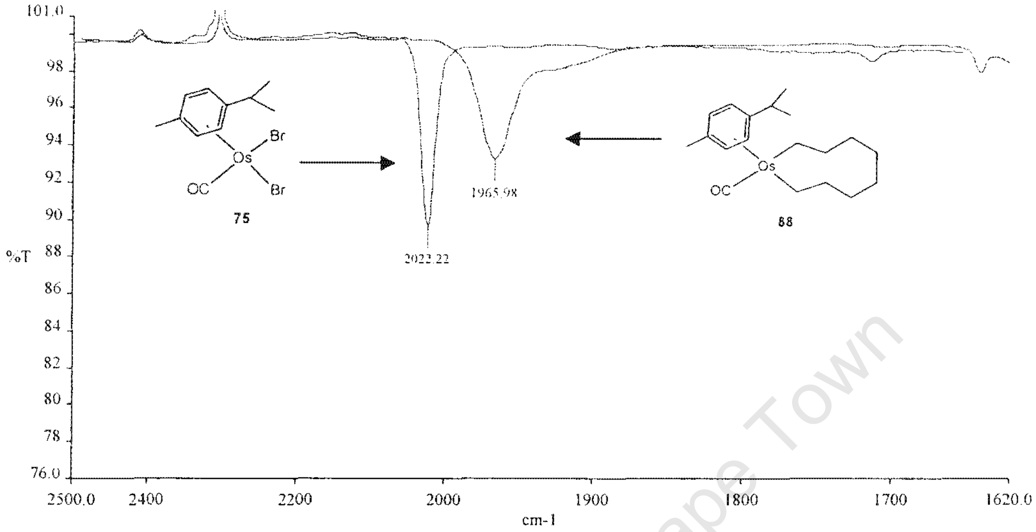


Figure 3.7 Comparison of the IR spectra of complexes **75** and **88**.

The shift of the ν(C≡O) band from a higher frequency (2022 cm^{-1}) in the dibromido starting material to lower regions in complexes **84** and **88**, may be attributed to a change in the electronegativity of the ligands on the osmium. The highly electronegative bromido ligands in complex **75** decrease electron density on the metal. This can result in less back donation to the CO ligand and hence a weaker Os-CO bond which results in a higher frequency ν(C≡O) band. On the other hand, when less electronegative carbon atoms are present as supporting ligands, more back donation to the CO ligand can be expected. This means that the Os-CO bond is stronger and this was indicated by a lower frequency ν(C≡O) band [8].

3.6 Conclusions

A series of new organo-osmium complexes of the type [(η^6-Ar)OsLBr$_2$] (Ar = *p*-cymene and C_6Me_6, L = CO, phosphines or phosphites) have been successfully prepared and characterized. They have been employed as precursors for the synthesis of osmium bis(alkenyl) complexes and osmacycloalkanes. These complexes were prepared using $K_2[OsO_2(OH)_4]$ as the starting material. The complexes were characterized by ^{1}H and ^{31}P NMR spectroscopy and elemental analysis. The characterization data that was obtained agreed well with the proposed formulations. For further characterization, mass spectrometry would be appropriate. The complexes were obtained in good to excellent yields and they proved to be fairly stable at ambient temperature and in solution.

Some osmium bis(alkenyl) complexes and osmacycloalkanes have been prepared by transmetallation of the osmium dibromido complexes with either an alkenyl Grignard reagent or a di-Grignard reagent. These complexes were obtained in good to low yields as oils, which proved to be very unstable both in and out of solution, and were thus not fully characterized. However, ^{1}H and ^{31}P NMR as well as IR data obtained for them suggest the proposed formulations. The bis(pentenyl) complexes **77**, **82** and **84** decompose at room temperature to give organic products 1-pentene and 1,4-pentadiene exclusively, as evidenced by GC analyses. This evidence is consistent with them being bis(pentenyl) complexes prior to their decomposition. More characterization data would indeed help in further confirming the formation of these complexes. The unstable nature of these complexes may be a result of the weak Os-CH_2R bonds. Due to the difficulty in handling the bis(alkenyl) complexes, preparation of osmacycles *via* the RCM route was not attempted.

3.7 References

1. (a) Y. Hung, W.-J. Kung, and H. Taube, *Inorg. Chem.,* (**1981**), 20, 457. (b) D.M. Heinekey, and T.G.P Harper, *Organometallics*, (**1991**), 10, 2891. (c) J.A. Cabeza, and P.M. Maitlis, *J. Chem. Soc., Dalton Trans.*, (**1985**), 573. (d) H. Werner, and K. Zenkert, *J. Organomet. Chem.,* (**1988**), 345, 151. (e) S Stahl, and H. Werner, *Organometallics*, (**1990**), 9, 1876. (f) H. Werner, R. Weinand, W. Knaup, K. Peters, and H.G. von Schnering, *Organometallics*, (**1991**), 10, 3967. (g) H.S. Clayton, (**2007**), *University of Cape Town, unpublished work.*
2. (a) T. Arthur, and T.A. Stephenson, *J. Organomet. Chem.,* (**1981**), 208, 369. (b) A. Demonceau, C.A. Lemoine, and A.F. Noels, *Tetrahedron Lett.*, (**1996**), 37, 1025. (c) A. Demonceau, A.W. Stumpf, E. Saive, and A.F. Noels, *Macromolecules*, (**1997**), 30, 3127. (d) A. Hafner, A. Muhlebach, and P.A. van der Schaaf, *Angew. Chem. Int. Ed.*, (**1997**), 36, 2121.
3. (a) J.R. Moss, and W.A.G. Graham, *Inorg. Chem.,* (**1977**), 16, 75. (b) W.A. Kiel, R.G. Ball, and W.A.G. Graham, *J. Organomet. Chem.,* (**1990**), 383, 481.
4. (a) A.G Bell, W. Koźmiński, A. Linden, and W. von Philipsborn, *Organometallics*, (**1996**), 15, 3124. (b) J. Huang, S. Serron, and S.P. Nolan, *Organometallics*, (**1998**), 17, 4004.
5. G.J. Perkins, M.I. Bruce, B.W. Skelton, and A.H. White, *Inorg. Chim. Acta*, (**2006**), 359, 2644.
6. (a) T. Mahamo, F. Zheng, A. Sivaramakrishna, G.S. Smith, and J.R. Moss, *J. Organomet. Chem.,* (**2008**), 693, 103. (b) A. Sivaramakrishna, H. Su, and J.R. Moss, *Angew. Chem., Int. Ed.,* (**2007**), 46, 3541.
7. F. Zheng, A. Sivaramakrishna, and J.R. Moss, *Inorg. Chim. Acta,* (**2008**), 361, 2871.
8. J.E. Ellis, and W. Beck, *Angew. Chem. Int. Ed Engl.,* (**1995**), 34, 2489.

Chapter 4: Synthesis, Characterization and Reactivity of Platinacycles

4.1 Introduction

Many platinacycloalkanes have been prepared and characterized (see Chapter 1). Recently an impressive number of stable large-ring platinacycles have been synthesized and characterized, from their bis(alkenyl)platinum(II) precursors, with up to 21-members in the ring [1].

It has been further established that these large-ring platinacycles decompose at high temperatures (>80°C) to give a mixture of organic products, including 1-alkenes, 2-alkenes, *n*-alkanes, α,ω-dienes and cycloalkanes [2].

In order to gain more knowledge regarding these complexes, we have embarked on studies of chemical reactivity on some platinacycles with elemental sulfur (S_8) and carbon monoxide (CO).
For this reason, we begin by briefly giving some background on the reactivity of transition metal complexes with CO and S_8.

4.1.1 CO insertion reactions

Carbon monoxide (CO) insertion reactions or carbonylation may be described by equation 4.1 (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. 4.1)

The first such reaction to have been observed was with methylmanganese pentacarbonyl in 1957 [4].

Ten years later Booth and Chatt [5] discovered that Pd(II), Pt(II), Ni(II) and Co(II) alkyl and aryl derivatives undergo reversible CO insertion.

Characterization techniques often employed in ascertaining the formation of metal acyl complexes include FT-IR and NMR spectroscopy. The molecular structures of some metal acyl complexes, including [MoCp(CO)$_2$(PPh$_3$)COMe] [6] and [Pd(P~N)(CH$_2$CH$_2$COMe)]OTf [7] (P~N = phosphinomethyl oxazoline), have been determined (Figure 4.1).

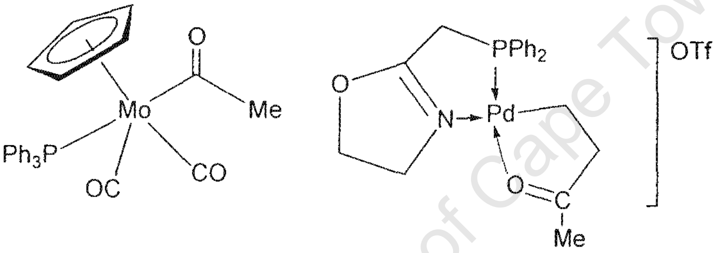
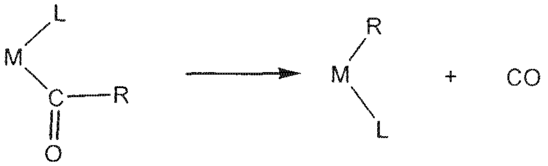


Figure 4.1 Two acyl complexes for which X-ray crystal structures have been determined

The reverse of CO insertion is termed decarbonylation and is also known (eq. 4.2) [4,5]. This process is often promoted by heating or photolysis [4].



(eq. 4.2)

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 a vast amount of information has been gathered regarding the kinetics and mechanism of CO insertion reactions [8,9].

Metallacycloalkanes containing Ti [10], Ru and Os [11], Co [12], and Pd [13] have been observed to undergo CO insertion, followed by reductive elimination to give cyclic ketones. In all these reactions no insertion of a second molecule of CO into the other metal-carbon bond of the metallacyclic ring was reported.

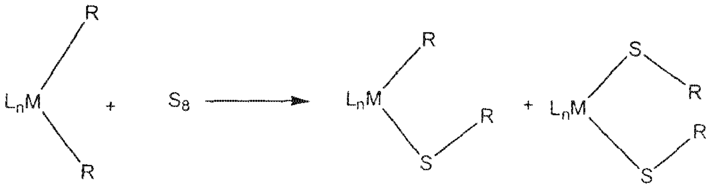
Our interest in CO insertion reactions resides in the scope they offer for the functionalization of hydrocarbons to give valuable organic compounds such as cyclic ketones (as was the case above) as well as the formation of interesting new acyl complexes upon insertion of CO.

4.1.2. Reaction of metal complexes with elemental sulfur

The reaction of organometallic complexes with elemental sulfur (S_8) has been documented in the literature [14-18].

There are two main ways in which S_8 has been seen to react with metal complexes.

In the first instance, one or two sulfur atoms can insert into the metal-carbon bonds of complexes to give metal thiolate derivatives (eq. 4.3) (where L_nM = metal and associated ligands and R = alkyl or σ-bonded carbon group)



(e.q. 4.3)

Early work by Legzdins [14] showed examples of $[(\eta^5\text{-}C_5H_5)W(NO)(CH_2SiMe_3)_2]$ reacting with S_8 to form $[(\eta^5\text{-}C_5H_5)W(NO)(SCH_2SiMe_3)(CH_2SiMe_3)]$ and $[(\eta^5\text{-}C_5H_5)W(NO)(SCH_2SiMe_3)_2]$.

Thiolate complexes are particularly useful in modeling intermediates in transition metal catalyzed biological processes. One such process is CO_2

fixation in anaerobic bacteria, mediated by a four-coordinate Ni complex containing S and N donor ligands [15].
Han and Hillhouse. [15] prepared some Ni thiolates using S_8 in order to model this biologically relevant Ni system.

In recent reports, S_8 has been seen to insert into lanthanide-carbon bonds to give lanthanide thiolate complexes, which have potential applications in catalysis and material science [16].

The second way in which S_8 can react with metal complexes is by insertion of sulfur chain fragments (S_x).
In 1970, Chatt and Mingos reported the synthesis of Pd and Pt complexes containing a chelating S_4 ligand of the type [L_2MS_4] (M = Pd or Pt and L = PPh_3 or L_2 = dppe) from the reaction of S_8 with either [$M(PPh_3)_4$] or [$M(dppe)_2$] [17]. The X-ray structure of [$dppePtS_4$] was later determined and it confirmed a 5-membered metal-tetrasulfide ring complex (Figure 4.2) [18].

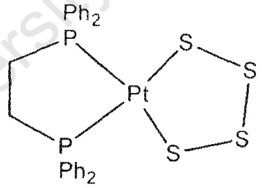
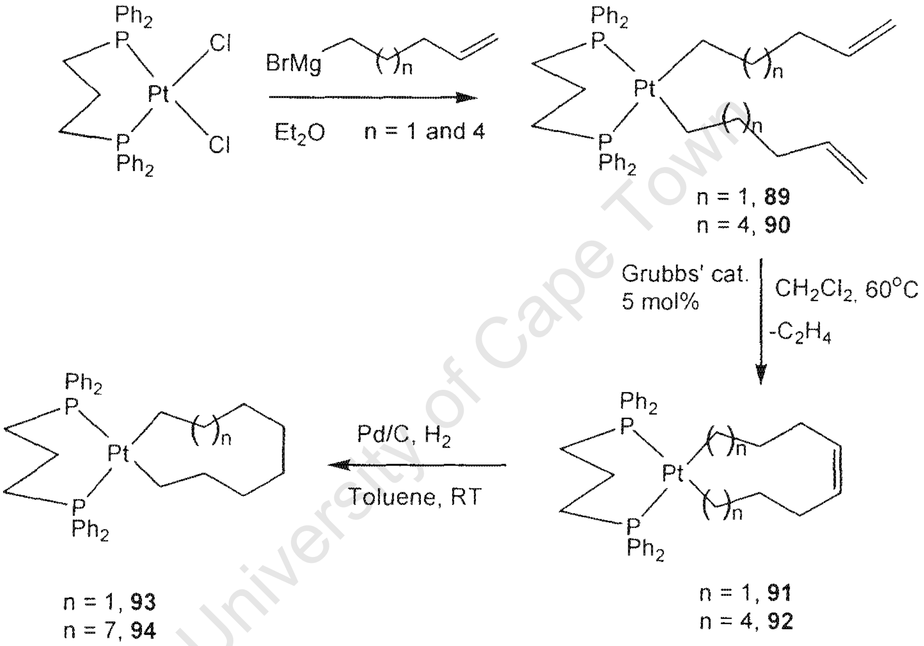


Figure 4.2 Structurally determined coordination of S_4 fragment in [$dppePtS_4$].

In section 4.3.3, we discuss the results of the reaction of a platinacycloalkane with S_8.

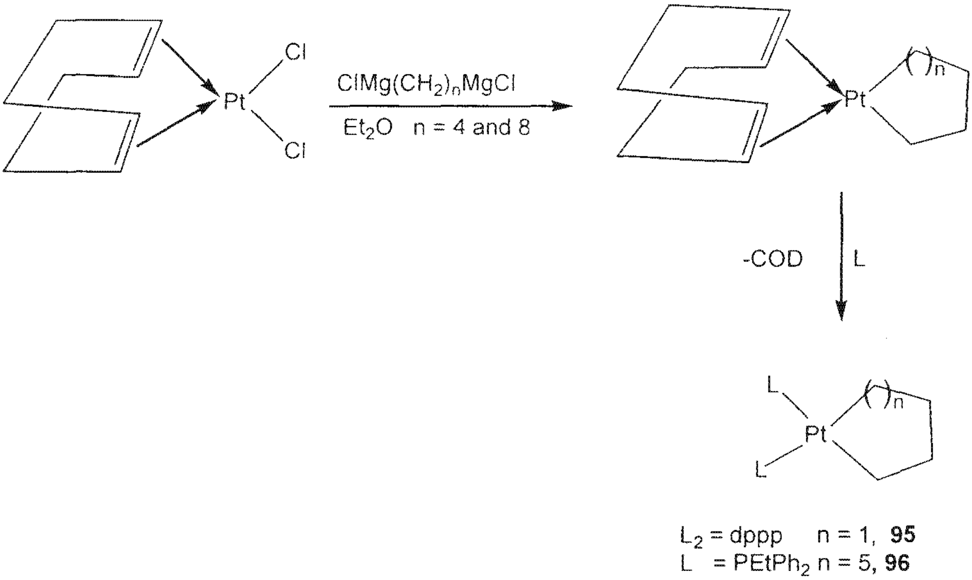
4.2 Synthesis and characterization of platinacycles and their precursors

Platinacycloalkenes **91** and **92** were prepared by the ring-closing metathesis reaction (RCM) of bis(alkenyl)platinum(II) complexes **89** and **90**, which were obtained from the transmetallation reaction of the dichloroplatinum(II) complex, [$PtCl_2$dppp], with the appropriate alkenyl Grignard reagent. These platinacycloalkenes were then hydrogenated to yield platinacycloalkanes **93** and **94** (Scheme 4.1) [1].



Scheme 4.1 Synthetic route for the preparation platinacycles **91**-**94**

Complexes **95** and **96** were prepared using the di-Grignard methodology, in which [(COD)$PtCl_2$] was treated with either $ClMg(CH_2)_8MgCl$ or $ClMg(CH_2)_4MgCl$ in dry diethyl ether, followed by displacement of the COD ligand with 2 molar equivalents of $PEtPh_2$ or 1 molar equivalent of dppp (Scheme 4.2). The new platinacyclononane **96** and platinacyclopentane **95** were obtained as light brown to colourless oils.



Scheme 4.2 Synthetic route for the preparation of platinacycles **95** and **96**

The bis(alkenyl)platinum(II) complexes **89** and **90** were obtained as white crystalline solids in yields of 80% and 62% respectively. They have been characterized by melting point, ^1H and ^{31}P NMR spectroscopy, elemental analysis, and mass spectrometry in the case of complex **90** (characterization data have been summarized in Tables 4.2-4.4, pages 79-81). 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).

4.2.1 Characterization of platinum bis(alkenyl) complexes

*X-ray crystal structure determination of $[(dppp)Pt\{(CH_2)_6CH{=}CH_2\}_2]$ complex **90***

Since no crystal structure has been previously reported on the bis(octenyl)platinum(II) complex **90**, single crystals for an X-ray study of this complex were obtained (by slow evaporation from diethyl ether) for determination of its molecular structure (Figure 4.3) [19a]. The molecular structure of complex **90** was then compared with the related bis(butenyl)platinum(II) complex (Table 4.1) [1].

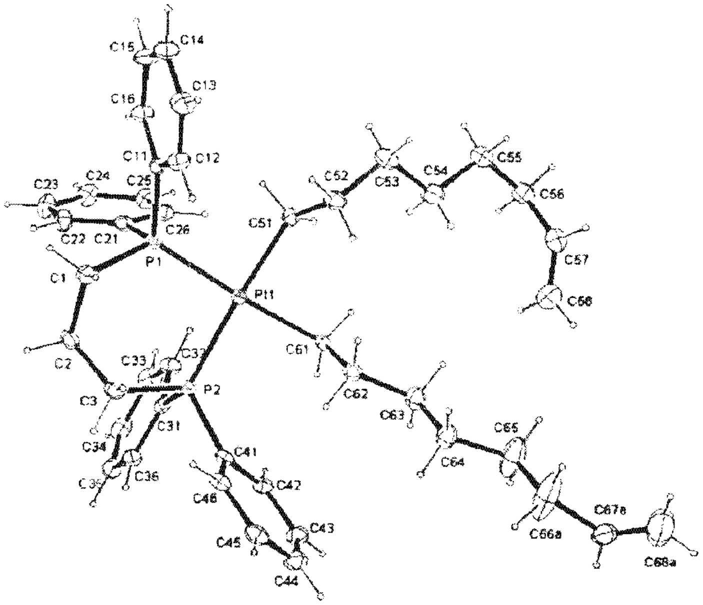


Figure 4.3 Molecular structure and atom labelling scheme for complex **90**. Displacement ellipsoids are drawn at 40% probability level and H atoms are shown as spheres of arbitrary radii. Atom C67 was displaced over two positions: C67A with Site Occupancy 0.535 and 67B with Site Occupancy 0.465. Atoms C66 and C68 also displaced over two positions.

The molecular structures of complex **90** and its bis(butenyl) counterpart are similar, as one would expect. Both complexes have a square planar geometry around their platinum centers. The two Pt-P bond lengths in complex **90** are slightly shorter than in the bis(butenyl) complex, possibly due to the different phosphine ligands present in these complexes (Table 4.1). The angles given in Table 4.1 are larger for complex **90** when compared with the PPh_3 complex, which may be due to steric crowding at the metal center. Both structures clearly reveal the presence of localized multiple bonding between the two terminal carbon atoms of each of their alkenyl chains. These have an average length of 1.251Å for complex **90** and 1.275Å for $[(PPh_3)_2Pt\{(CH_2)_2CH{=}CH_2\}_2]$. For further information regarding the bond angles and bond lengths of this structure, see reference 19a.

Table 4.1 Comparison of the X-ray crystal structures of complex **90** and a reported bis(butenyl)platinum(II) complex

	$(PPh_3)_2Pt\{(CH_2)_2CH{=}CH_2\}_2$[a]	$(dppp)Pt\{(CH_2)_6CH{=}CH_2\}_2$
$Pt_{(1)}$-$P_{(1)}$	2.300	2.2766(7)
$Pt_{(1)}$-$P_{(2)}$	2.304	2.2873(7)
$Pt_{(1)}$-$C_{(1)}$	2.127(2)	2.120(3)
$Pt_{(1)}$-$C_{(2)}$	2.095(3)	2.119(3)
Pt / \\ C C	83.07[b]	85.05[c]
Pt / \\ P P	99.65[b]	92.97[c]

[a] Reference : [1a], [b] C = C_1 and C_6, P = P_1 and P_2, [c] C = C_{51} and C_{61}, P = P_1 and P_2.

NMR Spectroscopy

^1H NMR spectra of complexes **89** and **90** both showed signals in the region of 0.88 and 1.11 ppm for the protons directly bonded to the platinum centre. The remaining methylene protons of the alkenyl chains appeared as broad multiplets in the region of 0.96 and 2.09 ppm as has been reported before for related complexes [1].

^{31}P NMR spectra of complexes **89** and **90** displayed singlets at 3.45 and 3.40 ppm with satellites corresponding to $^1J(^{195}Pt\text{-}^{31}P)$ coupling constants of 1623 and 1603 Hz respectively.

^{13}C NMR spectra for these complexes displayed singlets at 14.28 and 14.12 ppm which were assigned to the carbons directly bonded to the platinum centre (C_1) (Figure 4.4). The carbons labeled C_2-C_3 appeared as multiplets further upfield in the region of 27.63 to 34.04 ppm. Alkene carbons C_4 gave rise to singlets at 140.92 ppm for complex **89** and at 139.07 ppm in complex **90**, while the terminal carbons (C_5) resonated at 112.31 and 114.31 ppm.

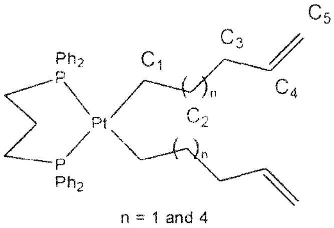


Figure 4.4 Labelling of methylene and alkene carbons in bis(alkenyl) complexes **89** and **90**.

Finally the dppp ligand gave rise to singlets in the region of *ca*. 22.0 and 25.0 ppm for its methylene carbons as well as broad multiplets at *ca*. 127.0-133.0 ppm for the carbons of the phenyl groups.

Mass Spectrometry

Complex **90** showed a parent ion at *m/z* = 829.2 $[M]^+$ (Figure 4.5), this compound displayed a fragmentation pattern involving the sequential loss of the octenyl chains, 717.5 $[M-\{(CH_2)_6CH=CH_2\}-(H)]^+$ and 606.1 $[M-2\{(CH_2)_6CH=CH_2\}-(H)]^+$.

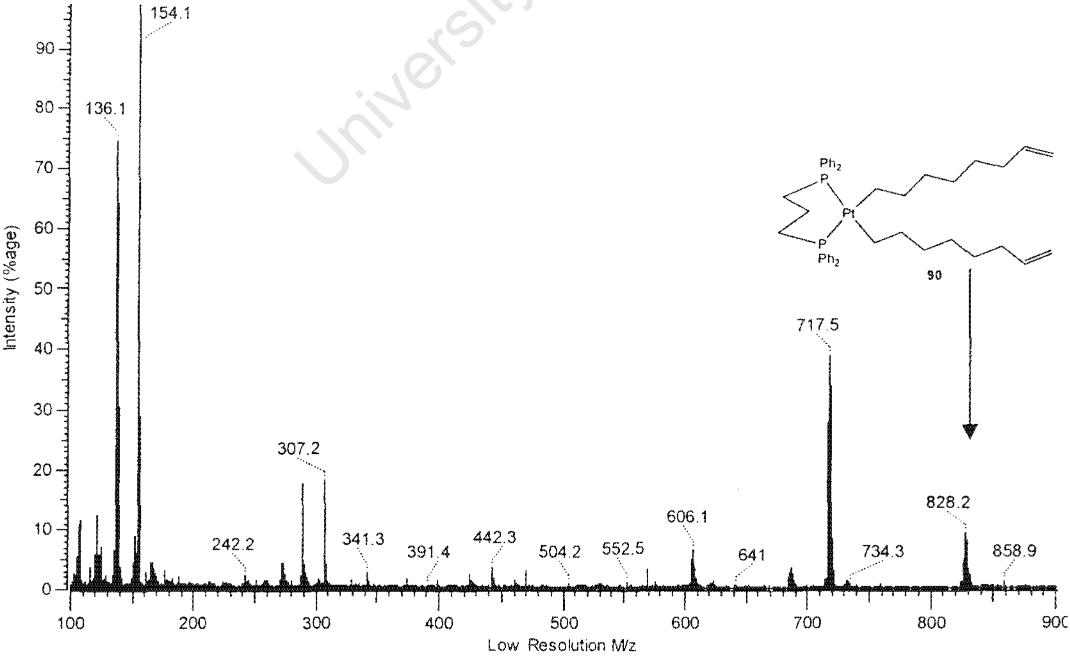


Figure 4.5 FAB mass spectrum of complex **90**.

4.2.2 Characterization of platinacycloalkenes

Platinacycloalkenes **91** and **92** were isolated as white crystalline solids in good yields of 76% and 96%, respectively. These complexes proved to be reasonably thermally stable, melting to brown unidentified oils between 161-164°C and 161-162°C, respectively. They were characterized using melting point, ^{1}H and ^{31}P NMR spectroscopy, elemental analysis, as well as mass spectrometry in the case of complex **92** (characterization data have been summarized in Tables 4.2-4.4, pages 79-81). The data obtained for these complexes agreed with the literature for the same complexes [1]. ^{13}C NMR data has been obtained for the first time for these complexes.

NMR Spectroscopy

The ^{1}H NMR spectra of complexes **91** and **92** displayed similar patterns to those observed for their precursors **89** and **90** except for the absence of resonances for the terminal alkene protons. These signals were replaced by internal alkene signals in the region between 5.15 and 5.54 ppm (Table 4.2).

^{31}P NMR spectra also displayed resonances similar to those of the starting materials (complexes **89** and **90**) in the region of *ca.* 3.0 ppm. It was interesting to see that platinacyclopentadecene **92** displayed the presence of different conformation of the metallacyclic ring, as evidenced by the presence of three signals and their corresponding platinum satellites in its ^{31}P NMR spectrum (Figure 4.6). Gibson and co-workers observed an unprecedented α-olefin distribution in their study of a chromium based homogeneous ethylene oligomerization precatalyst. They attributed this distribution to the intermediate chromacycloalkane assuming different conformations [19b].

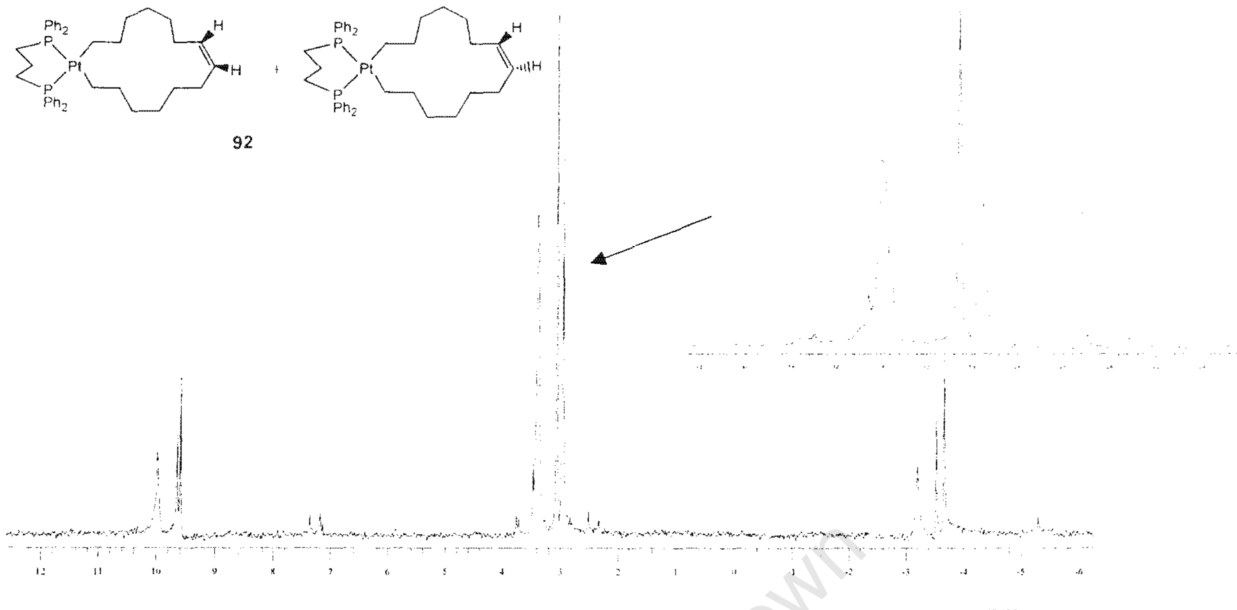


Figure 4.6 ^{31}P NMR spectrum of complex **90**

^{13}C NMR spectra for complexes **91** and **92** displayed similar patterns to their precursor complexes. The only difference was the absence of the peaks at *ca.* 112.0 and 114.0 ppm, for the terminal alkene carbons, which after the RCM reactions were expected to disappear. The internal alkene carbons resonated at 141.0 ppm for complex **91** and at 139.1 ppm for complex **92**. In all the ^{13}C NMR spectra of the platinum complexes **89-96**, no Pt-C or P-Pt-C couplings were seen; this may be partly due to the low abundance of ^{13}C.

Table 4.2 ^{1}H NMR data for complexes **89-96**

Complex	^{1}H NMR (δ ppm)[a]
89	0.96-1.11 (m, 4H) $Pt\{C\underline{H}_2(CH_2)_2CH=CH_2\}_2$; 1.09-1.31 (m, 6H) $Pt\{CH_2C\underline{H}_2CH_2CH=CH_2\}_2$ and $PCH_2C\underline{H}_2CH_2P$; 1.62 (q, 4H J = 7.02, 7.02 Hz) $Pt\{CH_2CH_2C\underline{H}_2CH=CH_2\}_2$; 2.44-2.54 (m, 4H) $PC\underline{H}_2CH_2C\underline{H}_2P$; 4.61-4.81 (m, 4H) $=C\underline{H}_2$; 5.46-5.64 (m, 2H) $C\underline{H}=$; 7.31-7.59 (m, 20H) $P\underline{\mathbf{Ph}}_2$.
90	0.88 (dd, 4H J = 12.87, 6.33 Hz) $Pt\{C\underline{H}_2(CH_2)_5CH=CH_2\}_2$; 0.93-1.05 (m, 2H) $PCH_2C\underline{H}_2CH_2P$; 1.11-1.24 (m, 12H) $Pt\{CH_2(C\underline{H}_2)_3(CH_2)_2CH=CH_2\}_2$; 1.85-1.96 (m, 4H) $Pt\{(CH_2)_4C\underline{H}_2CH_2CH=CH_2\}_2$; 2.00-2.09 (m, 4H) $Pt\{(CH_2)_5C\underline{H}_2CH=CH_2\}_2$; 2.45-2.53 (m, 4H) $PC\underline{H}_2CH_2C\underline{H}_2P$; 4.85 (td, 2H J = 1.22 Hz) $=C\underline{H}_2$; 5.02 (m, 2H) $=C\underline{H}_2$; 5.66-5.90 (m, 2H) $C\underline{H}=$; 7.29-7.62 (m, 20H) $P\underline{\mathbf{Ph}}_2$.
91	0.89-1.08 (m, 4H) $Pt\text{-}C\underline{H}_2$; 1.11-1.48 (m, 6H); 1.65-2.05 (m, 4H); 2.49-2.54 (m, 4H) $PC\underline{H}_2CH_2C\underline{H}_2P$; 5.38-5.45 (m, 2H) $C\underline{H}=$; 7.08-7.38 (m, 20H) $P\underline{\mathbf{Ph}}_2$.
92	0.79-0.95 (m, 4H) $Pt\text{-}C\underline{H}_2$; 0.98-1.11 (m 2H) $PCH_2C\underline{H}_2CH_2P$; 1.19-1.35 (m, 12H); 1.47-1.53 (m, 4H), 1.74-2.02 (m, 4H), 2.32-2.66 (m, 4H) $PC\underline{H}_2CH_2C\underline{H}_2P$; 5.15-5.54 (m, 2H) $C\underline{H}=$; 7.16-7.84 (m, 20H) $P\underline{\mathbf{Ph}}_2$.
93[b]	0.87-1.01 (m, 4H) $Pt\text{-}C\underline{H}_2$; 1.05-1.36 (m, 10H); 1.38-1.56 (m, 4H); 2.08-2.22 (m, 4H) $PC\underline{H}_2CH_2C\underline{H}_2P$; 6.97-7.66 (m, 20H) $P\underline{\mathbf{Ph}}_2$.

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

Table 4.2 continued

Complex	^{1}H NMR (δ ppm)[a]
94[b]	0.75-0.96 (m, 4H) Pt-C$\underline{\mathbf{H}}_2$; 0.98-1.12 (m, 2H) $PCH_2C\underline{\mathbf{H}}_2CH_2P$; 1.13-1.46 (br m, 16H); 1.48-1.74 (m, 8H) ; 2.13-2.25 (m, 4H) $PC\underline{\mathbf{H}}_2CH_2C\underline{\mathbf{H}}_2P$; 6.88-7.99 (m, 20H) P$\underline{\mathbf{Ph}}_2$.
95	0.78-0.95 (m, 4H) Pt-C$\underline{\mathbf{H}}_2$; 1.14-1.33 (m, 4H); 1.36-1.50 (m, 2H) $PCH_2C\underline{\mathbf{H}}_2CH_2P$; 2.36-2.62 (m, 4H) $PC\underline{\mathbf{H}}_2CH_2C\underline{\mathbf{H}}_2P$; 7.15-7.61 (m, 20H) P$\underline{\mathbf{Ph}}_2$.
96[b]	0.86-0.94 (m, 4H) Pt-C$\underline{\mathbf{H}}_2$; 0.96 -1.13 (m, 6H) P-$\{(CH_2C\underline{\mathbf{H}}_3)Ph_2\}$;1.20-1.42 (m, 12H); 1.46- 1.61(m, 4H) P-$\{(C\underline{\mathbf{H}}_2CH_3)Ph_2\}$; 7.01-7.40 (m, 20H) P-$\{(CH_2CH_3)\underline{\mathbf{Ph}}_2\}$.

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

Table 4.3 ^{31}P NMR data for complexes **89-96**

Complex	^{31}P NMR (δ ppm)[a]
89	3.45 {s, $^{1}J(^{195}\mathrm{Pt}\text{-}^{31}\mathrm{P})$ = 1623 Hz}
90	3.40 {s, $^{1}J(^{195}\mathrm{Pt}\text{-}^{31}\mathrm{P})$ = 1603 Hz}
91	3.45 {s, $^{1}J(^{195}\mathrm{Pt}\text{-}^{31}\mathrm{P})$ = 1623 Hz}
92	2.94 {s, $^{1}J(^{195}\mathrm{Pt}\text{-}^{31}\mathrm{P})$ = 1609 Hz}; 3.05 {s, $^{1}J(^{195}\mathrm{Pt}\text{-}^{31}\mathrm{P})$ = 1600 Hz}; 3.38 {s, $^{1}J(^{195}\mathrm{Pt}\text{-}^{31}\mathrm{P})$ = 1602 Hz}
93[b]	3.89 {s, $^{1}J(^{195}\mathrm{Pt}\text{-}^{31}\mathrm{P})$ = 1622 Hz}
94[b]	3.82 {s, $^{1}J(^{195}\mathrm{Pt}\text{-}^{31}\mathrm{P})$ = 1632 Hz}
95	3.30 {s, $^{1}J(^{195}\mathrm{Pt}\text{-}^{31}\mathrm{P})$ = 1608 Hz}
96[b]	19.35 {s, $^{1}J(^{195}\mathrm{Pt}\text{-}^{31}\mathrm{P})$ = 1725 Hz}

[a] All spectra were recorded in $CDCl_3$ at room temperature, using phosphoric acid as the external standard unless stated otherwise, [b] Spectrum recorded in C_6D_6 at room temperature.

Table 4.4 Yields, melting points and elemental analysis data for complexes **89-96**

Complex	Yield (%)	Melting Point (°C)	Elemental analysis[a] (%)
89	80	111-113	C 59.72 (59.59), H 5.74 (5.95)
90	62	67-70	C 62.82 (62.24), H 6.35 (6.75)
91	76	161-164	C 58.41(58.57), H 5.98 (5.62)
92	96	161-162	C 61.23 (61.41), H 6.69 (6.54)
93	90	oil	C 58.11 (58.41), H 5.65 (5.88)
94	60	oil	C 61.16 (61.26), H 6.59 (6.77)
95	52	oil	C 56.71 (56.11), H 5.29 (5.16)
96	42	oil	C 58.16 (58.77), H 6.59 (6.30)

[a] Calculated values in parentheses.

Mass Spectrometry

Complex **92** showed a parent ion at *m/z* = 801.3 $[M]^+$ and fragments by initial loss of the hydrocarbon ligand. A high intensity peak for $[\mathrm{dpppPt}]^+$ (*m/z* = 607.0) was also seen.

4.2.3 Characterization of platinacycloalkanes

Hydrogenation of complexes **91** and **92** using 10 wt % Pd on activated carbon support over 8 hours allowed the isolation of colourless oils of platinacycloalkanes **93** and **94** in yields of 90 and 60 % respectively.
The 5-membered- and 9-membered-ring platinacycloalkanes **95** and **96** obtained *via* the di-Grignard route both exist as fairly stable colourless to light brown oils. The yields of these compounds were relatively low (52% and 42%, respectively) when compared to the yields obtained for compounds **93** and **94**. This may be attributed to the different synthetic method employed in the syntheses of these complexes. The effect of synthetic method on the yields of products has also been seen in the preparation of other metallacycloalkanes [20].

In addition, the complex **96** proved to be less stable in solution than its diphosphine analogue **93**. This may be attributed to the positive chelate effect imposed by the diphosphine ligand, which plays a role in stabilizing complex **93**. The 5-membered ring complex **95** is known [20c]; however, platinacyclononane **96** is new (Scheme 4.2).

All the platinacycloalkane complexes **93**-**96** were characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and elemental analysis. These data agree well with the proposed formulations (characterization data have been summarized in Tables 4.2-4.4, pages 79-81 and Chapter 5)

NMR Spectroscopy

Apart from the signals which can be assigned to the tertiary phosphine ligands, the ^{1}H NMR spectrum of complex **96** displayed a multiplet at 0.86-0.94 ppm for the protons of the carbons directly bonded to the platinum atom. A broad multiplet in the region of 1.20-1.42 ppm, integrating for twelve protons, was assigned to the remaining methylene protons of the metallacyclic ring.

Similar broad signals have also been seen for related metallacycloalkane complexes containing PPh_3, dppe or dppp [1]. As well as the signals for the dppp ligand, ^1H NMR spectra for complexes **93-95** displayed expected downfield signals for Pt-C$\underline{H}_2$, as well as broad multiplets corresponding to the methylene protons of the metallacyclic rings in the aliphatic region (Table 4.2 pages 79-80).

The ^{31}P NMR spectrum of complex **96** displayed a singlet at 19.35 ppm, which can be assigned to the two phosphine ligands existing in the same environment. This peak was accompanied by platinum satellites with a $^1J(^{195}Pt-^{31}P)$ coupling constant of 1725 Hz, which is a similar value to the PPh_3 derivative which has a coupling constant of 1716 Hz [1]. Complexes **93-95** all displayed similar shifts at *ca.* 3.0 ppm in their ^{31}P NMR spectra. These shifts are characteristic of $[L_2PtR_2]$ (L_2 = dppp and R = alkyl, alkenyl or metallacyclic group) [1].

^{13}C NMR spectra for complexes **93-96** all displayed singlets in the region of *ca.* 14.0 and 15.0 ppm, assigned to the carbons directly bonded to the platinum centre. The remaining carbons in the metallacyclic rings appeared as multiplets, slightly more upfield in the region of *ca.* 26.0 to 32.0 ppm (see Chapter 5). In the ^{13}C NMR spectra for complexes **93-96** no coupling of ^{13}C to ^{31}P or ^{195}Pt was seen, again possibly due to the low abundance of ^{13}C.

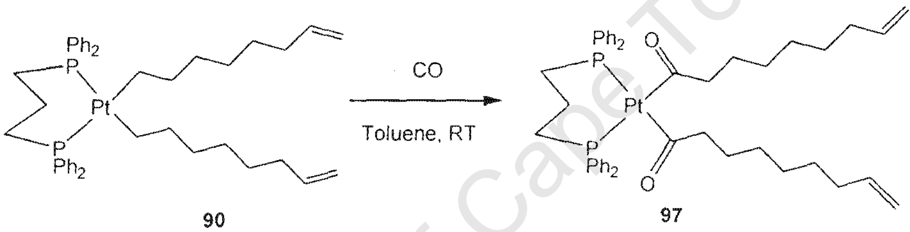
4.3 Reactivity of platinacycles

4.3.1 CO insertion with the bis(octenyl) complex 90

We have carried out a preliminary study on the reactions of CO with bis(octenyl)platinum(II) complex **90** at atmospheric pressure and room temperature.

It was observed that within 48 hours, CO inserted into both metal-carbon bonds of complex **90** as evidenced by the appearance of a strong carbonyl

band at 1676 cm^{-1} in its IR spectrum (eq. 4.4) [19a]. Pt-acyl bands have been reported in this region and at *ca*. 1700 cm^{-1} for complexes of the type *cis*-[Pt(COR)X(P~P)] (R = Me, Et, Cy or Ph, X = Cl or $SnCl_3$ and P~P = dppe, dppp, bdpp or dppb) [21]. The ^{13}C NMR data obtained also supported the formation of di-acyl **97**, by showing a new peak at 206 ppm which was assigned to the two acyl carbons. This new complex **97** was isolated as a colourless crystalline solid in a yield of 86% and was further characterized by melting point, ^{1}H and ^{31}P NMR spectroscopy as well as elemental analysis.



(eq. 4.4)

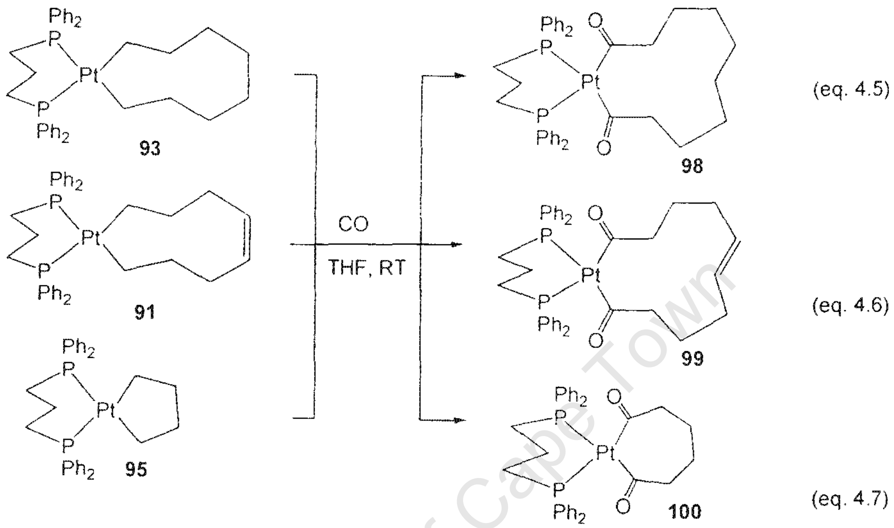
Based on the above findings, we set out to investigate whether metallacycles **91**, **93**, **95** and **96** would undergo similar reactions with CO.

4.3.2 CO insertion with metallacycles

Solutions of complexes **91**, **93** and **95** in dry THF were subjected to an atmosphere of CO contained in a balloon at room temperature with constant stirring (eq. 4.5-4.7). These reactions proved to be relatively slow, and this could principally be due to the strong metal-carbon bond seen in most 5d transition metal complexes [8b]. The progress of these reactions was monitored by IR spectroscopy. After 3 weeks, IR spectroscopy displayed strong bands in the acyl carbonyl region, as well as bands in the region of *ca*. 1600 cm^{-1} corresponding to vibrations associated with the phenyl groups of the dppp ligand (Figures 4.7). Complex **95** showed a similar reaction with CO to give di-acyl complex **100** within 1 week.

We have tentatively suggested the formation of complexes **98**-**100** as di-acyl complexes; however, molecular structures by X-ray crystallography would be essential in further ascertaining the proposed structures.

Complexes **98**-**100** were obtained as stable light pink oils in good yields ranging from 69-77%. Further characterization of these complexes was obtained from ^{1}H, ^{31}P and ^{13}C NMR spectroscopy and elemental analysis.



IR Spectroscopy

As was mentioned, the formation of products was monitored by IR spectroscopy. In addition to the ν(C=C) band at 1606 cm^{-1}, a new strong band was observed in the acyl carbonyl region (1673 cm^{-1}), suggesting that complex **98** had formed from insertion of two CO molecules into the metal-carbon bonds of platinacyclononane **93** (Figures 4.7 *a*,*b*). To further support the insertion of two CO molecules, the ^{31}P NMR spectrum of complex **98** displayed a new singlet with its corresponding Pt satellites for the two phosphorus atoms which are in the same environment. Similarly, formation of complexes **99** and **100** was evidenced by the appearance of IR bands in the acyl region (Figures 4.7 *c*-*f*).

Unexpectedly, the acyl groups in complexes **99** and **100** gave rise to carbonyl bands at higher frequencies (1732 and 1719 cm^{-1}, respectively) than complex **98**.

ν(C=O) bands for Pt-acyl complexes have been reported in this region for [Pt(COMe)Cl(bdpp)] (ν(C=O) = 1710 cm^{-1}) and [Pt(COMe)CO(bdpp)]$^{+}$ (ν(C=O) = 1706 cm^{-1}) (bdpp = (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane) [21a].

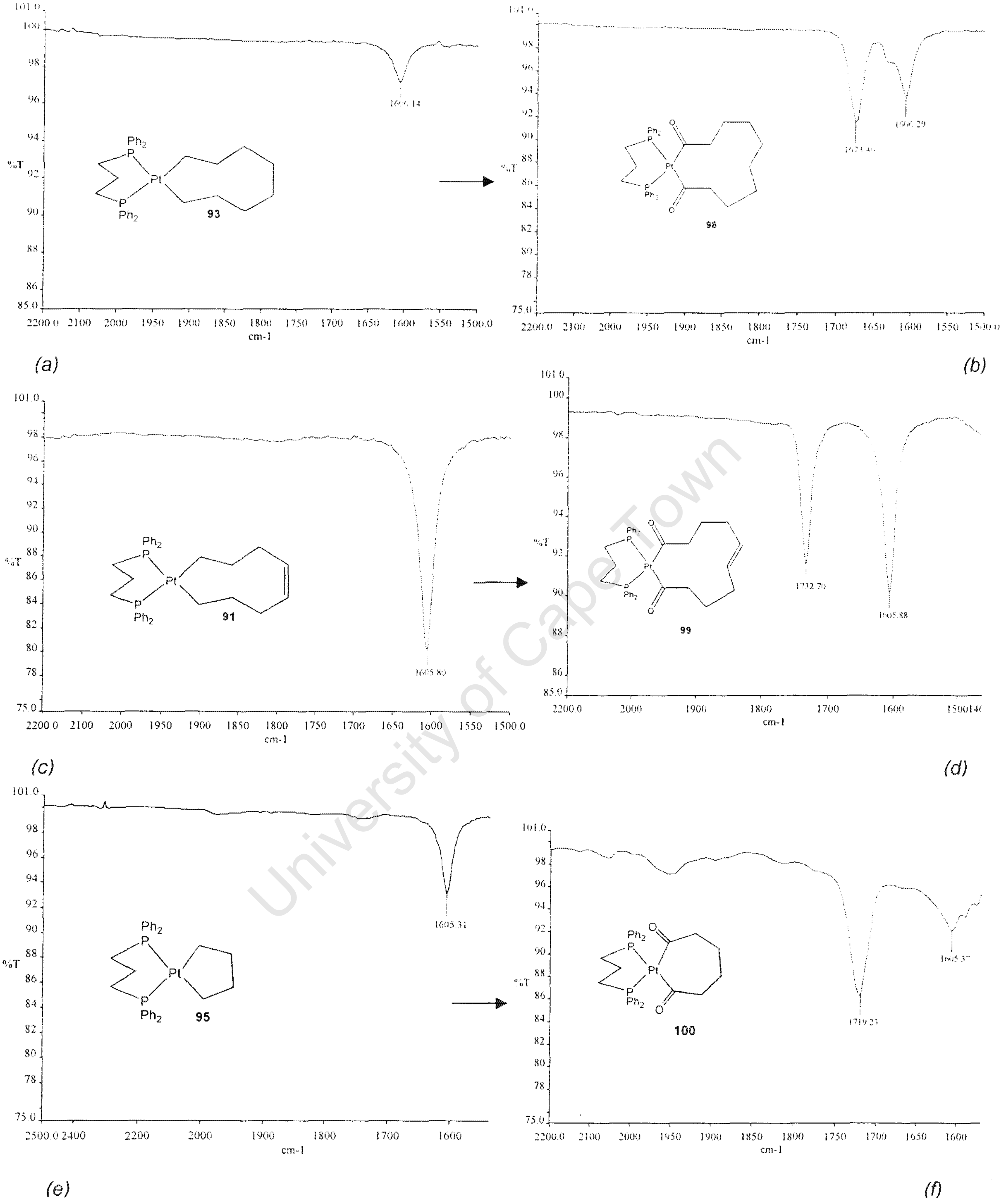


Figure 4.7 (*a*) IR spectrum of platinacyclononane **93** before carbonylation. (*b*) IR spectrum of complex **98**. (*c*) IR spectrum of platinacyclononene **91** before carbonylation. (*d*) IR spectrum of complex **99**. (*e*) IR spectrum of platinacyclopentane **95** before carbonylation. (*f*) IR spectrum of complex **100**.

NMR spectroscopy

The ^1H NMR spectrum of complex **98** displayed a broad multiplet in the region of 0.99-1.90 ppm, integrating for the 14 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 and the P-C$\underline{H}_2$ protons were represented by a multiplet at 2.03-2.57 ppm. Similar shifts have been observed for the protons α to the acyl carbon in related complexes [21]. The phenyl rings of the dppp ligand gave rise to a multiplet in the region of 6.93-7.73 ppm.

The ^1H NMR spectra of complexes **99** and **100** showed similar signals, with complex **99** differing by the presence of a signal at 5.04-5.29 ppm, which was assigned to the alkene protons.

^{13}C NMR spectra of complexes **98-100** displayed the envisaged signals for the carbon atoms of the metallacyclic rings in the aliphatic regions as well as phenyl group carbon signals. Anticipated signals for the acyl carbons (C=O) were observed at *ca.* 200 ppm (Table 4.5).

Table 4.5 ^{13}C NMR data for complexes **98-100**

Complex	^{13}C NMR (δ ppm)^a
98^b	22.72 (s, 1C) $PCH_2\underline{C}H_2CH_2P$; 26.01 (s, 2C) $P\underline{C}H_2CH_2\underline{C}H_2P$; 27.85-32.47 (m, 8C) $\underline{C}H_2$; 127.68-133.81 (m, 24C) **$\underline{Ph}$**; 203.68 (s, 2C) $\underline{C}$=O
99	22.55 (s, 1C) $PCH_2\underline{C}H_2CH_2P$; 25.49 (s, 2C) $P\underline{C}H_2CH_2\underline{C}H_2P$; 27.88-32.99 (m, 6C) $\underline{C}H_2$; 127.52-133.38 (m, 24C) **$\underline{Ph}$**; 138.71 (s, 2C) $\underline{C}$H=; 206.61 (s, 2C) $\underline{C}$=O
100	22.42 (s, 1C) $PCH_2\underline{C}H_2CH_2P$; 25.54 (s, 2C) $P\underline{C}H_2CH_2\underline{C}H_2P$; 28.01 (s, 2C) $\underline{C}H_2$; 32.16 (s, 2C) $\underline{C}H_2$; 128.22-133.74 (m, 24C) **$\underline{Ph}$**; 204.12 (s, 2C) $\underline{C}$=O

^{a}All spectra were recorded in $CDCl_3$ at room temperature, tetramethylsilane (TMS) as the external standard, ^{b} Spectrum recorded in C_6D_6 at room temperature.

All complexes showed deshielding of their ^{31}P NMR signals from *ca.* 3.0 ppm in the starting materials to *ca.* 15.0 ppm in the di-acyl products. These shifts were also accompanied by a decrease in the $^{1}J(^{195}Pt\text{-}^{31}P)$ coupling constant from *ca.* 1600 Hz to *ca.* 1400 Hz. $^{1}J(^{195}Pt\text{-}^{31}P)$ coupling constants at *ca.* 1400 Hz are characteristic of Pt-acyl complexes, such as $[Pt(COMe)CO(bdpp)]^+$ [21a], [PtCl(COPh)(dppp)] [21d], and [Pt(COMe)(dppp)Cl] [21c], in which the phosphorus donor ligand experiences the *trans* influence of an acyl ligand. Figures 4.8 *(a)* and *(b)* show the ^{31}P NMR spectra of complexes **93** and **98**, as a typical example of the shift in ^{31}P NMR signal and decrease in $^{1}J(^{195}Pt\text{-}^{31}P)$ in going from the platinacycle to the di-acyl complex.

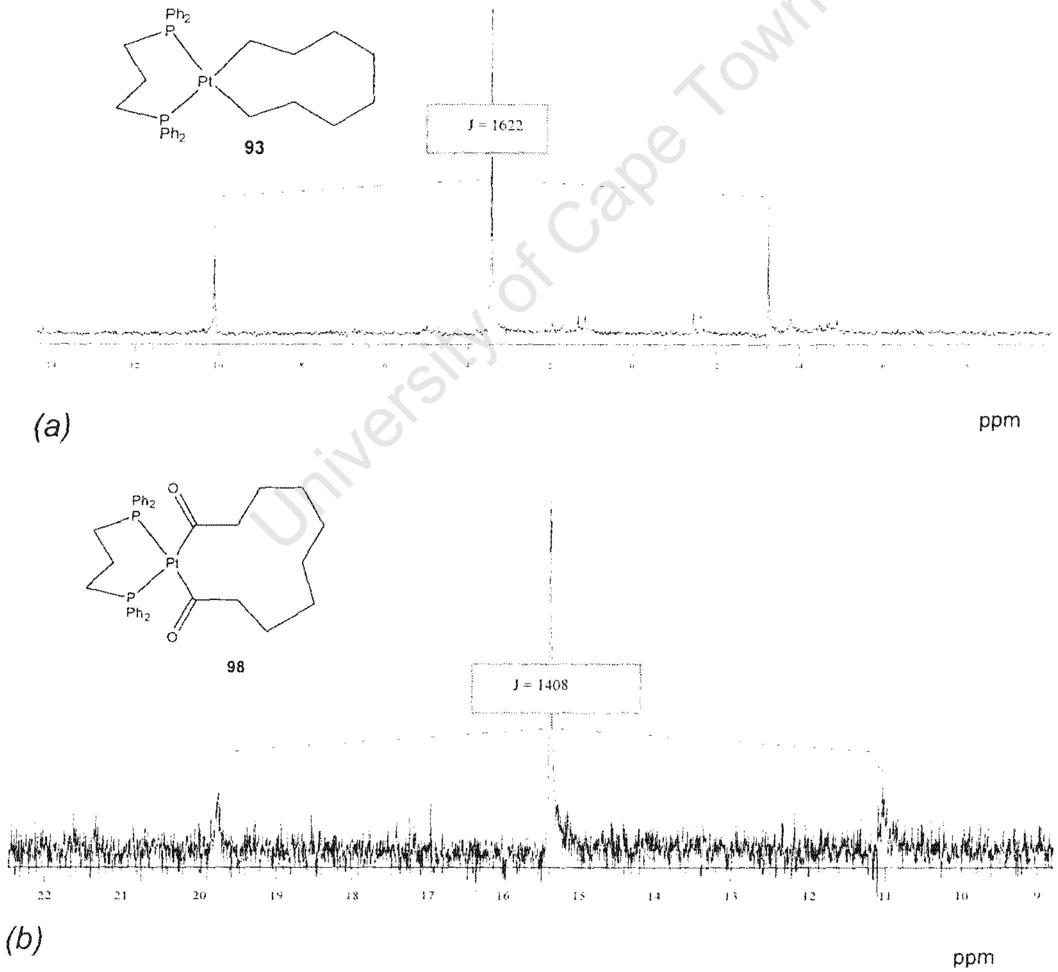


Figure 4.8 *(a)* ^{31}P NMR spectrum, showing $^{1}J(^{195}Pt\text{-}^{31}P)$ of complex **93** (b) ^{31}P NMR spectrum, showing $^{1}J(^{195}Pt\text{-}^{31}P)$ of complex **98**.

The elemental analyses of complexes **98-100** were in agreement with the proposed formulations (Table 4.6),

Table 4.6 Elemental analysis results and yields of complexes **98-100**

Complex	%C[a]	%H[a]	%Yield
98	57.38(57.29)	5.64(5.46)	77
99	57.28(57.43)	5.24(5.21)	69
100	56.71(56.11)	5.29(5.16)	65

[a] calculated values in parentheses.

4.3.2 Possible intermediates in CO insertion reactions

During the reactions of CO with platinacycles **91** and **93**, terminal carbonyl bands ν(C≡O) were observed in the region of 2037 cm^{-1} in their IR spectra after 7 days of reaction. These observations suggested that these reactions may proceed *via* five-coordinate platinum species or four-coordinate intermediates, in which one of the phosphorus donor atoms of the dppp ligand initially dissociates and CO subsequently coordinates to the platinum center (Figure 4.9).

A five coordinate platinum species has been proposed as the intermediate through which CO insertion proceeds in Pt(II) diphosphine complexes [21c].

A similar IR spectrum was observed in the reaction of CO with platinacyclopentane **95**, after 3 days of reaction.

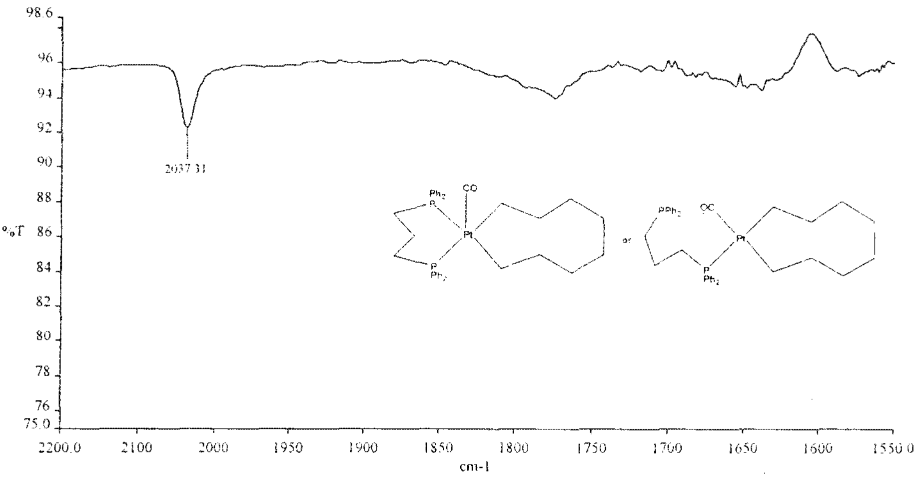


Figure 4.9 IR spectrum of possible intermediates formed during CO insertion

Further characterization of these intermediates by ^{31}P NMR spectroscopy in order to establish whether they were four- or five-coordinate species were unsuccessful as they proved to be unstable and thus difficult to isolate.
After 14 days of reaction additional bridging carbonyl bands ν(C=O) appeared together with the terminal carbonyl bands ν(C≡O) in the IR spectra of the reaction mixtures of complexes **91** and **93** (Figure 4.10). A similar IR spectrum was observed for the platinacyclopentane reaction mixture after 5 days.
In this instance, we suggest the formation of either four- or five-coordinate second intermediates. These species were also not isolated or further characterized due to their instability.

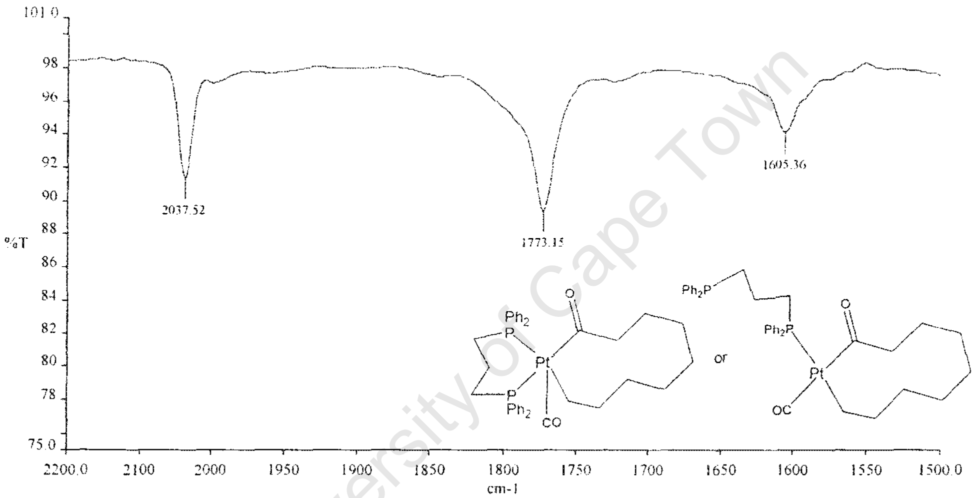


Figure 4.10 IR spectrum of a possible second intermediate formed during CO insertion

Platinacyclononane **96** with $PEtPh_2$ ligands dissolved in THF was also subjected to CO (contained in a balloon) at room temperature and atmospheric pressure. We observed that within 6 days no insertion occurred. However, we did see two terminal carbonyl bands ν(C≡O) at 2060 cm^{-1} and 1979 cm^{-1} in the IR spectrum (Figure 4.11), which we tentatively suggest is evidence, for a complex formed by dissociation of the labile tertiary phosphine ligands and subsequent coordination of two CO molecules to the platinum center. This species was not isolated or further characterized due to its instability. Platinum complexes of the type $[Pt(CO)_2R_2]$ (R = Me or Ph) are known and the carbonyl bands ν(C≡O) were reported in the region of 2000 to 2100 cm^{-1} [21f]. No acyl bands were seen in the reaction solution of complex

96 and further stirring resulted in the reaction mixture turning to a dark brown unidentified species.

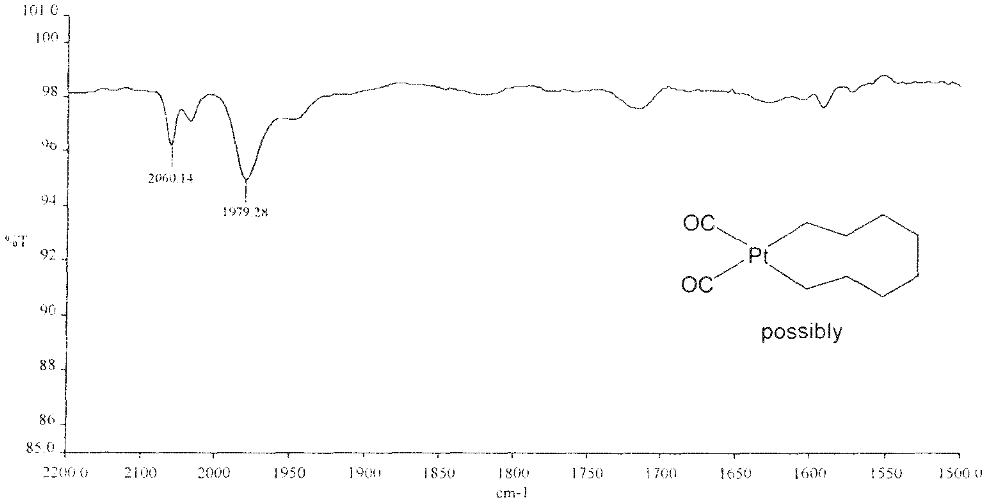
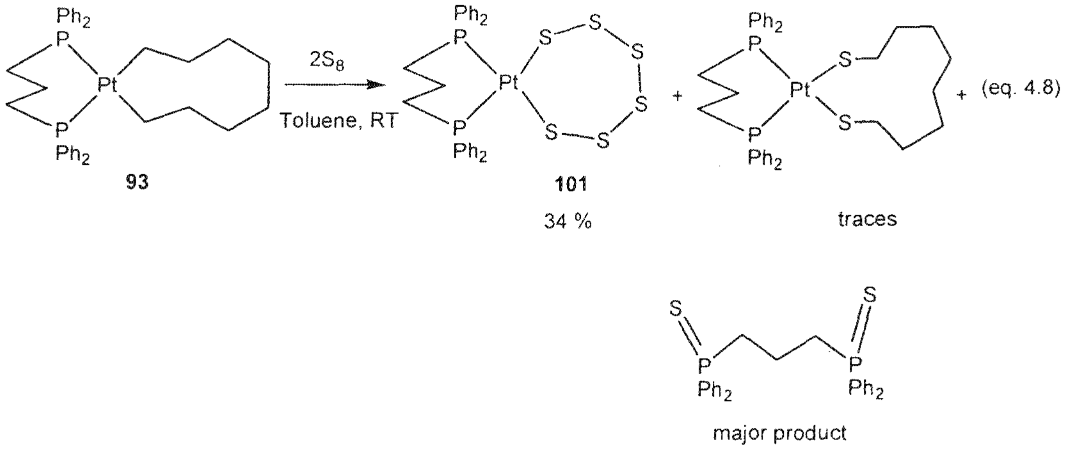


Figure 4.11 IR spectrum of reaction solution during carbonylation of complex **96**

4.3.3 Reaction of $[(dppp)P\overline{t\{(CH_2)_7CH_2\}}]$ complex 93 with elemental sulfur (S_8)

Platinacyclononane **93** was reacted with 2 equivalents of S_8 in toluene for 21 days (eq. 4.8). During this period the reaction progress was monitored by ^{31}P NMR spectroscopy. The reaction yielded a complex mixture of products including the phosphine disulfide, a 7-membered ring platinum complex containing a chelating S_6 ligand **101** and traces of the di-inserted product as evidenced by mass spectrometry (see later Fig. 4.13).

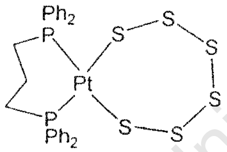


After separation of these products using column chromatography, a 7-membered platinacyclosulfide complex **101** was obtained as a stable, dark yellow to orange solid which melts at 121-126°C in 34% yield. The structure of a 5-membered-ring platinacyclosulfide prepared by a similar reaction of S_8 with $[(dppe)_2Pt]$ has been reported previously [18].

Complex **101** has been characterized by ^{31}P NMR, mass spectrometry and elemental analysis.

NMR Spectroscopy

The ^{31}P NMR spectrum of complex **101** in $CDCl_3$ displayed a shift of the singlet at 3.89 ppm in the starting material $[dpppPt(CH_2)_8]$ **93** to a lower frequency of -3.20 ppm (Figure 4.12). Along with this, an increase in $^1J(^{195}Pt-^{31}P)$ coupling constant from 1622 to 2688 Hz was observed. This typically large $^1J(^{195}Pt-^{31}P)$ coupling constant was seen in a similar sulfur-containing Pt complex, $[Pt(dppe)S_4]$ ($^1J(^{195}Pt-^{31}P)$ = 2814 Hz) [18].



101

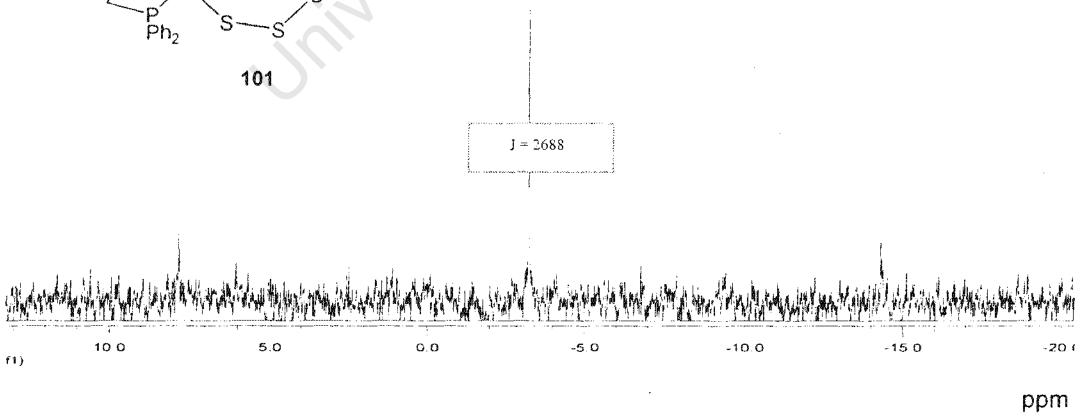


Figure 4.12 ^{31}P NMR spectrum of complex **101**, showing $^1J(^{195}Pt-^{31}P)$.

Mass Spectrometry

Mass spectral results showed a parent ion peak of *m/z* = 778.1. The mass spectrum also revealed that complex **101** fragments by sequential loss of sulfur atoms (Figure 4.13). A very weak peak, (*m/z* = 783.2) which may correspond to the product formed by insertion of two sulfur atoms into the Pt-C bonds of platinacyclononane **93**, was also observed (insert in Figure 4.13).

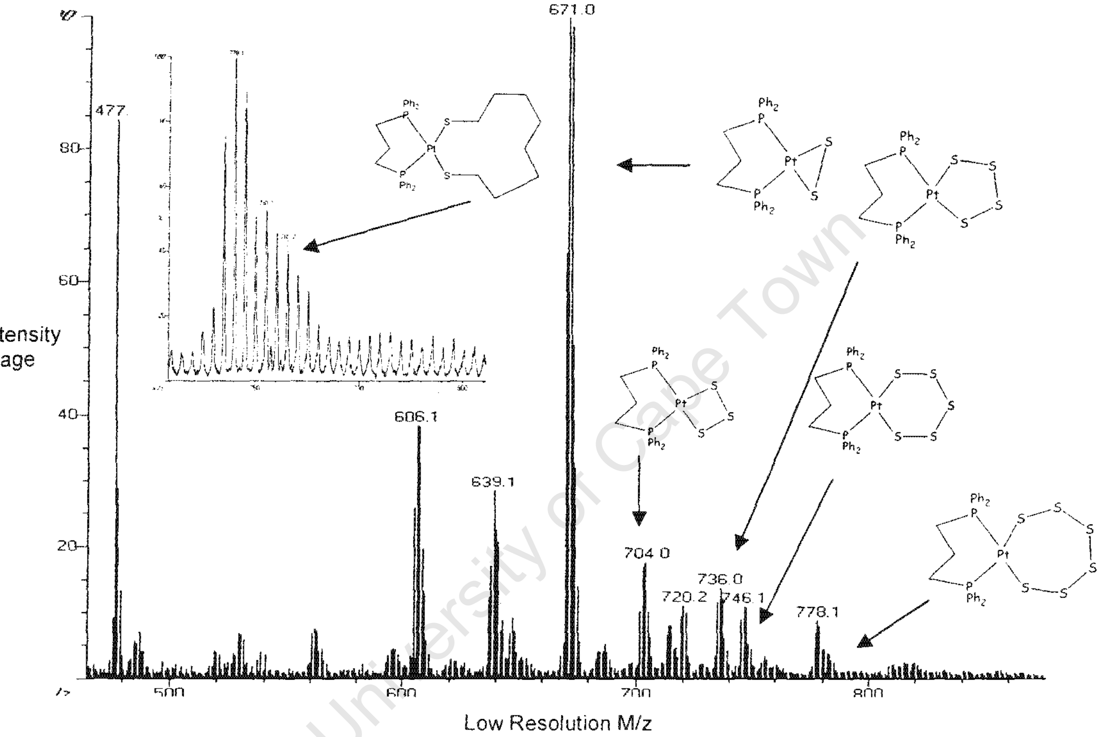


Figure 4.13 FAB mass spectrum of complex **101**.

4.4 Thermal decomposition of $[(PEtPh_2)_2\overline{Pt\{(CH_2)_7CH_2}\}]$ complex 96

4.4.1 Introduction

In 1977, Manyik *et al.* [22] suggested the involvement of metallacycles as key intermediates in the catalytic trimerization of ethylene for the first time. The chemistry of metallacycloalkane complexes has since developed immensely

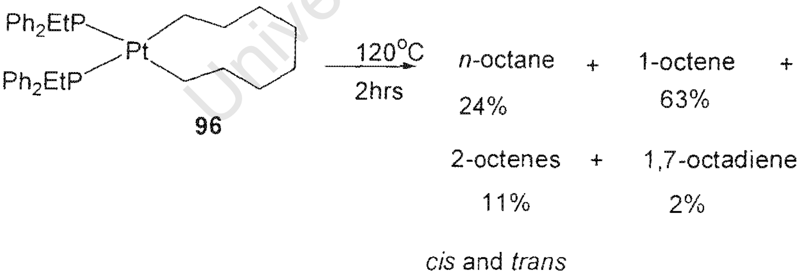
[23], with thermal decomposition studies being an important area investigated [24].

Much of the early work has been restricted to the decomposition of small metallacycloalkanes (four- to six-membered rings), primarily due to the difficulty of making medium and larger metallacycloalkanes [23,24]. It is only recently that thermolysis studies have been carried out on medium- and large-ring metallacycloalkanes, which were synthesized by a new route developed in our research group [1,2].

In this section, we report the products afforded and hence the thermal decomposition pathway of a new platinacyclononane complex **96**. These results are compared with thermolysis result of other similar platinacyclononanes containing mono- and diphosphine donor ligands.

4.4.2 Thermal decomposition of platinacyclononane 96

Solvent free thermolysis of a fresh sample of platinacyclononane **96** was carried out at 120˚C for 2 hours (eq. 4.9).



(eq. 4.9)

Complex **96** decomposed to yield a mixture of organic products (eq. 4.9). The complex also gave an intense red colour upon decomposition, which we believe could be a cluster of the type $Pt_n(PEtPh_2)_n$ [19a].

The major organic products were identified by comparison of their retention times with those of known (C_8) standards (Figures 4.14 (*a-c*).

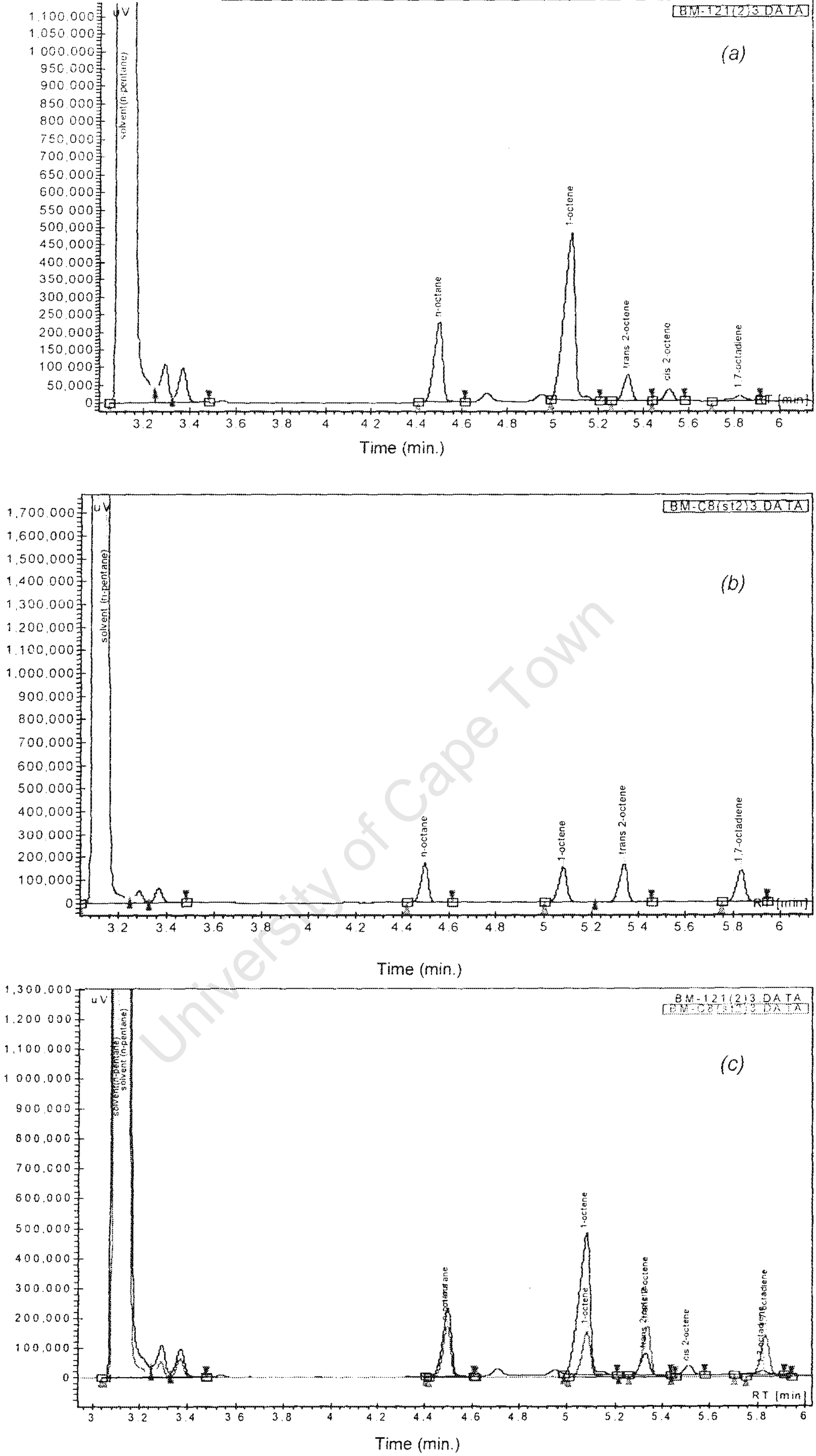
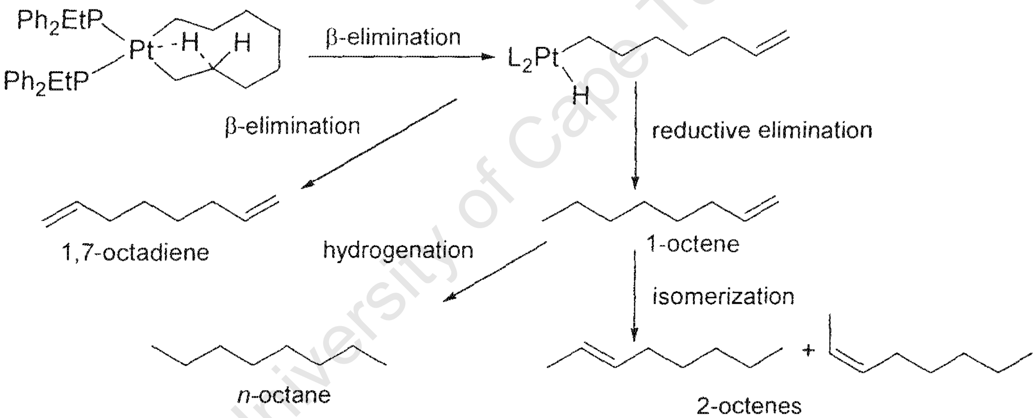


Figure 4.14 (*a*) Chromatogram for products formed from the thermal decomposition of complex **96**. (*b*) Chromatogram for a sample containing C_8 standards. (*c*) Comparison of the two chromatograms.

Formation of organic products

Platinacyclononane **96** decomposes to give 1-octene as the major product (63%). A possible mechanism for the formation of this product is by β-hydride elimination followed by reductive elimination (Scheme 4.3). Small amounts of 1,7-octadiene (2%) were present in the organic products and could be formed by a second β-hydride elimination reaction (Scheme 4.3) [2,24]. Formation of 2-octenes may be by isomerization of the initially formed 1-octene. Finally, *n*-octane could be a result of intermolecular hydrogenation reactions, with the hydrogen source coming from either metal hydride species or the coordinated ligand (Scheme 4.3) [2].



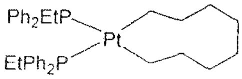
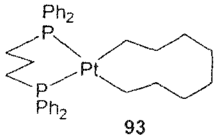
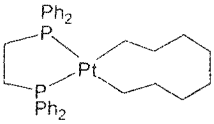
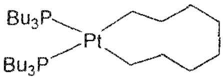
Scheme 4.3 Mechanism for the formation of organic products

Comparison of products obtained with similar platinacyclononanes

Comparison of the results obtained in this study with those of analogous 9-membered-ring platinum complexes containing dppp, dppe or $PBu_3{}^t$ donor ligands [2], reveals that the same decomposition routes occur, although in the literature results less 1-octene and more 2-octenes were formed (Table 4.7). Also, 1,7-octadiene formed to a slightly greater extent in the reports, than in the thermal decomposition of complex **96**.

For all the complexes in Table 4.7, no cyclooctane (an organic product resulting from reductive elimination) was observed.

Table 4.7 Solvent free decomposition products obtained for platinacyclononanes

Complex	Products (%) [a]				Ref
	1-octene	2-octenes *cis* & *trans*	1,7-octadiene	*n*-octane	
 **96**	63	11	2	24	this work
 **93**	49	21	4	26	2
	41	21	13	23	2
	51	24	5	20	2

[a] Error = +/-1%.

4.5 Conclusions

Some bis(alkenyl)platinum(II), platinacycloalkenes and platinacycloalkanes were successfully prepared using the RCM and di-Grignard routes. The products were isolated in moderate yields as reasonably stable colourless crystalline solids or oils. The complexes were characterized using melting points (for the known solid complexes), NMR spectroscopy, mass spectrometry and elemental analysis and all characterization data was in agreement with the formulations. ^{13}C NMR data has been obtained for the bis(alkenyl)platinum(II) complexes and the platinacycles for the first time. No $^{1}J(^{195}Pt-^{13}C)$ coupling was observed in the ^{13}C NMR spectra of all the complexes, and this may be partly due to the low abundance of ^{13}C and ^{195}Pt. The molecular structure of bis(octenyl) complex **90** was determined for the first time.

IR evidence gathered in these studies shows that the reactions with CO yield products consistent with the formation of di-acyl compounds. The products were characterized using NMR and IR spectroscopy as well as elemental analysis.

These studies have shown that the bis(octenyl)platinum complex **90** reacts faster (48 hours) than platinacyclopentane **95** (1 week), which in turn reacts faster than the 9-membered ring platinacycles (3 weeks).

Thus, the reactivity rate towards CO double-insertion for these complexes decreases in the order **90** > **95** > **91** ≈ **93**.

Possible four- or five-coordinate intermediates have been detected for these reactions using IR spectroscopy; however, these were found to be unstable and were thus not isolated or characterized further.

Platinacyclononane **96** containing the monodentate $PEtPh_2$ ligand, does not insert CO into its Pt-C bonds, and prolonged stirring results in this complex decomposing to a dark brown unidentified species.

The reaction of platinacyclononane **93** with S_8 resulted in a mixture of products including a 7-membered-ring platinacyclosulphide complex **101** in 34% yield, the undesired phosphine sulfide as the major product, and traces of the complex formed by insertion of two sulfur atoms into the Pt-C bonds of platinacyclononane **93**. Compound **101** was characterized using NMR spectroscopy, mass spectrometry and elemental analysis. (Data obtained was in agreement with the proposed formulation).

Thermal decomposition of platinacyclononane **96** gave 1-octene as the major organic product (63%), *n*-octane and 2-octene in 24 and 11% yields ,respectively, and traces of 1,7-octadiene. These results revealed that complex **96** decomposes via similar pathways to previously reported platinacyclononane complexes.

4.6 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**), 3865. (b) A. Sivaramakrishna. H. Su, and J.R. Moss, *Angew. Chem. Int. Ed.*, (**2007**), 46, 3541.
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. Braunstein, *Chem. Commun.*, (**2007**) , 58.
8. (a) B.L Booth, R.N. Haszeldine, and N.P. Woofenden, *J. Chem. Soc A.*, (**1970**), 1979. (b) F. Calderazzo, and K. Noack, *Coord. Chem. Rev.*, (**1966**), 1, 118. (c) M. Green, and R.I Hancock, and D.C. Wood, *J. Chem. Soc., A* (**1968**), 2718. (d) M. Green, and D.J. Westlake, *J. Chem. Soc., A* (**1971**), 367. (e) P.J. Craig, and M. Green, *J. Chem. Soc., A* (**1969**), 157. (f) R.W. Glyde, and R.J. Mawby, *Inorg. Chem.,* (**1971**), 10, 854. (g) P. Uguagliati, A. Palazzi, G. Deganello, and U. Belluco, *Inorg. Chem.,* (**1970**), 9, 724.
9. F. De Angelis, S. Fantacci, A. Sdamellotti, and N. Re, *Theor. 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**), 1633.

14. P. Legzdins, and L. Sánchez, *J. Am. Chem. Soc.*, (**1985**), 107, 5525.
15. R. Han, and G.L. Hillhouse, *J. Am. Chem. Soc.,* (**1998**), 120, 7657.
16. Z-X. Zhang, Y-R. Li, R-T. Liu, Z-X. Chen, L-H. Weng, and X-G. Zhou, *Polyhedron*, (**2007**), 26, 4986.
17. J. Chatt, and D.M.P. Mingos, *J. Chem. Soc. (A),* (**1970**), 1243.
18. (a) C.E. Briant, M.J. Calhorda, T.S.A. Hor, N.D. Howells, and D.M.P. Mingos, *J. Chem. Soc. Dalton Trans.*, (**1983**), 1325. (b) M.S. Morton, R.J. Lachicotte, D.A. Vicic, and W.D. Jones, *Organometallics*, (**1999**), 18, 227.
19. (a) A. Sivaramakrishna, B.C.E. Makhubela, F. Zheng, H. Su, G.S. Smith, and J.R. Moss, *Polyhedron*, (**2008**), 27, 44. (b) A.K. Tomov, J.J. Chirinos, R.J. Long, V.C. Gibson, and M.R.J. Elsegood, *J.Am. Chem. Soc.*, (**2006**), 128, 7704.
20. (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.
21. (a) I. Tóth, T. Kégl, C.J. Elsevier, and L. Kollár, *Inorg. Chem.*, (**1994**), 33, 5708. (a) M. Gómez, G. Muller, D. Sainz, J. Sales, and X. Solans, *Organometallics*, (**1991**), 10, 4036. (c) M. Gerisch, F.W. Heinemann, C. Bruhn, J. Scholz, and D. Steinborn, *Organometallics*, (**1999**), 18, 564. (d) G.K. Anderson, and G.J. Lumetta, *Organometallics*, (**1985**), 4, 1542. (e) A. Scrivanti, C. Botteghi, L. Toniolo, and A. Berton, *J. Organomet. Chem.*, (**1988**), 344, 261. (f) G.K. Anderson, H.C. Clark, and J.A. Davies, *Inorg. Chem.*, (**1981**), 20, 1636.
22. R.M. Manyik, W.E. Walker, and T.P. Wilson, *J. Catal.,* (**1977**), 47, 197.
23. B. Blom, H. Clayton, M. Kilkenny, and J.R. Moss, *Adv. Organomet. Chem.,* (**2006**), 56, 149.
24. F. Zheng, A. Sivaramakrishna, and J.R. Moss, *Coord. Chem. Rev.,* (**2007**), 251, 2056

Chapter 5: Experimental procedures

5.1 Experimental Details

5.1.1 General Experimental Procedures

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

1,3-bis(diphenylphosphinopropane), diphenylethylphosphine, triphenylphosphine, triethylphosphine, trimethylphosphite, tributylphosphite, α-phellandrene, hexamethylbenzene, Grubbs' 1st generation catalyst, 10 wt% palladium on activated carbon and all deuterated solvents were obtained from Aldrich and were used as received.

$K_2[PtCl_4]$ and $K_2[OsO_2(OH)_4]$ were obtained from Johnson Matthey and Anglo Platinum Corporation respectively.

$[Pt(COD)Cl_2]$ [1] and $[Pt(dppp)Cl_2]$ [2], were prepared according to previously reported methods.

5.1.2 Instrumentation

^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian XR300 MHz or XR400 MHz spectrometers using tetramethylsilane (TMS) as the internal standard (for ^1H and ^{13}C) and H_3PO_4 as the external standard (for ^{31}P). Mass spectra were recorded at the University of Witwatersrand using a VG70SE with 8kV acceleration and a Iontech Saddlefield FAB gun. Xenon gas operating at 8kV was used and all matrices were made with 3-nba. Microanalyses were conducted with a Thermo Flash 1112 Series CHNS-O Analyzer instrument. FTIR spectra were recorded on a Perkin Elmer.

Spectrum One FT-IR Spectrometer, using solution cells with NaCl windows. Melting points were recorded by a Kofler hot stage microscope (Riechert Thermovar). 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 was helium at 5.0 psi. The oven was programmed to hold at 32°C for 4 min and then to ramp to 200°C at 10 °C /min and hold 5 min.

5.2 Preparation of Grignard reagents

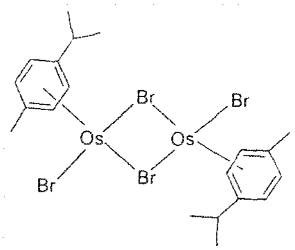
Alkenyl Grignard reagents were prepared by treatment of the appropriate alkenyl bromide with excess of magnesium turnings in freshly dried diethyl ether [3].

Freshly-distilled diethyl ether and an excess of magnesium turnings were placed in a two-neck round-bottom flask equipped with a reflux condenser. The contents of the flask were then cooled to -78°C and the appropriate bromoalkene was added slowly. After reaching room temperature, the reaction was then refluxed for 4 hours until the solution turned grey. Concentrations of the Grignard reagents were determined by hydrolyzing 1ml of the Grignard reagent with distilled water (2 ml). HCl (0.1 M, 20 ml) as well as phenolphthalein indicator (2-3 drops) was added to the hydrolyzed Grignard reagent and this was then back-titrated with NaOH (0.1 M).
The same procedure was followed for the preparation of di-Grignard reagents using α,ω-dichloroalkanes and freshly dried THF. In addition, these reactions were carried out in very dilute solutions with a large excess of magnesium turnings to prevent polymerization.

5.3 Preparation of osmium precursors

The complex $[(Cym)OsBr_2]_2$ **67** was prepared by a procedure developed in our research laboratory [4a].

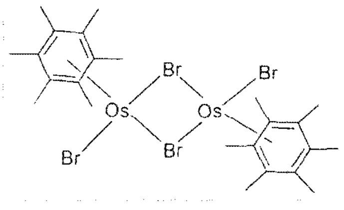
Synthesis of $[(Cym)OsBr_2]_2$ **67**



$K_2[OsO_2(OH)_4]$ (2.042 g, 5.54 mmol) was dissolved in HBr (20 ml, 48% aq). To this solution ethanol (100 ml 96%) was added and the solution was refluxed for 18 hours. α- Phellandrene (3 ml, 16.13 mmol) was added to the solution and it was refluxed for another 18 hours. The volatiles were removed using a rotary evaporator to give a red oil. The organic product was extracted with DCM (30 ml) and the solvent was removed once again using a rotary evaporator to give an orange red oil residue. Diethyl ether (15ml) was added to the residue, which resulted in the formation of an orange brown solid product which was filtered and washed with *n*-hexane (2 x 20 ml). Yield (1.422 g, 27%); m.p. 246-249°C; ^1H NMR (300 MHz, $CDCl_3$) δ ppm: 1.12-1.30 (m 6H) $CH(C\underline{H}_3)_2$, 2.17 (d, 3H J = 25.69 Hz) $C(C\underline{H}_3)$, 2.45-2.76 (m, 1H) $C\underline{H}(CH_3)_2$, 6.02 (d, 2H J = 5.65 Hz) $C_6\underline{H}_4$, 6.15 (d, 2H J = 5.64 Hz) $C_6\underline{H}_4$; Elemental analysis calculated for $C_{20}H_{28}Br_4Os_2$: C, 24.78; H, 2.89, Found: C, 24.01; H,2.82 %.

Synthesis of $[(\eta^6\text{-}C_6Me_6)OsBr_2]_2$ **68**

This compound was prepared by the procedure of ligand exchange with excess of hexamethylbenzene from *$[(Cym)OsBr_2]_2$* [4b].

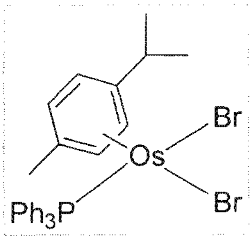


$[(Cym)OsBr_2]_2$ (500 mg, 0.516 mmol) and hexamethyl benzene (4.00 g 24.648 mmol) were transferred into a sealable tube. The tube was evacuated and heated at 175-180°C. After 24 hours the melt was allowed to reach room temperature and extracted with dichloromethane (25 ml). The solvent was removed using a rotary evaporator and a brown-orange solid was obtained and washed with (4 x 50) ml of *n*-

hexane to remove the excess hexamethylbenzene and dried under vacuum for 3 hours. Yield (315 mg, 60%); decomposes without melting at 280°C; ^{1}H NMR (300 MHz, CDCl$_3$) δ ppm: 2.25 (s 36H) 2{$C_6(C\underline{H}_3)_6$}, Elemental analysis calculated for $C_{24}H_{36}Br_4Os_2$: C, 28.13; H, 3.54, Found: C, 28.49; H, 3.57 %.

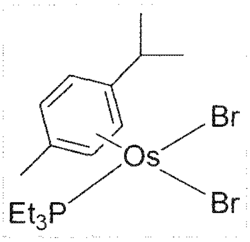
Synthesis of [(Cym)Os(PPh$_3$)Br$_2$] ***69***

Generally, the osmium precursors of the type [*(*Cym*)*OsLBr$_2$] (L = PPh$_3$, PMePh$_2$, P(OMe)$_3$, P(OBu)$_3$ or P(OPh)$_3$) were prepared by the method of heating [*(*Cym*)*OsBr$_2$]$_2$ in refluxing *n*-hexane for 4 hours. For example [*(*Cym*)*Os(PPh$_3$)Br$_2$] **69** was prepared as follows:



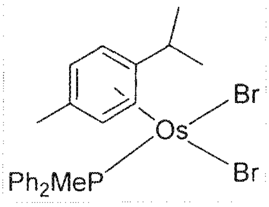
[*(*Cym*)*OsBr$_2$]$_2$ (1.070 g, 1.032 mmol) was transferred into a 250 ml round bottom flask and dissolved in *n*-hexane (80 ml). PPh$_3$ (560 mg, 2.064 mmol) was added to the flask and the solution was refluxed at the boiling point of *n*-hexane. After 4 hours the solvent was removed using a rotary evaporator to give an orange solid residue. The solid was dissolved in a minimum of DCM, filtered and the volatiles were once again removed using a rotary evaporator to afford a red-orange solid. Diethyl ether (15 ml) was added to the solid and it was cooled to 4°C for 11 hours after which red orange crystals of the product were formed. The crystals were dried under vacuum for 1 hour. Yield (1.424 g, 92%); m.p. 223-225°C; ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm: 1.19 (d, 6H J = 6.93 Hz) $CH(C\underline{H}_3)_2$, 1.97 (s, 3H) $C(C\underline{H}_3)$, 2.99 (q, 1H J = 7.04, 7.23, 7.23 Hz) $C\underline{H}(CH_3)_2$, 5.13 (d, 2H J = 5.82 Hz) $C_6\underline{H}_4$, 5.47 (d, 2H J = 5.90 Hz) $C_6\underline{H}_4$, 7.30-7.82 (m, 15H) $P\underline{Ph}_3$; ^{31}P NMR (121 MHz, CDCl$_3$) δ ppm: -17.57 (s), $^1J(^{187}Os-^{31}P)$ = 283 Hz; Elemental analysis calculated for $C_{28}H_{29}Br_2OsP$: C, 45.03; H, 3.88, Found: C, 45.86; H,3.81 %.

Synthesis of [(Cym)Os(PEt$_3$)Br$_2$] **70**



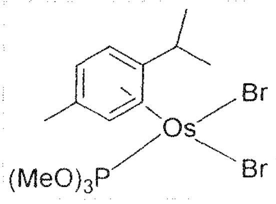
[(Cym)OsBr$_2$]$_2$ (200 mg, 0.206 mmol) was transferred into a 250 ml round bottom flask and dissolved in dry dichloromethane (35 ml). PEt$_3$ (48 mg, 0.413 mmol) was added to the flask and the solution was stirred at room temperature for 18 hours, during which time the solution had turned from dark orange to bright orange. After 18 hours the solvent was removed using a rotary evaporator to give an orange solid. The solid was washed with three portions of *n*-hexane (15ml) and an orange solid was obtained and dried under vacuum for 2 hour. Yield (191 mg, 73%); m.p. 119-122°C; ^{1}H NMR (300 MHz, CDCl$_3$) δ ppm: 1.04-1.22 (m, 9H) $P\text{-}(CH_2C\underline{H}_3)_3$, 1.27 (d, 6H J = 6.86 Hz) $CH(C\underline{H}_3)_2$, , 2.05-2.18 (m, 6H) $P\text{-}(C\underline{H}_2CH_3)_3$, 2.28 (s, 3H) $C(CH_3)$, 2.88 (q, 1H J = 7.04, 7.23, 7.23 Hz) $C\underline{H}(CH_3)_2$, 5.55 (d, 2H J = 4.98 Hz) $C_6\underline{H}_4$, 5.61 (d, 2H J = 5.71 Hz) $C_6\underline{H}_4$; ^{31}P NMR (121 MHz, CDCl$_3$) δ ppm: -28.35 (s) $^1J(^{187}Os\text{-}^{31}P)$ = 268 Hz; Elemental analysis calculated for $C_{16}H_{29}Br_2OsP$: C, 31.90; H, 4.85, Found: C, 31.02; H, 4.99 %.

Synthesis of [(Cym)Os(PMePh$_2$)Br$_2$] **71**



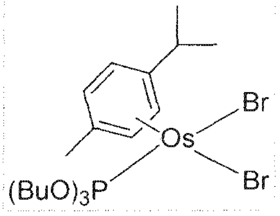
This compound was prepared using the same procedure as described for the preparation of compound **69**, using [(Cym)OsBr$_2$]$_2$ (460 mg, 0.475 mmol) and PMePh$_2$ (190 mg, 0.950 mmol). The product was isolated as an orange-yellow solid. Yield (566 mg, 87%); m.p. 196-198°C; ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm: 1.22 (d, 6H J = 6.97, Hz) $CH(C\underline{H}_3)_2$, 2.02-2.15 (m, 3H) $P\text{-}C\underline{H}_3Ph_2$, 2.18 (d, 3H J = 10.68 Hz) $C(C\underline{H}_3)$, 2.89 (q, 1H J = 7.04, 7.23, 7.23 Hz) $C\underline{H}(CH_3)_2$, 5.40 (d, 2H J = 5.75 Hz) $C_6\underline{H}_4$, 5.49 (d, 2H J = 5.71 Hz) $C_6\underline{H}_4$, 7.39-7.76 (m, 10H) $P\text{-}CH_3\underline{Ph}_2$; ^{31}P NMR (121 MHz, CDCl$_3$) δ ppm: -26.68 (s) $^1J(^{187}Os\text{-}^{31}P)$ = 274 Hz; Elemental analysis calculated for $C_{23}H_{27}Br_2OsP$: C, 40.36; H, 3.98, Found: C, 40.11; H, 3.52 %.

Synthesis of [(Cym)Os{P(OMe)$_3$}Br$_2$] **72**



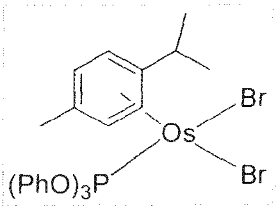
This compound was prepared using the same procedure as described for the preparation of compound **69**, using [(Cym)OsBr$_2$]$_2$ (200 mg, 0.206 mmol) and P(OMe)$_3$ (51 mg, 0.413 mmol). The product was obtained as a red-orange crystalline solid. Yield (185 mg, 74%); m.p. 154-157°C; ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm: 1.25 (d, 6H J = 6.95 Hz) $CH(C\underline{H}_3)_2$, 2.33 (d, 3H J = 1.71 Hz) $C(C\underline{H}_3)$, 2.99 (q, 1H J = 7.04, 7.23 , 7.23 Hz) $C\underline{H}(CH_3)_2$, 3.58 (d, 9H J = 10.90 Hz) $P\text{-}(OC\underline{H}_3)_3$, 5.49 (d, 2H J = 5.88 Hz) $C_6\underline{H}_4$, 5.64 (d, 2H J = 5.93 Hz) $C_6\underline{H}_4$; ^{31}P NMR (121 MHz, CDCl$_3$) δ ppm: 68.06 (s) $^1J(^{187}Os\text{-}^{31}P)$ = 455 Hz; Elemental analysis calculated for $C_{13}H_{23}O_3Br_2OsP$: C, 25.66; H, 3.78, Found: C, 25.29; H, 3.73 %.

Synthesis of [(Cym)Os{P(OBu^n)$_3$}Br$_2$] **73**



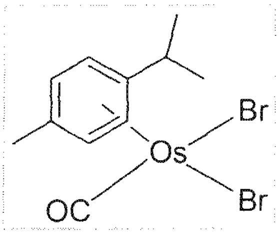
This compound was prepared using the same procedure as described for the preparation of compound **69**; using [(Cym)OsBr$_2$]$_2$ (1.000 g, 1.032 mmol) and P(OBu^n)$_3$ (516 mg, 2.065 mmol). The product was isolated as a bright orange solid. Yield (1.284 g, 85%); m.p. 57-60°C; ^{1}H NMR (400 MHz, CDCl$_3$) δ ppm: 0.83-0.95 (m, 9H) $P\text{-}\{O(CH_2)_3C\underline{H}_3\}_3$, 1.21 (d, 6H J = 6.95 Hz) $CH(C\underline{H}_3)_2$, 1.36 (qd, 6H J = 14.38, 7.24, 7.24, 7.15 Hz) $P\text{-}\{O(CH_2)_2C\underline{H}_2CH_3\}_3$, 1.52-1.69 (m, 6H) $P\text{-}\{OCH_2C\underline{H}_2CH_2CH_3\}_3$, 2.28 (s, 3H) $C(C\underline{H}_3)$, 2.87-2.92 (m, 1H) $C\underline{H}(CH_3)_2$, 3.76 (dd, 6H J = 6.90 , 13.90 Hz) $P\text{-}\{OC\underline{H}_2(CH_2)_2CH_3\}_3$, 5.43 (d, 2H J = 5.76 Hz) $C_6\underline{H}_4$, 5.57 (d, 2H J = 5.72 Hz) $C_6\underline{H}_4$; ^{31}P NMR (121 MHz, CDCl$_3$) δ ppm: 62.43 (s) $^1J(^{187}Os\text{-}^{31}P)$ = 449 Hz; Elemental analysis calculated for $C_{22}H_{41}O_3Br_2OsP$: C, 35.97; H, 5.58, Found: C, 35.95; H, 5.39 %;

Synthesis of $[(Cym)Os\{(P(OPh)_3\}Br_2]$ **74**



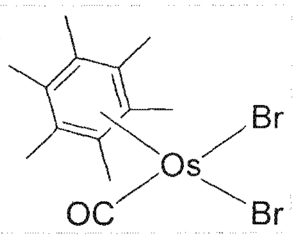
This compound was prepared using the same procedure as described for the preparation of compound **69**, using $[(Cym)OsBr_2]_2$ (500 mg, 0.516 mmol) and $P(OPh)_3$ (320 mg, 1.033 mmol). The product was isolated as an orange solid. Yield (662 mg, 81%); m.p. 175-177°C; ^1H NMR (300 MHz, $CDCl_3$) δ ppm: 1.20 (d, 6H $J = 6.99$ Hz) $CH(C\underline{\mathbf{H}}_3)_2$, 2.23 (s, 3H) $C(C\underline{\mathbf{H}}_3)$, 2.55-2.78 (m, 1H) $C\underline{\mathbf{H}}(CH_3)_2$, 5.16 (d, 2H $J = 5.92$ Hz) $C_6\underline{\mathbf{H}}_4$, 5.48 (d, 2H $J = 5.92$ Hz) $C_6\underline{\mathbf{H}}_4$, 7.09-7.36 (m, 15H) $P(O\underline{\mathbf{Ph}})_3$; ^{31}P NMR (121 MHz, $CDCl_3$) δ ppm: 52.28 (s), $^1J(^{187}Os\text{-}^{31}P) = 476$ Hz; Elemental analysis calculated for $C_{28}H_{29}Br_2O_3OsP$: C, 42.33; H, 3.68, Found: C, 42.45; H, 3.18 %.

Synthesis of $[(Cym)Os(CO)Br_2]$ **75**



CO gas was bubbled through a suspension of $[(Cym)OsBr_2]_2$ (500 mg, 0.195 mmol) in *n*-hexane (25 ml) at room temperature. After 45 min. the solvent was removed using a rotary evaporator to give a red-orange solid which was dried under vacuum for 1 hour. Yield (482 mg, 91%); decomposes without melting above 200°C; ^1H NMR (300 MHz, $CDCl_3$) δ ppm: 1.20 (d, 6H $J = 6.99$ Hz) $CH(C\underline{\mathbf{H}}_3)_2$, 2.13 (s, 3H) $C(C\underline{\mathbf{H}}_3)$, 2.77 (q, 1H $J = 7.04, 7.23, 7.23$ Hz) $C\underline{\mathbf{H}}(CH_3)_2$, 5.14 (d, 2H $J = 5.82$ Hz) $C_6\underline{\mathbf{H}}_4$, 5.47 (d, 2H $J = 5.90$ Hz) $C_6\underline{\mathbf{H}}_4$; Elemental analysis calculated for $C_{11}H_{14}Br_2OOs$: C, 25.79; H, 2.75, Found: C, 25.55; H, 2.66 %; FTIR (ν_{max}/cm^{-1}, DCM): 2022 s (C≡O).

Synthesis of $[(\eta^6\text{-}C_6Me_6)Os(CO)Br_2]$ **76**

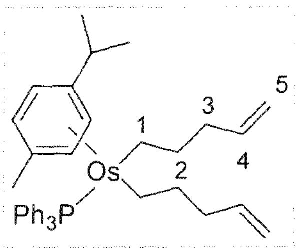


$[Os(\eta^6\text{-}C_6Me_6)Br_2]_2$ (200 mg, 0.195 mmol) was transferred into a 250 ml round bottom flask and dissolved in dry chloroform (40 ml). CO gas was then bubbled through the solution at room temperature. After 45 min. the solvent was removed using a rotary evaporator to give a dark orange solid which was dried under vacuum for 1 hour. Yield (89 mg, 42%); decomposes without melting above 280°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 1.98 (s, 18H) {$C_6(C\underline{H}_3)_6$}, Elemental analysis calculated for $C_{13}H_{18}Br_2OOs$: C, 28.90; H, 3.33, Found: C, 28.52; H, 3.85 %; FTIR (ν_{max}/cm^{-1}, $CHCl_3$): 2005 s (C≡O).

5.4 Preparation of osmium bis(alkenyl) complexes

Generally the bis(alkenyl) complexes **77**-**85** were prepared by treating the dibromide precursors with excess of the appropriate alkenyl Grignard reagent. These complexes were obtained in good yields but were not stable, thus they have only been characterized by ^{1}H and ^{31}P NMR spectroscopy, IR spectroscopy for complexes **84** and **85** and mass spectrometry in the case of complex **85**. Further characterization of these complexes could not be done due to their unstable nature.

Synthesis of [(Cym)(PPh$_3$)Os{(CH$_2$)$_3$CH=CH$_2$}$_2$] **77**

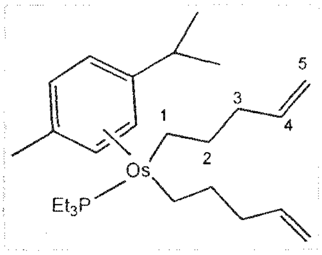


$[Os(Cym)(PPh_3)Br_2]$ (1.000 g, 1.420 mmol) was dried under vacuum in a Schlenk tube for 10 minutes and dissolved in freshly dried THF (30 ml). Then 5-pentenyl Grignard reagent (0.54 M, 10.56 ml, 5.690 mmol) was added to this orange solution under N_2 at -78°C. The solution was then allowed to reach room temperature and stirred for 18 hours, during which time the solution had turned from orange to yellow. A saturated NH_4Cl solution (15 ml) was added to the solution at -78°C in order to hydrolyze the excess Grignard reagent. After reaching room temperature dichloromethane (20 ml) was added and the organic layer was then separated, dried over anhydrous magnesium sulphate and filtered. The volatiles were removed using a rotary evaporator to give a yellow-brown oil which was dried under vacuum for 30 minutes. Yield (745 mg, 72%); ^{1}H NMR (300 MHz, C_6D_6) δ ppm: 0.82-0.91 (m, 4H) H1, 1.21 (d, 6H J = 6.99 Hz) $CH(C\underline{H}_3)_2$, 1.40-1.88 (m, 8H) H2-H3, 1.99 (s, 3H) $C(C\underline{H}_3)$, 2.98 (q, 1H J = 7.04, 7.23, 7.23 Hz) $C\underline{H}(CH_3)_2$, 4.52-5.04 (m, 4H) H5, 5.32 (d, 2H J = 5.90

Hz) $C_6\underline{H}_4$, 5.53 (d, 2H J = 5.88 Hz) $C_6\underline{H}_4$, 5.61-5.79 (m, 2H) H4, 7.28-7.82 (m, 15H) $P\underline{Ph}_3$; ^{31}P NMR (121 MHz, $CDCl_3$) δ ppm: 12.61 (s).

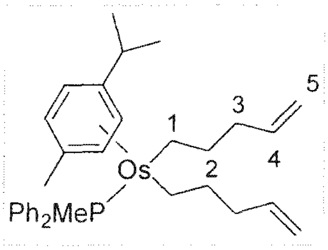
Synthesis of [(Cym)(PEt

Synthesis of $[(Cym)(PEt_3)Os\{(CH_2)_3CH{=}CH_2\}_2]$ **78**



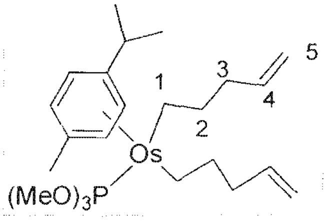
Compound **78** was prepared by a similar procedure as described for the preparation of compound **77**, using $[Os(Cym)(PEt_3)Br_2]$ (150 mg, 0.249 mmol) in dry THF (30ml) and 5-pentenyl Grignard reagent (0.21 M, 4.70 ml, 0.996 mmol). The product was isolated as a brown semi-solid, after the same work-up as outlined in the synthesis of complex **77**. Yield (141 mg, 95%); ^1H NMR (400 MHz, C_6D_6) δ ppm: 0.80-0.88 (m, 4H) H1, 1.02-1.30 (m, 15H) $CH(C\underline{H}_3)_2$ and $P\text{-}(CH_2C\underline{H}_3)_3$, 1.55-2.11 (m, 14H) H2-H3 and $P\text{-}(C\underline{H}_2CH_3)_3$, 2.26 (s, 3H) $C(C\underline{H}_3)$, 2.88 (q, 1H J = 7.04, 7.23 , 7.23 Hz) $C\underline{H}(CH_3)_2$, 4.86-5.13 (m, 4H) H5, 5.57 (d, 2H J = 5.96 Hz) $C_6\underline{H}_4$, 5.70 (d, 2H J = 5.81 Hz) $C_6\underline{H}_4$, 5.75-5.89 (m, 2H) H4; ^{31}P NMR (121 MHz, $CDCl_3$) δ ppm: -2.76 (s).

Synthesis of $[(Cym)(PMePh_2)Os\{(CH_2)_3CH{=}CH_2\}_2]$ **79**



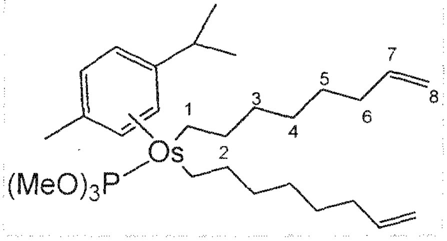
Compound **79** was prepared using a similar procedure as described for the preparation of compound **77**, using $[Os(Cym)(PMePh_2)Br_2]$ (150 mg, 0.218 mmol) in freshly dried THF (25 ml) and the 5-pentenyl Grignard reagent (0.32 M, 2.73 ml, 0.874 mmol). This compound was obtained as a dark brown oil. Yield (109 mg, 76%); ^1H NMR (300 MHz, C_6D_6) δ ppm: 0.79-0.89 (m, 4H) H1, 1.21 (dd, 6H J = 17.09, 10.07 Hz) $CH(C\underline{H}_3)_2$, 1.42-1.86 (m, 8H) H2-H3, 1.99-2.09 (m, 3H) $P\text{-}C\underline{H}_3Ph_2$, 2.22 (s, 3H) $C(C\underline{H}_3)$, 2.89 (q, 1H J = 7.04, 7.23, 7.23 Hz) $C\underline{H}(CH_3)_2$, 4.86-5.12 (m, 4H) H5, 5.19 (d, 2H J = 5.06 Hz) $C_6\underline{H}_4$, 5.43 (d, 2H J = 5.04 Hz) $C_6\underline{H}_4$, 5.65-5.84 (m, 2H) H4, 7.01-7.70 (m, 10H) $P\text{-}CH_3\underline{Ph}_2$; ^{31}P NMR (121 MHz, $CDCl_3$) δ ppm: -4.13 (s).

Synthesis of $[(Cym)\{P(OMe)_3\}Os\{(CH_2)_3CH=CH_2\}_2]$ **80**



$[Os(Cym)\{P(OMe)_3\}Br_2]$ (100 mg, 0.158 mmol) was dried under vacuum in a Schlenk tube for 10 minutes and dissolved in freshly dried THF (30 ml). Then 5-pentenyl Grignard reagent (0.54 $\underline{M}$, 1.2 ml, 0.632 mmol) was added to this orange solution under N_2 at -78°C. The solution was then allowed to reach room temperature and stirred at this temperature for 18 hours, during which time the solution had turned from orange to yellow. A saturated NH_4Cl solution (15 ml) was added to the solution at -78°C. After reaching room temperature dichloromethane (20 ml) was added and the organic layer was separated, dried over anhydrous magnesium sulphate and filtered. The volatiles were removed using a rotary evaporator to give a yellow oil which was dried under vacuum for 30 minutes. Yield (73 mg, 76%); ^{1}H NMR (400 MHz, C_6D_6) δ ppm : 0.86-0.89 (m, 4H) H1, 1.20 (dd, 6H *J* = 6.91, 2.21 Hz) $CH(C\underline{H}_3)_2$, 1.61-1.92 (m, 4H) H2, 2.07 (dd, 4H J = 13.92, 6.89 Hz) H3, 2.17 (s, 3H) $C(C\underline{H}_3)$, 2.99 (q, 1H J = 7.04, 7.23, 7.23 Hz) $C\underline{H}(CH_3)_2$, 3.69 (d, 9H J = 10.99 Hz) $P\text{-}(OC\underline{H}_3)_3$, 4.84-5.01 (m, 4H) H5, 5.16 (d, 2H J = 5.61 Hz) $C_6\underline{H}_4$, 5.42 (d, 2H J = 5.61 Hz) $C_6\underline{H}_4$, 5.81-5.98 (m, 2H) H4; ^{31}P NMR (121 MHz, $CDCl_3$) δ ppm: 82.65 (s) , $^1J(^{187}Os\text{-}^{31}P)$ = 487 Hz.

Synthesis of $[(Cym)\{P(OMe)_3\}Os\{(CH_2)_6CH=CH_2\}_2]$ **81**

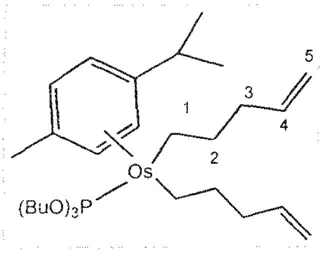


Compound **81** was prepared by a similar procedure as that described for the preparation of compound **80**, using $[Os(Cym)\{P(OMe)_3\}Br_2]$ (100 mg, 0.164 mmol) in freshly dried THF (30 ml) and 8-octenyl Grignard reagent (0.55 $\underline{M}$, 3.6 ml, 0.658 mmol). After the same work-up as outlined in the synthesis of complex **80**, the product was obtained as a light brown oil. Yield (79 mg, 75%); ^{1}H NMR (400 MHz, C_6D_6) δ ppm : 0.84-0.89 (m, 4H) H1, 1.20 (dd, 6H *J* = 6.91, 2.21 Hz) $CH(C\underline{H}_3)_2$, 1.61-2.03 (m, 16H) H2-H5, 2.07 (dd, 4H J = 13.92, 6.89 Hz) H6, 2.17 (s, 3H) $C(C\underline{H}_3)$, 2.99

(q, 1H J = 7.04, 7.23, 7.23 Hz) $C\underline{H}(CH_3)_2$ 3.72 (d, 9H J = 10.99 Hz) P-$(OC\underline{H}_3)_3$, 4.72-5.21 (m, 4H) H8, 5.16 (d, 2H J = 5.61 Hz) $C_6\underline{H}_4$, 5.42 (d, 2H J = 5.61 Hz) $C_6\underline{H}_4$, 5.83-5.98 (m, 2H) H7; ^{31}P NMR (121 MHz, $CDCl_3$) δ ppm: 84.20 (s) , $^1J(^{187}Os\text{-}^{31}P)$ = 479 Hz.

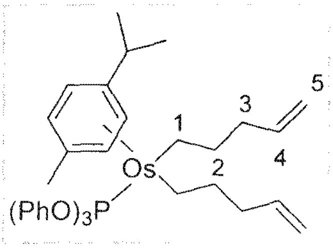
Synthesis of $[(Cym)\{P(OBu^n)_3\}Os\{(CH_2)_3CH{=}CH_2\}_2]$ **82**

Compound **82** was prepared by a similar procedure as described for the preparation of compound **80**, using $[Os(Cym)\{P(OBu^n)_3\}Br_2]$ (190 mg, 0.259 mmol) in freshly dried THF (35 ml) and 5-pentenyl Grignard reagent (2.0 $\underline{M}$, 0.5 ml, 1.035 mmol). The product was obtained as a yellow oil. Yield (178 mg, 97%); ^{1}H NMR (300 MHz, C_6D_6) δ ppm: 0.78-0.89 (m, 13H) H1 and P-$\{O(CH_2)_3C\underline{H}_3\}_3$, 1.24 (d, 6H J = 6.93 Hz) $CH(C\underline{H}_3)_2$, 1.40-1.70 (m, 16H) H2 and P-$\{OCH_2(C\underline{H}_2)_2CH_3\}_3$, 1.87-2.03 (m, 4H) H3, 2.28 (s 3H) $C(C\underline{H}_3)$, 2.92 (m, 1H) $C\underline{H}(CH_3)_2$, 3.77 (dd, 6H J = 6.90 , 13.90 Hz) P-$\{OC\underline{H}_2(CH_2)_2CH_3\}_3$, 4.72-5.05 (m, 4H) H5, 5.56 (d, 2H J = 5.76 Hz) $C_6\underline{H}_4$, 5.62 (d, 2H J = 5.72 Hz) $C_6\underline{H}_4$, 5.68-5.84 (m, 2H) H4; ^{31}P NMR (121 MHz, $CDCl_3$) δ ppm: 79.41 (s) , $^1J(^{187}Os\text{-}^{31}P)$ = 476 Hz.

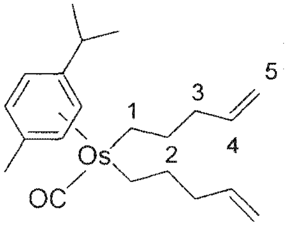


Synthesis of $[(Cym)\{P(OPh)_3\}Os\{(CH_2)_3CH{=}CH_2\}_2]$ **83**

Compound **83** was prepared using a similar procedure as described for the preparation of compound **77**, using $[Os(Cym)\{P(OPh)_3\}Br_2]$ (500 mg, 0.628 mmol) in freshly dried THF (30 ml) and 5-pentenyl Grignard reagent (0.32 $\underline{M}$, 7.80 ml, 2.512 mmol). The product was obtained as a brown oil. Yield (355 mg, 73%); ^{1}H NMR (300 MHz, C_6D_6) δ ppm: 0.76-0.94 (m, 4H) H1, 1.21 (d, 6H J = 6.99 Hz) $CH(C\underline{H}_3)_2$, 1.00-1.14 (m, 4H) H2, 1.96 (s, 3H) $C(C\underline{H}_3)$, 1.99-2.08 (m, 4H) H3, 2.78-2.98 (m, 1H) $C\underline{H}(CH_3)_2$, 4.48-4.85 (m, 4H) H5, 5.21 (d, 2H J = 5.41 Hz) $C_6\underline{H}_4$, 5.49 (d, 2H J = 5.41 Hz) $C_6\underline{H}_4$, 5.55-5.91 (m, 2H) H4, 6.68-7.41 (m, 15H) $P(O\underline{Ph})_3$; ^{31}P NMR (121 MHz, $CDCl_3$) δ ppm: 66.85 (s), $^1J(^{187}Os\text{-}^{31}P)$ = 520 Hz.

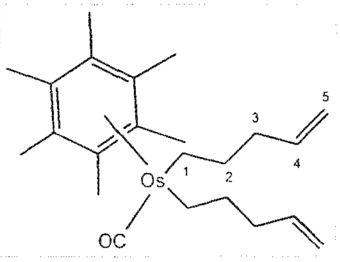


Synthesis of $[(Cym)(CO)Os\{(CH_2)_3CH=CH_2\}_2]$ **84**



Compound **84** was prepared using a similar procedure as described for the preparation of compound **77**, using $[Os(Cym)(CO)Br_2]$ (150 mg, 0.291 mmol) in freshly dried THF (25 ml) and 5-pentenyl Grignard reagent (0.32 $\underline{M}$, 3.64 ml, 1.167 mmol). This compound was obtained as a dark brown oil after an aqueous work-up. Yield (96 mg, 68%) ^1H NMR (300 MHz, C_6D_6) δ ppm: 0.77-0.91 (m, 4H) H1, 1.18 (d, 6H J = 6.99 Hz) $CH(C\underline{H}_3)_2$, 1.20-1.88 (m, 8H) H2-H3, 1.96 (s, 3H) $C(C\underline{H}_3)$, 2.68 (q, 1H J = 7.04, 7.23, 7.23 Hz) $C\underline{H}(CH_3)_2$, 4.83-5.08 (m, 4H) H5, 5.10 (d, 2H J = 5.67 Hz) $C_6\underline{H}_4$, 5.35 (d, 2H J = 5.77 Hz) $C_6\underline{H}_4$, 5.45-5.90 (m, 2H) H4; FTIR (ν_{max}/cm^{-1}, DCM): 1965 s (C≡O).

Synthesis of $[(\eta^6\text{-}C_6Me_6)(CO)Os\{(CH_2)_3CH=CH_2\}_2]$ **85**

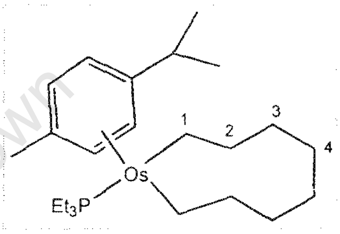


This compound was prepared in a similar method as that described for the preparation of compound **77**, using $[Os[(\eta^6\text{-}C_6Me_6)(CO)Br_2]$ (60 mg, 0.111 mmol) in dry benzene and 5-pentenyl Grignard reagent (1.66 $\underline{M}$, 0.26 ml, 0.444 mmol). The product was obtained as a brown oil. Yield (28 mg, 49%) ^1H NMR (300 MHz, C_6D_6) δ ppm: 0.82-0.89 (m, 4H) H1, 1.02-1.80 (m, 8H) H2-H3, 2.03 (s, 18H) $\{C_6(C\underline{H}_3)_6\}$, 4.93-5.20 (m, 4H) H5, 5.55 (d, 2H J = 5.18 Hz) H4; FTIR (ν_{max}/cm^{-1}, $CHCl_3$): 1897 s (C≡O); LRMS (FAB) $C_{23}H_{26}OOs$: m/z = 519.3 $[M]^+$, 451.2 $[M\text{-}(CH_2)_3CH=CH_2]^+$, 383.1 $[M\text{-}2((CH_2)_3CH=CH_2)]^+$.

5.5 Preparation of osmacycles

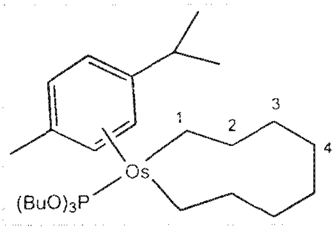
The osmacycles were prepared by treatment of the appropriate osmium dibromide complexes with a di-Grignard reagent. Products were obtained in low yields and were also unstable and were thus characterized only by ^{1}H and ^{31}P NMR spectroscopy and IR spectroscopy for complex **88**.

Synthesis of $[(Cym)(PEt_3)\overline{Os\{(CH_2)_7CH_2\}}]$ **86**



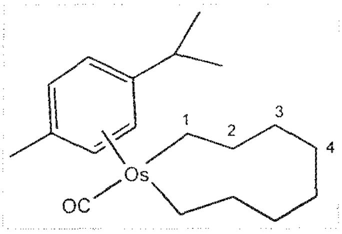
$[Os(Cym)(PEt_3)Br_2]$ (100 mg, 0.166 mmol) was dried under vacuum in a Schlenk tube for 10 minutes. Dry THF (35 ml) was added to the tube followed by $MgCl(CH_2)_8ClMg$ (0.37 <u>M</u>, 0.89 ml, 0.332 mmol) at -78°C and under a nitrogen atmosphere. The orange solution was then allowed to reach room temperature and stirred for 18 hours during which time the solution turned from orange to yellow. A saturated NH_4Cl solution (15 ml) was added to the solution at -78°C. After reaching room temperature, dichloromethane (20 ml) was added and the organic layer was separated, dried over anhydrous magnesium sulphate and filtered. The volatiles were removed using a rotary evaporator to give a brown semi-solid. This semi-solid was then dried under vacuum for 2 hours. Yield (49 mg, 52%); ^{1}H NMR (300 MHz, C_6D_6) δ ppm: 0.80-0.88 (m, 4H) H1, 1.02-1.38 (m 27H) H2-H4, $CH(C\underline{H}_3)_2$ and $P\text{-}(CH_2C\underline{H}_3)_3$, 2.06-2.20 (m, 6H) $P\text{-}(C\underline{H}_2CH_3)_3$, 2.26 (s, 3H) $C(C\underline{H}_3)$, 2.88 (q, 1H J = 7.04 H, 7.23, 7.23 Hz) $C\mathbf{H}(CH_3)_2$, 5.55 (d, 2H J = 5.96 Hz) $C_6\underline{H}_4$, 5.60 (d, 2H J = 5.81 Hz) $C_6\underline{H}_4$; ^{31}P NMR (121 MHz, $CDCl_3$) δ ppm: -2.80 (s).

Synthesis of $[(Cym)\{P(OBu^n)_3\}\overline{Os\{(CH_2)_7CH_2\}}]$ **87**



This compound was prepared using a similar method as compound **86** using, $[Os(Cym)\{P(OBu^n)_3\}Br_2]$ (130 mg, 0.177 mmol) in dry THF (35 ml) and $MgCl(CH_2)_8ClMg$ (0.37 $\underline{M}$, 0.95 ml, 0.354 mmol). After the same work-up as for compound **86**, a dark yellow oil was isolated. Yield (51 mg, 42%); ^1H NMR (400 MHz, C_6D_6) δ ppm: 0.78-0.91 (m, 13H) H1 and P-$\{O(CH_2)_3C\underline{H}_3\}_3$, 1.23 (d 6H J = 6.93 Hz) $CH(C\underline{H}_3)_2$, 1.40-1.70 (m, 16H) H2 and P-$\{OCH_2(C\underline{H}_2)_2CH_3\}_3$, 1.82-2.19(m, 8H) H3-H4, 2.28 (s 3H) $C(C\underline{H}_3)$, 2.92 (m, 1H) $C\underline{H}(CH_3)_2$, 5.43 (d, 2H J = 5.76 Hz) $C_6\underline{H}_4$, 5.57 (d, 2H J = 5.72 Hz) $C_6\underline{H}_4$; ^{31}P NMR (121 MHz, $CDCl_3$) δ ppm: 79.59 (s) , J(Os-P) = 476 Hz.

Synthesis of $[(Cym)(CO)\overline{Os\{(CH_2)_7CH_2\}}]$ **88**

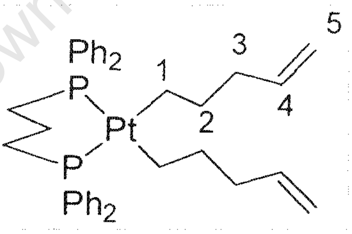


This compound was prepared in a similar method as compound **86** using, $[Os(Cym)(CO)Br_2]$ (200 mg, 0.389 mmol) in dry THF (30 ml) and $MgCl(CH_2)_8ClMg$ (0.65 $\underline{M}$, 2.39 ml, 1.556 mmol). After the same work-up as for compound **86**, a dark yellow oil was isolated. Yield (72 mg, 40%); ^1H NMR (300 MHz, C_6D_6) δ ppm: 0.76-0.88 (m, 4H) H1, 1.18 (d, 6H J = 6.99 Hz) $CH(C\underline{H}_3)_2$, 1.22-1.92 (m, 12H) H2-H4, 1.95 (s, 3H) $C(C\underline{H}_3)$, 2.72 (q, 1H J = 7.04, 7.23, 7.23 Hz) $C\underline{H}(CH_3)_2$, 5.12 (d, 2H J = 5.67 Hz) $C_6\underline{H}_4$, 5.35 (d, 2H J = 5.77 Hz) $C_6\underline{H}_4$; FTIR (ν_{max}/cm^{-1}, DCM): 1965 s (C≡O).

5.6 Preparation of platinum bis(alkenyl) complexes

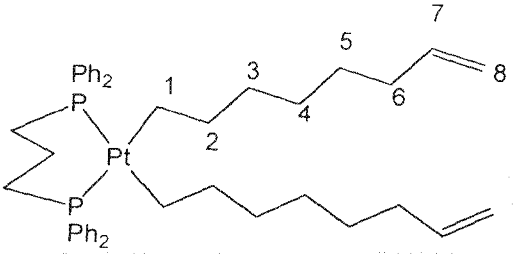
Platinum bis(alkenyl) complexes **89** and **90** were prepared by transmetallation of [(dppp)PtCl$_2$] in diethyl ether with either 5-pentenyl or 8-octenyl Grignard reagents. These compounds were obtained as stable white crystalline solids in good yields and have been characterized by melting point, elemental analysis, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy as well as mass spectrometry for complex **90**. Characterization data agrees well with literature reports [5].
The same atom numbering applies for both hydrogens and carbons.

Synthesis of [(dppp)Pt{(CH$_2$)$_3$CH=CH$_2$}$_2$] ***89*** [5]



[Pt(dppp)Cl$_2$] (508 mg, 0.746 mmol) was transferred into a Schlenk tube and dried under vacuum for 10 min, dry diethylether (50 ml) was then added followed by 5-pentenyl Grignard reagent (0.54 M, 6 ml, 2.94 mmol) at -78°C. The solution was then stirred at room temperature under N$_2$ for 16 hours, during which time the cloudy solution had become transparent. A saturated NH$_4$Cl solution (20 ml) was added to the solution at -78°C. After reaching room temperature dichloromethane (20 ml) was added to the solution and 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 dried under vacuum for 2 hours. Yield (441 mg, 80%); m.p. 111-113°C; ^{1}H NMR (300 MHz, CDCl$_3$) δ ppm: 0.96-1.11 (m, 4H) H1, 1.09-1.31 (m, 6H) H2 and $PCH_2C\underline{\mathbf{H}}_2CH_2P$, 1.62 (q, 4H J = 7.02 Hz, J = 7.02 Hz) H3, 2.44-2.54 (m, 4H) $PC\underline{\mathbf{H}}_2CH_2C\underline{\mathbf{H}}_2P$, 4.61-4.81 (m, 4H) H5, 5.46-5.64 (m, 2H) H4, 7.31-7.59 (m, 20H) $P\underline{\mathbf{Ph}}_2$; ^{13}C NMR (100 MHz, CDCl$_3$) δ ppm: 14.28 (s, 2C) C1, 23.93 (s, 1C) $PCH_2\underline{\mathbf{C}}H_2CH_2P$, 25.20 (s, 2C) $P\underline{\mathbf{C}}H_2CH_2\underline{\mathbf{C}}H_2P$, 27.63-28.02 (m, 2C) C2, 31.53 (s, 2C) C3, 112.31 (s, 2C) C5, 127.79-133.85 (m, 24C) $P\underline{\mathbf{Ph}}_2$, 140.92 (s, 2C) C4; ^{31}P NMR (121 MHz, CDCl$_3$) δ ppm: 3.45 (s), $^1J(^{195}Pt-^{31}P)$ = 1623 Hz; Elemental analysis calculated for $C_{37}H_{44}P_2Pt$: C, 59.59; H, 5.95, Found: C, 59.72; H, 5.74 %.

Synthesis of $[(dppp)Pt\{(CH_2)_6CH{=}CH_2\}_2]$ **90** [5]



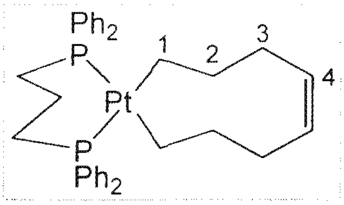
$[(dppp)PtCl_2]$ (1.014 g, 1.49 mmol) was dried under vacuum in a Schlenk tube. Dry Et_2O (50 ml) was added to the tube, followed by 8-octenyl Grignard reagent (0.5 $\underline{M}$, 9 ml, 2.86 mmol) of at -78°C, a pale white precipitate immediately resulted. The mixture was stirred at room temperature for 16 hours, during which time the precipitate disappeared. After 16 hours NH_4Cl solution (15 ml) was added to the solution at -78°C in order to remove excess Grignard reagent. On reaching room temperature, dichloromethane (20 ml) was added to the solution and the organic layer was separated, dried over anhydrous magnesium sulfate and the solvent was removed using a rotary evaporator to yield a residual colourless oil. The oil was recrystallized from Et_2O (30 ml). The solvent was once again removed using a rotary evaporator and dried under vacuum for 1 hour yielding the product as colourless crystals. Yield (763 mg, 62 %); mp 67-70 °C; ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 0.88 (dd, 4H J =12.87, 6.33 Hz) H1, 0.93-1.05 (m, 2H) $(PCH_2C\underline{\mathbf{H}}_2CH_2P)$, 1.11-1.24 (m, 12H) H2-H4, 1.85-1.96 (m, 4H) H5, 2.00-2.09 (m, 4H) H6, 2.45-2.53 (m, 4H) $(PC\underline{\mathbf{H}}_2CH_2C\underline{\mathbf{H}}_2P)$, 4.85 (td, 2H J=2.36, 1.22 Hz) H8, 5.02 (m, 2H) H8, 5.66-5.90 (m, 2H) H7, 7.29-7.62 (m, 20H) $P\underline{\mathbf{Ph}}_2$; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 14.12 (s, 2C) C1, 22.99 (s, 1C) $PCH_2\underline{\mathbf{C}}H_2CH_2P$, 25.80 (s, 2C) $P\underline{\mathbf{C}}H_2CH_2\underline{\mathbf{C}}H_2P$, 29.09-29.93 (br m, 8C) C2-C5, 33.92-34.04 (m, 2C) C6, 114.31 (s, 2C) C8, 127.53-133.64 (m, 24C) $P\underline{\mathbf{Ph}}_2$, 139.07 (s, 2C) C7; ^{31}P NMR (121 MHz, $CDCl_3$) δ ppm: 3.40 (s) $^1J(^{195}Pt\text{-}^{31}P)$ = 1603 Hz; Elemental analysis, calculated for $C_{43}H_{56}P_2Pt$: C, 62.24; H, 6.75; Found: C, 62.82; H, 6.35, %; LRMS (FAB) $C_{43}H_{56}P_2Pt$: m/z = 829.2 $[M]^+$, 718.2 $[M\text{-}(CH_2)_6CH{=}CH_2]^+$, 607.1 $[M\text{-}2((CH_2)_6CH{=}CH_2)]^+$.

5.7 Preparation of platinacycles

Platinacycles **91**- **94** were prepared by RCM of bis(alkenyl) complexes **89** and **90** at 60°C using Grubbs' 1st generation catalyst in dichloromethane followed by hydrogenation with 10 wt% Pd/C in toluene solvent. These compounds have been characterized by elemental analysis, ^1H, ^{13}C and ^{31}P NMR spectroscopy as well as mass spectrometry for complex **92**. Platinacycloalkanes **95** and **96** were synthesized in reasonable yields from the reaction of $[(COD)PtCl_2]$ with $ClMg(CH_2)_nMgCl$ (n = 4 and 8) followed by displacement of the COD with either $PEtPh_2$ or dppp in diethyl ether. These compounds have also been characterized by elemental analysis and ^1H, ^{13}C and ^{31}P NMR spectroscopy.

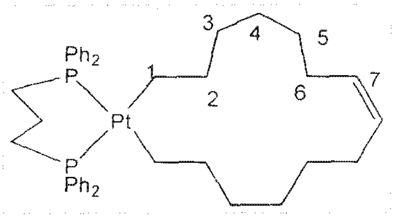
The same atom numbering applies for both hydrogens and carbons.

Synthesis of $[(dppp)Pt\{\overline{(CH_2)_3CH{=}CH(CH_2)_2CH_2}\}]$ ***91*** [5]



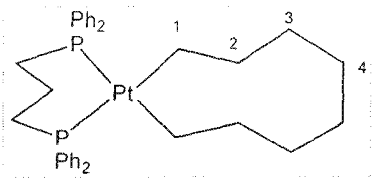
$[Pt(dppp)((CH_2)_3CH{=}CH_2)_2]$ (0.235 g, 0.315 mmol) was dissolved in dichromethane (20 ml). Grubbs' 1st generation catalyst (6 mg, 5 mol%) was added to the solution which was then refluxed at 60°C. After 8 hours the solvent was removed using a rotary evaporator to give a black oil as the crude product. The product was extracted with diethyl ether (5ml), filtered and dried under vacuum for 30 min. to give a white crystalline solid. Yield (171 mg, 76%); m.p. 161-164°C; ^1H NMR (300 MHz, $CDCl_3$) δ ppm: 0.89-1.08 (m, 4H) H1, 1.11-1.48 (m, 6H) H2 and $PCH_2C\underline{H}_2CH_2P$, 1.65-2.05 (m, 4H) H3, 2.49-2.54 (m, 4H) $PC\underline{H}_2CH_2C\underline{H}_2P$, 5.38-5.45 (m, 2H) H4, 7.08-7.83 (m, 20H) $P\underline{Ph}_2$; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 14.09 (s, 2C) C1, 22.64 (s, 1C) $PCH_2\underline{C}H_2CH_2P$, 25.52 (s, 2C) $P\underline{C}H_2CH_2\underline{C}H_2P$, 26.01-27.03 (m, 2C) C2, 30.28-31.57 (m, 2C) C3, 127.80- 133.41 (m, 24C) $P\underline{Ph}_2$, 141.02 (s, 2C) C4; ^{31}P NMR (121 MHz, $CDCl_3$) δ ppm: 3.45 (s), $^1J(^{195}Pt\text{-}^{31}P)$ = 1623 Hz, Elemental analysis calculated for $C_{35}H_{40}P_2Pt$: C, 58.57; H, 5.62, Found: C, 58.41; H, 5.98 %.

Synthesis of $[(dppp)\overline{Pt\{(CH_2)_6CH{=}CH(CH_2)_5CH_2}\}]$ ***92*** [5]



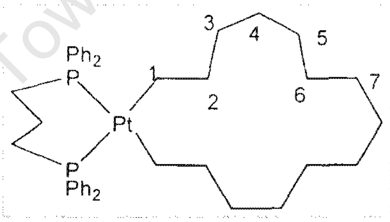
This complex was prepared in a similar method as complex **91** starting with compound **90** (302 mg, 0.36 mmol) in dichloromethane (35 ml) and (8 mg 5 mol%) of Grubbs' 1st generation catalyst. After refluxing for 8 hours the volatiles were removed using a rotary evaporator to afford a black oil. The oil was dissolved in dichloromethane (20 ml) and the solution was filtered, the solvent was once again removed using a rotary evaporator to yield a residual colourless oil, which was dried under vacuum for 1 hour, affording a colourless crystalline solid. Yield (280 mg, 96 %); mp 161-162 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 0.79-0.95 (m, 4H) H1, 0.98-1.11 (m, 2H) ($PCH_2C\underline{\mathbf{H}}_2CH_2P$), 1.19-1.35 (m, 12H) H2-H4, 1.47-1.53 (m, 4H) H5, 1.74-2.02 (m, 4H) H6, 2.32-2.66 (m, 4H) ($PC\mathbf{H}_2CH_2C\mathbf{H}_2P$), 5.15-5.54 (m, 2H) H7, 7.16-7.84 (m, 20H) $P\mathbf{Ph}_2$; ^{13}C NMR (100 MHz, C_6D_6) δ ppm: 15.03 (s, 2C) C1, 22.84 (s, 1C) $PCH_2\underline{\mathbf{C}}H_2CH_2P$, 25.98 (s, 2C) $P\underline{\mathbf{C}}H_2CH_2\underline{\mathbf{C}}H_2P$, 26.01-30.03 (br m, 8C) C2-C5, 31.18-31.77 (m, 2C) C6, 127.31- 133.38 (m, 24C) $P\underline{\mathbf{Ph}}_2$, 139.10 (s, 2C) C7; ^{31}P NMR (121 MHz, $CDCl_3$) δ ppm: 2.94 (s), $^1J(^{195}Pt\text{-}^{31}P)$ = 1602 Hz, 3.05 (s), $^1J(^{195}Pt\text{-}^{31}P)$ = 1600 Hz, 3.38 (s), $^1J(^{195}Pt\text{-}^{31}P)$ = 1602 Hz; Elemental analysis calculated for $C_{41}H_{52}P_2Pt$: C, 61.41; H, 6.54, Found: C, 61.23; H, 6.69 %; LRMS (FAB) $C_{41}H_{52}P_2Pt$: m/z = 801.3 $[M]^+$, 607.0 $[(dppp)Pt]^+$.

Synthesis of $[(dppp)\overline{Pt\{(CH_2)_7CH_2}\}]$ ***93*** [5]



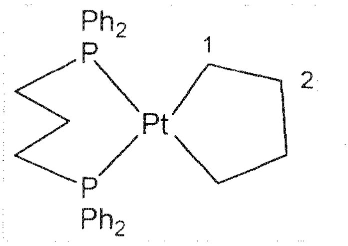
Platinacyclononene **91** (200 mg, 0.278 mmol) was transferred into a 100 ml round bottom flask and dissolved in dry toluene (35 ml). 10 wt% Pd/C (7 mg) was added to the flask. The flask was closed with a tap which was equipped with a H_2 gas filled balloon. The tap was opened thus allowing the H_2 gas to enter the flask and it was left to stir at room temperature. After 8 hours the solution was filtered and the solvent was removed under reduced pressure to give a colourless oil, which was dried under vacuum for 2 hours. Yield (180 mg, 90%); ^{1}H NMR (300 MHz, C_6D_6) δ ppm: 0.87-1.01 (m, 4H) H1, 1.05-1.36 (m,10H) H2-H3 and $PCH_2C\underline{H}_2CH_2P$, 1.38-1.56 (m, 4H) H4, 2.08-2.22 (m, 4H) $PC\underline{H}_2CH_2C\underline{H}_2P$, 6.97-7.66 (m, 20H) $P\underline{\mathbf{Ph}}_2$; ^{13}C NMR (100 MHz, C_6D_6) δ ppm: 15.00 (s, 2C) C1, 22.67 (s, 1C) $PCH_2\underline{C}H_2CH_2P$, 25.88 (s, 2C) $P\underline{C}H_2CH_2\underline{C}H_2P$, 28.13-29.44 (m, 4C) C2-C3, 30.15-31.98 (m, 2C) C4, 127.75- 133.38 (m, 24C) $P\underline{\mathbf{Ph}}_2$; ^{31}P NMR (121 MHz, C_6D_6) δ ppm: 3.89 (s), $^1J(^{195}Pt-^{31}P)$ = 1622 Hz; Elemental analysis calculated for $C_{35}H_{42}P_2Pt$: C, 58.41; H, 5.88, Found: C, 58.11; H, 5.65 %.

Synthesis of [(dppp)$\overline{Pt\{(CH_2)_{13}CH_2}$\}] ***94*** [5]



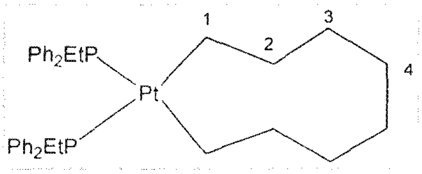
Platinacyclopentadecene **92** (200 mg, 0.250 mmol) was transferred into a 100 ml Schlenk round bottom flask and dried under vacuum for 10 minutes. Dry toluene 40 ml was transferred into the flask followed by Pd/C (8 mg). The flask and its contents were then immersed into liquid nitrogen for 15 min and evacuated. The flask was then closed with a stopper equipped with a hydrogen gas filled balloon. Upon reaching room temperature the tap on the stopper was opened thus allowing the H_2 to enter the flask. The solution was stirred at room temperature under a H_2 atmosphere for 10 hours. After 10 hours the solution was filtered and the solvent was removed using a rotary evaporator to give a colourless oil. The oil was washed with *n*-hexane (25 ml) and dried under vacuum for 2 hours, affording complex **94** as a colourless oil. Yield (120 mg, 60 %); ^{1}H NMR (300 MHz, C_6D_6) δ ppm: 0.75-0.96 (m, 4H) H1, 0.98-1.12 (m, 2H) ($PCH_2C\underline{H}_2CH_2P$), 1.13-1.46 (br m, 16H) H2-H5, 1.48-1.75 (m, 8H) H6-H7, 2.13-2.25 (m, 4H) ($PC\mathbf{H}_2CH_2C\mathbf{H}_2P$), 6.88-7.99 (m, 20H) $P\mathbf{Ph}_2$; ^{13}C NMR (100 MHz, C_6D_6) δ ppm: 15.02 (s, 2C) C1, 22.75 (s, 1C) $PCH_2\underline{C}H_2CH_2P$, 25.92 (s, 2C) $P\underline{C}H_2CH_2\underline{C}H_2P$, 26.42-30.15 (br m, 12C) C2-C7, 127.67- 133.81 (m, 24C) $P\underline{\mathbf{Ph}}_2$; ^{31}P NMR (121 MHz, C_6D_6) δ ppm: 3.82 (s), $^1J(^{195}Pt-^{31}P)$ = 1632 Hz; Elemental analysis calculated for $C_{41}H_{54}P_2Pt$: C, 61.26; H, 6.77, Found: C, 61.16; H, 6.59 %.

Synthesis of $[(dppp)\overline{Pt\{(CH_2)_3CH_2}\}]$ **95** [6]



$[Pt(COD)Cl_2]$ (800 mg, 1.167 mmol) and dry diethyl ether (30 ml) was transferred into a Schlenk tube under a N_2 atmosphere. The tube was brought to -78°C and $MgCl(CH_2)_4ClMg$ (0.20 $\underline{M}$, 11.67 ml, 4.671 mmol) was added to the solution. This was then left to stir for 10 min. during which time the solution had turned colourless. dppp (480 mg, 1.167 mmol) was then added to this clear solution and it was stirred for 16 hours at room temperature. After 16 hours the same work-up procedure as that described for the synthesis of compound **89** was followed. A colourless oil was isolated and dried under vacuum for 3 hours. Yield (406 mg, 52%); ^1H NMR (300 MHz, $CDCl_3$) δ ppm: 0.78-0.95 (m, 4H) H1, 1.14 -1.33 (m, 4H) H2, 1.36-1.50 (m, 2H) $PCH_2C\underline{H}_2CH_2P$, 2.36-2.62 (m, 4H) $PC\underline{H}_2CH_2C\underline{H}_2P$, 7.15-7.61 (m, 20H) $P\underline{\mathbf{Ph}}_2$; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 14.02 (s, 2C) C1, 22.57 (s, 1C) $PCH_2\underline{C}H_2CH_2P$, 25.72 (s, 2C) $P\underline{C}H_2CH_2\underline{C}H_2P$, 28.63 (s, 2C) C2, 127.66- 133.32 (m, 24C) $P\underline{\mathbf{Ph}}_2$; ^{31}P NMR (121 MHz, $CDCl_3$) δ ppm: 3.30 (s), $^1J(^{195}Pt-^{31}P)$ = 1608 Hz; Elemental analysis calculated for $C_{31}H_{34}P_2Pt$: C, 56.11; H, 5.16, Found: C, 56.71; H, 5.29 %.

Synthesis of $[(Ph_2EtP)_2\overline{Pt\{(CH_2)_7CH_2}\}]$ **96**



$[Pt(COD)Cl_2]$ (160 mg, 0.427 mmol) and dry diethyl ether (30 ml) was transferred into a Schlenk tube under N_2 gas atmosphere. The tube was brought to -78°C and $MgCl(CH_2)_8ClMg$ (0.65 $\underline{M}$, 2.63 ml, 1.711 mmol) was added to the solution. This was then left to stir for 10 min. during which time the solution had turned colourless. $PEtPh_2$ (182 mg, 0.854 mmol) was then added to this clear solution and it was stirred for 16 hours at room temperature. After 16 hours the same work-up procedure as that described for the synthesis of compound **89** was followed. A light brown oil was isolated and dried under vacuum for 2 hours. Yield (132 mg, 42%); ^{1}H NMR (300 MHz, C_6D_6) δ ppm: 0.86-0.94 (m, 4H) H1, 0.96 -1.13 (m, 6H) P-$\{(CH_2C\underline{\mathbf{H}}_3)Ph_2\}$, 1.20-1.42 (m, 12H) H2-H4, 1.46-1.61 (m, 4H) P-$\{(C\underline{\mathbf{H}}_2CH_3)Ph_2\}$, 7.01-7.40 (m, 20H) P-$\{(CH_2CH_3)\underline{\mathbf{Ph}}_2\}$; ^{13}C NMR (100 MHz, C_6D_6) δ ppm: 10.47 (s, 2C) P-$\{(CH_2\underline{\mathbf{C}}H_3)Ph_2\}$, 15.03 (s, 2C) C1, 24.70 (s, 2C) P-$\{(\underline{\mathbf{C}}H_2CH_3)Ph_2\}$, 28.58-29.45 (m, 4C) C2-C3, 31.81-32.02 (m, 2C) C4, 127.50- 134.00 (m, 24C) P-$\{(CH_2CH_3)\underline{\mathbf{Ph}}_2\}$; ^{31}P NMR (121 MHz, C_6D_6) δ ppm: 19.35 (s), $^1J(^{195}Pt\text{-}^{31}P)$ = 1725 Hz; Elemental analysis calculated for $C_{36}H_{46}P_2Pt$: C, 58.77; H, 6.30, Found: C, 58.16; H, 6.59 %.

5.8 Reactivity of platinacycles

5.8.1 Carbonylation of platinacycles and complex **90**.

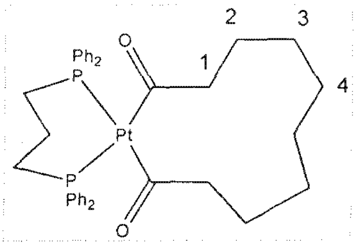
The same atom numbering applies for both hydrogens and carbons.

Preparation of complex ***97***

Complex **90** (262 mg, 0.358 mmol) was transferred into a round bottom flask and 25 mL of toluene was added. After bubbling the contents of the flask with CO gas for 5-6 min, the solution was stirred at room temperature under ambient pressure of carbon monoxide (balloon). After 72 h, the solvent was removed under reduced pressure. The residue was filtered and recrystallized from a CH_2Cl_2/hexane mixture (2:1 v/v) to give **97**. Yield (163 mg, 62%), mp 118-126 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 7.24-7.91 (m, 20H, Ph); 5.54-5.69 (m, 2H, =C$\underline{\mathbf{H}}$); 4.61-4.80 (m, 4H, =C$\underline{\mathbf{H}}_2$); 1.98-2.40 (m, 4H, P-C$\underline{\mathbf{H}}_2$); 1.16-1.86 (m, 12H, C$\underline{\mathbf{H}}_2$); ^{31}P NMR (121 MHz, $CDCl_3$) δ ppm: 15.77 (s) , $^1J(^{195}Pt\text{-}^{31}P)$ = 1408 Hz; Elemental analysis calculated for $C_{38}H_{42}O_2P_2Pt$: C, 57.94; H, 5.37. Found: C, 58.16; H, 5.42 %; FTIR (ν_{max}/cm^{-1}, DCM): 1608 s (C=C), 1680 s (C=O).

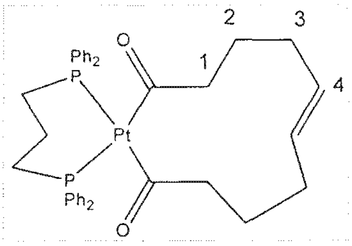
Preparation of complex ***98***

Complex **93** (242 mg, 0.336 mmol) was transferred into a 100 ml round bottom flask and dissolved in dry THF (25 ml). CO was then bubbled through the



solution for 10 minutes. The flask was then closed with a stopper containing a tap, which was in turn equipped with a CO gas filled balloon. The tap was opened allowing the gas to enter the flask while stirring at room temperature for 21 days, during which time the progress of the reaction was monitored by IR spectroscopy. After 21 days the solvent was removed from the now pale pink solution to give a light pink oil. Yield (200 mg, 77%); ^{1}H NMR (300 MHz, C_6D_6) δ ppm: 0.99-1.90 (m, 14H) H2-H4 and $PCH_2C\underline{\mathbf{H}}_2CH_2P$, 2.03-2.27 (m, 8H) H1 and $PC\underline{\mathbf{H}}_2CH_2C\underline{\mathbf{H}}_2P$, 6.93-7-75 (m, 20H) $P\underline{\mathbf{Ph}}_2$; ^{13}C NMR (100 MHz, C_6D_6) δ ppm: 22.72 (s, 1C) $PCH_2\underline{\mathbf{C}}H_2CH_2P$, 26.01 (s, 2C) $P\underline{\mathbf{C}}H_2CH_2\underline{\mathbf{C}}H_2P$, 27.85-32.47 (br m, 8C) C1-C4, 127.68- 133.81 (m, 24C) $P\underline{\mathbf{Ph}}_2$, 203.68 (s, 2C) $\underline{\mathbf{C}}$=O; ^{31}P NMR (121 MHz, C_6D_6) δ ppm: 15.41 (s), $^1J(^{195}Pt\text{-}^{31}P)$ = 1408 Hz; Elemental analysis calculated for $C_{37}H_{42}O_2P_2Pt$: C, 57.29; H, 5.46, Found: C, 57.38; H, 5.64 %; FTIR (ν_{max}/cm^{-1}, DCM): 1606 m (C=C), 1673 s (C=O).

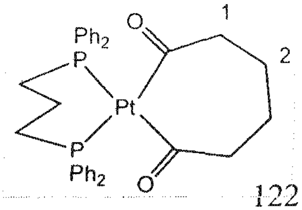
*Preparation of complex **99***



This compound was prepared in a similar method as compound **98** using, (100 mg, 0.139 mmol) of compound **91**. The product was isolated as a pale pink oil. Yield (74 mg, 69%); ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 1.00-2.09 (m, 10H) H2-H3 and $PCH_2C\underline{\mathbf{H}}_2CH_2P$, 2.38-2.62 (m, 8H) H1 and $PC\underline{\mathbf{H}}_2CH_2C\underline{\mathbf{H}}_2P$, 5.04-5.29 (m, 2H) H4, 7.11-7.91 (m, 20H Ph) $P\underline{\mathbf{Ph}}_2$; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 22.55 (s, 1C) $PCH_2\underline{\mathbf{C}}H_2CH_2P$, 25.49 (s, 2C) $P\underline{\mathbf{C}}H_2CH_2\underline{\mathbf{C}}H_2P$, 27.88-32.99 (br m, 6C) C1-C3, 127.52 -133.38 (m, 24C) $\underline{\mathbf{Ph}}_2$; 138.71 (s, 2C) C4, 206.61 (s, 2C) $\underline{\mathbf{C}}$=O; ^{31}P NMR (121 MHz, $CDCl_3$) δ ppm: 15.04 (s), $^1J(^{195}Pt\text{-}^{31}P)$ = 1407 Hz; Elemental analysis calculated for $C_{37}H_{40}O_2P_2Pt$: C, 57.43; H, 5.21, Found: C, 57.28; H, 5.24 %; FTIR (ν_{max}/cm^{-1}, DCM): 1605 s (C=C), 1732 s (C=O).

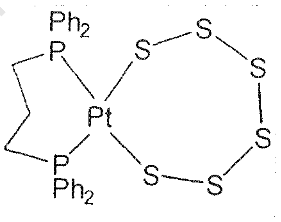
*Preparation of complex **100***

This compound was prepared in a similar method as compound **98** using, (350 mg, 0.527 mmol) of



compound **95**. The product was isolated as a light pink oil. Yield (245 mg, 65%); ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 1.14 -1.37 (m, 6H) H2 and $PCH_2C\underline{\mathbf{H}}_2CH_2P$, 2.36-2.65 (m, 8H) H1 and $PC\underline{\mathbf{H}}_2CH_2C\underline{\mathbf{H}}_2P$, 7.22-7.87 (m, 20H) $P\underline{\mathbf{Ph}}_2$; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 22.42 (s, 1C) $PCH_2\underline{\mathbf{C}}H_2CH_2P$, 25.54 (s, 2C) $P\underline{\mathbf{C}}H_2CH_2\underline{\mathbf{C}}H_2P$, 28.01 (s, 2C) C2, 32.16 (s, 2C) C1, 128.22 -133.74 (m, 24C) $P\underline{\mathbf{Ph}}_2$, 204.12 (s, 2C) $\underline{\mathbf{C}}$=O; ^{31}P NMR (121 MHz, $CDCl_3$) δ ppm: 15.08 (s), $^1J(^{195}Pt\text{-}^{31}P)$ = 1407 Hz; Elemental analysis calculated for $C_{37}H_{40}O_2P_2Pt$: C, 57.43; H, 5.21, Found: C, 57.28; H, 5.24 %; FTIR (ν_{max}/cm^{-1}, DCM): 1605 m (C=C), 1719 s (C=O).

5.8.2 Reaction of platinacyclononane **93** with elemental sulphur (S_8).



101

Platinacyclononane **93** (292 mg, 0.406 mmol) was transferred into a 100 ml round bottom flask and dissolved in dry toluene (30 ml). Elemental sulfur (S_8) (25 mg, 0.812 mmol) was added to the solution and it was stirred at room temperature for 21 days, during which time the progress of the reaction was monitored by ^{31}P NMR spectroscopy. The solution turned from colourless to orange-yellow. The solvent was removed using a rotary evaporator to give a semi-solid crude product, which was passed through an alumina column eluting with a 50:50 mixture of dichloromethane and *n*-hexane. The dark-yellow to orange and light yellow bands were collected separately and after removal of the volatiles form the solutions the light yellow band was found to be phosphine disulfide as identified by ^{31}P NMR and mass spectrometry (*m/z* = 477 see Fig 4.13). A yellow solid of compound **101** was obtained from the dark-yellow to orange band. Yield (111 mg, 34%); m.p. 121-126°C; ^{31}P NMR (121 MHz, $CDCl_3$) δ ppm: -3.20 (s), $^1J(^{195}Pt\text{-}^{31}P)$ = 2688 Hz; Elemental analysis calculated for $C_{27}H_{26}S_6P_2Pt$: C, 40.60; H, 3.25; S, 24.06, Found: C, 40.33; H, 3.23; S, 24.13; LRMS (FAB) $C_{27}H_{26}S_6P_2Pt$: m/z = 778.1 $[M]^+$, 766.7 $[M\text{-}S]^+$, 735.0 $[M\text{-}2S]^+$, 703.2 $[M\text{-}3S]^+$, 671.5 $[M\text{-}4S]^+$.

5.9 Thermal Decomposition

Thermal decomposition was carried out in the solid state under vacuum at 120°C following a protocol similar to the one reported by Whitesides *et al.* [6], for the thermal decomposition of a series of platinacyclopentanes.
A thermal decomposition study was carried out on a fresh sample of the 9-membered ring complex **96**, where 12 mg of the sample was transferred into a thoroughly cleaned, oven-dried sealable tube. The tube was degassed 3 times and sealed under vacuum. The sample was then immersed into a heated oil bath (maintained at 120°C) for 2 hours. After 2 hours the reaction was quenched by immersing the tube in liquid nitrogen for 5 minutes. Chlorobenzene (internal standard, 5 µl) was then added to another tube with a 0.5 ml mark.

The decomposition products in the cooled tube were then extracted with *n*-pentane and added to the tube containing chlorobenzene and marked up to the 0.5 ml mark.

The products were analyzed by gas chromatography (GC), by injecting a 1 µl portion of the sample. Products were identified by comparison of their retention times with those of known samples used as internal standards, and product yields were determined by the response relative to the chlorobenzene standard (response factors obtained from known samples).

5.10 Crystallographic data

Single crystals for an X-ray study of complex **90** were obtained by slow evaporation from diethyl ether.

Intensity data for complex **90** (CCDC number 631341) were collected at 113 K on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å).

Table 5.1. Crystal parameters, data collection, and refinement details for complex **90**.

Empirical formula	=	$C_{43}H_{56}P_2Pt$	*Volume*	=	1943.33(3) Å^3
Crystal system	=	Triclinic	*Z*	=	2
Space group	=	P -1	*F(000)*	=	844
Unit cell dimensions		a = 12.597(10) Å α= 110.33(10)° b = 12.987(10) Å β= 90.64(10)° c = 14.536(2) Å γ= 117.12 (10) °	*ρ*	=	2, 1.418 mg/m^3
Absorption coefficient	=	3.720 mm^-1	*Crystal size*	=	0.18 x 0.10 x 0.05 mm
Color	=	colourless	*θ range for data collection*	=	2.89-25.70°
Limiting indices	=	-15<=h<=15, -15<=k<=15, -17<=l<=17	*Reflections collected/ unique*	=	55624 / 7391 [R(int) = 0.0467]
Completeness to θ	=	25.70 99.6 %	*max & min. trans*	=	0.8358 & 0.5540
Refinement Method	=	Full-matrix least-squares on F^2			
Data/restraints/ Parameters	=	7391/4/426	*Goodness-of-fit on F^2*	=	1.034
Final R indices wR$_2$ = 0.0433	=	*R_1* = 0.0210, *(all data)*	*R indices* wR$_2$ = 0.0452	=	*R_1* = 0.0265, *[I>2σ(I)]*
Extinction coefficient	=	0.00114(14)	*Largest diff. peak and hole*	=	1.303 & -0.586 e.A^{-3}

Chapter 6: General Conclusions and Future work

In this project, a series of new osmium(II) dibromido complexes containing *p*-cymene and hexamethylbenzene with various phosphorus donor ligands were synthesized and characterized by ^{1}H and ^{31}P NMR spectroscopy, elemental analysis and IR spectroscopy. These include complexes **69-76**.

The bis(alkenyl) complexes **77-85** were then prepared by reaction of the dibromido complexes with the appropriate Grignard reagent. These complexes proved to be very unstable and were thus only characterized using ^{1}H, ^{31}P NMR and IR spectroscopy. The characterization data obtained and decomposition products supported the formation of bis(alkenyl) complexes. RCM reactions were not carried out on these complexes due to the difficulty associated with handling them caused by their instability. Osmacycles **86-88** were prepared *via* the di-Grignard methodology and they were also found to be very unstable. The osmacycles were thus also not fully characterized. However, the spectroscopic evidence was consistent with their formation.

Platinacyclic complexes were prepared using either the RCM or di-Grignard methods. These include complexes **93-96**. Complexes **93-95** are known and have been prepared *via* the RCM and di-Grignard routes [1]; however, complex **96** is new.

The thermal decomposition of complex **96** indicated that this complex decomposes to yield similar organic products when compared to related complexes with diphosphine ligands.

Reaction of platinacycles **91**, **93** and **95** with CO yielded products that correspond to the formation of di-acyl complexes **98-100**, as evidenced by the characterization data obtained. These include data from IR spectroscopy, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, as well as elemental analysis. The reactions with CO proved to be relatively slow, and the resulting products were stable at ambient temperature.

The reaction of platinacyclononane **93** with S_8 resulted in the formation of a mixture of products, including undesired phosphine disulfide, a platinum complex containing a chelating S_6 ligand **101** and very small amounts of the di-inserted product. Complex **101** was characterized by ^{31}P NMR spectroscopy, mass spectrometry and elemental analysis.

Future work in this study could include:

- Reactivity studies on the new osmium dibromido complexes.
- Further attempts could be made to try and stabilize the osmium bis(alkenyl) complexes (by choosing a different system of ligands) in order to carry out RCM reactions and obtained osmacycles *via* this route.
- Attempts to obtain good crystals for the characterization by X-ray crystallography of the products obtained from the CO insertion reactions and platinaheptacyclosulphide **101**.
- Thermal decomposition studies on the CO inserted products, to establish what organic products will be given upon decomposition.

1. K. Dralle, N.L. Jaffa, T. le Roex, J.R. Moss, S. Travis, N.D. Watermeyer, and A. Sivaramakrishna, *Chem. Commun,* (**2005**), 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.