Pyrazolyl palladium(II) complexes as phenylacetylene oligomerization and polymerization catalysts.

By

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Submitted in partial fulfillment of the requirements for the degree of

Master of Science in the Faculty of Science

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May 2004

DECLARATION

I declare that "*Pyrazolyl palladium(II) complexes as phenylacetylene oligomerization and polymerization catalysts*" is my own work, and it has not been submitted for any degree or examination in any other university, and all the sources I have used or quoted have been indicated and acknowledged by means of complete reference.

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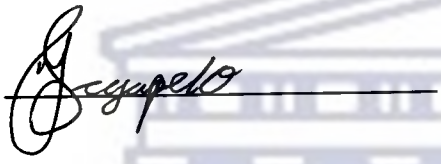
Signature: 

DEDICATION

To my parents on their *25th Wedding Anniversary*, may the Lord bless you on this special milestone and may he bless you with many more years.

TABLE OF CONTENTS

Abstract

Pyrazolyl compounds have been extensively used to prepare metal complexes, but it is only recently that they have been investigated as catalysts for the polymerization of unsaturated hydrocarbons. In catalyzing the polymerization of ethylene, the electrophilicity of the metal centre plays an important role since the key step in the polymerization is coordination of the ethylene. A similar facile coordination would be expected for acetylene and one would therefore expect pyrazolyl palladium complexes to be good catalysts for the transformation of acetylenes. This thesis is an investigation of pyrazolyl palladium complexes as catalysts for the polymerization and oligomerization of substituted acetylenes.

Chapter 2 is on the synthesis and characterization of palladium complexes that were used to catalyse the acetylenes. The pyrazolyl ligands, 1,4-(3,5-R_2pzC(O))$_2C_6H_4$ (**L1-L4**), 1,3-(3,5-Ph_2pzC(O))$_2C_6H_4$ (**L5**) and X{Y(CH_2)R_2pz}$_2$ (**L6-L8**) {R = ^{t}Bu (**L1**), Me (**L2**), H (**L3**), Ph (**L4**); X = NH, O; Y = CH_2, $SiMe_2$}, were prepared from a reaction in which a chloro compound containing the 1,4-benzenedicarbonyl (**L1-L4**), 1,3-benzenedicarbonyl (**L5**), or X{Y(CH_2)} (**L6-L8**) linker was reacted with the appropriate pyrazole. Compounds **L1-L8** were subsequently used to prepare their corresponding palladium complexes **1-8** by reacting **L1-L8** with [$PdCl_2$(NCMe)$_2$]. The ligands **L1-L4** form complexes of the type [Pd_2L(μ-Cl)$_2Cl_2$]$_2$ while the former 1,3-(3,5-Ph_2pzC(O))$_2C_6H_4$ ligand forms the same type of complexes as their ^{t}Bu and Me analogues, which form bimetallic complexes of the type [Pd_2L(μ-Cl)$_2Cl_2$]. All compounds were characterized by multinuclear NMR and IR spectroscopy, mass spectrometry and elemental analysis. The latter two techniques were pivotal in the elucidation of structural mode of bonding in the 1,4-(3,5-R_2pzC(O))$_2C_6H_4$ complexes.

The proposed structures for **L1**, **L5** and complex **5** from the spectroscopy were confirmed by X-ray crystallography.

Chapter 3 describes the use of new palladium complexes prepared in this project as catalysts in the oligomerization and polymerization of substituted acetylenes. Complexes **1**, **5** and **6** were investigated as catalysts precursors for the polymerization of substituted acetylenes. To do this, the complexes were converted to the cationic forms $[Pd_2L(\mu\text{-}Cl)_2(NCMe)_2]_2(OTf)_2$, $[Pd_2L(\mu\text{-}Cl)_2(NCMe)_2](OTf)_2$ and $[PdL(NCMe)_2](OTf)_2$ respectively by reacting complexes **1**, **5** and **6** with the appropriate equivalents of Ag(OTf) in the presence of NCMe. These cationic forms of the precursors were found to be active catalysts in the polymerization and oligomerization of phenylacetylene and its derivative p-tolylacetylene. The catalysts produced poly(phenylacetylene) with molecular weight as high as 12 000 Da. However, attempts to use these compounds to polymerize other acetylenes resulted in only low molecular weight oligomers being formed. When complex **6** was used as catalyst precursor, polymerization proceeded with very high stereoselectivity producing only *cis-transoidal* poly(phenylacetylene) and selectivity was independent of the polymerization conditions used. The other catalysts gave poly(phenylacetylenes) which were a mixture of *cis-transoidal* and *trans-cisoidal* geometry. It was thus conclusive evidence that polymerization was initiated through an insertion mechanism rather than a metathesis mechanism.

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS

3,5–Me_2PzH = 3,5-dimethylpyrazole

3,5-$^tBu_2$pzH = 3,5- ditertiarybutylpyrazole

AgOTf = Silver trifluoromethanesulfonate

Da. = Daltons

GPC = Gel Permeation Chromatography

EI = Electron Impact

IR = Infrared

MALDI- TOF = Matrix-Assisted Laser Desorption Ionization-Time of Flight

$MoCl_5$ = Molybdenum pentachloride

M_n = Number average molecular weight

M_w = Weight average molecular weight

M_w/M_n = Polydispersity index

NMR = Nulear Magnetic Resonance

PA = Phenylacetylene

Ph = Phenyl

Ph_4Sn = Tetraphenyltin

PPA = poly(phenylacetylene)

Pz/ pzH =pyrazole

UV-Vis = Ultra Violet Visible

WCl_6 = Tungsten hexachloride

ACKNOWLEGEMENTS

I would like to express my sincere appreciation and gratitude to my supervisor, Professor James Darkwa, under whose guidance this research was conducted; his invaluable advice, guidance and unconditional support is highly acknowledged. I also wish to thank Mr. Pierro Bincassa (University of Cape Town) for elemental analysis of samples, Mr. Andre Van Zyl and Ms. Valerie Grumel (University of Stellenbosch) for GPC analysis of poly(phenylacetylenes), Dr Ilia Guzei (University of Winconsin-Madison) for X-ray structural analysis of the ligands and complexes reported in this thesis. I am grateful to the National Research Foundation (NRF) and Eskom for the funding of this project. My special thanks are due to Professor Selwyn F. Mapolie and to my co-researchers from the *Organometallics* group (U.W.C) for their helpful suggestions during the project. My thanks are also due to the Department of Chemistry, University of the Western Cape, where this research was carried out, its staff members and fellow post-graduates for making me feel at home away from home. Finally I thank the Lord for affording me with the chance to study and guiding me through challenges I came across during my studies.

CHAPTER 1

LATE TRANSITION METAL COMPLEXES AS PHENYLACETYLENE POLYMERIZATION CATALYSTS AND REVIEW OF PYRAZOLE AND PYRAZOLYL COMPLEXES

1.1 Polymerization of acetylenes

Over the past few years, one of the main fields of research in homogenous catalysis has been the development of catalysts for the polymerization of unsaturated substrates, with special interest towards formation of π-conjugated polymers. Attention towards producing such compounds is due to their unique physico-chemical properties. Polyacetylenes are among such polymeric materials. Thus polyacetylenes possessing alternating olefinic bonds along the main chain are of intense interest because of their unique physical properties such as photoconductivity,[1] non-linear optical behaviour,[2,3] magnetic susceptibility.[4] The simplest of the polyenes is polyacetylene, $(-H_2C{=}CH_2-)_n$; but polyacetylene has not been extensively investigated owing to its insolubility and infusibility, as such applications of polyacetylene have been restricted due to functionality peculiar to its simple chemical structure.

Acetylene was first polymerized to a linear π-conjugated polymer by Natta *et al.* using $Ti(O\text{-}Pr)_4/Et_3Al$ in 1958.[5] Watson *et al.* studied the polymerization of acetylene with various Ziegler-type catalysts and gave the first account of the preparation of *cis*-polyacetylene.[6] To increase the processability and provide various functionalities of polyacetylene, synthesis and characterization of substituted polyacetylenes have been the subject of extensive investigations.[7-13]

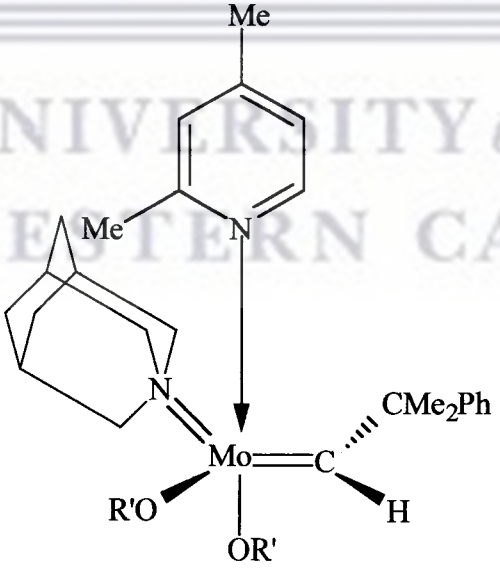
1.2 Polymerization of monosubstituted acetylenes

The introduction of functional substituents into polyacetylene causes a drastic change in various properties of the polymers. The presence of aryl or alkyl substituents is crucial for obtaining sufficient stability, appropriate chain conformation and stiffness, and high solubility in organic solvents.

Phenylacetylene has been the most often used monosubstituted acetylene in polymerization of this class of compounds. Conventional radical, cationic, or anionic initiation methods give only low yields of phenylacetylene oligomers with number-average molecular weight (M_n) below 900 Da.[14] Ziegler catalysts yield relatively high molecular weight oligomers (M_n = 7000) having a large insoluble fraction.[15,16] In 1974 Masuda and Higashimura found that phenylacetylene could be polymerized to give high molecular weight polymer in good yields with WCl_6 and $MoCl_5$ as catalysts.[17] These catalysts have also been used for olefin metathesis reactions and polymerization of cycloolefins via a metathesis mechanism.[18-20] Since then various types of group 5 and 6 transition metal catalysts have been reported for the polymerization of monosubstituted and disubstituted acetylenes, and numerous kinds of high molecular weight polymers with unique properties have been discovered. The M_n of poly(phenylacetylene) obtained from WCl_6 is about 15 000 while that obtained from $MoCl_5$ is 12000.[17]

The polymerization with WCl_6 is significantly accelerated by the presence of tetraphenyltin (Ph_4Sn) as a cocatalyst.[21] It is clear from literature reports that polymer molecular weight is greatly influenced by the method used in preparing the polymer. For instance poly(phenylacetylenes) having high molecular weight (M_n = 100 000) are

prepared by using solvents containing active hydrogens such as 1,4-dioxane, cyclohexenes, and tetralin in the polymerization of phenylacetylene and WCl_6-Ph_4Sn as the catalyst system.[22] The active hydrogens of the solvents seems to prevent polymer degradation reaction by a radical mechanism and/or modify the nature of the active species. This ensures chain growth and hence high polymer molecular weight. While polymerizations of 1-phenyl-1-propyne (PP) and 1-phenyl-1-butyne (PB) initiated by WCl_6-Ph_4Sn at room temperature yield small amounts of polymers (0.05-5.3%) with low molecular weights (M_n 8000-15000) and high polydispersity indexes (PDI up to 109), addition of C_{60} into the initiator mixture dramatically boosts its catalytic activity, producing polymers with high M_ns (up to 171 000) and low PDIs (down to 2.2) in high yields (up to 99.5%). The resultant polymers are soluble, stable, and film-forming.[23]

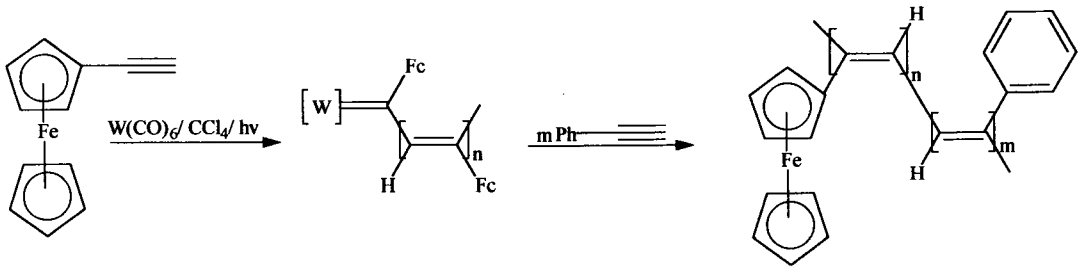


OR' = OCF_5 or $OCH(CF_3)_2$

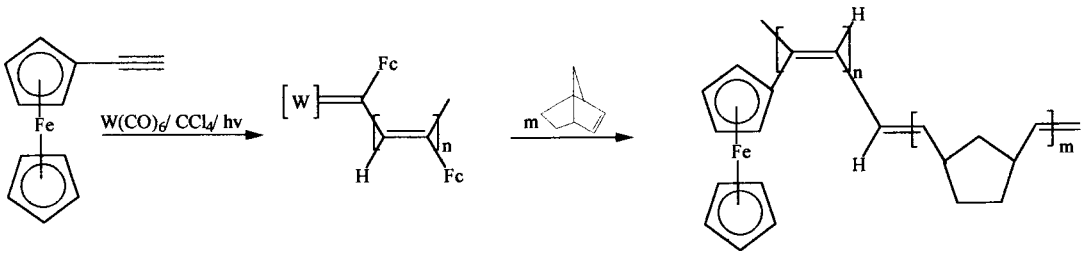
Figure 1.1: Typical structure of a Schrock carbene

Recently, living polymerization of substituted acetylenes have also been carried out using Schrock carbenes,[24-26] tantalum catalysts such as Ta[C(Me)CHCMe](DIPP)$_3$(py) where DIPP = 2,6-diisopropylphenoxide and py = pyridine,[27] rhodium complexes,[28] and $MoCl_4$-based catalysts.[29-31] Living polymerizations are polymerizations in which propagating centers do not undergo either termination or chain transfer. Living polymerization thus offers potential for producing structures with defined end groups by deliberate termination of a living system with appropriate reagents.

Living polymerization can also be used to produce block copolymers by sequential addition of two or more different monomers.[32-34] Important advantages of controlled living polymerization reactions of acetylene derivatives are greater tolerance of functionalities, control over the nature of the capping groups, and the ability to prepare block or random copolymers which contain other monomers that can be polymerized by the well defined alkylidene complexes.[35] A report by Sundarajan *et al.* provides two excellent examples in which ferocenylacetylene forms co-polymers with phenylacetylene and norbornene, respectively.[36]



Scheme 1: Copolymerization of ferrocenylacetylene and phenylacetylene



Scheme 2: Copolymerization of ferrocenylacetylene and norbonene

They further showed the versatility of $W(CO)_6$ catalyst system and employed it to synthesize poly(phenylacetylene) anchored to redox-active ferrocenyl moieties at both ends of the polymer chain.[37]

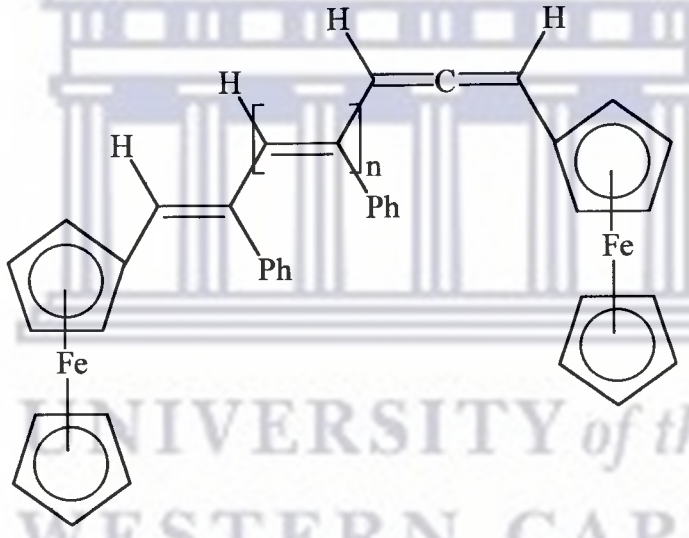


Figure 1.2: PPA with ferrocenyl end groups

Polymerization of monosubstituted acetylenes having aromatic heterocycles such as thienyl, furyl, and pyridyl substituents have also been carried out with W and Mo based catalysts.[38-40] Catalysts activities were generally better when organotin compounds, such as Ph_4Sn, *n*-Bu_4Sn, and Me_4Sn, were added to the reactions. The exception to this is the polymerization of 2-ethynylpyridine in which organoaluminum compounds, such as Et_2AlCl and $EtAlCl_2$, are very good cocatalysts in polymerization reactions catalyzed by WCl_6 and $MoCl_5$. The aluminium co-catalysts were found to be

much better co-catalysts than the tin compounds and suggest that the Lewis acidity of the aluminium compounds might be the source of the improved activity; a fact that seems to be underscored by the highly active $TiCl_4$-$EtAlCl_2$ catalytic system for the same monomers.

Despite the excellent ability of late transition metals to induce polymerizations of various cyclic and acyclic monomers, they are generally not suitable for acetylene polymerization. This is mainly due to the fact that oligomerization tends to dominate over polymerization to give cyclotrimers and linear oligomers as main products when late transition metals catalysts are used.[41,42] Nickel and palladium catalysts in particular are known to mostly produce 6, 8 and 12-membered cyclic oligomers.[43]

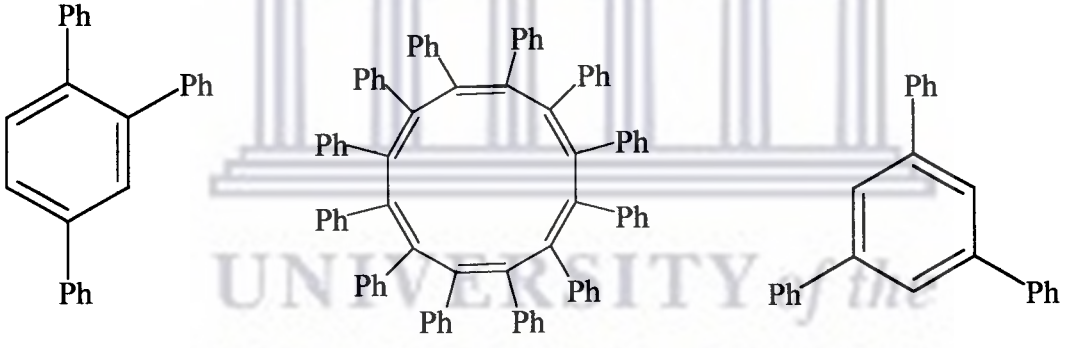


Figure 1.3: Cyclic oligomers of PA and diphenylacetylene

It is therefore an interesting and challenging problem to polymerize substituted acetylenic monomers with late transition metal catalysts, especially with Ni and Pd catalysts.

There are, however, a few late transition metal complexes that polymerize monosubstituted acetylenes. Recently two new Ni catalysts were reported to catalyze the polymerization of phenylacetylene polymers with molecular weight of 12 000-48 000.[44,45] But very high molecular weight polymers from the polymerization of

substituted acetylenes are only known for Rh[46] and Ir[47] catalytsts; up to molecular weights of 900 000 have been found with these catalysts. The Rhodium catalysts, in particular, are effective for the polymerizations of monosubstituted acetylenes, including aryl acetylenes, 1-alkynes, and propiolates but are inactive in polymerizing any disubstituted acetylenes. The Rhodium catalysts polymerize monosubstituted acetylenes via an insertion mechanism to give *cis-transoidal* polymers (Fig. 1.4).[48]

However, these Rhodium catalyst systems require the addition of the base, 4-(dimethylamino)pyridine, to prevent the formation of a less active dinuclear complex.[49] The role of base as cocatalyst in the phenylacetylene polymerization has been a source of controversy. Tabata *et al.* reported that using triethylamine as solvent in the $[(nbd)RhCl]_2$ enhances catalytic activity and selectivity.[50] The base has been linked to the formation of an active monomeric species, $(nbd)RhCl(NEt)_3$. Escudero *et al.* on the other hand proposed in their mechanism that the presence of the base promotes proton transfer that is believed to be the key step of chain growth.[51] It is however, interesting to note that high stereoregularity has been found in polymers obtained from THF as polymerization solvent without triethylamine as cocatalyst. Hence, it is still not clear what role the addition of a base plays in the polymerization of substituted acetylenes, if any.

1.3 Stereochemistry of poly(phenylacetylene)

Polymerization of monosubstituted acetylene with head-to-tail regiochemistry can in principle produce four isomeric polyenes, depending on the configuration of the C=C bond as well as on the conformation (cisoidal or transoidal) of the single carbon-

carbon bond of the main chain. For example the polymerization of phenylacetylene produces four stereochemical forms of poly(phenylacetylene) (Fig. 1.4).

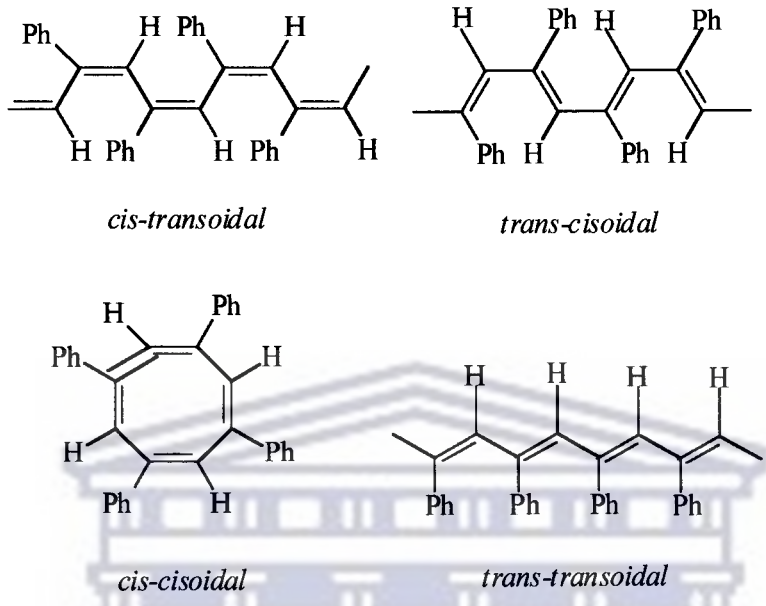
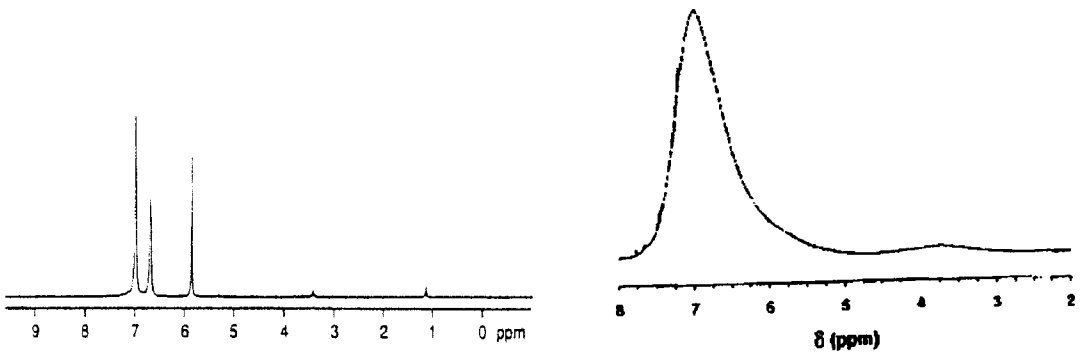


Figure 1.4: Stereochemical forms of poly(phenylacetylene)

^{1}H NMR spectroscopy is a simple analytical technique that is used to assign stereochemistry of poly(phenylacetylene). Figure 1.5 depicts the ^{1}H NMR spectra of *cis-transoidal* (Fig. 1.5a) and *trans-cisoidal* (Fig. 1.5b) polyacetylene. However, most poly(phenylacetylene)s are isolated as mixtures of two more stereoisomers. It has recently been established that solutions of poly(phenylacetylene) results in polymer rearrangement or polymer degradation.[52] Solubility of poly(phenylacetylene) is also depended upon the polymer conformation and molecular weight, e.g *cis-cisoidal* poly(phenylacetylene) exhibits low solubility compared to the other conformations.[53] Assigment of stereoregularity is therefore important in the study of poly(phenylacetylene).



a b

Figure 1.5: (a) ^{1}H NMR spectra of *cis-transoidal* and (b) *trans-cisoidal* PPA

Several methods have been used to determine the stereoregularity in poly(phenylacetylene). One of the most widely used methods was developed in the late 1970s by Percec and co-workers.[53] This method determines the *cis* content of poly(phenylacetylene) on the basis of ^{1}H NMR spectra. The *cis* content is determined from the equation:

$$cis\ \% = [A_{5.82}/(A_{total}/6)] \times 100\% \quad \textbf{OR} \quad \%\ cis\ = A_{5.82}.10^{4} / A_{total} \cdot 16.66$$

where $A_{5.82}$ is the integrated peak area of the vinyl proton in the *cis* isomer and A_{total} is the total integrated peak area of the polymer spectrum. It should be noted that use of NMR spectroscopy to determine the *cis* content of poly(phenylacetylene) could lead to a somewhat distorted estimate. This was clearly demonstrated in the experiments carried out by Mastrorilli *et al.*[54] in which they showed a polymer in solution could degrade from a pure *cis-transoidal* isomer to a nearly 50:50 mixture of *cis-transoidal* and *trans-cisoidal* over time (Fig. 1.6).

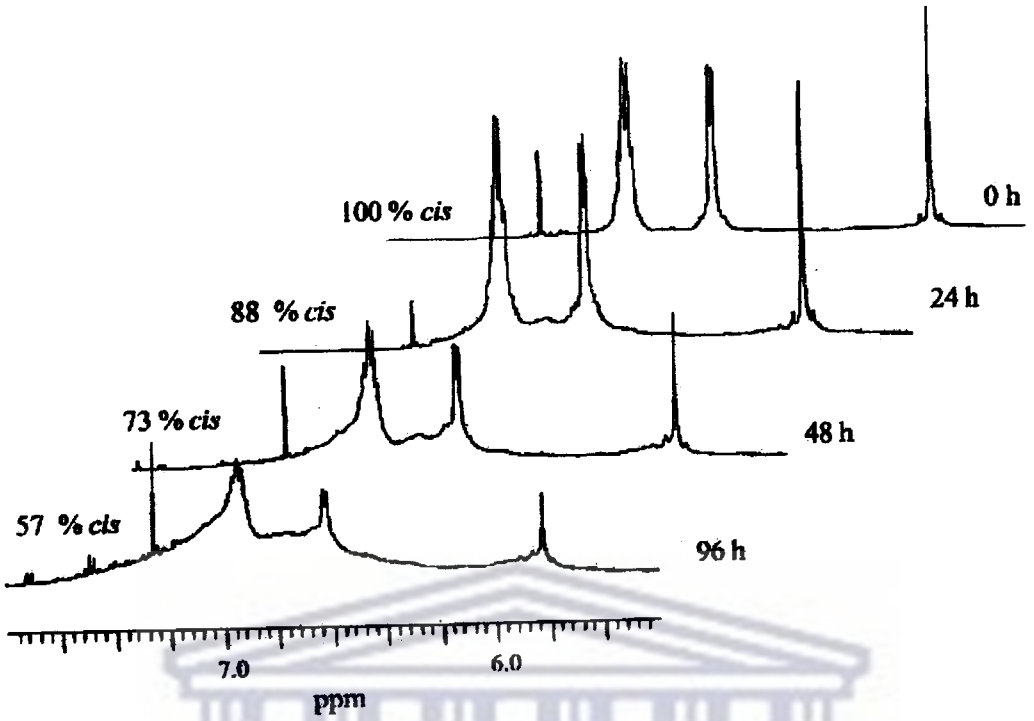


Figure 1.6: ^{1}H NMR spectra showing poly(phenylacetylene) degradation in $CDCl_3$.

An alternate method is Infrared spectroscopy. The intensity ratios of the peaks at 760 and 740 cm^{-1} (I_{760}/I_{740}) or the bands at 910 and 870 cm^{-1} (I_{870}/I_{910}) are used to determine what proportion of *cis-transoidal* and *trans-cisoidal* is in a sample of poly(phenylacetylene) (Fig 1.7 and 1.8). Other useful bands in determining the presence of *trans-cisoidal* poly(phenylacetylene) appear at 912, 970 and 1265 cm^{-1}; while peaks at 740 , 885 and 1380 cm^{-1} are specific to *cis-transiodal* poly(phenylacetylene).[55] According to Kern, models of the planar *cis-transoidal* chain of PPA reveal a strong interaction between the hydrogen atoms of a monomeric unit and phenyl protons two monomeric units away. This interaction is responsible for the infrared band at 740 cm^{-1} that disappears when the interaction is reduced by rotation of the monomeric unit around the single bonds and by the formation of *cis-cisoidal*

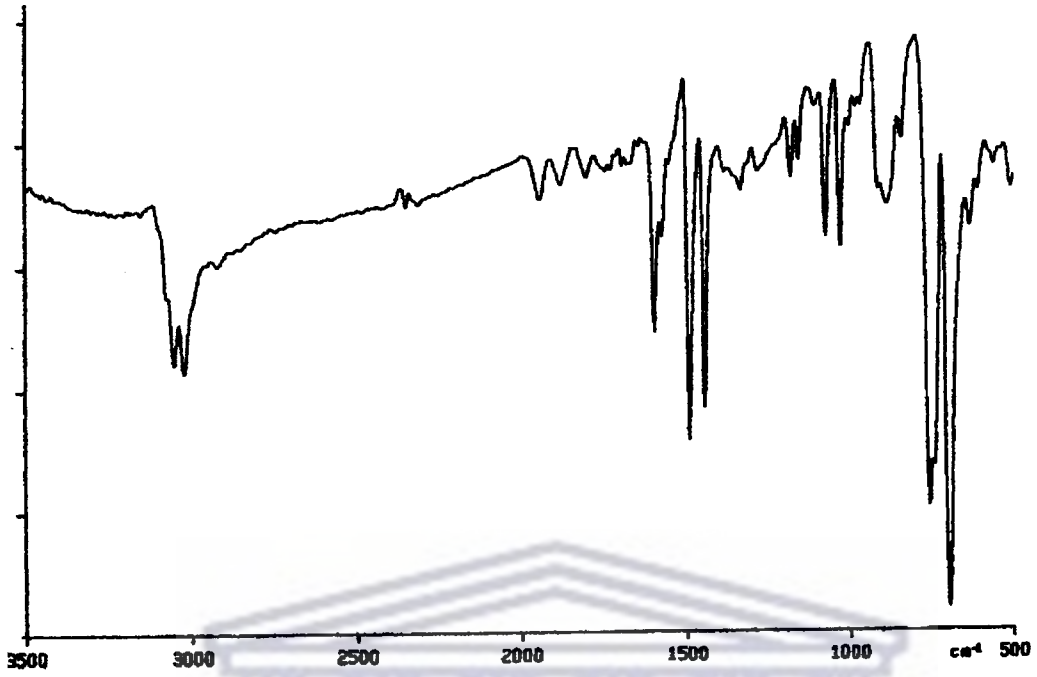


Figure1.7: IR spectrum of a polyphenylacetylene sample.

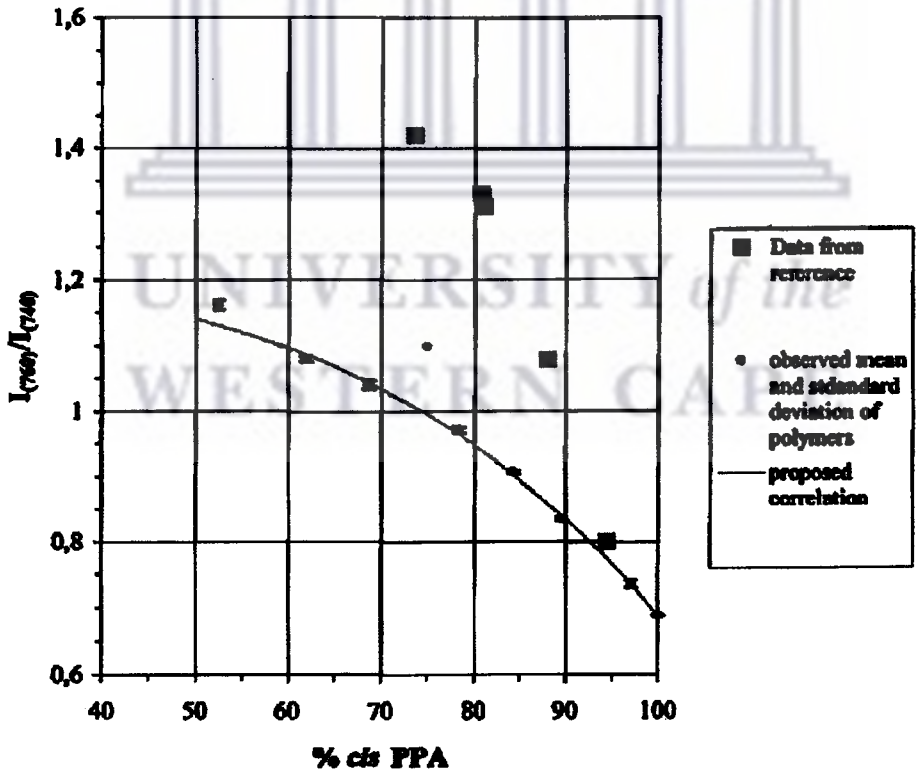


Figure 1.8: Correlation between cis percentage and I_{760}/I_{740} ratio.

helicoidal chain. However, it has been reported by Simineoscu and co-workers that the doublet at 740 cm^{-1} is present in IR spectra of both the *cis-transoidal* and *trans-cisoidal* polymers.[53] Furthermore their theoretical calculations based on ^1H NMR spectrum revealed that the *cis-transoidal* polymers is different from *cis-cisoidal* polymer. Despite their claims, these authors did not report supporting experimental evidence for the ^1H NMR spectrum of *cis-cisoidal* poly(phenylacetylene).

It was noted that heating of the polyphenylacetylene sample was found to decrease the band at 740 cm^{-1}. In addition, Kern also observed the disappearance of the band at 740 cm^{-1} and an increase in crystallinity when the *cis-transoidal* polymers were treated with toluene. This renders the IR spectroscopic approach to stereoregular determination less exact compared to the ^1H NMR spectroscopic route.

1.4 Isomerization of poly(phenylacetylene)

Thermal isomerization from *cis* to *trans* form in polymer chains of poly(phenylacetylenes) is a common phenomenon and has been well-studied.[56,57] Pressure-induced *cis* to *trans* isomerization of poly(phenylacetylene) derivatives has also been reported.[58] Recently isomerization behaviour of poly(phenylacetylene) thin solid films under an electric field have been studied. This recent study has been of great interest considering the fact that poly(phenylacetylene) are usually used in solid state as sandwiched devices working under applied electric field.[59]

According to Simineoscu, *cis-transoidal* poly(phenylacetylene) is converted by thermal treatment in solution or in solid state during or after polymerization into a *trans-cisoidal* structure.[60] On heating a poly(phenylacetylene) sample, the sample

starts isomerizing at temperatures above 100 °C. This isomerization process can be followed by techniques such as ^{1}H NMR and UV-visible spectroscopy. The UV-visible spectra below show the thermal isomerization process when a poly(phenylacetylene) sample of 96.8% *cis*-concentration was heated at 130°C.

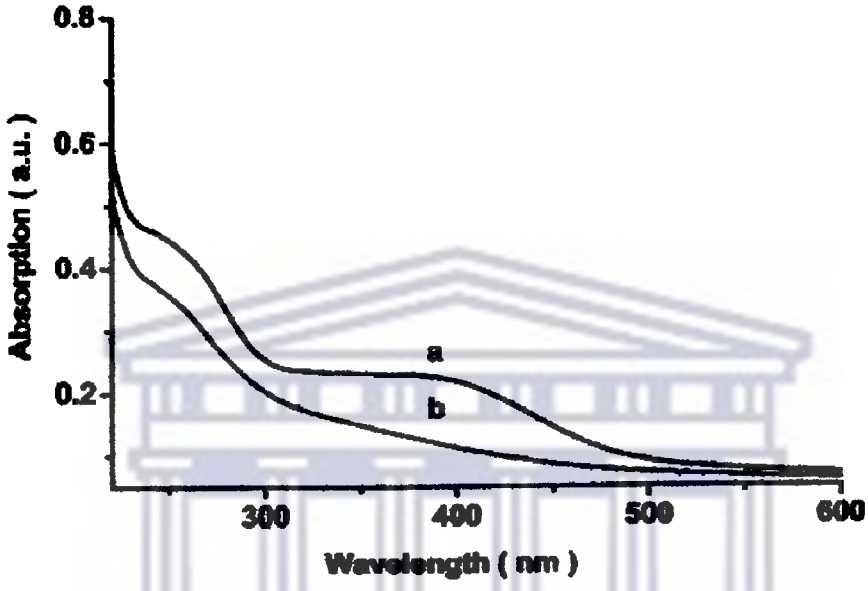


Figure 1.9: UV-visible absorption spectra of PPA with (a) *cis*, (b) *trans* content.

Ishii *et al.*[61] reported that the absorption spectrum of *cis*-transoidal (*cis*) segments in poly(phenylacetylene) polymer chains are found to show the feature of a plateau peak with a shoulder at around 390 nm, which is attributed to the π-π* transition of the main chain, and a peak at about 260 nm, which is a π-π* transition due to the side chain. The absorption bands of the main chain and side chain for *trans-transoidal* (*trans*) segments shift to about 250 and 220 nm respectively. This was clearly illustrated in the experiments conducted by Tang *et al.*[59] when they exposed polyphenylacetylene film samples an the electric field. Absorption spectra of the thin film of 96.8% *cis*-concentration before and after corona charging for 30 s are shown in Fig. 1.10, together with ^{1}H NMR spectra (Fig 1.11). The change in the spectral feature (Fig. 10) is almost identical to that in Fig. 1.9 and strongly confirms that there

is an electric field induced isomerization. The absorption plateau peak at around 390 nm becomes increasingly weak. This indicates the decrease of the concentration of *cis*-segments on poly(phenylacetylene) molecular chains.

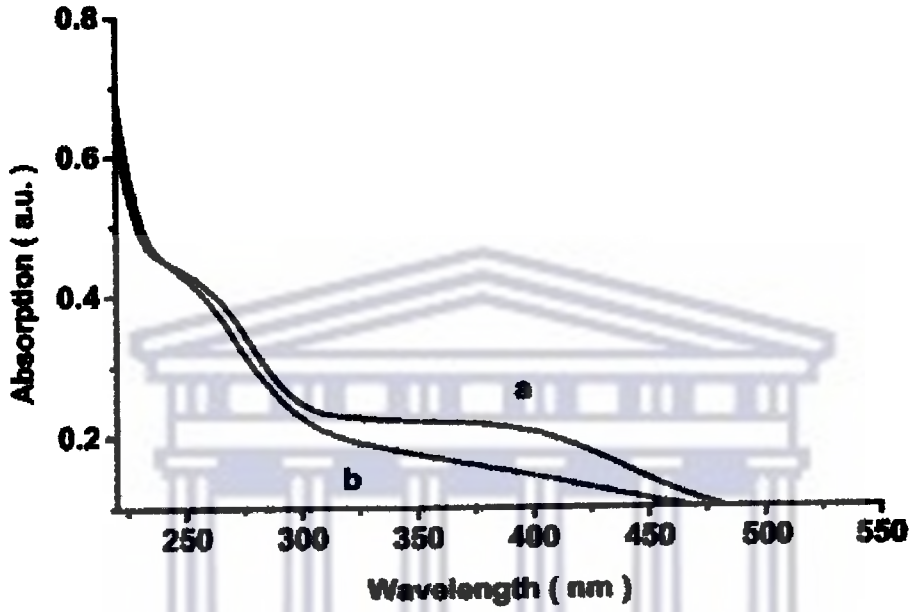


Figure 1.10: UV-visible absorption spectra of cis PPA (a) before and (b) after isomerization.

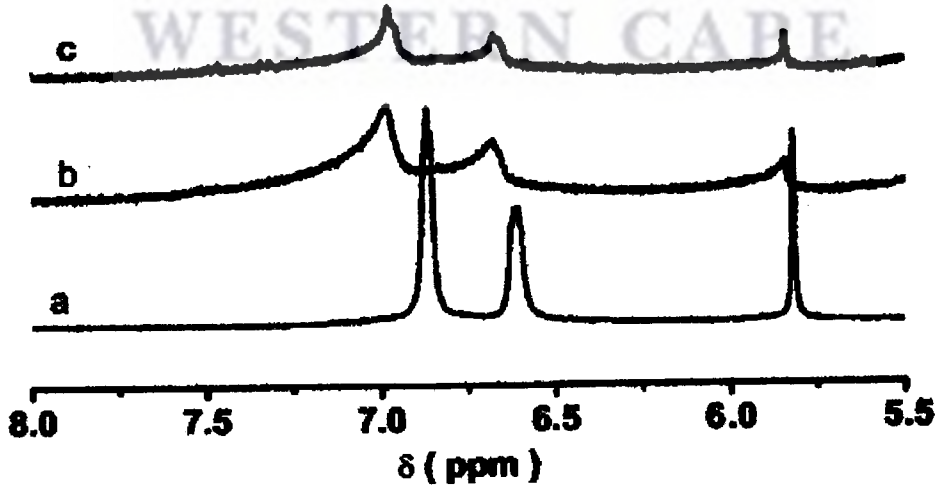
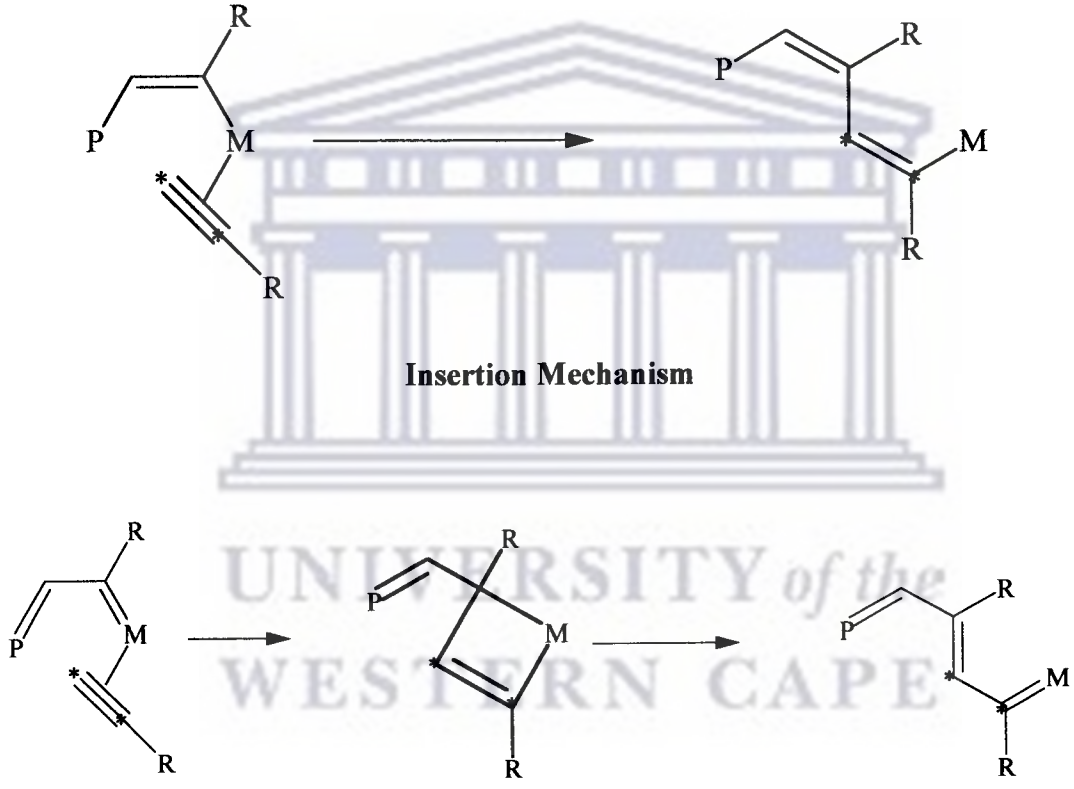


Figure 1.11: ^{1}H NMR spectra of *cis* PPA solution after charging for (a) 0s, (b) 5s and (c) 10s.

1.5 Mechanisms for acetylene polymerization

There are three main steps in the polymerization of any substrate. These are initiation, propagation and termination; but it is the propagation step that determines the microstructures of polymers. For phenylacetylene polymerization, two possible propagation mechanisms have been proposed: a metathesis mechanism via a metal-carbene intermediate and an insertion mechanism via a metal-vinyl complex. Scheme 3 depicts the important sequences in the propagation steps in these two mechanisms.



P = growing polymer chain

Metathesis mechanism

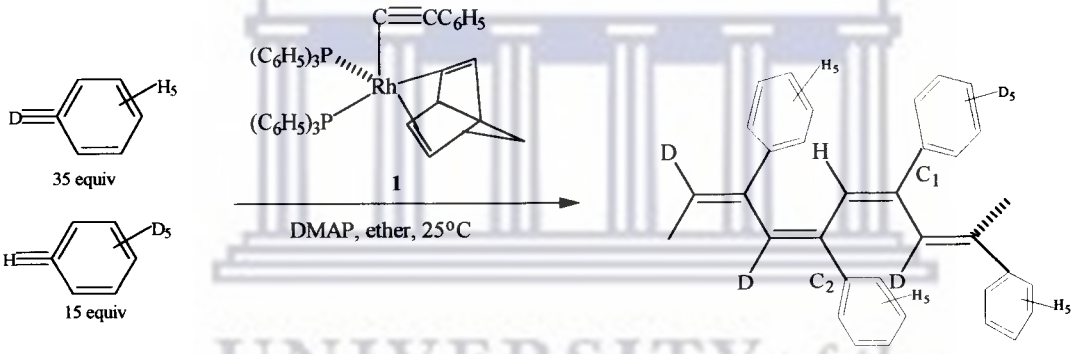
Scheme 3: Two possible propagation mechanisms for the transition metal mediated polymerization of acetylenes.

^{13}C labelling can be used to distinguish between the two mechanisms, in which the triple bond of the monomer changes to a single bond in the metathesis mechanism,

while it becomes a double bond in the insertion mechanism. The insertion route leads to the formation of the polymers containing a mixture of *cis* and *trans* configurated double bonds, while the metathesis mechanism provides only *cis* polymers.

1.5.1 Insertion mechanism

Isotope labelling experiments provided more information concerning the details of the structure (Scheme 4). The results obtained are consistent with the C1 carbon being *cis* to the vinyl proton and the C2 carbon occupying a transoidal position, as would be expected of the insertion mechanism.



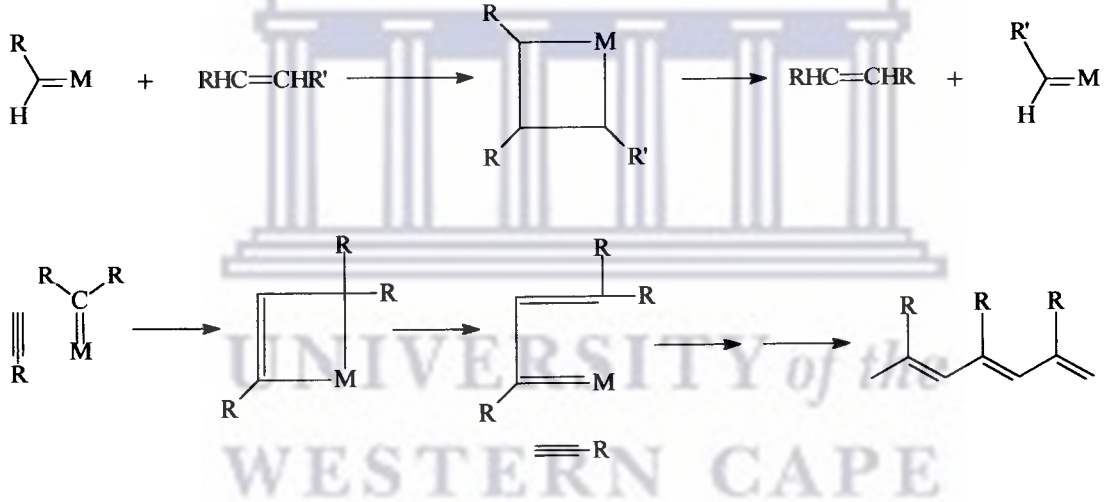
Scheme 4

When an isotope labelled complex, Rh(^{13}C≡C^{13}CC$_6$H$_5$)(nbd)[P(C$_6$H$_5$)$_3$]$_2$ (Scheme 4), was used as an initiator, no ^{13}C-enriched polymeric products were isolated.[49] This implies that polymerization does not start via a direct insertion of phenylacetylene into the rhodium–carbon bond. Valuable information for the initiation step was provided by detection of 1,4-dipenyl-1,3–butadiyne. The formation of C$_6$H$_5$C≡CC^{13}C≡^{13}CC$_6$H$_5$ by reaction of **1** and **PA** was explained by oxidative addition of **PA** to the tetracoordinate alkynyl complex and subsequent reductive coupling of two alkynyl units. The reaction would in turn probably generate a rhodium hydride

species, which would act as an initiator for the polymerization and subsequent insertion of monomer.

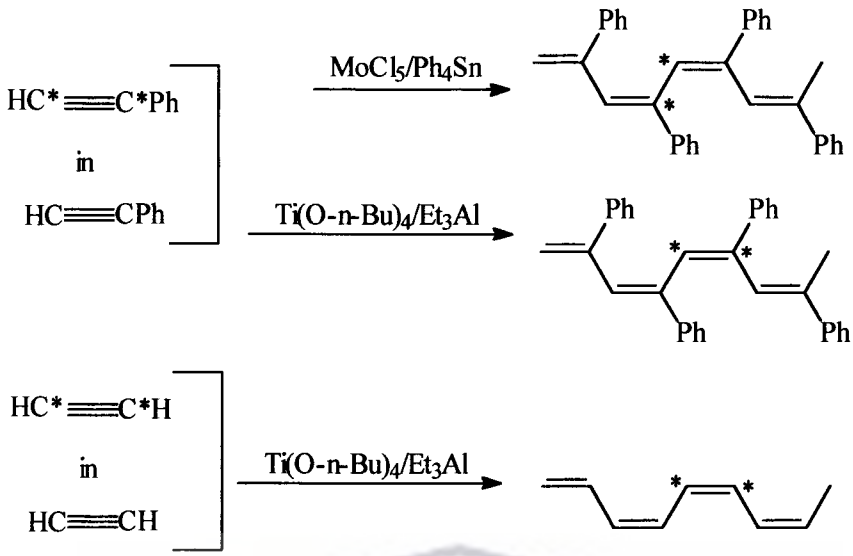
1.5.2 Metathesis mechanism

In 1975, Masuda *et al.* proposed a metal-carbene mechanism for the polymerization of substituted acetylenes.[62] The propagation stage is depicted by Scheme 5. In this polymerization mechanism a 2+2 cycloaddition occurs, as with olefins, forming a metallacyclobutene as an intermediate. When the metallacycle opens in a productive way it results in a growing polymer chain.



Scheme 5

Support for Masuda's proposed mechanism was provided by Katz in a series of experiments shown in Scheme 6.[63] When a mixture of ^{13}C-labeled and ^{13}C-unlabeled phenylacetylenes is polymerized by $MoCl_5$-Ph_4Sn, the labeled carbons in the polymer are separated by single bonds according to ^{13}C-nutation NMR (Scheme 6).



Scheme 6

This observation means that there is cleavage of the two π-bonds in the acetylene monomer during polymerization. In contrast, only one bond of phenylacetylene or acetylene cleaves in the case of polymerization by $Ti(OBu)_4/EtAl_3$.[63,64] These findings clearly show that polymerization of acetylenes by the Mo catalyst proceeds *via* the metal-carbene mechanism, whereas that by the Ziegler catalyst occurs via the metal alkyl (insertion) mechanism.[65]

It is now generally accepted that groups 5 and 6 metals catalyze acetylenes *via* a metathesis mechanism, whilst late transition metal catalysts promote polymerization by an insertion route.

1.6 Nitrogen donor ligands

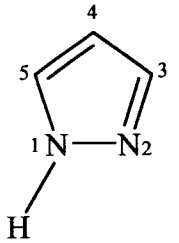
Bidentate and tridentate nitrogen heterocyclic compounds containing 6-membered rings such as 2,2'-bipyridine, 1,10-phenanthroline, and terpyridine have dominated transition metal chemistry for many decades.[66-68] The main feature of these heterocycles is their π-electron deficiency. They behave as excellent π-acceptors and provide soft sites for metal coordination. On the other hand, the π-excessive 5-

membered nitrogen heterocycles such as pyrazole are poor π-acceptors. In fact, they are better π-donors and hence act as hard donor sites.

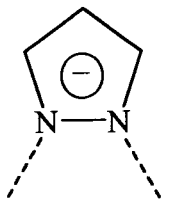
Pyrazole-based chelating ligands form a variety of coordination complexes with a number of metal ions, providing varying coordination geometry and nuclearity. Recent years have seen considerable interest in the designing of various pyrazole-based ligands and to study their structural properties. The ease of synthesis of various substituted pyrazoles has lead to the utilization of pyrazole moieties in the design of new ligands and offers the opportunity of both electronic and steric control of the properties of the metal complexes. The properties of coordination compounds, whether in classical inorganic coordination complexes or in organometallic compounds or in bioinorganic model compounds, are known to be determined to a large extent by the nature of ligands bound to the metal ion.[69,70]

1.6.1 Pyrazole as ligand

As a ligand, the thermally and hydrolytically stable pyrazole, binds to metals and metalloids through the N atom in position 2. When deprotonated pyrazole becomes the pyrazolide ion **2**, which can coordinate through both nitrogen atoms as an exobidentate ligand.



1

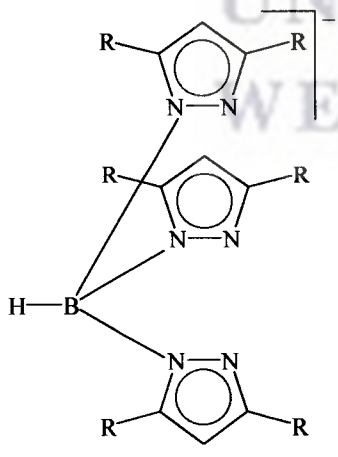


2

The nucleophilicity of the nitrogen atoms in pyrazole and their accessibility to bind are usually varied through an appropriate choice of substituents on the ring, normally at 3-C and 5-C positions of the ring. A substituent in position 3 introduces steric hindrance and limits the number of pyrazole ligands that can be coordinated via the 2-N to the metal. To circumvent steric hindrance 3-methylpyrazole tautomerises to 5-methylpyrazole before coordination. However, when pyrazole has substituents on 1-N the steric effect produced could lead to different mode of coordination and a modification of electronic properties of metal complexes formed. This class of ligands is referred to as pyrazolyl ligands. Thus pyrazolyl metal complexes offer opportunities to prepare new compounds that could be tuned for specific uses, such as catalysts.

1.6.2 Pyrazolyl compounds as ligands

Tris(pyrazolyl)hydroborates, $[HB(3,5\text{-}RR'pz)_3]^-$ (**3**), are among the most popular ligands in coordination chemistry since their introduction almost 40 years ago.[71-73]



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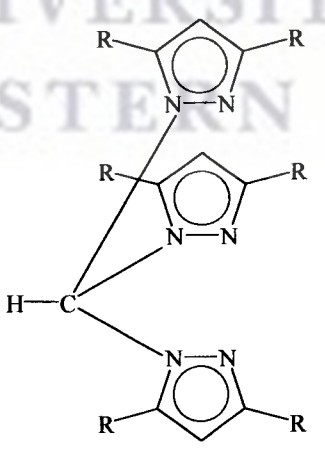

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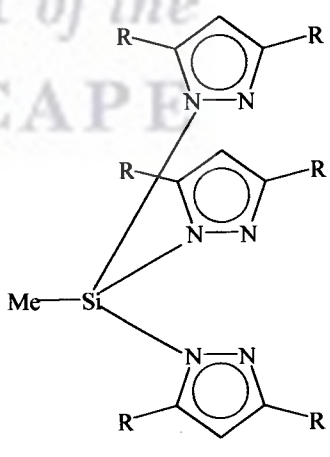


5

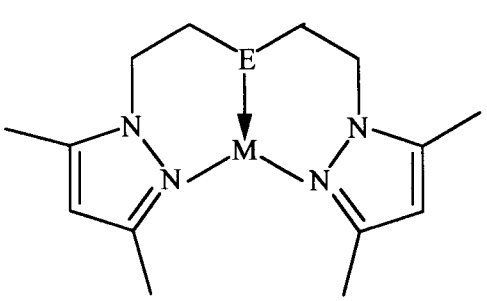
Their popularity stems from the distinctive steric and electronic effects that can be attained by changing the nature, number, and position of the substituents on the

pyrazole rings, thus allowing the reactivity at the metal centers they support to be fine-tuned. Not surprisingly, these ligands have been used to prepare complexes with metals all across the periodic table, some of which have found interesting applications in catalysis and bioinorganic chemistry.[74]

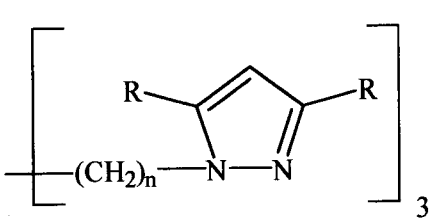
The chemistry of their neutral, carbon centered analogs, the tris(pyrazolyl)methanes (**4**), is considerably less developed, and deals mainly with the $HC(pz)_3$ and $HC(3,5Me_2pz)_3$ ligands.[75] Only recently have bulkier tris(pyrazolyl)methanes ligands bearing alkyl (^{i}Pr, ^{t}Bu) or aryl (Ph) substituents in the 3-position been developed.[76,77] These sterically demanding ligands are attractive in view of the success of the corresponding tris(pyrazolyl)hydroborates as tetrahedral enforcers.[78,79]

1.6.3 Nongeminal polypyrazolyl ligands

Pyrazoles can bear donating groups attached to any position of the aromatic ring, thus affording a large family of polydentate ligands referred to as nongeminal. Studies of the coordination chemistry of these ligands include modeling of metalloenzymes and organometallic chemistry of polypyrazolylborate ligands.[80,81] Ligands in this category contain two or more pyrazolyl groups at the end of a flexible chain, which occasionally contain other coordinating heteroatoms as exemplified by structures **6** and **7**.



6

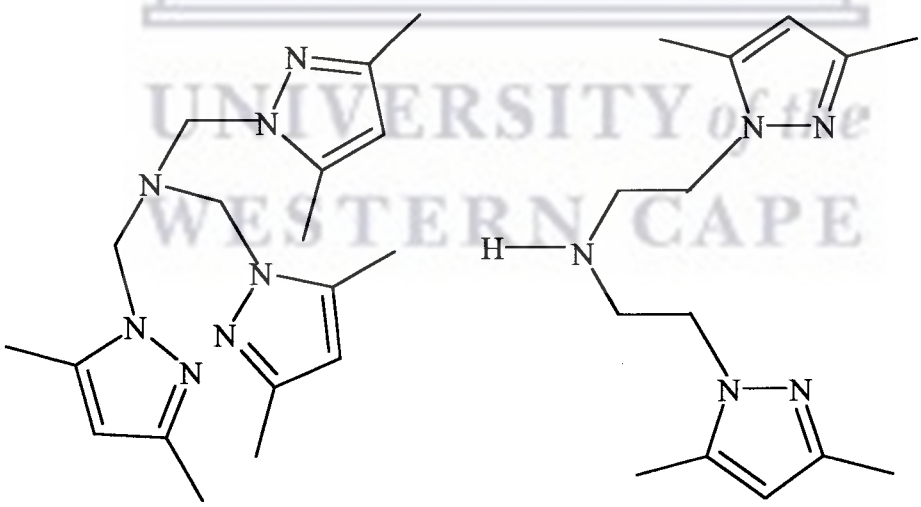


7

A number of reports on other pyrazole-based chelating ligands have appeared in the literature.[82] The ligands consist of pyrazole heterocycles linked by NR (R=H or alkyl or benzyl), O or S group(s), with incorporation of 'insulating spacer(s)' between the coordinating sites. A review of the chemistry of some of these ligands is given below.

1.6.4. 1. 1-Alkylaminopyrazolyl ligands

Ligand **9** forms two different types of compounds, $M^{II}(\mathbf{8})X_2(H_2O)n$ and $M^{II}_3(\mathbf{8})_2X_6$, with Co, Ni, and Cu.[83] In the compounds $M^{II}(\mathbf{8})X_2(H_2O)n$, with X = Cl^-, NCS^- and/or NO_3^- and n = 0 or 1, the anions take part in the coordination of the metal ion resulting in penta- or hexa coordination. In the compounds $M^{II}_3(\mathbf{8})_2X_6$, where M = Co, Cu, Zn and X = Cl^- and NCS^-, autoanion formation occurs, resulting in $[M(\mathbf{8})X]_2[MX_4]$ with both four-coordinate and five-coordinate metal ions.



R = H **8**

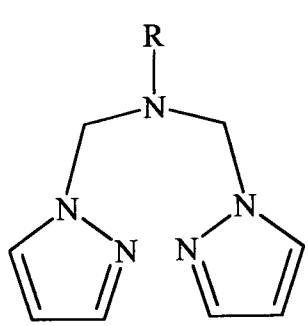
R = Me **9**

R= H **10**

The crystal structures of three compounds of composition $M^{II}(\mathbf{9})(NO_3)_2$ (M = Cu, Ni or Cd) were reported by Reedijk and co-workers.[84] In each compound the ligand utilizes each of its four potential donor sites. The structures of Cu and Ni compounds comprise of $[M(\mathbf{9})(NO_3)]^+$ cationic species, and NO_3^- anions.

Complexes having **9** as the ligand, with general formula $[M(\mathbf{9})(H_2O)(OAc)][ClO_4]$ (M = Co(II) or Ni(II); octahedral) and $[M(\mathbf{9})(OAc)][ClO_4]$ [M=Co(II) or Cu(II)] are known.[85] The X-ray structure of $[Co(\mathbf{9})(H_2O)(OAc)][ClO_4]$ reveals that the cobalt ion is approximately octahedral; with one O atom of the acetate ion, the O atom of the water molecule, the amine N atom of the amine in the axial positions. The coordinated acetate anion is both intra- and inter-molecular hydrogen bonded to the hydrogen atom of the coordinated water molecule, thus forming infinite chains of cation. When ligand **9** in $[M(\mathbf{9})(OAc)][ClO_4]$ undergoes partial hydrolysis it forms $[Cu(\mathbf{10})dmpz)(OAc)(H_2O)][ClO_4]$.

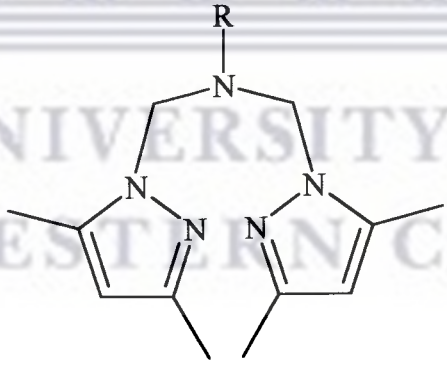
Partial hydrolysis of the ligand tris(1-pyrazolylmethyl)amine[83,86] in solution with some of the metal salts results in the formation of bis(1-pyrazolylmethyl)amine (**11**).



R = H **11**

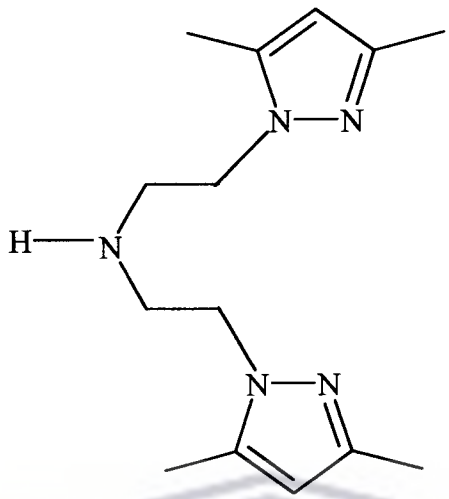
R= $-CH_2Ph$ **12**

Using **11**, with M = Co^{2+} and Ni^{2+}, and X = Cl^- and NO_3^- octahedral complexes of formulation $M(\mathbf{11})_2(X)_2$ have been prepared. In addition copper(II) compounds of formulation $Cu(\mathbf{11})(X)_2(H_2O)_n$ with X = Cl^- (n =1) and NO_3^- (n = 0) and $Cu(\mathbf{11})(pz)X_2(H_2O)$ with X = Cl^-, NCS^- and NO_3^- and pz = pyrazole have also been prepared.[86] The compound $[Co(\mathbf{11})_2][NO_3]_2$ was structurally characterized[86] to reveal that the cobalt(II) ion is coordinated in a slightly distorted octahedral array. The ligand chelates in the vicinal mode to the cobalt(II) ion and the coordination angles spanned by the pyrazole N to amine N bites of the ligands range from ~ 78.3 to 78.8°. The copper(I) ion in $[(Cu(\mathbf{12})I)_2]$ has two pyrazole nitrogen atoms and two bridging iodide ions. Two copper(I) ions and the two bridging iodide ions form a planar Cu_2I_2 four-membered ring. Interestingly, a Cu_2I_2 bridge was observed here because there is no ligand steric hindrance in contrast to the mononuclear complex [Cu(**13**)I] (see below) where methyl groups prevent association of the [Cu(**13**)I] moieties.



R = CH_2CH_3 **13**

Cobalt(II), copper(II) and zinc(II) complexes with the ligand **14** and chloride and/or tetrafluoroborate as the anion have been isolated and characterized by spectroscopic techniques. Some of the complexes were structurally characterized.[87]



R = H **14**

R = -CH_2CH_3 **15**

The coordination sphere of the metal(II) atom in [M(**14**)Cl][BF_4] (M = Co, Cu) is satisfied by two pyrazole nitrogens and one amine nitrogen. The coordination geometry around the cobalt(II) atom can be described as a distorted tetrahedral; while that around the copper(II) atom can be described as square planar distorted towards tetrahedral, with the largest angle N(pyrazole)–Cu N(pyrazole) now being 155°. The metal(II) atom in the [M(**14**)Cl]$^+$ cation of [M(**14**)Cl]$_2$[MCl_4] (M = Co, Cu) is surrounded by three nitrogens from the ligand and one chloride anion. The coordination geometry around the copper(II) atom can be described as distorted tetrahedral, where the distortion is towards square planar although the largest angle of 141° is still far from the 180° for a square. Interestingly, experiments designed to obtain M:L = 1:2 compounds using excess of ligand resulted solely in the formation of 1:1 compounds.

The nickel compound $[Ni(\mathbf{15})(NO_3)_2]$ is isomorphous with the cobalt nitrate compound, as shown by X-ray powder diffraction. Interestingly, attempts to synthesize coordination compounds with a metal to ligand ratio of 1:2 were not successful. Model studies on octahedral $[M(\mathbf{15})_2]^{2+}$ indicated that methyl substituents on the 3- and 5-positions of pyrazole rings of a facially or of a meridionally coordinated **15** ligand protrude to such an extent that a second ligand cannot approach the M^{2+} ion. This steric hindrance is due to the four-bond chelate bites of **15**, which cause the N–M–N coordination angles to be somewhat larger than 90°, thereby pushing the methyl substituents inward. Similar ligands with unsubstituted pyrazole groups are able to form M:L = 1:2 compounds, as for example, $[Ni(\mathbf{13})(NO_3)_2]$.[88]

In spite of the potential of the amino nitrogen in these ligands, the above review illustrates the inability of the alkylpyrazolyl compounds with amino linkers to act as tridentate ligands.

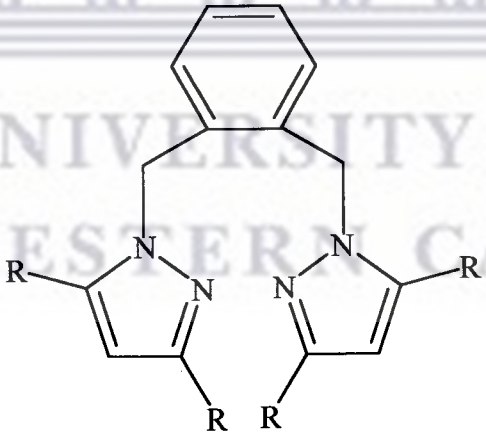
1.6.4.2 Poly(pyrazol-1-ylmethyl)benezene ligands

When a six-membered heterocycle such as pyridine and a five-membered heterocycle such as pyrazole are directly linked in a single ligand system, complexes formed give rise to significantly different electronic properties. A study of these classes of compounds was done in 1989 by Constable and Steel,[89] and recently by Darkwa *et al.*[90] An even more interesting situation arises when the electronic communication between these two heterocycles is either induced or prevented. Communication can be prevented by incorporation of an 'insulating spacer' such as a methylene group between the rings, while communication can be induced by the introduction of an electron withdrawing spacer such as a carbonyl group between the rings.

The poly(pyrazol-1-ylmethyl)benzene will be discussed in this section. These ligands are expected to exhibit a variety of modes of coordination, including participation by the benzene ring as a donor group. A sizeable number of *m*-xylyl-based pyrazolyl ligands and their coordination compounds, have been pepared as models of dinuclear copper proteins, hemocyanin and tyrosinase .[91-93]

1.6.4.2.1 o-xylyl-based ligands

The ligand 1,2-bis(pyrazol-1-ylmethyl)benzene (**16**), with two pyrazolyl coordinating sites separated by a *o*-xylyl spacer, has been prepared[94,95] and its coordination chemistry investigated.[96] It reacts with copper(II) chloride affording two types of complexes, the green monomer $[Cu(\mathbf{16})Cl_2]\cdot 0.5CH_3OH$ and the yellow–green dimer $[Cu_2(\mathbf{16})_2Cl_4]$, which have been structurally characterized.

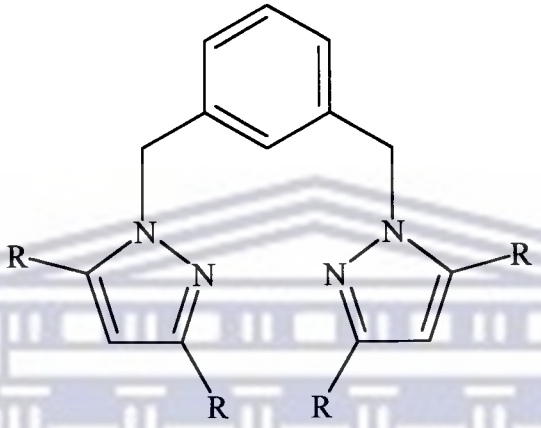


16

In the monomeric complex the copper(II) ion is coordinated by two pyrazole nitrogen atoms and two chloride ions, and the copper ion in this complex has a distorted tetrahedral geometry. In the dimeric complex the two copper(II) ions and two bridging chloride ions form a centrosymmetric planar 4-membered ring. In this case

each copper(II) ion is coordinated by five donors: two pyrazolyl nitrogen atoms, two bridging chloride ions and a non-bridging chloride ion that occupies the fifth (axial) coordination site. The copper(II) ion is 0.403 Å, above the basal plane. Thus here the geometry at each copper(II) centre is distorted square pyramidal.

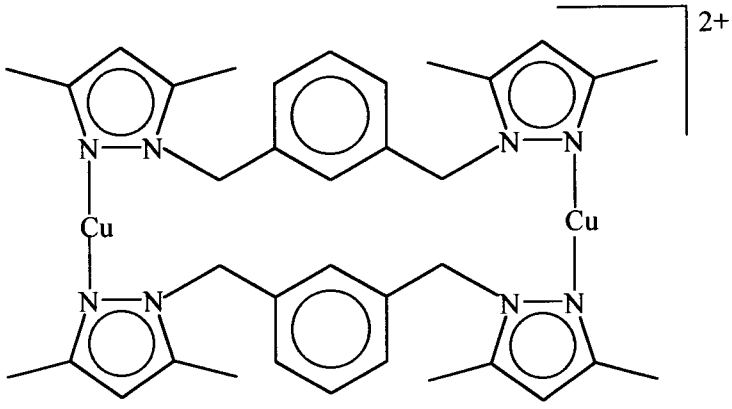
1.6.4.2.2 m-xylyl-based ligands



R = H **17**

R = Me **18**

Although the synthesis of the ligand **17** has been reported in the literature,[95] its coordination chemistry has not been explored. However, The dinuclear cation **19** was produced from m-xylenebis(3,5-Me2pzH) **18** and $[Cu(CH_3CN)_4][BF_4]$ yielding $[Cu_2(\mathbf{18})_2][BF_4]_2$.[97]

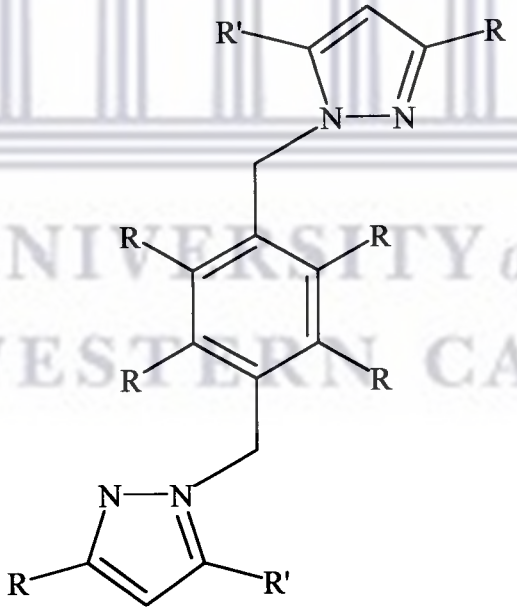


19

The X-ray structure of **19** shows extremely short Cu–N(pyrazole) distances, resulting from the low coordination number, although back-donation into the π^* orbital of the aromatic pyrazole ring cannot be ruled out. The N(pyrazole)–Cu– N(pyrazole) angle of 160° is smaller than the expected linear arrangement of donors in two-coordinate Cu(I). The Cu···Cu distance [6.350(3) Å] is large enough to presume that each copper atom acts as it would in a monomeric complex.

1.6.4.2.3 p-xylyl-based ligands

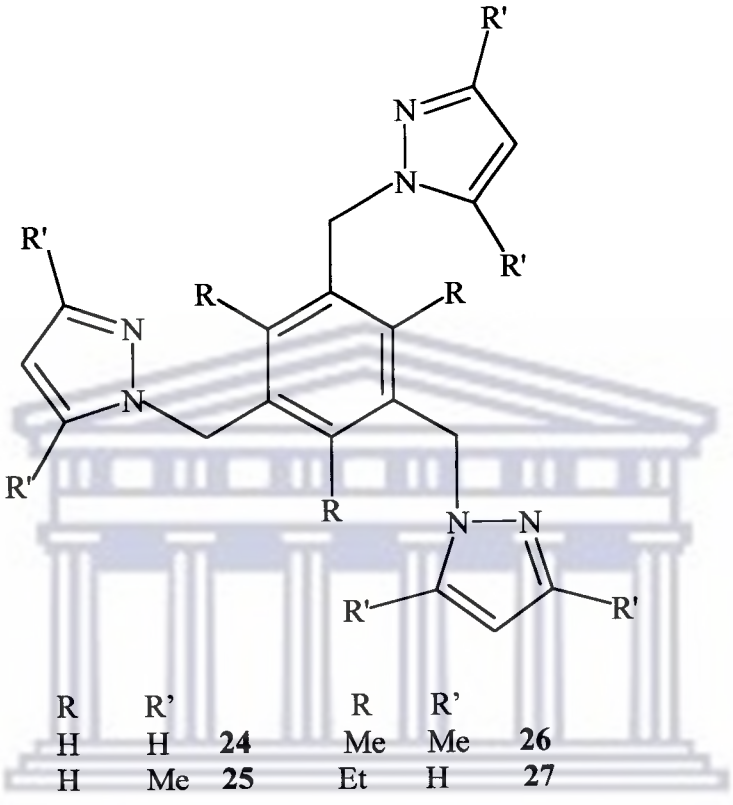
Ligands **20-23** were synthesized[94] and reaction of a methanol solution of **23** with $PdCl_2$ in 2M HCl resulted in the isolation of a deprotonated ligand coordinated to a $PdCl_4^{2+}$ unit. The X-ray structure reveals that the ligand di-cation is hydrogen bonded to the $PdCl_4^{2-}$ anion.



R	R'		R	R'	
H	H	**20**	Me	H	**22**
H	Me	**21**	Me	Me	**23**

1.6.4.2.4. Mesityl-based ligands

New trifunctional pyrazolyl ligand, 1,3,5-tris(pyrazol-1-ylmethyl)benzene ligand (**24**) and its substituted derivatives **25–27** have also been synthesized.[94,96,98]



R	R'		R	R'	
H	H	**24**	Me	Me	**26**
H	Me	**25**	Et	H	**27**

Copper(II) and cobalt(II) complexes of **24** have been reported.[96] X-ray analysis reveals that the complex $[Cu(\mathbf{24})_2(ClO_4)(H_2O)_2][ClO_4]$ is a mononuclear copper(II) compound. The copper atom is coordinated by two pyrazolyl nitrogen atoms from two ligands, two water molecules in the square plane and an oxygen atom of a perchlorate ion at the apical position. This gives rise to a distorted square pyramidal coordination sphere of copper(II). Thus each ligand has two dangling pyrazole arms.

Reaction of **25** with $[Ru_2(DMSO)_4Cl_2]$ affords a complex in which a coordinated metal is simultaneously involved in η^6-bonding to the benzene ring [average Ru–C bond:2.129(9) Å] and tripodal pyrazole coordination to suitably placed ligand [average Ru–N: 2.097(8) Å].[99] The coordination about the ruthenium atom is a

distorted octahedral. The distance of the ruthenium atom from the centroid of the benzene ring is 1.579 Å. This indicates a stronger metal–arene interaction in this compound, given the corresponding distances (1.67–1.70 Å) in the previously reported structures.[100] The benzene ring is measurably distorted towards a chair conformation.

Ligand **27** was designed to reorganize the three pyrazole rings on the same side of the benzene ring. In fact, reaction of **27** with $PdCl_2$ results in the self-assembly of a three-dimensional cage.[97] X-ray structure of this compound $(PdCl_2)_6(\mathbf{27})_{4\cdot 8}(CH_3)_2SO\cdot_8H_2O$ reveals that it consists of a ten-component, three-dimensional metallosupra-molecular adamantanoid cage compound of six *trans*-dichloro palladium units bridged by four molecules of **27**. The six palladium atoms are arranged in a pseudo-octahedral array, while the four molecules of **27** form a tetrahedrally disposed internal core of benzene rings of approximately 4.7 Å, internal radius. Within this core resides a single (disordered) $(CH_3)_2SO$ molecule (used in the recrystallization step). One of the ligands has all three terminal methyl groups directed towards the internal core, while the other three ligands have one methyl group directed outside the core. The diagonally opposite palladium atoms have separations ranging from 13.26 to 15.54 Å.

1.7 Objectives of this project

The review in this chapter covers two aspects of this project. Firstly, a review of different catalysts shows that very few late transition metal complexes catalyses the polymerization of phenylacetylene to form poly(phenylacetylene). Some of the best phenylacetylene polymerization catalysts are pyrazolyl ligands complexes that are electrophilic.[28b] We believe the key steps in late transition metal catalyzed acetylene polymerization reaction are coordination of the monomer and the subsequent insertion

processes. Our catalysts design takes cognisance of the ability of the active catalyst to coordinate the monomer. Secondly, the review of pyrazolyl late transition metal complexes provides insights into the formation of different metal complexes as substituents and linkers are varied. These suggest that a judicious choice of substituents and linker variation could provide late transition metal complexes that could be used as catalysts for phenylacetylene polymerization. The objectives of this project, therefore, were the following: (i) to prepare new pyrazolyl ligands with alkyl linkers and their palladium complexes. (ii) A second aspect of the ligand modification involves substituents on the pyrazole as well as the linkers. (iii) All new complexes that are fully characterized would be investigated as phenylacetylene polymerization catalysts. The rest of this thesis describes how we set out to realize these objectives.

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CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF PYRAZOLYL PALLADIUM COMPLEXES

2.1 Introduction

There is considerable interest in the development of new nitrogen donor ligands for late transition metal complexes. Motivations in this area of chemistry are diverse and include the preparation of new single site catalysts[1] for synthetic transformations such as olefin[2] and alkyne polymerization[3]. One of the new nitrogen donor ligands is the pyrazolato ligand. The relative ease of tuning the steric and electronic properties by the selection of substituents at the 3 and 5-position of the pyrazolyl rings makes pyrazolato compounds interesting ligands. Such ligand modifications could produce highly electrophilic metal centres necessary for active single site catalysts for transformations involving unsaturated substrates. Despite all the possibilities to fine-tune pyrazolato ligands and their complexes, studies related to their catalytic activity for organic transformation are still limited.

However, some metal pyrazolyl derived complexes have recently attracted considerable interest not only because of their extensive coordination chemistry, but also their catalytic and biological properties.[4] These complexes include the bidentate (NN') and tridentate (NN'N) alkylaminopyrazole ligands that were developed by Driessen *et al.*[5] So far their coordination chemistry has mainly focused on metalloenzyme mimics. Ros *et al.* have recently revived this class of compounds from the viewpoint of potential application in homogeneous catalysis.[6]

Darkwa *et al.* have also been interested in the unique properties of pyrazolato ligands, and examined the reactivity of coordinated transition metal complexes in catalytic

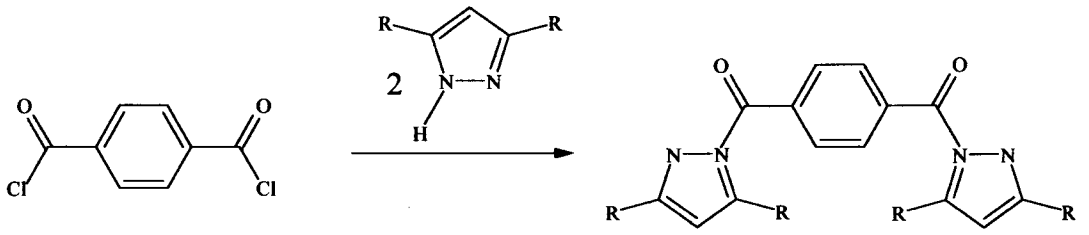
systems such as polymerization of ethylene.[7a,b] They have recently reported that pyrazolyl palladium complexes of 1,3-bis(3,5-alkylpyrazolyl-1-carbonyl)benzene are highly active catalysts for ethylene polymerization[7b] because of the highly electrophilic metal centre that is promoted by the presence of carbonyl functional groups in the pyrazolyl ligand. This facilitates coordination of the ethylene monomer and hence the high catalytic activity.

This chapter reports the synthesis of 1,4-bis(3,5-alkylpyrazolyl-1-carbonyl)benzene palladium complexes and new silicon containing alkylaminopyrazole ligands and their metal complexes as well as their characterization using various spectroscopic techniques. The intent for synthesizing these complexes is to use them as catalyst precursors for the polymerization of substituted acetylenes. The polymerization studies are reported in chapter 3 of this thesis.

2.2 Results and discussion

2.2.1 Synthesis of 1,4-benzenedicarbonylpyrazolyl ligands and complexes

Compounds **L1**- **L4** were synthesized according to Scheme 1 from the reaction of 1,4-benzenedicarbonyl dichloride (terephthaloyl chloride) and two equivalents of the appropriate pyrazole. Preparation of **L1-L4** proved to be tricky when compared to their 1,3- benzenedicarbonylpyrazolyl analogues. In the latter case, ligands were soluble in the solvent in which they were prepared, whereas in the former case the ligands precipitated out of solution. This heterogeneity of the procedure for **L1-L4** made the work-up easier than that of their 1,3-benzenedicarbonylpyrazolyl analogues.



R = ^{t}Bu **L1** R = H **L3**

R = Me **L2** R = Ph **L4**

Scheme 1

The ^{1}H NMR spectra of **L1** and **L2** reveal a clear separation of 0.237 and 0.41 ppm respectively for the non-equivalent substituents at position 3 and 5 of the pyrazole. This effect is due to the electron withdrawing effect of the carbonyl linker between the pyrazolyl units and the benzene rings. Typical ^{1}H NMR spectra are shown in Figure 2.1 and 2.2. In **L3** there seem to be some interaction between the protons on the 3 position of the pyrazole and those on the benzene ring. These protons on the pyrazole also appear more deshielded than other protons on the 4 and 5 position (Figure 2.1). The protons in positions 4 and 5 of the pyrazole are also more downfield than the protons of the benzene ring, which typically appear more downfield than protons of the pyrazole in **L1** and **L2**. When the more bulkier phenylpyrazole was used to prepare **L4** the phenyl protons on the 3 and 4 position appeared as two multiplets that are centred at 8.88 ppm and 7.50 ppm. However, the two peaks give an integration ratio of 1:4 contrary to what was expected.

Infrared spectroscopy was used to identify functional groups in both ligand and complexes. Due to the insoluble nature of complex **3**, infrared spectroscopy became one of the major analytical techniques in elucidating the structure of this compound. Hence the infrared spectra of the ligand **L3**, and its corresponding complex **3**, have

been used to illustrate how this analytical tool helps in the identification of the pyrazolyl compounds reported in this chapter.

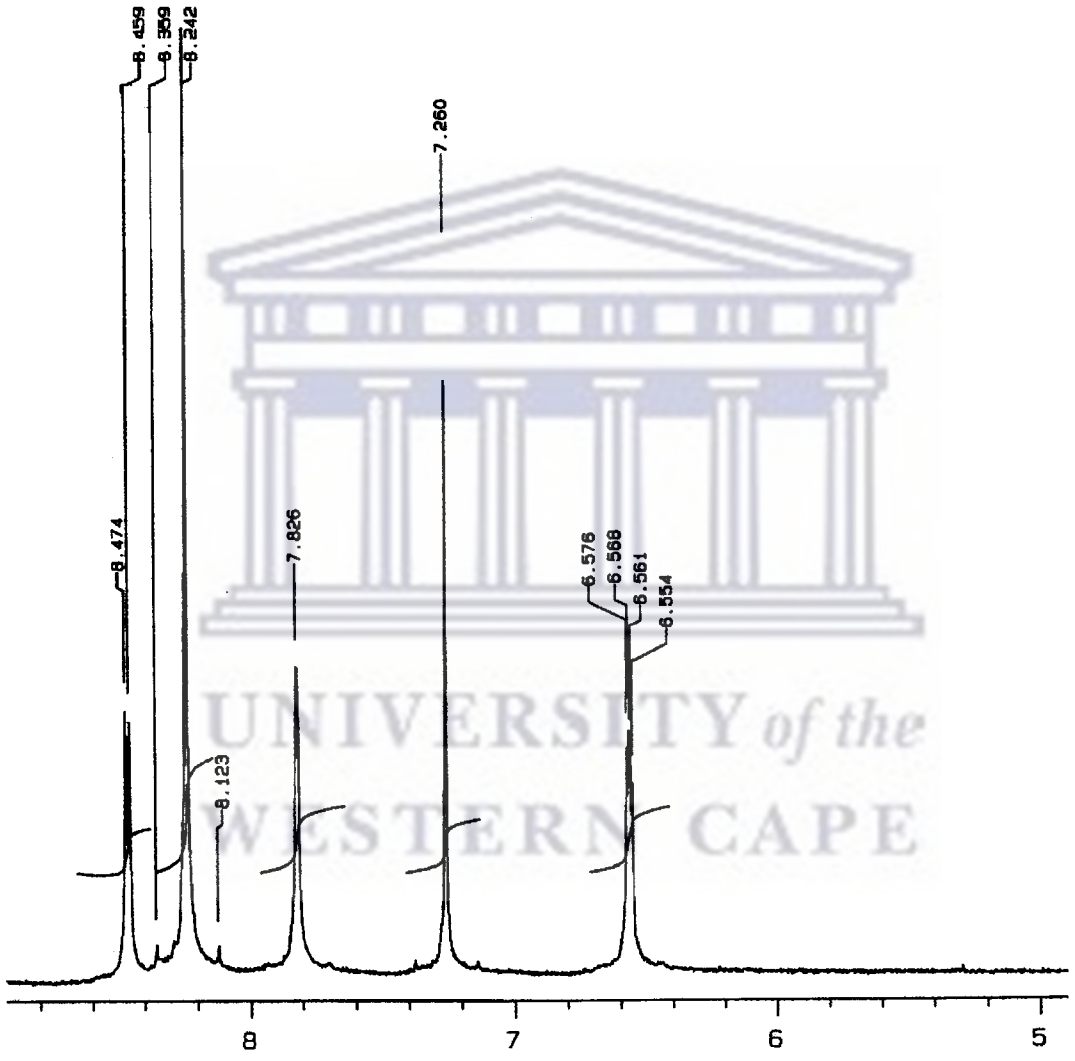


Figure 2.1: ^{1}H NMR spectrum of 1,4-bis(pyrazolyl-1-carbonyl)benzene **(L3)**

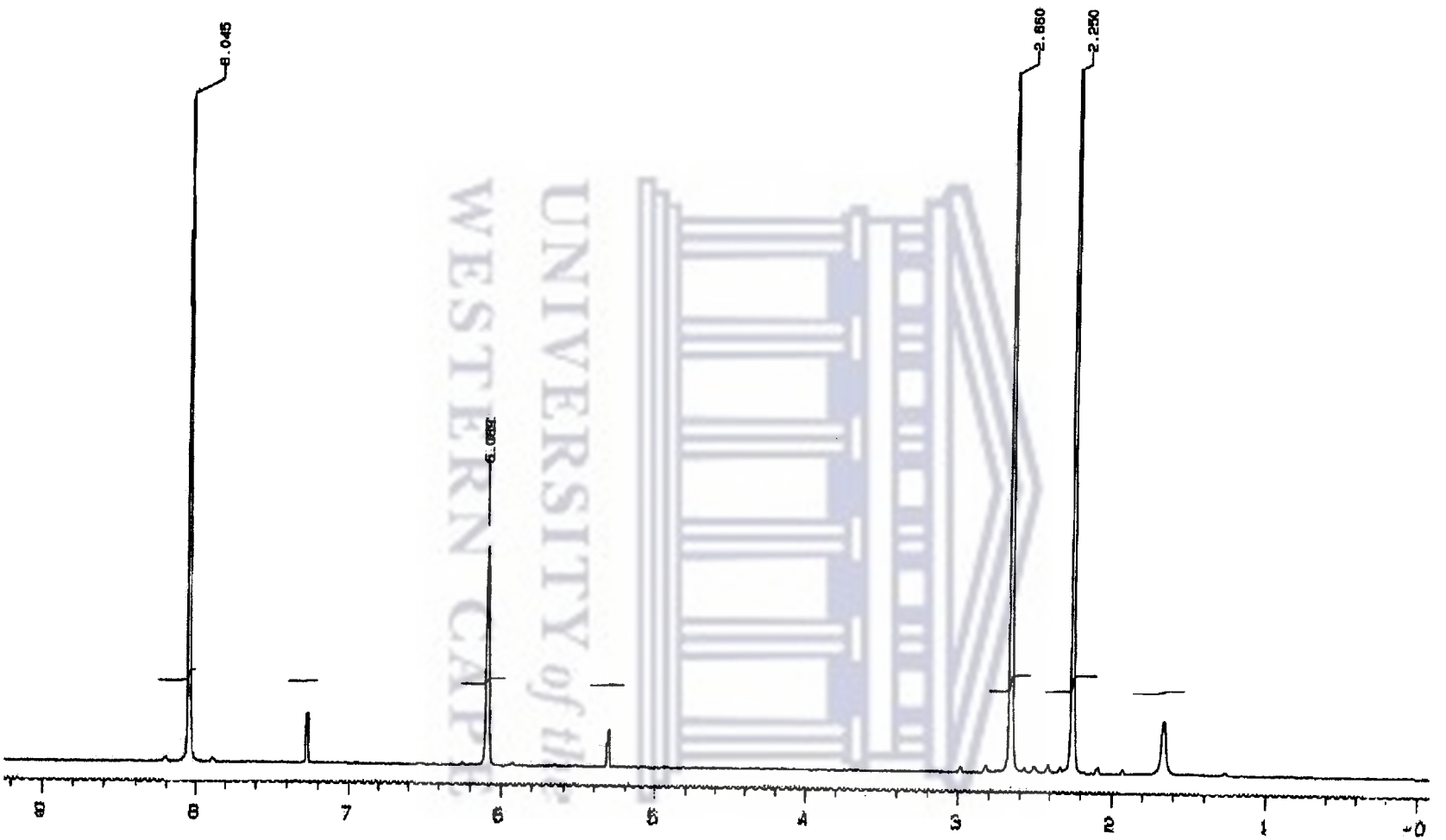


Figure 2.2: ^{1}H NMR spectrum of 1,4-Bis(3,5-dimethylpyrazolyl-1-carbonyl)benzene (**L2**)

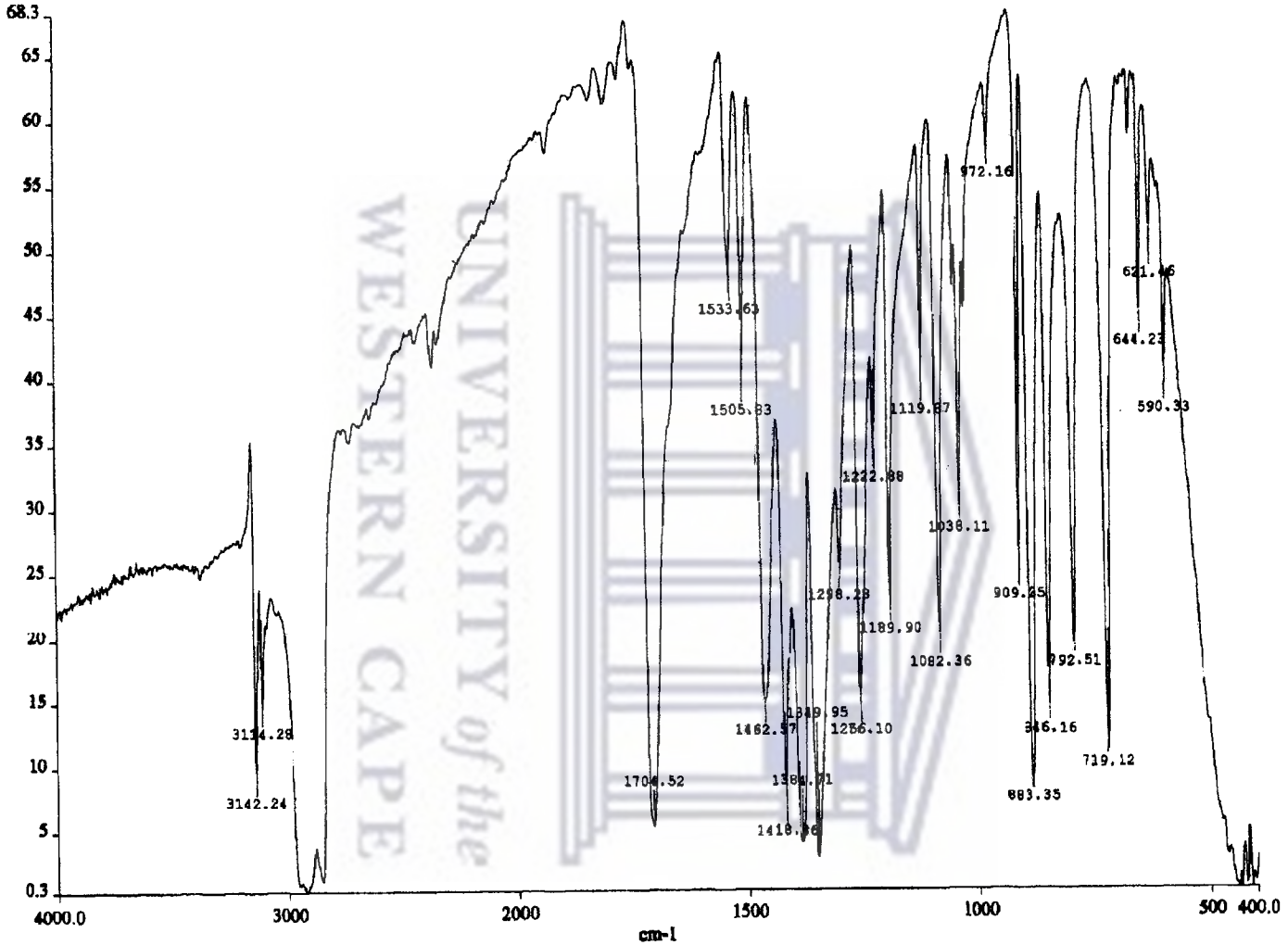


Figure 2.3: IR spectrum of 1,4-Bis(pyrazolyl-1-carbonyl)benzene **(L3)**

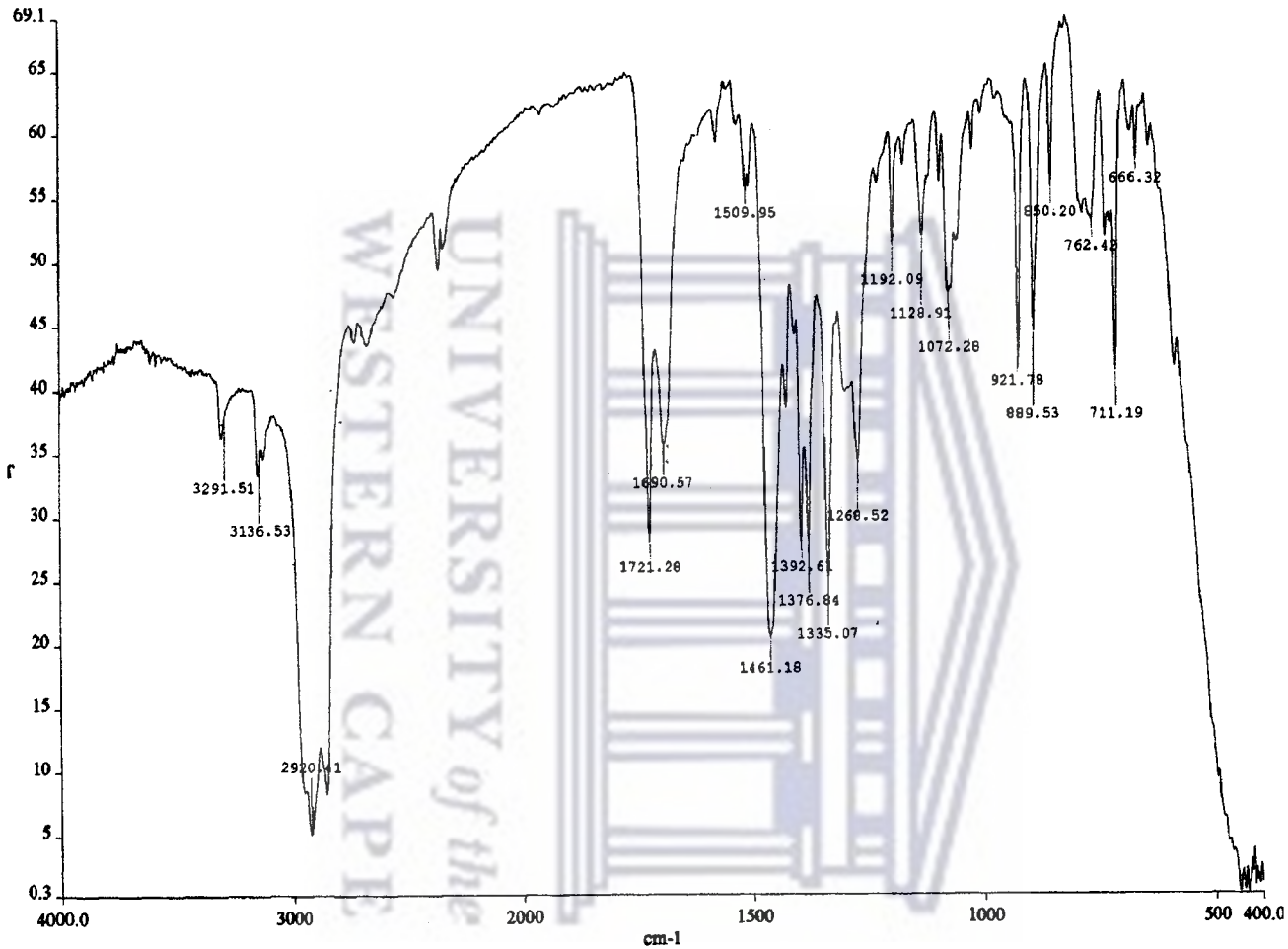


Figure 2.4: IR spectrum of dichloro[1,4-bis(pyrazolyl-1-carbonyl)benzene] dipalladium(II) complex **(3)**

The most important stretching frequencies in L3 were at 1705 cm^{-1} for ν(C=O), 1534 cm^{-1} for ν(C=C) and 1506 cm^{-1} for ν(C=N). For complex **3** the corresponding frequencies were found at1721 cm^{-1} for ν(C=O), 1564 cm^{-1} for ν(C=C) and 1509 cm^{-1} for ν(C=N), these stretching frequencies were higher than those obtained for the ligands indicating that complexation has indeed occurred. The full spectra for both compounds are shown in Figures 2.3 and 2.4. The ν(C=O) peaks confirmed the presence of the carbonyl linker.

Mass spectrometry is generally used to derive structural information about a compound by looking at its fragmentation pattern. The mass spectral fragmentation patterns of large molecules are usually complex. The molecular ion is never the base peak as it undergoes extensive fragmentation. In addition, many other fragment ions are observed. It is therefore often difficult to assign definite structures to fragment ions. The positive charge remains with the fragment that is more likely to stabilize it.

Generally all ligands prepared in this study showed similar fragmentation patterns. In a typical fragmentation pathway, the ligand first loses sequentially both of its substituents on one of the two pyrazoles. This is then followed by the loss of the remaining pyrazole moiety. The C=O linker is then cleaved and the second pyrazole is cleaved in a similar pattern as described above.The mass spectrum of **L2** is used here to illustrate how this analytical technique was used in the characterization of similar ligands. Molecular ion (*m/z* = 322) was observed in the case of **L2** (Figure 2.5). Scheme 2 is also an illustration of how compounds **L1-L4** fragment in the mass spectrometer under electron impact ionization, and follows the fragmentation pattern described above.

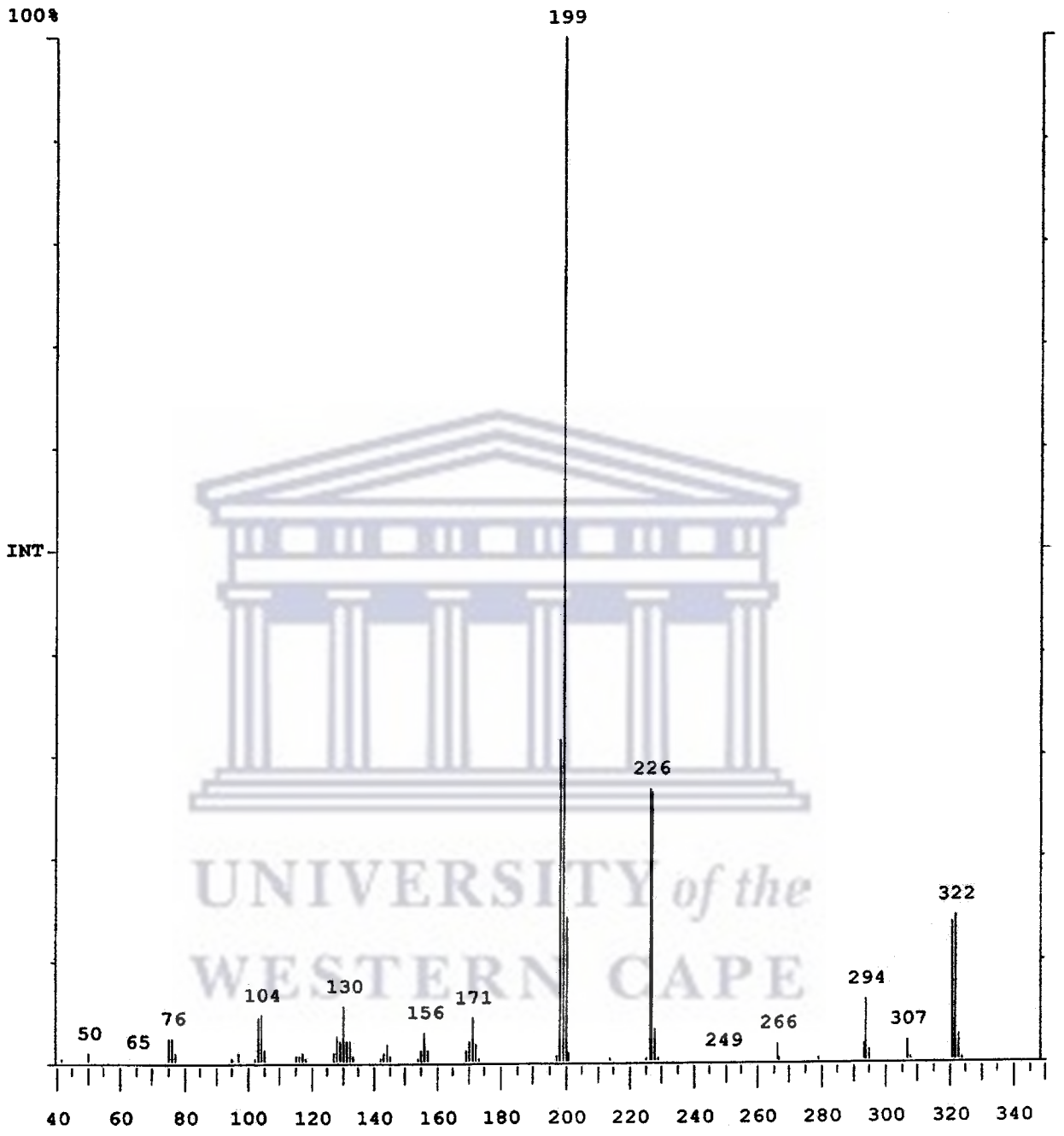
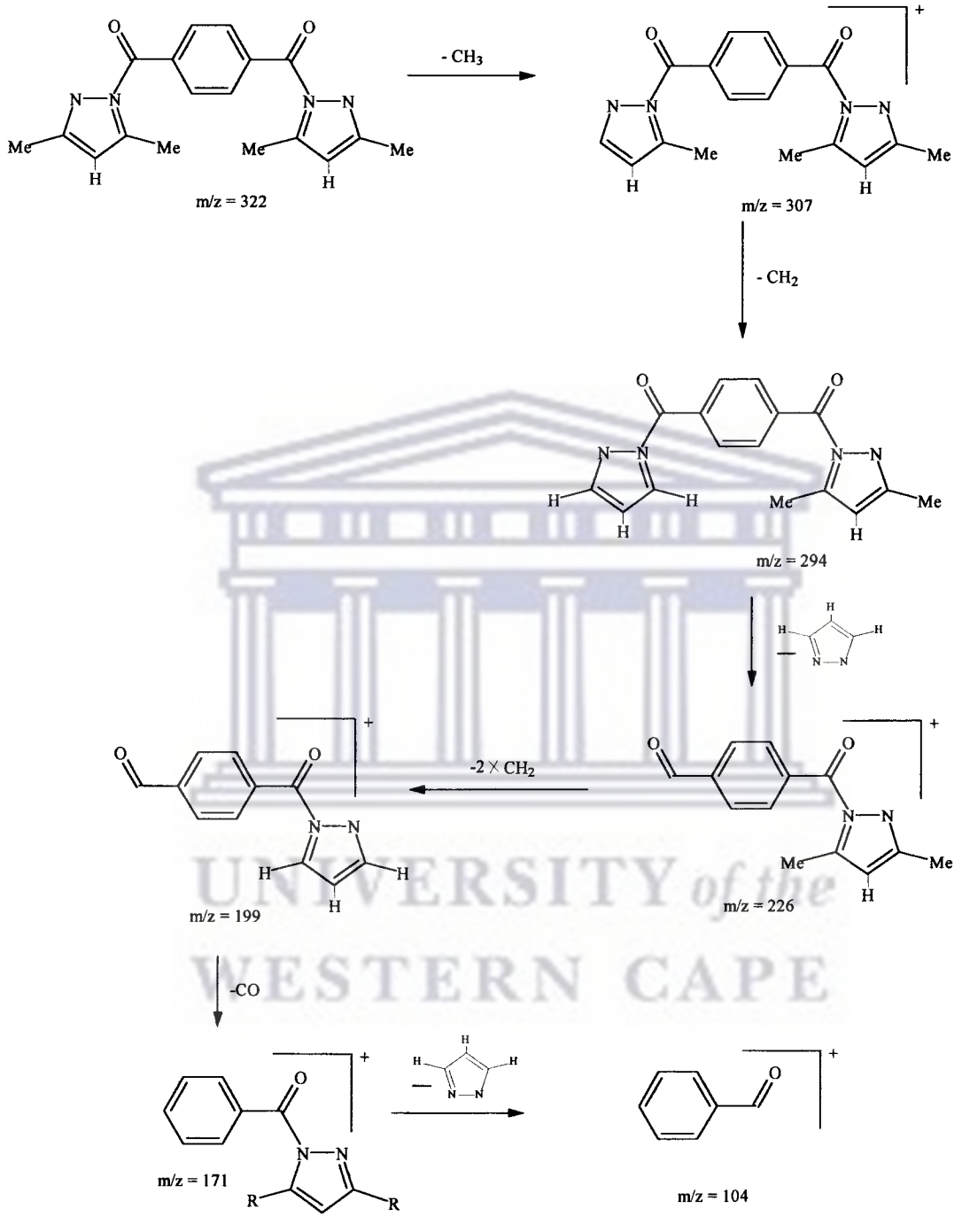
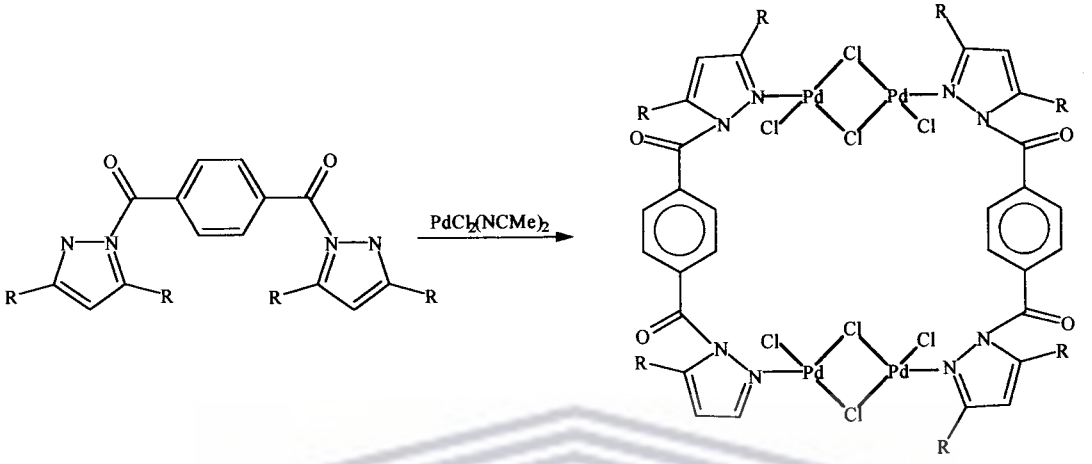


Figure 2.5: Mass spectrum of Ligand, **L2**



Scheme 2: Fragmentation pattern of Ligand, **L2**

Compounds **L1-L4** were reacted with $[PdCl_2(CH_3CN)_2]$ in a 1:1 ratio to form light yellow complexes **1**, **2**, **3** and **4** respectively.



R = ^{t}Bu **1** R = H **3**

R = Me **2** R = Ph **4**

Scheme 3

Complexes **1** and **2** were partially soluble in common organic solvents and were obtained in low yields (20% and 19% respectively), while complexes **3** and **4** were completely insoluble. ^{1}H and ^{13}C NMR, IR spectroscopy and elemental analysis were used to characterize the former complexes, while only IR and elemental analyses were used to characterize the latter. An interesting feature of the ^{1}H NMR spectra of complexes **1** and **2** is that they are nearly superimposable with those of the free ligand; however, their elemental analyses support the structural assignment proposed. Although the ^{1}H NMR spectra of **1** and **2** are identical to the spectra of their respective ligands, the ^{13}C NMR spectra of the complexes showed chemical shifts whose differences between ligand and complex peaks are in the 0.8 to 1.4 ppm range. This rare phenomenon is not unprecedented, especially for complexes containing nitrogen heterocycles. Newkome *et al.* also observed the same phenomenon when they prepared Ni(II) complexes of bipyridine ligands.[8]

The mode of bonding in the proposed structure is based on similar mode of bonding found in the 1,3-benzenedicarbonyl analogues of complexes **1-4**. The complexes are thus postulated to have the dimeric structure shown in the Scheme 3 above based on elemental analyses results.

Mass spectrometry was useful in proposing the structure for complex **1**. Under the highly energetic conditions of Electron Impact (EI) ionization extensive rearrangement occurs in **1**, complicating the interpretation. Alternative soft ionization method that does not use electron bombardment such as MALDI-TOF was utilized to prevent extensive fragmentation. Although, no molecular ion (*m/z* = 1691) was observed, substantial information was obtained from the base peak (*m/z* = 739) which corresponds to a dinuclear metal centre with two pyrazoles attached to it and a carbonyl linker is attached to one of the pyrazole moieties. This confirmed that the 1,4-(3,5-R_2pzC(O))$_2C_6H_4$ and 1,3-(3,5-R_2pzC(O))$_2C_6H_4$ palladium complexes contains basically the same mode of bonding and geometry around the Pd atoms. This observation supports the elemental analysis data. Scheme 4 outlines some of the major fragments resulting from the proposed structure. Mass spectrum of **1** (Fig. 2.6) yielded substantial information in support of the proposed structure; but attempts to grow crystal of these complexes to confirm the proposed structure were unsuccessful.

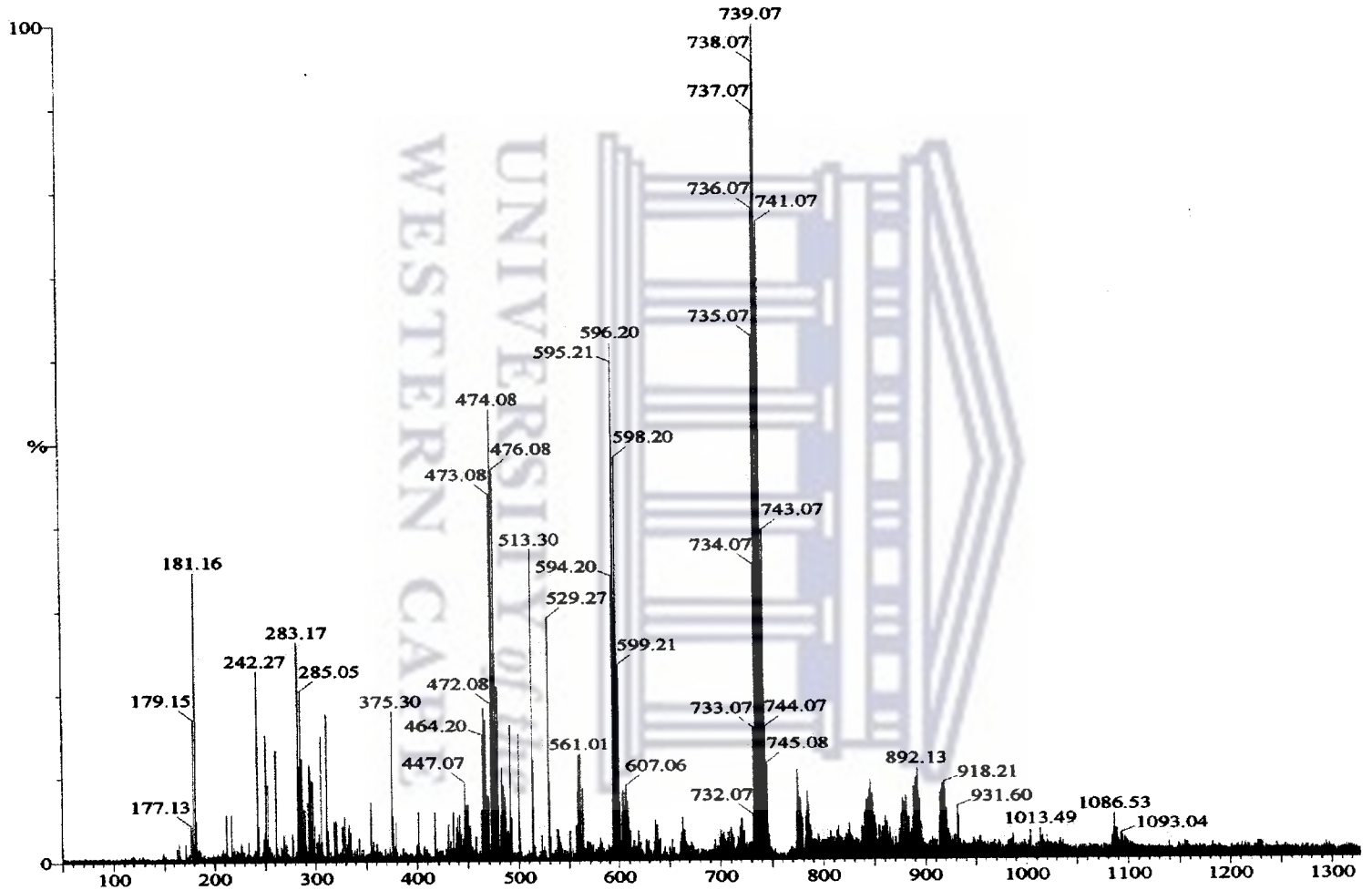
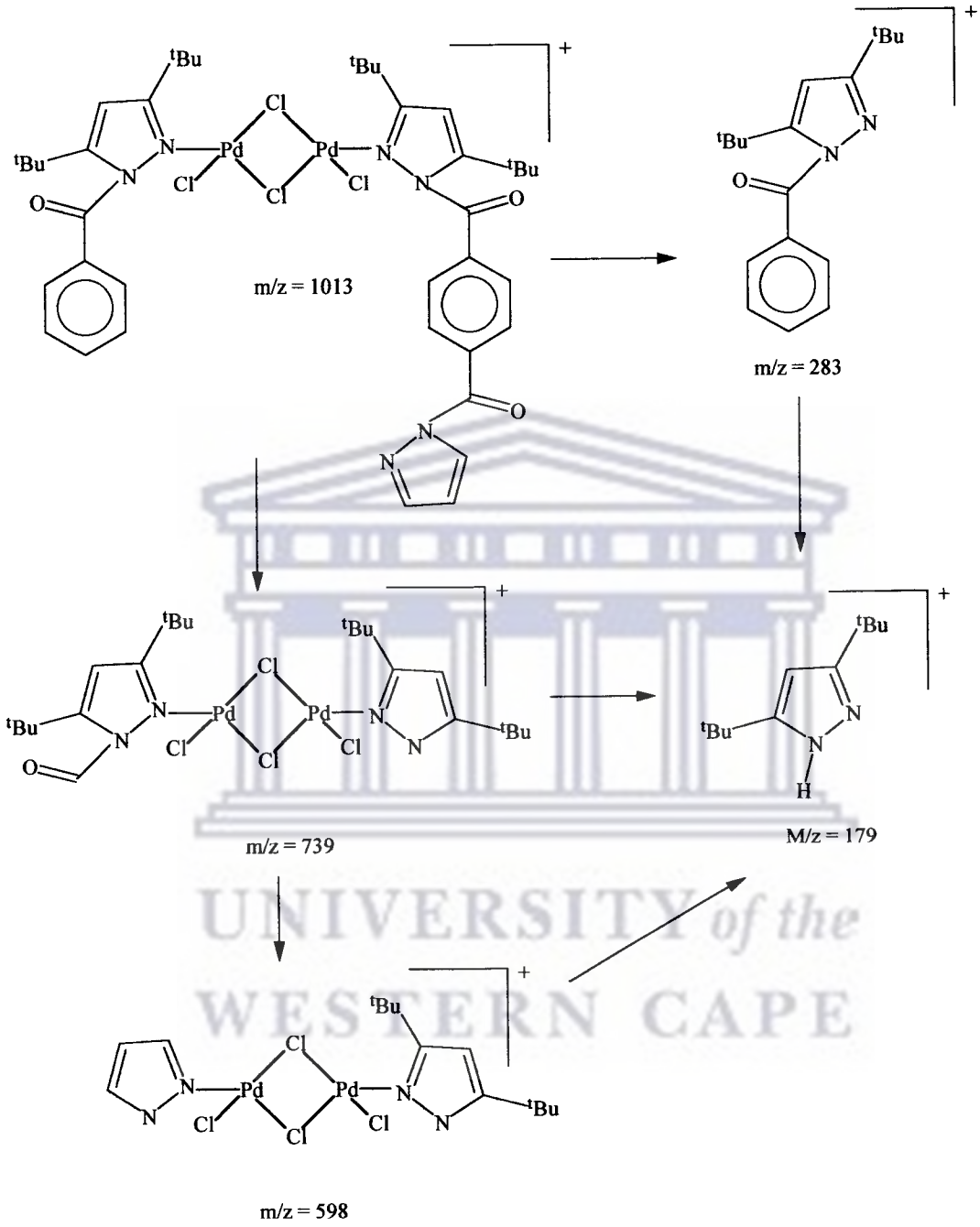


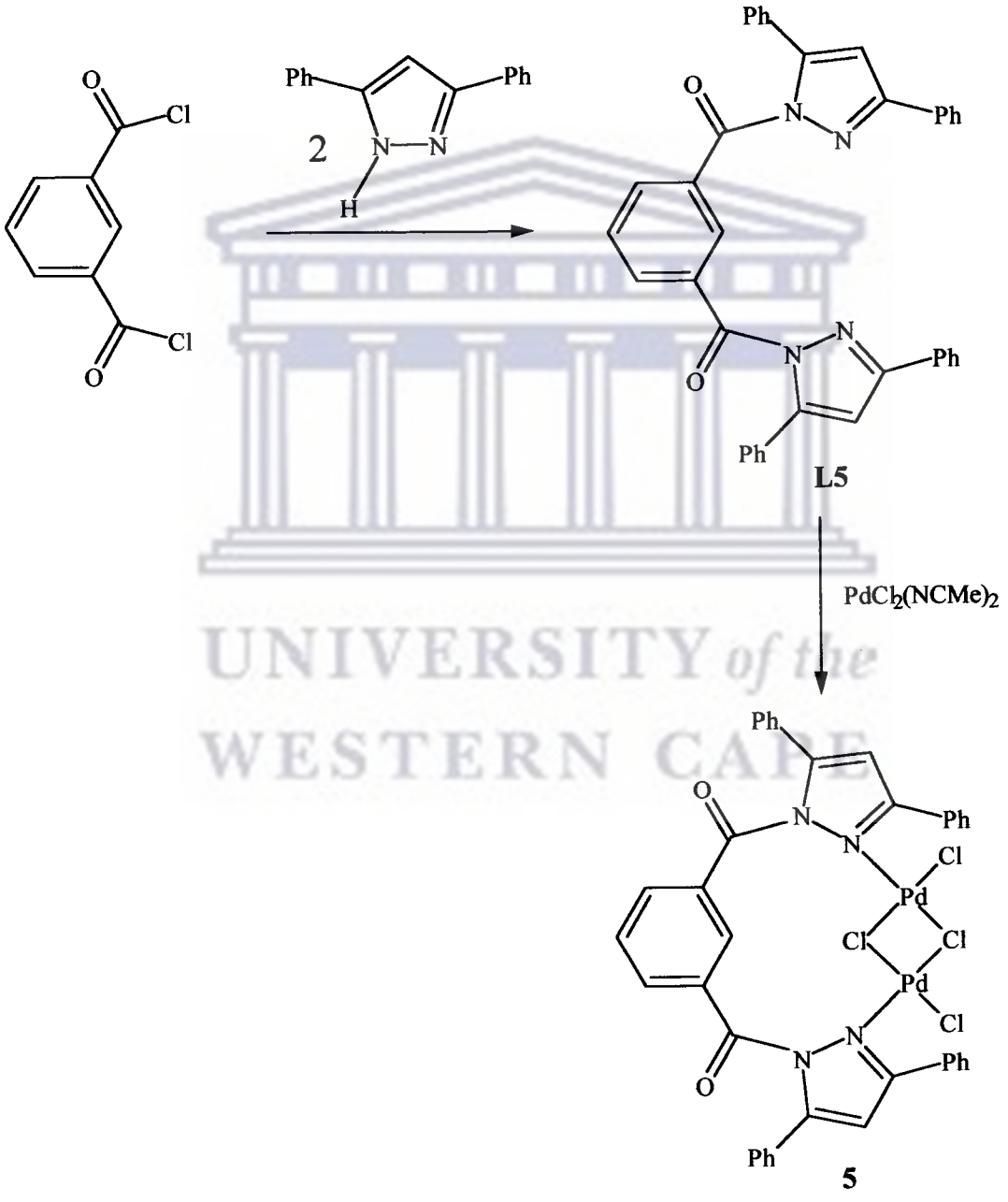
Figure 2.6: Mass spectrum of complex **1**



Scheme 4: Fragmentation of **1**

2.2.2 Synthesis of 1,3-bis(3,5-diphenylpyrazolyl-1-carbonyl)benzene ligand (L5) and its palladium complex (5).

L5 was prepared using the same methodology as the one described earlier for **L1-L4**. Scheme 5 describes the synthesis of **L5** and its reaction with $[PdCl_2(CH_3CN)_2]$ to produce complex **5**.



Scheme 5

The ^{1}H NMR spectrum obtained for **L5** is typical of ^{1}H NMR spectral pattern associated with 1,3 benzenedicarbonyl pyrazolyl ligands. The C2, C4 and C5 protons on the benzene appear as a triplet (7.69 ppm), doublet (8.42 ppm) and doublet of a doublet (8.56 ppm) respectively. The triplet is sandwiched between the two peaks associated with substituents on the pyrazole.

The NMR spectra of **5** (Fig. 2.7 and 2.8) suggest that **L5** binds to the Pd in a similar fashion as recently reported on the literature,[7b] forming dinuclear complexes. The binuclear structure was confirmed by X-ray crystallography (Fig. 2.12). It was proposed that this bonding mode could either be the result of poor donor ability of the pyrazolyl nitrogen or the bite angle between the two pyrazolyl units might be too big to allow bridging by one metal atom. The structure of $[\{(2\text{-}ClC_6H_4(CO)(3,5\text{-}Me_2pz)\}PdCl(\mu\text{-}Cl)]_2$ recently determined in our laboratory supports the weaker donor ability of the pyrazolyl nitrogen and the reason for the dinuclear complex structure.[9]

2.3 Molecular structures of L1, L5 and 5

Single crystals of **L1** and **L5** suitable for X-ray structural analysis were obtained from recrystallization of the ligands from CH_2Cl_2 and ether at room temperature for **L1**, and at −15 °C for **L5**. Molecular structures of the two ligands are shown in Figures 1.10 (**L1**) and 1.11 (**L5**). Their crystal data, together with the data collection and refinement parameters are presented in Table 2.1 and selected bond length and angles are given in Table 2.2 for **L1** and Table 2.3 for **L5**.

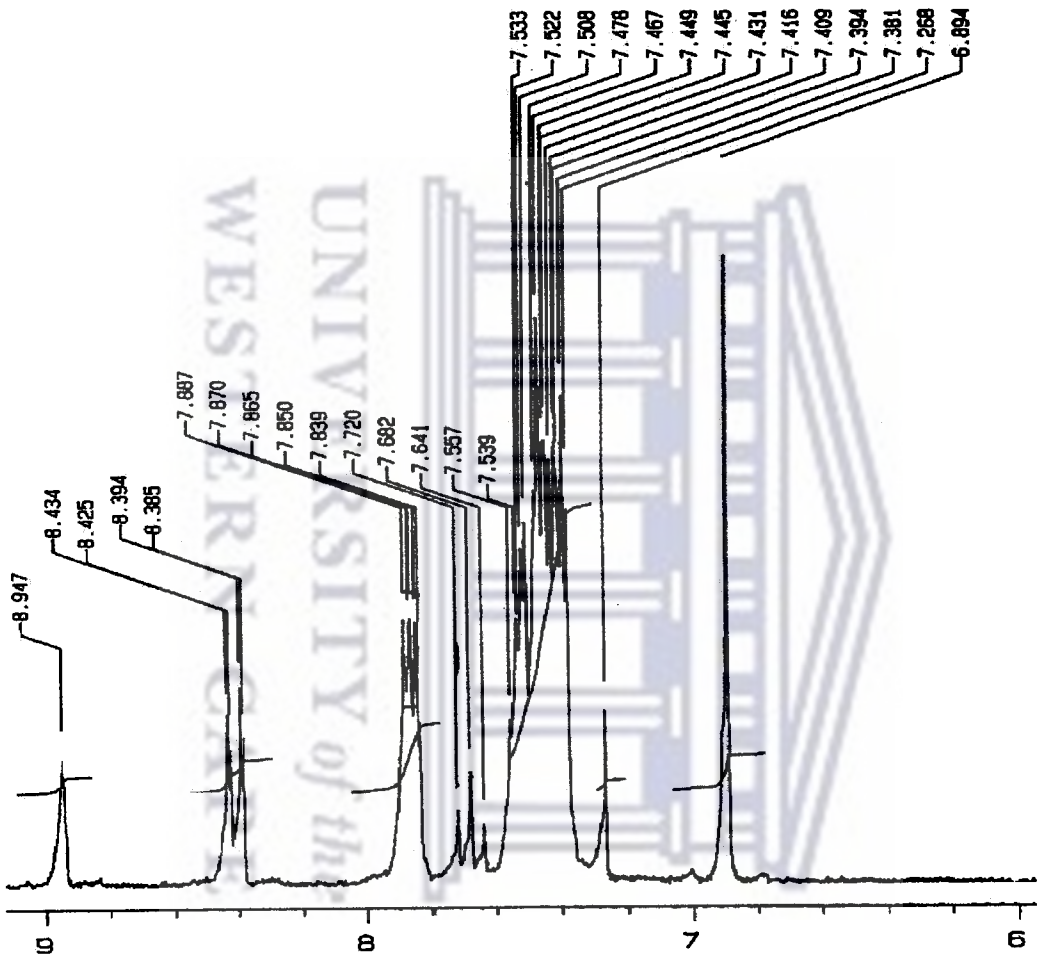


Figure 2.8: 1,3-Bis(3,5-diphenylpyrazolyl-1-carbonyl)benzene (L5)

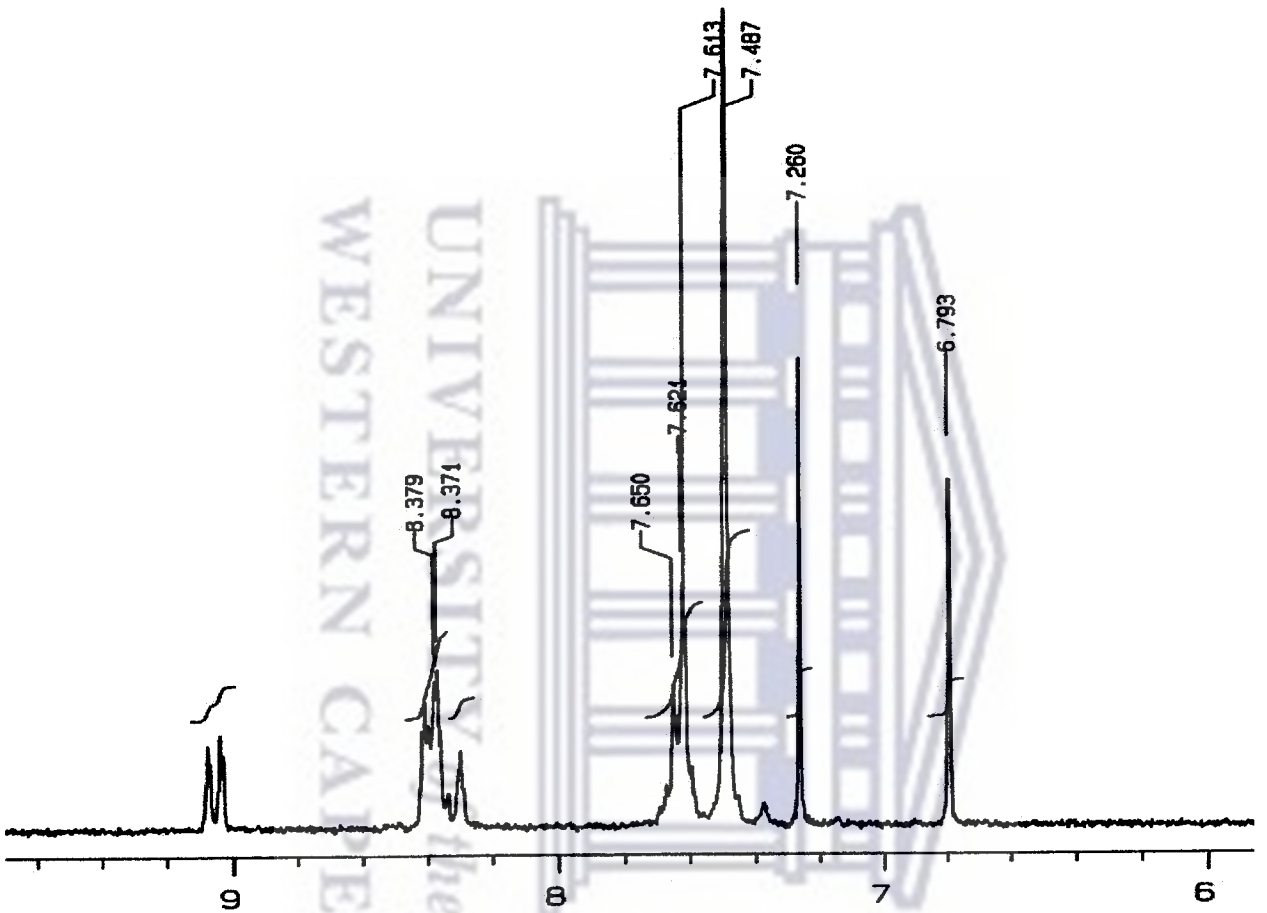


Figure 2.9: ^{1}H NMR spectrum of Di-μ-chloro-dichloro[1,3-bis(3,5-dipheylpyrazolyl-1-carbonyl)benzene] dipalladium(II) (**5**)

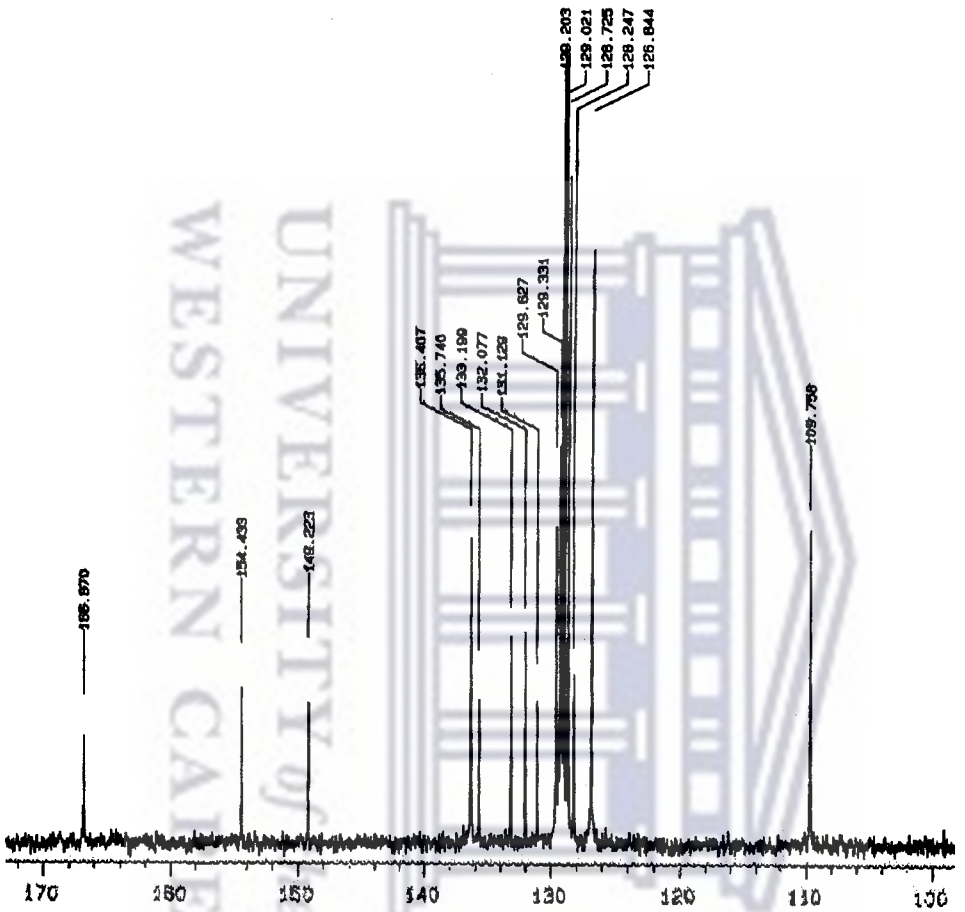


Figure 2.10: ^{13}C NMR spectrum of Di-μ-chloro-dichloro[1,3-bis(3,5-dipheylpyrazolyl-1-carbonyl)benzene] dipalladium(II) **(5)**

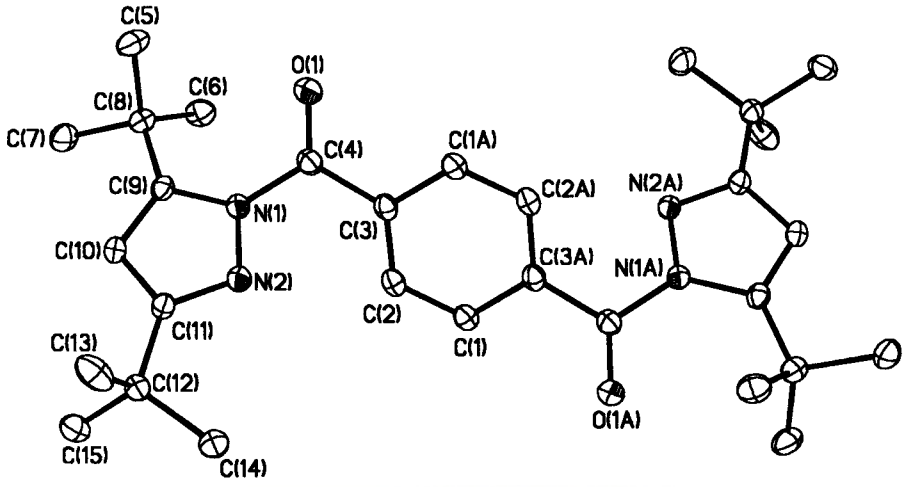


Figure 2.10: molecular structure of 1,4-Bis(3,5-ditertbutylpyrazolyl-1-carbonyl) benzene **(L1)**

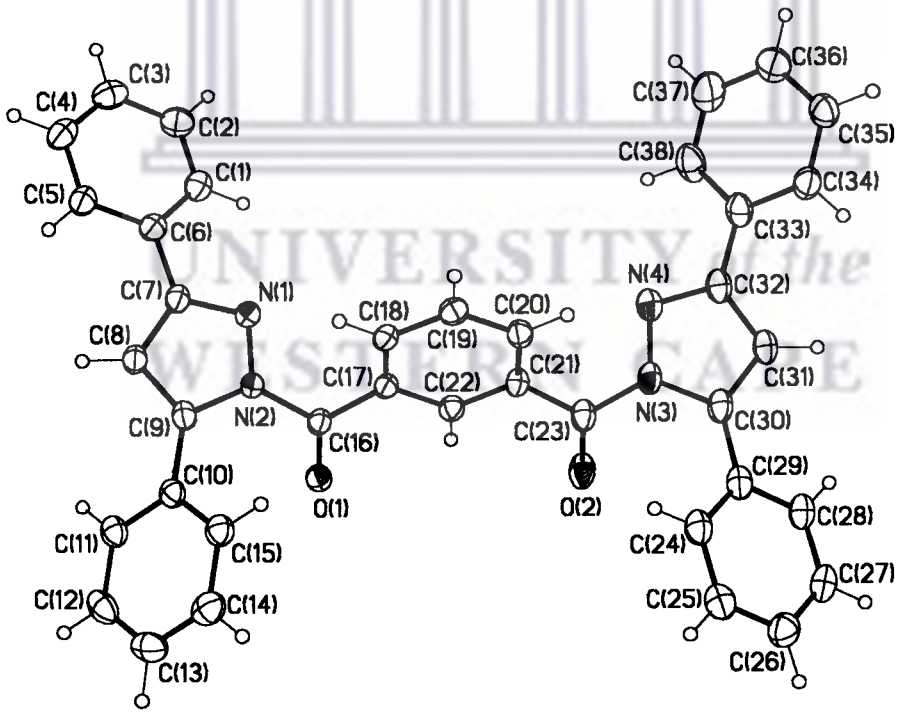


Figure 2.11: molecular structure of 1,3-Bis(3,5-diphenylpyrazolyl-1-carbonyl) benzene **(L5)**

Table 2.1: Crystal data and structure refinement for **L1** and **L5**

	L1	**L5**
Empirical formula	C_{30} H_{42} N_4 O_2	C_{38} H_{26} N_4 O_2
Formula weight	490.68	570.63
Temperature/ K	173(2) K	173(2)
Wavelength	0.71073 Å	0.71073 Å
Space group	$P\bar{1}$	$P2_1/n$
Crystal system	Triclinic	Monoclinic
a/Å	9.7835(7)	9.6723(16)
b/Å	9.8619(8)	28.979(5)
c/Å	15.5527(12	10.1433(17)
α/°	105.0810(10)	90
β/°	90.186(2)	92.980(3)
γ/°	98.9710(10)	90
V/Å	1429.67(19)	2839.3(8)
Z	2	4
Dc/Mg m^{-3}	1.140	1.335
(Mo-K) mm^{-1}	0.072	0.084
Crystal size	0.40 x 0.30 x 0.20	0.44 x 0.34 x 0.17
Reflections collected	9316	21409
T_{max}/T_{min}	0.9857 / 0.9718	0.9859 / 0.9640
Goodness-of-fit on F^2	1.050	0.992
Final R indices [I>2sigma(I)]	R1 = 0.0440, wR2 = 0.1231	R1 = 0.0501, wR2 = 0.1333
R indices (all data)	R1 = 0.0538, wR2 = 0.1290	R1 = 0.0575, wR2 = 0.1388

Table 2.2: Selected bond lengths [Å] and angles [°] for **L1**

L1			
Bond lengths [Å]			
C(1)-C(2)	1.380(2)	N(2)-C(11)	1.3189(17)
C(2)-C(3)	1.395(2)	C(9)-C(10)	1.3618(19)
C(3)-C(4)	1.495(2)	C(10)-C(11)	1.4204(19)
O(1)-C(4)	1.2038(18)	C(11)-C(12)	1.510(2)
N(1)-N(2)	1.3824(16)	C(12)-C(14)	1.530(2)
N(1)-C(9)	1.3946(17)	C(12)-C(13)	1.553(2)
N(1)-C(4)	1.4199(17)	C(12)-C(15)	1.536(2)
Bond angles [°]			
C(2)-C(1)-C(3)#1	120.55(13)	C(11)-N(2)-N(1)	105.12(11)
C(1)-C(2)-C(3)	120.09(12)	N(2)-C(11)-C(12)	120.61(12)
C(2)-C(3)-C(1)#1	119.36(13)	N(2)-C(11)-C(10)	110.60(12)
C(2)-C(3)-C(4	124.28(12)	C(10)-C(9)-N(1)	104.47(12)
O(1)-C(4)-C(3)	121.94(13)	C(9)-C(10)-C(11)	107.83(12)
N(1)-C(4)-C(3)	117.04(12)	C(11)-C(12)-C(14)	110.11(12)
N(2)-N(1)-C(4)	116.45(11)	C(11)-C(12)-C(13)	108.54(12)
C(9)-N(1)-C(4)	131.14(12)	C(11)-C(12)-C(15)	109.54(12)

Table 2.3: Selected bond lengths [Å] and angles [°] for **L5**

		Bond lengths [Å]	
N(1)-C(7)	1.330(2)	O(1)-C(16)	1.2059(19)
N(1)-N(2)	1.3744(18)	C(6)-C(7)	1.478(2)
N(2)-C(9)	1.381(2)	C(9)-C(10)	1.476(2)
N(2)-C(16)	1.4331(19)	C(16)-C(17)	1.485(2)
		Bond angles [°]	
N(1)-N(2)-C(16)	117.31(12)	N(2)-C(9)-C(10)	123.58(14)
C(9)-N(2)-C(16)	128.68(13)	O(1)-C(16)-N(2)	120.03(14)
C(1)-C(6)-C(7)	120.39(15)	O(1)-C(16)-C(17)	124.22(14)
N(1)-C(7)-C(6)	119.40(14)	N(2)-C(16)-C(17)	115.65(13)
C(8)-C(7)-C(6)	129.13(14)	C(18)-C(17)-C(16)	121.17(14)

It has been reported that the structures of 1,3-(3,5-R_2pzC(O))$_2C_6H_4$ and 1,2-(3,5-R_2pzC(O))$_2C_6H_4$ compounds in the solid state possess either C_2 or C_S.[7b] These observation can easily be extended to include 1,4-(3,5-R_2pzC(O))$_2C_6H_4$ compounds. The C_2 symmetry is attained when the pyrazolyl substituents on the benzene ring reside on the opposite sides of its plane. The C_s symmetry is observed when both substituents are on the same side of the ring with the mirror plane perpendicular to the plane of the ring. Based on the above assessment **L1** has a C_2 symmetry whilst **L5** has a C_S symmetry. Molecular modeling calculations revealed that the two symmetry conformations are energetically equivalent and are close in energy to a number of calculated energetic minima corresponding to various C_i arrangements. It has also

been established that the most energetically favourable conformations are those in which the carbonyl is coplanar with the pyrazole ring.

Compounds **L1** and **L5** cannot achieve planarity due to either close proximity of the pyrazolyl substituents in the 2-position to the *ortho* hydrogen of the phenyl ring, or due to unfavorable interactions between the nitrogen lone pair and the *ortho* hydrogen. The C=O group can, however, be coplanar with either ring since both pyrazolyl and phenyl groups possess a delocalized π-system, with the preferred ring being the pyrazole.

The C–N bond in the O=*C*–*N*–N linkage is shorter than the generic C_{sp2}–N_{sp2} single bond due to electronic resonance. The C–N bond is the shortest when the torsion angle O–C–N–N is 180° and longest when the angle is 90°. The C–N bonds in **L1** averaged 1.4157 Å while those in **L5** averaged 1.4271 Å. These values fall within the range of bond distances for compounds reported by Darkwa *et al.*[7b]

Single crystals of **5** were obtained from recrystallization of the complex from CH_2Cl_2 and ether at –15 °C. The crystal quality was poor but an X-ray diffraction analysis could be carried out and revealed clearly the structure of the complex **5**.The molecular structure of **5** is shown in Figure 2.12. Crystallographic information is tabulated in Table 2.4, and the selected bond lengths and angles of the molecule are listed in Table 2.5.

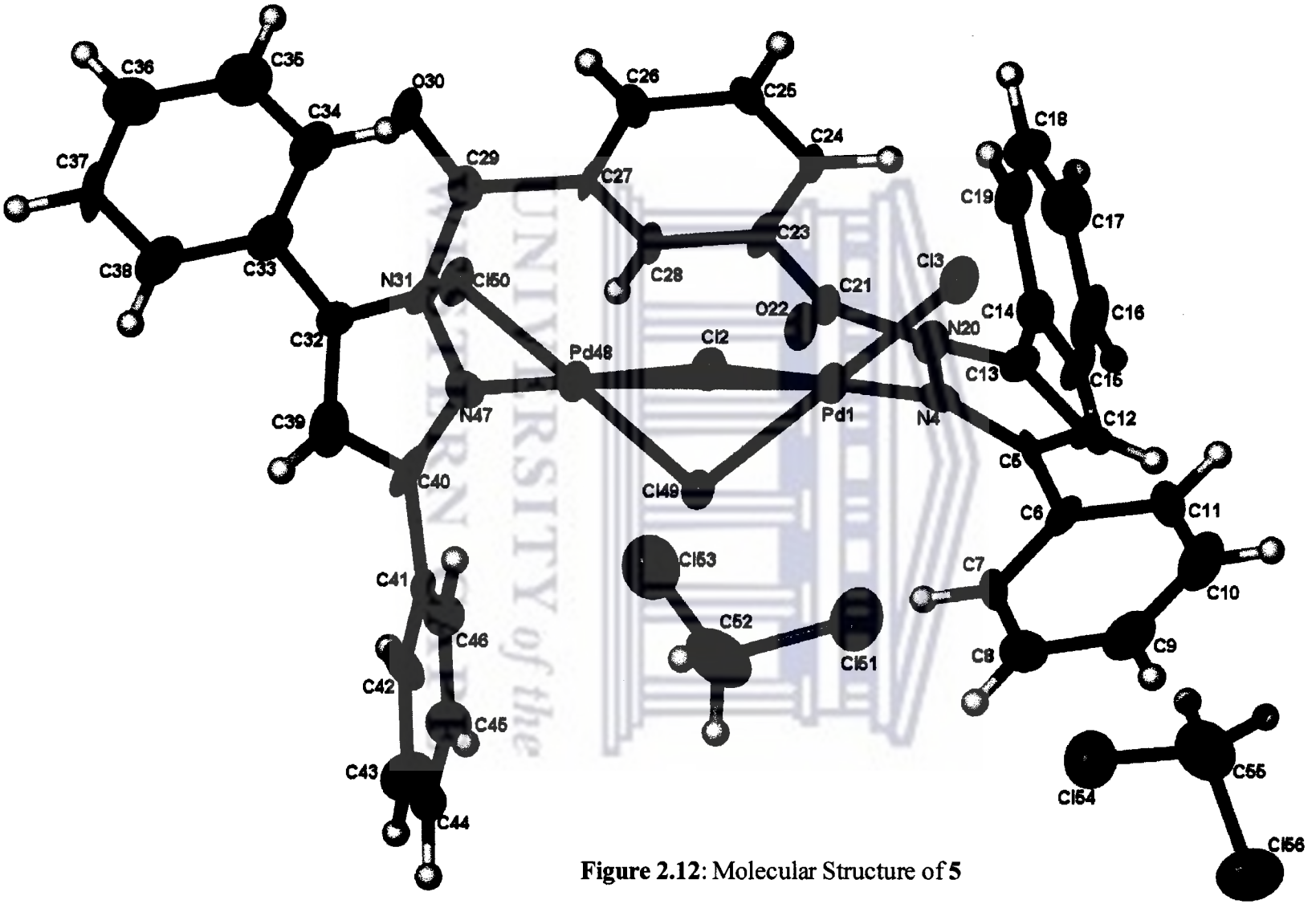


Figure 2.12: Molecular Structure of **5**

Table 2.4: Crystal data and structure refinement for **5**

Complex	**5**
Empirical formula	$C_{40}H_{30}Cl_8N_4O_2Pd_2$
Formula weight	1095.08
Temperature/ K	100(2)
Wavelength/ Å	0.71073
Space group	$P2_1/n$
Crystal system	Monoclinic
a/Å	12.819(6)
b/Å	16.503(8)
c/Å	19.401(9)
α/°	90
β/°	94.703(8)
γ/°	90
V/ Å^3	4091(3)
Z	4
Dc/Mg m^{-3}	1.778
(Mo-K) mm^{-1}	1.444
Crystal size/ mm^3	0.10 x 0.10 x 0.05
Reflections collected	21736
T_{max}/T_{min}	0.9313 / 0.8691
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1 = 0.1167, wR2 = 0.2850
R indices (all data)	R1 = 0.2058, wR2 = 0.3450

Table 2.5: Selected bond lengths [Å] and angles [°] for **5**

	5		
	Bond lengths [Å]		
Pd(1)-N(4)	2.040(12)	N(47)-Pd(48)	2.033(12)
Pd(1)-Cl(3)	2.264(4)	Cl(2)-Pd(48)	2.308(4)
Pd(1)-Cl(2)	2.305(4)	Pd(48)-Cl(50)	2.275(4)
Pd(1)-Cl(49)	2.342(4)	Pd(48)-Cl(49)	2.321(4)
	Bond angles [°]		
N(4)-Pd(1)-Cl(3)	88.2(3)	N(47)-Pd(48)-Cl(50)	90.5(4)
N(4)-Pd(1)-Cl(2)	178.6(3)	N(47)-Pd(48)-Cl(2)	175.6(4)
Cl(3)-Pd(1)-Cl(2)	93.10(14)	Cl(50)-Pd(48)-Cl(2)	92.51(14)
N(4)-Pd(1)-Cl(49)	94.4(3)	N(47)-Pd(48)-Cl(49)	92.5(4)
Cl(3)-Pd(1)-Cl(49)	177.35(14)	Cl(50)-Pd(48)-Cl(49)	176.05(14)
Cl(2)-Pd(1)-Cl(49)	84.27(13)	Cl(2)-Pd(48)-Cl(49)	84.68(13)
Pd(1)-Cl(2)-Pd(48)	87.22(13)	Pd(48)-Cl(49)-Pd(1)	86.05(13)

The Pd atoms in complex **5** are in slightly distorted square planar configurations with the bond angles about the Pd atoms ranging between 84.35(5) and 94.4(3)°. Each Pd metal has four atoms comprising its coordination sphere, three chlorine atoms and one nitrogen atom. The Pd–Cl(terminal), Pd–Cl(bridging trans to N) and Pd–Cl- (bridging *trans* to Cl), bond lengths average of 2.236 Å in **5** is shorter than the 2.310 Å reported for the same series of compounds. Due to the *trans* influence of the pyrazolato ligands their good π-donor ability is not reflected in these structures. The metal–chloride distance *trans* to the pyrazolato ligand is shorter than would be anticipated, as the latter is a weaker σ-donor than the chloride. The average Pd–N

bond distance (2.036(12) Å) is somewhat shorter than the average value of 2.1(1) Å calculated for 59 Pd–N(pz) bond lengths reported to the Cambridge Structural Database (CSD).[10]

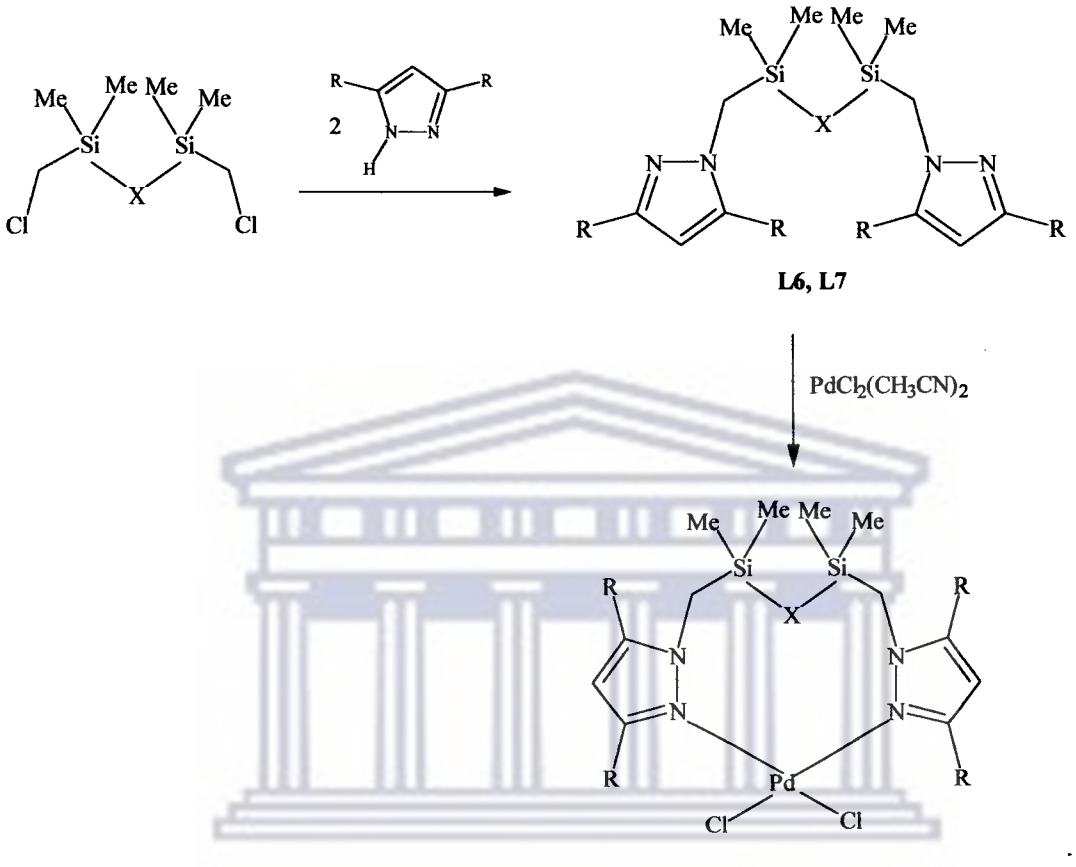
The distinguishing feature of these series of compounds that sets them apart from almost all dinuclear Pd complexes with the $L_2Pd(\mu_2\text{-}Cl)_2\text{-}PdL_2$ core is the smaller dihedral angle between the planes defined by the Pd centres and two bridging Cl atoms. This results in folding which shortens the Pd–Pd separation to 3.1818(19) Å. Undoubtedly, such strained ligand arrangement stems from the incorporation of a bidentate bridging ligand into the system. In 21 other relevant complexes reported to the CSD the $Pd\text{–}(\mu\text{-}Cl)_2\text{–}Pd$ rhombuses were planar with the Pd–Pd distances averaging 3.45(5) Å.

2.4 Synthesis of alkylpyrazolyl ligands and complexes

In order to study the effect of various linkers on the donor ability of pyrazolyl nitrogen and the stability of their complexes, we changed the benzenecarbonyl linkers in the **L1-L5** above to alkylsilizane and alkylsiloxane. Three ligands, **L6**, **L7** and **L8**, were targeted for this investigation.

Compounds **L6** and **L7** were synthesized according to Scheme 5 from the reaction of 1,3-bis(chloromethyl)tetramethyldisilazane (X = NH) or 1,3-bis(chloromethyl)tetra methyldisiloxane (X = O) and two equivalents of the appropriate pyrazole. The pure ligands were isolated as white solids in moderate yields. The compounds are stable in dry air for several weeks but, as a precautionary measure, were stored under a nitrogen atmosphere. The ligands are soluble in common organic solvents, including

aliphatic and aromatic hydrocarbons, but they slowly decompose in presence of solvents having acidic protons such as alcohols and water.



Scheme 5

The ^{1}H NMR spectra of **L6** (Fig. 2.13) and **L7** revealed the equivalent 3 and 5 methyl protons of the pyrazolyl units in these alkylaminopyrazolyl ligands which appear as single peaks at 2.17 and 1.33 ppm respectively, in addition to the peaks of the alkyl protons. There was no sign of the NH peak in **L6**.

Further characterization of **L6** (Fig. 2.14) and **L7** by mass spectrometry produced no molecular ion, but fragmentation pattern (Scheme 6) provide evidence for the formulation of compounds in Scheme 5. In the silicon containing alkylaminopyrazole ligand **L6** the base peak (*m/z* = 241) corresponds to a structure in which a pyrazolylmethine unit is lost.

Compounds **L6** was reacted with $[PdCl_2(CH_3CN)_2]$ in a 1:1 ratio to form a light yellow complex in low yield. The complex was characterized by ^1H (Fig. 2.14) and ^{13}C NMR spectroscopy. The telltale sign that complexation of **L6** has occurred is the separate singlets observed for 3 and 5-methyl protons of the pyrazolyl units in **L6**. The separation of 3 and 5-CH_3 signals is a confirmation of metal binding to the ligand while the appearance of a single peak for a proton at C-4 on the pyrazole suggests that the metal is bonded through the nitrogen of the each pyrazole rings.

Contrary to our observation of the absence of a signal due to the amine proton of **L6** when using ^1H NMR spectroscopy, infrared spectroscopy could detect this functional group in the ligand and in the complex formed by this ligand. The ν(N-H) band was found at 3417 cm^{-1} in free ligand **L6** and shifts to 3188 cm^{-1} in complex **6**.

During attempts to grow single crystals of complex **6**, the complex was found to disproportionate to the known compound $(3,5\text{-}Me_2pzH)PdCl_2$. This decomposition product was readily detected by its characteristic ^1H NMR chemical shift of the pyrazole NH proton at 11.40 ppm. In order to avoid this decomposition, complex **6** was not left in solution for longer than 24 h.

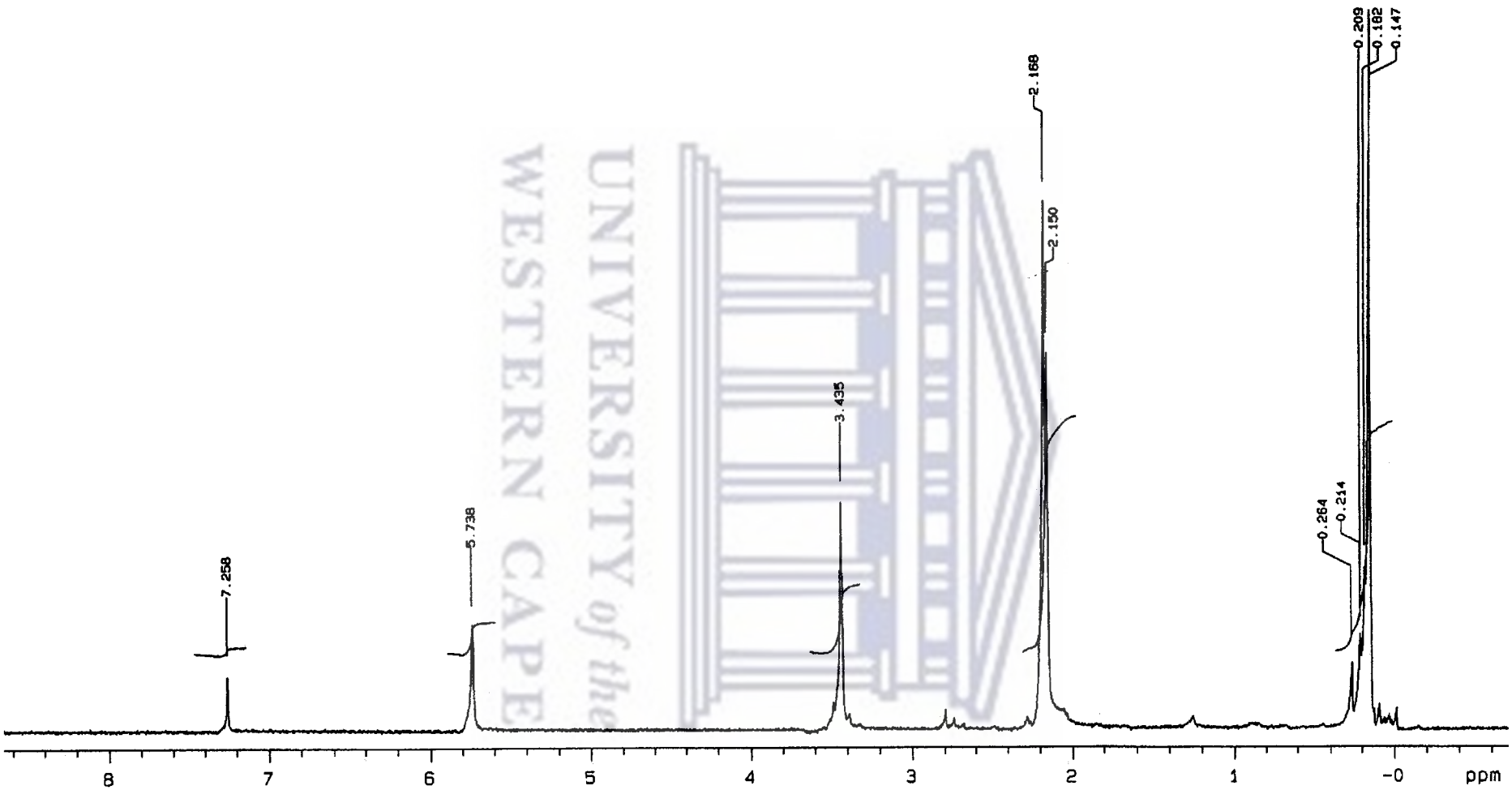


Figure 2.13: ^{1}H NMR spectrum of 1,3-Bis(3,5-dimethylpyrazolyl-1-methyl)tetramethyldisilazane (**L6**)

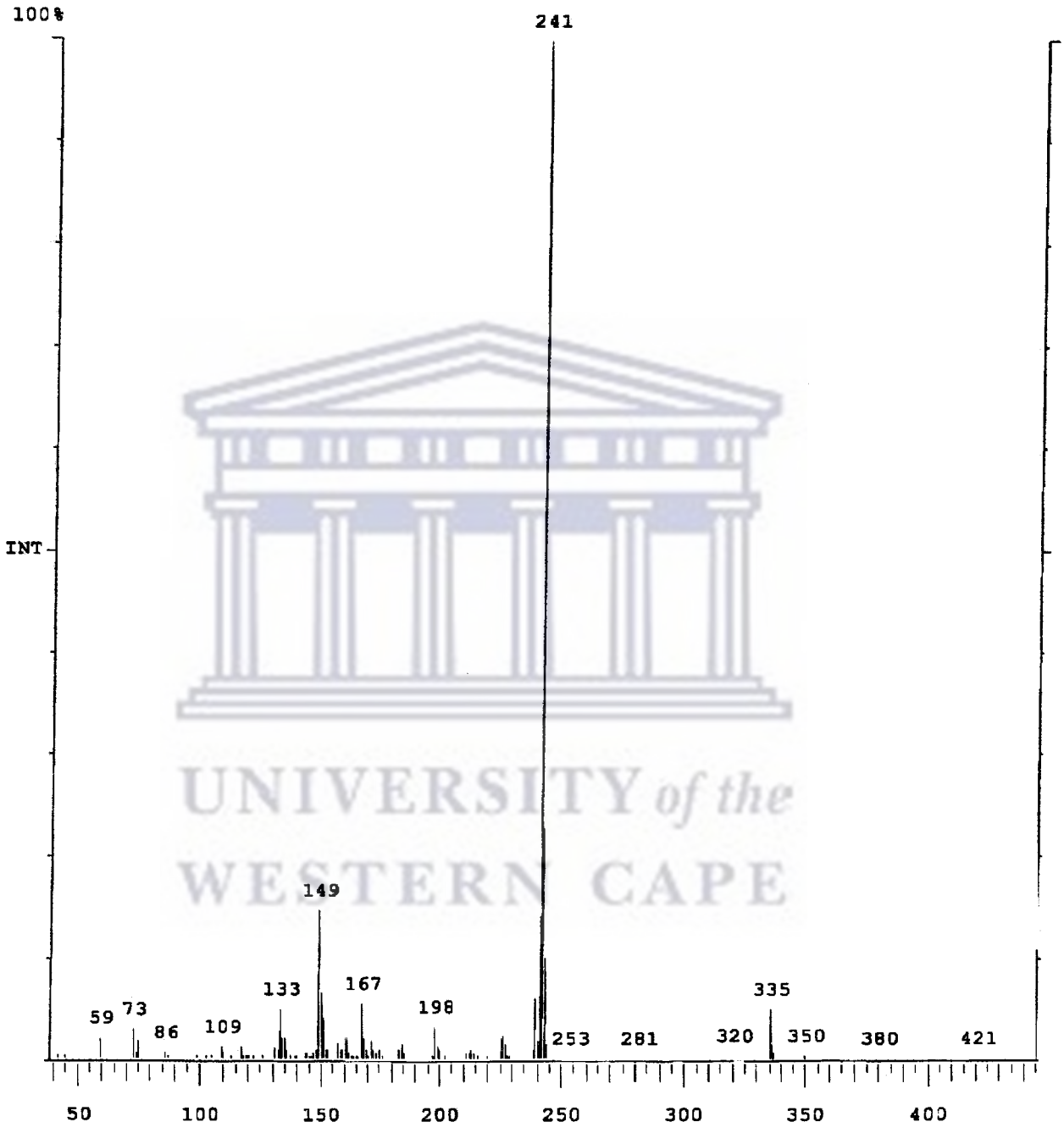
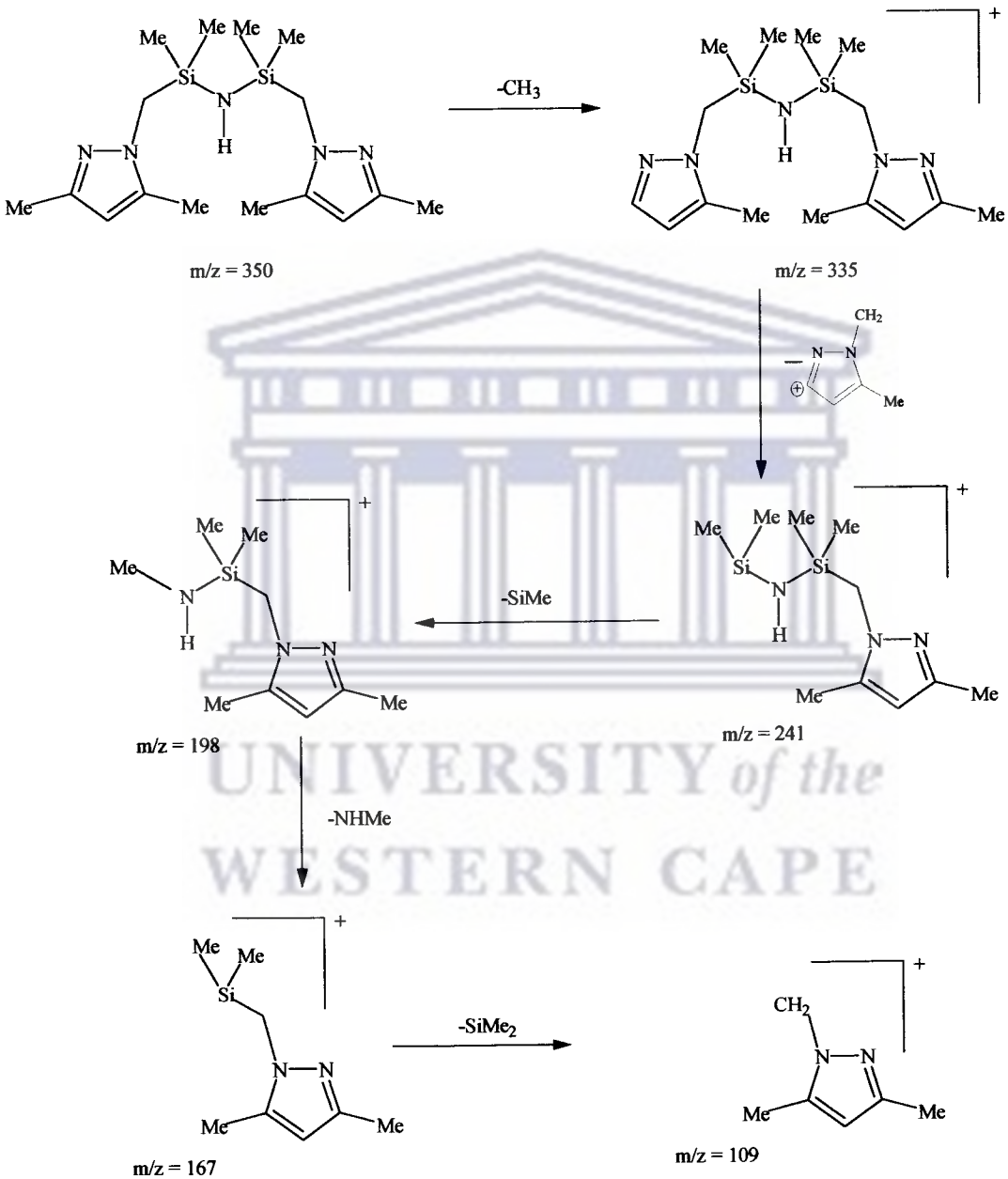


Figure 2.14: Mass spectrum of Ligand, **L6**



Scheme 6: Fragmentation pattern for ligand **L6**

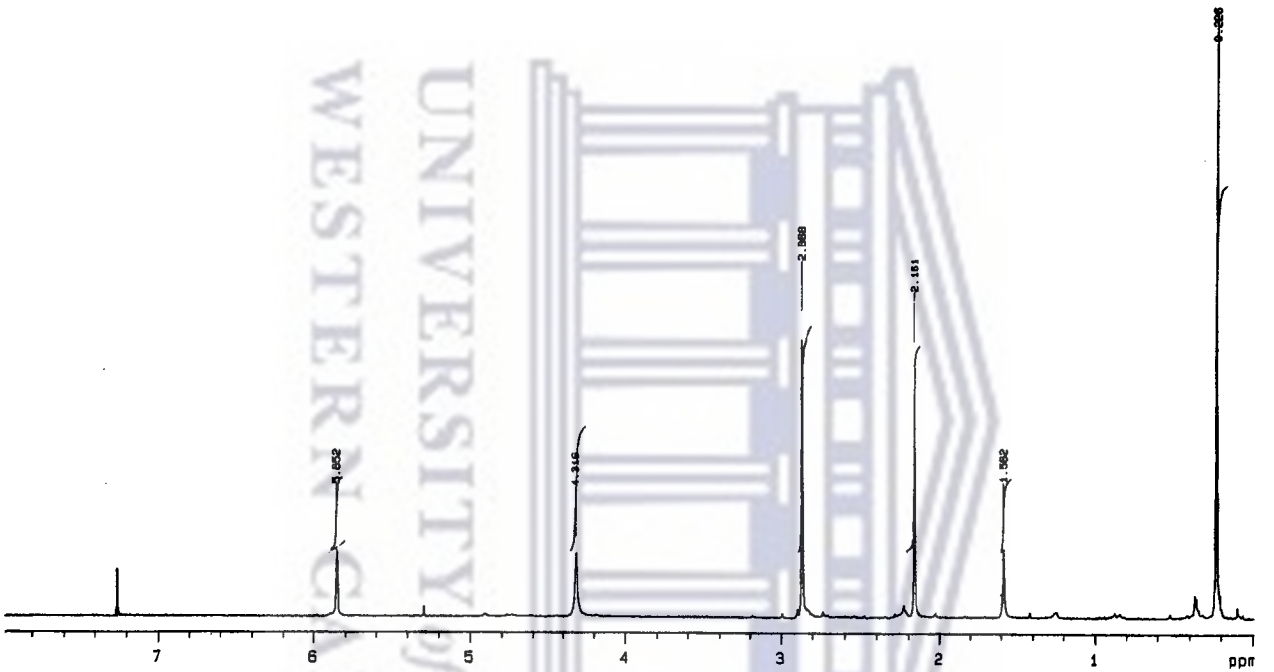
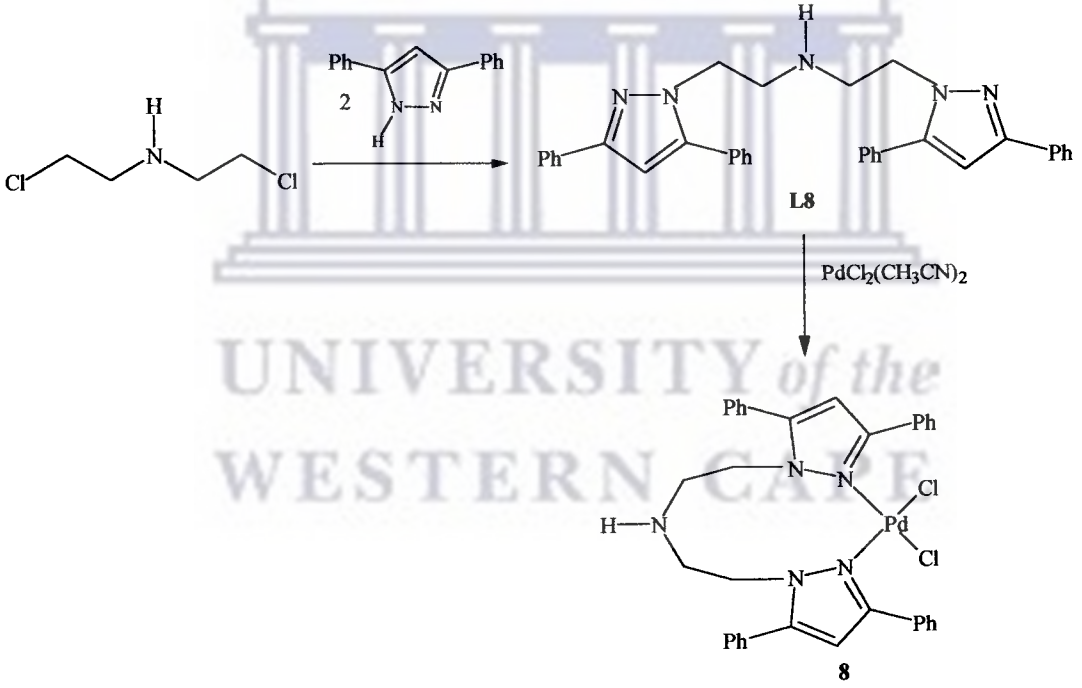


Figure 2.15: ^{1}H NMR spectrum of 1,3-Bis(3,5- dimethylpyrazolyl-1-methyl)tetramethyldisilazane Palladium(II) dichloro complex (**6**)

Compound **L8** was synthesized according to Scheme 7 from the reaction of bis(2-chloroethyl)amine hydrochloride and two equivalents of the phenylpyrazole. Attempts to prepare methyl analogues using literature procedures were unsuccessful. ^{1}H NMR spectrum of **L8** (Fig. 2.16) confirms the presence of the amine (N-H) functional group appearing as a broad peak at 4.40 ppm. Other protons of the molecule, namely the methine and phenyl protons, have all their usual characteristics. The two pyrazolyl phenyl groups appear as two sets of multiplets centred at 7.30 and 7.70 ppm in a 2:3 intensity ratio. The methine groups are observed as two triplets at 3.41 and 3.95 ppm. These NMR peaks together with elemental analysis provide analytical data to support the successful synthesis of **L8**.



Scheme 7

The reaction between **L8** and $[PdCl_2(NCMe)_2]$ in a 1:1 ratio yielded complex **8**, which, once isolated, was insoluble in common organic solvents such as CH_2Cl_2, toluene, DMSO and THF. Thus, it was characterized by elemental analysis. The insolubility of **8** is a sign that it might have dimerize to $[(L8)PdCl(\mu\text{-}Cl)]_2$.

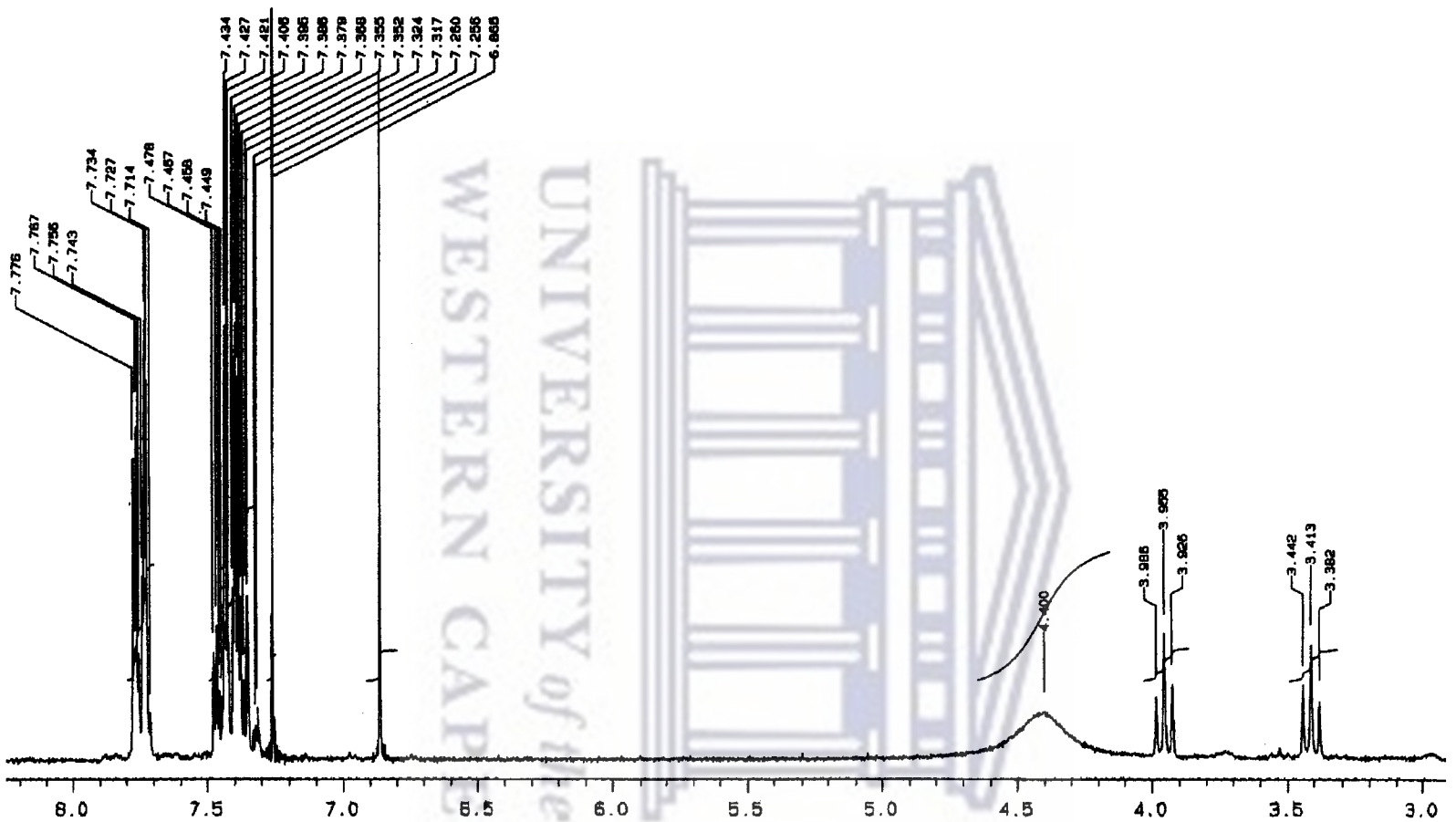


Figure 2.16: ^{1}H NMR spectrum of Bis[2-(3,5diphenylpyrazolyl)ethyl]amine (**L8**)

2.5 Conclusions

Compounds **L1-L8** were successfully prepared in low to moderate yields (16-56%) using the same methodology that has been used to prepare their 1,3-(3,5-$R_2pzC(O))_2C_6H_4$ analogues. These compounds were subsequently reacted with $[PdCl_2(NCMe)_2]$ to form mostly orange complexes in low yields. All these compounds were successfully characterized by a combination of analytical techniques such as multinuclear NMR spectroscopy, elemental analysis and in some instances single crystal X-ray analyses. The insolubility of most palladium complexes in organic solvents limits the use of other analytical techniques for their characterization.

Generally the 1,4-(3,5-$R_2pzC(O))_2C_6H_4$ complexes are found to be either sparingly soluble or completely insoluble, when compared to their 1,3-(3,5-$R_2pzC(O))_2C_6H_4$ analogues. They also display interesting contrast in colour, the latter are known to produce mostly red complexes while the former gives mostly orange complexes. Despite all these differences, present data at our disposal seem to suggest that there are similarities in the mode of bonding between the two classes of compounds.

In forming the Pd complexes (**1**–**5**) it is clear from the types of products that the bonding modes of ligands **L1**, **L2** and **L5** are different compared to other pyrazolyl ligands.[11] It has been shown by Steel *et al.*[11] and Lee *et al.*[12] that pyrazolyl units in 1,3,5-tris(pyrazolyl-1-ylmethyl)benzene form complexes that have only one metal bonded to two pyrazolyl units, contrary to what we observed in complexes **1**, **2** and **5**. Thus the bonding mode in **L1**, **L2** and **L5** to palladium is likely to be determined by two main factors, namely electron-withdrawing groups on the linkers and steric hindrance by the substituents on the pyrazolyl units. In chapter 3 we use some of these

synthesized complexes and other related complexes to generate active catalysts that have been used to study the oligomerization and polymerization of substituted acetylenes.

2.6. Experimental

2.6.1 Materials and Instrumentation

All manipulations were performed under dry, deoxygenated nitrogen atmosphere using standard Schlenk techniques. NMR spectra were recorded on a Gemini 2000 instrument (^{1}H at 200 MHz, ^{13}C at 50 MHz). The chemical shifts are reported in δ (ppm) referenced to residual protons and ^{13}C signals of deuterated chloroform as internal standard. Et_3N was dried over KOH, and toluene was dried with sodium/benzophenone, distilled and stored under a nitrogen atmosphere. 3,5-ditertbutylpyrazole[13] and 3,5-diphenylpyrazole[14] were prepared by literature procedures. All other chemicals were obtained from Aldrich and used as received. Elemental analysis was performed in-house on a Carlo Erba NA analyzer in the department of chemistry, University of the Western Cape.

2.6.2 Crystallographic structure determination

Crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.9 cm. The initial cell constants were obtained from three series of ω scans at different starting angles. The reflections were successfully indexed by an automated indexing routine built in the SMART program. These highly redundant datasets were corrected for Lorentz and polarization effects.

The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[15] The structures were solved by direct methods and refined by least-squares techniques using SHELXTL program.[16] All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighbouring atoms with relative isotropic displacement coefficients.

2.6.3 Preparation of ligands

2.6.3.1 1,4-Bis(3,5-di-*tert*-butylpyrazolyl-1-carbonyl)benzene (L1)

To a solution of terephthaloyl chloride (1.14 g, 5.62 mmol) in dry toluene (50 cm^3) was added 3,5-^{t}Bu$_2$pzH (2.03 g, 11.24 mmol). The colourless solution turned yellow upon addition of Et_3N (8 cm^3). The solution was vigorously stirred under nitrogen at room temperature for 24 h. After the specified time the mixture was filtered and the filtrate was evaporated to dryness under reduced pressure to give a yellow solid, which was purified by column chromatography using silica gel and CH_2Cl_2:Et_2O (8:1) as eluent. Yield = 1.46 g, 53%. Anal. Calc. for $C_{30}H_{42}N_4O_2$: C, 73.43; H, 8.63; N, 11.42. Found: C, 73.85; H, 10.01; N, 11.54%. ^{1}H NMR ($CDCl_3$): δ 7.93 (s, 4H, Ph); 6.20 (s, 2H, 4-pz); 1.48 (s, 18H, 5-^{t}Bu); 1.25 (s, 18H, 3-^{t}Bu).

Compounds **L2**, **L4** and **L5** were prepared using a similar procedure as described for **L1**. Starting materials and quantities are indicated for each reaction.

2.6.3.2 1,4-bis(3,5-dimethylpyrazolyl-1-carbonyl)benzene (L2)

Terephthaloyl chloride (1.14 g, 5.62 mmol) and 3,5-Me$_2$pzH (1.10 g, 11.24 mmol) were used. Yield = 0.68 g, 38%. Anal. Calc. for $C_{18}H_{18}N_4O_2$: C, 67.07; H, 5.63; N,

17.38. Found: C, 67.01; H, 5.94; N, 16.56%. ^{1}H NMR ($CDCl_3$): δ 8.05 (s, 4H, Ph); 6.07 (s, 2H, 4-pz); 2.65 (s, 6H, 5-CH_3); 2.24 (s, 6H, 3-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 167.70; 152.52; 145.13; 136.61; 130.46; 111.35; 14.28; 13.76

2.6.3.3 1,4-Bis(pyrazolyl-1-carbonyl)benzene (L3)

To a solution of terephthaloyl chloride (0.45 g, 5.62 mmol) in dry toluene (50 cm^3) was added pyrazole (pzH) (0.30 g, 11.24 mmol). Extra 40 cm^3 of toluene were added to wash the pyrazole on the sides of the Schlenk tube, then Et_3N (3 cm^3) was added and the milky solution coagulated. The coagulated solution was vigourously stirred under nitrogen at room temperature for 24 h. After the specified time the solution was filtered. The precipitate was washed with distilled water to remove the Et_3N.HCl salt and dried in air. The water insoluble solid was extracted with dichloromethane and the resulting filtrate was evaporated to dryness under reduced pressure to give analytically pure product as a white solid. Yield = 0.33 g, 56%. Anal. Calc. for $C_{14}H_{10}N_4O_2$: C, 63.15; H, 3.79; N, 21.04. Found: C, 63.33; H, 3.50; N, 20.24%. ^{1}H NMR ($CDCl_3$): δ 8.47-8.46 (d, 2H, 5-CH_3, $^2J_{HH}$ = 3); 8.24 (s, 4H, Ph); 7.83 (s, 2H, 3-CH_3) 6.57-6.55 (dd, 2H, 4-pz, $^2J_{HH}$ = 4). IR (nujol mull): ν (C=O) = 1705, cm^{-1}, ν (C=C) = 1534 cm^{-1}, ν (C=N) = 1506 cm^{-1}

2.6.3.4 1,4-Bis(3,5-diphenylpyrazolyl-1-carbonyl)benzene (L4)

Terephthaloyl chloride (0.50 g; 2.46mmol) and diphenylpyrazole (1.08 g; 4.92 mmol) were used. Yield = 0.23 g, 31%. Anal. Calc. for $C_{38}H_{26}N_4O_2$: C, 79.98; H, 4.59; N, 9.82. Found: C, 79.91; H, 4.33; N, 9.90%. ^{1}H NMR ($CDCl_3$): δ 8.24(s, 4H, Ph); 7.58-7.405(m, 16H, Ph of pz); 6.91(s, 2H, 4-pz).

2.6.3.5 1,3-Bis(3,5-diphenylpyrazolyl-1-carbonyl)benzene (L5)

Isophthaloyl dichloride (0.50 g; 2.46 mmol) in dry toluene (30 cm^3) and diphenylpyrazole (1.08g; 4.92 mmol) were used. Yield = 0.64 g, 46%. Anal. Calc. for $C_{38}H_{26}N_4O_2$: C, 79.98; H, 4.59; N, 9.82. Found: C, 79.96; H, 4.57; N, 9.65%. ^1H NMR ($CDCl_3$): δ 8.95(s, 1H, Ph); 8.44-8.39 (dd, 2H, Ph, $^2J_{HH}$ = 10); 7.69 (t, 1H, Ph); 7.53-7.38 (m, 20H, Ph on pz); 6.90(s, 2H, 4-pz).

2.6.3.6 1,3-Bis(3,5-dimethylpyrazolyl-1-methyl)tetramethyldisilazane (L6)

To a solution of 3,5–Me_2PzH (2.20 g, 22.95 mmol) in dry toluene (100 cm^3) was added Et_3N (15 cm^3) and 1,3-bis(chloromethyl)tetramethyldisilazane (2.64 g, 11.45 mmol, 2.5 cm^3). The colourless solution was vigourously stirred under reflux at 90 °C for 72 h. After the specified time the solution was found to have turned red, with a large amount of precipitate on the sides of the Schlenk tube. The solution was left to cool to room temperature and then filtered. The filtrate was evaporated under reduced pressure to give a red oily material, which solidified upon standing at room temperature overnight. The crude product was purified by column chromatography and eluted using a mixture of diethyl ether:dichloromethane:hexane (1:1:3). Yield = 1.78 g, 44%. Anal. Calc. for $C_{16}H_{31}N_5Si_2$: C, 54.97; H, 8.94; N, 20.03. Found: C, 53.92; H, 8.63; N, 14.81%. ^1H NMR ($CDCl_3$): δ 5.74 (s, 2H, 4-pyrazole); 3.44 (s, 4H, $-CH_2-$); 2.17 (s, 12H, 3- & 5-CH_3); 0.15 (s, 12H, Si – CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 145.9; 138.4; 104.1; 40.5; 13.3; 11.3; 0.1. IR (nujol mull): ν (N-H) = 3417 cm^{-1}, ν (C=C) = 1580 cm^{-1}, ν (C=N) = 1549 cm^{-1}.

2.6.3.7 Synthesis of 1,3-Bis(3,5-di-*tert*-butylpyrazolyl-1-methyl) tetramethyl disiloxane (L7)

To a solution of 3,5 – $^{t}Bu_2pzH$ (0.40 g, 2.22 mmol) in dry toluene (40 cm^3) was added NEt_3 (3 cm^3) and 1,3 Bis(chloromethyl)tetramethyldisiloxane (0.26g, 1.11 mmol, 0.244 cm^3). The colourless solution was vigourously stirred under reflux at 100 °C for 72 h. After 72 h the solution was found to have turned yellow. The solution was left to cool to room temperature and then filtered. The filtrate was evaporated under reduced pressure to give wet brown solid that was kept under vacuum. Yield = 1.98 g, 43%. ^1H NMR ($CDCl_3$): δ 5.91 (s, 2H, 4-pyrazole); 2.75 (s, 4H, -CH_2-); 1.33 (s, 36H, 3- & 5-^{t}Bu); 0.23 (s, 12H, Si – CH_3).

2.6.3.8 Synthesis of Bis{2-(3,5-diphenylpyrazolyl)ethyl}amine (L8)

To a solution of 3,5-diphenylpyrazole (0.54 g; 5.60 mmol) bis(chloroethyl)amine hydrochloride (0.50 g; 2.80 mmol) in dry toluene was added Et_3N (2 cm^3). The solution was heated to 70 °C and stirred at that temperature for 18 h. It was then filtered and filtrate evaporated to give a pale yellow solid. The solid was recrystallized from $CHCl_2$ and hexane at -15 °C to afford a peach solid. Yield = 0.23 g, 16.%. Anal. Calc. for $C_{35}H_{33}N_5Cl$: C, 70.70; H, 5.59; N, 11.77. Found: C, 70.38; H, 5.63; N, 11.90%. ^1H NMR ($CDCl_3$): δ 7.78-7.71 (m, 8H, Ph); 7.48-7.716 (m, 12H, Ph); 5.87 (s, 2H, 4H-pz); 4.40 (s, 1H, NH); 3.96 (t, 4H, -CH_2-, $^2J_{HH}$ = 5.8); 3.41 (t, 4H, -CH_2-, $^2J_{HH}$ = 5.8).

2.6.4 Preparation of complexes

2.6.4.1 Di-μ-chloro-dichloro{1,4-bis(3,5-di-*tert*-butylpyrazolyl-1-carbonyl)-benzene}dipalladium(II) (1)

To **L1** (1.25 g, 2.55 mmol) and $[PdCl_2(NCMe)_2]$ (0.66 g, 2.55 mmol) was added dry dichloromethane (70 cm^3). The resulting dark red solution was stirred at room temperature under nitrogen for 18 h, turning yellow with formation of a small amount of precipitate. The reaction mixture was filtered and the filtrate was evaporated to dryness to give an orange solid. Yield = 0.84 g; 20%. Anal. Calc. for $C_{60}H_{84}N_8O_4Pd_4Cl_8$: C, 42.63; H, 5.01; N, 6.63. Found: C, 42.70; H, 5.10; N, 6.46%.

2.6.4.2 Di-μ-chloro-dichloro{1,4-bis(3,5-dimethylpyrazolyl-1-carbonyl)-benzene}dipalladium(II) (2)

Complex **2** was prepared following the procedure for **1** above but using **L2**. Yield = 0.48 g; 19.5%. ^1H NMR ($CDCl_3$): δ 8.13 (s, 4H, phenyl); 6.16 (s, 2H, 4-pyrazole); 2.74 (s, 6H, 5-CH_3); 2.33 (s, 6H, 3-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 167.67; 152.48; 145.13; 136.55; 130.42; 14.28; 13.76

2.6.4.3 Dichloro{1,4-bis(pyrazolyl-1-carbonyl)benzene}dipalladium(II) (3)

Complex **3** was prepared following the procedure for **1** above but using **L3.** Yield = 0.40 g; 60%. Anal. Calc. for $C_{28}H_{20}N_8O_4Pd_2Cl_4$: C, 37.91; H, 2.27; N, 12.63. Found: C, 36.98; H, 2.40; N, 12.35%. IR (nujol mull): ν (C=O) = 1721,1691 cm^{-1}, ν (C=C) = 1564 cm^{-1}, ν (C=N) = 1509 cm^{-1}.

2.6.4.4 Di-μ-chloro-dichloro{1,4-bis(3,5-diphenylpyrazolyl-1-carbonyl)-benzene}dipalladium(II) (4)

Complex **4** was prepared following the procedure for **1** above but using **L4**. Yield = 0.07 g, 13%. Anal. Calc. for $C_{76}H_{52}N_8O_4PdCl_2$: C, 69.23; H, 3.97; N, 8.50. Found: C, 69.55; H, 3.91; N, 8.55%.

2.6.4.5 Di-μ-chloro-dichloro{1,3-bis(3,5-dipheylpyrazolyl-1-carbonyl)benzene} dipalladium(II) (5)

Complex **3** was prepared following the procedure for **1** above but using **L5.** Yield = 0.40 g, 53.3%. Anal. Calc. for $C_{40}H_{30}Cl_8N_4O_2Pd_2$: C, 47.06; H, 2.91; N, 5.78. Found: C, 47.79; H, 2.46; N, 5.78%. ^{1}H NMR ($CDCl_3$): 9.10-9.08 (dd, 2H, Ph, $^2J_{HH}$ = 4); 8.38-8.37 (m, 5H, Ph of pz); 8.31 (s, 1H, Ph); 7.62 (s, 6H, Ph of pz); 7.49 (s, 10H, Ph of pz); 6.79 (s, 2H, 4H- pz).

2.6.4.6 Synthesis of 1,3-bis(3,5-dimethylpyrazolyl-1-methyl)tetramethyl disilazane-palladium(II) dichloro complex (6)

To ligand **L6** (0.39 g, 1.16 mmol) and $[PdCl_2(NCMe)_2]$ (0.29 g, 1.16 mmol) was added dry dichloromethane (30 cm^3). The resulting orange solution was stirred at room temperature under nitrogen for 3 h. The solution was concentrated to ~5 cm^3 and slowly layered with hexane. The pure product was allowed to precipitate for 1h. Yield = 0.17 g; 22%. Anal. Calc. for $C_{16}H_{31}Cl_2N_5PdSi_2$: C, 36.47; H, 5.93; N, 13.29. Found: C, 37.13; H, 5.73; N, 10.13%. ^{1}H NMR ($CDCl_3$): δ 5.85 (s, 2H, 4-pyrazole); 4.32 (s, 4H, -CH_2-); 2.87 (s, 6H, 5-CH_3); 2.16 (s, 6H, 3-CH_3); 0.23 (s, 12H, Si – CH_3). IR (nujol mull): ν (N-H) = 3188 cm^{-1}, ν (C=C) = 1576 cm^{-1}, ν (C=N) = 1550 cm^{-1}.

2.6.4.7 Bis{2-(3,5-diphenylpyrazolyl)ethyl}aminepalladium(II) (8)

To **L8** (0.10 g; 0.20 mmol) and $[PdCl_2(NCMe)_2]$ (0.05 g; 0.20 mmol) was added dry CH_2Cl_2 (20mL). The reaction turned yellow with formation of a precipitate. The reaction mixture was filtered to isolate a yellow solid. Yield = 0.13 g, 81%. Anal. Calc. for $C_{34}H_{31}N_5PdCl_2.CH_2Cl_2$: C, 54.45; H, 4.31; N, 9.07. Found: C, 54.45; H, 3.94; N, 9.08%.

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CHAPTER 3

POLYMERZATION AND OLIGOMERIZATION OF PHENYLACETYLENE AND OTHER SUBSTITUTED ACETYLENES BY CATIONIC PALLADIUM COMPLEXES AS CATALYSTS

3.1 Introduction

Since the first *trans-cisoidal* poly(phenylacetylene) was described by Natta *et al.*,[1] poly(phenylacetylene) has continued to attract considerable interest. Later developments showed that poly(phenylacetylene) has four different isomers. These isomers were first described by Kern,[2] Berlin *et al.*, [3] and Simionescu *et al.*[4] Different methodologies have been used to obtain isomers of poly(phenylacetylene). These include radical[5,6] and cationic[7,8] polymerization, and the classical metathesis catalysts WCl_6 and $MoCl_5$.[9] It has recently been reported that polycondensation of phenylacetaldehyde is an efficient methodology in preparing *trans-cisoidal* poly(phenylacetylene).[10]

One of the interesting current developments in phenylacetylene polymerization is the work done by Tang *et al.*[11] on liquid-crystalline acetylene monomers. To design the molecular structures of the liquid-crystalline acetylene monomers they inevitably had to use functional groups to glue together the building blocks of mesogens, spacers, tails, triple bonds, and so forth. Introduction of these functional groups, however, made the polymer synthesis difficult given the fact that only few catalyst systems for acetylene polymerizations were known to be functionality tolerant at the time Tang *et al.*[11] started their research. Some Rhodium based catalysts such as $[Rh(nbd)Cl]_2$ are tolerant to functional groups but are generally only effective for the polymerization of phenylacetylene derivatives.[12,13]

Although classical metathesis catalysts such as WCl_6 and $MoCl_5$ can initiate the ring-closing polymerizations of functional diacetylenes or diynes (e.g., 1,6-heptadiynes) to give cyclic poly(acetylenes),[14a,b] attempts by other groups using W and Mo based catalysts to synthesize linear poly(acetylenes) from functional (mono)acetylenes or monoynes have been unsuccessful and resulted in insoluble or oligomeric products in low yields.[15-22] This pioneering work started with the development of new functionality-tolerant catalysts with the general formulae of $M(CO)_xL_y$ (where M is W or Mo and L is a ligand)[23] and Rh(diene)LL',[24] some of which can work even in tap water and in air.

The Mo-based catalysts can polymerize not only the monosubstituted acetylenes but also certain types of disubstituted ones such as *n*-alkynes, 2-alkynates, and alkyl 3-arylpropiolates. The W-based catalysts are also good for the polymerizations of the monosubstituted acetylenes and can also polymerize disubstituted acetylenes such as 1-phenyl-1- alkynes, diarylacetylenes, *n*-alkynes, and aryl 3-arylpropiolates. The high activities of some of the catalyst systems are manifested by the high polymer yields ~ 90% and high molecular weights of the polymers weight-average molecular weights (*M*w's) up to and greater than 1×10^6 Da.

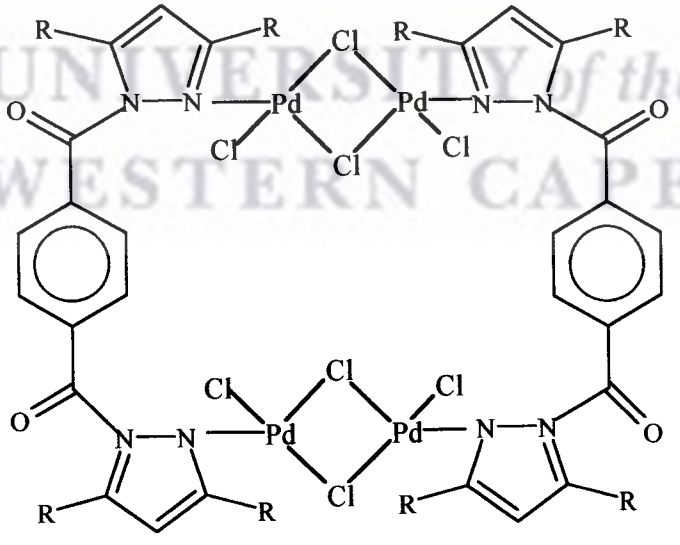
Using appropriate monomer–catalyst combinations, it is now possible to synthesize functional poly(acetylenes) from monosubstituted and disubstituted acetylenes containing all kinds of polar moieties: ester, sterol, carbazole, siloxane, and silole among others.[25]

It should be stressed that success in the development of liquid crystal poly(acetylenes) was achieved not only by molecular engineering but also through catalysts development. It was

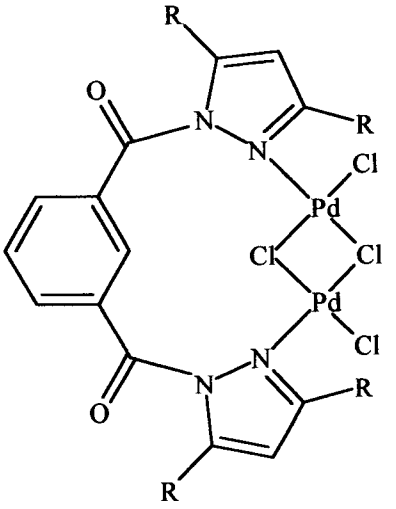
through the optimization of polymerization conditions that a broad utility of the old metal-halide catalyst systems based on $MoCl_5$ and WCl_6 for the polymerizations of functional acetylenes was achieved. Catalysts development has therefore been very crucial in forming new poly(acetylenes). This chapter describes our attempt to use pyrazolyl palladium complexes as catalysts for substituted acetylene monomers.

3.2 Results and Discussion

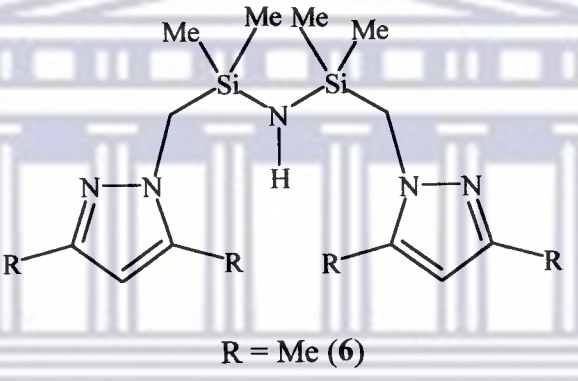
Selected complexes synthesized in chapter 2 of this thesis (Fig. 3.1) were used as catalysts precursors for the polymerization of substituted acetylenes. Polymerization reactions were performed as illustrated in Scheme 1. The effect of polymerization parameters, such as solvent type, solvent mixtures ratios and temperature, were investigated. The most extensively used substituted acetylene in this study is phenylacetylene as would be seen in the discussion below.



R = ^{t}Bu (**1**)

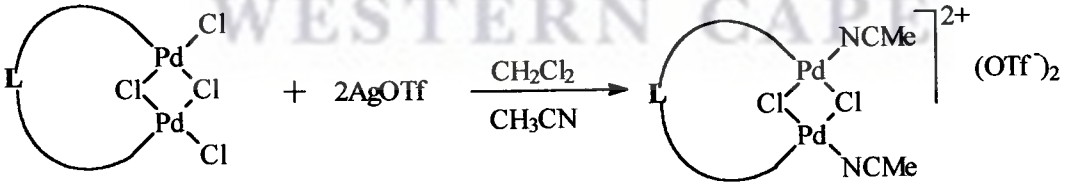


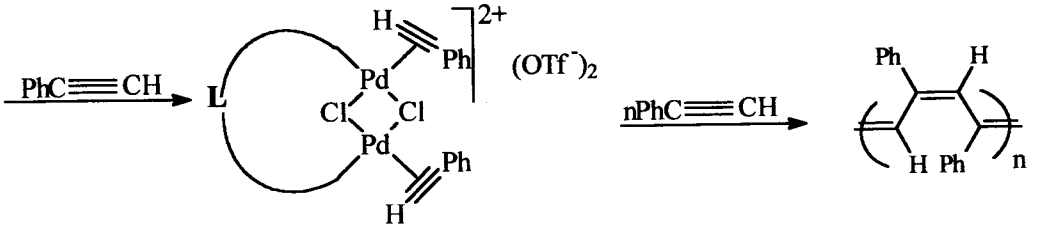
R = Ph (**5a**); ^{t}Bu = (**5b**); Me = (**5c**)



R = Me (**6**)

Figure 3.1: Selected complexes used as catalyst precursors for generating active acetylene polymerisation catalysts.





Scheme 1: Schematic representation of polymerization process

In preparing the active catalysts, the first step preceeding polymerization, involved the abstraction of two chlorides by silver triflate dissolved in a mixture of CH_2Cl_2/CH_3CN. In the generated catalyst the chlorides anions are replaced by a weakly coordinating acetonitrile solvent molecules, which can easily be displaced by phenylacetylene. This leads to the generation of our catalyst *in situ*. Different solvent mixtures were obtained by varying $CH_2Cl_2\backslash CH_3CN$ ratio. For example a final composition of 5:1 was obtained by adding 20 cm^3 of $CH_2Cl_2\backslash CH_3CN$ (2:1) to any of the complexes dissolved in 20 cm^3 of dichloromethane, taking the total volume of solvent used in all such reactions to $40cm^3$. Acetonitrile plays a dual role in preparing the catalyst. First it is used to solubilise silver triflate, in which it is readily dissolved; and secondly it stabilizes the catalyst formed *in situ* by occupying the free coordination sites. In reactions where neat solvents used were unable to dissolve silver triflate, the active catalyst was prepared using a mixture of CH_2Cl_2 and CH_3CN. The solvent mixture was then evaporated *in vacuo* and then the desired solvent was added in appropriate quantity. Upon addition of substituted acetylene monomer, the coordinated acetonitrile was easily displaced by the monomer. In all cases the dark red solids, which represent the combined yield of both polymers and oligomers, were obtained in high yields. The polymers obtained from the polymerization reactions are soluble in dichloromethane but insoluble in methanol and readily precipitated from it while oligomers are soluble in methanol and were generally obtained by evaporation of methanol filtrates.

Generally the point at which one refers to a homologous series as an oligomer as opposed to a polymer has been controversial. In fact, different authors have designated values of 20 monomer units, 1000, 6000, or 10 000 Da, as the oligomer/polymer distinction point.[26] The reasons for such demarcations are synthesis or property related. However, data obtained showed that all the polymers produced in this study are methanol insoluble fractions whose

molecular weights are greater than 900 Da. The methanol soluble fractions are in fact, oligomers with average degree of polymerization of between 4 and 7. It seems that if the average DP is 9 or greater, the material becomes methanol insoluble. It was also found that spectra of insoluble and ~~in~~soluble fractions are nearly identical to each other confirming that the methanol solubility differences of the two fractions are due to differences in molecular weight.

When polymers were left in solution over long periods we observed degradation. Percec *et al.*[27] carefully investigated the degradation processes of poly(phenylacetylene) and found that the intramolecular cyclization of the polymer results in conformational isomerization and that its subsequent chain cleavage produces 1,3,5-triphenylbenzene. The intramolecular cyclization is accelerated by the presence of air, particularly when the reaction takes place in solution. Therefore exposures of polymer solutions to air were minimized to avoid conversion to trisubstituted benzene derivatives.

3.2.1 Characterization of polymers

3.2.1.1 Stereochemistry determinations using ^{1}H and ^{13}C NMR spectroscopy

NMR spectroscopy is one of the best analytical tools to characterize the type of polymers obtained. Hence it was the main characterization method used in this study. The ^{1}H NMR spectra of polymers obtained showed a sharp singlet due to the vinylic protons in the polymer at 5.85 ppm in addition to a set of broad peaks at 6.64 (2H, ortho) and 6.95 ppm (3H, meta and para) (Fig. 3.2a). These peaks are associated with the regular head to tail structure of *a cis-transoidal* poly(phenylacetylene) structure.

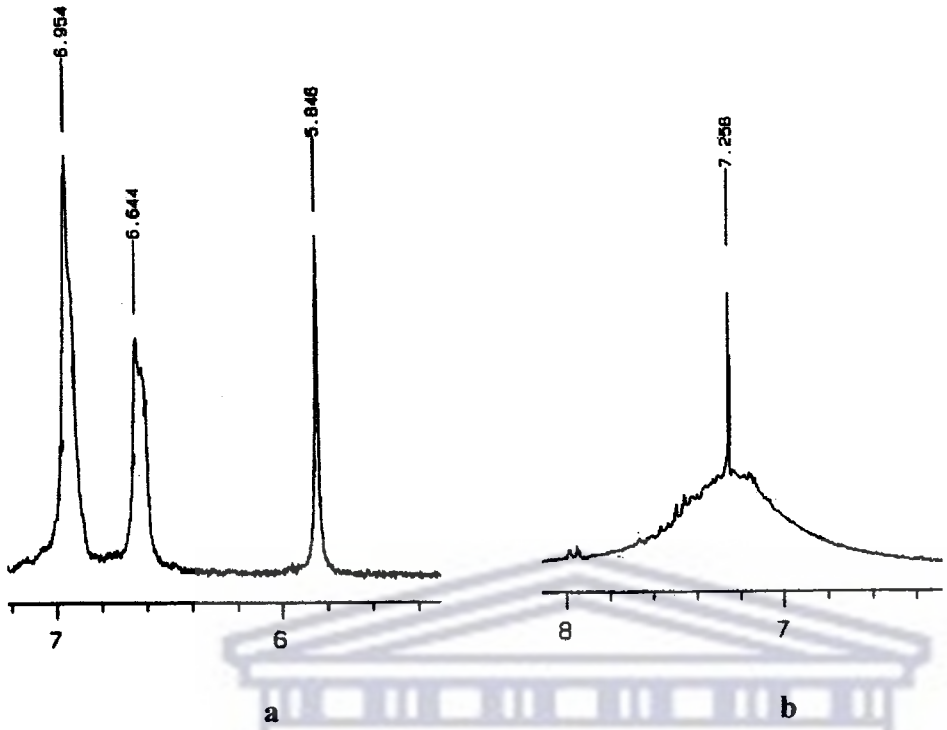


Figure 3.2: ^{1}H NMR spectra of (a) cis- and (b) trans-poly(phenylacetylene).

The ^{1}H NMR spectrum (Fig. 3.2a) is typical of polymers obtained in neat solvents using **6** as catalyst. The polymers were further characterized by ^{13}C NMR spectroscopy, which also gave some information regarding the structure of the polymer. It gave six peaks as anticipated (Fig. 3.3); the main peaks being the two signals at 132 and 139 ppm for the chain carbons C_1 and C_2 as indicated in the Figure 3.4. On the other hand when **5b** and **1** were used to generate the active catalysts, the polymers obtained gave a broad ^{1}H NMR signal centred at 7 ppm (Fig. 3.2b) and broad ^{13}C NMR peaks in the range 125-131 ppm and centred at 127.3 ppm, typical of *trans-cisoidal* poly(phenylacetylene).

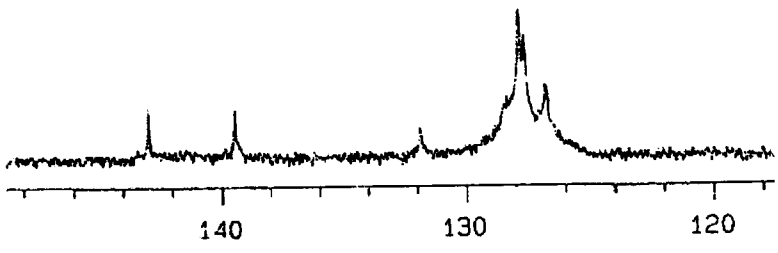


Figure 3.3: ^{13}C NMR spectrum of *cis-transoidal* poly(phenylacetylene)

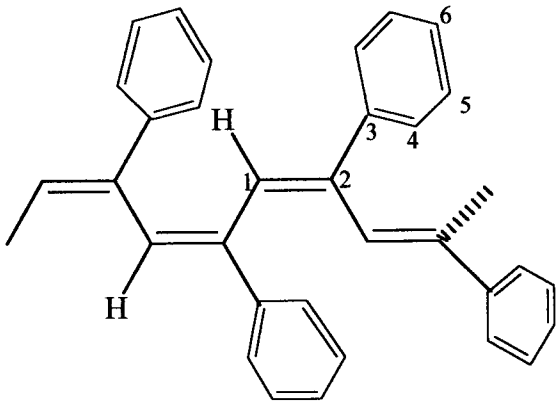


Figure 3.4: The six resonating carbons on the polymer chain

Interestingly, when polymerization reactions were performed in solvent mixtures all catalysts produced a mixture of *cis-transoidal* and *trans-cisoidal* poly(phenylacetylene); but the dominant isomer was always *cis-transoidal* poly(phenylacetylene). Typical ^{1}H and ^{13}C NMR spectra for the polymer mixtures isolated are shown in Figure 3.5. This suggests that the mechanism of polymerization involves a 1,2 insertion as opposed to a 2,1 insertion of the phenylacetylene to produce *cis-transoidal* poly(phenylacetylene) and that the formation of *trans-cisoidal* poly(phenylacetylene) is likely to be the result of isomerization when the initial *cis-transoidal* polymer is formed in solution. Marigo *et al.*[28] have proposed that alkyne insertion to produce mixtures of *cis-transoidal* or *trans-cisoidals* poly(phenylacetylene) stereochemistry depend on the reaction temperature. It is difficult to see how temperature could be responsible for consistently producing predominantly one isomer irrespective of the solvent mixture ratios and temperature. A 1,2-insertion is supported by observation by Mastrorilli *et al.*[29] that pure *cis-transoidal* poly(phenylacetylene) degrades to a nearly 50:50 mixture of *cis-transoidal* and *trans-cisoidal* isomers over time.

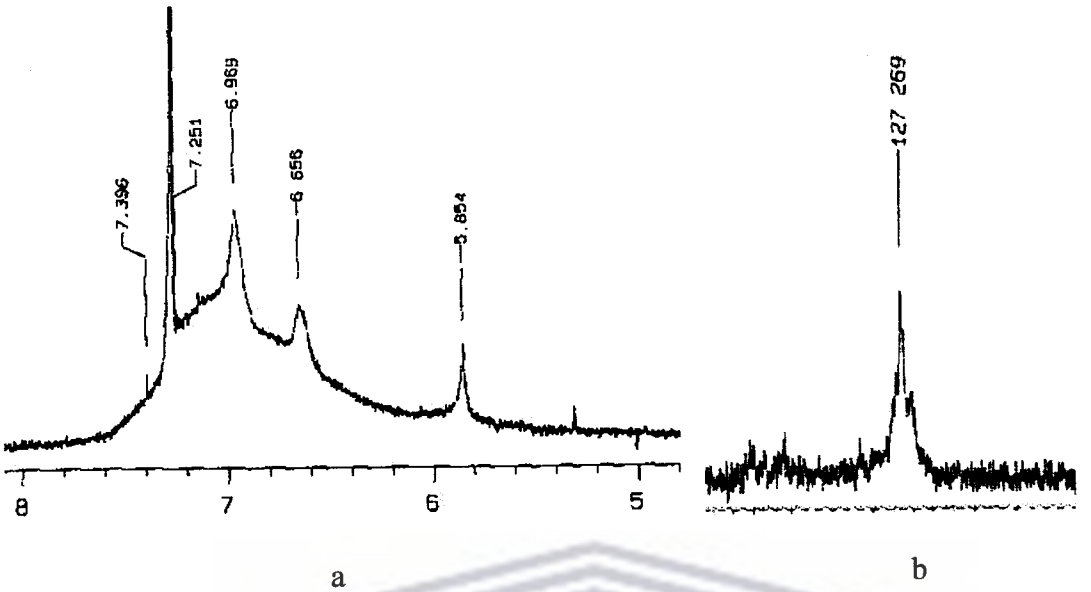


Figure 3.5: (a) ^{1}H NMR and (b) ^{13}C NMR spectra of a mixture of *cis-transoidal* and *trans-cisoidal* poly(phenylacetylene).

In general colours of polymers isolated varied from reddish brown to yellow. Polymers are soluble in common organic solvents such as toluene, dichloromethane and acetone. The yellow polymers were found to be *cis-transoidal* poly(phenylacetylene). The brown polymers were mostly *trans-cisoidal* poly(phenylacetylene) while the reddish brown polymers were mixtures. The colour of a polymer thus gave a hint of the isomeric forms of poly(phenylacetylene) isolated. The polymers are also stable in air. Their stability is due to the tri-substituted C=C bonds, which are less reactive than their double-substituted counterparts. The presence of substituents along the polymer chain leads to steric hindrance and this determines deviations from a planar structure that decreases π electron delocalization. The loss of such delocalization has many consequences, such as a variation in the colour; for example polyacetylene is known to be dark grey and poly-*t*-butylacetylene is white.

3.2.1.2 Determination of poly(phenylacetylene) stereochemistry by IR spectroscopy

Infrared spectroscopy is another analytical technique that has been used to determine the stereochemistry of poly(phenylacetylene). The diagnostic feature of this technique is stretching frequency of the double bonds in the polymer backbone. The absorbances due to stretching frequencies of polyconjugated double bonds are observed at around 1591 cm^{-1}. Additional absorbances are observed at 691 cm^{-1} and 754 cm^{-1}, which are characteristic of the C-H out of plane deformation of a monosubstituted benzene ring. The above set of peaks are characteristic of both *cis-transoidal* and *trans-cisoidal* poly(phenylacetylene) and thus difficult to use in distinguishing between the two isomers. However, peaks at 870 - 895cm^{-1} are characteristic of *cis-transoidal* poly(phenylacetylene) while those at 910 - 920cm^{-1} are specific to *trans-cisoidal* poly(phenylacetylene). Additionally most spectra show weak absorbances in the range 1250 - 1270cm^{-1}. These absorbances are also specific to *trans-cisoidal* poly(phenylacetylene). It has been demonstrated both experimentally and theoretically that the absorption at 740cm^{-1} is specific to the cis isomer in polyacetylenes.[18]

Figure 3.6 is a typical spectrum of products from phenylacetylene reactions from methanol soluble and insoluble fractions. The spectrum has peaks that are characteristic of both *cis* and *trans* isomers discussed above. Therefore both the methanol soluble and insoluble fractions are considered to be linear polymers with a conjugated polyene structure since they gave the same spectra. Their spectra also reveal three peaks in the 840 - 920cm^{-1} range, which are due to stereochemical features in poly(phenylacetylene).

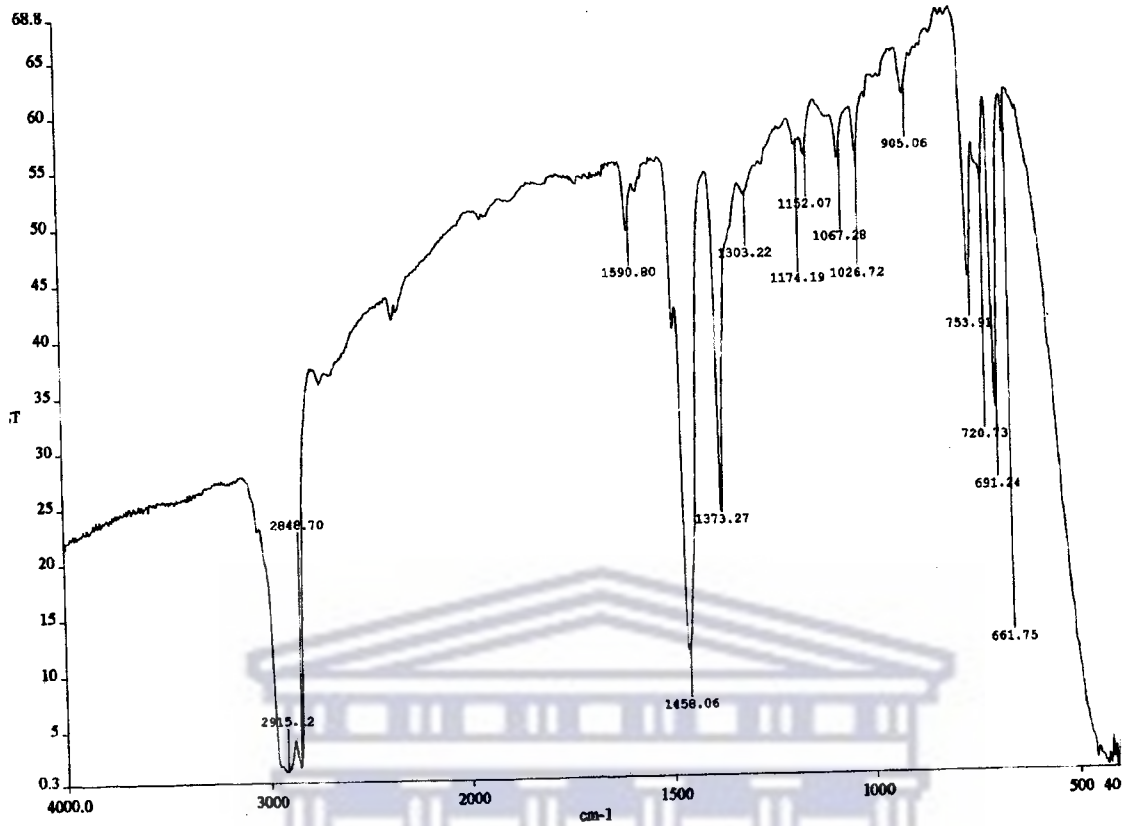


Figure 3.6: IR spectrum of a polymer isolated from a reaction run in a mixture of CH_2Cl_2:CH_3CN

3.2.2 Optimization studies

Activities of the catalysts tested strongly depend on the solvent used. The effect of solvent on conversion of phenylacetylene, selectivity, molecular weight and structure of polymer was examined in different mixtures of CH_2Cl_2 and CH_3CN, and neat solvents such as CH_3CN, toluene, Et_2O and THF. The polymerization reaction of phenylacetylene was never 100% selective in the catalyst systems tested. It was always accompanied by oligomerization reaction. The results of these reactions are presented below.

3.2.2.1 Polymerization of phenylacetylene using 6

Table 3.1 shows the results of polymerisation reactions carried out with catalyst precursor **6**. Figure 3.7 is a plot of the effect of solvent ratio on molecular weight from the data in Table 3.1, which suggests that higher CH_2Cl_2:CH_3CN ratios favoured high percentage conversions. On the contrary, lower CH_2Cl_2:CH_3CN ratios favour high molecular weights. This was found to be true with the only exception being entry 2, which gave a molecular weight of 4077. The highest molecular weight polymer was obtained when equal amounts of CH_2Cl_2 and CH_3CN were used (entry 1).

Table 3.1: Polymerization of phenylacetylene catalyzed by **6** in mixture of solvents

Entry	Solvent	%Conv.	M_w[a]	M_n[a]	M_w/M_n[a]
1	1:1	16.80	6962	2189	3.18
2	3:1	6.72	4077	1213	3.36
3	5:1	47.00	6002	1099	5.46
4	7:1	47.00	5521	1747	3.16

All reactions were run for 6 h in mixtures of CH_2Cl_2/CH_3CN; [Pd] = 2.92×10^{-3} mol/L; Pd/PA = 1:50; temperature = 25 °C; [a]determined by GPC.

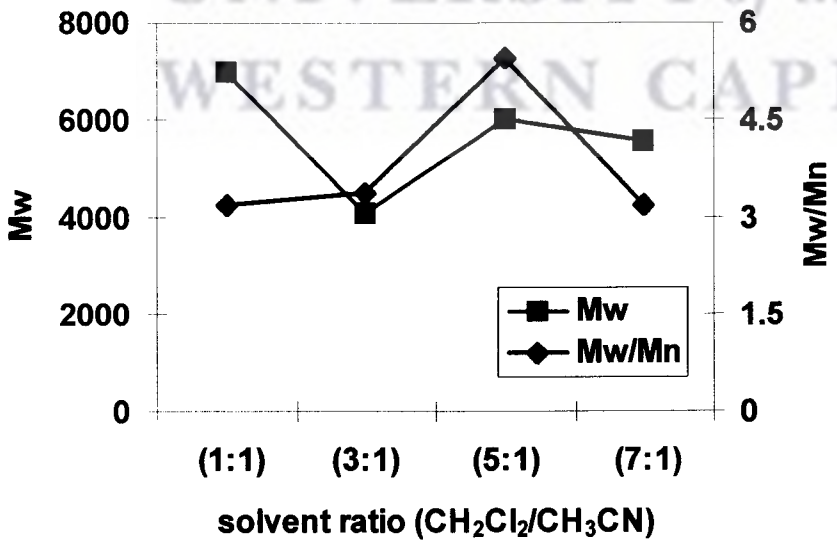


Figure 3.7: Effect of solvent mixtures on polymer molecular weight and polydispersity.

The polydispersity indices in all cases were around 3, with the exception being entry 3. From these results it was concluded that the role of CH_2Cl_2 was merely to help to solubilize the active species and hence improve the overall percentage conversion of the monomer into oligomers and subsequently polymers. The active catalysts were stabilized by coordination of the vacant sites by CH_3CN. As such higher concentrations of CH_3CN were required in the solvent mixture to obtain poly(phenylacetylene) of reasonable molecular weight, this finding suggests that using neat CH_3CN as polymerization solvent could help to improve polymer molecular weights. When the effects of neat solvents on polymerization were investigated, it was found that neat polar solvents gave lower percentage conversions compared to mixture of solvents. However, the polymer molecular weights were higher in neat solvents than in the CH_2Cl_2/CH_3CN mixtures (Table 3.2). Although, the best monomer conversions were obtained with THF, CH_3CN gave the highest polymer molecular weight as predicted.

Table 3.2: Polymerization of phenylacetylene catalyzed by **6** in different solvents.

Entry	Temp.	Solvent	%Conv.	M_w[a]	M_n[a]	M_w/M_n[a]
1	r.t	THF	36.0	7974	2484	3.21
2	r.t	MeCN	24.0	8901	2220	4.01
3	r.t	Et_2O	24.0	5169	1705	3.03
4	r.t	Toluene	18.0	-	-	-

All reactions were run for 6h in mixtures of CH_2Cl_2:CH_3CN unless indicated otherwise [Pd] = 2.92×10^{-3} mol/L; Pd/PA = 1:50 , [a] determined by GPC.

THF gave the second highest molecular weight of 7974 while the non-coordinating solvent ether gave poly(phenylacetylene) with molecular weights lower than those obtained from most solvent mixtures. The other non-coordinating solvent, toluene, was found to give only oligomers whose molecular weights were below 900 as determined by mass spectroscopy. The polydispersity indices were directly proportional to molecular weight as they increased

increased with an increase in molecular weight and vice versa. These polydispersity indexes range was similar to that obtained from solvent mixtures.

It was also observed that while polymerization rate increased at temperatures higher than room temperature the catalyst deactivated rapidly as the temperature increased. At lower temperature (0°C) catalyst deactivation was reduced drastically (Fig. 3.8) and higher molecular weight polymers, M_w = 12043, M_w/M_n = 1.71 (entry1) having narrow molecular distribution were formed (Table 3.3). These results suggest that at room temperature polymerization is not favoured. Low temperatures allow monomer insertion into growing polymer chain and chain termination is reduced hence high molecular weight polymers were obtained. Figure 3.9 depicts the effect of temperature on polymer molecular weight. The higher molecular weight polymers obtained at high temperatures were unexpected, in fact, according to Percec, an increase in reaction temperature facilitates the termination reactions of poly(phenylacetylene) .[30] Thus low molecular weight PPA would be expected.

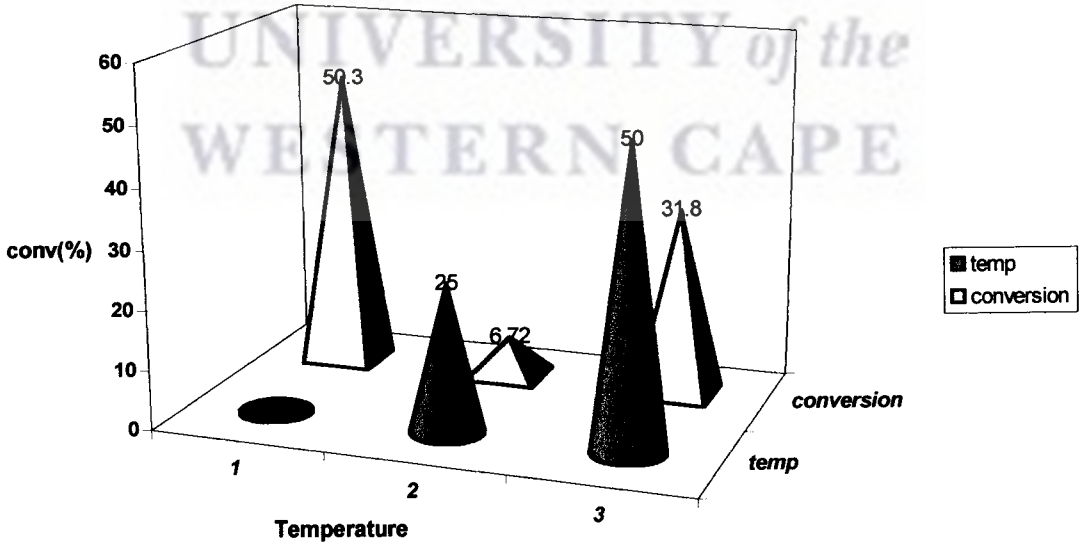


Figure 3.8: The effect of temperature on monomer conversion.

Table 3.3: Polymerization of phenylacetylene catalyzed by **6** at different temperatures.

Entry	Temp. (°C)	Solvent	%Conv.	M_w[a]	M_n[a]	M_w/M_n[a]
1	0	3:1	50.3	12043	7043	1.71
2	50	3:1	31.8	6396	2190	2.92
3	0	7:1	58	7742	1950	3.70
4	0	MeCN	50	8779	2140	4.10

All reactions were run for 6 h in mixtures of CH_2Cl_2:CH_3CN unless indicated otherwise ; [Pd] = 2.92×10^{-3} mol/L; Pd/PA = 1:50; [a]determined by GPC.

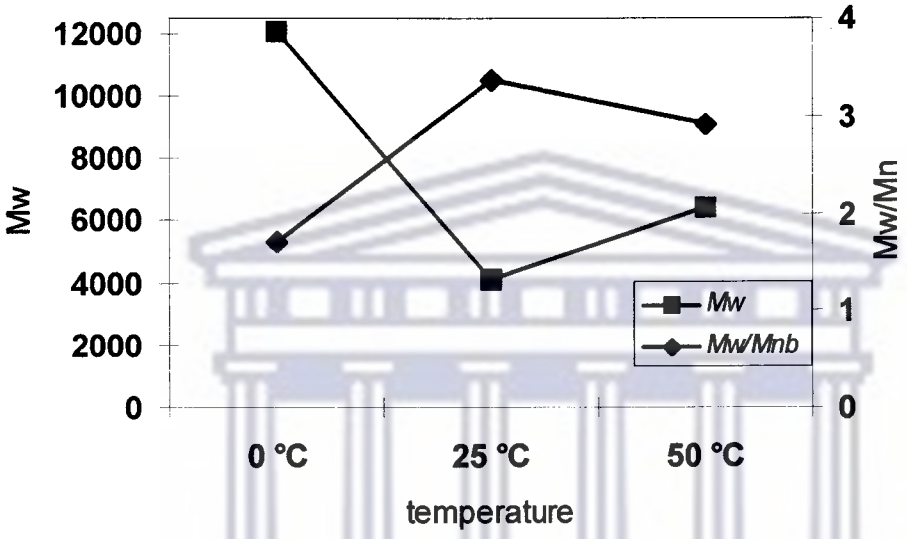


Figure 3.9: Effect of temperature on molecular weight and polydispersity

Another interesting feature of catalyst **6** was its high selectivity. It afforded mostly *cis-transoidal* poly(phenylacetylene) with percentage *cis* content ranging between 80 and 89%. However some solvents such as acetonitrile, which afforded high molecular weight polymers, resulted in rapid degradation of the polymer. Interestingly poly(phenylacetylene) obtained from this catalyst was found to be stable even at higher temperatures, 50 °C. (entry 4, Table 3.3). Poly(phenylacetylene) produced at elevated temperature ie. 50 °C, was found to have a high percentage *cis* conversion of 80%. Based on this data, it was concluded that temperature played no role in the degradation of the polymer. Therefore the effect of solvent was largely responsible for degradation observed in case of acetonitrile.

3.2.2.2 Polymerization of phenylacetylene using 5a

When **5a** was used as catalyst, a decrease in solvent ratio led to a steady increase in polymer molecular weight (Table 3.4, entries 1-4). However, percentage conversion of monomer dropped as solvent ratio decreases. The polydispersity index decreased by a small margin, (entries 1-4). Polymer molecular weight distribution from catalyst **5a** is higher compared to other catalysts that were used in this study. According to Kunzler, when the initiation rate of polymerization is lower than the rate of propagation, this leads to polymers with broad polydispersity.[31]

Table 3.4: Polymerization of phenylacetylene catalyzed by **5a**

Entry	Solvent	% Conver	Temp.	M_w[a]	M_n[a]	M_w/M_n[a]
1	7:1	100	r.t	10237	2238	4.57
2	5:1	72	r.t	9603	2139	4.49
3	3:1	69	r.t	9767	2223	4.39
4	1:1	67	r.t	9974	2279	4.37
5	MeCN	93	r.t	5257	3190	3.78
6	THF	100	r.t	1610	944	1.71
7	DCM	77	r.t	2705	1220	2.22
8	7:1	100	0°C	6552	1496	4.38
9	MeCN	83	0°C	6295	1484	4.24
10	THF	100	0°C	1646	997	1.65

All reactions were run for 3 h in mixtures of CH_2Cl_2:CH_3CN unless indicated otherwise [Pd] = 1.97×10^{-3} mol/L; Pd/PA = 1:50 [a] determined by GPC.

Low polydispersity indices were only obtained when neat solvents were used (Table 3.4, entries 5-7). These low polydispersity indices are accompanied by low molecular weights. THF as a solvent at low temperatures gave poly(phenylacetylene) with low polydispersity of 1.71 (entry 10). Surprisingly, even solvent mixtures at low temperatures (entry 8) afforded poly(phenylacetylene) with lower molecular weight than those obtained at room temperature. Similar results have been reported by Furlani *et al.*. when using [Rh(COD)bipy]PF6 at –40°C.[12] In fact, according to Percec, an increase in reaction

temperature facilitates the termination reactions of poly(phenylacetylene).[30] This phenomenon was also observed in the catalytic system where **5c** was used as catalyst contrary to catalyst **6**.

3.2.2.3 Polymerization of phenylacetylene using 5b

When **5b** was used as catalyst it was observed that an increase in the monomer concentration leads to a general decrease in percentage conversion and a consistent decrease in molecular weight (Table 3.5, Fig. 3.10). Percentage conversion decreases from a maximum of 90% (entry 1) to 58% (entry3).

Table 3.5: Polymerization of phenylacetylene catalyzed by **5b** at different monomer concentrations.

Entry	Solvent	[PA]/[Pd]	%Conver.	M_w[a]	M_n[a]	M_w/M_n[a]
1	7:1	50	90	11890	5038	2.36
2	7:1	100	58	8955	2995	2.99
3	7:1	200	60	6444	2929	2.20

All reactions were run for 24 h in mixtures of CH_2Cl_2:CH_3CN unless indicated otherwise [Pd] = 1.97×10^{-3} mol/L; Pd/PA = 1:50, room temperature, [a] determined by GPC.

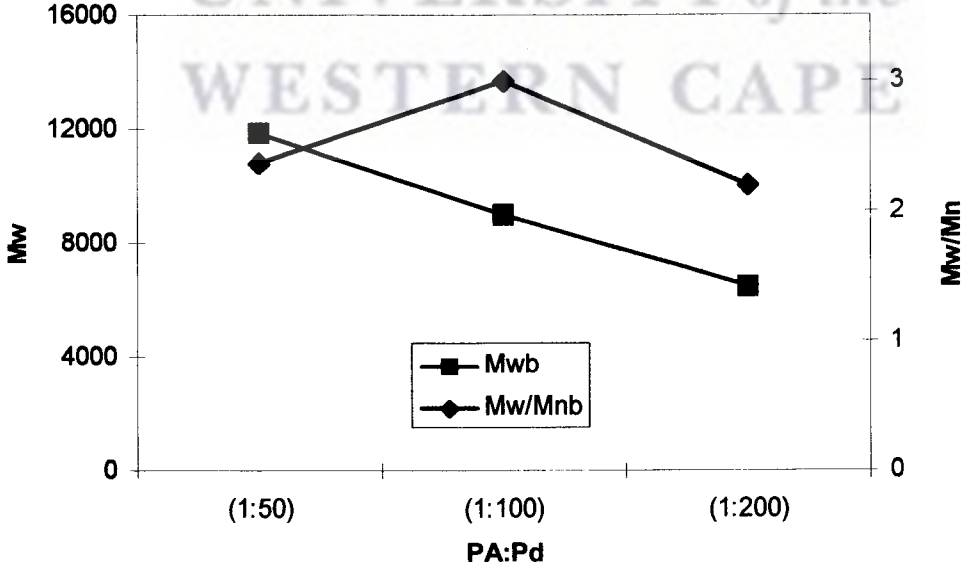


Figure 3.10: Effect of different monomer concentration on polymer molecular weight.

A threshold concentration is obtained when 50 equivalents of phenylacetylene (entry 1) are reacted with one equivalent of the catalyst. Beyond this an excess of phenylacetylene favours the production of low molecular weight polymers and oligomers. It is clear that the polymer chain propagates in a non-living manner. The catalyst was also observed to be highly active during initiation stages but gradually died during polymerization process (Table 3.6 entry 1 and 4).

Polymerization reactions were also performed using solvent mixtures (Table 3.6). Polymerization reactions seem to occur very rapidly with this catalyst. The reactions were found to be complete in a minimum period of two minutes without compromising the yield and molecular weight of the resultant polymer as can be seen from Table 3.6 and Fig. 3.11. Interestingly the polydispersity indices and molecular weights decreased consistently as the time increased. It looks like there is a competition between the monomer and the solvent to bind to the catalyst, especially when the acetonitrile concentration is increased. However, the monomer wins but a little bit less of it is polymerized as indicated by the little drop in the percentage conversion.

Table 3.6: Polymerization of phenylacetylene catalyzed by **5b** in mixtures with different solvent ratios over time

Entry	solvent	Time(min)	%Conver.	M_w[a]	M_n[a]	M_w/M_n[a]
1	7:1	2	90	11890	5038	2.36
2	7:1	30	85	11609	5160	2.25
3	7:1	60	87	12919	5872	2.20
4	7:1	120	92	12114	5714	2.12
5	5:3	1440	86	11521	5539	2.08
6	1:3	1440	76	8546	4748	1.80

All reactions were run in mixtures of CH_2Cl_2:CH_3CN unless indicated otherwise [Pd] = 1.97×10^{-3} mol/L; Pd/PA = 1:50, room temperature.[a] determined by GPC.

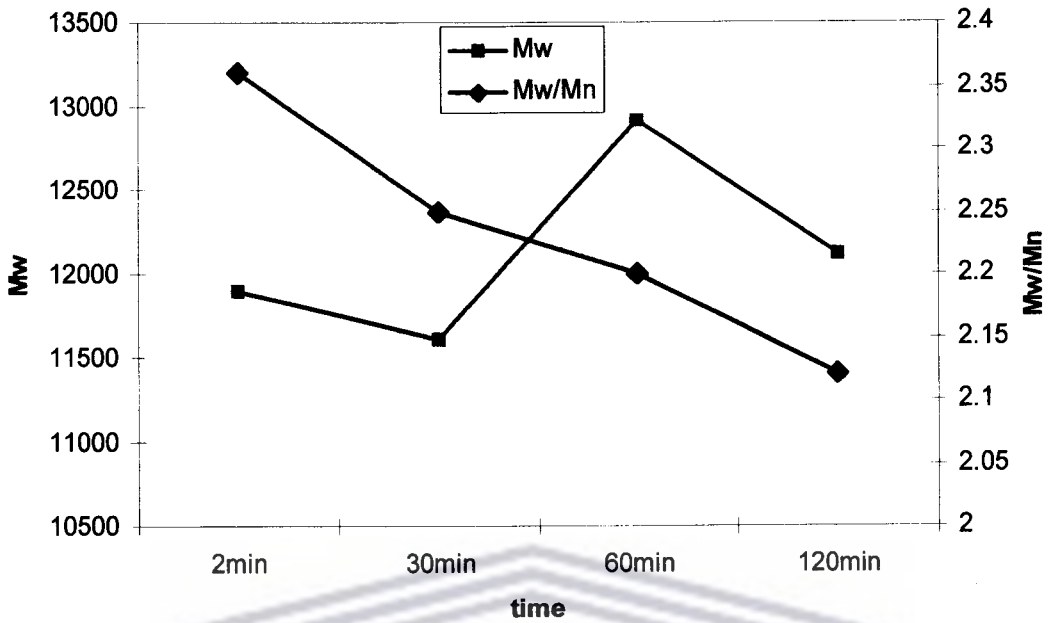


Figure 3.11: Effect of time on polymer molecular weight and polydipersity

3.2.2.4 Polymerization of phenylacetyelene and other substituted acetylenes using 5c as catalyst

In order to test the generality of pyrazolyl palladium complexes as catalysts for acetylene polymerisation, we investigated the polymerisation of phenylacetylene and other substituted acetylenes. The types of acetylenes used in this study are shown in below:

R = H **1a**

R = CH_3 **1b**

R = R' = H **2a**

R = R' = CH_3 **2b**

R = R' = Ph **2c**

Using **5c** in catalytic transformation of acetylenes produces mainly lower molecular weight polymers. However, in the majority of the reactions the polydispersity indexes were low in comparison to other catalysts investigated. The exception to this general trend was

polymers obtained when THF was used as polymerization solvent (Table 3.7, entry 10) and when the reaction was performed at low temperatures (entry 13). Attempts to optimise both the percentage conversion and subsequently the molecular weights by combining the two optimum conditions resulted in low molecular weights poly(phenylacetylene) with low polydispersity indices being formed (entry 18).

Despite the ability of catalyst 5c to polymerize phenylacetylene, 1a, and p-tolylacetylene. 1b, (entry 13) at low temperatures to appreciable molecular weights, it could not polymerize 2c under any given conditions (entry 12, 15 & 17). It should be noted that the M_w data in Table 3.7 are relative to polystyrene standards. Percec *et al.*[32] found that polystyrene calibration often underestimates the molecular weights of polyacetylenes, with up to fivefold differences. The real or absolute molecular weights of our polyacetylenes, therefore, could be much higher than the relative values given in Table 3.7. Remarkably, 2c was the only acetylene that could be transformed quantitatively. The polymer obtained from 2a was found to be insoluble in all organic solvents except hot DMSO, while that obtained from 2b was found to be soluble in almost every solvent including MeOH, which is used to separate polymers from oligomers. It was observed that upon washing some samples of poly(phenylacetylene) with pure methanol a good portion of the polymer also dissolved. By using 25% HCl in methanol, Trumbo *et al.*[33] were able to precipitate the methanol soluble polymers from reactions mixtures. We used acidified methanol (3M) to recover methanol soluble polymers in some of our reactions. For example we found in entry 4 that when 3M acidified methanol solution was used 65% of the total converted material was isolated as polymer and oligomers accounted for the remaining 35%.

Table 3.7: Polymerization of phenylacetylene and other alkynes catalyzed by **5c**

Entry	Monomer	Solvent	Temp. (°C)	% Conv.	M_w[b]	M_n[b]	M_w/M_n[b]
1	**1a**	7:1	25	45	1203	716	1.68
2	**1a**	5:1	25	44	1715	692	2.48
3	**1a**	5:3	25	61	1787	695	2.57
4	**1a**	3:1	25	65	991	703	1.41
5	**1a**	1:1	25	60	1297	697	1.86
6	**1a**	1:3	25	55	1027	750	1.37
7	**1a**	Toluene	25	30	1431	678	2.11
8	**1a**	MeCN	25	43	1581	561	2.82
9	**1a**	NEt_3	25	42	2019	990	2.04
10	**1a**	THF	25	50	3949	1207	3.27
11	**2b**	3:1	25	50	904	636	1.45
12	**2c**	3:1	25	100	1482	760	1.95
13	**1a**	3:1	0	60	3084	988	3.12
14	**1b**	3:1	0	51	3382	983	3.44
15	**2c**	3:1	0	100	1571	745	2.11
16	**1b**	3:1	50	50.0	1002	659	1.52
17	**2c**	3:1	50	96	1810	801	2.26
18	**1a**	MeCN	0	56	1829	1008	1.18

All reactions were run for 2 h in mixtures of CH_2Cl_2:CH_3CN unless indicated otherwise [Pd] = 2.92×10^{-3} mol/L; Pd/PA = 1:50, [b] determined by GPC.

3.2.2.5 Polymerization of phenylacetylene using 1

When solvent optimization studies were performed using **1** as catalyst it was found that the percentage conversion was higher when a mixture of solvents was used (entry1-4) and when high ratios of CH_2Cl_2/CH_3CN were used. The percentage conversion also showed dependence on the concentration of monomer used and seems to increase with a decrease in monomer concentration (entry 5 and 6).

Table 3.8: Polymerization of Phenylacetylene catalyzed by **1**

Exp	Solvent	(%)Conversion	M_w[b]	M_n[b]	M_w/M_n[b]
1	7:1	59	7410	2225	3.33
2	5:1	54	7027	2274	3.09
3	3:1	46	6756	2138	3.16
4	1:1	31	6313	1902	3.32
*5	7:1	80	6716	1489	4.51
*6	3:1	61	6511	1255	5.19
7	CH_3CN	46	4931	1586	3.11
8	THF	49	5527	1253	4.41

All reactions were run for 14 h in mixtures of CH_2Cl_2:CH_3CN unless indicated otherwise [Pd] = 9.23×10^{-4} mol/L; Pd/PA = 1:50 *[Pd] = 4.615×10^{-4} mol/L; Pd/PA = 1:25, [b] determined by GPC.

On the contrary the polydispersities are higher but the molecular weights are comparable to those obtained when PA:Pd of 50 was used at lower CH_2Cl_2/CH_3CN ratios (entry 3 & 4). The broad polydispersity indices obtained indicates that the initiation rate was lower than the rate of propagation. [31]

The low percentage conversions attained in pure solvents could be attributed to competition between polar solvents used and phenylacetylene. It was apparent that phenylacetylene was unable to completely replace the solvent coordinated before polymerization.

One of the limitations of the polymerization catalysts in pure solvents was the deactivation of the catalyst, since traces of metal could be seen after filtering once the polymerization was complete. Part of the ligand was also isolated with polymer. The presence of the ligand in the polymer seems to masks the polymer peak thus creating the dual distributions, resulting in broad polydispersity indices.

3.3 Conclusion

All the complexes showed some catalytic activity towards polymerization of phenylacetylene. Importantly we observed no catalytic activity in the absence of the catalyst. Thus catalysis occurred only in the presence of the metal complexes. Complex **5c** gave mainly low molecular weight polyphenylacetylene. It was found that complexes with bulky substituents were better catalyst than their less bulky counterparts. Comparing activity of the complexes from 1,3-(3,5-R_2pzC(O))$_2C_6H_4$ system it is evident that activity increase in the order **5c** < **5a** < **5b**. However, the polydispersity indices dramatically increased with an increase in the bulkiness of the catalyst used. The more strained and bulky catalyst, **5a**, produced polymers with the highest polydispersity values. Silylalkylamino pyrazolyl complex **6** showed high selectivity in polymerizing phenylacetylene to *cis-transoidal* poly(phenylacetylene) under all given reaction conditions. The other catalysts gave poly(phenylacetylene) that was a mixture of cis-transoidal and trans-cisoidal poly(phenylacetylene).

3.4 Materials and instrumentation

All manipulations were performed under dry, deoxygenated nitrogen atmosphere using standard Schlenk techniques. Triethylamine was dried over KOH, toluene and tetrahydrofuran (THF) were dried with sodium/benzophenone, distilled and stored under a

nitrogen atmosphere, while acetonitrile was distilled before use and was stored over 4Å molecular sieves. Phenylacetylene (98%) and silver trifluoromethanesulfonate (AgOTf) were obtained from Aldrich and used as received.

NMR spectra were recorded on a Gemini 2000 instrument (^1H at 200 MHz, ^{13}C at 50 MHz). The chemical shifts are reported in δ (ppm) and referenced to residual protons and ^{13}C signals of deuterated chloroform as internal standard. IR spectra were recorded as NaCl plates on a PERKIN ELMER, Paragon 1000PC FT-IR spectrometer. The number- and weight-average molecular weights were determined by gel permeation chromatography (THF, 30 °C, rate = 1.0 cc/min) with PL mixed–C column using polystyrene standards.

3.5 Polymerization procedure for phenylacetylene

3.5.1 Polymerization of phenylacetylene using solvent mixtures of CH_2Cl_2 and CH_3CN

In a typical experiment a colourless solution of silver triflate, AgOTf, (0.060 g, 0.234 mmol) in 15cm^3 of CH_2Cl_2\$CH_3CN$ (in a 2:1 ratio) was added to a yellow solution of **6** (0.040 g, 0.117 mmol) in 25 cm^3 of degassed CH_2Cl_2 for a final CH_2Cl_2\$CH_3CN$ ratio of 7:1. A white precipitate of AgCl appeared immediately. The mixture was stirred for 20 min and filtered to give a light yellow solution, generating the active catalyst *in situ*. Phenylacetylene (0.63 cm^3, 5.84 mmol, 50 equiv) was added to the system via a syringe and the resultant solution was stirred for 6 h. Generally the initial yellow solution changed to dark red within 30 min. The red solution was filtered and the filtrate evaporated to give a dark red residue. The residue is allowed to dry overnight in air. The crude residue was redissolved in a minimum amount of CH_2Cl_2 and methanol (40cm^3) added to precipitate the polymer. The polymer was isolated by filtration,dried and weighed.

Other polymerisation reaction were performed using the same general procedure as in 3.5.1 except for the following specific modifications or conditions:

3.5.2 Procedure for polymerization of Phenylacetylene using neat solvents (Et_2O, THF, CH_3CN and Toluene)

The active catalysts was generated from $CH_2Cl_2\backslash CH_3CN$ (2:1), but the solution of the catalysts was evaporated in *vacuo* and the appropriate solvent added to the residue of the catalyst before addition of monomer.

3.5.3 Temperature variation in phenylacetylene polymerization reactions

In high temperature experiments the catalyst generated in 3.5.1 of (3:1) was placed in an oil bath that had been set at 50 °C before phenylacetylene (0.63 cm^3, 5.84 mmol, 50 equiv) was added via a syringe once the reaction mixture reached the desired temperature.

The same protocol was followed for polymerization at 0 °C; but instead of an oil bath, an ice bath was used and phenylacetylene was added once the temperature of catalyst solution reached 0 °C.

3.6 Polymerization procedure for other acetylenes.

3.6.1 Procedure for polymerization of propargyl alcohol (2a), 2-methyl-3-butyn-ol (2b) and diphenyl-2-propyn-ol (2c) using neat solvents (THF and CH_3CN)

A typical experiment was performed as follows: A solution of AgOTf (0.040 g, 0.157 mmol) in 20 THF (cm^3) was added to a solution of **5c** (0.06 g, 0.079 mmol) in degassed THF (20 cm^3). A white precipitate of AgCl appeared immediately. The mixture was stirred for 30 min and filtered to give a yellow solution. Polymerization was triggered by addition

of 2-methyl-3-butyn-ol (0.33 cm^3, 3.93 mmol, 50 equiv) via a syringe. The initial yellow solution changed to dark red within 10 min. The resultant solution was stirred for 6 h and the reaction worked up as in 3.5.1 above.

Temperature variation reactions were performed as described in 3.5.3

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CHAPTER 4

4.1 Conclusions

This work extends the range of pyrazolyl palladium complexes that can be used as catalytic precursors for the transformation of unsaturated hydrocarbons recently reported by Darkwa *et al.*[1] This includes the preparation of silylalkylamino, alkylamino and 1,4-(3,5-R_2pzC(O))$_2C_6H_4$ pyrazolyl ligands and their complexes. The alkylamino and 1,4-(3,5-R_2pzC(O))$_2C_6H_4$ compounds are less soluble when compared to the silyl alkylamino pyrazolyl compounds and were thus isolated in low yields. The dimethysilyl groups in the alkylaminopyrazolyl compounds play a crucial role in conferring solubility to the prepared compounds especially since most of the compounds were prepared with a viewpoint of using them as homogenous catalysts. The down side of the presence of the dimethysilyl groups, however, is that they also made the compounds susceptible to hydrolysis.

Data from spectroscopic techniques gave major insight on the bonding mode of 1,4-(3,5-R_2pzC(O))$_2C_6H_4$ ligands in the complexes and its analysis revealed that the mode of bonding is basically the same as what pertains in 1,3-(3,5-R_2pzC(O))$_2C_6H_4$ complexes.

Complexes **1**, **5a-c** and **6** were successfully tested for their catalytic activity in the polymerization and oligomerization of phenylacetylene. Since complex **1** was not satisfactorily soluble to be used in a homogenous system, it was decided that all complexes would first be converted into their cationic salts to enhance their solubility. These cationic complexes were found to promote oligomerization and polymerization of phenylacetylene. It was found that the activity of the catalysts is influenced by a

number of factors. The stereochemistry, molecular weight and yield of poly((phenylacetylene) formed strongly depends on the polymerization conditions, with the major contributing factors being temperature and the type of solvent used. The use of neat solvents always produced polyphenylacetylene that was a mixture of *cis* and *trans* isomers.

However, it was interesting to observe that the silylalkylamino pyrazolyl complex **(6)** showed high selectivity in polymerizing phenylacetylene to *cis-transoidal* poly(phenylacetylene) irrespective of the reaction conditions used. When neat acetonitrile was used in this system it was found to promote rapid degradation of the polymer *cis* content. In fact the least *cis* content using **6** was obtained using acetonitrile.

Another interesting observation is that polymerization tends to dominate over oligomerization at lower temperatures. Poly(phenylacetylene) with a higher *trans* content were observed at room temperature and at elevated temperatures. Catalyst architecture also played a vital role in determining the most likely products to be formed. It was found that complexes with bulky substituents were better catalysts than their less bulky counterparts. Comparing activity of the complexes from 1,3-(3,5-$R_2pzC(O))_2C_6H_4$ system, it is evident that catalytic activity increase in the order **5c** < **5a** < **5b**. Interestingly **5c** favoured the formation of lower molecular weight polymer while the other two bulky catalysts **5a** and **5b** favoured formation of higher molecular weight polymers.

Poly(phenylacetylene) produced from **5b** and **5c** had acceptable polydispersity indexes with an average $M_w/M_n \geq 2$, and are comparable to many in literature.[2] Complex **1**, **5a** and **6** produced polymers with high polydispersity indexes averaging $M_w/M_n \geq 3$ but are comparable to some observed in literature.[3] These polydispersity indexes are way above that obtained using most Rhodium catalysts $M_w/M_n \geq 1$.[4] Despite the phenomenal ability of Rhodium catalysts to produce highly stereoregular polymers, there are few reports in which rhodium catalysts produced polymer with $M_w/M_n \geq 3$.[5]

In general pyrazolyly compounds tested in this study are good catalysts for preparing poly(phenylacetylene) and linear phenylacetylene oligomers. No cyclic trimers were observed throughout the whole study.

4.2 References

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APPENDIX

Calculations for the *cis* content of polyphenylacetylene obtained using complex **6**

A

$\%\ cis = [A_{5.82} / (A_{total} / 6)] \times 100\%$ $\quad A_{total} = A_{5.82} + A_{6.64} + A_{6.95}$

$= [6.41 / (46.4 / 6)] \times 100\%$ $\quad = 27.22 + 12.77 + 6.41$

$= 6.41 / 7.73 \times 100\%$ $\quad = 46.4$

$= 82.82\%$

$\approx 83\%$

OR

$\%\ cis = A_{5.82}.10^4 / A_{total} \cdot 16.66$

$= 6.41 \times 10^4 / 46.4 \times 16.66$

$= 82.92$

$\approx 83\%$

B

$\%\ cis = [A_{5.82} / (A_{total} / 6)] \times 100\%$ $\quad A_{total} = A_{5.82} + A_{6.64} + A_{6.95}$

$= [9.65 / (64.86 / 6)] \times 100\%$ $\quad = 34.85 + 20.36 + 9.65$

$= 9.65 / 10.81 \times 100\%$ $\quad = 64.86$

$= 89.27\%$

$\approx 89\%$

OR

$\%\ cis = A_{5.82}.10^4 / A_{total} \cdot 16.66$

$= 9.65 \times 10^4 / 64.86 \times 16.66$

$= 89.30$

$\approx 89\%$

Clearly both equations give equivalent answers, therefore any one of them can be used. All calculations from here on will be based on the first equation.

C

$\%\ cis = [A_{5.82} / (A_{total} / 6)] \times 100\%$ $\quad A_{total} = A_{5.82} + A_{6.64} + A_{6.95}$

$= [8.29 / (86.18 / 6)] \times 100\%$ $\quad = 53.60 + 24.29 + 6.28$

$= 8.29 / 14.36 \times 100\%$ $\quad = 86.18$

$= 57.72\%$

$\approx 58\%$

D

$cis = [A_{5.82} / (A_{total} / 6)] \times 100\%$ $\quad A_{total} = A_{5.82} + A_{6.64} + A_{6.95}$

$= [7.98 / (60.23 / 6)] \times 100\%$ $\quad = 32.65 + 19.60 + 7.98$

$= 7.98 / 10.04 \times 100\%$ $\quad = 60.23$

$= 79.69\%$

$\approx 80\%$

E

$cis = [A_{5.82} / (A_{total} / 6)] \times 100\%$ $\quad A_{total} = A_{5.82} + A_{6.64} + A_{6.95}$

$= [8.13 / (56.04 / 6)] \times 100\%$ $\quad = 29.35 + 18.46 + 8.13$

$= 8.13 / 9.34 \times 100\%$ $\quad = 56.04$

$= 87.04\%$

$\approx 87\%$

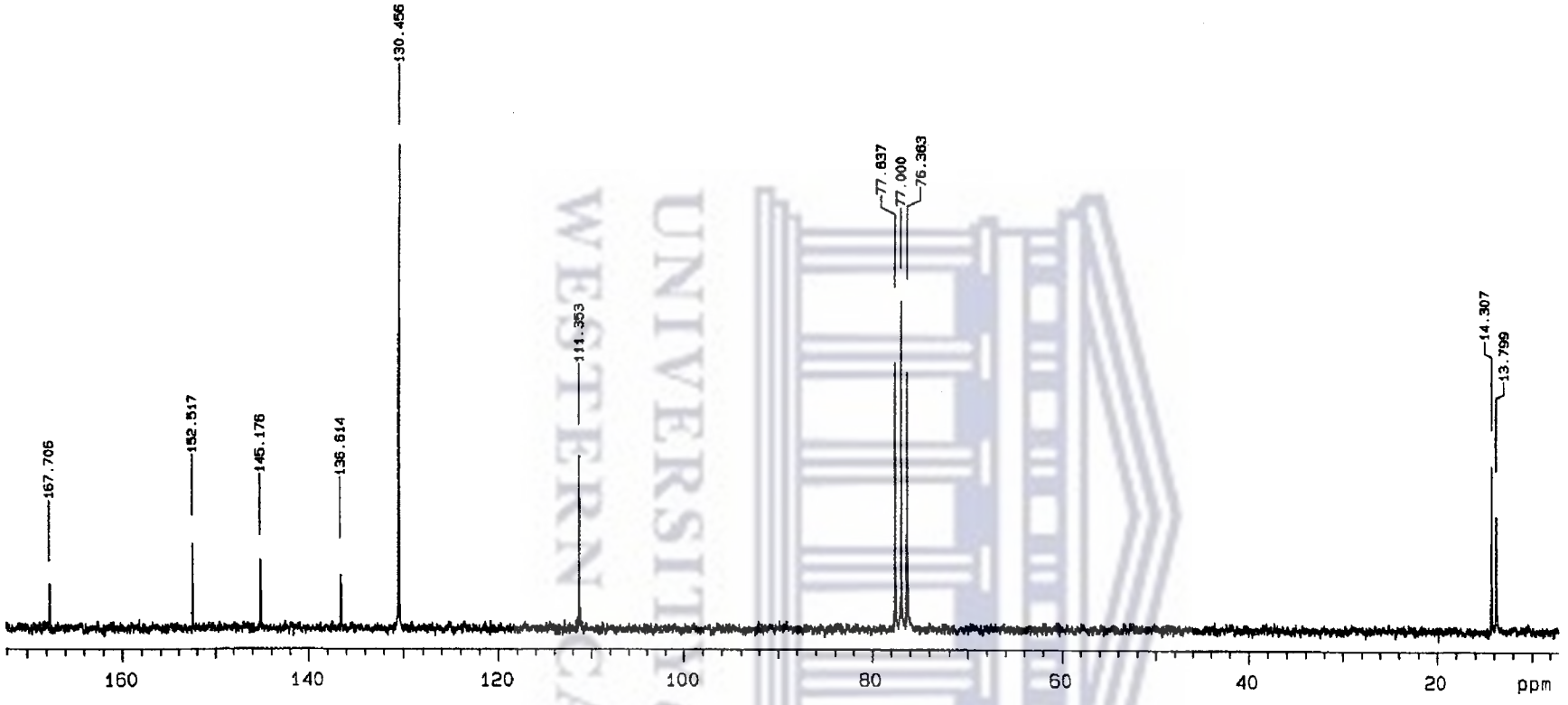

Figure A1: ^{13}C NMR spectrum of 1,4-Bis(3,5-dimethylpyrazolyl-1-carbonyl)benzene (**L2**)

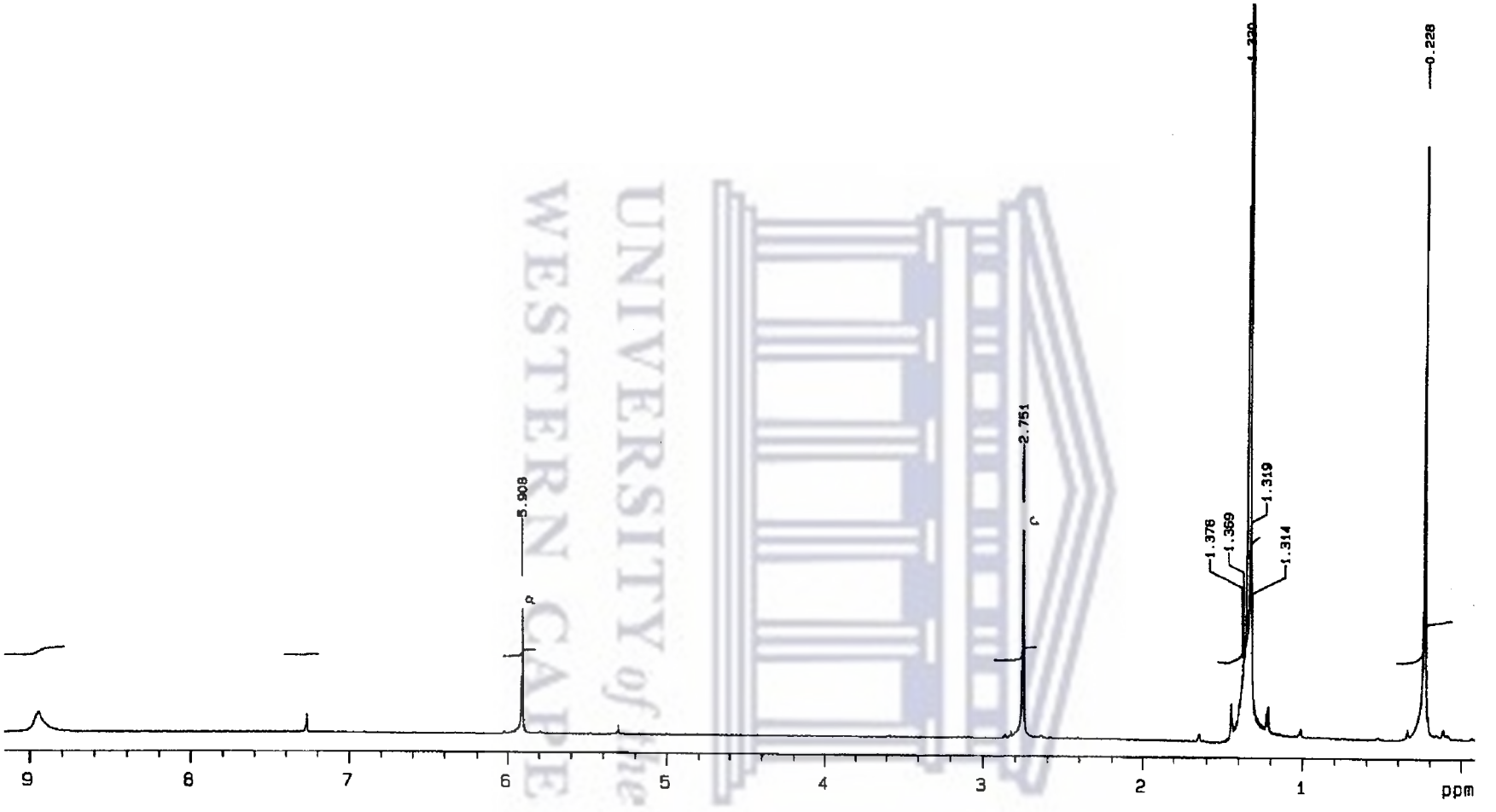

Figure A2: ^{1}H NMR spectrum of 1,3-Bis(3,5-dimethylpyrazolyl-1-methyl)tetramethyldisiloxane (**L7**)

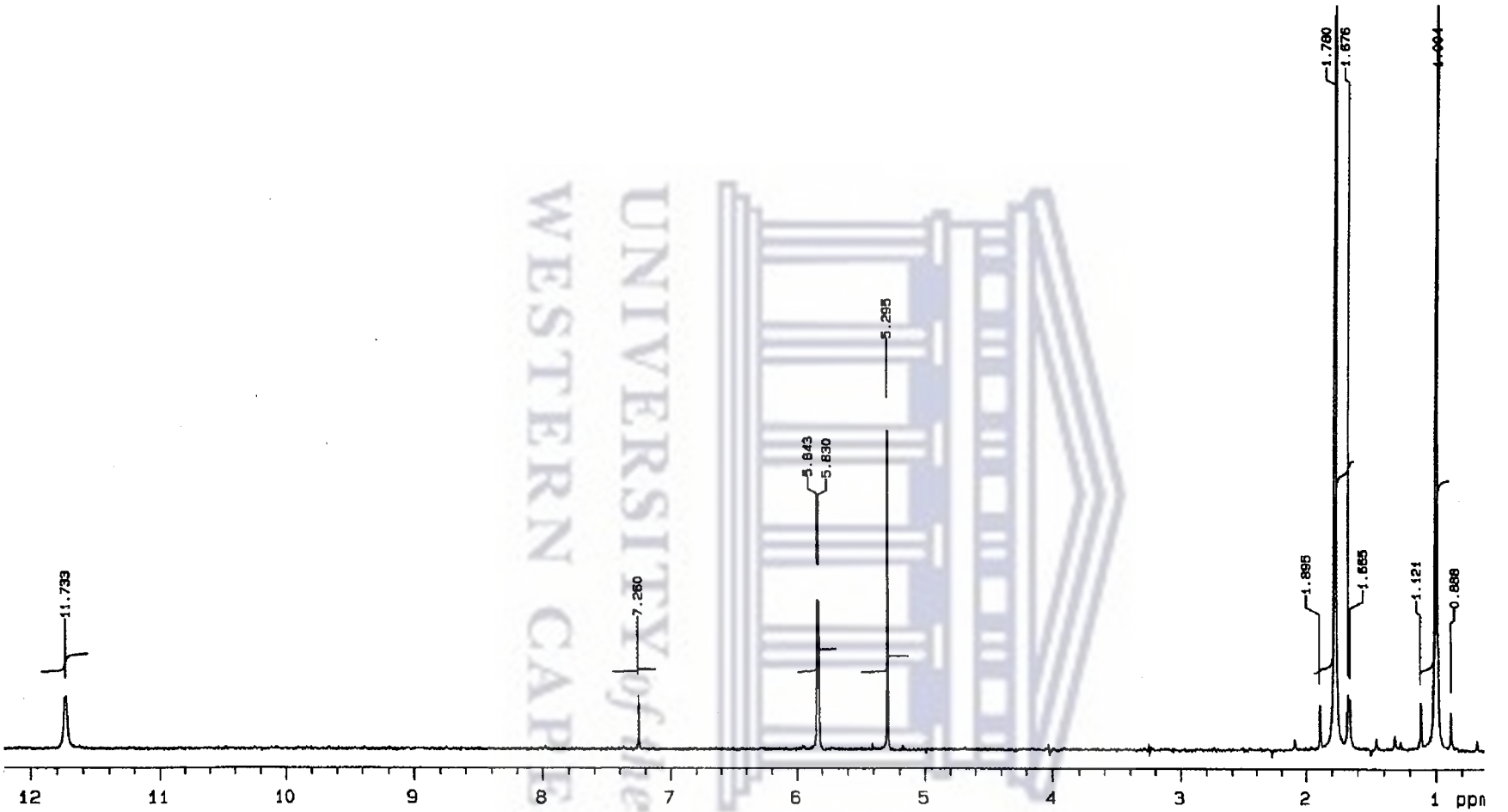

Figure A3: ^{1}H NMR spectrum of Bis(3,5-di-*tert*-butylpyrazole) Palladium(II) dichloro complex (hdrolysis product formed between **L7** and $[PdCl_2(NCMe)_2]$)

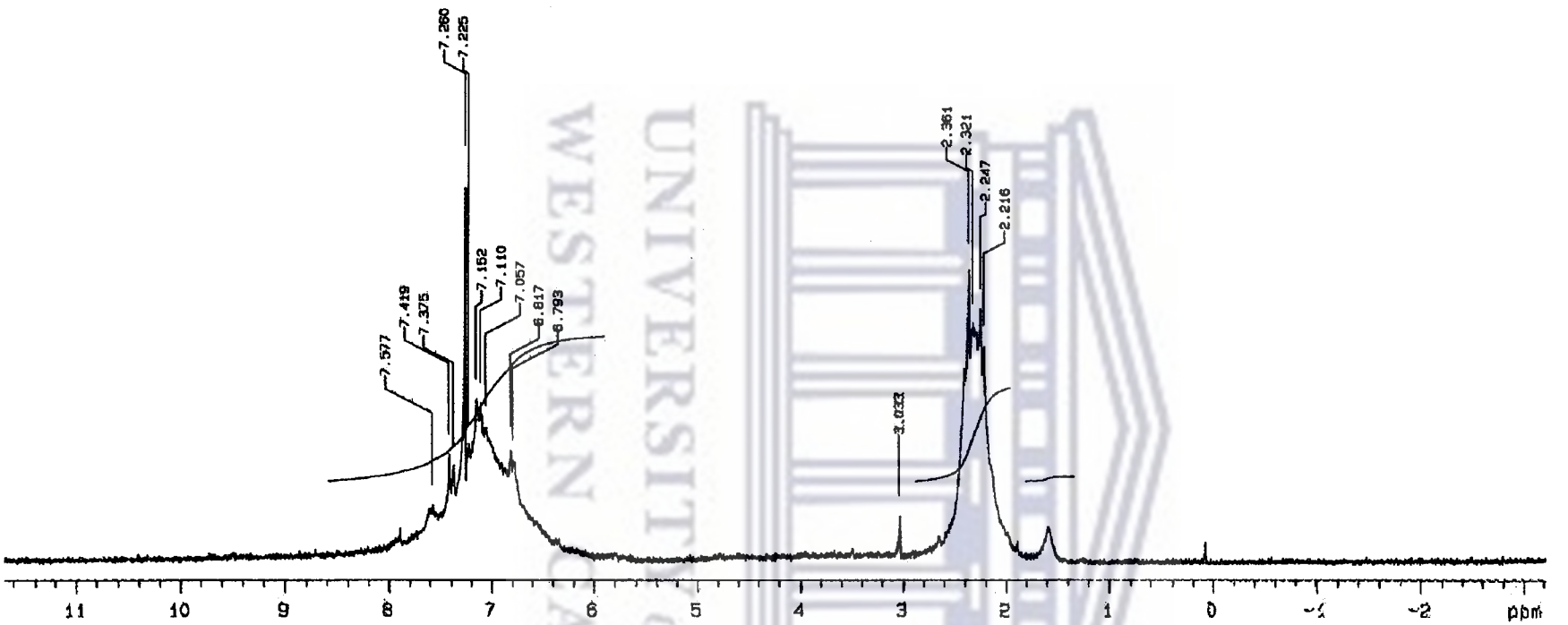

Figure A4: ^{1}H NMR spectrum of *trans*-poly(*p*-tolylacetylene).

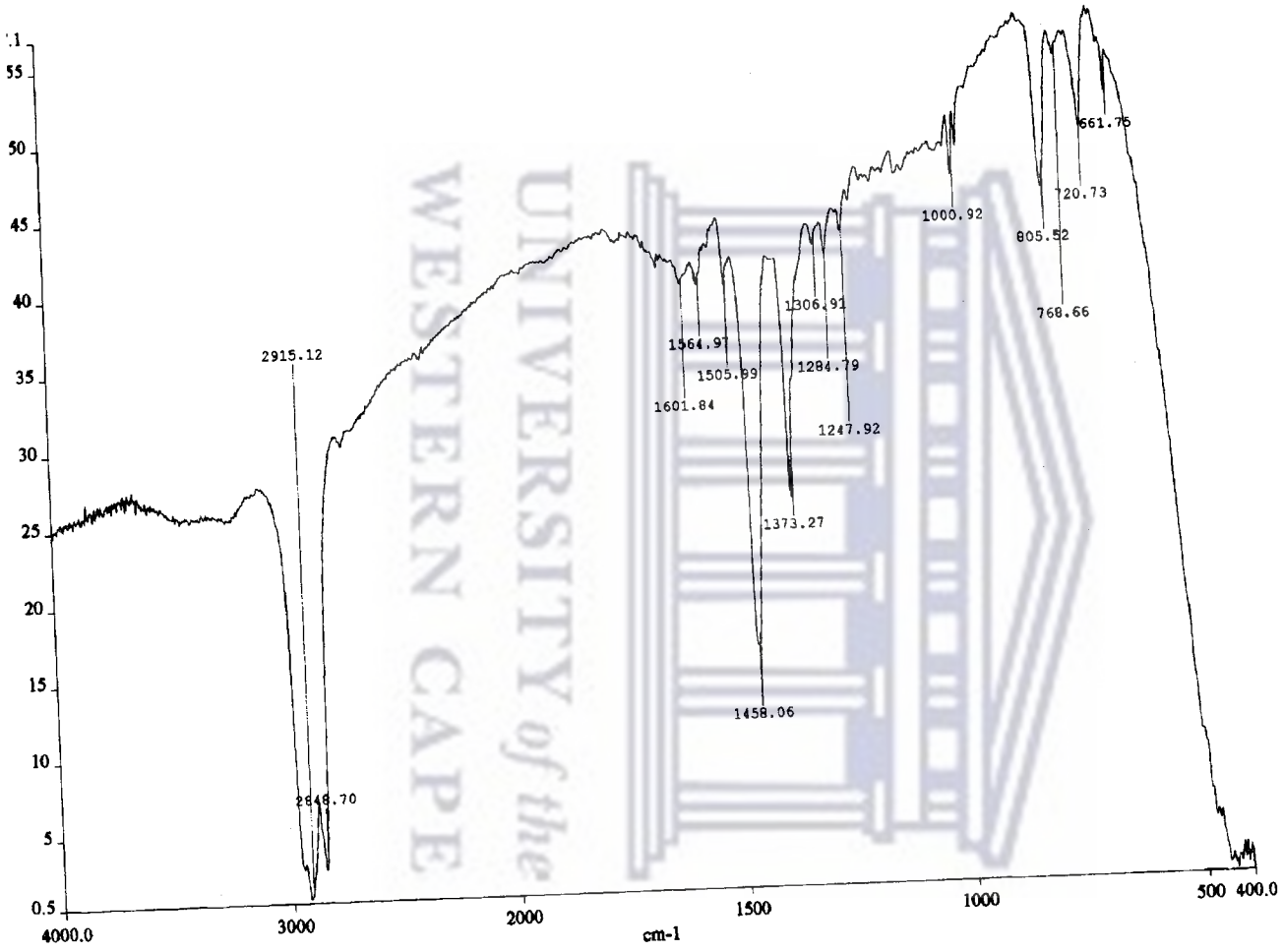

Figure A5: IR spectrum of *trans*-poly(*p*-tolylacetylene).

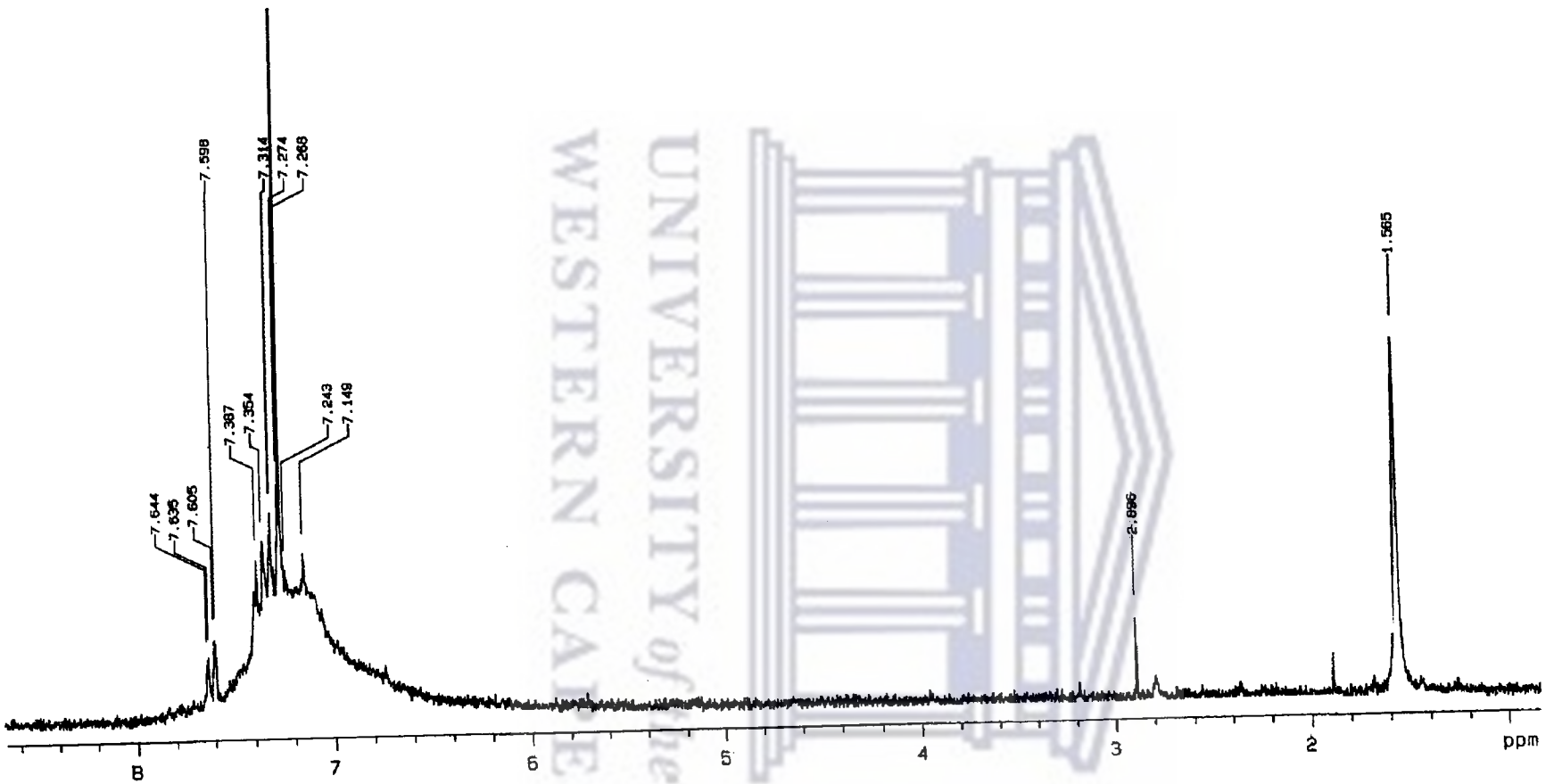

Figure A6: ^{1}H NMR spectrum of product obtained from polymerization of diphenyl-2-propyn-ol (**2c**)

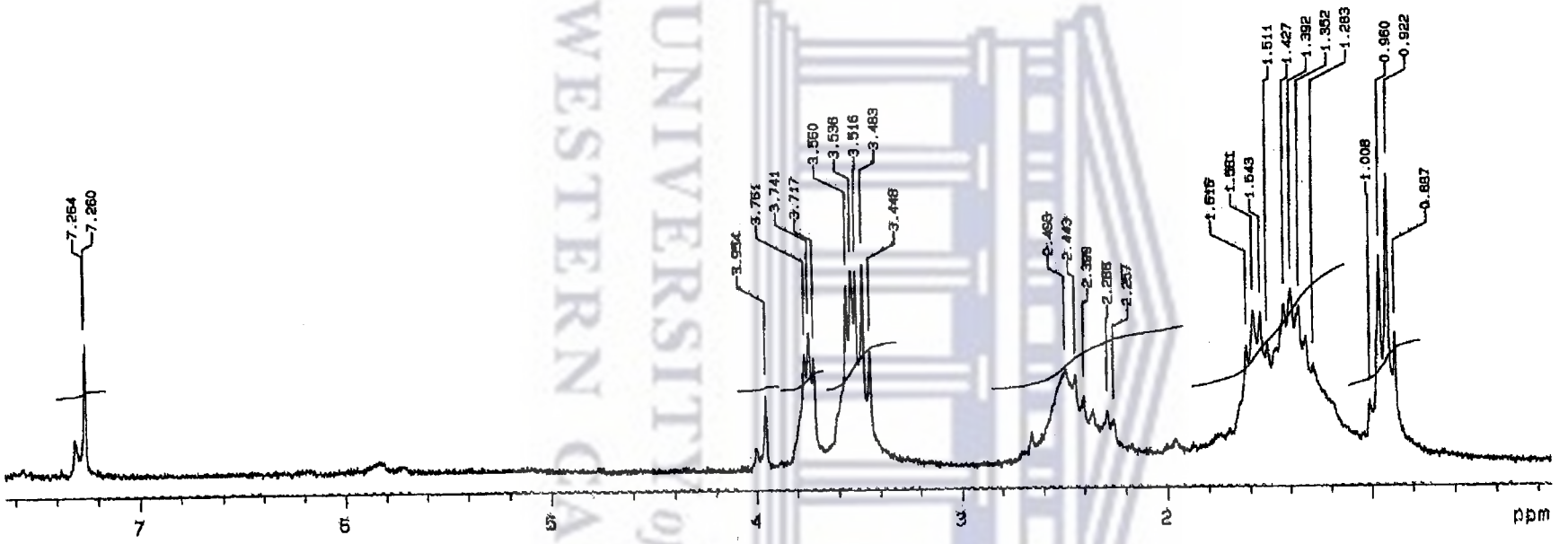

Figure A7: ^{1}H NMR spectrum of product obtained from polymerization of 2-methyl-3-butyn-ol (**2b**)