The Synthesis, Characterization and Decomposition Studies of Novel Palladacycloalkanes and their Precursors.

Tebello Mahamo
BSc(Hons)

University of Cape Town
2007

A thesis submitted to the

University of Cape Town

In fulfillment of the requirements for the degree of

Master of Science

By

Tebello Mahamo

Department of Chemistry

University of Cape Town

Rondebosch 7701

South Africa

March 2007

Table of Contents

Acknowledgements

I would like to take this opportunity to extend my heartfelt gratitude to the following people, without whom I would not have been able to make to this point:

Firstly, to my supervisors, Prof. John R. Moss and Dr. Gregory Smith, thank you very much for your constant guidance, encouragement, motivation and constructive criticism throughout this project. I would also like to thank Dr. Akella Sivaramakrishna for his help and encouragement in the lab and for proof-reading this manuscript. Special thanks also go to Feng Zheng, who carried out all the decomposition studies and recorded the GC and GC-MS results presented in this report.

Many thanks to the technical staff at UCT for their help. Thanks to Noel and Pete for recording all the NMR spectra and Pierro for all the elemental analyses. To Tommie van der Merwe at Wits University for recording all the mass spectra. Without your input this project would not have reached its successful completion.

To my dear friends: thank you guys for being part of my life, and (to those of you who are also my colleagues) thanks for making the lab a great working environment and for the useful and informative discussions and your input into this project. The time I've spent with you guys has been a real blast and I hope that it will continue to be for many more years. I have truly been blessed to have you in my life.

To my family: my mother, 'M'abo, you're truly the best, my sisters Aus' Ma and Aus' M'lebo, and my brother, Ab'ti Kamoho, thank you guys so much for your constant support and prayers. This work is dedicated to you.

Many thanks to my sponsors, NRF-DST Centre of Excellence in Catalysis (C* Change) and the National Manpower Development Secretariat, Lesotho, for financial support.

Finally, I would like to thank God Almighty for all His blessings and for carrying me through to this point.

Abbreviations

OAc	Acetoxy, $CH_3C(=O)$-O-
DMA	Dimethylamine, $HN(CH_3)_2$
NEt_3	Triethyl amine, $N(CH_2CH_3)_3$
DBU	1,8-diazabicyclo(5.4.0)undec-7-ene, $C_9H_{16}N_2$
DMF	N,N-dimethylformamide, $HCON(CH_3)_2$
THF	Tetrahydrofuran, (C_4H_8O)
TMEDA	N,N,N',N'-tetramethylethylenediamine,$C_6H_{16}N_2$
HMPA	Hexamethylphosphoramide, $\{(CH_3)_2N\}_3PO$
P(o-Tol)$_3$	Tri(*o*-tolyl)phosphine, $C_{21}H_{21}P$
OMe	Methoxy, OCH_3
Ph	Phenyl, C_6H_5
MeCN	Acetonitrile, $NCCH_3$
Et_2O	Diethyl ether, $O(CH_2CH_3)_2$
DCM	Dichloromethane, CH_2Cl_2
EtOH	Ethanol, CH_3CH_2OH
MeOH	Methanol, CH_3OH
Me	Methyl, CH_3
Et	Ethyl, -CH_2CH_3
iPr	Isopropyl, -$CH(CH_3)_2$
^{t}Bu	Tertiary butyl, -$C(CH_3)_3$
Bu	Butyl, -$CH_2(CH_2)_2CH_3$
COD	1,5-cyclooctadiene, C_8H_{12}
PPh_3	Triphenylphosphine, $C_{18}H_{15}P$
PMe_3	Trimethylphosphine, C_3H_9P
dppe	1,2-bis(diphenylphosphino)ethane, $C_{26}H_{24}P_2$
dmpe	1,2-bis(dimethylphosphino)ethane, $C_6H_{16}P_2$
bipy	2,2'-bipyridine, $C_{10}H_8N_2$
phen	1,10-phenanthroline, $C_{12}H_8N_2$
DMSO	Dimethylsulfoxide, $(CH_3)_2S=O$

L	Ligand
R	Alkyl
Ar	Aryl
Nu	Nucleophile
RCM	Ring closing metathesis
o	ortho
m	meta
p	para
NMR	Nuclear Magnetic Resonance
s	singlet
d	doublet
t	triplet
m	multiplet
br m	broad multiplet
J	coupling constant
FAB	fast atom bombardment
M^+	parent molecular ion
m/z	mass to charge ratio
°C	degrees Celsius
mmol	millimoles
mg	milligrams
ppm	parts per million
min.	minutes
hr	hours
ca.	approximately
equiv.	equivalent
wt	weight
lit	literature

Conference Contributions

Mahamo, T., Moss, J. R. Smith, G. and Sivaramakrishna, A., October, 2005, **Synthesis and characterization of novel palladacycloheptanes**. The 3rd Cape Organometallic Symposium, Cape Town, South Africa. Poster presentation.

Mahamo, T., Moss, J. R. Smith, G. and Sivaramakrishna, A., May, 2006, **Synthesis and characterization of simple palladacycloalkanes and their precursors**. South African Chemical Institute Young Chemists Symposium, Cape Town, South Africa. Oral presentation.

Mahamo, T., Moss, J., Smith, G., Sivaramakrishna, A. and Zheng, F., August, 2006, **A new route to novel palladacycloalkanes**. Organometallics And Their Applications, Cape Town, South Africa. Poster presentation.

Mahamo, T., Moss, J. R., Smith, G. and Sivaramakrishna, A., August, 2006, **A new route to novel palladacycloalkanes**. 37th International Conference of Coordination Chemistry, Cape Town, South Africa. Poster presentation.

Mahamo, T., Moss, J. R., Smith, G. and Sivaramakrishna, A., August, 2006, **A new route to novel palladacycloalkanes**. 15th International Symposium on Homogeneous Catalysis, Sun City, South Africa. Poster presentation.

Mahamo, T., Moss, J., Smith, G., Sivaramakrishna, A. and Zheng, F., November, 2006, **Synthesis and characterization of simple palladacycloalkanes and their precursors**. C* Change Meeting, Mossel Bay, South Africa. Oral Presentation.

Mahamo, T., Moss, J. R., Smith, G., Sivaramakrishna, A. and Zheng, F., November, 2006, **A new route to novel palladacycloalkanes**. Catalysis Society of South Africa 2006, Mossel Bay, South Africa. Poster presentation.

Abstract

The synthesis and characterization of palladacycloheptane and palladacyclononane complexes based on 1,5-cyclooctadiene (COD), 2,2'-bipyridine (bipy), triphenylphosphine (PPh_3), and 1,2-bis(diphenylphosphino)ethane (dppe), and their precursors were successfully carried out. The complexes were characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, mass spectrometry as well as elemental analysis. The palladacycloalkanes were prepared from the bis(alkenyl) complexes of the type *cis*-[Pd{$(CH_2)_nCH=CH_2$}$_2L_2$] (n = 2, 3; L = PPh_3; L_2 = COD, bipy, dppe) by ring closing metathesis (RCM) reactions followed by hydrogenation.

Bis(butenyl) and bis(pentenyl) complexes based on COD, bipy, PPh_3 and dppe were successfully prepared and characterized. These complexes showed very low stability in solution, but upon isolation their stability is greatly improved, thereby allowing for their characterization. The yields obtained for the bis(alkenyl) complexes showed the following trend: bipy > COD > PPh_3 > dppe. Preparation of the bis(pentenyl) complex based on 1,0-phenanthroline (phen) was attempted, but, the complex decomposed to give palladium black and 1,9-decadiene when isolation was attempted. The decomposition product was characterized by ^{1}H and ^{13}C NMR spectroscopy as well as GC-MS.

Decomposition studies were carried out on the complex *cis*-[Pd{$(CH_2)_3CH=CH_2$}$_2$(dppe)]. This complex gave 1,9-decadiene and decane as the only decomposition products, suggesting that reductive elimination is the major decomposition mechanism for this complex. Decomposition studies were also carried out on fresh samples of the palladacycloheptanes and palladacyclononanes based on PPh_3 and dppe at 165°C. The product mixtures from these reactions consist mainly of straight-chain organic hydrocarbons, with olefins forming the bulk of the product mixture.

In addition, decomposition studies were further carried out on samples of the palladacyclononane complex that had been kept under argon at room temperature for three weeks. These reactions consistently yielded organic products that had one carbon atom less than the expected number, suggesting that another decomposition mechanism, α-carbon abstraction, is active in these complexes under mild conditions. All decomposition products were characterized by GC or GC-MS.

To the best of our knowledge, all the bis(alkenyl), palladacycloalkene and palladacycloalkane complexes reported in this work have not yet been reported in the literature.

Chapter 1

A Review of Selected Palladium-Catalyzed Reactions

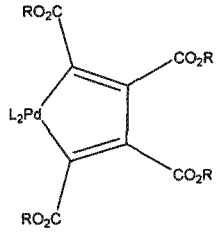
1.1 Introduction

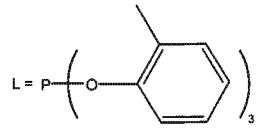
Palladium complexes form some of the most versatile and useful catalysts in organic transformations. The facile interchange between the two stable Pd(II) and Pd(0) oxidation states, and the compatibility of many palladium compounds with most functional groups, are mainly responsible for the rich chemistry enjoyed by palladium compounds.[1] Organo-palladium complexes have been known to display remarkable catalytic activity in a wide variety of organic transformations, especially in carbon-carbon bond formation reactions[2] including carbon monoxide-olefin co-polymerization reactions,[3,4] ethylene oligomerization and polymerization reactions, as well as the Heck, Suzuki, and Negishi coupling reactions[5] amongst others.

It is now widely recognized that palladium has significantly changed and improved organic synthesis over the last three to four decades.[6] Palladium-catalyzed reactions often proceed through the formation of palladacyclic complexes as key intermediates in the reaction. This feature has opened up many short and efficient pathways from simple starting materials to complex target molecules,[7] especially in the construction of ring systems (both carbocyclic and heterocyclic) in organic synthesis.[8]

Considering the large number of reactions catalyzed by palladium compounds, it is remarkable that a high degree of selectivity is achieved by the correct choice of ligand systems and reaction conditions.[8] In some cases it has even been discovered that certain five-membered palladacyclic complexes with enhanced thermodynamic and kinetic stability are valuable catalysts with unique properties.[8] Thermodynamic as well as kinetic stability are essential in order for these complexes to be applicable as catalysts and complexes **1a** and **1b** fulfill these requirements.[8] Complex **1a** (Figure 1.1) was found to catalyze the intramolecular

Alder-ene reaction of enynes whilst complex **1b** was found to catalyze intramolecular enyne metathesis.[8]





1a R = CH_3

1b R = CH_2CF_3

Figure 1.1: Palladacyclic catalysts.

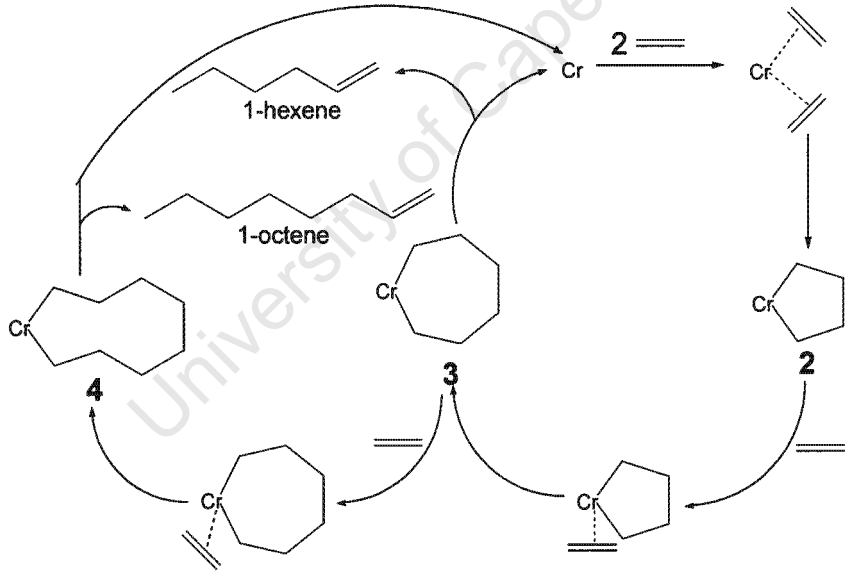
As already mentioned, palladacyclic complexes have been proposed as key intermediates in palladium-catalyzed reactions such as the intramolecular Stille reaction, coupling reactions that proceed via C-H activation,[8] as well as dimerization and telomerization reactions of 1,3-butadiene and its derivatives.[6] One of the most interesting classes of reactions that proceed via palladacyclic intermediates is that of "Heck-type" reactions, where the final step in the reaction, the *syn*-β-hydrogen elimination step, is inhibited due to lack of suitable β-hydrogen atoms.[8]

Many other transition metal catalyzed processes such as ethylene oligomerization have been proposed to involve metallacycloalkanes as key intermediates.[9,10] Metallacyclic compounds of the transition metals can be defined as 'carbocyclic systems in which one or more carbon atoms have been substituted by a transition metal'.[9,10] For the purposes of this review, this definition is limited to those complexes in which the metal centre is bonded to two carbon atoms in a cyclic system, and therefore excludes complexes formed by chelating ligands such as diphosphines and diimines in which the metal centre is bonded to heteroatoms.[11]

Metallacyclic compounds of the transition elements have become a subject of considerable research interest due to the important role they play in catalytic reactions such as alkene metathesis, isomerization of strained carbocyclic rings as

well as oligomerization and polymerization of olefins.[12] The metallacycloalkanes have been shown to be key intermediates in these catalytic reactions and their subsequent thermolysis or substitution reactions have been used to simulate catalytic cycles.[13]

A good example is the chromium PNP system recently developed by the group at Sasol, for the selective trimerization and tetramerization of ethylene to 1-hexene and 1-octene respectively. Their high selectivity for α-olefins has led to increased interest in the mechanism of these systems. Ethylene labeling experiments have proved that these reactions proceed via metallacyclopentane (**2**), metallacycloheptane (**3**) and metallacyclononane (**4**) intermediates as shown in Scheme 1.1.[13,14] A similar metallacyclic pathway, supported by computational studies, has also been proposed for homogeneous titanium catalysts for ethylene oligomerization.[15,16]



L = $Ph_2PN(R)PPh_2$

Scheme 1.1: Catalytic cycle for ethylene trimerization and tetramerization by chromium catalysts.

This review covers three main areas of interest. The first section deals with "Heck-type" intramolecular cyclization reactions that proceed via palladacyclic

inetermediates. Palladium-catalyzed ethylene oligomerization will also be discussed briefly, and the review will be concluded with a brief look at mechanisms of decomposition for palladacycloalkanes as shown below:

1. Heck-type Intramolecular Cyclization Reactions.

2. Palladium-Catalyzed Ethylene Oligomerization.

3. Decomposition Mechanisms Observed in Palladacyclic Complexes.

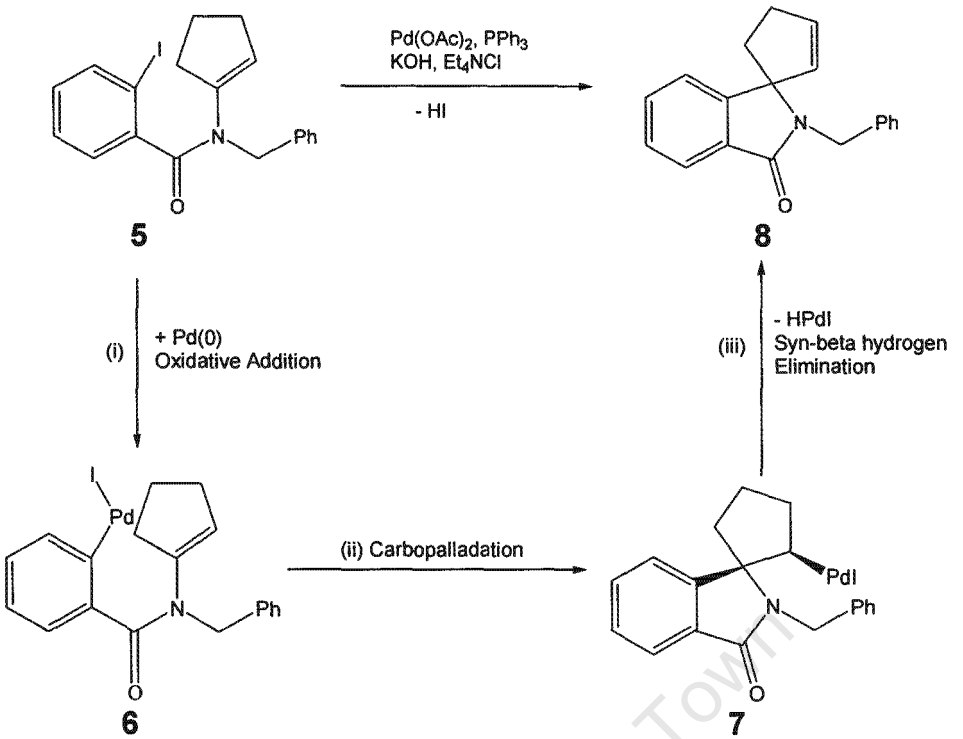
1.2 Heck-type Intramolecular Cyclization Reactions

Among the numerous palladium-catalyzed processes for carbon-carbon bond formations, the Heck reaction is one of the most versatile and widely used methods in modern organic synthesis.[17] The reaction proceeds through three mechanistic steps (see (i) – (iii) in Scheme 1.2):[8]

1. Oxidative addition of the C-X bond (where X = halogen) to the Pd(0) catalyst to produce a Pd(II) intermediate (**6**); the active Pd(0) catalyst is generated *in situ* from palladium salts such as $PdCl_2$ and $Pd(OAc)_2$.

2. *Syn*-carbopalladation of an appropriate C=C bond that results in the ring-closing C-C bond formation.

3. The ring-closed intermediate (**7**) rapidly undergoes *syn*-β-hydrogen elimination to form the final product (**8**). The resulting HPd(II)X species undergoes base-mediated reductive elimination to regenerate the active Pd(0) catalyst.

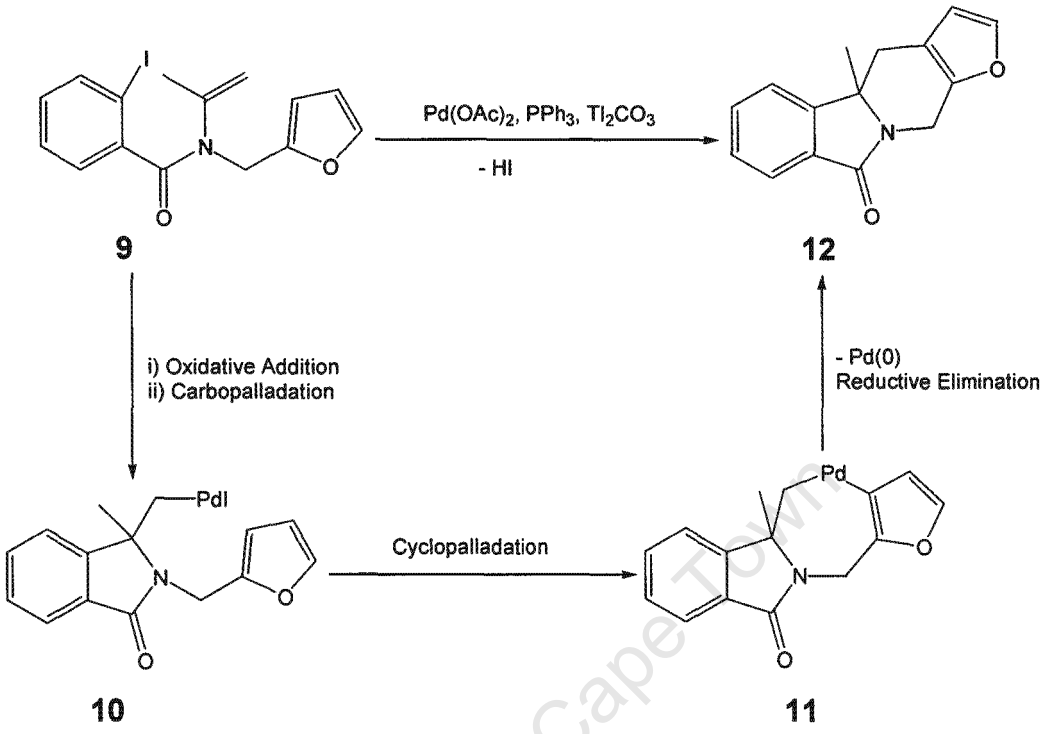


Scheme 1.2: Normal steps in a typical intramolecular Heck reaction.

The final step, the *syn*-β-hydrogen elimination of **7** to form **8**, is crucial to the completion of the catalytic cycle in a normal Heck reaction. However, with certain substrates this step is not possible because these substrates do not have suitable β-hydrogen atoms that can undergo *syn*-β-hydrogen elimination. However, under these conditions an alternative reaction pathway to the β-hydrogen elimination is the cyclopalladation/reductive elimination reaction sequence. This pathway results in the formation of a palladacyclic complex (e.g. complex **11** in Scheme 1.3) as a key intermediate in these reactions.[8,17]

Depending on the structure of the substrates, palladacycles of different ring sizes are formed, and the ring size in these intermediates plays an important role in determining the pathway that the reaction follows after the cyclopalladation step, and hence the products that will be obtained.[7,8] The reaction involving six-membered and larger palladacycles with carbon-palladium σ-bonds typically

undergo the reductive elimination reaction, as shown in the final step of the example in Scheme 1.3 below. [8]

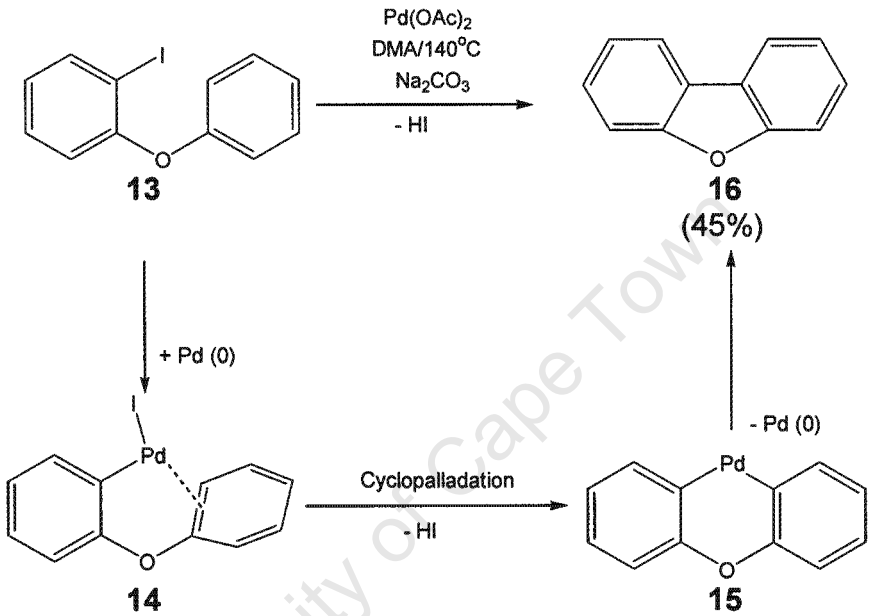


Scheme 1.3: Normal mechanism of "Heck-type" reactions that involve six-membered or larger palladacyclic intermediates.

1.2.1 Palladacyclohexanes and Larger Rings as Intermediates

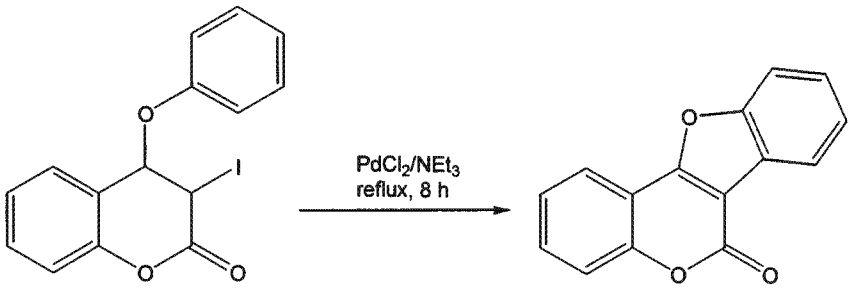
Ames and co-workers[18,20] were the first researchers, in the early 1980s, to report six- and seven-membered palladacyclic complexes as proposed key intermediates in intramolecular aryl-aryl coupling reactions. For instance, the biaryl ether, **13**, is cyclized to give the dibenzofuran **16** via a cyclopalladation/reductive elimination sequence (Scheme 1.4).[18,20] The formation of the η^2-bound arene palladium complex, **14**, is presumed to preceed the C-H activation in the formation of palladacycle **15**.[18] Complexes with a related structure to **14** have been isolated and fully characterized. Cheng and co-workers have shown by X-ray crystallography that the aromatic ring in the complex is weakly bound to the palladium centre through η^2-coordination.[21]

Catellani and co-workers later showed that an ortho substituent on the aryl ring coordinated in η^2-fashion to the metal centre causes a shift towards η^1-coordination.[22] Thus the presence of an ortho substituent on the aryl ring enhances the formation of the palladacyclic intermediate **15** in the reaction in Scheme 1.4. The palladacycle **15** then undergoes facile reductive elimination resulting in the formation of the dibenzofuran **16**.



Scheme 1.4: Palladium-catalyzed aryl-aryl coupling via a palladacyclic intermediate.

This type of aryl-aryl coupling reaction has found wide application in the preparation of polycyclic hydrocarbons as well as in natural products synthesis.[8] The key step in these syntheses is often the formation of the palladacyclic intermediates. In the total synthesis of coumestan, (**18**, Scheme 1.5) Laschober and Kappe used $PdCl_2$ as the pre-catalyst for the final step of the reaction, presumably via a palladahexacyclic intermediate, and obtained the product in very good yields (75 – 95%).[23]

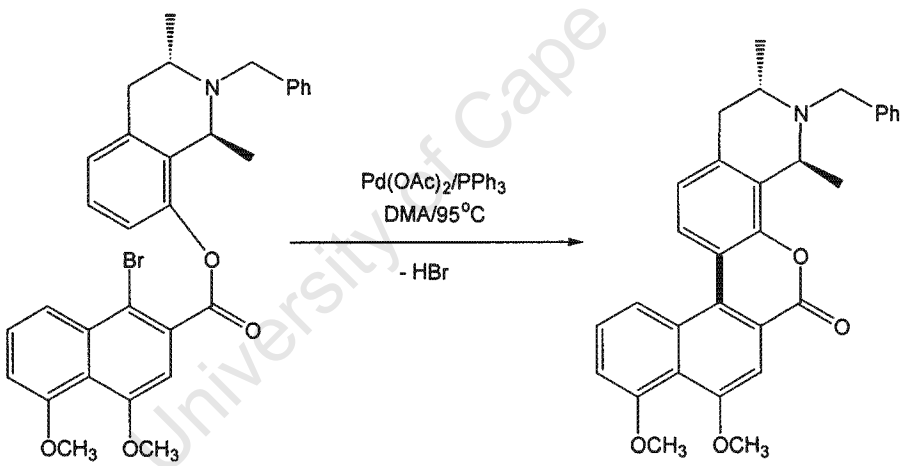


17 **18**

(75 – 95%)

Scheme 1.5: Palladium-catalyzed synthesis of coumestan.

In the synthesis of compound **20** (Scheme 1.6) the key step was the formation of the biaryl axis (marked in bold). The C-C bond was introduced by the palladium-catalyzed step in compound **19**.[24]

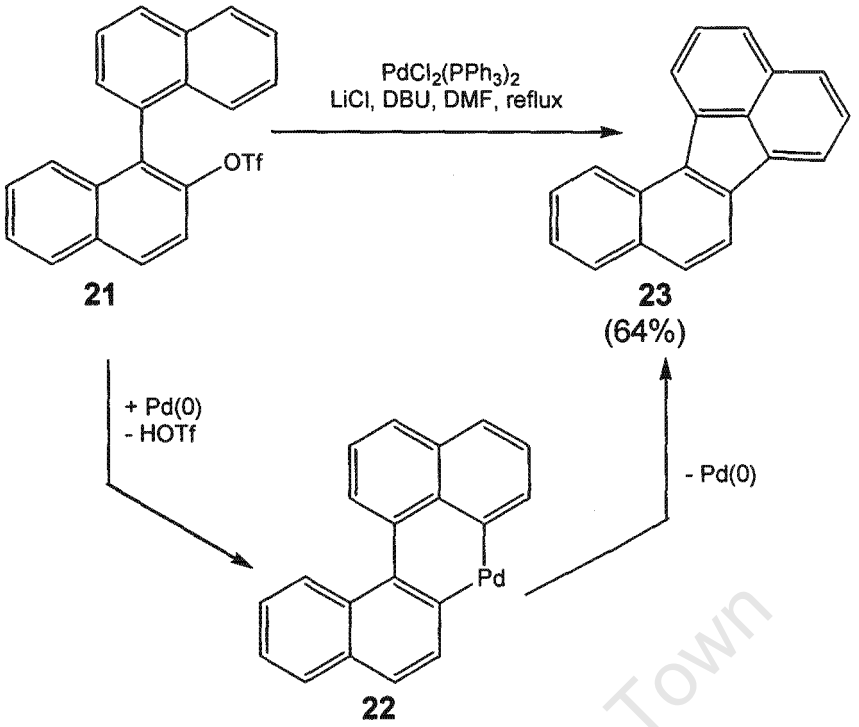


19 **20**

(82%)

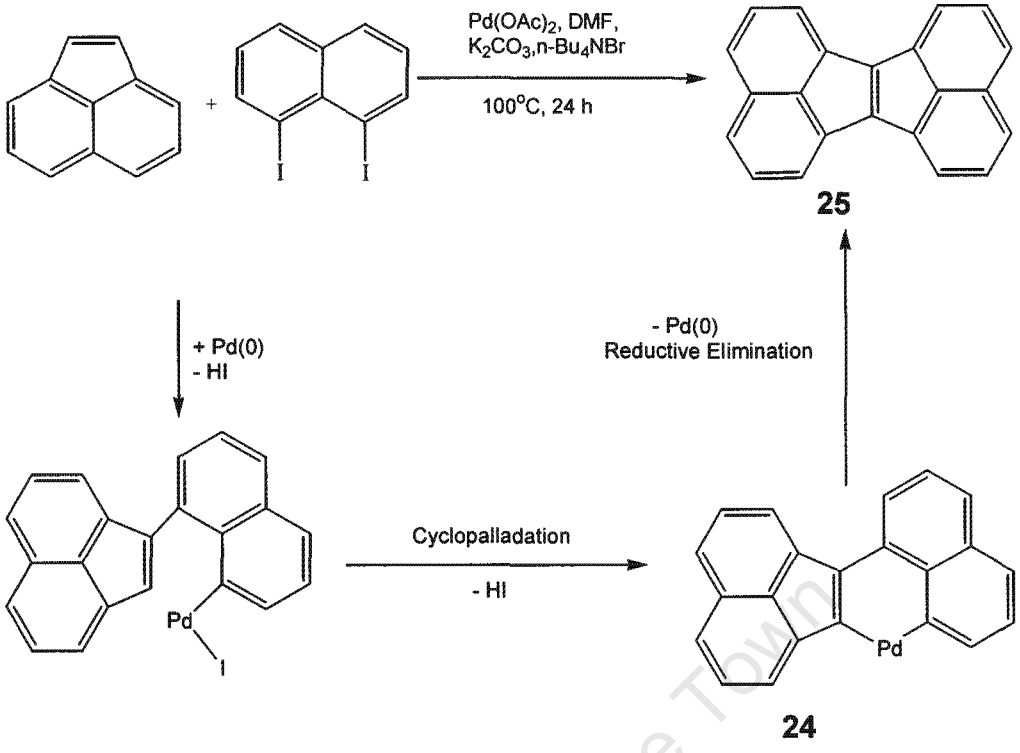
Scheme 1.6: Palladium-catalyzed C – C coupling.

Palladium catalysis has also found wide application in the synthesis of strained carbocyclic systems such as those shown in Schemes 1.7 and 1.8,[25,26] as well as use in the isomerization of these strained systems.[12] The benzofluoranthene **23** (Scheme 1.7) was prepared from **21**, by Rice and Cai, by a reaction that proceeds via the six-membered palladacycle **22** as the key intermediate.[25]



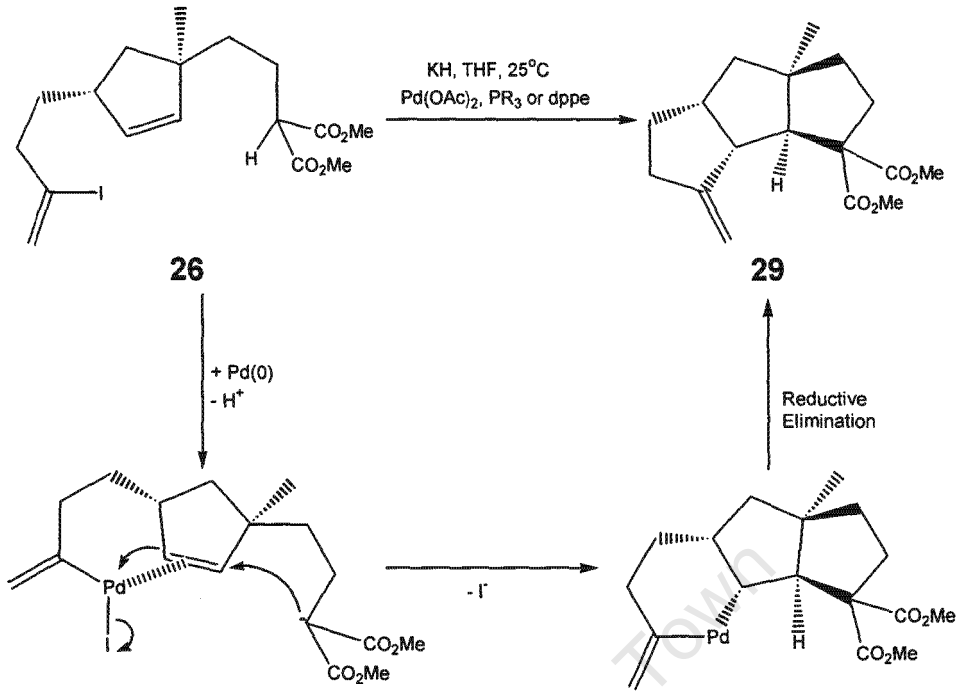
Scheme 1.7: Palladium-catalyzed triflate-arene coupling reaction.

The annelated pentalene system **25** (Scheme 1.8) was synthesized in a single step by the coupling reaction of acenaphthylene with 1,8-diiodonaphthalene.[26] The reaction proceeds via the cyclopalladation/reductive elimination sequence and the six-membered palladacycle **24** is a key intermediate in the reaction.



Scheme 1.8: Palladium-catalyzed synthesis of the annelated pentalene system, 25.

Remarkable selectivity can be achieved in palladium-catalyzed reactions.[8] Compound **29** (Scheme 1.9)[27] was synthesized in a single preparative step from the cyclopentene **26**. All the three functional groups in the starting material are involved in this transformation.[8] Oxidative addition of the catalyst to the C-I bond in **26** results in the vinylpalladium iodide intermediate **27**, which polarizes the neighboring olefinic double bond by complexation. Nucleophilic attack by malonate on the olefinic double bond results in the formation of the palladacyclohexane intermediate **28**. The palladacycle then reductively eliminates to give the target molecule and the active Pd(0) catalyst can then be regenerated by the potassium hydride in the reaction mixture.[27] The reaction proceeds at room temperature with retention of chirality at all the stereogenic centers in the product.

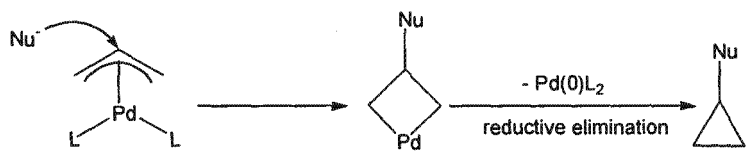


PR_3 = tri(2-furyl) phosphine, ligands on Pd omitted for clarity.

Scheme 1.9: Palladium-catalyzed bis-cyclization reaction.

1.2.2 Palladacyclobutanes as Intermediates

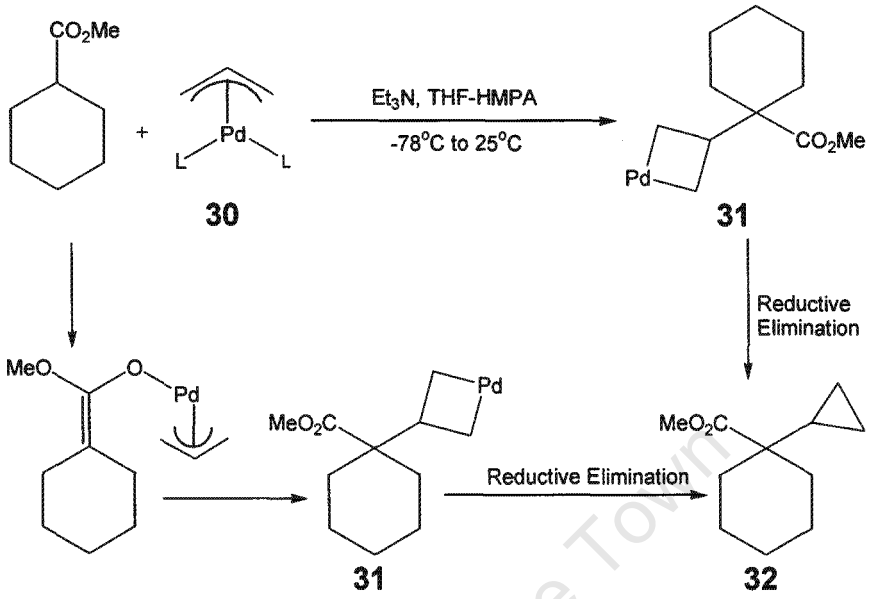
Like six-membered and larger palladacyclic intermediates, palladacyclobutanes also undergo reductive elimination to give substituted cyclopropanes as products. Palladacyclobutanes are often presumed to be key intermediates in nucleophilic addition reactions involving π-allyl palladium complexes. In these reactions the nature of the ligands bonded to the palladium as well as the nucleophile, play an important role in both the rate and the regioselectivity of the reaction.[28] Hegedus and co-workers reported the first example of this type of reaction and proposed its mechanism (Scheme 1.10) in 1980.[29]



Nu^- = ester-enolate, L = TMEDA, HMPA

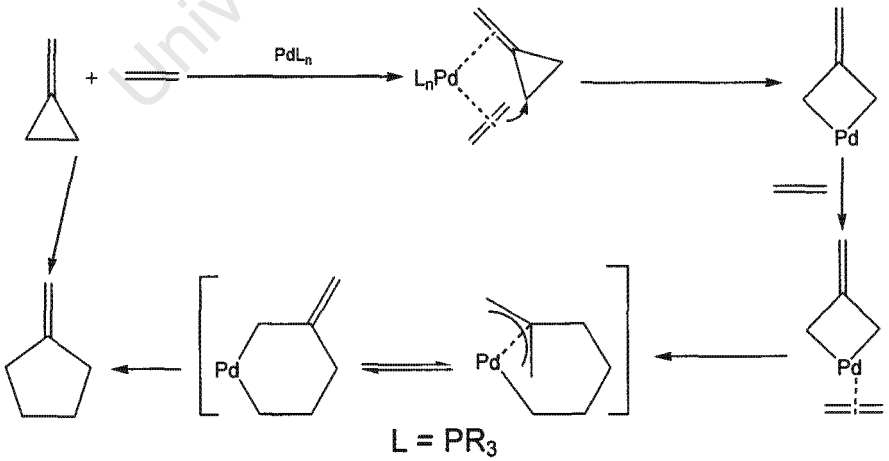
Scheme 1.10: Mechanism of nucleophilic substitution on a (π-allyl)palladium complex involving a palladacyclobutane as an intermediate.

In the cyclopropanation reaction of **30** (Scheme 1.11), the reaction is presumed to proceed via the palladacyclobutane **31** as the key intermediate. This complex then undergoes reductive elimination to give the final product, **32**.[30,31]



Scheme 1.11: Formation of the substituted cyclopropane, 32.

Palladacyclobutanes have also been proposed as intermediates in the [3 + 2] cycloaddition reaction of methylenecyclopropane with olefins to give methylenecyclopentane (Scheme 1.12).[32]

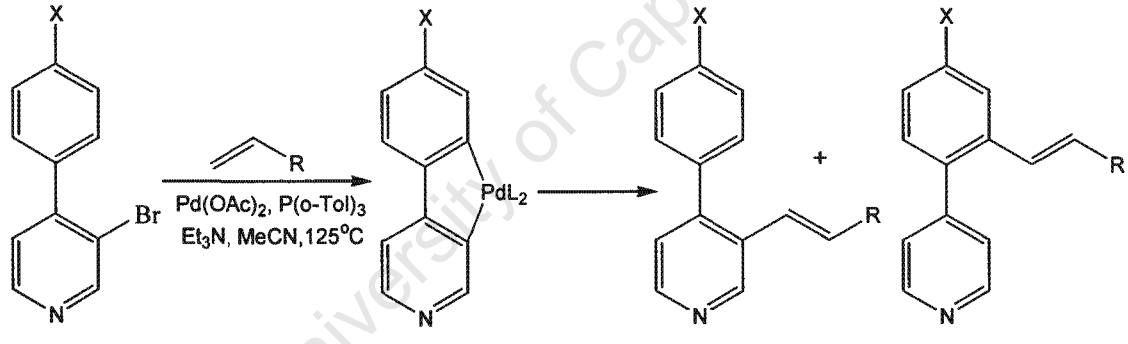


Scheme 1.12: Binger's proposed palladacyclo- mechanism for the [3 + 2] cycloaddition reaction of methylenecyclopropane with olefins.

In this case, however, the coordinated alkene inserts into the palladium-carbon bond to give a palladacyclohexane intermediate, which then undergoes reductive elimination to give the final product.[32]

1.2.3 Palladacyclopentanes as Intermediates

Unlike the reactions discussed so far, reactions that involve five-membered palladacycles follow a different pathway. The formation of cyclobutanes from the reductive elimination of these intermediates is unfavorable and restricted to special cases.[7,8] Gallagher *et al* described the Heck reaction of pyridyl-based biaryls of the type **33**, which lead to the formation of the expected cross coupling products **35** (Scheme 1.13).[33] In addition to these products, the more unusual "cross-over Heck" products, **36** were observed in significant amounts. The "crossover" reaction was proposed to proceed via the palladacycle **34** as an intermediate.[34]

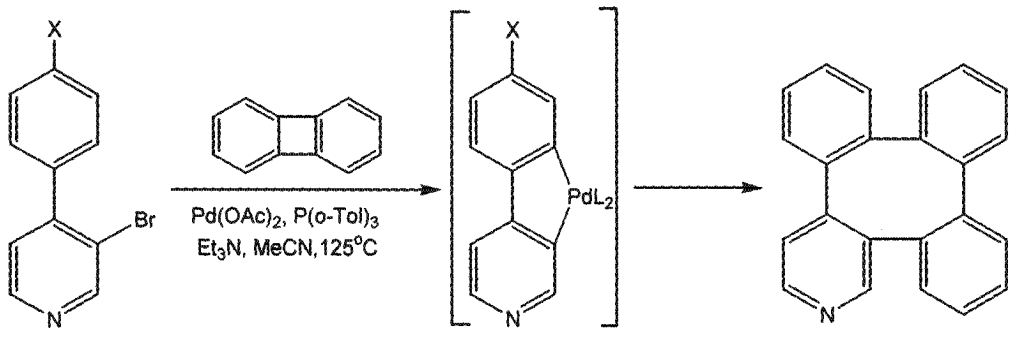


33 **34** **35** **36**

X = H, NO_2, OMe; R = CO_2Et, Ph

Scheme 1.13: "Cross-over" Heck reaction.

To gain support for the involvement of the palladacycle in the reaction, the researchers reacted the biaryls with the biphenylene (Scheme 1.14) and obtained the desired tetracycle **37** as the product. The formation of the tetracycle provided support for the formation of **34** as an intermediate in the reaction.[34] Analogous complexes to **34**, based on nickel have been synthesized and characterized.[11]

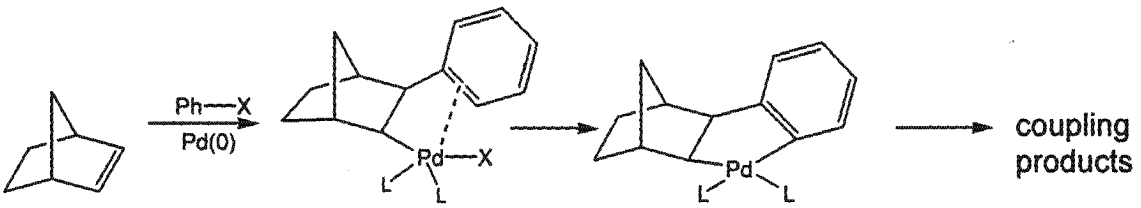


33 34 37

Scheme 1.14: Palladium-catalyzed coupling reaction of biaryl halides, 33, with the biphenylcyclobutane.

Five-membered palladacyclic intermediates open up pathways to domino (cascade) reactions by reacting with a second molecule of the substrate or with added reagents as shown in the reactions in Schemes 1.13 and 1.14. In these reactions the competing reductive elimination reaction that would produce cyclobutane products is relatively slow. Various polycyclic hydrocarbons can be prepared by these processes.[7]

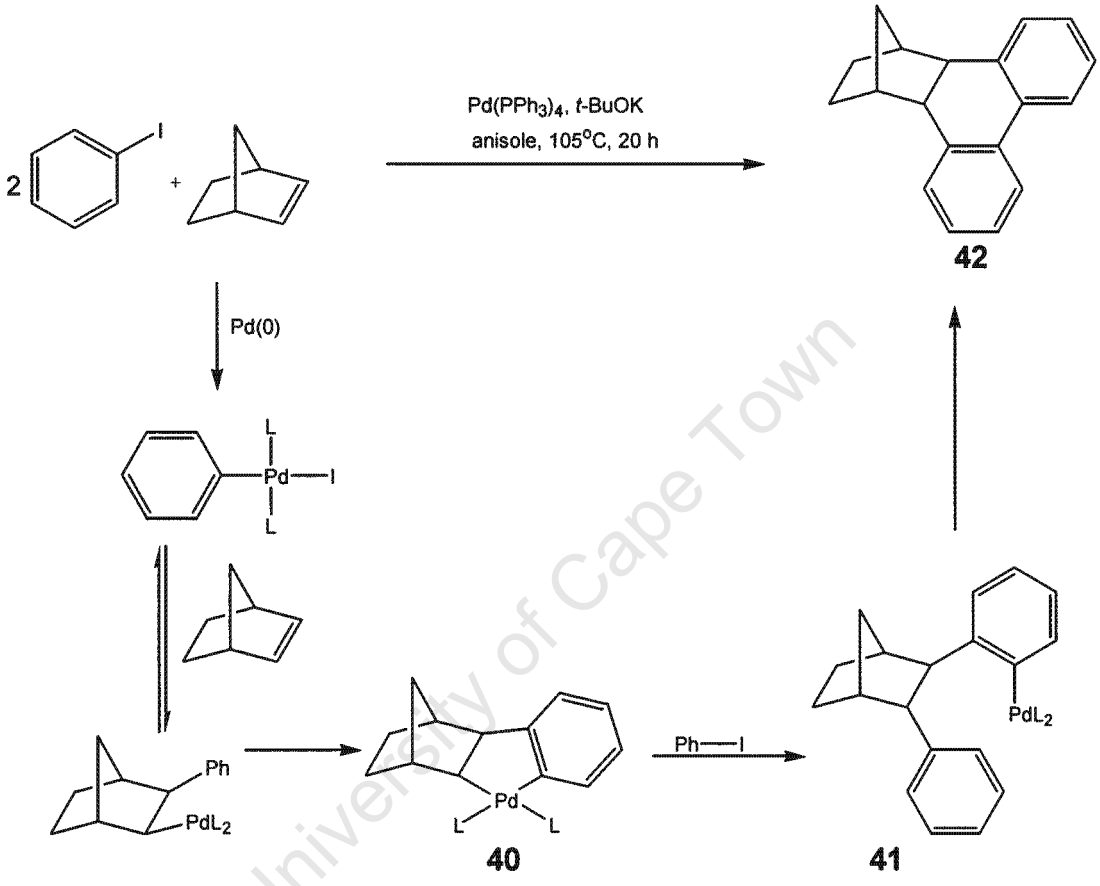
The domino reaction has been studied in the palladium catalyzed coupling reaction of aryl halides with norbonene. In these reactions the oxidative addition generates a long-lived σ-alkylpalladium intermediate **38** (Scheme 1.15). This intermediate then undergoes intramolecular aromatic C-H activation reaction with the formation of the palladacycle **39**.



38 39

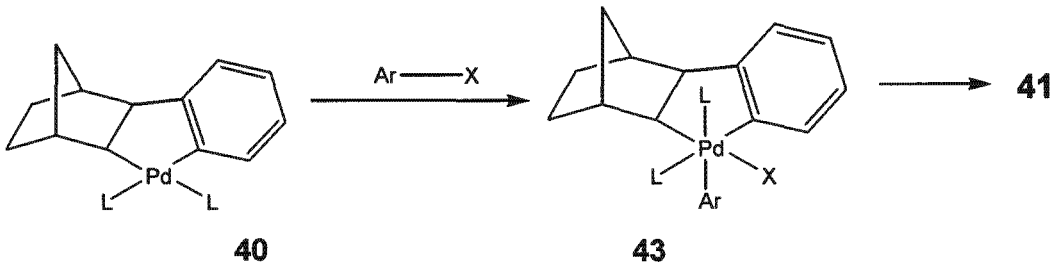
Scheme 1.15: Palladium catalyzed coupling reaction of aryl halides with norbonene.

Catellani and co-workers proposed that the reactions proceed via both Pd(II) and Pd(IV) metallacycles as intermediates,[22,35-37] although an alternative mechanism, supported by computational studies, has recently been proposed.[38] Compound **42** (Scheme 1.16) can be prepared by a reaction between iodobenzene and norbonene in a 2:1 reaction ration.[35]



Scheme 1.16: One of the proposed mechanisms for the coupling reaction of norbonene and aryl halides.

It has been proposed that intermediate **40** can undergo oxidative addition of aryl halides to form Pd(IV) metallacycles (complex **43**, Scheme 1.17) by S_N2 processes. Examples of these Pd(IV) metallacycles have been successfully isolated in the presence of suitable stabilizing ligands and characterized.[22,37]

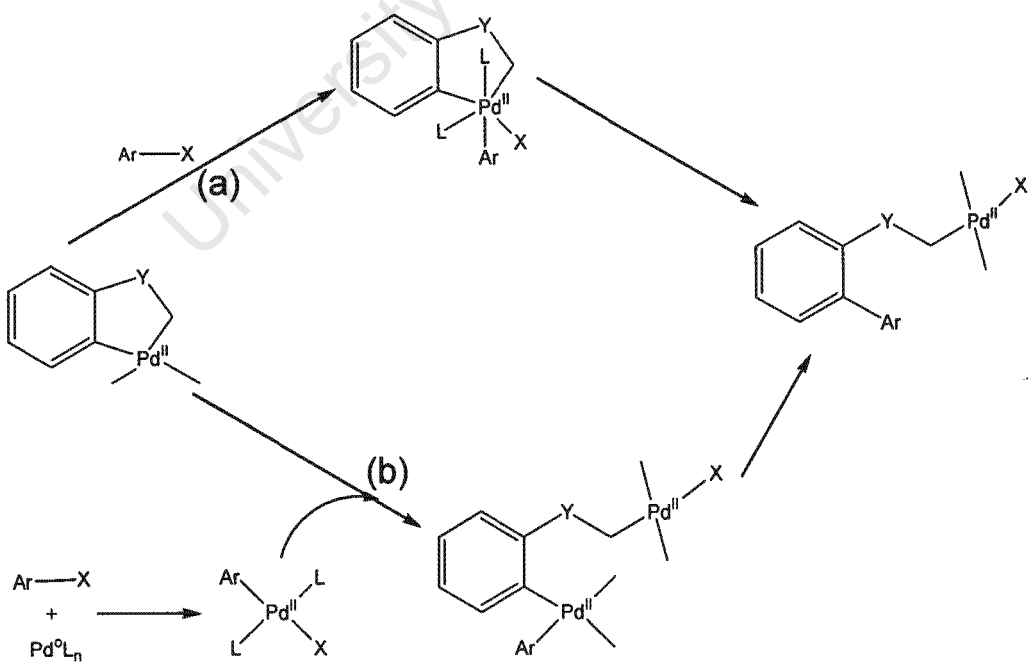


40 **43**

L = OAc

Scheme 1.17: Proposed formation of a Pd(IV) palladacycle from a Pd(II) palladacycle in the coupling reaction of norbonene and aryl halides.

Reductive elimination of complex **43** can readily occur through migration of the Ar group to the bicycloheptyl unit and results in the formation of complex **41**.[36] Although there is compelling experimental evidence for the formation of Pd(IV) metallacycles as intermediates in these reactions, some computational studies have suggested that a more energetically favorable pathway is possible.[38] The authors of these studies propose that, since the activation barriers for the oxidative addition of aryl halides to Pd(0) is much lower than that of Pd(II), the formation of the Pd(IV) palladacycle from the Pd(II) intermediate is unlikely.[38]



Scheme 1.18: Proposed mechanisms for coupling reactions involving aryl halides.

An alternative pathway that involves a transmetallation-type exchange of aryl ligands between different Pd(II) centres has been suggested (pathway (b) in Scheme 1.18). Exchange of carbon ligands between two Pd(II) centers or Pd(II) and Pt(II) has been reported before.[39]

Although the involvement of Pd(IV) species as intermediates in domino reactions is still under investigation, palladium-catalyzed reactions are an important component of synthetic organic chemistry as they provide access to otherwise inaccessible valuable carbocyclic and heterocyclic systems. The presence of Pd(II) metallacycles as key intermediates in these reactions has, however, been established.

1.3 Palladium-Catalyzed Ethylene Oligomerization

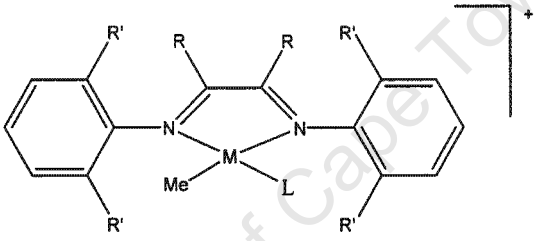
In recent years, extensive efforts have been made to develop catalytic systems that achieve selective oligomerization of ethylene to higher α-olefins. Of special interest is the selective trimerization and tetramerization of ethylene to form 1-hexene and 1-octene respectiely.[12c-15] These olefins are used extensively as comonomers in the production of linear low density polyethylene, detergents and plasticizers.[40,41]

Early work in catalytic ethylene oligomerization mainly focused on the early transition metal catalysts such as titanium and zirconium compounds. Ethylene oligomerization by these catalysts was presumed to proceed via metallacycloalkanes as key intermediates which then undergo β-hydrogen elimination followed by reductive elimination to give the observed α-olefins.[13,14] Involvement of large metallacycloalkane intermediates has also been proposed in the formation of higher α-olefins with chain lengths of up to thirty carbon atoms,[15] using chromium catalyst systems.

In recent years, however, the focus has shifted to include late transition metal compounds such as palladium and nickel complexes. To date, an impressive

number of late transition metal complexes based on different ligand systems have been developed and tested for activity in catalytic ethylene oligomerization.[40]

The discovery, by Brookhart and co-workers in the mid-1990s, of versatile highly active cationic Ni(II)- and Pd(II)-α-diimine complexes with the general structure **44** (Figure 1.2)[42] was a significant advance in the development of late transition metal catalyzed ethylene oligomerization and polymerization.[43,44] As a result, a large number of palladium complexes based on different ligand systems such as P-P, P-N, P-O and N-N chelating ligands have been developed for ethylene oligomerization.[40] Some of these complexes have been shown to catalyze oligomerization of ethylene to short α-olefins with chain lengths in the range between C_4 and C_{14+}.[2,41,45]



44

M = Ni, Pd

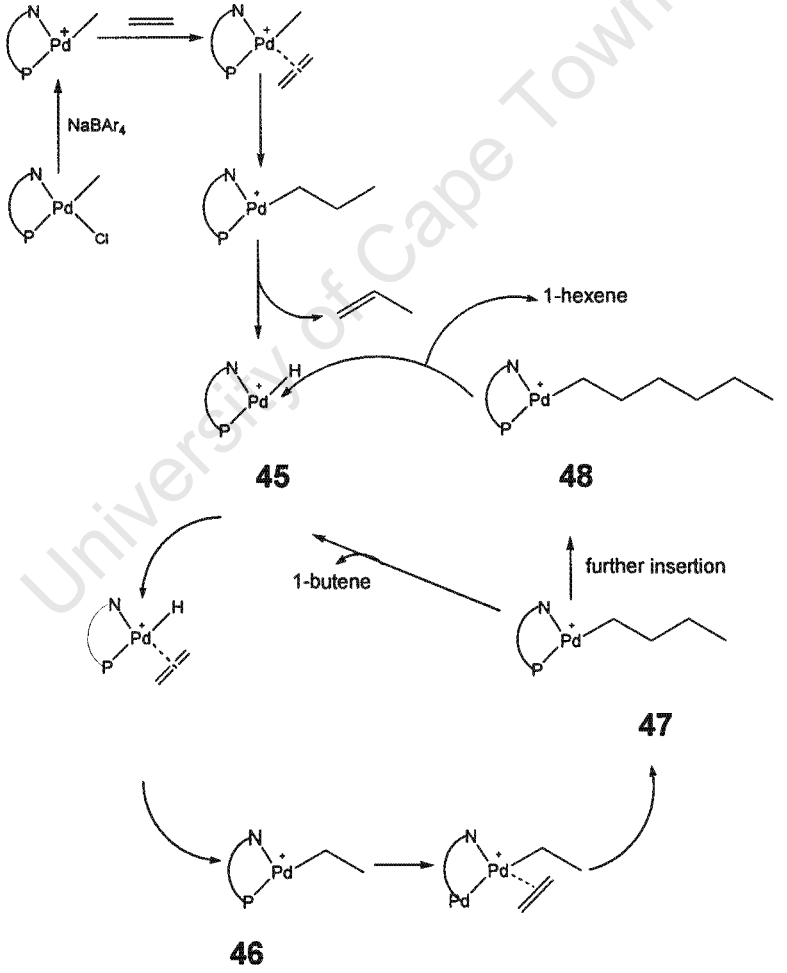
L = Et_2O, MeCN

Figure 1.2: General structure of Brookhart's Ni(II)- and Pd(II)-α-diimine catalysts for ethylene oligomerization and polymerization.

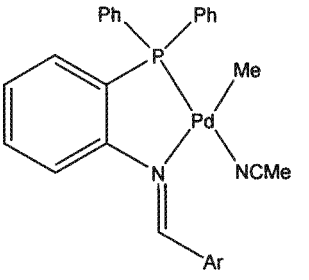
Concerted effort has also been put into determining the mechanism of these palladium-catalyzed reactions. These studies reveal that palladium-catalyzed reactions involve a different mechanism (Scheme 1.19).[46,47] Unlike in early transition metal catalyzed ethylene oligomerization, in palladium-catalyzed reactions metallacyclic intermediates have not yet been observed, although metallacycles could possibly be involved. Instead, these reactions have been proposed to proceed via the formation of palladium alkyl species such as complexes **46 - 48** in Scheme 1.19. These complexes can then undergo β-hydride elimination to give the α-olefins as products together with the metal hydride

complex, **45**. Complex **45** can then coordinate another ethylene molecule and the catalytic cycle is repeated.[46,47]

Chen and co-workers studied phosphino-imino palladium complexes of the type **49** (Figure 1.3) for ethylene oligomerization and found that these complexes only catalyze the dimerization and trimerization of ethylene to mainly 1-hexene and 1-butene.[46] The nature of products obtained was found to be dependent on reaction conditions such as temperature, pressure and solvent. Increase in temperature and ethylene pressure as well as use of aromatic solvents seemed to favor the formation of 1-butene over 1-hexene.[46]



Scheme 1.19: Proposed mechanism for palladium-catalyzed ethylene oligomerization.

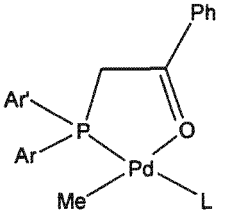


49

Figure 1.3: P,N-based palladium catalyst for ethylene oligomerization.

Studies done by other researchers show that, depending on the steric bulk of the ligands in phosphino-imino palladium complexes, different α-olefin products in the range C_6 – C_{16} are obtained. Van den Beuken and co-workers found that under appropriate conditions of temperature pressure and solvent, the main product obtained was 1-hexene although some C_8 – C_{16} α-olefins were also obtained in reactions catalyzed by complexes with more bulky ligands.[48] Catalytic activity was found to be influenced by electronic effects in the imino donor site, with electron-releasing groups enhancing reaction rates.[48]

Complexes of the type **50** (Figure 1.4)[45] were found to be active only in dimerization and trimerization of ethylene to give butenes and hexenes, respectively. These complexes are selective for α-olefins as >90% of the products obtained were found to be α-olefins. Similar ligand systems have been used extensively in nickel-catalyzed ethylene oligomerization in the SHOP process.[2,45]



50

Figure 1.4: P,O-based palladium catalyst for ethylene oligomerization.

Investigation into the electronic effects of the ligands revealed that the addition of electron-withdrawing groups such as CF_3 on either the arylphosphine or phenacyl moeties of the ligands slightly lowered the activation barrier to migratory insertion.[45] Addition of electron-donating groups such as the methoxy group slightly increased the activation barrier in the catalyst resting state.[45]

It has been suggested that the magnitude of the insertion barrier in these systems is determined by the overall electrophilicity of the metal center and not the donor properties of the phosphine or keto binding sites.[45] Another important factor in the activities of these (P,O)Pd(II) complexes is the ring size in the resulting complexes.[2] Five-membered chelate complexes show higher activities and selectivities for α-olefins than complexes with larger rings.[2]

Abraham *et al.* studied ethylene oligomerization catalyzed by dendritic N,N palladium complexes and observed that these complexes were active catalysts.[47] 1-Butene and 1-hexene were found to be the major products and the catalysts were selective for α-olefins, especially 1-hexene. As in the reactions catalyzed by phophino-imino complexes, decreasing the reaction temperature favors the formation of 1-hexene over 1-butene. At lower temperatures, chain propagation is favored over β-hydride elimination, resulting in the increase in relative amounts of 1-hexene.[47]

Moss *et al.* also found that palladium complexes based on Brookhart-type ligands with dendritic wedges were active ethylene olgomerization catalysts with α-olefinic products up to C_{20}.[41]

1.4 Decomposition Mechanisms in Palladacycloalkanes

The last stage in the mechanism of every synthetically useful catalytic or stoichiometric reaction in which metallacyclic intermediates are involved is its decomposition to give the desired organic products. The understandimg of this decomposition process is therefore of great importance in the design of new

catalyst systems. This is an aspect of the chemistry of metallacycles which differs considerably from that of their open-chain analogs.[11] A typical decomposition process for group 10 dialkyl complexes is the β-hydride elimination, which requires a transition state in which the M-C_α-C_β-H dihedral angle is almost 0°.[50] This transition state is not readily reached in medium and small ring-sized metallacycloalkanes such as metallacyclobutanes, metallacyclopentanes and metallacyclohexanes.[11]

Another decomposition route frequently observed in metallacycloalkanes and their dialkyl counterparts is reductive elimination, which is thermodynamically unfavorable in metallacycles of small ring sizes as the process gives rise to strained organic products such as cyclopropanes and cyclobutanes.[11] Other decomposition processes observed in metallacycloalkanes include α-hydride elimination as well as retro-cycloaddition (β-C-C fission) reactions (Figure 1.5).[11]

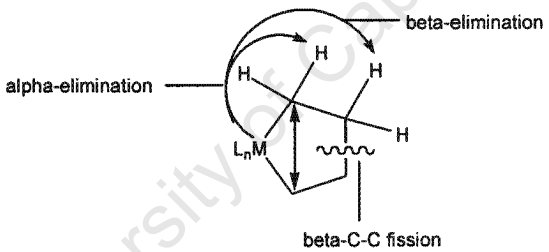
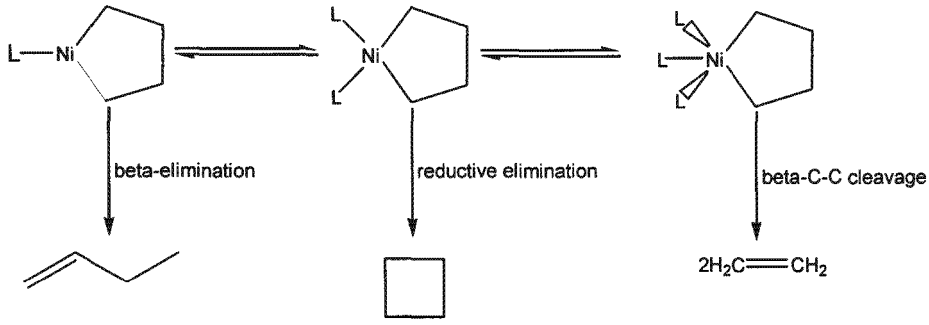


Figure 1.5: Decomposition mechanisms observed in metallacycloalkanes.

A number of platinum(II) and nickel(II) metallacycles have been synthesized and characterized.[11] Extensive studies have been carried out on the decomposition reactions of these complexes and these studies show that, in general, platinum(II) metallacycles decompose via β-elimination to give product mixtures of 1-alkenes and 2-alkenes (after a β-elimination/isomerization processes).[11] The decomposition patterns of nickel-based metallacycles are, on the other hand, dependent on the coordination number of the metal center. The main decomposition route in the nickel complexes, however, is reductive elimination, giving cycloalkanes as the main organic products (Scheme 1.20).[49]

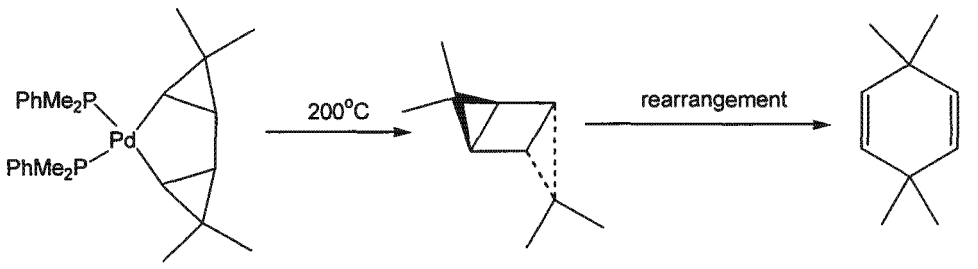


L = PR_3, R = alkyl or aryl group

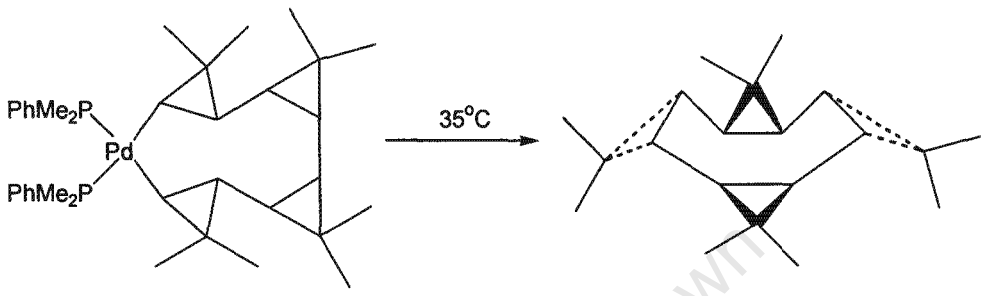
Scheme 1.20: Decomposition mechanisms observed in nickelacycloalkanes.

Unlike their nickel and platinum counterparts, the metallacycloalkanes of palladium have not been as extensively studied.[9,10] The limited number of studies that have been carried out to date indicate that the decomposition mechanisms observed in palladacycloalkanes seem to be midway between the platinum and nickel complexes. Both reductive elimination and β-hydride elimination are observed.[11] Although decomposition of palladacycloalkanes via β-elimination has been reported,[11,50] most reports on the decomposition of these complexes indicate that the majority of organic products from palladacycloalkanes are formed by reductive elimination processes.[10,11,51]

In the intramolecular reactions discussed in Section 1.1, the key steps in the catalytic cycles are the formation and subsequent decomposition of the palladacyclic complexes. In these types of reactions, the complexes decompose via reductive elimination as the β-elimination is blocked by the absence of suitable β-hydrogen atoms. Binger and co-workers also prepared and studied the decomposition products of the palladacyclopentane, **51**, and palladacyclononane, **52** (Scheme 1.21).[51] The thermal decomposition of these complexes yielded substituted cyclobutane and cyclooctane via reductive elimination.[51] In this case, β-elimination was also prevented by lack of suitable β-hydrogen atoms.



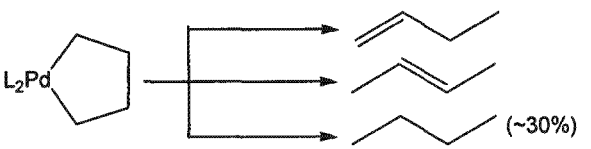
51



52

Scheme 1.21: Substituted palladacycloalkanes and their thermal decomposition products.

Diversi *et al.* reported that thermal decomposition reactions of the palladacyclopentanes **53** (Scheme 1.22) gave a mixture of 1-butene, 2-butene and n-butane, presumably via β-elimination and β-elimination/isomerization or β-elimination/hydrogenation processes.[52,53] A review of the literature shows that very little work has been done on the synthesis and decomposition studies of simple palladacycloalkanes with larger rings, but the expectation is that as ring size increases, these complexes will show behaviour that approaches that of their dialkyl analogues,[11] and more palladacycles that decompose via β-elimination will perhaps be reported in the future.



53

L = PPh_3, L_2 = dppe, bipy, tmen

Scheme 1.22: Thermal decomposition products of different palladacyclopentanes.

The other decomposition routes such as α-hydride elimination and β-C-C cleavage (retro-cycloaddition) have not yet been reported for palladacycoalkanes.

1.5 Concluding Remarks

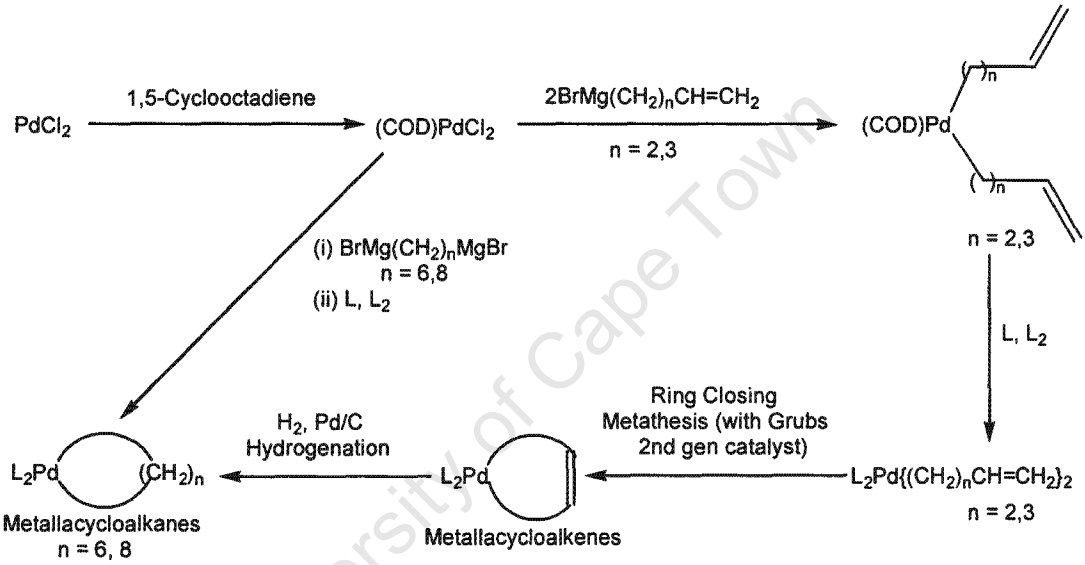
Palladium complexes catalyze a wide variety of reactions, especially in the field of carbon-carbon bond forming reactions such as polymerization, as well as Heck, Suzuki, and Stille coupling reactions. For most of these reactions palladacyclic complexes have either been proposed or shown to be key intermediates in the catalytic process. The types of organic products formed from the decomposition reactions of the palladacycles depend on the structure and ring size of the palladacycles.

The final stage in the mechanism of every catalytic or stoichiometric reaction in which metallacyclic intermediates are involved is the decomposition of these metallacycles to give organic products. Understanding the mechanisms by which the palladacyclic intermediates are formed, and their decomposition reactions is therefore of great importance in the development of new applications for palladium catalysts. Although a number studies have been carried out on the synthesis, characterization and decomposition reactions of palladacycloalkanes, more work still needs to be done in this area as relatively little work has been on these complexes compared to the other metals in the nickel triad.

1.6 Aims and Objectives of the Project

The aim of this project was to develop a new route for the synthesis of simple palladacycloalkanes of medium ring sizes. Palladacycloheptanes and palladacyclononanes were prepared. These complexes could be possible intermediates in palladium-catalyzed ethylene trimerization and tetramerization. Similar complexes based on chromium and titanium have been shown to be key intermediates in Cr- and Ti-catalyzed ethylene oligomerization.[13-16]

The palladacycloalkanes and their precursors were then characterized (as fully as possible) and thermal decomposition studies were carried out on some of the palladacycloalkanes and their precursors. The complexes were characterized using the ^{1}H, ^{13}C and ^{31}P NMR, microanalysis, mass spectrometry as well as melting points. The thermal decomposition products were characterized using gas chromatography/mass spectrometry. Scheme 1.23 below outlines the synthetic routes that were used in the synthesis of the palladacycloalkanes (see Chapter 2 for experimental details).



Scheme 1.23: Synthesis of the palladacycloalkanes in this study.

1.7 References

1. Dupont, J., Consorti, C. S. and Spencer, J., *Chem. Rev.*, 2005, **105**, 2527.
2. Brassat, I., Keim, W., Killat, S., Möthrath, M., Mastrorilli, P., Nobile, C. F. and Suranna, G. P., *J. Mol. Catal. A: Chem.*, 2000, **157**, 4.
3. Sen, A. and Lai, T. W., *J. Am. Chem. Soc.*, 1982, **104**, 3520.
4. Knight, J. G., Dorhety, S., Harriman, A., Robins, E. G. Betham, M., Eastham, G. R., Tooze, R. P., Elsegood, M. R. J., Champkin, P. and Clegg, W., *Organometallics*, 2000, **19**, 4957.
5. (a) Daugulis, O., Brookhart, M. and White, P. S., *Organometallics*, 2002, **21**, 5935. (b) De Vries, J. G., De Vries, A. H. M., Tucker, C. E. and Miller, J. A., *Innovations in Pharmaceutical Technology*, 2001, **1**, 125 and references therein. (c) Miura, M. and Nomura, M., *Top. Curr. Chem.*, 2002, **219**, 211 and references therein. (d) Huang, R. and Shaughnessy, K. H., *Organometallics*, 2006, **25**, 4105.
6. Negishi, E. (Ed), *Handbook of Organopalladium Chemistry for Organic Synthesis*, John Wiley and Sons Inc., New York, 2002, Vol 1, p3.
7. Dyker, G., Korning, J., Nerez, F., Siemen, P., Sostmann, S., Weigand, A., Jones, P. G. and Bubenitschek, P. *Pure and Appl. Chem.*, 1996, **68**, 323.
8. (a) Dyker, G., *Chem. Ber.*, 1997, **130**, 1567. (b) Trost, B. M., *Acc.Chem. Res.*, 1990, **23**, 34. (c) Trost, B. M. and Trost, M. K., *Tetrahedron Lett.*, 1991, **32**, 3647. (d) Trost, B. M. and Trost M. K., *J. Am. Chem. Soc.*, 1991, **113**, 1850. (e) Trost, B. M. and Chang, V. K., *Synthesis*, 1993, 824.
9. Collman, J. P., Hegedus, L. S., Norton, J. R. and Finke, R. G., *Principles and Applications of Organometallic Chemistry*, University Science Books, Mill Valley, 1987.
10. Blom, B., Clayton, H., Kilkenny, M. and Moss, J. R., *Adv. Organomet. Chem.*, 2005, **54**, 149.

11. Cámpora, J., Palma, P. and Carmona, E., *Coord. Chem. Rev.*, 1999, **193 -195**, 207.
12. (a) Chapell, S. D. and Cole-Hamilton, D. J., *Polyhedron*, 1982, **1**, 739. (b) McDermott, J. X., White, J. F. and Whitesides, G. M., *J. Am. Chem. Soc.*, 1973, **95**, 4451. (c) Elowe, P. R., McCann, C., Pringle, P. G., Spitzmesser, S. K. and Bercaw, J. E., *Organometallics*, 2006, **25**, 5255.
13. Overett, M. J., Blann, K., Bollmann, A., Dixon, J. T., Haasbroek, D., Killian, E., Maumela, H., McGuinness, D. S. and Morgan, D. H., *J. Am. Chem. Soc.*, 2005, **127**, 10723.
14. Bollmann, A., Blann, K., Dixon, J. T., Hess, F. M., Killian, E., Maumela, H., McGuinness, D. S., Morgan, D. H., Neveling, A., Otto, S., Overett, M., Slawin, A. M. Z., Wasserscheid, P. and Kuhlmann, S., *J. Am. Chem. Soc.*, 2004, **126**, 14712.
15. Tomov, A. K., Chirinos, J. J., Jones, D. J., Long, R. J. and Gibson, V. C., *J. Am. Chem. Soc.*, 2005, **127**, 10166.
16. Tobisch, S and Zeigler, T., *Organometallics*, 2003, **22**, 5392.
17. Alonso, I, Alcami, M., Mauleon, P. and Carretero, J. C., *Chem. Eur. J.*, 2006, **12**, 4576.
18. Ames, D. E. and Bull, D., *Tetrahedron*, 1982, **38**, 383.
19. Ames, D. E. and Opalko, A., *Synthesis*, 1983, 234.
20. Ames, D. E. and Opalko, A., *Tetrahedron*, 1984, **40**, 1919.
21. Li, C.-S., Cheng, C.-H., Liao, F.-L. and Wang, S.-L., *J. Chem. Soc. Chem. Commun.*, 1991, 710.
22. Catellani, M., Mealli, C., Motti, E., Paoli, P., Perez-Carreno, E. and Pregosin, P. S., *J. Am. Chem. Soc.*, 2002, **124**, 4336.
23. Laschober, R. and Kappe, T., *Synthesis*, 1990, 387.
24. Bringmann, G., Walter, R. and Weirich, R., *Angew. Chem. Int. Ed. Engl.*, 1990, **29**, 977.
25. Rice, J. E. and Cai, Z.-W., *J. Org. Chem.*, 1993, **58**, 1415.
26. Dyker, G., *J. Org. Chem.*, 1993, **58**, 234.
27. Balme, G. and Bouyssi, D., *Tetrahedron*, 1994, **50**, 403.

28. Szabo, A. A. K. J., Castana, A. M. and Backvall, J.-E., *Organometallics*, 1997, **16**, 1058.
29. Hegedus, L. S., Darlington, W. H. and Russell, C. E., *J. Org. Chem.*, 1980, **45**, 5193.
30. Jennings, P. W. and Johnson, L. L., *Chem. Rev.*, 1994, **94**, 2241.
31. Bernadi, F., Bottoni, A. and Miscione, P. G., *Organometallics*, 2001, **20**, 2751.
32. Suzuki, T. and Fujimoto, H., *Inorg. Chem.*, **39**, 1113.
33. Masselot, D., Charmant, J. P. H. and Gallagher, T., *J. Am. Chem. Soc.*, 2006, **128**, 694.
34. Satoh, T. and Jones, W. D., *Organometallics*, 2001, **20**, 2916.
35. Catellani, M., Motti, E. and Paterlini, L., *J. Organomet. Chem.*, 2000, **593 – 594**, 240.
36. Catellani, M. and Motti, E., *New J. Chem.*, 1998, 759.
37. Catellani, M., *Synthesis*, 2003, 298.
38. Cardenas, D. J., Martin-Matute, B. and Echavarren, A. M., *J. Am. Chem. Soc.*, 2006, **128**, 5033.
39. Suzaki, Y. and Osakada, K., *Bull. Chem. Soc. Jpn.*, 2004, **77**, 139.
40. Axenov, K. V., Leskalä, M. and Repo, T., *J. Catal.*, 2006, **238**, 96.
41. Blom, B., Overett, M. J., Meijboom, R. and Moss, J. R., Inorg. Chimica. Acta, 2005, 358, 3491.
42. Rix, F. C. and Brookhart, M., *J. Am. Chem. Soc.*, 1995, **117**, 1137.
43. Johnson, L. K., Killian, C. M. and Brookhart, M., *J. Am. Chem. Soc.*, 1995, **117**, 6414.
44. Tempel, D. J., Johnson, L. K., Huff, R. L., White, P. S. and Brookhart, *J. Am. Chem. Soc.*, 2000, **122**, 6686.
45. Malinoski, J. M. and Brookhart, M., *Organometallics*, 2003, **22**, 5324.
46. Chen, .J-T., Liu, S.-T. and Zhao, K.-Q., *J. Chin., Chem. Soc.*, 2000, **47**, 279.
47. Abraham, S., Ha, C.-S. and Kim, I., *Macromol. Rapid Commun.*, 2006, **27**, 1386.

48. Van den Beuken, E. K., Smeets, W. J. J., Spek, A. L. and Feringa, B. L., *Chem. Commun.*, 1998, 223.
49. Grubbs, R. H. and Miyashita, A., *J. Am. Chem. Soc.*, 1978, **100**, 1300.
50. Huang, X., Zhu, J. and Lin, Z., *Organometallics*, 2004, **23**, 4154.
51. Binger, P., Buech, H. M., Benn, R. and Mynott, R., *Angew. Chem. Int. Ed. Engl.*, 1982, **21**,62.
52. Diversi, P., Ingrosso, G., Lucherini, A. and Murtas, *J. Chem. Soc. Dalton Trans.*, 1980, 1633.
53. Diversi, P., Ingrosso, G., Lucherini, A., Lumini, T. and Marchetti, F., *J. Chem. Soc. Dalton Trans.*, 1988, 133.

Chapter 2

Experimental

2.1 Experimental Details

2.1.1 General Experimental Procedures

All reactions were carried out under a nitrogen or argon atmosphere using a dual vacuum/nitrogen line and standard Schlenk line techniques unless otherwise stated. All solvents were analytical grade and were dried and purified by refluxing under an inert atmosphere over a suitable drying agent. Diethyl ether and tetrahydrofuran were dried over sodium wire with benzophenone. Dichloromethane was dried over calcium hydride (CaH_2). Hexane and pentane were dried over ^{t}BuLi and 2,2'-bipyridine. Benzene was dried over sodium melt. All solvents were freshly distilled before use.

$PdCl_2$ was obtained from Johnson Matthey. All other reagents were obtained commercially from Aldrich and, unless otherwise stated, were used as received without further purification.

2.1.2 Instrumentation

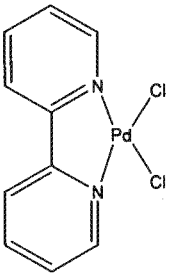
Microanalysis was carried out at the University of Cape Town using a Fisons EA 1108 CHNS Elemental Analysis apparatus. Melting points were recorded using a Kofler hot stage microscope (Riechert Thermovar). ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on Varian XR300 MHz and XR400 MHz spectrometers using deuterated chloroform, benzene or dimethylsulfoxide purchased from Aldrich as solvents. Tetramethylsilane (TMS) was used as the internal standard. Mass spectra were recorded at the University of Witwatersrand. GC studies were carried out at the University of Cape Town using a Varian 3900 gas chromatograph equipped with an FID and a 30 m x 0.32 mm CP-Wax 52 CB column (0.25 μm film thickness). The carrier gas used was helium at 5.0 psi. The oven was programmed to hold at 32°C for 4 minute and then to ramp to 200°C at

10°C/min and then hold for 5 minutes. GC-MS analyses were performed using an Agilent 5973 gas chromatograph equipped with MSD and a 60 m x 0.25 mm Rtx-1 column (0.5 μm film thickness). The carrier gas was helium at a flow rate of 0.9 ml/min. The oven was programmed to hold at 50°C for 2 minutes and then ramp to 250°C at 10 °C/minute and then hold for 8 minute. HPLC-grade compounds purchased from Aldrich were used as internal standards for the GC and GC-MS studies.

2.2 Preparation of Grignard Reagents

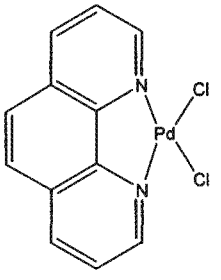
Alkenyl Grignard reagents were synthesized by reaction of the appropriate alkenyl bromide and excess magnesium turnings in dry diethyl ether.[1] A three-necked round-bottomed flask fitted with a dropping funnel and a reflux condenser, was charged with the appropriate amount magnesium turnings. The system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

2.3.3 Synthesis of *cis*-[(2,2'-bipyridine)dichloropalladium(II)]



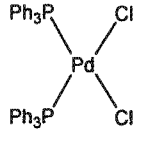
2,2'-bipyridine (0.55 g, 3.50 mmol) was dissolved in DCM (25 ml). To the colorless solution, a solution of $PdCl_2(COD)$ (1.01 g, 3.50 mmol) in DCM (25 ml) was added. A further 20 ml of DCM was added and the solution was refluxed at 50 °C for 3 hrs during which time a yellow precipitate formed. The precipitate was filtered on a Hirsch funnel, washed with DCM (50 ml) and dried under vacuum. The product was obtained as yellow solid (1.15 g, 98 %), melting point: >300 °C. δ_H(400 MHz, DMSO-d_6): 7.79 (2H, t, bipy), 8.35 (2H, t, bipy), 8.55 (2H, d, J_H = 8.42 Hz, bipy), 9.14 (2H, d, J_H = 5.86 Hz, bipy). δ_C(75 MHz, DMSO-d_6): 123.8 (2C, bipy), 127.2 (2C, bipy), 141.2 (2C, bipy), 149.7 (2C, bipy), 156.4 (2C, bipy). Anal. Calc. for $C_{10}H_8Cl_2N_2Pd$: C, 36.01; H, 2.42; N, 8.40. Found: C, 36.69; H, 2.18; N, 8.44. The elemental analysis and ^{1}H NMR spectral data agree with literature values.[3,4]

2.3.4 Synthesis of *cis*-[(1,10-phenanthroline)dichloropalladium(II)]



$PdCl_2(phen)$ was prepared from $PdCl_2(COD)$ following the procedure described for $PdCl_2(bipy)$. The product was obtained as a bright yellow crystalline solid (0.62 g, 92 %), melting point: >300 °C. δ_H(400 MHz, DMSO-d_6): 8.14 (2H, t, phen), 8.28 (2H, d, J_H = 9.75 Hz, phen), 8.96 (2H, dd, J_H = 4.88 Hz, phen), 9.35 (2H, d, J_H = 7.80 Hz, phen). δ_C(75 MHz, DMSO-d_6): 125.8 (C, phen), 131.9 (C, phen), 133.6 (C, phen), 140.7 (C, phen), 155.0 (C, phen). Anal. Calc. for $C_{12}H_8Cl_2N_2Pd$: C, 40.31; H, 2.25; N, 7.83. Found: C, 40.60; H, 2.22; N, 7.25. All data agree wit literature reports.[5]

2.3.5 Synthesis of *cis*-[bis(triphenylphosphine)dichloropalladium(II)]



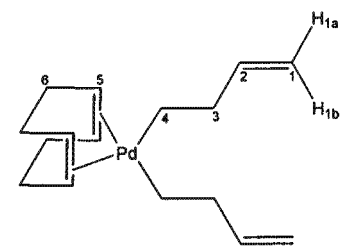
Triphenylphosphine (1.01 g, 3.85 mmol) was dissolved in dry Et_2O (10 ml) and stirred. To this solution, $PdCl_2(COD)$ (0.51 g, 1.79 mmol) was added. The mixture was stirred for 3 hours at room temperature. The yellow solid obtained was then filtered and washed with Et_2O and dried under vacuum for 3 hours. The product was obtained as a pale yellow solid (1.12 g, 90

%), melting point: 268 – 271 °C (with decomposition), (lit[6] 267 – 270 with decomposition). δ_H(400 MHz, $CDCl_3$): 7.38 (18H, m, Ph), 7.70 (12H, m, Ph). δ_P(120 MHz, $CDCl_3$): 23.5 (2P, $\underline{P}Ph_3$). Anal. Calc for $C_{36}H_{30}Cl_2P_2Pd$: C, 61.59; H, 4.32. Found: C, 61.25; H: 4.06. All data agrees with literature reports.[6,7]

2.4 General Procedure for the Synthesis of bisalkenyl Palladium Complexes, 54 – 55

The COD and bipy complexes, **54a**, **54b**, **55a** and **55b**, were synthesized by reacting the precursors, $PdCl_2L_2$, with excess alkenyl Grignard reagents to give the bisalkenyl complexes.[8] The phosphine complexes, **54c**, **54d**, **55c** and **55d**, were prepared by the reaction of $PdCl_2$(COD) with the Grignard reagents followed by displacement of COD by the phosphine ligands.[9] Microanalysis results of the complexes showed that a few solvent molecules were trapped in the products. Attempts to completely remove the solvent under vacuum resulted in the products decomposing.

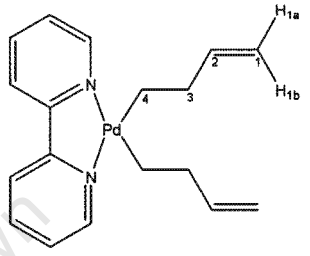
2.4.1 Synthesis of *cis*-[Pd($CH_2CH_2CH{=}CH_2$)$_2$(COD)], 54a



$PdCl_2$(COD) (0.51 g, 1.79 mmol) was suspended in dry Et_2O (15 ml) and the mixture was cooled to -78°C. A solution of butenyl magnesium bromide in Et_2O (2.39 $\underline{M}$, 2.3 ml, 5.36 mmol) was added drop-wise to the cold suspension and the mixture was stirred for 40 minutes, during which time the mixture was warmed to -30°C. Product formation was indicated by the dissolution of the palladium species and the reaction solution turning brown. At this point excess Grignard reagent was hydrolyzed by adding a saturated solution of NH_4Cl (5 ml). The product was extracted with hexane and the organic layer was collected and dried over anhydrous $MgSO_4$. Excess solvent was removed under reduced pressure and the product was obtained as a bright yellow oil, which was then dried under vacuum (0.26 g, 45%). δ_H(400 MHz, $CDCl_3$): 1.41 (4H, t, H4), 2.05 (4H, m, H3), 2.38 (8H, m, H6), 4.93 (2H, t, H1a), 5.03 (2H, m, H1b), 5.61 (4H, m, H5), 5.85

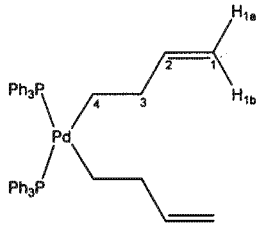
(2H, m, H2). δ_C(75 MHZ, $CDCl_3$): 19.9 (C4), 29.3 (C6), 33.9 (C3), 112.4 (C5), 114.6 (C1), 139.6 (C2). Anal. Calc. for **54a**.$2C_6H_{14}$, $C_{26}H_{50}Pd$: C, 66.57; H, 10.74. Found: C, 66.71; H, 7.76. Mass spec. (FAB): m/z 323.7 $[M]^+$, 215.6 $[M\text{-}COD]^+$, 268.7 $[M\text{-}CH_2CH_2CH{=}CH_2]^+$, 214.6 $[M\text{-}2CH_2CH_2CH{=}CH_2]^+$, 54.1 $[CH_2CH_2CH{=}CH_2]^+$, 107.2 $[2CH_2CH_2CH{=}CH_2]^+$.

2.4.2 Synthesis of *cis*-[Pd($CH_2CH_2CH{=}CH_2$)$_2$(bipy)], 54b



Complex **54b** was synthesized using the same procedure used for complex **54a** above. $PdCl_2$(bipy) (0.50 g, 1.50 mmol) was suspended in dry Et_2O (10 ml) at -78°C. A solution of butenyl magnesium bromide (2.39 M, 2.0 ml, 4.78 mmol) was added drop-wise to the cold suspension and the mixture was warmed to -30°C while stirring for 45 minutes. After work-up (as outlined for **54a** in Section 2.4.1) the product was obtained as a bright yellow oil (0.21 g, 35%). δ_H(400 MHz, CDl_3): 1.49 (4H, t, H4), 2.28 (4H, m, H3), 4.79 (2H, t, H1a), 4.92 (2H, m, H1b), 5.91 (2H, m, H2), 7.31 (2H, t, bipy), 7.80 (2H, t, bipy), 8.38 (2H, d, J_H = 8.67 Hz, bipy), 8.67 (2H, d, J_H = 6.01 Hz, bipy). δ_C(75 MHz, $CDCl_3$): 29.4 (C4), 35.7 (C3), 118.7 (C1), 120.3 (C, bipy), 124.1 (C, bipy), 137.2 (C, bipy), 141.2 (C2), 149.1 (C, bipy), 155.2 (C, bipy). Anal.Calc. for **54b**.$2C_6H_{14}$, $C_{30}H_{50}N_2Pd$: C, 66.10; H, 9.24; N, 5.14. Found: C, 66.53; H, 8.82; N, 5.22. Mass spec. (FAB): m/z 371.8 $[M]^+$, 215.0 $[M\text{-}bipy]^+$, 316.7 $[M\text{-}CH_2CH_2CH{=}CH_2]^+$, 260.9 $[M\text{-}2CH_2CH_2CH{=}CH_2]^+$.

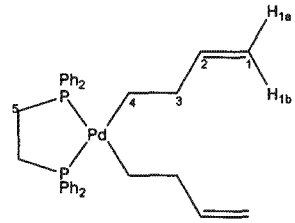
2.4.3 Synthesis of *cis*-[Pd($CH_2CH_2CH{=}CH_2$)$_2$(PPh_3)$_2$] 54c



Complex **54c** was prepared by substitution of 1,5-cyclooctadiene from complex **54a** by triphenylphosphine. After work-up (as outline in Section 2.4.1) the product was obtained as a bright yellow oil (0.67 g, 50%). δ_H(400 MHz, $CDCl_3$) 1.43 (4H, t, H4), 2.34 (4H, m, H3), 4.94 (2H, t, H1a), 5.07 (2H, m, H1b), 5.84 (2H, m, H2), 7.47 (12H, m, Ph), 7.54 (12H, m, Ph), 7.70 (6H, m, Ph). δ_P(120 MHz, $CDCl_3$): 29.2 ($\underline{P}Ph_3$). Anal. Calc. for **54c**.$2.5C_6H_{14}$,

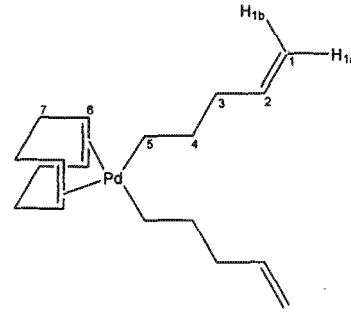
$C_{59}H_{80}P_2Pd$: C, 74.00; H, 8.42. Found: C, 73.51; H, 5.67. Mass spec. (FAB): m/z 740.1 $[M]^+$, 687.1 $[M\text{-}CH_2CH_2CH{=}CH_2]^+$, 629.8 $[M\text{-}2CH_2CH_2CH{=}CH_2]^+$, 477.8 $[M\text{-}PPh_3]^+$, 215 $[M\text{-}2PPh_3]^+$.

2.4.4 Synthesis of *cis*-[Pd(CH$_2$CH$_2$CH=CH$_2$)$_2$(dppe)], 54d



Complex **54d** was prepared using the same procedure as **54c**. After work-up (see Section 2.4.1) the product was obtained as yellow oil (0.52 g, 48%). δ_H(400 MHz, $CDCl_3$): 1.72 (4H, t, H4), 2.36 (4H, m, H3), 3.44 (4H, t, H5), 4.96 (2H, t, H1a), 5.10 (2H, m, H1b), 5.82 (2H, m, H2), 7.44 (12H, m, Ph), 7.62 (8H, m, Ph). δ_P(120 MHz, $CDCl_3$) 31.0 (-$\underline{P}Ph_2$). Anal. Calc. for **54d**.2C_6H_{14}, $C_{46}H_{66}P_2Pd$: C, 70.17; H, 8.45. Found: C, 70.12; H, 9.76. Mass spec. (FAB): m/z 614.0 $[M]^+$, 560.0 $[M\text{-}CH_2CH_2CH{=}CH_2]^+$, 502.9 $[M\text{-}2CH_2CH_2CH{=}CH_2]^+$, 215.4 $[M\text{-dppe}]^+$.

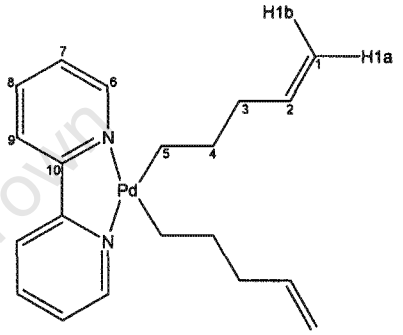
2.4.5 Synthesis of *cis*-[Pd(CH$_2$CH$_2$CH$_2$CH=CH$_2$)$_2$(COD)], 55a



Complex **55a** was prepared in a similar way to **54a** using pentenyl magnesium bromide as the Grignard reagent instead of butenyl magnesium bromide. A suspension of $PdCl_2$(COD) (0.50g, 1.75 mmol) in anhydrous diethyl ether (10 ml) was cooled to -78°C and a solution of $BrMg(CH_2)_3CH{=}CH_2$ (1.3 $\underline{M}$, 4.1 ml, 5.25 mmol) in anhydrous Et_2O was added drop-wise to this suspension. The mixture was stirred for 45 minutes, during which time the mixture was warmed to -30°C and dissolution of the palladium species was observed. The solution turned brown, indicating product decomposition. The reaction was then quenched by adding a saturated solution of NH_4Cl (5 ml). The organic product was extracted with hexane and the organic layer was collected and dried over anhydrous $MgSO_4$. Excess solvent was removed under reduced pressure and the product was dried under vacuum for three hours. The product was obtained as a bright yellow oil (0.30 g, 48%). δ_H(400 MHz, $CDCl_3$): 1.28 (4H, t, H5), 1.36 (4H, m, H4),

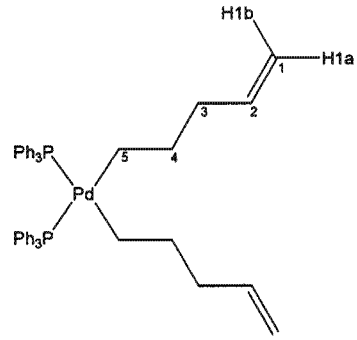
2.03 (4H, m, H3), 2.37 (8H, m, H7), 4.91 (2H, t, H1a), 5.02 (2H, m, H1b), 5.58 (4H, m, H6), 5.77 (2H, m, H2). δ_C(75 MHz, $CDCl_3$): 25.7 (C5), 29.8 (C4), 34.1 (C7), 36.1 (C3), 113.1 (C6), 114.3 (C1), 139.0 (C2). Anal. Calc. for **55a**·C_6H_{14}, $C_{24}H_{44}Pd$: C, 65.66; H, 10.10. Found: C, 65.94; H, 11.71. Mass spec. (FAB): m/z 351.9 $[M]^+$, 282.7 $[M\text{-}CH_2CH_2CH_2CH{=}CH_2]^+$, 243.6 $[M\text{-}COD]^+$, 214.6 $[M\text{-}2CH_2CH_2CH_2CH{=}CH_2]^+$, 140.3 $[2CH_2CH_2CH_2CH{=}CH_2]^+$, 70.2 $[CH_2CH_2CH_2CH{=}CH_2]^+$.

2.4.6 Synthesis of *cis*-[Pd($CH_2CH_2CH_2CH{=}CH_2$)$_2$(bipy)], 55b



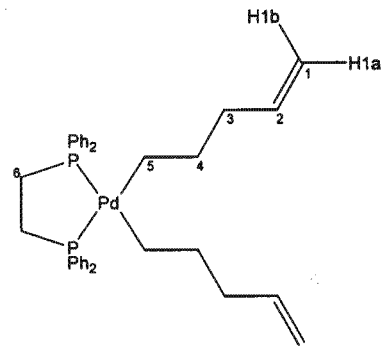
Complex **55b** was prepared following the same procedure used for complex **54b**. $PdCl_2$(bipy) (0.21 g, 0.60 mmol) was suspended in anhydrous Et_2O and cooled to -78°C. A solution of $BrMg(CH_2)_3CH{=}CH_2$ (1.3M, 1.4 ml, 1.80 mmol) was added drop-wise to the suspension and the mixture was stirred for 40 minutes. After work-up (as ouline for **55a** in Section 2.4.5) the product was obtained as a yellow solid (0.068 g, 28%), melting point: 48 - 52°C. δ_H(300 MHz, $CDCl_3$): 1.19 (4H, m, H5), 1.29 (4H, m, H4), 1.95 (4H, m, H3), 4.96 (2H, m, H1a), 5.03 (2H, m, H1b), 5.76 (2H, m, H2), 6.66 (2H, t, H7), 7.21 (2H, t, H8), 8.51 (2H, d, J_H = 4.88 Hz, H9), 8.70 (2H, d, J_H = 7.80 Hz, H6). δ_C(75 MHz, $CDCl_3$): 29.0 (C5), 32.1 (C4), 38.1 (C3), 115.5 (C1), 119.6 (C7), 123.3 (C9), 137.8 (C8), 141.4 (C2), 145.2 (C6), 152.3 (C10). Anal. Calc. for **55b**.1.5C_6H_{14}, $C_{29}H_{48}N_2Pd$: C, 65.58; H, 9.11; N, 5.27. Found: C, 65.58; H, 6.59; N, 4.35. Mass spec. (FAB): m/z 399.8 $[M]^+$, 330.7 $[M\text{-}CH_2CH_2CH_2CH{=}CH_2]^+$, 261.6 $[M\text{-}2CH_2CH_2CH_2CH{=}CH_2]^+$, 243.8 $[M\text{-bipy}]^+$.

2.4.7 Synthesis of *cis*-[Pd($CH_2CH_2CH_2CH=CH_2$)$_2$(PPh_3)$_2$], 55c



Complex **55c** was prepared using the same procedure as **54c**, except that pentenyl magnesium bromide was used as the alkylating agent instead of butenyl magnesium bromide. $PdCl_2$(COD) (0.52 g, 1.82 mmol) was suspended in anhydrous Et_2O and cooled to -78°C. To the cold suspension, a solution of $BrMg(CH_2)_3CH=CH_2$ (1.3M, 4.2 ml, 5.6 mmol) was added drop-wise. Complex **55a** was isolated, dissolved in Et_2O (15 ml) and PPh_3 (0.47 g, 1.78 mmol) was added. After work-up the product was obtained as a bright yellow oil (0.67 g, 49%) . δ_H(400 MHz, $CDCl_3$): 1.63 (4H, m, H5), 1.99 (4H, m, H4), 2.10 (4H, m, H3), 4.86 (2H, m, H1a), 4.96 (2H, m, H1b), 5.80 (2H, m, H2), 7.01 – 7.88 (30H, m, Ph). δ_P(120 MHz, $CDCl_3$): 29.7 ($\underline{P}Ph_3$). Anal. Calc. for **55c**.$5C_6H_{14}$, $C_{76}H_{118}P2Pd$: C, 76.06; H, 9.91. Found: C, 76.84; H, 10.66. Mass spec. (FAB): m/z 767.9 $[M]^+$, 698.1 $[M\text{-}CH_2CH_2CH_2CH=CH_2]^+$, 629.8 $[M\text{-}2CH_2CH_2CH_2CH=CH_2]^+$, 505.9 $[M\text{-}PPh_3]^+$, 243.5 $[M\text{-}2PPh_3]^+$, 135.1 $[2CH_2CH_2CH_2CH=CH_2]^+$, 68.2 $[CH_2CH_2CH_2CH=CH_2]^+$.

2.4.8 Synthesis of *cis*-[Pd($CH_2CH_2CH_2CH=CH_2$)$_2$(dppe)], 55d



Complex **55d** was prepared following the same procedure used for **55c**. $PdCl_2$(COD) (0.50 g, 1.75 mmol) was suspended in dry Et_2O (15 ml) and cooled to -78°C. $BrMg(CH_2)_3CH=CH_2$ was slowly added to the cold suspension and the mixture was warmed to -78°C. The COD complex, **55a**, was isolated and then dissolved in dry Et_2O (30 ml). 1,2-bis(diphenylphosphino)ethane (0.35 g, 0.88 mmol) was added to this solution. After work-up the product was obtained as a yellow oil (0.56 g, 50%). δ_H(400 MHz, $CDCl_3$): 1.31 (4H, t, H5), 1.39 (4H, m, H4), 2.37 (4H, m, H3), 2.52 (4H, t, H6), 4.94 (2H, m, H1a), 5.01 (2H, m, H1b), 5.81 (2H, m, H2), 7.45 – 7.89 (20H, m, Ph).

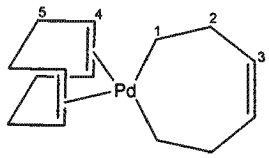
δ_P(120 MHz, $CDCl_3$): 30.1 (-$\underline{P}Ph_2$). Anal. Calc. for **55d**.4C_6H_{14}, $C_{60}H_{98}P_2Pd$: C, 72.96; H, 10.00. Found: C, 73.11; H, 9.67. Mass spec. (FAB): m/z 642.1 $[M]^+$, 572.9 $[M\text{-}CH_2CH_2CH_2CH{=}CH_2]^+$, 503.8 $[M\text{-}2CH_2CH_2CH_2CH{=}CH_2]^+$, 243.6 [M-dppe]$^+$.

2.5 Synthesis of Palladacycloalkenes, 57 – 58

The palladacycloalkene complexes, **57** – **58**, were prepared by ring closing metathesis (RCM) reactions of the bisalkenyl complexes, **54** – **55**, using Grubbs' second generation catalyst.[8,10-12] The catalyst was added in batches of 5 mol% after every five hours during the course of each RCM reaction. The reaction time ranged between 18 and 30 hours, depending on the different ligands in the complexes. All reactions were carried out at 50°C using benzene as a solvent. The products were obtained as brown oils in good to excellent yields (60 – 90%). All RCM reactions were carried following the procedure outlined for complex **57a** below.

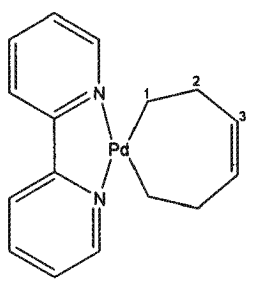
All compounds were characterized by ^1H and ^{31}P NMR spectroscopy (in the case of phosphine-based complexes) as well mass spectrometry. Product formation was indicated by the disappearance of the two signals at *ca.* 5.0 and 5.8 ppm, and appearance of the signal at *ca.* 5.4 ppm in the ^1H NMR spectra of the products. Well-resolved signals corresponding to the Pd-C$\underline{H}_2$- and =C$\underline{H}$- protons in the palladacycloalkenes were observed. However, signals for the methylene further away from the metal centre in the palladacyclononenes (complexes **58a** – **58d**) were not very well resolved and appeared as broad multiplets,[13] but the integrations for these peaks correspond to the expected number of methylene protons in these complexes.

2.5.1 Synthesis of *cis*-[Pd(C_6H_{10})(COD)], 57a



In a round-bottomed flask, complex **54a**, cis-Pd{$(CH_2)_2CH=CH_2$}$_2$(COD) (0.15 g, 0.46 mmol) was dissolved in benzene (20 ml) and Grubbs' second generation catalyst was added to the solution. The resulting solution was refluxed with stirring at 40°C for a total of 20 hrs. The catalyst was added in batches of 5 mol% at five hour intervals throughout the course of the reaction. Reaction progress was monitored by ^{1}H NMR spectroscopy and a sample was taken for ^{1}H NMR analysis after every two hours. After 20 hrs the solution was cooled to room temperature and excess solvent was removed on the rotary evaporator and a maroon residue was obtained. The product was extracted with hexane (4 x 5 ml) by adding hexane stirring the mixture for *ca.* 5 min. The mixture was then allowed to stand for a further 5 min. to allow for Grubb's catalyst (which is insoluble in hexane) to settle down and the supernatant was then decanted into a clean round-bottomed flask. When this process was complete, hexane was removed on the rotary evaporator and the product was obtained as brown oil (0.10 g, 70%). δ_H(300 MHZ, C_6D_6): 1.42 (4H, m, H1), 2.04 (4H, m, H2), 2.37 (8H, m, H5), 5.33 (2H, br m, H3), 5.58 (4H, m, H4). Mass spec. (FAB): m/z 295.7 $[M]^+$, 189.1 $[M\text{-COD}]^+$, 213.4 $[M\text{-}C_6H_{10}]^+$.

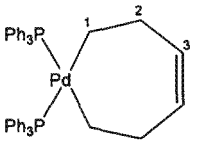
2.5.2 Synthesis of *cis*-[Pd(C_6H_{10})(bipy)], 57b



Complex was prepared from complex **54b**, cis-Pd{$(CH_2)_2CH=CH_2$}$_2$(bipy) (0.21 g, 0.56 mmol) as the starting material. The complex was prepared using the same procedure used for the synthesis of complex **57a**, however, the reaction mixture was refluxed in benzene (25 ml) at 50°C for 24 hrs. After work-up (as outlined for **57a**) the product was obtained as a brown oil (0.16 g, 85%). δ_H(300 MHz, C_6D_6): δ_H(400 MHz, C_6D_6): 1.46 (4H, m, H1), 2.28 (4H, m, H2), 5.42 (2H, br m, H3), 7.33

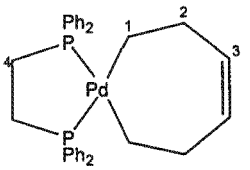
(2H, m, bipy) 7.81 (2H, m, bipy), 8.38 (2H, m, bipy), 8.69 (2H, m, bipy). Mass spec. FAB): m/z 343.6 $[M]^+$, 261.6 $[M\text{-}C_6H_{10}]^+$, 189.6 $[M\text{-bipy}]^+$.

2.5.3 Synthesis of *cis*-[Pd(C_6H_{10})(PPh_3)$_2$], 57c



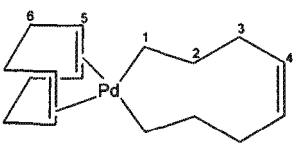
Complex **57c** was prepared by the RCM reaction of complex **54c**, cis-Pd{$(CH_2)_2CH{=}CH_2$}$_2$(PPh_3)$_2$ (0.32 g, 0.45 mmol) following the same procedure used for the preparation of **57a**. The reaction mixture was refluxed in benzene (30 ml) at 50°C for 18 hrs. After work-up (as for **57a**) the product was obtained as a brown oil (0.25 g, 80%). δ_H(300 MHz, C_6D_6): 1.62 (4H, m, H1), 2.31 (4H, m, H2), 5.44 (2H, br m, H3), 7.44 – 7.71 (30H, m, Ph). δ_P(120 MHz, C_6D_6): 29.3 ($\underline{P}Ph_3$). Mass spec. (FAB): m/z 712.1 $[M]^+$, 629.1 $[M\text{-}C_6H_{10}]^+$, 449.8 $[M\text{-}PPh_3]^+$, 188.9 $[M\text{-}2PPh_3]^+$.

2.5.4 Synthesis of *cis*-[Pd(C_6H_{10})(dppe)], 57d



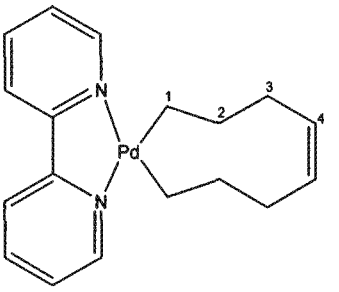
Complex **57d** was synthesized by the RCM reaction of complex **54d**, cis-Pd{$(CH_2)_2CH{=}CH_2$}$_2$(dppe) (0.24 g, 0.39 mmol) following the same procedure used for the synthesis of **57a**. The reaction mixture was refluxed in benzene (30 ml) at 50°C for 20 hrs. After work-up (as for **57a**) the product was obtained as a brown oil (0.18 g, 82%). δ_H(300 MHz, C_6D_6): 1.79 (4H, m, H1), 2.05 (4H, m, H2), 2.54 (4H, t, H4), 5.40 (2H, br m, H3), 7.46 – 8.01 (20H, m, Ph). δ_P(120 MHz, C_6D_6): 32.9 (-$\underline{P}Ph_2$). Mass spec. (FAB): 585.9 $[M]^+$, 503.8 $[M\text{-}C_6H_{10}]^+$, 189.4 $[M\text{-dppe}]^+$.

2.5.5 Synthesis of *cis*-[Pd(C_8H_{14})(COD)], 58a



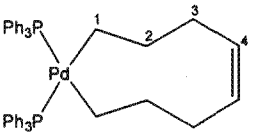
Complex **58a** was prepared by the RCM reaction of the bispentenyl complex, **55a**, cis-Pd{$(CH_2)_3CH{=}CH_2$}$_2$(COD) (0.20g , 0.57 mmol). The reaction mixture was stirred at 40°C for 20 hrs using benzene (25 ml) as the solvent. After work-up (as for **57a**) the product was obtained as a dark brown oil (0.12 g, 63%). δ_H(400 MHz, C_6D_6): 1.39 (4H, m, H1), 1.47 – 2.19 (8H, br m, H2 – H3), 2.38 (8H, m, H6), 5.39 (2H, br m, H4), 5.57 (4H, m, H5). Mass spec. (FAB): m/z 323.8 $[M]^+$, 216.8 $[M\text{-COD}]^+$, 213.1 $[M\text{-}C_8H_{14}]^+$.

2.5.6 Synthesis of *cis*-[Pd(C_8H_{14})(bipy)], 58b



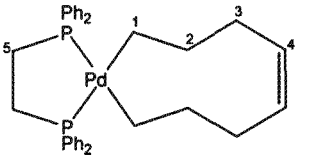
Complex **58b** was prepared by RCM reaction of complex **55b**, cis-Pd{$(CH_2)_3CH=CH_2$}$_2$(bipy) (0.10g , 0.25 mmol). The reaction mixture was refluxed at 40°C for 30 hrs and benzene (20 ml) was used as the solvent. After work-up (as outlined for **57a**) the product was obtained as a dark brown oil (0.08 g, 87%). δ_H(400 MHz, C_6D_6) 1.45 (4H, m, H1), 1.56 – 2.31 (8H, br m, H2 – H3), 5.36 (2H, br m, H4), 7.31 (2H, t, bipy), 7.85 (2H, t, bipy), 8.47 (2H, d, J_H = 8.67 Hz, bipy), 8.69 (2H, d, J_H = 5.77 Hz, bipy). Mass spec. (FAB): m/z 371.8 $[M]^+$, 217.0 $[M\text{-bipy}]^+$, 260.0 $[M\text{-}C_8H_{14}]^+$.

2.5.7 Synthesis of *cis*-[Pd(C_8H_{14})(PPh_3)$_2$], 58c



Complex **58c** was prepared by the RCM reaction of **55c**, cis-Pd{$(CH_2)_3CH=CH_2$}$_2$(PPh_3)$_2$ (0.31g, 0.40 mmol). The reaction was carried out by refluxing in benzene (30 ml) at 50°C for 20 hrs. After work-up (as outlined for **57a**) the product was obtained as a dark brown oil (0.21 g, 71%). δ_H(400 MHz, C_6D_6): 1.51 (4H, m, H1), 1.70 – 2.27 (8H, br m, H2 – H3), 5.45 (2H, br m, H4), 7.47 – 7.90 (30H, m, Ph). δ_P(120 MHz, C_6D_6): 28.6 ($\underline{P}Ph_3$). Mass spec. (FAB): m/z 740.2 $[M]^+$, 628.9 $[M\text{-}C_8H_{14}]^+$, 477.8 $[M\text{-}PPh_3]^+$, 217.1 $[M\text{-}2PPh_3]^+$.

2.5.8 Synthesis of *cis*-[Pd(C_8H_{14})(dppe)], 58d



Complex **58d** was prepared by the RCM reaction of **55d**, cis-Pd{$(CH_2)_3CH=CH_2$}$_2$(dppe) (0.23 g, 0.36 mmol). The reaction was carried out at by refluxing in benzene (30 ml) at 50°C for 26 hrs. After work-up (as outlined for **57a**) the product was obtained as brown oil (0.17 g, 79%). δ_H(400 MHz, C_6D_6): 1.87 (4H, m, H1), 2.01 – 2.38 (8H, br m, H2 – H3), 2.58 (4H, t, H5), 5.41 (2H, br m, H4), 7.45 –

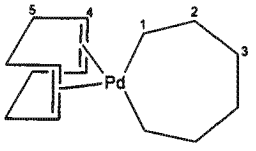
7.76 (20H, m, Ph). δ_P(120 MHz, C_6D_6): 32.9 (-$\underline{P}Ph_2$). Mass spec. (FAB): m/z 614.1 $[M]^+$, 503.9 $[M\text{-}C_8H_{14}]^+$, 216.9 [M-dppe]$^+$.

2.6 Synthesis of Palladacycloalkanes, 59 – 60

The palladacycloalkanes, **59 – 60** were synthesized by hydrogenation of the palladacycloalkenes **57 – 58**.[8] The hydrogenation reactions were all carried out by stirring a solution of appropriate palladacycloalkenes in benzene under atmospheric pressure of hydrogen gas at room temperature as outlined for complex **59a**. The reaction time ranged between 40 and 50 hours, depending on the different ligands used. 10 wt% of 10% Pd/C was used as the catalyst in all reactions and reaction progress was monitored by ^{1}H NMR spectroscopy and a sample of the reaction mixture was submitted for ^{1}H NMR spectroscopy after every two hours. Product formation was indicated by the gradual disappearance of the signal at *ca.* 5.4 ppm, which is attributed to the alkene protons, =C$\underline{H}$-, in the palladacycloalkenes.

Signals for the methylene protons in the ^{1}H NMR spectra of the palladacycloheptanes are well resolved and were assigned. On the other hand, signals the methylene protons in the ^{1}H NMR spectra of the palladacyclononanes appear as broad multiplets. Integrations for these multiplets, however, agree with the expected number of the methylene protons in the products. All products were identified by ^{1}H NMR spectroscopy, mass spectrometry and, in the case of phosphine-based complexes, ^{31}P NMR spectroscopy.

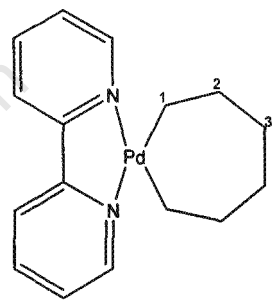
2.6.1 Synthesis of *cis*-[Pd(C_6H_{12})(COD)], 59a



In a round-bottomed flask, a solution of complex **57a**, Pd(C_6H_{10})(COD) (0.08 g, 0.27 mmol) in Et_2O (20 ml) was added. 10% Pd/C (8 mg) was then added to this solution. A take-off fitted with a tap was attached to a balloon and this balloon was filled with hydrogen gas. The take-off at the mouth of the balloon was attached to the mouth of the round-bottomed flask and the tap was opened.

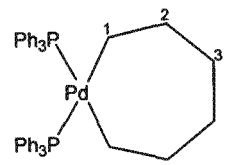
The mixture was stirred at room temperature for 40 hrs. During the course of the reaction, the balloon was refilled with hydrogen gas when the gas was running low. The mixture was then filtered and excess solvent was removed under reduced pressure and the product was obtained as a brownish yellow oil that was dried for half an hour under vacuum. (0.063 g, 78%). δ_H(400 MHz, C_6D_6): 1.39 (4H, m, H1), 2.06 (8H, m, H2 - H3), 2.39 (8H, m, -C<u>H</u>$_2$- (COD)), 5.61 (4H, m, =C<u>H</u>$_2$- (COD). Mass spec. (FAB): m/z 297.8 $[M]^+$, 213.7 $[M\text{-}C_6H_{12}]^+$, 189.5 [M-COD]$^+$.

2.6.2 Synthesis of *cis*-[Pd(C_6H_{12})(bipy)], 59b



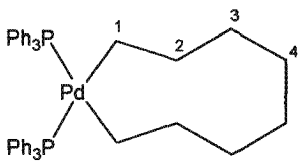
The procedure used for the preparation of complex **59a** was followed for the synthesis of complex **59b**. Complex **57b** (0.13 g, 0.38 mmol) was dissolved in Et_2O (20 ml) and 10% Pd/C (12 mg) was added to the solution. A balloon filled with hydrogen gas was attached and the solution was stirred under hydrogen for 50 hrs. After work-up (as outlined for **59a**) the product was obtained as a brownish yellow oil (0.11 g, 83%). δ_H(300 MHz, C_6D_6): 1.26 (4H, m, H1), 1.62 (8H, m, H2 - H3), 7.26 (2H, m, bipy), 7.81 (2H, t, bipy), 8.41 (2H, d, J_H = 8.78 Hz, bipy), 8.68 (2H, d, J_H = 3.90 Hz, bipy). Mass spec. (FAB): m/z 345.8 $[M]^+$, 261.6 $[M\text{-}C_6H_{12}]^+$, 189.6 [M-bipy]$^+$.

2.6.3 Synthesis of *cis*-[Pd(C_6H_{12})(PPh_3)$_2$], 59c



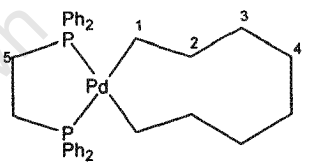
Complex **59c** was prepared following the procedure used for the synthesis of **59a**. Complex **57c** (0.21 g, 0.29 mmol) was dissolved in Et_2O (20 ml) and 10% Pd/C (20 mg) was added to the solution. The solution was stirred under hydrogen gas for 46 hrs. After work-up (as for **59a**) the product was obtained as a brownish yellow solid (0.19 g, 90%), melting point: 48 - 59°C (with decomposition). δ_H(300 MHz, C_6D_6): 2.05 (4H, m, H1), 2.30 (8H, m, H2 and H3), 7.35 – 7.82 (30H, m, Ph). δ_P(120 MHz, C_6D_6): 27.3 (<u>P</u>Ph_3). Mass spec. (FAB): m/z 714. 2 (M^+), 451.8 (M-PPh_3)$^+$, 189.7 (-2PPh_3)$^+$, 629.1 (M-C_6H_{12})$^+$.

2.6.7 Synthesis of *cis*-[Pd(C_8H_{16})(PPh_3)$_2$], 60c



Complex **58c** (0.18g, 0.24 mmol) was dissolved in Et_2O (20 ml) and 10% Pd/C (20 mg) was added. The solution was stirred under hydrogen gas for 44 hrs. After work-up (as for **57a**) the product was obtained as a brownish yellow solid (0.14 g, 83%), melting point 39 - 49°C (with decomposition). δ_H(300 MHz, C_6D_6): 0.87 (4H, m, H1), 1.22 – 1.62 (12H, m, H2 – H4), 7.64 – 7.98 (20H, m, Ph). δ_P(120 MHz, C_6H_6): 25.5 (2P, $\underline{P}Ph_3$). Mass spec. (FAB): m/z 742.9 $[M]^+$, 630.0 $[M-C_8H_{16}]^+$, 489.9 $[M-PPh_3]^+$, 216.9 $[M-2PPh_3]^+$.

2.6.8 Synthesis of *cis*-[Pd(C_8H_{16})(dppe)], 60d

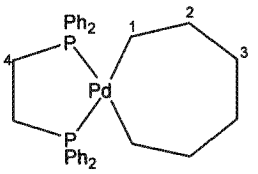


Complex **58d** (0.14 g, 0.22 mmol) was dissolved in Et_2O (20 ml) and 10% Pd/C was added. The solution was stirred under hydrogen gas for 46 hrs. After work-up the product was obtained as a pale yellow solid (0.10 g, 76%), 55 - 67°C (with decomposition). δ_H(300 MHz, C_6D_6): 0.90 (8H, br m, H1 – H2), 1.33 (8H, br m, H3 – H4), 2.24 (4H, t, H5), 7.10 – 7.85 (20H, m, Ph). δ_P(120 MHz, C_6D_6): 33.5 (2P, -$\underline{P}Ph_2$). Mass spec. (FAB): m/z 616.0 $[M]^+$, 503.4 $[M-C_8H_{16}]^+$, 217.5 $[M-dppe]^+$.

2.7 Di-Grignard Reactions

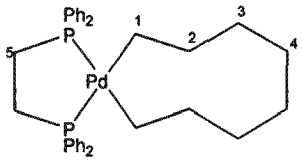
The dppe-based palladacycloalkanes, **59d**, and **60d**, were also prepared by reacting $PdCl_2$(COD) with appropriate di-Grignard reagents followed by ligand displacement.[14,15] The products were obtained as very pale yellow (almost white) solids in very modest yields (11 – 15%). These compounds were identified by ^1H and ^{31}P NMR spectroscopy and their spectra were found to be the same as the spectra obtained for the same complexes prepared by the hydrogenation reactions of the corresponding palladacycloalkenes as indicated in Sections 2.6.4 and 2.6.8.

2.7.1 Synthesis of *cis*-[Pd(C_6H_{12})(dppe)], 59d



In a Schlenk tube, $PdCl_2$(COD) (0.50 g, 1.75 mmol) was suspended in anhydrous Et_2O (30 ml) and cooled to -78°C. To the cold suspension, a solution of $BrMg(CH_2)_6MgBr$ in anhydrous THF (1.5 ml, 2.6 M, 3.50 mmol) was added drop-wise. The solution mixture was then stirred for 30 minutes, during which time dissolution of the palladium species was observed and the solution turned dark brown, with palladium black precipitating out of solution. Pentane (5 ml) was then added to the tube and excess di-Grignard reagent precipitated out of solution. The supernatant was transferred into a clean roun-bottomed flask and filtered. Excess solvent was removed from the filtrate under reduced pressure and the COD complex, **59a**, was obtained as yellow oil. The oil was dissolved in Et_2O (20 ml) and dppe (0.12 g, 0.31 mmol) was added. The product immediately precipitated out of solution. The mixture was stirred for a further 30 minutes and the supernatant was removed. The pale yellow solid obtained was washed with diethyl ether (4 x 5 ml). The solid was dried under vacuum for half an hour. (0.15 g, 15%), melting point 69 - 72°C (with decomposition). δ_H(300 MHz, C_6D_6): 2.01 (4H, br m, H1), 2.51 (8H, m, H2 – H3), 3.37 (4H, t, H4), 7.41 – 7.71 (20H, m, Ph). δ_P(120 MHz, C_6D_6): 32.9 ($\underline{P}Ph_2$).

2.7.2 Synthesis of *cis*-[Pd(C_8H_{16})(dppe)], 60d



Complex **60d** was prepared following the procedure outlined in Section 2.7.1 above. $PdCl_2$(COD) (0.51 g, 1.75 mmol) was suspended in anhydrous Et_2O (30 ml) and cooled to -78°C. To the cold suspension, a solution of $BrMg(CH_2)_8MgBr$ in anhydrous THF (10 ml, 0.33 M, 3.50 mmol) was added drop-wise. Dppe (0.11 g, 0.28 mmol) was added to the bright yellow oil obtained after work-up (complex **60a**). The product was obtained as a very pale yellow (almost white) solid (0.12 g, 11%), melting point 66 - 68°C (with decomposition). δ_H(400 MHz, C_6D_6): 0.88 (8H, br m, H1 – H2), 1.30 (8H, br m, H3 – H4), 2.21 (4H, t, H5), 6.98 – 7.81 (20H, m, Ph). δ_P(120 MHz, C_6D_6): 33.4 (2P, -$\underline{P}Ph_2$).

2.8 Thermal Decompositions

All thermal decomposition reactions were carried out in the solid state under vacuum at 165°C following a procedure similar to the one reported by Whitesides *et. al* for the thermal decomposition of a series of platinacyclopentanes.[9] Decomposition studies were carried out on fresh samples of complexes **55d**, **59d**, **60c** and **60d**, as well as on three-week old samples of the nine-membered ring complexes, **60c** and **60d**. In each reaction *ca.* 10 mg of the sample was dissolved in DCM and transferred into a thoroughly cleaned, oven-dried sealable tube. Solvent was removed under vacuum. The tube was then degassed and sealed under vacuum. The sample was immersed in a heated oil bath (held constant at 165°C) for 2 hours. After two hours, the reaction was quenched by immersing the decomposition tube in liquid nitrogen for 5 minutes. Chlorobenzene (internal standard, 5 µl) was placed in a tube with a 0.5 ml mark on it.

The decomposition products in the cooled tube were then extracted by adding small amounts of *n*-pentane and these extractions were added to the marked tube until the volume reached the 0.5 ml mark. The products were analyzed using GC-MS by injecting a 2 µl sample into the GC-MS machine. Products were identified by comparison of their retention times to those of known samples used as internal standards. Product yields were determined by the response relative to the chlorobenzene standard, and the response factors were obtained from known samples.

The proposed 1,10-phenanthroline complex, *cis*-[Pd{$(CH_2)_3CH=CH_2$}$_2$(phen)] from the reaction of $PdCl_2$(phen) and pentenyl magnesium bromide decomposed upon attempted isolation. Its decomposition product was obtained as a colorless oil and, in addition to GC-MS analysis, the product was also characterized by ^1H and ^{13}C NMR spectroscopy.

2.9 References

1. Silverman, G. S. and Rakita, P. E. (Eds), *Handbook of Grignard Reagents*, Marcel Dekker, Inc., New York, 1996.
2. Bailey, C. T. and Linsesky G. C., *J. Chem Edu.*, 1985, **62**, 896.
3. Wehman, P., Dol, G. C., Moorman, E. R., Kamer, P. C., Van Leeuwen, P. W. M. N., Fraanje, J. And Goubitz, K., *Organometallics*, 1994, **13**, 4856.
4. Giannoccaro, P., *J. Organomet. Chem*, 1994, **470**, 249.
5. Newkome, G. R., Gupta, V. K., Taylor, H. C. R. and Fronczek, F. R., *Organometallics*, 1984, **3**, 1594 and references therein.
6. Herrmann, W. A. and Slazer, A. (Eds), *Synthetic Methods of Organometallic and Inorganic Chemistry*, Georg Thieme Verlag, Stuttgart, 1996, Vol. 1, p.160.
7. Mann, F. G. and Purdie, D., *J. Chem. Soc.*, 1935, 1549.
8. Dralle K., Jaffa, N. L., le Roux, T., Moss, J. R., Travis, S., Watermeyer, N. D. and Sivaramakrishna, A., *Chem. Commun.*, 2005, 3865.
9. McDermott, J. X., White, J. F and Whitesides, G. M., *J. Am. Chem. Soc.*, 1976, **98**, 6521.
10. Shima, T., Hampel, F. and Gladyz, J. A., *Angew. Chem. Int. Ed.*, 2004, **43**, 2.
11. Sivaramakrishna, A., Clayton, H. S., Kaschula, C. And Moss, J. R., *Coord. Chem. Rev.*, 2007, **251**, 1294.
12. Sivaramakrishna, A., Su, H. and Moss, J. R., *Angew. Chem. Int. Ed.*, 2007, in press.
13. Diversi, P., Ingrosso, G., Lucherini, A. Porzio, W. and Zocchi, M., *Inorg. Chem.*, 1980, **19**, 3590.
14. Diversi, P., Ingrosso, G., Lucherini, A., Lumini, T.and Marchetti, F., *J. Chem. Soc. Dalton Trans.*, 1988, 133.
15. Diversi, P., Ingrosso, G., Lucherini, A. and Murtas, S., *J. Chem. Soc. Dalton Trans.*, 1980, 1633.

Chapter 3

Synthesis and Characterization of Palladium Bis(alkenyl) Complexes

3.1 Introduction

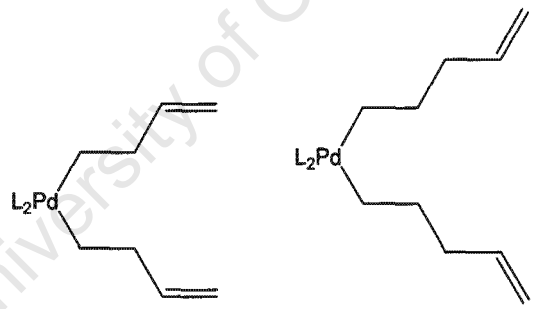
Transition metal-alkyl complexes in which the metal centre is σ-bonded to an alkyl chain have been known for a long time as key intermediates in many catalytic industrial processes.[1] Their involvement in other fundamental organic transformations such as C-H activation and α- and β-hydride elimination has also been extensively studied.[2] However, there are relatively fewer reports on corresponding complexes where the alkyl chain has been replaced by an alkenyl chain.[3]

Transition metal-alkenyl complexes can be described as ligand supported metal carbon systems in which the metal is σ-bonded to an aliphatic group containing at least two methylene units and a pendant $-CH=CH_2$ group.[3] Metal-alkenyl complexes are emerging as an important class of organometallic compounds and have found use in organic synthesis and some have been postulated as key intermediates in the Fischer-Tropsch process,[3,4] as well as ethylene oligomerization.[5]

While the synthesis and characterization of a range of metal monoalkenyl complexes have been reported, the known bis(alkenyl) complexes are limited to platinum, molybdenum and zircomium, and these complexes were all prepared by the reaction of the metal halides with Grignard reagents.[3,6-9] These metal bis(alkenyl) complexes have found application in various fields. For example, due to the importance of thin platinum films for micro-electronic and catalytic applications, the platinum bis(alkenyl) complexes have been used as precursors for chemical vapor deposition (CVD).[6] Transition metal bis(alkenyl) complexes

have also been found to be useful precursors for the preparation of other important classes of compounds, particularly metallacycloalkanes.[3,10]

This chapter deals with the synthesis and characterization of bis(alkenyl) palladium complexes containing 1,5-cyclooctadiene (COD), 2,2'-bipyridine (bipy), triphenylphosphine (PPh_3) and 1,2-bis(diphenylphosphino)ethane ligands (dppe). The complexes discussed are the bis(butenyl) (**54a – d**) and bis(pentenyl) (**55a – d**) palladium (II) complexes (Figure 3.1). Preparation of the bis(pentenyl) complex with 1,10-phenanthroline as the ligand was also attempted, but the complex decomposed completely in the reaction mixture to give 1,9-decadiene. Product formation was indicated by dissolution of the palladium species followed by decomposition.The identity of the decomposition products from these reactions was confirmed by ^1H NMR as well as GC-MS studies. Details of the thermal decomposition of some of the complexes discussed in this chapter and the characterization of the decomposition products will be reported in Chapter 5.



54a – d **55a – d**

a) L = COD, **c)** L = PPh_3

b) L = bipy, **d)** L = dppe

Figure 3.1: Bis(1-butenyl) and bis(1-pentenyl) palladium(II) complexes.

The palladium starting material in these reactions was $PdCl_2$. $PdCl_2$ exists in two forms, the α- and the β- forms.[11] The α-$PdCl_2$ (Figure 3.2) is polymeric and diamagnetic, and its structure is stabilized by chloride bridges rather than metal-metal bonds.[1] This compound is soluble in concentrated hydrochloric acid, forming

$[PdCl_4]^{2-}$ ions. The ions react with different donor ligands including amines, phosphines, imines and carbon monoxide to give complexes of the types $PdCl_2L_2$ and $[LPdCl_2]_2$.[12]

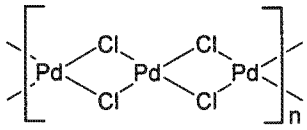


Figure 3.2: Structure of α-$PdCl_2$.

Two synthetic methods were used for the synthesis of the bisalkenyl palladium complexes. In the first method (Equations 3.1 – 3.3), complexes of the type L_2PdCl_2 (L = PPh_3, L_2 = bipy, dppe) were prepared by the reaction of $PdCl_2$ with 1,5-cyclooctadiene (Equation 3.1)[13] followed by ligand displacement with the different ligands (Equation 3.2). These complexes were then reacted with excess alkenyl Grignard reagents, BrMgR, to give the corresponding bis(alkenyl) complexes (Equation 3.3)[10]

In the second approach (Equation 3.4), $PdCl_2(COD)$ was reacted with excess alkenyl Grignard reagents, the products were isolated and then reacted with the different ligands to give the corresponding bis(alkenyl) complexes (Equation 3.4).[14] In general, the second method was found to work better for the phosphine-based complexes in that the products obtained using the second method were of higher purity (judging by the quality of NMR spectra obtained) than those obtained using the first method.[14]

$PdCl_2 + COD \longrightarrow PdCl_2(COD)$ Equation 3.1

$PdCl_2(COD) + L_2 \longrightarrow PdCl_2L_2$ Equation 3.2

$PdCl_2L_2 + 2BrMgR \longrightarrow L_2PdR_2$ Equation 3.3

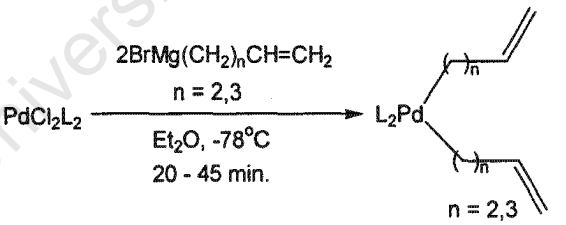
$PdCl_2(COD) + 2BrMgR \longrightarrow PdR_2(COD) \xrightarrow{L_2} L_2PdR_2$ Equation 3.4

This could be due to the reaction times being longer when the reactions were carried out with $PdCl_2L_2$ as starting materials, thereby allowing more time for product decomposition. On the other hand, when the phosphine-based complexes were prepared according to Equation 3.4, the ligand displacement reactions carried out on $PdR_2(COD)$ were very fast and relatively little decomposition occurred, leading to faster product separation and good NMR spectra. Attempts to purify the complexes prepared using the first method, by column chromatography or recrystallization were unsuccessful as these materials appear highly unstable, especially in solution, decomposing on the column. Furthermore, the products are oily materials and this makes them even more difficult to purify.

3.2 Results and Discussion

3.2.1 Synthesis of *cis*-[Pd{$(CH_2)_nCH=CH_2$}$_2L_2$], 54 – 55 (n = 2,3)

Complexes **54a** and **54b** were prepared by the reaction of the corresponding $PdCl_2L_2$ precursors (L_2 = COD, bipy) with butenyl magnesium bromide (Scheme 3.1). Complexes **55a** and **55b** were prepared by the same procedure used for complexes **54a** and **54b**, but the Grignard reagent used was pentenyl magnesium bromide.



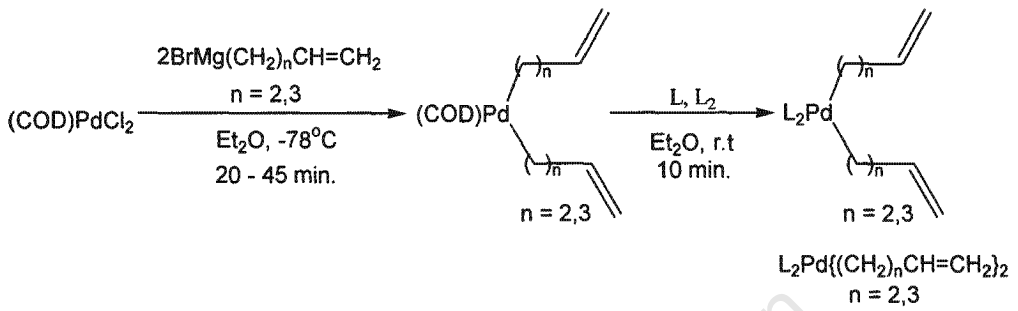
54a, 55a: L_2 = COD; n = 2

54b, 55b: L_2 = bipy; n = 3

Scheme 3.1: Preparation of complexes 54a, 54b, 55a and 55b.

The phosphine-based complexes, **54c** and **54d** were prepared by ligand displacement of 1,5-cyclooctadiene from **54a** whilst **55c** and **55d** were prepared by ligand displacement from complex **55a** (Scheme 3.2). All reactions were carried out in anhydrous diethyl ether as the solvent, at -78°C. Product formation was

signaled by dissolution of the palladium species. The reactions were then quenched using either a saturated solution of ammonium chloride, or using water. The products were extracted with hexane and dried under vacuum for a limited amount of time (5 – 10 minutes). Leaving the complexes under vacuum at room temperature for longer periods resulted in product decomposition.



54c, 55c: L = PPh_3

54d, 55d: L_2 = dppe

Scheme 3.2: Preparation of complexes 54c, 54d, 55c and 55d.

These complexes were found to be thermally unstable in the reaction mixture, giving reductive elimination products, 1,7-octadiene in the case of **54a – d** and 1,9-decadiene in the case of **55a – d**, as well as some elemental palladium (palladium black). The decomposition studies are discussed in detail in Chapter 5. As a result of the low thermal stability of the complexes, relatively low yields were obtained. The yields ranged between 28% and 50%. The complexes were characterized by ^{1}H, ^{13}C and ^{31}P NMR, elemental analysis and mass spectrometry.

In all reactions, product formation resulted in dissolution of the palladium species and immediate product decomposition was signaled by the reaction mixture turning brown and precipitation of elemental palladium from the reaction mixture.[15] All complexes were obtained as bright yellow materials after work-up. A comprehensive review of the literature revealed that the bis(alkenyl) complexes in this study have not yet been reported. Some bis(alkyl) complexes such as diethyl palladium complexes have been reported.[16,17] Brookhart and co-workers also

prepared palladium bis(propyl) and bis(butyl) complexes based on α-diimine ligands.[17] Keister and Parsons reported decomposition studies of dioctyl palladium complexes based on several phosphine and imine ligands although they did not report the characterization of these complexes.[15]

3.2.2 Characterization of *cis*-[Pd{$(CH_2)_nCH=CH_2$}$_2$$L_2$], 54 – 55 (n = 2,3)

Complexes **54a – d** and **55a, c, d** were obtained as bright yellow oils and complex **55b** was obtained as a yellow solid (m. p. 48 – 52°C). The complexes were characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, microanalysis, as well as mass spectrometry. ^{1}H and ^{13}C NMR data for the complexes in this study complexes compare favorably with data obtained by Denner and Alt for similar complexes based on chromium.[18] Satisfactory elemental analyses could not be obtained and this could be due to the low thermal stability of the complexes even at low temperature. Because both the expected products and their decomposition products are either oily materials or low melting point solid (complex **55b**), product separation and purification was difficult and this could have contributed to the disagreement observed between the found and the calculated microanalysis values. Due to the products being oils, complete removal of solvents from the products was also difficult even though the products were dried under vacuum for short periods.

The microanalysis values obtained for the bis(alkenyl) complexes were found to agree with the calculated values only when a few molecules of hexane were included in the calculations. For example, for the bipy complexes, **54b** and **55b**, agreement between calculated and observed values was obtained when 2 and 1.5 hexane molecules were included in the calculations for **54b** and **55b** respectively. Hexane is the solvent that was used to extract the products during work-up. The CHN values obtained for complex **54b** (values calculated for **54b** with 2 molecules of hexane in brackets) are: C, 66.53 (66.10); H, 8.82 (9.24); N, 5.22 (5.14). The CHN values obtained for complex **55b** (calculated values for **55b** with 1.5 molecules of hexane are in brackets) are: C, 65.58 (65.58); H, 6.59 (9.11); N, 4.35

(5.27). Attempts at purifying and completely drying the compounds in order to improve the microanalysis results resulted in the complexes decomposing. All other spectroscopic data, however, agree very well with those expected for bisalkenyl complexes.

^{1}H NMR Spectroscopy

The bis(alkenyl) complexes prepared have characteristic patterns in the ^{1}H NMR spectra that are common to all the complexes. As a result ^{1}H NMR spectroscopy proved to be a very useful diagnostic tool in these syntheses. These trends are also observed in the ^{13}C NMR spectra of the complexes, and the ^{13}C NMR data will be discussed in more detail later in this section.

The ^{1}H NMR spectra of all bis(butenyl) complexes, **54a – d**, show five characteristic signals for the fourteen protons in the butenyl chains (Figure 3.4, Table 3.1). The furthest downfield signals appear as triplets between 1.41 and 1.72 ppm and are assigned to the methylene protons on the carbons next to the metal centre. These signals integrate for four protons. The signals for the methylene protons on the carbon atoms β- to the metal centre appear as multiplets in the region between 2.05 and 2.36 ppm. These signals also integrate for four protons. The metal centre has a shielding effect on the methylene protons adjacent to it, as a result the signals for these atoms appear further downfield compared to the other protons in the alkenyl chains.[19,20]

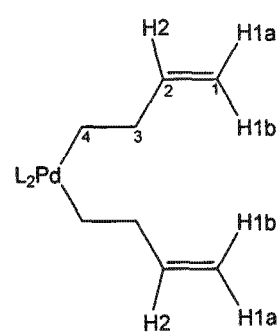


Figure 3.3: Atom numbering used in Table 3.1

Table 3.1: ^{1}H NMR data for the butenyl chains in complexes 54a – d[a]

Ligand	H1a	H1b	H2	H3	H4
COD	4.93	5.03	5.85	2.05	1.41
bipy	4.79	4.92	5.91	2.28	1.49
PPh_3	4.94	5.07	5.84	2.34	1.43
dppe	4.96	5.10	5.82	2.36	1.72

[a]The same numbering system used for carbon and hydrogen atoms.

Changing the ligand on the metal also has an effect on the chemical shifts of the methylene protons on the carbon atoms α- and β- to the metal centre. The methylene protons in the bipy and phosphine-based ligands are more shielded than the same protons in the COD complex. The signals for the protons on the carbon atoms adjacent to the metal centre appear between 1.49 and 1.72 ppm in complexes **54b – d** and the same protons appear 1.41 ppm for the COD complex, **54a** (Table 3.1). The signals for the protons β- to the metal centre appear between 2.28 and 2.36 ppm for complexes **54b – d** and this signal appears at 2.05 ppm in the COD complex. A similar trend is observed in the spectra of the bispentenyl complexes, **55a – d**.

This pattern can be explained, based on the basicity and therefore donor ability of the ligands on the metal centre. Nitrogen- and phosphorus- based ligands are more basic than their olefin based counterparts and therefore N- and P-based ligands are better donors.[15] As a result, the signals for the methylene protons adjacent to the metal centre in the complexes based on N- and P-donor ligands appear further upfield than the signals for the same protons in the COD complexes. Comparing the chemical shifts of the methylene protons α- to the metal centre in the bipy and dppe complexes, the resonances for these protons appear at 1.49 ppm in **54b** and at 1.72 ppm in **54d**, further confirming that more basic donor ligands on the metal center result in stronger M – C bonds, resulting in the methylene protons next to the metal centre, M – CH_2, becoming more

Table 3.1: ^{1}H NMR data for the butenyl chains in complexes 54a – d[a]

Ligand	H1a	H1b	H2	H3	H4
COD	4.93	5.03	5.85	2.05	1.41
bipy	4.79	4.92	5.91	2.28	1.49
PPh_3	4.94	5.07	5.84	2.34	1.43
dppe	4.96	5.10	5.82	2.36	1.72

[a]The same numbering system used for carbon and hydrogen atoms.

Changing the ligand on the metal also has an effect on the chemical shifts of the methylene protons on the carbon atoms α- and β- to the metal centre. The methylene protons in the bipy and phosphine-based ligands are more shielded than the same protons in the COD complex. The signals for the protons on the carbon atoms adjacent to the metal centre appear between 1.49 and 1.72 ppm in complexes **54b – d** and the same protons appear 1.41 ppm for the COD complex, **54a** (Table 3.1). The signals for the protons β- to the metal centre appear between 2.28 and 2.36 ppm for complexes **54b – d** and this signal appears at 2.05 ppm in the COD complex. A similar trend is observed in the spectra of the bispentenyl complexes, **55a – d**.

This pattern can be explained, based on the basicity and therefore donor ability of the ligands on the metal centre. Nitrogen- and phosphorus- based ligands are more basic than their olefin based counterparts and therefore N- and P-based ligands are better donors.[15] As a result, the signals for the methylene protons adjacent to the metal centre in the complexes based on N- and P-donor ligands appear further upfield than the signals for the same protons in the COD complexes. Comparing the chemical shifts of the methylene protons α- to the metal centre in the bipy and dppe complexes, the resonances for these protons appear at 1.49 ppm in **54b** and at 1.72 ppm in **54d**, further confirming that more basic donor ligands on the metal center result in stronger M – C bonds, resulting in the methylene protons next to the metal centre, M – CH_2, becoming more

shielded. The signal for analogous protons in the complex [$PdEt_2$(dppe)], reported by Ito *et al.* appears at 1.96 ppm.[19]

The signals for the olefin protons, H1 and H2, (see Figure 3.3 for atom numbering) appear in the region between 4.79 (integrating for four protons) and 5.91 ppm (integrating for two protons) respectively. There are two separate multiplets for the terminal alkenyl protons in all complexes. The triplets observed at *ca.* 4.90 ppm (see Figure 3.4 for example) have been assigned to the terminal alkenyl protons *cis*- to H2, H1a, and the multipltes at *ca.* 5.0 ppm have been assigned to the protons *trans*- to H2, H1b.

The signal due to the two terminal alkenyl protons on the butenyl chains is expected to be a doublet as geminal coupling is not usually observed for these protons.[21] However, a more complex splitting pattern is observed and this can be explained by the fact that the double C=C bonds are connected to aliphatic chains and not an aromatic ring as in styrene, and also these signals are due to protons on two different butenyl chains that are not stationary. These two multiplets together integrate for four protons as is expected for the bisbutenyl complexes. It is interesting to note that the symmetry of these peaks at *ca.* 5.9 ppm is still maintained though (see inserts in Figure 3.4).

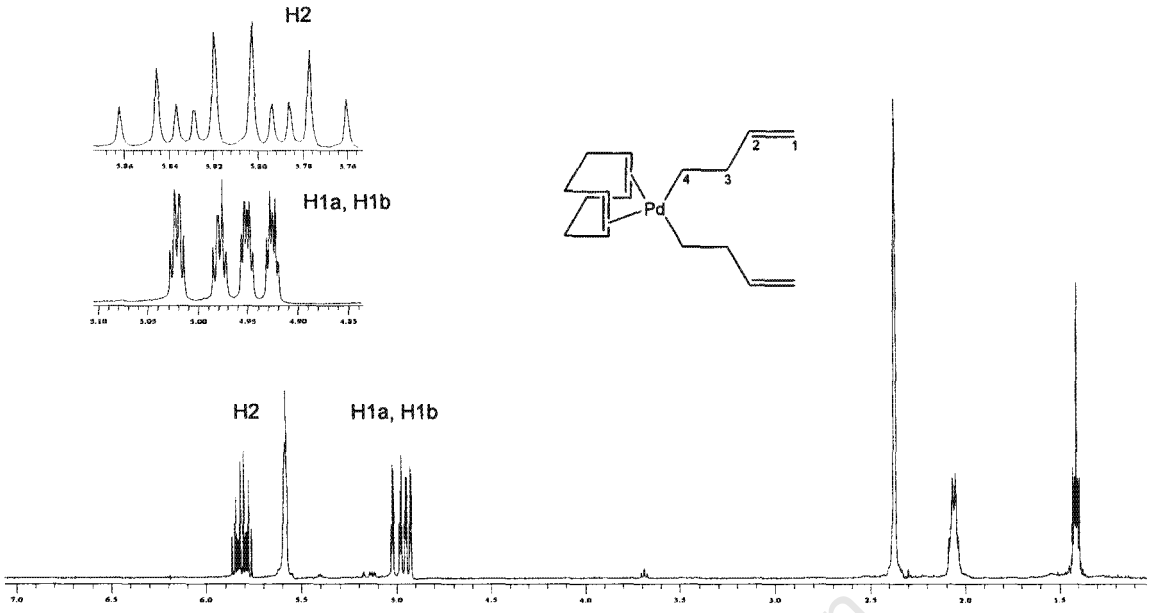


Figure 3.4: ^{1}H NMR spectrum of complex 54a.

The ^{1}H NMR spectra of the bis(pentenyl) complexes show a similar pattern (see Figure 3.6 for example), the only difference being that there is an extra multiplet at in the region between 1.95 and 2.37 ppm, which is due to the methylene protons adjacent to the carbon-carbon double bond. These signals integrate for four protons, which agrees very well with what is expected for the proposed structures of the products. Another difference is that the chemical shifts for the methylene protons adjacent to and methylene protons β- to the metal centre have shifted upfield in the bis(pentenyl) complexes compared to their positions in their bis(butenyl) counterparts Table 3.2 (see Figure 3.5 for atom numbering).

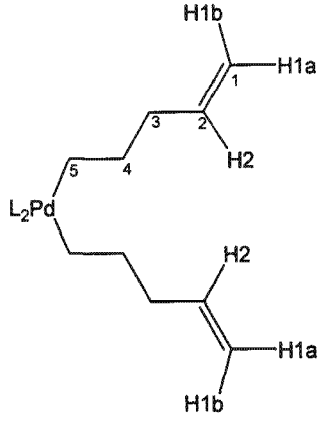


Figure 3.5: Atom numbering used in Table 3.2

Table 3.2: ^{1}H NMR data for the pentenyl chains in complexes 55a – d[a]

Ligand	H1a	H1b	H2	H3	H4	H5
COD	4.91	5.02	5.77	2.03	1.36	1.28
bipy	4.96	5.03	5.76	1.95	1.29	1.19
PPh_3	4.86	4.96	5.80	2.10	1.99	1.63
dppe	4.94	5.01	5.81	2.37	1.39	1.31

[a]The same numbering system is used for carbon and hydrogen atoms.

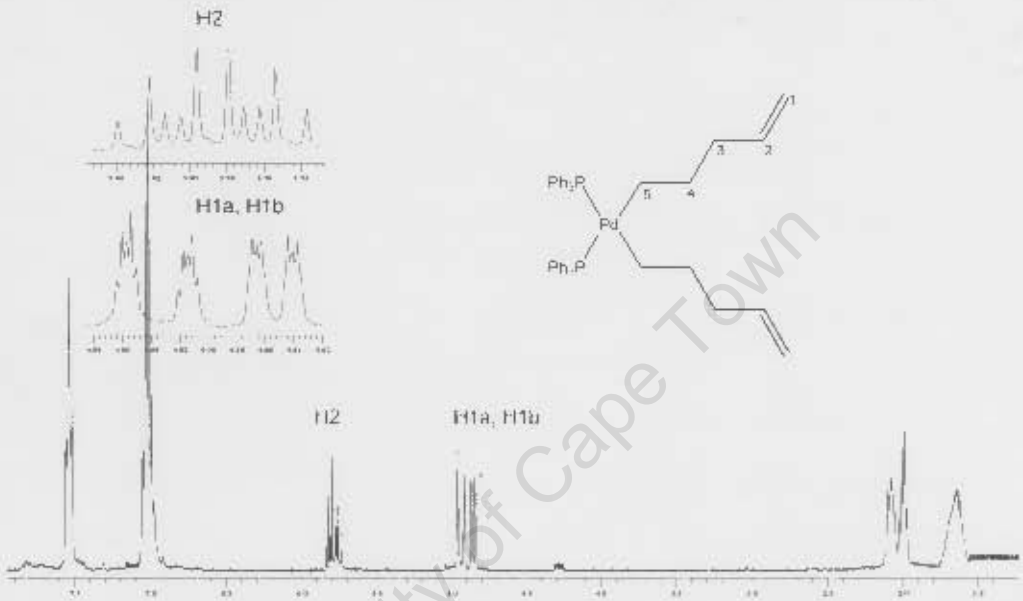


Figure 3.6: ^{1}H NMR spectrum of complex 55c.

The above-mentioned trends in the proton NMR spectra of the complexes are expected for the bis(alkenyl) complexes where the olefin groups are not coordinated to the metal center in a η^2- fashion. Carre *et al.* prepared group 4B metal monoalkenyl complexes and the signals for the =C<u>H</u>- and =C<u>H</u>$_2$- protons appear at ca. 5.9 and 5.0 ppm respectively.[8] Signals for coordinated olefin protons in complexes such as the iron complexes [$L_xFe(\eta^2$-C<u>H</u>$_2$=CH(CH$_2$)$_n$CH=CH$_2$] reported by Dooling *et al.* appear at *ca.* 3.6 for the *trans*-protons and at *ca.* 4.1 ppm for the *cis*-protons.[22] The signals for the =C<u>H</u>- protons, [$L_xFe\{\eta^2$-CH$_2$=C<u>H</u>(CH$_2$)$_n$CH=CH$_2$}] appear at *ca.* 5.2 ppm.[22] The signals for the protons on the uncoordinated olefin groups appear *ca.* 5.8 ppm for the =C<u>H</u>- protons and *ca.*

5.0 ppm for the -C<u>H</u>$_2$- protons as was observed for the palladium complexes in this study.[22]

Proton NMR spectra of the complexes also show the expected signals for the protons in the ligands. In the spectra of the COD complexes, **54a** and **55a**, the signals for methylene protons, -C<u>H</u>$_2$-, appear as multiplets at 2.38 and 2.37 ppm in the COD ligand respectively. These signals integrate for eight protons whilst the multiplets at 5.61 and 5.58 ppm, integrating for four protons, have been assigned to the =C<u>H</u>- protons in the ligand for the two complexes. The spectrum for the bipy complex, **54b**, shows four signals in the aromatic region between 7.31 and 8.67. The signals for the phenyl protons in the phosphine-based complexes, **54c**, **54d**, **55c** and **55d** appear in the region between 7.01 and 7.88 ppm and these multiplets integrate for thirty protons for the triphenylphosphine complexes and twenty protons for the dppe complexes.

^{13}C NMR Spectroscopy

The COD complexes, **54a** and 55a, as well as the bipy complexes, **54b** and **55b** were also characterized by ^{13}C NMR spectroscopy. The ^{13}C NMR spectra of these complexes show a similar pattern to that observed in the proton NMR spectra. The methylene carbons adjacent to the metal centre (Pd-<u>C</u>H$_2$-) in the bis(alkenyl) chains are more shielded than the other carbon atoms in these chains. The signals for these carbons appear in the region between 19 and 30 ppm (Table 3.3, see Figures 3.3 and 3.5 for atom numbering). The effect of changing the donor ligand on the metal centre is also noticed in the chemical shifts of the methylene carbons next to the metal centre, where these carbons are less shielded in the bipy complexes than they are in the COD complexes. As a result the signals for these carbons in the bipy complexes appear further upfield (29 ppm for both **54b** and **55b**) than in the COD complexes (19.ppm for **54a** and 25 ppm for **55a**).

Table 3.3: ^{13}C NMR data for the alkenyl chains in complexes 54a – 55d

Complex	Ligand	C1	C2	C3	C4	C5
54a	COD	114.6	139.6	33.9	19.9	-
54b	bipy	118.7	141.2	35.7	29.4	-
55a	COD	114.3	139.0	36.1	29.8	25.7
55b	bipy	115.5	141.4	38.1	32.1	29.0

Two more peaks due to the carbon atoms in the ligand are also observed in the ^{13}C NMR spectra of the COD complexes. The signals at *ca.* 112 in the spectra of the two complexes are assigned to the =**C**H- carbons while the peaks at 29 ppm are due to the -**C**H_2- carbons in the ligand. The ^{13}C NMR spectra of the bipy complexes also show four peaks in the aromatic regions and the peaks were assigned to the ten carbon atoms in the ligand.

^{31}P NMR Spectroscopy

The phosphine-based complexes, **54c**, **54d**, **55c** and **55d** were also characterized by ^{31}P NMR spectroscopy. The peaks for the phosphorus atoms in the complexes appear at *ca.* 30 ppm for all four complexes (Table 3.4). Absence of peaks at -4.03 ppm for the triphenylphosphine complexes and at -12.0 ppm for the dppe complexes indicates that there are no free ligands in the products.

Table 3.4: ^{31}P NMR data for complexes 54c – d and 55c –d

Complex	Ligand	δ(ppm)
54c	PPh_3	29.2
54d	Dppe	31.0
55c	PPh_3	29.7
55d	Dppe	30.1

All complexes except for the PPh_3 complexes are expected to be cis- complexes due to the rigidity in the structure of the chelating ligands used. However, in the case of the PPh_3 complexes, both *cis*- and *trans*- structures are possible. Since

the structure of these complexes could not be determined by X-ray crystallography, the proposed structure of the PPh_3 complexes in this study is the *cis-* structure based on the color of the complexes and the ^{31}P NMR data. *Trans-* palladium complexes based on triphenylphosphine are usually more intensely colored than their *cis-* palladium counterparts.[1,21] Since both the PPh_3 and dppe complexes were obtained as yellow oils, we suggest that the PPh_3 complexes have a *cis-* structure. Furthermore, the chemical shifts for all the phosphine- based complexes in this study are very similar, further suggesting the structural similarity between the PPh_3 and the dppe complexes.

Mass Spectrometry

The complexes were further characterized by mass spectrometry. The mass spectra (FAB) of the complexes show very similar fragmentation patterns. All spectra show parent molecular ions, M^+, corresponding to the molecular masses of the expected products (Table 3.5) as well as peaks corresponding to the loss of the ligands. In addition, the spectra for the bis(butenyl) complexes also show peaks corresponding to the loss of one and two butenyl chains, $[M - CH_2CH_2CH{=}CH_2]^+$ and $[M - 2CH_2CH_2CH{=}CH_2]^+$ respectively. These spectra also show peaks at m/z 54.1 and 107.2 corresponding to the molecular masses of the fragments $[CH_2CH_2CH{=}CH_2]^+$ and $2[CH_2CH_2CH{=}CH_2]^+$ respectively. The mass spectra of the PPh_3-based complexes also show peaks corresponding to the loss of one molecule of PPh_3 together with one alkenyl chain. These peaks appear at m/z 423.0 for complex **54c** and at m/z 436.8 for complex **55c**.

A similar pattern is observed in the mass spectra of the bis(pentenyl) complexes, where in addition to peaks corresponding to the molecular masses of the expected products, there are also peaks corresponding to loss of ligands as well as peaks corresponding to loss of the pentenyl chains. The spectra also show peaks at m/z 68.2 and 137.6, which correspond to the molecular masses of the fragments $[(CH_2)_3CH{=}CH_2]^+$ and $2[(CH_2)_3CH{=}CH_2]^+$.

Table 3.5: Mass Spectrometry data of complexes 54 and 55

Complex	Ligand	m/z[a]			
		M	M – ligand	M – R	M – 2R
54a	COD	323.7	215.6	268.5	213.6
54b	bipy	371.8	215.0	316.7	260.9
54c	PPh_3	740.1	477[b].8;215.5[c]	687.1	629.8
54d	dppe	614.0	215.5	560.0	502.9
55a	COD	351.9	243.7	282.5	213.6
55b	bipy	399.8	243.7	330.7	261.6
55c	PPh_3	767.9	505.9[b];243.6[c]	698.1	629.9
55d	dppe	642.1	243.6	572.9	503.8

[a]R is $(CH_2)_2CH=CH_2$ for complexes **54a – d** and R is $(CH_2)_3CH=CH_2$ for complexes **55a – d**.

[b]m/z corresponds to the structure M – PPh_3.

[c]m/z corresponds to the structure M – $2PPh_3$.

3.3 Conclusion

Bis(alkenyl) complexes of the type *cis*-PdR_2L_2 (where L = PPh_3, L_2 = 1,5-cyclooctadiene, 2,2'-bipyridine, 1,2-diphenylphosphinoethane and R = butenyl and pentenyl chains) were successfully synthesized and characterized. Confirmation of product formation was obtained primarily from the NMR as well as mass spectral data of the complexes. The compounds showed very low thermal stability in solution, with some product decomposition occurring at temperatures as low as -30°C.

Judging from the yields obtained for the complexes, the length of the alkenyl chains in the bis(alkenyl) complexes does not seem to have any effect on the stability of the complexes formed. With the exception of complexes **54b** and **55b**, the 2,2'-bipyridyl complexes, the yields obtained for all the complexes were almost the same, ranging from 45% to 50%. The yields obtained for the bipy complexes are 35% and 28% for complexes **54b** and **55b** respectively.

The following trend was observed in the yields obtained for both the bis(butenyl) and bis(pentenyl) complexes, bipy < COD < PPh_3 < dppe, with the lowest yields obtained for the 2,2'-bipyridyl complexes, **54b** and **55b**, and the highest yields obtained for the 1,2-bis(diphenylphosphino)ethane complexes, **54d** and **55d**. This trend is to be expected as literature reports show that palladium alkyl complexes based on phosphine ligands such as diphenylphosphinoethane are more stable than analogous complexes based on imine ligands like 2,2'-bipyridine and phenanthroline.[15,23] Complexes based on chelating ligands are also expected to have a higher degree of stability than their counterparts based on non-chelating ligands.[24] To the best of our knowledge, the bis(alkenyl) palladium complexes discussed in this chapter have not been reported yet.

3.4 References

1. Wilkinson, G., Stone, F. G. A. and Abel, E. W. (Eds), Comprehensive Organometallic Chemistry, Pergamon, Oxford, 1982, vol 8, p285.
2. Cotton, F. A., Wilkinson, G., Murillo, C. A. and Bochmann, M. Advanced Inorganic Chemistry, John Wiley and Sons Inc., New York, 1999, p1194.
3. Sivaramakrishna, A., Clayton, H. S., Kaschula, C. and Moss, J. R., *Coord. Chem. Rev.*, 2007, Article in press, and references therein.
4. Turner, M. L., Marsih, N., Mann, B. E., Quyoum, R., Long, H. C. and Maitlis, P. M., *J. Am. Chem. Soc.*, 2002, **124**, 10456.
5. Briggs, J. R., *J. Chem. Soc. Chem. Commun.*, 1989, **11**, 674.
6. Tagge, C. D., Simpson, R. D., Bergman, R. G., Hostetler, M. J., Girolami, G. S. and Nuzzo, R. G., J. *Am. Chem. Soc.*, 1996, **118**, 2634.
7. Benn, R., Reinhardt, R. and Rufinska, A., *J. Organomet. Chem.*, 1985, **282**, 291.
8. Carre, F., Colomer, E., Corriu, R. J. and Vioux, A., Organometallics, 1984, **3**, 970.
9. Vetter, W. M. and Sen, A., Organometallics, 1991, **10**, 244.
10. Dralle K., Jaffa, N. L., le Roux, T., Moss, J. R., Travis, S., Watermeyer, N. D and Sivaramakrishna, A., *Chem. Commun.*, 2005, 3865.
11. Sharpe, A. G., Inorganic Chemistry, Longman, New York, 1981, p631.
12. Cotton, F. A. and Wilkinson, G., Advanced Inorganic Chemistry, 5th Ed., John Wiley and Sons, New York, 1988, p878.
13. Bailey, C. T. and Linsesky, G. C., *J. Chem. Edu.*, 1985, **62**, 896.
14. Mahamo, T., Sivaramakrishna, A. and Moss, J. R., unpublished results.
15. Keister, J. W. and Parsons, E. J., *J. Organomet. Chem.*, 1995, **487**, 23.
16. a) Sustmann, R. and Lau, J. *Chem. Ber.*, 1986, **119**, 2531. b) Lau, J. and Sustmann, R. *Tet. Lett.*, 1985, **26**, 4907.
17. Shultz, L. H., Tempel, D. J. and Brookhart, M., *J. Am. Chem. Soc.*, 2001, **123**, 11539.
18. Denner, C. E. and Alt, H. G., *J. Appl. Pol. Sci.*, 2003, **89**, 3379.
19. Ozawa, F., Ito, T. and Yamamoto, A., *J. Am. Chem. Soc.*, 1980, **102**, 6457.

20. Luo, H-K., Kou, Y., Wang, X-W. and Li, D-G., *J. Mol. Catal. A: Chem.*, 2000, **151**, 91.
21. Dyer, J. R., Applications of Absorption Spectroscopy of Organic Compounds, Prentice-Hall, New Jersey, 1965.
22. Dooling, D., Joorst, G. and Mapolie, S. F., *Polyhedron*, 2001, **20**, 467.
23. Ozawa, F., Ito, T. Nakamura, Y. and Yamamoto, A., *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1868.
24. Zhang, L. and Zetterberg, K., *Organometallics*, 1991, **10**, 3806.

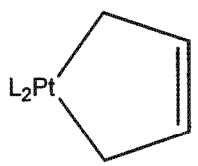
Chapter 4

Synthesis and Characterization of Palladacyclic Complexes

4.1 Introduction

Metallacyclic complexes of the transition elements can be defined as "carbocyclic systems in which one or more atoms have been replaced by a transition metal".[1] These compounds have become a subject of considerable research interest due to the important role they play in catalytic reactions such as alkene metathesis, olefin oligomerization, as well as isomerization of strained carbocyclic rings.[2,3] Metallacycloalkenes have been proposed as precursors in ring opening metathesis polymerization reactions in the preparation of metal-containing polymers[4] as well as precursors for metallacycloalkanes[6] while metallacycloalkanes are key intermediates in olefin metathesis[4] as well as ethylene trimerization and tetramerization.[7-10]

An impressive number of metallacyclic complexes have been synthesized and characterarized, and there are several reviews that have been written on these complexes.[1,2,5] Of the nickel triad metals, only a few metallacycloalkenes such as those reported by Benn *et al.* (Figure 4.1) have been reported.[1,11] However, a large number of metallacycloalkanes based on these metals have been reported and their reactivity has been studied.[1]



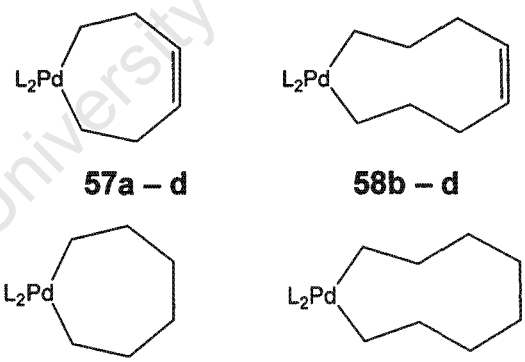
56

$L_2 = (^iPr)_2PCH_2CH_2P(^iPr)_2$

Figure 4.1: Platinum(II) metallacyclopentene reported by Benn *et al.*[11]

Of the palladacycloalkanes reported in the literature, a few simple palladacyclopentanes[12,13] as well as one highly substituted palladacyclononane have been reported.[14] The palladacyclopentanes were synthesized by reaction of $PdCl_2$(tmen) with 1,4-dilithiobutane followed by ligand displacement.[12] The palladacyclononane was formed by the oxidative coupling of 3,3-dimethylcyclopropene with a latent palladium(0) complex.[5,14] Palladacycloalkanes of other ring sizes have only been proposed as intermediates in palladium-catalyzed reactions.[15]

The complexes discussed in this chapter are palladacycloalkene and palladacycloalkane complexes with ancillary ligands consisting of 1,5-cyclooctadiene, 2,2'-bipyridine, triphenylphosphine and 1,2-bis(diphenylphosphino)ethane, complexes **57 – 60** (Figure 4.2). The first part of the chapter discusses the synthesis and characterization of palladacycloheptene complexes, **57a – d**, and palladacyclononene complexes, **58a – d**, whilst the second part deals with the synthesis and characterization of palladacycloheptanes, **59a – d** and palladacyclononanes **60a – d**.



57a – d **58b – d**

59a – d **60a – d**

a) L = COD, **b)** L = bipy

c) L = PPh_3, **d)** L = dppe

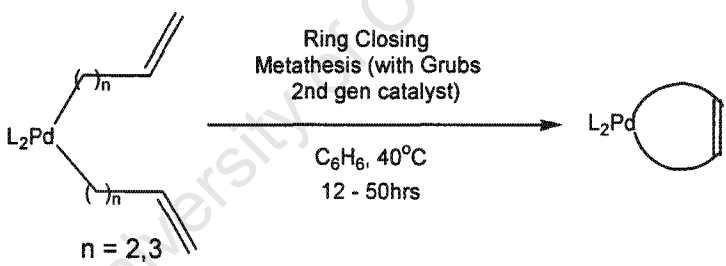
Figure 4.2: Palladacycloalkene and palladacycloalkane complexes discussed in this chapter.

A comprehensive review of the literature showed that none of the complexes discussed in this section have been reported before, although some analogous platinum(II) systems have been reported by Moss, Sivaramakrishna and co-workers.[16,17]

4.2 Results and Discussion

4.2.1 Synthesis of Palladacycloalkenes, Complexes 57 – 58

Complexes **57 – 58** were prepared by the ring closing metathesis reactions of the bis(alkenyl) complexes **54** and **55** (see Chapter 3) using Grubbs' second generation catalyst to yield the palladacycloalkenes (Scheme 4.1). Gladysz and co-workers reported the preparation of "molecular gyroscopes" using Grubbs' catalysts for ring closing metathesis (RCM) of alkene groups bonded to phosphorus,[18] and Moss *et al.* extended this concept to the RCM reactions of bis(alkenyl) platinum complexes to form platinacycloalkenes analogous to the palladacycloalkenes reported in this chapter.[16]



54 – 55 **57 – 58**

L = PPh_3, L_2 = COD, bipy, dppe

Scheme 4.1: Preparation of palladacycloalkenes by RCM reaction of Pd(II) bisalkenyl complexes.

The reactions in this study were initially tried with the Grubbs' first generation catalyst, $RuCl_2(PCy_3)_2(=CHPh)$, but the reaction times were long and this resulted in both the precursors and the products decomposing before the reactions were complete. The complexes were obtained as brown oils in good to excellent yields (60 – 90%) using the second generation catalyst. The catalyst was added in a

batch-wise manner during the course of the reaction so as to avoid the products not forming due to catalyst decomposition. The catalyst was added in batches of 5 mmol% every five hours throughout the course of each RCM reaction. All reactions were carried out at 40°C, with benzene as the solvent. Chlorinated solvents such as chloroform and dichloromethane were avoided because in preliminary studies it was observed that these solvents were reactive and resulted in the formation of $PdCl_2L_2$ as by-products.

Yields obtained for the bipy, PPh_3 and dppe complexes were in excess of 80%. The COD complexes (**57a** and **58a**) gave lower yields and this is attributed to the relatively lower stability of these complexes compared to the complexes based on the P- and N-ligands. The yields obtained for the COD complexes are 70% for the seven-membered ring complex, **57a** and 60% for the nine-membered ring complex, **58a**. The yields obtained for the COD complexes are low due to the fact that the ring closing metathesis reactions for these complexes did not go to completion. The products and the bis(alkenyl) precursors started decomposing with extended reaction times. Carrying out the reactions at higher temperatures also resulted in the decomposition of both the products and the precursors. Under similar conditions, the reactions with bipy- and phosphine-based complexes gave very good yields and this can be expected as N- and P-ligands are better donors than the alkene-donor ligands and form more stable complexes.

Lower yields were obtained for the nine-membered rings and this can be expected as literature reports indicate that as the ring size increases, the behavior of metallacycles approaches that of metal-alkyl complexes.[1] Palladacyclic complexes undergo both β-hydride elimination and reductive elimination. For β-hydride elimination to occur the dihedral angle M-C-C-H has to be nearly 0° in the transition state.[1,19] As ring size increases, this ideal angle is more easily attained, making the decomposition of medium and large metallacycles easier than that of small metallacycles.

4.2.2 Characterization of Palladacycloalkenes

The complexes were characterized by ^{1}H and ^{31}P NMR spectroscopy as well as mass spectroscopy. Proton NMR spectroscopy proved to be a very useful diagnostic tool as these complexes have certain characteristics that are common to all the palladium complexes in this study as well as analogous platinum complexes reported by Moss, Sivaramakrishna and co-workers. As a result reaction progress was monitored by ^{1}H NMR spectroscopy. All spectroscopic data obtained agrees with the proposed structures for the products obtained.

^{1}H NMR Spectroscopy

Formation of the ring-closed complexes was indicated by the appearance of the broad multiplet at *ca.* 5.4 ppm, which is due to the alkene protons in the cyclized products. Appearance of this new peak was accompanied by the disappearance of the peaks at *ca.* 4.9 ppm and 5.8 ppm, which are assigned to the alkene protons in the bis(alkenyl) precursors (compare Figure 4.3 (i) and 4.3 (ii)).

The proton NMR spectra of the complexes also show signals in the region 1.1 - 2.5 ppm which are due to the methylene protons in the metallacycloalkenes. These signals integrate for ten protons in the case of the palladacycloheptenes, **57a – d**, whilst the integration in the case of the palladacyclononenes, **58a – d,** is for fourteen protons. This information agrees very well with what is expected for the proposed structures of the products. As in the bis(alkenyl) complexes, the signals for the methylene protons on the carbon atoms α- to the metal centre appear furthest down field. These signals appear as triplets integrating for four protons.

Studies carried out on similar platinum complexes show that the bis(alkenyl) complexes can isomerize to internal bis(alkenyl) complexes during the RCM reaction.[20] The isomerized bis(alkenyl) complexes were not observed in this present study. The signals due to the protons on the internal olefin appear *ca.* 5.5 ppm in the platinum systems and the signals due to the terminal methyl group

appears at *ca.* 1.7 ppm. The absence of these signals in the ^{1}H NMR spectra of the complexes in this study suggests that isomerisation did not occur in the palladium complexes. Similar studies carried out on analogous rhodium complexes showed that these complexes also undergo ring closing metathesis instead of isomerization to internal bis(alkenyl) complexes.[21] The integration observed in the ^{1}H NMR spectra of the complexes also agrees very well with the palladacycloalkene complexes. Considering, for example, the integration in the ^{1}H NMR spectrum of complex **57a** (Figure 4.3 (ii)), the signals in the spectrum would not integrate for ten protons (excluding the protons in COD) as observed because the isomerized bis(alkenyl) complex would have fourteen protons. A much more complex spectrum would have been obtained.

The ^{1}H NMR spectra also show the expected peaks for the protons in the ligands. The signals for the protons in COD appear as multiplets at *ca.* 2.37 and 5.58 ppm for the -C$\underline{H}_2$- and =C$\underline{H}$- protons in the complexes **57a** and **58a** respectively. These signals integrate for eight protons and four protons respectively. The signals for the protons in the bipy ligand, integrate for eight protons and appear in the region 7.2 - 8.5 ppm while the signals for the phenyl protons in the phosphine ligands appear as multiplets in the aromatic region 7.0 - 8.0 ppm.

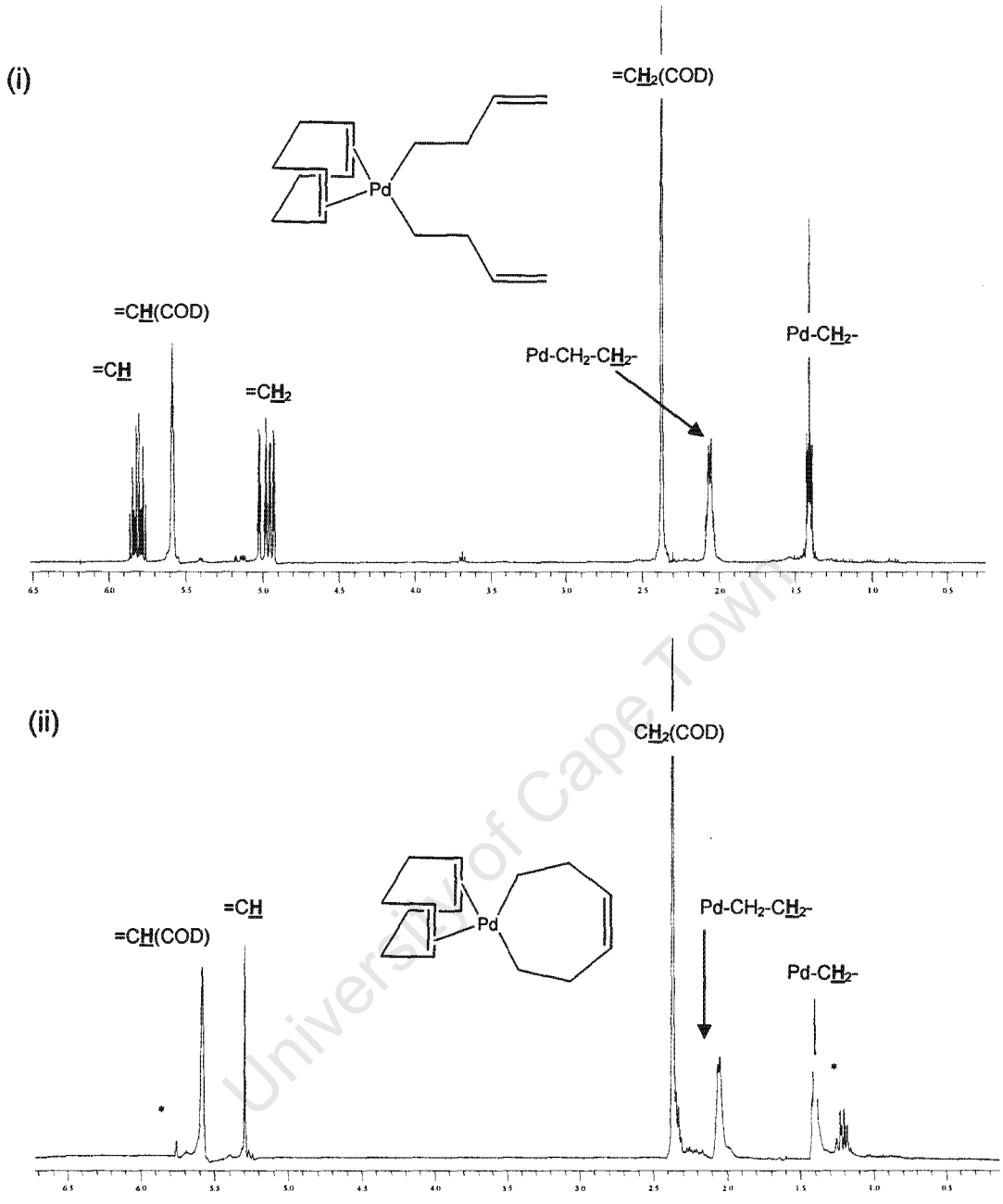


Figure 4.3: ^{1}H NMR spectra of complex 57a (ii) and its precursor, complex 54a, (i) (* denotes impurities).

^{31}P NMR Spectroscopy

The phosphine complexes were also characterized by ^{31}P NMR spectroscopy. The signals for the phosphorus atoms appear at *ca.* 30 ppm in all the complexes (Table 4.1). The chemical shifts for these complexes are very similar to the resonances for these atoms in the bisalkenyl complexes. This is because these

complexes have very similar structures in that all of them are *cis*-palladium complexes. The fact that complexes **57** and **58** are ring-closed compounds while complexes **54** and **55** have open chains connected to the metal centre seems to have little effect on the environment around the metal centre and this is reflected in the similar chemical shifts of the phosporus atoms in these complexes. This trend is also observed in the metallacycloalkane complexes reported in Section 4.2.3 and 4.2.4 later in this chapter.

Table 4.1: Yields, ^{1}H and ^{31}P NMR data for complexes 57 and 58.

Complex	Ligand	Yield	δ(Pd-C<u>H</u>$_2$-,ppm)	δ(=C<u>H</u>,ppm)	δ(P, ppm)
57a	COD	70	1.42	5.33	-
57b	bipy	85	1.46	5.42	-
57c	PPh_3	80	1.62	5.44	29.3
57d	dppe	82	1.79	5.40	32.9
58a	COD	63	1.39	5.39	-
58b	bipy	87	1.45	5.36	-
58c	PPh_3	71	1.51	5.45	28.6
58d	dppe	79	1.87	5.41	33.4

Mass Spectrometry

The complexes were also characterized by mass spectrometry and the mass spectra all show a parent ion peak of the expected product for each complex. The fragmentation pattern for each compound also shows peaks corresponding to successive loss of the ligands as well as the alkenyl groups. The spectra also show peaks corresponding to loss of the alkenyl rings as expected (Table 4.2), further confirming the proposed structures of the complexes. The mass spectrum of complex **60a**, the palladacyclononene with COD as the ligand, shows two peaks very close together at m/z 216.8 and 213.2. These peaks were assigned to the fragments M – COD and M – R (where R is cyclooctene). These peaks are so close together because the ligand (1,5-cyclooctadiene) and the alkyl group (cyclooctene) have very similar structures and molecular weights.

Table 4.2: Mass Spectrometry data of complexes 57 and 58

Complex	Ligand	m/z		
		M	M – ligand	M – R[a]
57a	COD	295.7	187.1	213.4
57b	bipy	343.6	187.6	261.6
57c	PPh_3	712.1	449.8,[b] 188.0[c]	629.1
57d	dppe	585.9	187.4	503.8
58a	COD	323.8	215.4	213.1
58b	bipy	371.8	215.0	260.9
58c	PPh_3	740.2	447.8,[b] 215.1[c]	628.9
58d	dppe	614.1	214.9	503.9

[a]R = cyclohexene for complexes **57a – d** and R = cyclononene for complexes **58a – d**.

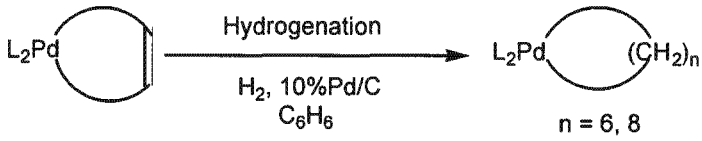
[b]m/z corresponds to M^+ - PPh_3.

[c]m/z corresponds to M^+ - $2PPh_3$.

4.2.3 Synthesis of Palladacycloalkanes, Complexes 59 – 60

Several methods have been reported for the synthesis of known metallacycloalkanes. These include the use of di-Grignard and dilithio reagents.[2,22]

Two methods were used for the preparation of the palladacycloalkanes in this study. In the first method the complexes were prepared by hydrogenating the palladacycloalkene complexes, **57** and **58**. The hydrogenation reactions were carried out at room temperature using benzene as a solvent, as illustrated in Scheme 4.2. This method was first reported by Moss *et al.* for the preparation of platinacycloalkanes of medium to large rings.[16] The palladium COD and bipy complexes were obtained as yellow oils while the PPh_3 complexes were obtained as pale yellow solids. The dppe complexes were obtained as very pale, almost white low melting solids. These reactions proceed quantitatively with yields higher than 90%.



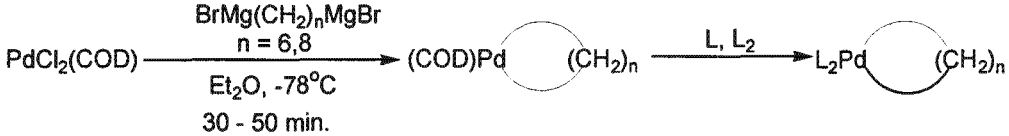
57 – 58 **59 – 60**

L = PPh_3, L_2 = COD, bipy, dppe

Scheme 4.2: Preparation of complexes 59 and 60 by hydrogenation of complexes 57 and 58.

The phosphine-based complexes were also prepared by the reaction of di-Grignard reagents using the method reported by Whitesides *et al* for the synthesis of a series of platinacyclopentanes and a platinacycloheptane.[19] $PdCl_2$(COD) was reacted with the di-Grignard reagents followed by displacement of COD by the tertiary phosphine ligands.[2,22]

In the current study di-Grignard reagents were used as alkylating reagents because these reagents are easier to handle than dilithio- or di-mercury reagents. Complexes **60c** and **60d** were also prepared by the reaction of $PdCl_2$(COD) with the di-Grignard reagents {$BrMg(CH_2)_6MgBr$ for **60c** and $BrMg(CH_2)_8MgBr$ for **60d**}, followed by ligand substitution as outlined in Scheme 4.3. The products were obtained in very low yields. All products were obtained in yields less than 15%. The reactions were carried out at -78°C in diethyl ether as the solvent even though the di-Grignard reagents themselves were stored as solutions in THF. The reactions were carried out in highly dilute reaction mixtures in order to avoid polymerization instead of metallacycloalkane formation. The complexes were found to be reasonably stable at room temperature. However, prolonged exposure to these conditions resulted in decomposition.



L = PPh_3, L_2 = COD, bipy, dppe

Scheme 4.3: Preparation of palladacycloalkanes using di-Grignard reagents.

4.2.4 Characterization of Palladacycloalkanes

The complexes were characterized by ^{1}H and ^{31}P NMR spectroscopy as well as mass spectrometry. Reaction progress of the hydrogenation reactions was monitored by ^{1}H NMR spectrometry. Product formation was indicated by the reduction and eventual disappearance of the peak at *ca.* 5.4 ppm (compare Figure 4.3 (ii) and Figure 4.4). This peak is assigned to the alkenyl protons in the palladacycloalkenes. The ^{1}H NMR NMR spectra of the complexes also show a clear distinction between the methylene protons on the carbon atoms next to the metal centre and those that are further away from the metal centre.

As in the bisalkenyl and palladacycloalkene complexes, the methylene protons next to the metal centre are more shielded and their chemical shifts appear further downfield. The signals for these protons appear as multiplets in the region between 1.2 and 1.5 ppm and integrate for four protons. Because of the symmetrical nature of the complexes, the signals for these protons are expected to be triplets, but a more complex splitting pattern is observed as these signals are due to the methylene protons on both sides of the metal centre. In additions, due to the sizes of the palladacycloalkanes, the complexes are expected to assume different conformations, further causing the splitting pattern for these protons to deviate from the expected pattern.

Comparison of the NMR spectra of the palladaheptacycles, **59**, and the palladanonacycles, **60**, shows that the spectra of the palladaheptacycles have a much simpler pattern in the aliphatic region (compare Figure 4.4 and Figure 4.5). This is due, firstly, to the fact that complexes **60a – d** have more methylene protons than complexes **59a – d**. It is therefore expected that the spectra for the larger metallacycle would have more signals in the aliphatic region. Secondly, the larger metallacycles, **60a – d** can have many more conformations than the palladaheptacycles, leading to more complicated spectra in the aliphatic region for the palladacyclononanes.

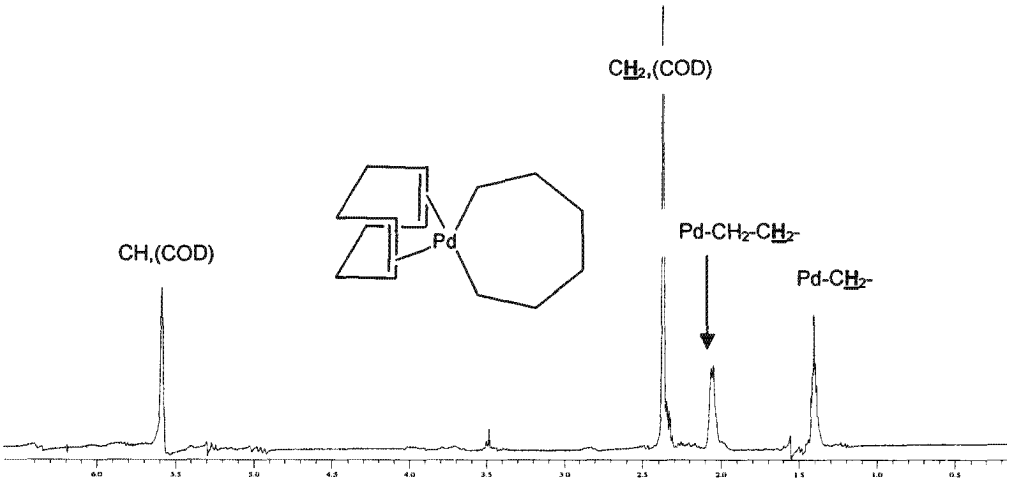


Figure 4.4: ^{1}H NMR spectrum of complex 59a.

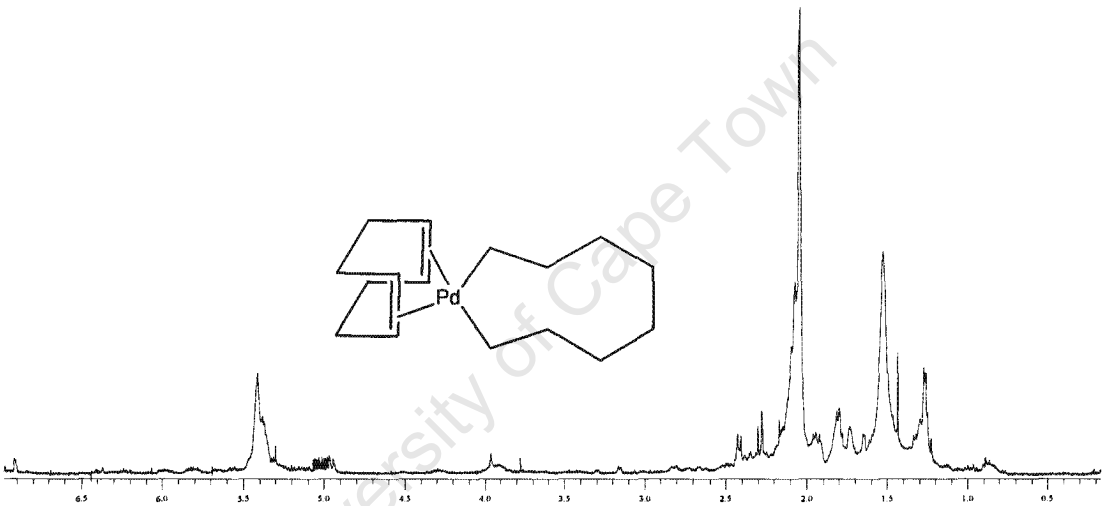


Figure 4.5: ^{1}H NMR spectrum of 60a.

The signals in the aliphatic region of the of the spectra integrate for twelve protons in the case of the palladaheptacycles and sixteen protons in the case of the palladacyclononanes, which agrees with what is expected for the proposed structures of the products.

Preparing the palladacycloalkanes using the di-Grignard method gave products of higher purity judging from the ^{1}H NMR spectra obtained (see Figures 4.4 and 4.6 for example) even though the overall yields were much lower than those obtained when the complexes were prepared from the bisalkenyl complexes by ring closing

metathesis followed by hydrogenation. The higher purity can be attributed to the fact that there are fewer reaction steps involved in the di-Grignard method.

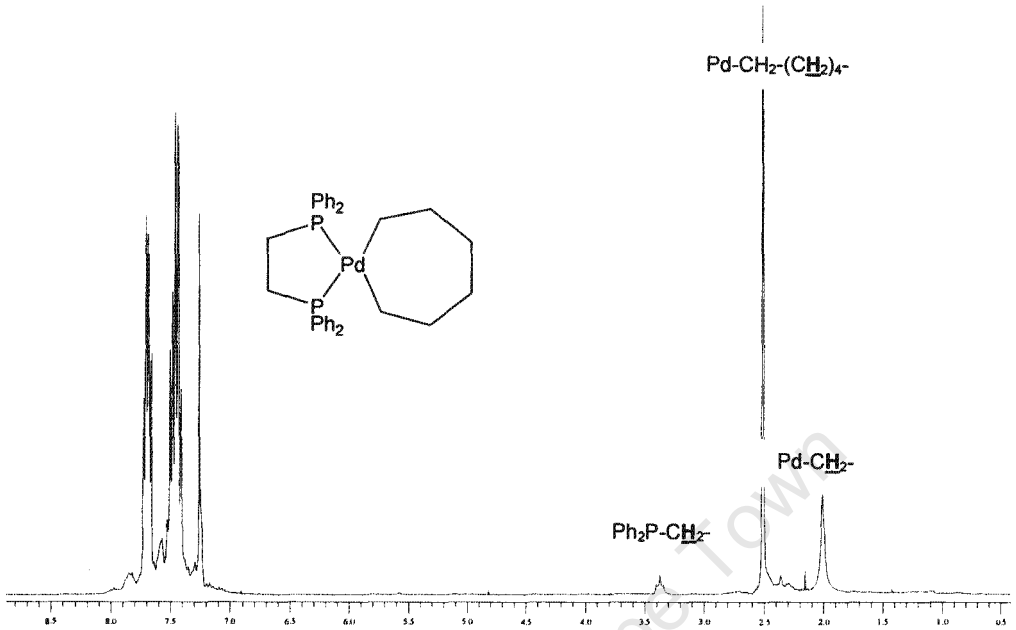


Figure 4.6: ^{1}H NMR spectrum of 59d at the end of the hydrogenation reaction.

The proton NMR spectra of the complexes show the expected signals for the protons in the ligands with the correct integrations. The spectra for the COD complexes show the peaks *ca.* 2.3 and *ca.*5.6 ppm for the -C<u>H</u>$_2$- and =C<u>H</u>- protons respectively. These peaks together integrate for twelve peaks as expected. The spectra for the bipy complexes show the signals for the ligand in the region between 6.5 and 9.0 ppm, integrating for eight protons. The multiplets for the phenyl protons in PPh_3 and dppe complexes appear between 7.0 and 8.0 ppm. These multiplets integrate for twenty protons in the case of the dppe complexes and thirty protons in the case of the PPh_3 complexes. In addition, the spectra for the dppe complexes also show a triplet at ca. 3.4 ppm, which is assigned to the methylene protons in the dppe ligand backbone. These signals integrate for four protons.

Table 4.3: Yields, melting points and ^{31}P NMR data for complexes 59 – 60

Complex	Ligand	Yield	m.p. (°C)	δ(P, ppm)
59a	COD	78	oil	-
59b	bipy	83	oil	-
59c	PPh_3[a]	97	48 - 59	27.3
59d	dppe[a]	96	65 - 73	32.7
60a	COD	60	oil	-
60b	Bipy	78	oil	-
60c	PPh_3[a]	83	39 - 47	25.5
60d	dppe[a]	76	55 - 67	33.5

[a]The yields reported are for the hydrogenation reactions. The yields for the reactions with the di-Grignard reagents were all lower than 15%.

^{31}P NMR spectroscopy

Complexes **59c**, **59d**, **60c** and **60d** were also characterized by ^{31}P NMR spectroscopy. The spectra of the complexes show a similar pattern to those of the bisalkenyl complexes presented in Chapter 3 as well as the palladacycloalkene complexes presented earlier in this chapter. The signals for the phosphorus atoms in the palladacycloalkane complexes appear *ca.* 30 ppm (Table 4.3). The similarity in the ^{31}P NMR spectra of all these complexes is due to the fact that the environments around the metal centres in these complexes are all very similar.

Mass Spectrometry

Complexes **59 – 60** were also characterized by mass spectrometry. The mass spectra of the complexes show molecular ion peaks corresponding to the molecular masses of the expected products foe each complex. The fragmentation patterns of the complexes also show peaks corresponding to the loss of the ligands as well as the cycloalkyl fragments (Table 4.4).

Table 4.4: Mass spectral data for palladacycloalkanes, complexes 59 - 60

Complex	Ligand	m/z		
		M	M – ligand	M – R[a]
59a	COD	297.8	189.5	213.7
59b	bipy	345.8	189.9	257.6
59c	PPh_3	714.2	451.8,[b] 189.7[c]	629.1
59d	dppe	587.9	189.9	503.8
60a	COD	325.9	217. 6	213.6
60b	bipy	373.8	217.5	256.9
60c	PPh_3	742.9	489.9,[b] 217.6[c]	630.0
60d	dppe	616.0	216.9	503.4

[a]R = cyclohexane for complexes **59a – 59d** and R = cyclooctane for complexes **60a – 60d**.

[b]m/z corresponds to $M^+ - PPh_3$.

[c]m/z corresponds to $M^+ - 2PPh_3$.

4.3 Conclusion

Palladacycloheptene and palladacyclononene complexes with COD, bipy, PPh_3 and dppe as ligands were successfully prepared and characterized. The complexes were synthesized by ring closing metathesis reactions of the bisalkenyl complexes reported in Chapter 3. The complexes were characterized by ^1H and ^{31}P NMR spectroscopy as well as mass spectrometry. All spectral data obtained agrees with what is expected for the proposed structures of the products.

The complexes were found to be fairly stable at ambient temperatures the products were obtained in good to excellent yields. The COD complexes were obtained in lower yields than the complexes based on bipy and the phosphine ligands. This trend was expected as the COD complexes are expected to be less stable than analogous complexes based on nitrogen and phosphorus donor ligands.

The palladacycloalkane complexes, **59 – 60**, were prepared by hydrogenation reactions of the palladacycloalkenes. The hydrogenation reactions were carried out at room temperature and the complexes were found to be stable at room temperature if they were not left for prolonged periods at room temperature. The phosphine-based complexes, **59c**, **59d**, **60c** and **60d**, were also prepared from the reaction of $PdCl_2(COD)$ with corresponding di-Grignard reagents followed by ligand substitution. ^{1}H and ^{31}P NMR spectra obtained for the compounds prepared by these two routes were the same, confirming that the same products were obtained by these two routes.

Satisfactory elemental analysis results could not be obtained for the complexes. This is due to the complexes being unstable. Some of the compounds are also oily materials and purification and removal of solvent from the products was difficult. However, all other data obtained for the compounds agrees very well with what is expected for the proposed structures of the complexes. For both the palladacycloalkene and palladacycloalkane complexes, the nine-membered rings were found to be less stable than the seven-membered rings. To the best of our knowledge, the compounds reported in this chapter have not been reported in the literature before.

4.4 References

1. Cámpora, J., Palma, P. and Carmona, E., *Coord. Chem. Rev.*, 1999, **193 - 195**, 207.
2. Chappel, S. D. and Cole-Hamilton, *Polyhedron*, 1982, **1**, 739.
3. McDermott, J. X., White, J. F. and Whitesides, G. M., *J. Am.Chem. Soc.*, 1973, **95**, 4451.
4. (a) Carlise, J. R. and Weck, M., *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 2973. (b) Abd-El-Aziz, A. S., May, L. J., Hurd, J. A. and Okasha, R. M., *J. Polym. Sci., Part A: Polym. Chem.*, 2001, **39**, 2716. (c) Alaa, S., Okasha, R. M., Afifi, T. H. and Todd, E. K., 2003, **20**, 555.
5. Blom, B., Clayton, H., Kilkenny, M and Moss, J. R., *Adv. Organomet. Chem.*, 2006, **54**, 149.
6. Grubbs, R. H., *Tetrahedron*, 2004, **60**, 7117.
7. Overett, M. J., Blann, K., Bollmann, A., Dixon, J. T., Haasbroek, D., Killian, E., Maumela, H., McGuinness, D. S. and Morgan, D. H., *J. Am. Chem. Soc.*, 2005, **127**, 10723.
8. Bollmann, A., Blann, K., Dixon, J. T., Hess, F. M., Killian, E., Maumela, H., McGuinness, D. S., Morgan, D. H., Neveling, A., Otto, S., Overett, M., Slawin, A. M. Z., Wasserscheid, P. and Kuhlmann, S., *J. Am. Chem. Soc.*, 2004, **126**, 14712.
9. Tomov, A. K., Chirinos, J. J., Jones, D. J., Long, R. J. and Gibson, V. C., *J. Am. Chem. Soc.*, 2005, **127**, 10166.
10. Tobisch, S and Zeigler, T., *Organometallics*, 2003, **22**, 5392.
11. Benn, R., Reinhart, R.-D. and Rufinska, A., *J. Organomet. Chem.*, 1985, **282**, 291.
12. Diversi, P., Ingrosso, G., Lucherini, A. and Murtas, S., *J. Chem. Soc. Dalton Trans.*, 1980, 1633.
13. Diversi, P., Ingrosso, G., Lucherini, A., Lumini, T. and Marchetti, F., *J. Chem. Soc. Dalton Trans.*, 1988, 133.
14. Buch, H. M. And Kruger, C., *Acta Cryst.*, 1984, C**40**, 28.
15. See references in Chapter 1 of this thesis.

16. Dralle K., Jaffa, N. L., le Roux, T., Moss, J. R., Travis, S., Watermeyer, N. D and Sivaramakrishna, A., *Chem. Commun.*, 2005, 3865.
17. Sivaramakrishna, A., Su, H. and Moss, J. R., *Angew. Chem. Int. Ed. Engl.*, 2007, in press.
18. Shima, T., Hampel, F. and Gladyz, J. A., *Angew. Chem. Int. Ed.*, 2004, **43**, 2.
19. Huang, X., Zhu, J. and Lin, Z., *Organometallics*, 2004, **23**, 4154.
20. Sivaramakrishna, A., Su, H. and Moss, J. R., 2007, *Organometallics*, under revision.
21. Hager, E., Sivaramakrishna, A. and Moss, J. R., unpublished results.
22. McDermot, J. X., White, J. F. and Whitesides, G. M., *J. Am. Chem. Soc.*, 1976, **98**, 6521.

Chapter 5

Decomposition Studies of Selected Palladium Complexes

5.1 Introduction

The last step in the mechanism of every synthetically useful catalytic or stoichiometric reaction that involves a metallacycle, is its decomposition to give the desired organic products.[1] This is an aspect of the chemistry of metallacycles that differs considerably from that of their open-chain analogues.[1] The understanding of this process is therefore of great importance in the design of new applications of metallacycles.[1]

The most commonly observed decomposition process for group-10 dialkyl complexes is the β-hydride elimination. This process requires the transition state in which the dihedral angle M-C-C-H is nearly 0°C.[2] This transition state is not readily achieved in medium and small ring-sized metallacycles.[1] As a result, β-hydride elimination is not as common in metallacycles of small and medium ring sizes such as metallacyclobutanes, metallacyclopentanes and metallacyclohexanes as is in dialkyl complexes.[1]

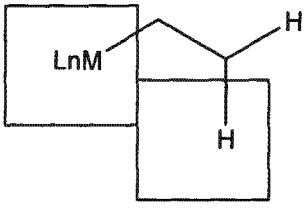


Figure 5.1: The dihedral angle M-C-C-H is 0° when the planes containing the metal centre and the hydrogen atom are parallel.

Another frequently observed decomposition route in group-10 dialkyl complexes is the reductive elimination process. However, this process is thermodynamically unfavorable in metallacycles of small and medium sized rings. The process gives rise to strained organic products such as cyclopropanes and cyclobutanes.[1] Other

decomposition processes observed in metallacycloalkanes include α-hydride elimination as well as retro-cycloaddition (β-C-C fission) reactions (Figure 5.2).[1] Of these decomposition processes, the two most important concerted thermolysis pathways of dialkyl palladium complexes relevant to organic synthesis are reductive elimination and β-hydride elimination.[3]

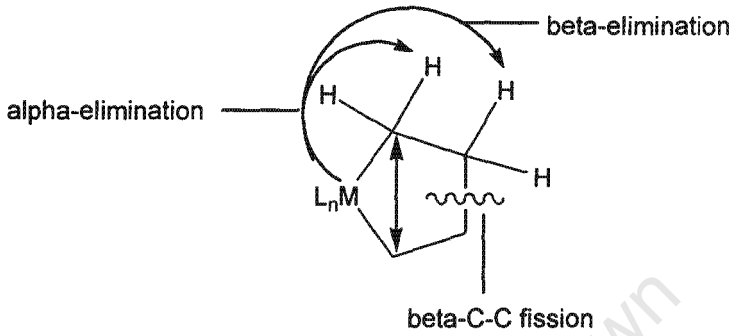


Figure 5.2: Decomposition mechanisms observed in metallacycloalkanes.[1]

A number of platinum(II) and nickel(II) metallacycles have been synthesized and characterized.[1] Extensive studies have been carried out on the decomposition reactions of these complexes and these studies show that, in general, platinum(II) metallacycles decompose via β-elimination to give product mixtures of 1-alkenes and 2-alkenes (after a β-elimination/isomerization processes).[1] The decomposition patterns of nickel-based metallacycles are, on the other hand, dependent on the coordination number of the metal center. The main decomposition route in the nickel complexes, however, is reductive elimination, giving cycloalkanes as the main organic products.[4]

Unlike their nickel and platinum counterparts, the metallacycloalkanes of palladium have not been as extensively studied.[5,6] The limited number of studies that have been carried out to date indicate that the decomposition mechanisms observed in palladacycloalkanes seem to be midway between the platinum and nickel complexes. Both reductive elimination and β-hydride elimination are observed.[1] Although decomposition of palladacycloalkanes via β-elimination has been reported,[1,2] most reports on the decomposition of these complexes indicate that

the majority of organic products from palladacycloalkanes are formed by reductive elimination processes.[1,6,7]

The decomposition studies reported in this chapter are of some bisalkenyl and metallacycloalkane complexes reported in Chapters 3 and 4. The types of products obtained from the decomposition reactions were observed to depend on how long after complex synthesis the decomposition reactions were carried out. The thermal decomposition reactions described in this thesis were all carried out at 165°C in the solid state. The products were analyzed using GC or GC-MS. In addition, the decomposition products of the proposed 1,10-phenanthroline complex, [cis-Pd{$(CH_2)_3CH=CH_2$}$_2$(phen)] were also characterized by ^{1}H and ^{13}C NMR spectroscopy.

5.2 Decomposition of bis(alkenyl) complexes

Synthesis of the bis(pentenyl) complex, *cis*-[Pd{$(CH_2)_3CH=CH_2$}$_2$(phen)] was attempted. The procedure used for the synthesis of complex **55a**, *cis*-[{$(CH_2)_3CH=CH_2$}$_2$(COD)] was followed except that $PdCl_2$(phen) was used as the starting material instead of $PdCl_2$(COD). Product formation was indicated by the dissolution of the palladium precursors to form an orange solution. However this solution immediately turned brown indicating that the complex had decomposed considerably in the reaction mixture. After work-up a product was obtained as a colorless oil that was characterized by ^{1}H and ^{13}C NMR spectroscopy (Figure 5.2) as well as GC-MS.

All data confirmed that the obtained oil is 1,9-decadiene, which is the reductive elimination product from the proposed 1,2-phenanthroline complex. The ^{1}H NMR spectrum of the product shows no signals for the protons due to the phenanthroline ligand while all the expected signals for the protons in the aliphatic chain are observed in the expected regions. The ^{13}C NMR spectra also showed the same pattern, with signals in the aromatic region which would have been due to the carbon atoms in the ligand being absent.

The GC-MS results further confirmed the identity of the product to be 1,9-decadiene. The mass spectrum showed the parent molecular ion at m/z 137.2, which corresponds to the molecular mass of 1,9-decadiene. A peak at m/z 423.9, which would have corresponded to the molecular mass of $[Pd\{(CH_2)_3CH=CH_2\}_2(phen)]^+$, was not observed.

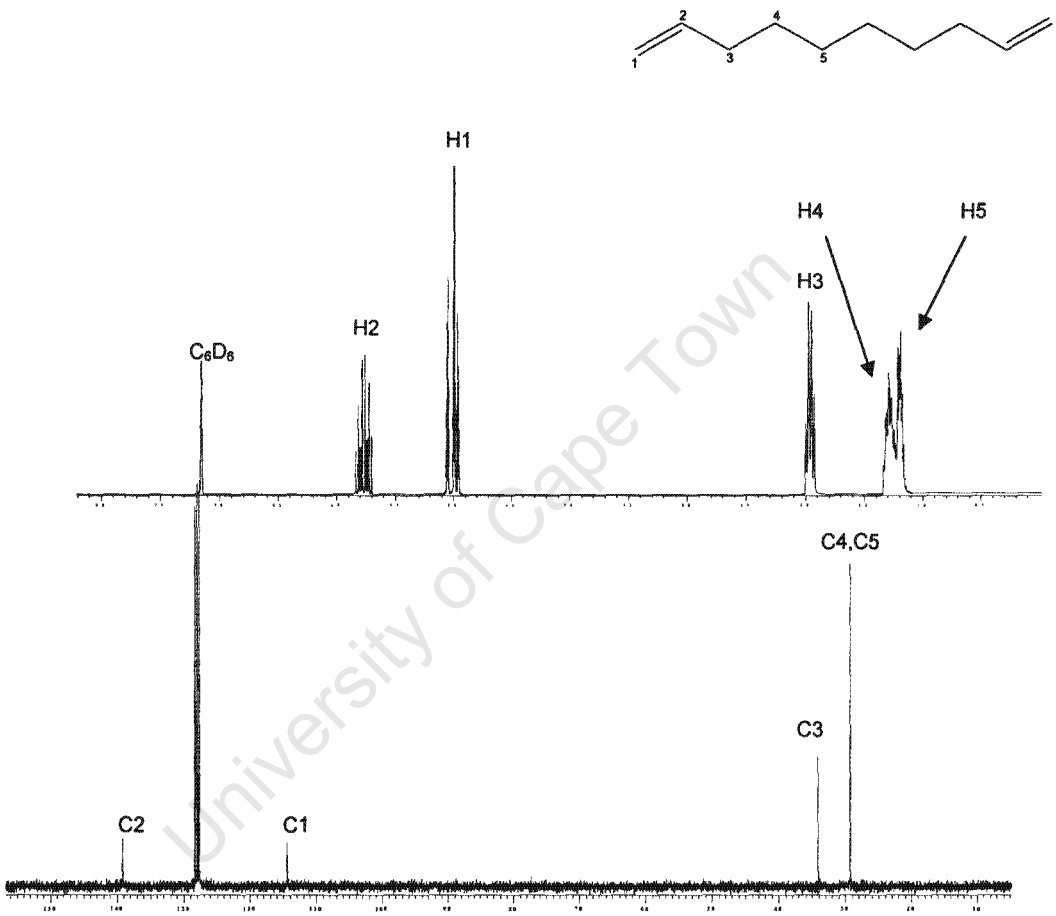
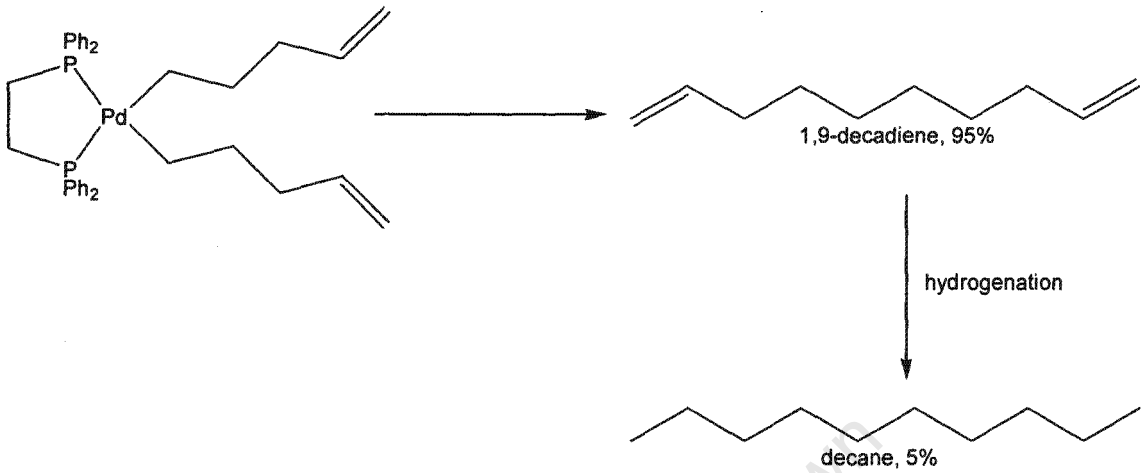


Figure 5.3: ^1H and ^{13}C NMR spectra of 1,9-decadiene obtained from the decomposition of the palladium complex, [cis-$Pd\{(CH_2)_3CH=CH_2\}_2(phen)$}.

The decomposition of a fresh sample of the bis(pentenyl) complex, **55d**, was carried out at 160°C for 2 hours. The reaction gave the reductive elimination products, 1,9-decadiene (95%) and decane (5%) exclusively. The decane could be

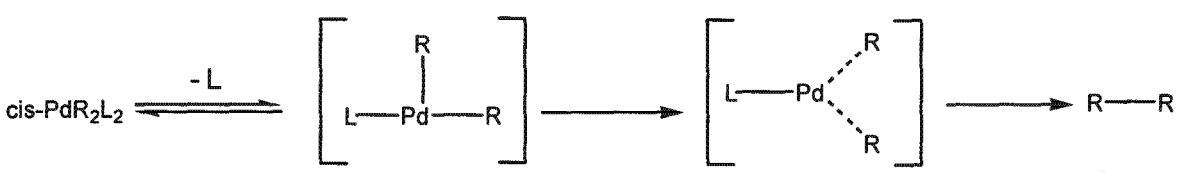
the result of reductive elimination followed by hydrogenation. The hydrogen could come from the palladium hydride species (Scheme 5.1).



Scheme 5.1: Decomposition of complex 55d.

These results are in agreement with the results obtained by Ozawa and Yamamoto for the decomposition studies carried out on PdR_2L_2 complexes (where L_2 are tertiary phosphine ligands and R are methyl or ethyl groups).[8] They observed that decompositions of the *trans*-$PdEt_2L_2$ complexes gave ethene and ethane exclusively, indicating a β-hydride elimination pathway. The *cis*- isomers, on the other hand, afforded reductive elimination products exclusively.[8]

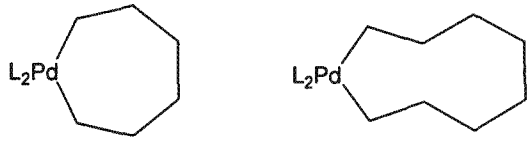
Ozawa and Yamamoto proposed a reaction mechanism in which the rate determining step is the dissociation of the tertiary phosphine ligand as outlined in Scheme 5.2 below.



Scheme 5.2: Proposed mechanism for the reductive elimination of cis-PdR_2L_2.[3]

5.3 Decomposition studies of palladacycloalkanes

Decomposition reactions were carried out on the phosphine-based complexes, **59c**, **59d**, **60c** and **60d** (Figure 5.3). For the palladacycloheptanes, **59c** and **59d**, the decomposition reactions were carried out on fresh samples while for the palladacyclononanes, **60c** and **60d**, the decomposition reactions were carried out on both fresh and three-week old samples.



59d **60c, 60d**

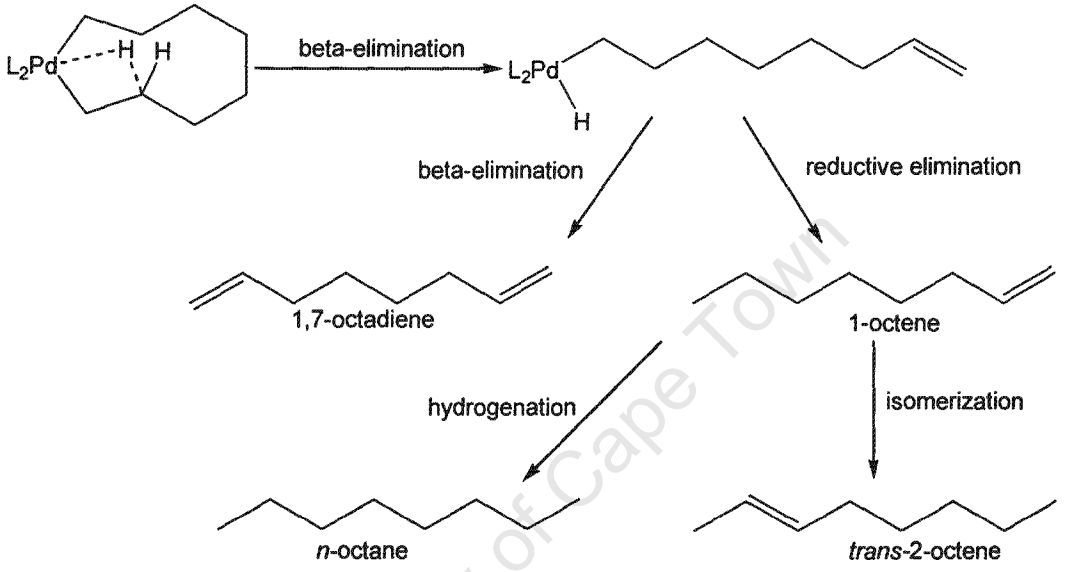
c) L = PPh_3, **d)** L = dppe

Figure 5.4: Complexes used in the decomposition studies.

As already mentioned, the types of products obtained from the decomposition reactions of the palladacycloalkanes depend on how long after their synthesis the decomposition reactions were carried out. Decomposition of fresh samples gave organic products with the expected numbers of carbon atoms (six for the palladacycloheptanes and eight for the palladacyclononanes). However, if the decomposition reactions were carried out three weeks after the synthesis of the palladacycloalkanes with storage of the sample under argon at room temperature, the organic products obtained were consistently one carbon atom short of the expected number.

The decomposition of fresh samples of the nine-membered palladacycles gave predominantly straight-chain organic products as indicated in Table 5.1. The product profiles for both complexes **60c** and **60d** are more or less the same, with the decomposition reactions yielding *n*-octane, 1-octene, *trans*-2-octene and 1,7-

octadiene. No *cis*-2-octene was observed for both complexes. The initial step in the decomposition process is possibly the β-hydride elimination step that results in the formation of a palladium hydride species as outlined in Scheme 5.3. This step is probably then followed by the reductive elimination of the palladium hydride species to yield 1-octene. The 1,7-octadiene could be a product of a second β-elimination from the palladium hydride species.

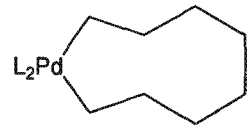


Scheme 5.3: Decomposition of palladacyclononanes.

The *trans*-2-octene is formed from the isomerization of 1-octene while *n*-octane is formed by the hydrogenation of the olefinic products. The proposed mechanism for the isomerization reaction is similar to the one proposed by Brookhart and co-workers for branching observed in palladium-catalyzed ethylene oligomerization and polymerization products (Scheme 5.4).[9] The olefinic products (both mono- and di-olefins) from the decomposition reactions of both complexes **60c** and **60d** make up more than 80% of the product mixture. In this 80%, *ca*. 30% consists of 1-octene.

Comparison of the results obtained in this study with those obtained for analogous platinum complexes with the same ligand systems[10] reveals that the same

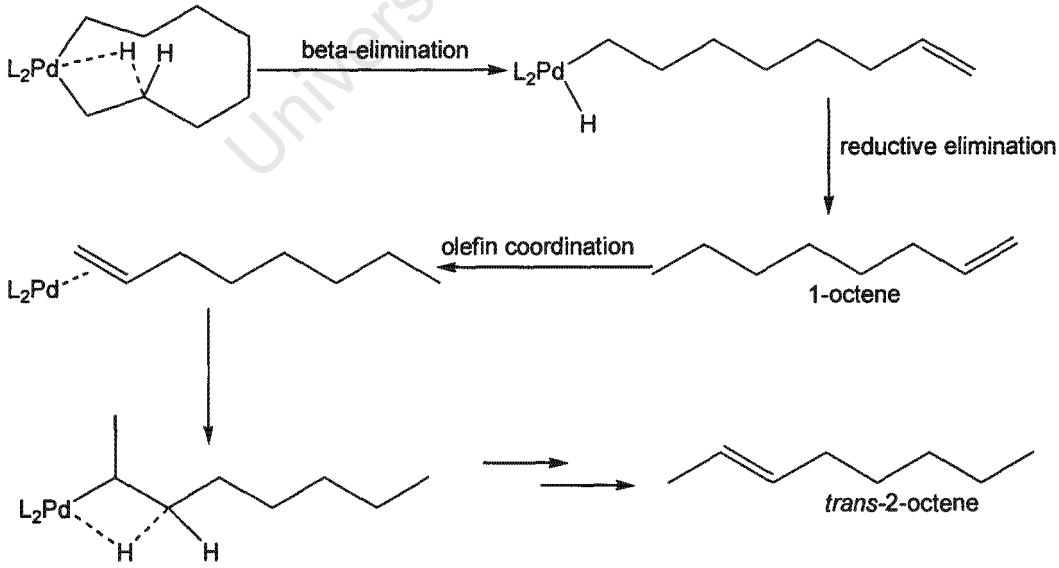
decomposition routes occur in palladium and platinum, although in these complexes isomerization of 1-octene to *trans*-2-octene was observed to occur to a smaller extent while hydrogenation to octane occurs to a greater than in palladacycloalkanes. For instance, the decomposition of the dppe- and PPh_3-based platinacycloalkanes (Figure 5.4) gave *n*-octane (38 %), 1-octene (45 %), *trans*-2-octene (15 %) as well as cyclooctane (2 %) as products. Similar results were obtained for the analogous PPh_3 platinum complex.



L = PPh_3, L_2 = dppe

Figure 5.5: Structure of platinacyclononanes.

Comparing the palladium complexes reported in this study and the chromium systems for ethylene trimerization and tetramerization shows that the decomposition of the palladium complexes is not as selective for α-olefins as the chromium systems.[11-14] In the chromium systems, selectivities as high as 90% percent were achieved for α-olefins.[15]



Scheme 5.4: Proposed mechanism for the isomerization of 1-octene to internal olefins.

A similar decomposition process is expected for the palladacycloheptane, **59d**. The majority of the decomposition products is made up of the straight-chain six-carbon organic products (n-hexane, 1-hexene, trans-2-hexene and 1,5-hexadiene). However, in addition to these, the GC results show that the product mixture for these complexes also has significant amounts of cyclohexane (*ca.* 20%), which suggests that reductive elimination is also an important decomposition route for palladacycloheptanes. Palladacyclononanes, on the other hand, gave very small amounts of the reductive elimination process, i.e. cyclooctane (*ca.* 3%). Olefinic products in the palladacycloheptanes make up *ca.* 60% of the product mixture, and of this 60%, 1-hexene comprises only *ca.* 20%. Comparing these results with those obtained for analogous platinum systems, a similar trend is observed. Cyclohexane comprises *ca.* 20% of the products in these systems, while the other 80% is made up of olefins.[10]

The observed differences in the decomposition mechanisms of the palladacycloheptanes and palladacyclononanes can be explained by the fact that as ring size increases the metallacycles behave more and more like metal alkyls.[1] β-elimination, which is the main decomposition process observed for group-10 metal alkyls requires a transition state in which the dihedral angle M-C-C-H is close to 0° (see Figure 5.1). This angle is more easily achieved in larger metallacycles than in smaller ones.[1] The reductive elimination of palladacycloheptanes gives thermodynamically stable cyclohexane as a product, which is another reason why reductive elimination occurs to a greater extent in the seven-membered than in the nine-membered palladacycles.

Table 5.1: Decomposition products obtained from fresh samples of complexes 59d, 60c and 60d.

Complex	Ligand	n[a]	Products (%)[b]				
59d	dppe	6	n-hexane (22)	1-hexene (21)	*trans*-2-hexene (19)	1,5-hexadiene (18)	cyclohexane (20)
60c	PPh_3	8	n-octane (15)	1-octene (33)	*trans*-2-octene (32)	1,7-octadiene (17)	cyclooctane (3)
60d	dppe	8	n-octane (16)	1-octene (29)	*trans*-2-octene (34)	1,7-octadiene (18)	cyclooctane (3)

[a]n is the number of carbon atoms in the metallacyclic complex.

[b]Error = +/-1%.

Table 5.2: Decomposition products obtained from old samples of complexes 60c and 60d.[a]

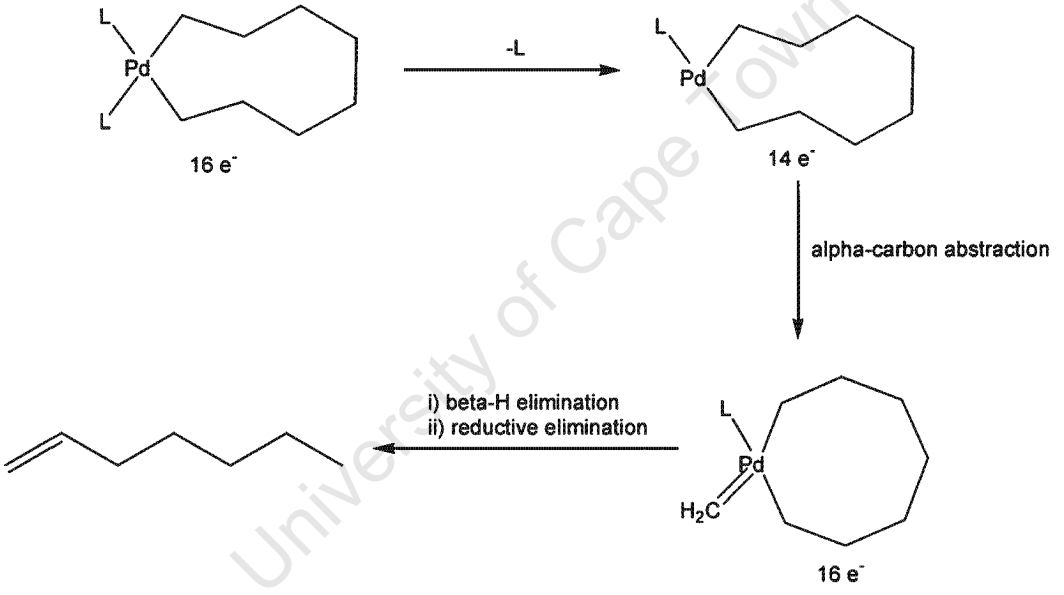
Complex	Ligand	n[b]	Products (%)[c]	
			1-Heptene	Heptane
60c	PPh_3	8	50	50
60d	dppe	8	65	35

[a]The decomposition reactions were carried out three weeks after the synthesis of the pallacycles.

[b]n is the number of carbon atoms in the palladacycles.

[c]Error = +/-1%.

Decomposition reactions carried out on three weeks old samples of the palladacyclononanes, **60c** and **60d**, consistently gave seven-membered open-chain organic products (Table 5.2). This observation could be explained using the α-C-C mechanism reported by Grubbs and Miyashita for the decomposition of some nickel complexes (Scheme 5.5).[4] The process most likely starts with the dissociation of the phosphine ligand, which results in an unstable 14-electron species. The metal centre then abstracts the methylene group α- to the metal in the metallacyclic ring, thereby forming a carbene species.[4] This species then undergoes β-elimination followed by reductive elimination to give 1-heptene. Heptane is a secondary product in the reaction resulting from the hydrogenation of 1-heptene.



Scheme 5.5: α-carbon abstraction decomposition mechanism for palladanonacycles.

We believe that the α-carbon abstraction decomposition mechanism occurs over a longer period of time and under milder conditions than β-elimination in the palladacycloalkanes. As a result, it is highly possible that the samples that were submitted for decomposition studies after three weeks were no longer the nine-membered rings that were initially prepared, but palladacyclooctanes. Further

observed to occur to a very limited extent. Products from this process comprised only *ca.* 3% of the product mixture. Comparison with analogous platinacycloalkanes shows that the same decomposition mechanisms operate between palladium and platinum complexes.

5.5 References

1. Cámpora, J., Palma, P. and Carmona, E., *Coord. Chem. Rev.*, 1999, **193 - 195**, 207.
2. Huang, X., Zhu, J. and Lin, Z., *Organometallics*, 2004, **23**, 4154.
3. Ozawa, F., Kurihara, K., Yamamoto, T. and Yamamoto, A., *Bull. Chem. Soc. Jpn.*, 1985, **58**, 399.
4. Grubbs, R. H. and Miyashita, A., *J. Am. Chem. Soc.*, 1978, **100**, 7148.
5. Collman, J. P., Hegedus, L. S., Norton, J. R. and Finke, R. G., *Principles and Applications of Organometallic Chemistry*, University Science Books, Mill Valley, 1987.
6. Blom, B., Clayton, H., Kilkenny, M. and Moss, J. R., *Adv. Organomet. Chem.*, 2005, **54**, 149.
7. Binger, P., Buech, H. M., Benn, R. and Mynott, R., *Angew. Chem. Int. Ed. Engl.*, 1982, **21**,62.
8. Ozawa, F. and Yamamoto, A., *Organometallics*, 1982, **1**, 1481.
9. Tempel, D. J., Johnson, L. K., Huff, R. L., White, P. S. and Brookhart, M., *J. Am. Chem. Soc.*, 2000, **122**, 6686.
10. Sivaramakrishna, A., unpublished results.
11. Bollmann, A., Blann, K., Dixon, J. T., Hess, F. M., Killian, E., Maumela, H., McGuinness, D. S., Morgan, D. H., Neveling, A., Otto, S. Overett, M., Slawin, A. M. Z., Wasserscheid, P. and Kuhlmann, S., *J. Am. Chem. Soc.*, 2004, **126**, 14712.
12. Tomov, A. K., Chirinos, J. J., Jones, D. J., Long, R. J. and Gibson, V. C., *J. Am. Chem. Soc.*, 2005, **127**, 10166.
13. Overett, M. J., Blann, K. Bollmann, A., Dixon, J. T., Haasbroek, D., Killian, E., Maumela, H., McGuinness, D. S. and Morgan, D. H., *J. Am. Chem. Soc.*, 2005, **127**, 10723.
14. Agapie, T., Schofer, S. J., Labinger, J. A. and Bercaw, J. E., *J.Am. Chem. Soc.*, 2004, **126**, 1304.
15. Elowe, P. R., McCann, C., Pringle, P. G., Spitzmesser, S. K. and Bercaw, J. E., *Organometallics*, 2006, **25**, 5255.

Chapter 6

General Conclusions and Future Work

In this project, a series of new palladium(II) complexes based on 1,5-cyclooctadiene, 2,2'-bipyridine, triphenylphosphine and 1,2-bis(diphenylphoshino)ethane were synthesized and characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, mass spectrometry and elemental analysis. These complexes include the bis(butenyl), bis(pentenyl), palladacycloheptene, palladacyclononene, palladacycloheptane and palladacyclononane complexes.

The bis(alkenyl) complexes, **54a – 55d**, were prepared by the reaction of the different $PdCl_2L_2$ complexes with appropriate Grignard reagents. RCM reactions with Grubbs' second generation catalyst were then carried out on the bisalkenyl complexes to obtain the palladacycloalkenes, **57a – 58d**. The RCM reactions were followed by hydrogenation reactions to prepare the palladacycloalkanes, **59a – 60d**. Complex stability seemed to be dependent on the donor ligand attached to the metal centre.

In addition to their synthesis and characterization, thermal decomposition reactions were carried out on some of the palladium complexes and the decomposition products were characterized mainly by GC and GC-MS. The decomposition products obtained from bis(pentenyl) complexes revealed that reductive elimination is the predominant mode of decomposition for these complexes.

Decomposition reactions carried out on palladacycloalkanes, on the other hand, gave a mixture of products, indicating that for these complexes both reductive elimination and β-hydride elimination occur. Analysis of the product mixtures for palladacyclononanes and palladacycloheptanes revealed that reductive elimination occurs to a greater extent in palladacycloheptanes than it does for

palladacyclononanes. The mode of decomposition observed for the palladacyclononanes also seemed to be dependent on the conditions under which the decomposition occurred. Slow decomposition of these complexes at ambient temperature gave organic products with one carbon atom less than the expected number, indicating that under these conditions α-carbon abstraction is the major decomposition mechanism operating.

Future work in this study could include:

- Optimization of yields for the bis(alkenyl) complexes.
- Further attempts could be made to purify all compounds in order to get satisfactory elemental analysis for all complexes.
- Use of other ligands (such as PMe_3 or dmpe) in order get crystalline compounds that could be characterized by X-ray crystallography.
- More decomposition reactions could be carried out on the other complexes in order to observe whether these complexes show the same trends shown by the complexes whose decomposition was studied.
- Further reactivity studies, such as insertion reactions, with both the palladacycloalkanes and their precursors.