Pyrazolyl palladium complexes with heterocyclic carbonyl linkers as catalyst precursors for ethylene and phenylacetylene polymerization.

By

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DECLARATION

I declare that "*Pyrazolyl palladium complexes with heterocyclic carbonyl linkers-as catalyst precursors for ethylene and phenylacetylene polymerization*" 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 references.

Name: Matshwenyego Sarah Mohlala (Ms) Date: June 2003

Signature: ______________________

DEDICATION

TO MY DAUGHTER MOLOGADI, THE MOHLALA AND THE MASEMOLA FAMILIES

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ABSTRACT

The pyrazolyl ligands 2,6-bis(3,5-R_2pyrazolylcarbonyl)pyridine {R = ^{t}Bu (**L1**), Me (**L2**)}, 2,6-bis(3-methylpyrazolylcarbonyl)pyridine (**L3**), 2,6-bis(pyrazolylcarbonyl)pyridine (**L4**) and 2,5-bis(3,5-R_2pyrazolylcarbonyl)thiophene { R = ^{t}Bu (**L5**), Me (**L6**) were prepared by the reaction of 2,6-pyridinedicarbonyl dichloride and 2,5-thiophenedicarbonyl dichloride with the appropriate pyrazoles and were characterized by ^{1}H, ^{13}C{^{1}H} NMR, IR spectroscopy and elemental analysis. Reactions of the ligands **L1-L3**, **L4** and **L5** and $PdCl_2(MeCN)_2$ in a ratio of 1:1 yielded mononuclear and binuclear complexes [2,6-bis(3,5-R_2pyrazolyl-1-carbonyl)pyridine]palladium(II) dichloride {R = ^{t}Bu (**1**), Me (**2**)}, [2,6-bis(3-methylpyrazolyl-1-carbonyl)pyridine]palladium(II) dichloride (**3**) and di-μ-chloro-dichlorobis[2,5-bis(R_2pyrazolyl-1-carbonyl)thiophene]dipalladium(II) {R = ^{t}Bu (**4**), R = Me (**5**)}. Complex **1** was characterized by ^{1}H, ^{13}C{^{1}H} NMR, IR spectroscopy and elemental analysis while complexes **2-5**, which were insoluble in most common organic solvents, were characterized by elemental analysis and IR spectroscopy. The structures of the ligands **L3**, **L6** and complex **1**, deduced from spectroscopic studies, were confirmed by single crystal X-ray diffraction analysis.

The activation of [2,6-bis(3,5-R_2pyrazolyl-1-carbonyl)pyridine]palladium(II) dichloride {R = ^{t}Bu (**1**), Me (**2**)} and di-μ-chloro-dichlorobis[2,5-bis(3,5-R_2pyrazolyl-1-carbonyl)thiophene]dipalladium(II) {R = ^{t}Bu (**4**), Me (**5**)} with methylaluminoxane

(MAO) formed palladium complexes which were active catalysts for ethylene copolymerization, yielding linear high-density polyethylene (HDPE). The effects of co-catalyst (MAO) to catalyst (Al:Pd) molar ratio and temperature on catalytic activity were investigated. The best catalytic activity was obtained when co-catalyst:catalyst **1** molar ratio of 3000:1 was used at 25 °C. The polymers were characterized by high temperature ^{1}H, ^{13}C {^{1}H} NMR spectroscopy and high temperature gel permeation chromatography (GPC). The linearity of the polyethylene formed was confirmed by the presence of only one peak in the ^{1}H and ^{13}C {^{1}H} NMR data.

The complexes were also tested as catalysts for phenylacetylene polymerization. The active catalysts for phenylacetylene polymerization were generated *in situ* from the reaction of [2,6-bis(3,5-R$_2$pyrazolyl-1-carbonyl)pyridine]palladium(II) dichloride {R = ^{t}Bu (**1**), Me (**2**)} and di-μ-chloro-dichlorobis[2,5-bis(3,5-R$_2$pyrazolyl-1-carbonyl)thiophene]dipalladium(II) {R = ^{t}Bu (**4**), Me (**5**)} with silver triflate (AgTOf) in CH_2Cl_2/CH_3CN solvent mixtures. These catalyst systems polymerized phenylacetylene to produce brownish polymers and oligomers in low to good yields. The effect of solvents was investigated and showed that the highest molecular weight polyphenylacetylene was formed when THF and catalyst **2** were used. The resulting polyphenylacetylenes were characterized by ^{1}H, ^{13}C {^{1}H} NMR, IR spectroscopy and GPC. The ^{1}H, ^{13}C {^{1}H} NMR spectra of the polymers produced showed the polymers produced to be a mixture of *cis-transoidal* and *trans-cisoidal* polyphenylacetylene.

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ABBREVIATIONS

DSC = differential scanning calorimetry

DTA = differential thermal analysis

GPC = gel permeation chromatography

HDPE = high density polyethylene

LDPE = low density polyethylene

LLDPE = linear low density polyethylene

MAO = methylaluminoxane

PPA = polyphenylacetylene

py = pyridine

pz = pyrazole

TGA = thermogravimetric analysis

th = thiophene

AKNOWLEGDEMENTS

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CHAPTER 1

REVIEW OF HETEROCYCLIC NITROGEN DONOR LIGANDS AND LATE TRANSITION METAL COMPLEXES AS CATALYST PRECURSORS FOR ALKENE AND ALKYNE POLYMERIZATION

1.1 Introduction

Metal complexes containing nitrogen donor ligands have been known for a long time and are pivotal in coordination chemistry. The preparation of the 2,2′-bipyridine (bipy) ligand and the description of the first transition metal complex of this ligand was first reported by Blau [1] more than 100 years ago. Since then bipy and the related ligand 1,10-phenanthroline (phen) have been continuously and extensively used in both analytical and preparative coordination chemistry [2]. It is only recently that systematic studies of substituted derivatives of bipy and other α–diimine ligands have been undertaken. Mostly this work has been initiated by the intense interest in the redox and photocatalytic properties of the $[Ru(bipy)_3{}^{2+}]$ cation. Recently work done by Brookhart and co-workers [3], as well as that of Gibson et al [4], show the use of nitrogen donor ligand metal complexes as catalysts for olefin oligomerization and polymerization. This has raised the interest in the synthesis and properties of such compounds.

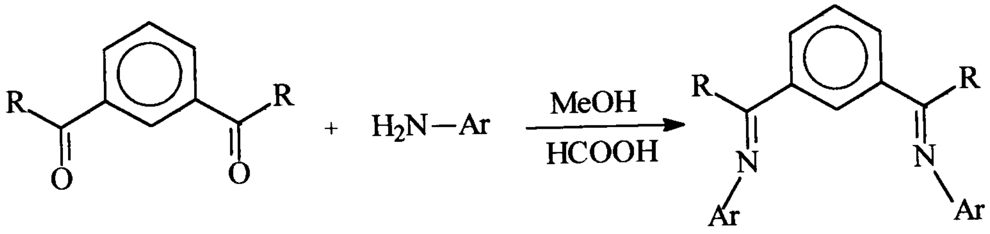
1.2 Nitrogen donor ligands

Aromatic nitrogen heterocycles represent an important class of ligands in coordination chemistry [2]. Monodentate ligands, such as pyridine, and chelating ligands, such as 2,2'-bipyridine, readily form stable complexes with most transition metal ions and have been extensively used in both analytical and preparative coordination chemistry. Nitrogen heterocycles with six membered rings have relatively low energy π^* orbitals and act as good acceptors of metal *d*-orbital electron density in metal-ligand back-bonding. The five membered ring nitrogen heterocycles are π excessive therefore are π donors rather than π acceptors and are relatively strong σ–donors and can also exist as anionic ligands by deprotonation of acidic N-H groups in the free ligand. This report surveys mainly the pyrazole derived ligands with few examples of pyridine and imidazole ligands, which are capable of forming metal complexes wherein metal ions are coordinated to the nitrogen atoms contained in a five- or six-membered aromatic heterocycles.

Metal nitrogen bonds are mainly σ-type, therefore the nitrogen ligand in coordination chemistry and other divisions of chemistry, form strong σ-bonds to metal centres. The strength of the bonds depends on their donor ability and the important contribution from the ionic character of the bond itself.

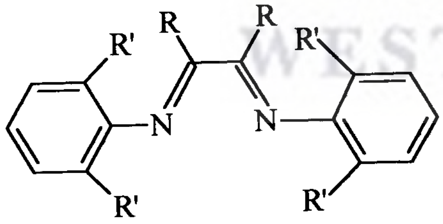
1.2.1 Pyridine and imine derived ligands

The most studied nitrogen donor ligands are diimine ligands because of their easily varied steric and electronic properties. They are also known to stabilize organometallic complexes [5]. Their synthesis involves simple condensation of a diketone with two equivalents of an alkyl- or arylamine, often catalyzed by a Lewis or Bronsted acid (Scheme I) with various R groups and aryl groups.



Scheme I: Synthetic route to diimine ligands

There are wide ranges of diimine complexes of nickel and palladium and some of them are highlighted below. Different diimine ligands (**1, 2**) with different substituents, varying from methyl to isopropyl groups coordinate with nickel(II) and palladium(II) to form complexes that are highly active for ethylene polymerization [3a,d]. Bidentate pyridinylimine ligands (**3**) react with nickel(II) and palladium(II) to produce dimeric nickel(II) and monomeric palladium(II) complexes [6]. The nickel complex was activated for ethylene polymerization while the palladium complex was highly active for norbornene polymerization after being activated.



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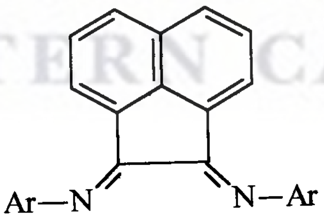

Ar = 3,5-$C_6H_3(CF_3)_2$

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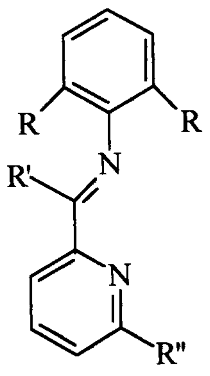

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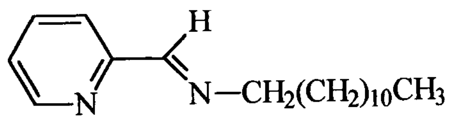

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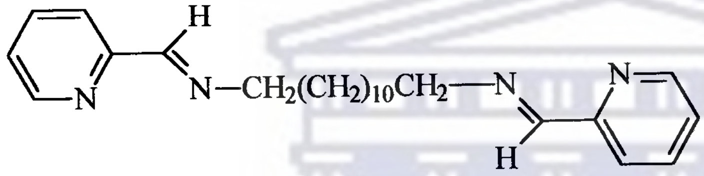

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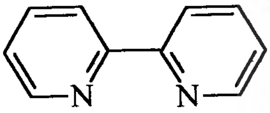
The synthesis and characterization of mono- and bi-nuclear pyridylimine-palladium(II) complexes with long chain alkyl groups attached to the imino nitrogen were recently reported by Mapolie *et al.* [7] with the ligands, N-(dodecyl)pyridyl-2-methanimine (**4**) and *N,N'*-(1,12-dodecanediyl)-bis(pyridyl-2-methanimine) (**5**) which were reacted with $PdCl_2(COD)$ (cycloctadiene), to form palladium chloride complexes that were tested for activity in ethylene polymerization.

The prototype diimine ligands, 2,2'-bipyridine (bipy) (**6**) [8] and 2,2':6',2''-terpyridine (terpy) (**7**) [9] have been used extensively as bidentate and tridentate chelating ligands in both preparative and analytical coordination chemistry. In terms of ruthenium(II) chemistry, many 3-, 4-, 5- and 6-substituted derivatives of bipy have been prepared along with their complexes [10]. Chiral derivatives of bipy and phen have been synthesized for potential application in asymmetric catalysis [11]. There are also ligands formed by the replacement of one of the pyridine rings of bipy with other heterocycles. The chemistry of 2-(2′-pyridyl)quinoline (**8**) has also been studied, with the complexes of manganese, iron, ruthenium, osmium, copper and gold [12] being predominant. As for other 6-substituted bipyridines, fusion of the benzo ring makes ligand **8** more sterically demanding than bipy. X-ray structures of manganese and gold complexes have shown a significant elongation of the metal nitrogen bond to the quinoline ring relative to that of the pyridine nitrogen [12a,g]. The replacement of one of the pyridine rings of bipy by five-membered pyrazole and imidazole rings have been reported. There have been a number of reports where pyrazolyl unit is fused with pyridine to form 2-(1′-pyrazolyl)pyridine. This ligand and its dimethyl derivative form complexes that include those of tin, mercury and ruthenium [13]. Complexes of the methyl derivative with nickel, cobalt, copper, ruthenium, palladium, platinum, gold, tin and uranium have also been described. Ligand Ru^{2+} complexes of 2-(1′-pyrazolyl)pyridine and bipy have been studied, and it was deduced from their reactions that 2-(1′-pyrazolyl)pyridine is a much weaker π–acceptor than bipy [14]. Although the unsubstituted 3-pyrazolylpyridine ligand (**9a**) is not known, the methyl (**9b**), phenyl (**9c**), and tert-butyl derivatives (**9d**) have been reacted with various metal ions including ruthenium [15]. These ligands can also act as anionic bidentate ligands after deprotonation of the N-H nitrogen and both neutral and anionic modes of coordination are known [16]. Other pyrazolylpyridine type ligands are mentioned in section 1.2.3.

Complexes of various metals with 2-(2′-imidazolyl)pyridine (**10**), which can also act as both a neutral and an anionic ligand have been studied. It was concluded in a study of Ru^{2+} complex that the deprotonated form of ligand **10** is a stronger π–donor than the protonated form which in turn is stronger than bipy [17]. Benzimidazole(**11**) is commercially available and has been studied as a ligand for numerous transition metals. It was found in the studies of Ru^{2+} complexes that ligand (**11**) has better π–donor properties compared to those of bipy and the imidazolylpyridine (**10**) [17].



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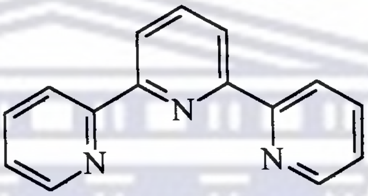

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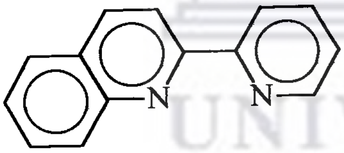

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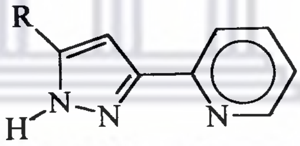

R = H (a), Me (b), Phe (c), ^{t}Bu (d)

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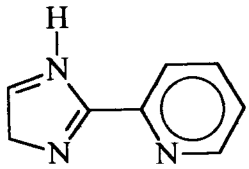

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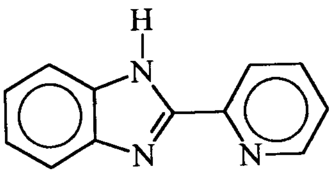

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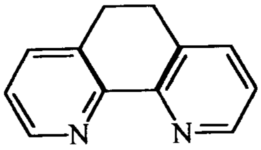
The terpy ligand coordinate with copper metal to form six coordinates complexes of the type [Cu(terpy)$_2$]X$_2$ (X=NO_3^-, PF_6^-, Br^-) [18]. Dicopper(I) complexes that utilizes neutral dinucleating ligands in which two tridentate pyridine units, (bis[2-(2-pyridyl)ethyl]amine), are connected by a variable alkyl chain have been synthesized [19]. Palladium(II), nickel(II) and cobalt(II) complexes bearing the unsymmetrical, bidentate nitrogen ligand 2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene)phenylamine have been studied with the palladium compound existing in the monomeric form, and nickel complexes observed as centrosymmetric dimers with a slightly distorted square-pyramidal coordination sphere around each nickel centre [20].

The pyridine ligand, 2,6-tetra[2-(2-pyridyl)ethyl]aminomethyl-*p*-cresol providing three nitrogen donors to each Cu ion, has been used to prepare many useful biomimics of the type III copper protein sites [21]. The (Py)$_4$N$_6$OH ligands can be used either protonated or deprotonated to give different types of Cu(I) complexes and these ligands are able to stabilize Cu(I) complexes that show reactivity with oxygen [22]. The influence of bridging of bipy at 3,3'-positions to allow some conformational control of the chelating environment, leading to different systems such as **(12-14)** as well as homologues with longer or shorter polymethylene bridges [23] have been studied by Thummel *et al.* [24]. The ligands 3,3'-dimethylene-2,2'-bibenzoquinoline **(14)** and bisbenzo[2,3:9,8]-1,10-phenanthroline are coordinated to ruthenium(II) to form both tris- and mixed ligand complexes.



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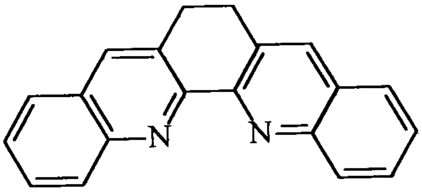

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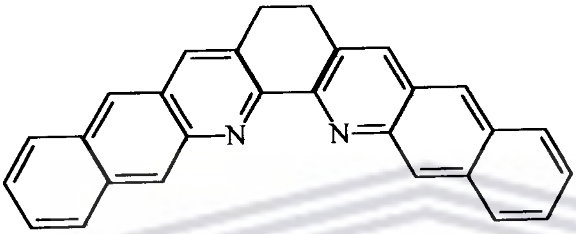

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These species are highly congested about the metal centre but can be formed through the use of microwave irradiation *in situ*, hence the steric factors to stop complexation is minimized. The ruthenium(II) complexes both as $[RuL_3]^{2+}$ and $[Ru(L)(bipy)_2]^{2+}$ (L=**12**, **13**) have been examined and it has been found that as the ligand became more sterically encumbering, the formation of the tris-complex was sterically hindered and even the formation of the mixed ligand complexes was sluggish [24].

1.2.2 Imidazole derived ligands

The imidazole ring is an ubiquitous essential metal binding site in different metalloproteins [25], occurring as histidine side chains in blue copper proteins, hemocyanin, tyrosinase, multicopper oxidases, and cytochrome c oxidase. Imidazole can be deprotonated to give imidazolate anion (**15**), which is capable of acting as a bridging ligand.

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The 1,3-arrangement of the nitrogen atoms imposes geometrical constraints such that, unlike pyrazolate, only one imidazole bridge is possible between two metal centres, therefore imidazolate-brigded transition metal complexes show higher linearity than the pyrazolate-bridged complexes discussed below. Many oligomeric and polymeric complexes have been known for long time to contain imidazolate bridges [26]. Imidazole can also act as a bridging ligand between different metal centres, as in the Cu(II), Zn(II) superoxide dismutase [27]. Hence a considerable number of imidazole metal complexes, specially those involving imidazole-bridged dicopper centres, have been prepared and characterized, in order to understand the peculiar properties of these natural systems better. Active sites, which incorporate an imidazolate bridge between two copper ions, have also been synthesized. Since the additional bridging between the copper atoms increases the stability of imidazolate bridge, many copper models have been prepared wherein the imidazolate ring is incorporated into a multidentate ligand or where the two copper atoms are held within a macrocyclic ligand [28]. X-ray crystal structures have been reported for heterobimetallic complexes containing Cu-Co and Cu-Ni [29] pairs bridged by an imidazolate ring. Imidizolate-bridged Fe-Cu binuclear complexes have also been prepared [30]. Imidazolate bridging have also been found to exist in the cobalt(III) complexes of a synthetic analogue of the important antitumor drug bleomycin [31]. Other imidazole-bridged complexes include homobimetallic complexes of ruthenium, mercury, nickel, and rhodium [32]. Imidazolate has also been used to bridge iron and manganese porphyrins [33]. Other imidazolate-bridged heterobimetallic complexes include Co-Ru, Cu-Ni, Rh-Au and Rh-Pt [34] examples. Mani *et al.* reported on hexacoordinate vanadium(II) complexes with the ligands N-methylimidazole (Nmiz), 1,2-dimethylimidazole (dmiz) and benzimidazole (benziz) [35] and complexes of Nmiz with chromium have also been studied [36].

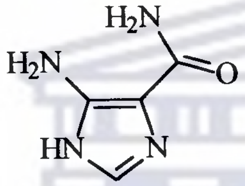
Imidazole groups were found to be relatively difficult to incorporate into synthetic ligand, therefore many researchers have used other nitrogen donors (pyridine, pyrazole and benzimidazole) in designing copper chelates to study enzyme models that have copper centers. Polydentate ligands (2-imidazolylethyl)amino and (2-benzimidazolylethyl)amino groups have been prepared via the imidate esters derived from *N*-(2-cyanoethyl)benzamides. These chelating ligands form stable copper(I) complexes that react with dioxygen at low temperature to give adducts presumed to be dinuclear peroxo complexes [37]. Most of these compounds were stabilized by incorporating the dicopper-imidazolate moiety into macrocyclic ligands, while others were stabilized by polycoordinating imidazole derivatives. Some of these investigations of were done in order to obtain stable dioxygen species [$LCuO_2CuL$], analogous to oxyhemocyanin [38]. The stability and the catalytic activity of these complexes in oxidation reactions of suitable substrates were not as widely investigated as compared to the analogous pyridyl and pyrazolyl derivatives.

Da Costa *et al.* [39] reported on the stability and catalytic activity towards the aerobic oxidation of phenolic substrates of some copper(II) complexes, $[Cu(apip)(imH)]^{2+}$, containing an imidazole ligand, in addition to a tridentate imine (apip = 2-[2-(2-pyridyl)ethyl]pyridine). The tetranuclear species, $[Cu_4(apip)_4im_4]^{4+}$, and binuclear species were observed to behave as good functional models of the tyrosine enzyme, catalyzing the aerobic oxidation of 2,6-di-*tert*-butylphenol and 3,4-dihydroxyphenylalanine. Mononuclear copper(II) complexes of salicylate derivatives with basic ligands containing nitrogen donors have been previously reported [40], these include the mononuclear copper(II) salicylate imidazole complexes derived from copper(II) aspirate [41]. In this report imidazole reacts with binuclear copper(II) aspirinate to form bis-, *pentakis*-, and *hexakis*(imidazole) mononuclear copper(II) complexes that contain the salicylate ions. The copper complexes exist in different geometries depending on the number of salicylate ions and imidazole groups.

The coordination of cyanamidonitriate in the presence of the neutral ligands of imidazole type with nickel(II) and cobalt(II) as central atoms was reported by Hvastijova et. al. [42]. Cyanamidonitrate complexes with imidazole (iz) and its methyl derivatives (meiz) of the type $[M(NO_2NCN)_2L_4]$ (M = Ni, L = iz, 1-,2-, 4-meiz; M = Co, L = iz, 1-, 4-meiz) and $[CoL_4](NO_2NCN)_2$ (L= iz, 2-meiz) have been prepared and the metal(II) environment was found to be octahedral, with four tertiary nitrogens from the imidazole ligands and two nitrile nitrogens from the cyanamidonitrate groups.

Structural studies of nickel(II), copper(II), and zinc(II) complexes of four imidazole derivatives 4(2)-aminoimidazole-5(4)-carboxamide (aic) (**16**), 2,2'-biimidazole (biim) (**17**), imidazole-4-acetic acid (iaa) (**18**) and bis(1,1'-imidazol-2-yl)(4-imidazol-4(5)-yl)-2-

aza-butane (biib) (**19**) having different coordination environments around the imidazole ring(s) were reported by Gajda *et al.* [43] with the biim offering a stable bidentate metal-binding site which is comparable to 2,2'bipyridine. This is due to the 5-membered chelate rings formed with the participation of two imidazole rings and the probably strong π–interaction between the imidazole rings and metal ions. Both aic and iaa are good models for studying the coordination behavior of imidazole ring in the presence of oxygen donors.



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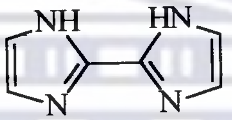

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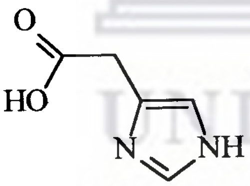

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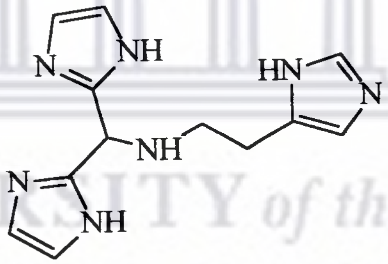

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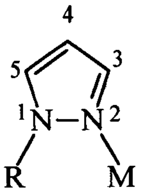
Other imidazole ligands that provide potential coordinating oxygen donors, are 4-methyl-5-imidazolecarboxaldehyde (4-Me-5-CHOIm) and 1-benzyl-2-hydroxymethylimidazole (1-Bz-2-CH_2OHIm). These bidentate ligands coordinate to Cu(II) to form eight and six coordinate compounds [44]. The coordination of the six coordinate complex [Cu(1-Bz-2-CH_2OHIm)$_4$]$(NO_3)_2$ was shown to be a slightly distorted tetragonal bipyramid with the ligands binding in a monodentate and bidentate fashion.

Copper(II) α,β-unsaturated carboxylate complexes of imidazoles, $[Cu(CH_2=CH-COO)_2(ImH)_2]$, $[Cu_2(CH_2=CH-COO)_4(ImH)_2]$, $[Cu\{CH_2=C(CH_3)-COO\}_2(ImH)_2]$ and $[Cu_2\{CH_2=C(CH_3)-COO\}_4(ImH)_2]$ (ImH = imidazole) were reported by Wang *et al.* [45]. The complexes $[Cu(CH_2=CH-COO)_2(ImH)_2]$ and $[Cu\{CH_2=C(CH_3)-COO\}_2(ImH)_2]$ have a mononuclear square planar configuration, while complexes $[Cu_2(CH_2=CH-COO)_4(ImH)_2$ and $[Cu\{CH_2=C(CH_3)-COO\}_2(ImH)_2]$ show a binuclear cage structure.

The above is the extent of imidazole and imidazole derived ligand chemistry. The discussion shows that imidazole chemistry is dominated by biological mimics and has little links to the catalysts studied in this thesis, though it constitutes one of the best studied nitrogen ligand chemistry.

1.2.3 Pyrazole derived ligands

Pyrazole functions like an imine donor ligands by coordinating to metals and metalloids through unsubstituted nitrogen (N2) (**20**), but when deprotonated, pyrazole becomes the pyrazolide ion, which can coordinate through both nitrogen atoms as an exobidentate ligand (**21**). Pyrazole ligands are attractive ligands because the donor ability of the nitrogen and steric ability may be varied through appropriate ring substitution through 2-N, 3-C, 4-C, and 5-C atoms of the pyrazole. Because of their attractive features, pyrazole ligand has been reported to exhibit a variety of modes of coordination to transition metal. The chemistry of pyrazole and pyrazolate metal complexes is quite extensive.



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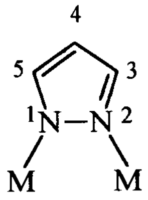


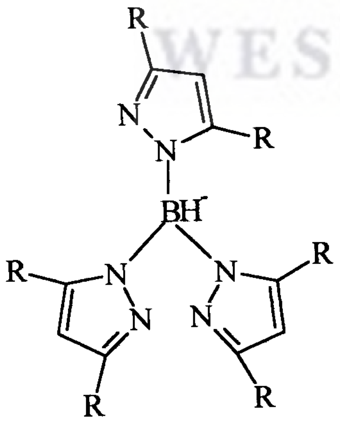
21

Unsubstituted pyrazoles coordinate to late transition metals such as palladium(II), cobalt(II), nickel(II) to produce complexes with different geometries. Simple substituted pyrazole palladium complexes [(3,5-tert-butylpyrazolyl)$_2$PdCl$_2$], [(3,5-methylpyrazolyl)$_2$PdCl$_2$], [(3-methylpyrazolyl)$_2$PdCl$_2$], [(3,5-tert-butylpyrazolyl)PdClMe] and unsubstituted pyrazolyl palladium complex [(pyrazolyl)$_2$PdCl$_2$] were recently reported by Darkwa et al [46] as catalyst precursors for the ethylene polymerization. Cobalt(II) coordinates to pyrazole, 3-methylpyrazole (mpz), 3,5-dimethypyrazole (dmpz), 3-methyl-5-phenyl pyrazole (mphpz), 1,3,5–trimethyl pyrazole (tmpz) and pyrazolato-anions [47]. The reaction of cobalt salts with pyrazole or 3-methylpyrazole gave complexes of the type [Co(pz)$_4$X$_4$] (X = univalent anion) with octahedral geometry. The *hexakis*pyrazolyl [Co(pz)$_6$(NO$_3$)$_2$] complexes were isolated when using the nitrate salts. The maximum number of pyrazolyl units on the di- and tri-substituted pyrazole coordinating to the Co(II) ion is two [Co(pz)$_2$X$_2$]. The reaction of Co(II)X$_2$ with dmpz, mphpz, tmpz, produced [CoL$_2$X$_2$] complexes. The complex [*cis*-PtCl$_2$(pzH)$_2$] was prepared from the reaction of [K$_2$PtCl$_4$] with pzH producing [Pt(pzH)$_4$][PtCl$_4$] as side product. This *cis*-complex acts as another example of antitumor-active platinum compounds [48]. Rhodium(III) complexes with unsubstituted pyrazoles and their cytostatic activity against HCV29T tumor cells have been reported by Pruchnik *et al.* [49]. The ligand 1-hydroxymethyl-3,5-dimethylpyrazole react with Cu(II) ion in a 1:4

metal to ligand molar ratio to form a binuclear complex [50,] with the ligand showing some decomposition properties when reacted with the metal ion, but decomposition was not observed for the imidazole analogue. Torralba *et al.* reported on the linear palladium(II) complexes based on the pyrazoles containing long chain substituents at the third position, with their mesomorphic properties been studied [51].

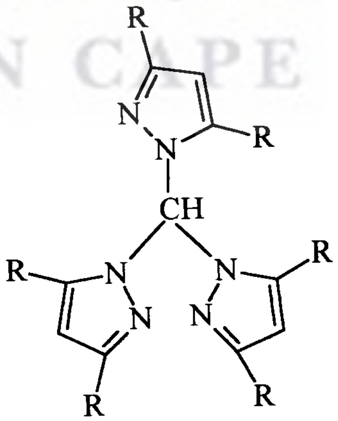
It is therefore clear from the above discussion that simple pyrazole metal complexes have ranges of properties from catalytic and anti-tumor to liquid crystallinity. The project here relates to its catalytic behaviour and this is investigated with its derivatized compounds.

Tris(pyrazol-1-yl)borate anion (HB(pz)$_3$) (**22**) as a ligand in transition metal complexes was introduced by Trofimenko [52]. HB(pz)$_3$ is often compared with C_5H_5 and C_5Me_5 due to the same charge and number of electrons donated (six electron donors). It was found that their electron donating ability varies with the coordinating metal and its coordination state [53].



R= H, Me

22



R = H, Me

23

Poly(pyrazol-1-yl)borate ligands coordinates with a variety of metals to give different coordination geometries. These ligands react with complexes of the type $[Os(C_6H_5)Cl(CO)(PPh_3)_2]$ and $[RuHCl(CO)PPh_3)_3]$ to give products in which the poly(pyrazol-1-yl)borate ligand binds to the metal centre in a bidentate mode [54]. It can also bind in a tridentate mode to a ruthenium metal. Copper hydrotris (pyrazol-1-yl)borate complexes display catalytic properties towards cyclopropanation and aziridination [55].

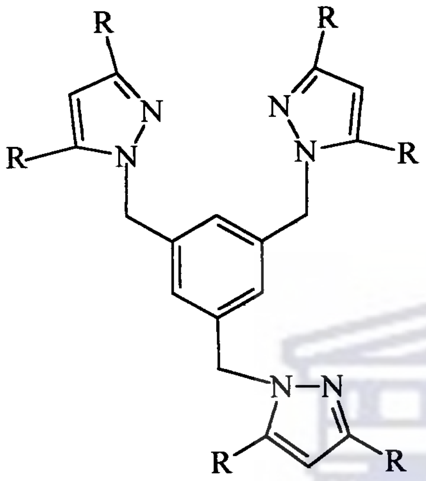
Dihydrogenobis(pyrazol-1-yl)borate anion has been found to coordinate to chromium(II) and manganese(II) to form anionic complexes, having the general formula $A[MX\{H_2B(pz)_2\}_2]$ (M = Cr(II) or Mn(II), A = NEt_4 , PPh_4, or $AsPh_4$, X= halide or pseudo halide) [56]. Oxidation of Cr(II) produced a pure crystalline compound of chromium (III) formulated as $[NEt_4][Cr_2(EtO)_3\{H_2B(pz)_2\}_2(NCS)_2]$ [57]. These ligands also coordinate to copper(II) metals to form bridged copper complexes with the ratio of 2:2 of metal to ligand. The neutral bis chelates $[Cu (H_2B(pz)_2)_2]$ complex is obtained from the reaction of $KH_2B(pz)_2$ with copper halides in polar solvents [58]. It has also been found that ethanolic solutions of $Et_4NH_2B(pz)_2$ and some metal (II) salts in 3:1 molar ratio give the anionic tris chelate $(Et_4N)[M(H_2B(pz)_2)_3]$ M = Fe, Co, Ni salts [59]. The boron derivative has dominated pyrazolyl ligand chemistry even though other derivatives are known.

The coordination chemistry of poly(pyrazol-1-yl)alkane ligands was discovered more than forty years ago. The interest in the tripodal tris(pyrazol-1-yl)alkanes **(23)** and the analogous isosteric anionic poly(pyrazol-1-yl)borates arise from the fact that regiospecific substituents in the pyrazole rings allow considerable control of the steric factors. Tris(pyrazol-1-yl)methane copper (II) complexes with different substituents on pyrazole and different counter ions were reported by Martini *et al.* [60]. The nitrato and perchlorato complexes were found to be ionic and six- coordinated. The chloride adducts display a 1:1 metal to ligand coordination and are neutral with a five-coordinated copper environment. Two different stochiometries were obtained for the bromide complexes. When less basic and less hindered $HC(pz)_3$ was employed as a donor, a 1:1 ligand to metal ratio was found to form a five coordinate complex (two bromide groups and the tripodal N_3 donor). In the case of the methyl substituted ligand, an ionic species being six coordinate was obtained. Copper (II) acetato complexes gave 1:1 and 2:3 adducts with the ligand acting as a bridging ligand. Tris(pyrazol-1yl)methane reacts with copper(I) and the reactivity of copper complex towards dioxygen has been studied [61]. The reaction of AgX (X = ClO_4, NO_3 or SO_3CH_3) acceptors with excesses of tris(pyrazol-1-yl)methane ligands L (L = $CH(pz)_3$, $CH(4\text{-}Mepz)_3$, $CH(3,5\text{-}Me_2pz)_3$, $CH(3,4,5\text{-}Me_3pz)_3$ or $CH(3\text{-}Mepz)_2(5\text{-}Mepz)$) yields 1:1 [AgX(L)], 2:1 $[Ag(L)_2]X$ or 3:2 $[(AgX_2)_2(L)_3]$ complexes [62]. The ligand to metal ratio in all complexes depends on the number and the position of the Me substituents on the pyrazole ring of the neutral ligand and on the nature of the Ag(I) acceptor.

Bis(pyrazol-1-yl)methane ligands binds to ruthenium(I) metals to form neutral and cationic rhodium complexes and it also coordinates with chromium, molybdenum or tungsten to form complexes of general formula $[M(H_2C(pz)_2)(CO)_4]$ [63]. Bis(pyrazol-1-

yl)methane and bis(3,5-dimethylpyrazol-1-yl)methane ligands react with palladium chloride to form [Pd(N–N)Cl_2] complexes [64]. The chloride atoms are replaced by the weakly coordinated ligand acetonitrile by treating dichloro complexes with $AgClO_4$ to form palladium acetonitrile complexes, [Pd(N–N)(CH_3CN)$_2$][ClO_4]$_2$. The reactivity of the new precursors [Pd(N–N)(CH_3CN)$_2$][ClO_4]$_2$ towards a variety of neutral N- and P- donor ligands (L = pyridine, triphenylphosphine, triethylphosphine or L_2 = 1,2-bis(diphenylphosphine)ethane, ethylenediamine) has also been studied.

Multidentate poly(pyrazol-1-yl)benzene ligands were reported by Steel *et al.* [65] with a benzene ring linked by methylene groups to the nitrogens of pyrazole rings. These types of ligands exhibit various modes of coordination, including participation of the benzene ring as a donor group. A trifunctional ligand 1,3,5-tris(pyrazol-1-ylmethyl)benzene (**24**) reacts with different equivalents of copper(II) perchlorate to form mono-, bi-, and tri-nuclear copper complexes and it also react with cobalt(II) [66]. For the mononuclear complex [Cu(**24**)$_2$(ClO_4)(H_2O)$_2$][ClO_4], the copper atom is coordinated to 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. The ligand 1,3-bis(pyrazol-1-ylmethyl)benzene has been shown to readily undergo cyclopalladation reactions to produce fused ring six membered metallocycles [67]. The ligand 1,2,4,5-tetrakis(pyrazol-1-ylmethyl)benzene undergo double cyclopalladation reaction to produce complexes incorporating 1,4-dipalladated benzene rings. Such compounds have recently been shown to possess interesting mesogenic properties. 1,3-bis(pyrazol-1-ylmethyl)-4,6-dimethylbenzene (**25**) undergoes cycloruthenation *via* an interesting intermediate containing an aryl C-H Ru interaction. There are many more poly(pyrazolyl)benzenes with pyrazolyl coordination sites separated by *o*-xylyl, *m*-xylyl, *p*-xylyl, mesityl spacers that are reported along with their coordination towards different metals [68].



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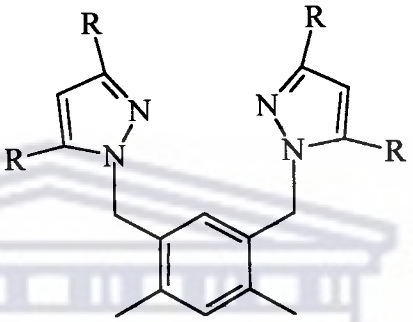
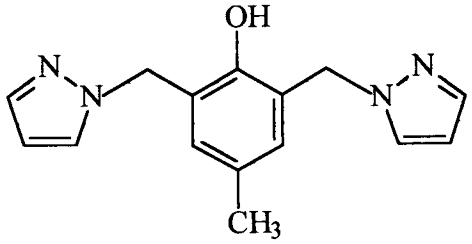


25

There are phenol-based ligands that contain two or more pyrazolyl units as nitrogen donor ligands and because of availability of an anionic phenolate group, this class of ligands provide extra stability to the resulting complexes. The synthesis and characterization of a zinc(II) complex of the new bifuntional ligand, 4-methyl-2,6-bis (pyrazol-1-ylmethyl)phenol (**26**) have also been reported [69]. The ligand reacts with zinc chloride to form a macronuclear complex with a tetrahedral geometry. In basic solution, binuclear zinc(II) complexes with distorted square pyramidal geometry are obtained under different reaction conditions. Other phenol-based ligands with one bridging phenol, two/four terminal pyrazoles and two tertiary amines have been reported to coordinate with copper to form different complexes [70].



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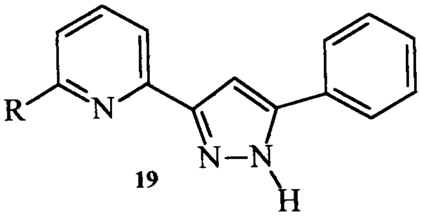
The tridentate ligand *N,N*-bis(3,5-dimethylpyrazolmethyl)aminoethane (bdmpae) coordinates with transition metals to form compounds of the general formula: [M(bdmpae)X_2] (M= Co, Ni, Cu or Zn; X= Cl, Br, or NO_3) [71]. Coordination of this ligand to metal halides and nitrates results in five coordinate (halides) and six coordinate (nitrates) compounds. With metal perchlorates, six coordinate compounds were obtained with two ligands per metal ion in which the anions are not bonded to the metal ions.

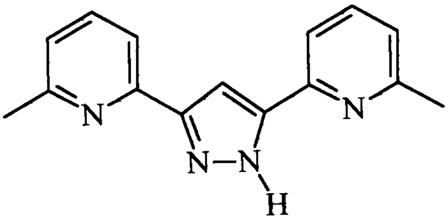
Cobalt(II) complexes with the tetradentate ligand tris(1-pyrazolylethyl)amine (TpyEA), and a variety of co-ligands have been reported. The complexes with formula [CoX(TpyEA)]BPh_4 are mononuclear and five coordinate when X = NCS, NCO, I, ClO_4, or binuclear with six-coordinate metal centres when X = F, Cl, Br, N_3 [72]. In a binuclear complex, each cobalt atom is coordinated to four nitrogen donor atoms of the TpyEA ligand and to two bridging bromine atoms in a distorted octahedral geometry. The bis-acetone adduct $[Co(Me_2CO)_2(TpyEA)](BPh_4)_2$, has been synthesized and characterized in the solid state with the cobalt atom in a six coordinated geometry, by the four nitrogen atoms of the TpyEA ligand and by the two oxygens of the acetone molecules [73]. The reaction of hydrated $CuBr_2$ and the ligand TpyEA in a 1:1 ratio of metal to ligand produced complex $Cu_4Br_7(TpyEA)_3.3H_2O$ and the X-ray structure revealed that the compound contains three non-equivalent five-coordinate $[CuBr(TpyEA)]^{+}$ cations, a discrete $[CuBr_3]^{2-}$ anion, and interposed a bromine ion and water molecules [74]. Tetradentate ligand tris(3,5-dimethyl-1-pyrazolyl-ethyl)amine (MeTPyEA), have been prepared and complexed with nickel(II) and cobalt(II) metals forming $[NiBr(MeTPyEA)]BPh_4.C_2H_5OH$, $[NiBr(MeTPyEA)]BPh_4.(CH_3)_2CO$, and $[(Co(MeTPyEA)](BPh_4)_2$ complexes [75]. Nickel complexes form trigonal bipyramid and square pyramid geometry with the cobalt complex occurring in a four coordinate. The ligand bind in a tetradentate mode, with three nitrogen atoms from a pyrazole group and the fourth nitrogen been the amine nitrogen. Tris(3,5-dimethyl-1-pyrazolylmethyl)amine (MeTPyA) ligand coordinate with iron(II), cobalt(II), and nickel(II) to form complexes, with the formulae $M(MeTPyA)XBPh_4$ (M = Fe, X = Cl, Br, M = Co, X = Cl, Br, I, NCS; M = Ni, X = Cl, Br) $[Ni(MeTPyA)FBPh_4.acetone]$, $[Fe(MeTPya)(NCS)_2]$ and $[Co(MeTPyA)(NO_3)_2]$. The iron complexes are penta- and hexa-coordinated, with the cobalt complexes having coordination geometry intermediate between trigonal-bipyramidal and tetrahedral and the nickel derivatives having a dimeric hexa-coordinate structure [76].

There are pyrazolyl ligands that are coordinated to pyridine rings to form pyrazolylpyridine ligands. The reaction of the pyrazolylpyridine derived ligands 3-phenyl-5-(2-pyridyl)pyrazole and 3-phenyl-5-(6-methyl-2-pyridyl)pyrazole (**27**) with $M(CH_3COO)_2$ (M = Cu, Co and Ni) produce different complexes with a nature of the complexes depending on the metal, ligand, and the metal to ligand ratio [77]. The study indicates that Ni(II) form compounds with neutral ligands while Cu(II) and Co(II) form compounds with ionic ligands. Tetranucleating ligand, 3,5-bis(6-methyl-2-pyridyl)pyrazole (**28**) form a pentanuclear complex with cobalt (II) metal [78].



R = H, Me

27



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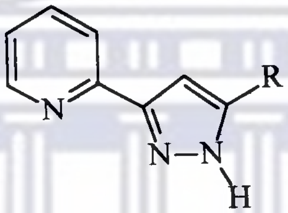
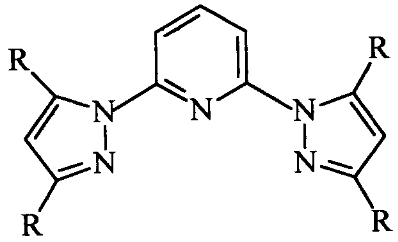


R = Me, ^{t}Bu

29

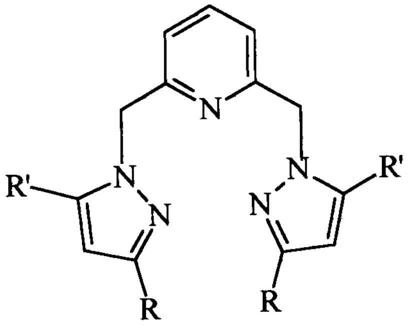
The reaction of pyrazolylpyridine derived ligand, 3-alkyl-5-(2-pyridinyl)pyrazole (**29**) and η^3-allyl palladium chloride forms a cationic η^3–allyl palladium pyrazolylpyridine complex which are converted to neutral complex under basic conditions [79]. Neutral complexes were found to have high catalytic activity towards cyclopropanation of ketone silyl acetals.

In addition to polypyrazolyl ligands, bidentate ligands and many other pyrazolyl ligands, there are large varieties of pyrazole-based ligands, which have tridentate chelation at each metal centre. The ligand 2,6-bis(pyrazolyl)pyridine (**30**) binds ruthenium(II) resulting in complexes that could be completely characterized. These complexes act as redox mimics for the analogous terpyridine compounds [80]. Variation of the number of methyl groups on the ligand allows four systematic variations of the redox and spectroscopic properties of the complexes. Coordination of the ligand to copper(II) halides produced the copper complex with copper bonded to two nitrogens of the pyrazole and pyridine nitrogen. The 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine ligand (**31**) complex with iron(II) to form distorted octahedral Fe(II)N6 coordination with 1:2 metal to ligand ratio [81]. Bis-ligand complexes $[M(II)(\mathbf{31a})_2]^{2+}$(M= Fe, Ni and Ru) have been reported [82]. The X-ray structure for the nickel complex $[Ni(\mathbf{31a})_2][ClO_4]_2$ revealed that the geometry around the nickel is close to being octahedral, with the Ni-N(pyridine) bond length being longer that Ni-N(pyrazole) bond lengths. The synthesis of the complexes $[M(II)(\mathbf{31a})(NCS)_2]$ (M= Ni and Cu) and $[Pd_3(\mathbf{31a})_2Cl_6]$ were also reported. A tripodal ligand, (**31c**) coordinate with copper(I) to give copper complexes with the formula $[Cu(\mathbf{31c})(OClO_3)].CH_2Cl_2$ and $[Cu(\mathbf{31c})(PPh_3)]ClO_4$ [83]. In $[Cu(\mathbf{31c})(OClO_3)].CH_2Cl_2$ the copper(I) is coordinated to two pyrazole nitrogens, one pyridyl nitrogen and one perchlorate oxygen. The geometry around the Cu is a highly distorted tetrahedron and can be described as distorted trigonal-planar coordination if perchlorate coordination is excluded while in $[Cu(\mathbf{31c})(PPh_3)]ClO_4$, the copper(I) is coordinated to two pyrazole nitrogens, pyridyl nitrogen and to PPh_3. There are other tridentate ligands that contain two pyrazoles and one imidazole, furan, thiophene, thioether, ether, that have been reported [84], for example ligands with one imidazole and two pyrazoles have the tendency of forming organometallic complexes of platinum [84a].



R = H, Me

30

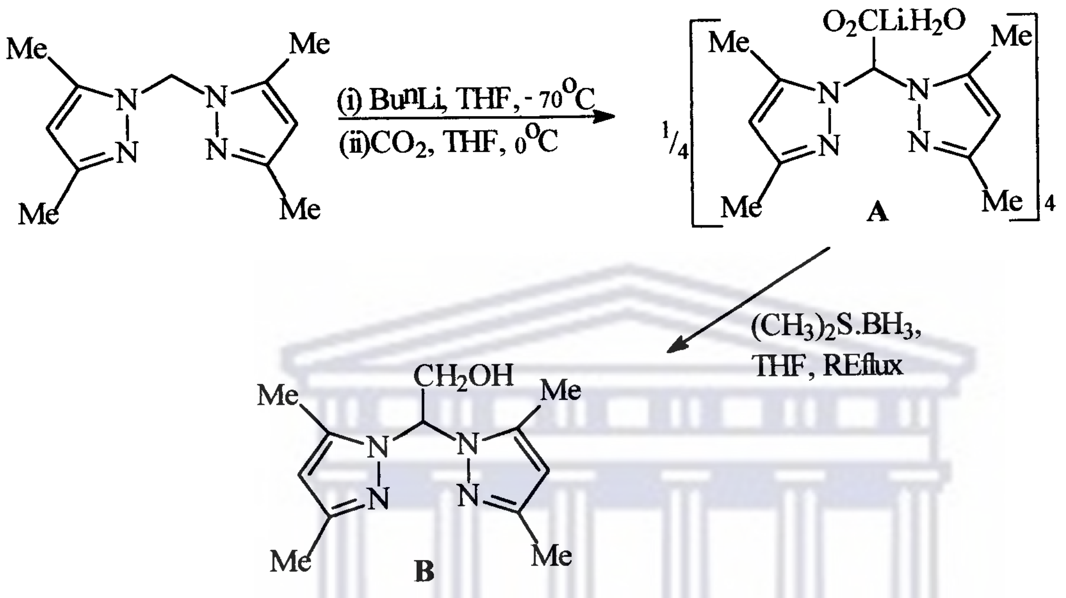


R = R’ = H (a); R =H, R’ = Me (b);

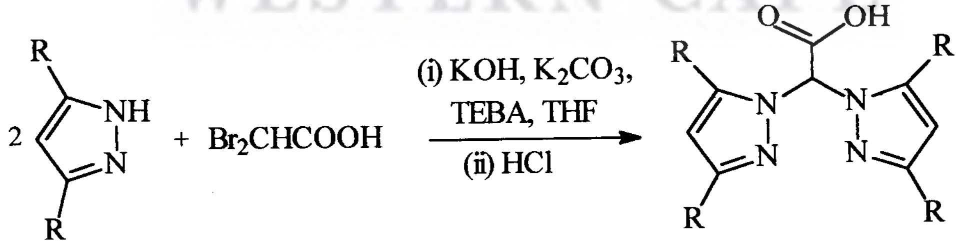
R = R’ = Me (c) **31**

The tridentate ligands, 2,6-bis(1-(pyridin-2-yl)pyrazolyl-3-yl)pyridine and 2,6-bis(pyrazol-3-yl)pyridine have been found to coordinate with cobalt(II) chloride to form five coordinate cobalt (II) complexes [85]. The cobalt is bound to ligand using the 2,6-bis(pyrazol-3-yl)pyridine fragment and the two terminal pyridine rings left uncoordinated. The above discussion demonstrates that multidentate pyrazolyl compounds can be prepared by linking the pyrazolyl units with either a benzyl group or pyridine. A pyrazolyl unit can act as a linker to two pyridine moieties and still produce bidentate ligands.

New pyrazolyl ligands with spacers other than benzyl or pyridyl groups have been prepared recently. This includes a new class of scorpionate ligands, bis(pyrazol-1-1yl)acetates (**32**). Bis(pyrazolyl)acetates ligands can be synthesized in a multistep [86] or simple one-step procedures [87] (Scheme II, III). Due to their facial binding properties, they can be compared with cyclopentadienyl or hydrotris(pyrazol-1-yl)borato ligands. The ligands bis(pyrazol-1-yl)acetates (bpza) and bis(3,5(-dimethyl pyrazol-1-yl)acetates (bdmpza) have shown to coordinate strongly to group VII transition metal carbonyl compounds affording complexes of the form: $[LM(CO)_3]$ (L = bpza, bdmpza; M = Re, Mn) [87].



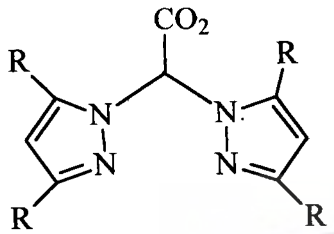
Scheme II: Summary of reactions leading to lithium derivative **A**$[\{Li(H_2O)(bdmpza)\}_4]$ and alcohol derivative **B** 2,2-bis(3,5- dimethylpyrazolyl)ethanol (Hbdmpze)



R = H, Me

Shceme III: Synthetic route leading to bis(pyrazolyl)acetic acid (R = H) and bis(3,5-dimethylpyrazolyl)acetic acid (R = Me).

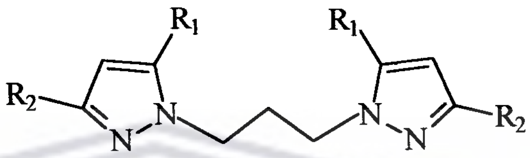
This type of ligands can also react with perrhenic acid to yield trioxorhenium complexes, for example: bpza and bdmpza react with perrhenic acid ($HOReO_8$) to produce the trioxorhenium complexes [(bpza)ReO_3] and [(bdmpza)ReO_3] respectively with a distorted octahedral geometry [88].



bpza: R= H

bdmpza: R = Me

32



bpp: $R_1 = R_2 = H$; bmpp: $R_1 = Me$, $R_2 = H$

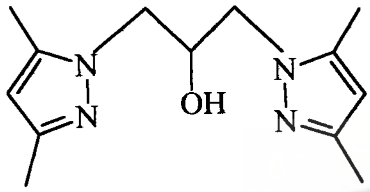
bdpp: $R_1 = R_2 = Me$

33

Another new class of pyrazolyl compounds has alkane linkers. This includes 1,3-bis(pyrazol-1-yl)propane (dpp), 1,3-bis(5-methylpyrazol-1-yl)propane (bmpp), and 1,3-bis(3,5-dimethyl pyrazol-1-yl) propane (bdpp) ligands which were synthesized by Tarrago [89]. They consist of two pyrazolyl units linked by a flexible spacer (**33**). These ligands may either bridge to two different metal ions, or act as a bidentate chelate to single metal ion in analogy to the ligand bis(2-benzimidazole)propane (tbz), which was reported to occur in a range of copper complexes [90]. They form M(II) compounds with the general formula: [M(L)(X_2)], X= Cl or NO_3, and M= Cu, Zn, or Co [91]. The ligands act as bidentate chelates forming an unusual eight chelate ring with the metal ion.

The preparation of the new tridentate ligand 1,3-bis(3,5-dimethyl pyrazol-1-yl)propan-2-ol (Hdpzhp) (**34**) and its coordination with copper metals was reported by Gamez *et al.* [92] producing the complexes [Cu_2(μ-dpzhp-O,N,N')$_2$]X_2 with X= Cu(MeOH)Cl_3, NO_3,

BF_4 and $[Cu_2(\mu\text{-dpzhp-O,N,N'})(\mu\text{-OH})Cl_2]$. The ligand forms binuclear complexes and act as an N_2O donor with a bridging alkoxo group.



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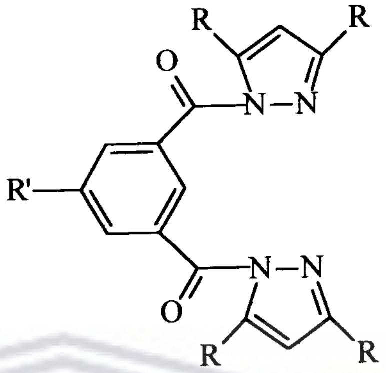


R = H, Me, ${}^tBu$; R' = H or 3,5-bis(pyrazolylcarbonyl)

35

Darkwa *et al.* synthesized pyrazolyl compounds with pyrazolyl units linked by benzenedicarbonyl and benzenetricarbonyl (**35**) [93]. The ligands coordinate to $PdCl_2(MeCN)_2$ to form bimetallic palladium complexes,$\{(3,5\text{-}R_2pzCO\}_2\text{-}1,3\text{-}C_6H_4\}Pd_2Cl_2(\mu\text{-}Cl)_2$ (R= ${}^tBu$ and Me) and $\{(3,5\text{-}{}^tBu_2PzCO)_3\text{-}1,3,5\text{-}C_6H_4\}PdCl_2(\mu\text{-}Cl)_2$; with each palladium metal bonded to one pyrazolyl nitrogen and the complex stabilized with the palladium atoms bridged by chlorine atoms. The benzenecarbonyl linker complexes are especially interesting because when activated by methylaluminoxane (MAO) they are highly active ethylene polymerization catalysts. The high activity has been attributed to the electron-withdrawing ability of the carbonyl groups, which makes the activated complexes very nucleophilic. In the light of pyridine having been used as a spacer for pyrazolyl compounds, it was reasoned that the pyridinecarbonyl spacers could also be used to prepare pyrazolyl compounds.

The project reported in this thesis is an investigation of two heterocycle carbonyl compounds, pyridinedicarbonyl and thiophenedicarbonyl, as linkers for pyrazolyl compounds and their activity for both ethylene and phenylacetylene polymerization.

1.3 Ethylene polymerization

1.3.1 Types of ethylene polymers and characterization

There are three major classes of polyethylene namely, low-density polyethylene (LPDE), high-density polyethylene (HDPE), and linear low-density polyethylene (LLPDE) [94]. HDPE is a linear high density (0.94-0.967 g/cm^3) polyethylene prepared by different catalytic systems including Ziegler-Natta and metallocene catalysts and exhibit melting temperatures between 130-140 °C. LDPE is a low density (0.915-0.935 g/cm^3) polyethylene prepared by a high-temperature and high-pressure free-radical process with melting points between 106-115 °C. LLDPE is a linear low density (0.880-0.925 g/cm^3) polyethylene produced commercially by Zieglar-Natta, chromium, and metallocene catalysts with a melting point at 125 °C. The polyethylenes (LDPE, HDPE, and LLPDE) are represented schematically in Fig. 1.1.

There are two different types of polymerization: (i) addition or chain growth and (ii) condensation or step growth polymerization. In addition polymerization, polymers are formed by the addition of one unsaturated unit to another resulting in the loss of multiple bonds. Examples of addition polymers include low-density polyethylene, polyvinyl chloride, polymethyl methacrylate and polybutadiene. In the condensation method, polymers are formed by condensing their monomers to form a repeat functional group (e.g., esters, amides, ethers) interspersed by alkyl chains, aromatic rings, or a combination of both. Examples of condensation polymers include polyesters, polyurethanes, polycarbonate and polyphenyleneoxide.

Figure 1.1 Schematic representations of LDPE, HDPE and LLDPE

Polyethylene can be characterized by some of the following techniques:

(a) Gel Permeation Chromatography (GPC)

(b) High temperature Nuclear Magnetic Resonance (NMR)

(c) Thermal analysis

(a) Gel Permeation Chromatography

Gel permeation chromatography, also known as size exclusion chromatography (SEC), is a separation method for polymers and provides information on relative molecular weights of a polymer relative to a standard sample, usually polystyrene [95]. It is a continuous technique, which can be applied to both analytical and preparative work with a wide variety of systems ranging from low to very high molecular weights [95]. Applications of GPC are for separation of high molecular weight, natural product molecules from low molecular weight species and are also used for the separation of homologs and oligomers. A major application of GPC is for the determination of weight average molecular weight (M_w), number average molecular weight (M_n) and molecular weight distribution (polydispersity) (M_w/M_n) of polymers. The difference between number and weight average molar masses gives an estimate of the width of the molar mass distribution (MMD). The broader the distribution, the larger is the difference between M_n and M_w. The ratio of M_w/M_n is thus a measure of the breadth of the molar mass and is termed polydispersity. A typical gel permeation chromatogram is shown in Fig.1.2 below.

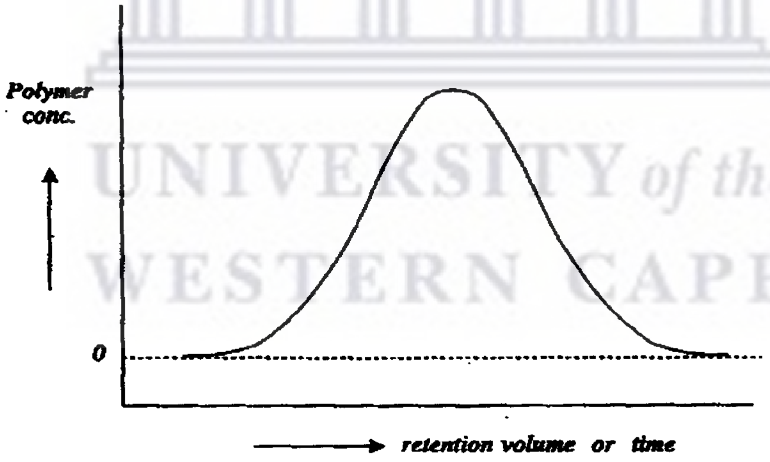
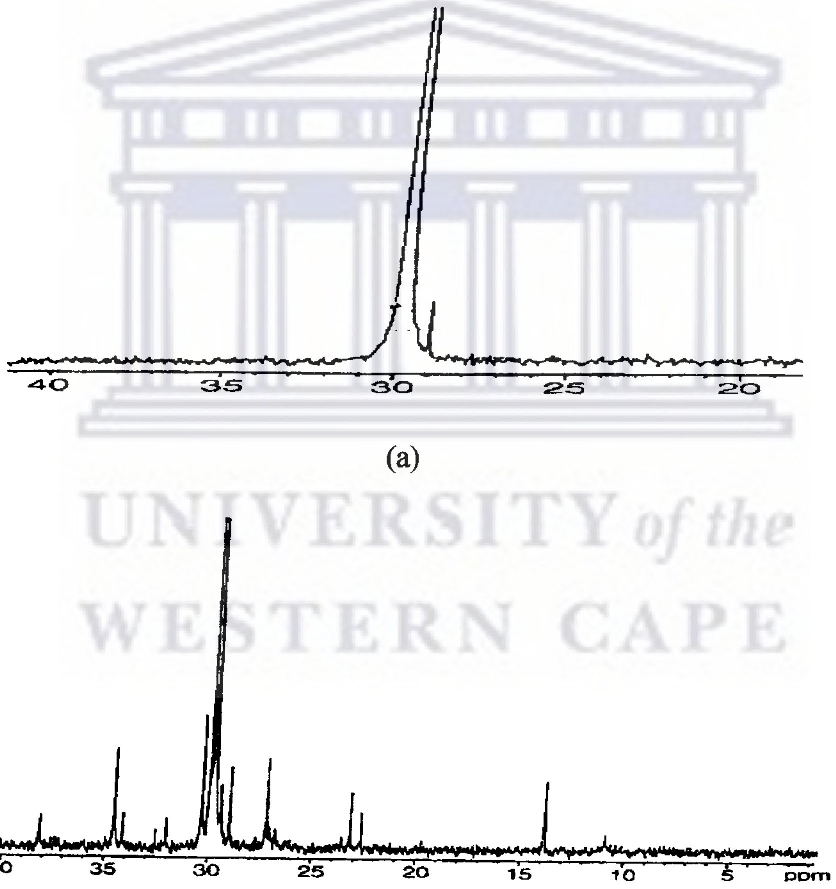


Figure 1.2 Typical elution curve, obtained during GPC of a solution of a polydisperse polymer

(b) High temperature Nuclear Magnetic Resonance

NMR spectroscopy is the most effective and significant method for observing the structure and dynamics of polymer chains both in solution and in the solid state [95a]. NMR spectroscopy is sensitive to polymer composition and stereochemistry, branching, isomerism, head-to-head and head-tail additions, and chain ends. Figures 1.3a and 1.3b show ^{13}C NMR spectra of HDPE and LDPE respectively with their ^{1}H NMR spectra exhibiting similar patterns.



(a)

(b)

Figure 1.3 ^{13}C NMR spectra of HDPE (a) and LDPE (b)

For HDPE, ^{1}H NMR spectrum has only one signal at $\delta = 1.47$ ppm while the spectrum of LDPE gives several signals depending on the number of branches along the polymer chain.

(c) Thermal analysis

Thermal analysis is a group of techniques in which a physical property of a substance and/or its reaction products is measured as a function of temperature. Thermal analysis methods that are used for polymer characterization include (i) Thermogravimetric Analysis (TGA), (ii) Differential Thermal Analysis (DTA) and (iii) Differential Scanning Calorimetry (DSC). In TGA the change in mass of a sample in a controlled atmosphere is recorded due to dehydration, decomposition, or oxidation of a polymer with time and temperature. Since different polymers have different thermal stabilities, TGA has an advantage in that it provides a rapid means to differentiate one polymer from another on the basis of the temperature range over which mass loss occurs. The most important applications of TGA are found in the study of the decomposition of various polymers. The decomposition patterns are characteristic of each kind of polymer and can be used for identification purposes.

A TGA curve can be plotted in either (a) the weight loss of the sample or (b) in differential form (the change of sample weight with time) as a function of temperature (Fig 1.4)

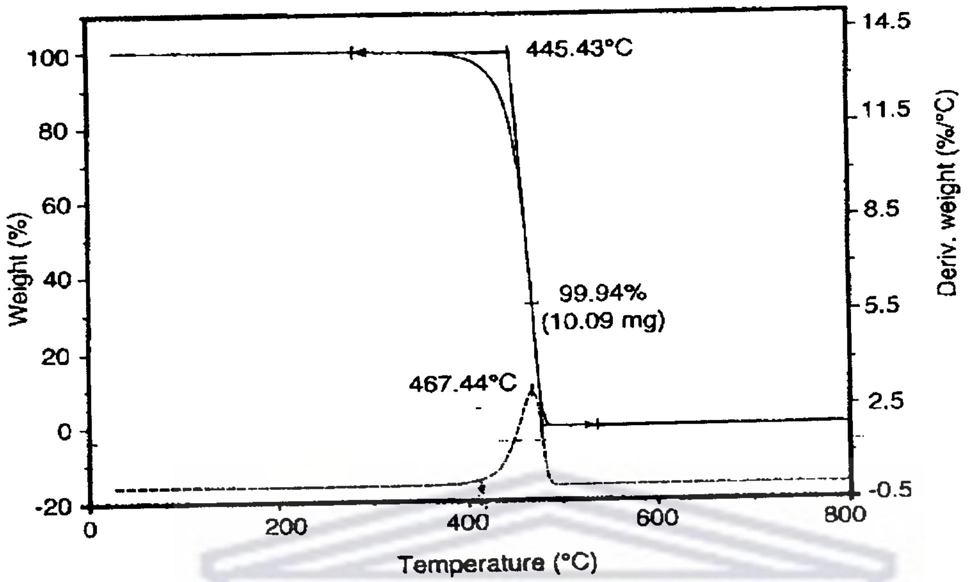


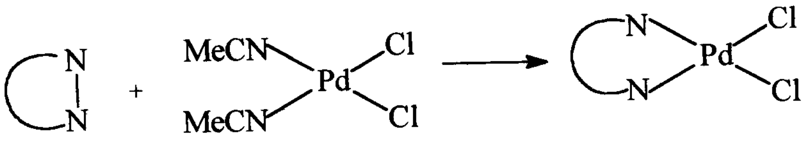
Figure 1.4 A thermogram loss of a sample of polyethylene when heated at a constant rate.

DTA and DSC are analytical techniques in which the difference in temperature between the substance and the reference is measured as a function of temperature. The basic differences between DSC and DTA is that the DSC is a calorimetric method in which differences in energy are measured and in DTA differences in temperature are recorded. The temperature programmes for both methods are similar. DSC has by now become the most widely used of all thermal methods for polymer characterization. DSC measures important physical changes in the polymer including the glass transition temperature (T_g), the crystallization temperature (T_c), the melting temperature (T_m) and the degradation or decomposition temperature (T_D). The most common application of DSC is for polymer characterization and melting point determination, which provides information on both the quality (temperature) and the quantity (peak area) of crystallinity in a polymer [95c].

1.3.2 Late transition metal complexes as catalysts for ethylene polymerization

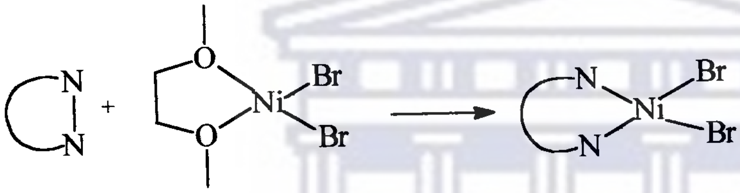
The development of organometallic complexes that have been applied as olefin polymerization catalysts has increased interest in understanding the factors that are important in the development of highly active and selective catalysts. The developments include the industrially important discovery that active catalysts may be readily generated and used *in situ* by reaction of the complex with co-catalyst methylaluminoxane (MAO). Early transition and lanthanide-based catalysts for the polymerization of ethylene and α-olefins are of interest in industry and academic research [96]. These homogeneous early transition metal-based catalysts have advantages over the traditional heterogeneous Ziegler-Natta catalysts in that their homogenous nature leads to lower polydipersities and lead to more uniform incorporation of α–olefin comonomers than obtained with heterogeneous Ziegler-Natta catalysts. This results in improvements in the properties of the polymers produced and it leads to greater insight into polymerization mechanisms. However because of the oxophillic nature and air or moisture sensitive of the early transition metals, the search for new catalysts continues, included amongst those are the nitrogen donor ligand late transition metal complexes.

Nitrogen donor ligands coordinate with late transition metals to form complexes that act as catalyst precursors for olefin polymerization. The simplest catalyst precursors are the metal dihalides, which are prepared simply by addition of the appropriate ligands to preformed starting materials for instance the reaction of ligand and $PdCl_2(MeCN)_2$ with the displacement of MeCN. The reaction shown in equation 1 is one of the examples of preparing a nitrogen donor ligand catalyst.



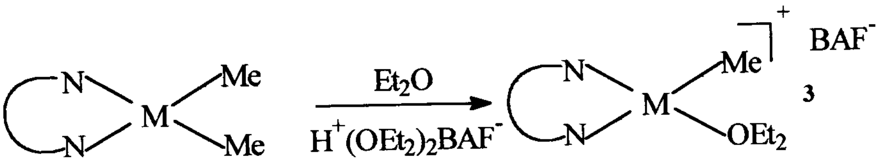
(1)

These metal dihalides can also be prepared similarly by the addition of ligands to $PdCl_2(COD)$ or $NiBr_2(DME)$ with the displacement of cycloctadiene (COD) and dimethoxyethane (DME) respectively if the nitrogen containing ligand has better donor ability than COD or DME (eq. 2).



(2)

In generating catalytically active species for olefin polymerization halides complexes are reacted with MAO to form cationic species. Therefore cationic form of organometallic complexes is generally of interest in ethylene polymerization reactions since it determines how active is the catalyst. Protonation of palladium and nickel dimethyl precursors with $H^+(OEt_2)_2 BAF^-$ [3a], which results in the loss of methane and formation of the diethyl ether adducts shown in equation 3, is another route to generate catalytically active species if the catalyst precursor is a dimethyl complex. The most intensively studied catalysts of the two types incorporate diimine or bipyridine ligands.



(3)

The diimine late transition metal catalysts have some advantages over the homogenous early metal catalysts. One of the advantages is the low oxophilicity of late transition metal catalysts, which gives them the ability to polymerize oxygen-containing olefins.

The following subsections describe the late transition metal complexes incorporating diimine and pyrazolyl ligands as catalyst precursors for ethylene polymerization.

1.3.2.1 Diimine late transition metal polymerization catalysts

The major advance of diimine late transition metal catalysts in ethylene polymerization was described by Brookhart and co-workers, who showed that Ni(II) and Pd(II) complexes incorporating bulky α–diimine ligands are capable of polymerizing ethylene and α–olefins to high molar mass polymers [3]. Diimine late transition metal polymerization catalysts have three important features: (i) highly electrophillic cationic nickel and palladium metal centres, for the rapid rates of olefin insertion, (ii) the use of sterically bulky ligands, which favour insertion over chain transfer, (iii) the use of noncoordinating counterions, for providing an accessible coordination site for the incoming olefins. Because of these three features high molecular weight polyethylene have been produced with nickel ($M_n = 1.03 \times 10^6$) [3a- c, 6, 97] and palladium ($M_n = 3.1 \times 10^4$) [3a, 98] α–diimine catalysts. The key discovery appears to be the use of sterically bulky ligands, which blocks the axial coordination sites effectively thus, hindering chain termination. Besides Ni and Pd catalysts, there are other diimine late transition metal catalysts. For example bis(imino)pyridine iron(II) and cobalt(II)-based catalysts that have been described by Brookhart [4] and Gibson [99] to be active for ethylene polymerization. Some of these have been shown to be extremely active for the synthesis of linear polyethylene. Other research groups [100] have also reported on these types of catalysts and found that high molar mass polyethylene could be obtained. It was also reported that by reducing the steric bulk of the pyridinebisimine ligands the iron catalyst oligomerize ethylene to linear α–olefins with high activity and selectivity [99b]. A recent review by Brookhart and coworkers summarized late transition metal catalysts that have been used for ethylene polymerization [101]. Gibson and coworkers also reported recently on non-metallocene olefin polymerization catalysts [102].

1.3.2.2 Pyrazole and pyrazolyl late metal polymerization catalysts

Substituted pyrazole palladium(II) complexes, $[(3,5\text{-}{}^t\mathrm{Bu_2pz})_2\mathrm{PdCl_2}]$, $[(3,5\text{-}\mathrm{Me_2pz})_2\mathrm{PdCl_2}]$, $[(3\text{-}\mathrm{Mepz})_2\mathrm{PdCl_2}]$, $[(\mathrm{pz})_2\mathrm{PdCl_2}]$ and $[(3,5\text{-}{}^t\mathrm{Bu_2pz})_2\mathrm{PdCl(Me)}]$ reported by Darkwa *et al.* have shown moderate activity (1006 kg PE/mol Pd.h) towards ethylene polymerization [47]. Activation of these palladium complexes by MAO resulted in palladium complexes, which were used as catalysts for polymerization of ethylene giving linear high-density polyethylene (HDPE). The activity of neutral and cationic palladium(II) complexes incorporating bis(pyrazolyl)methane ligands towards ethylene polymerization reported by Jordan *et al.* [103] was however lower than the catalyst of Darkwa *et al.* [47]. In the report by Jordan *et al.* their neutral palladium complexes, $[\{\mathrm{Ph_2C}(3\text{-}{}^t\mathrm{Bupz})_2\}\mathrm{PdCl_2}]$,

[{$Ph_2C(pz)_2$}$PdCl_2$] had no activity towards polymerization of ethylene even after being activated by MAO. However the cationic complex, {$Me_2C(pz)_2$}$PdMe(L)^+$ (L = NMe_2Ph) oligomerize ethylene producing C_8-C_{24} internal olefins. This demonstrates that electrophilicity of the cationic complex {$Me_2C(pz)_2$}$PdMe(L)^+$ is considered crucial to the activity of the catalyst since the first step in oligomerization reaction involves the formation of a palladium-olefin complex. Therefore in order to increase the catalytic activity of the complexes the presence of a strong electrophilic metal is essential. We have explored this requirement in our research group.

1.3.2.3 Electron withdrawing pyrazolyl compounds as polymerization catalysts

The first project in preparing electrophilic metal centres by our group made use of electron-withdrawing linkers. Palladium(II) complexes with pyrazolyl units linked by benzenedicarbonyl and benzenetricarbonyl were prepared and used as catalysts for ethylene polymerization [93]. These electrophilic complexes have shown much better activity towards ethylene polymerization, after being activated with MAO, relative to Jordan catalysts and simple pyrazole palladium complexes. Even here the tertiary butyl benzenedicarbonyl palladium catalyst exhibited higher activity (2591 kg PE/mol Pd.h) than the benzenetricarbonyl analogue (1099 kg PE/mol Pd.h). The reason behind this activity difference is because in the latter catalyst there is an uncoordinated pyrazlolylcarbonyl unit, which reacts with MAO and therefore reduces the amount of activator in solution. The benzenecarbonyl linker study raised interest in the investigation of palladium(II) complexes with pyrazolyl units linked by different heterocyclic carbonyl compounds as catalysts for ethylene polymerization. My project therefore started with a single goal of comparing benzene linker compounds with those of heterocycle pyridine and thiophene.

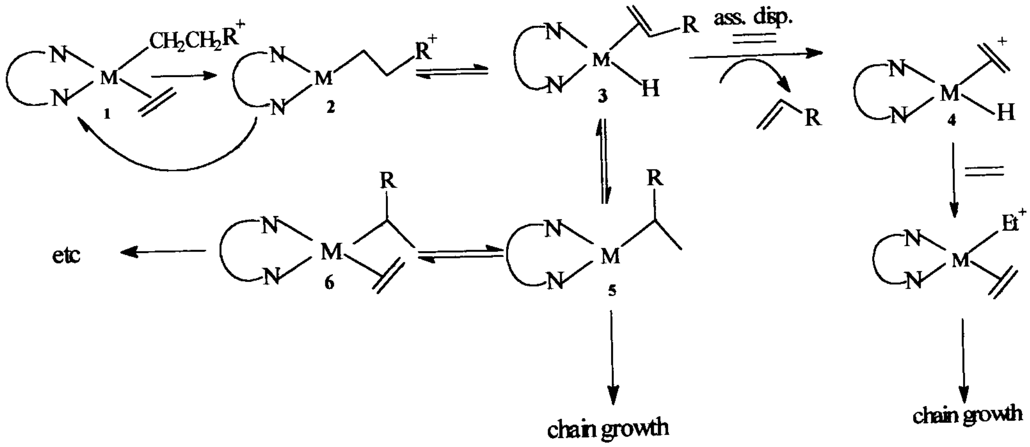
1.3.2.4 The use of pyrazolyl compounds with heterocyclic carbonyl linkers as polymerization catalysts

Ligands with pyrazolyl units linked by pyridine and thiophene dicarbonyl were synthesized and reacted with $PdCl_2(MeCN)_2$ to yield palladium(II) complexes that were used as precatalysts for ethylene polymerization. The resulting complexes were activated by MAO to provide alkylation on the palladium(II) complexes and generate cationic site for the ethylene monomer to coordinate. HDPE was produced from these complexes with moderate catalytic activity. This is reported in chapter 3 of this thesis.

1.3.3 Polymerization mechanism

The mechanism for olefin polymerization has been extensively investigated. It is generally accepted that an insertion process is the chain growth mechanism. The generally accepted mechanism for the ethylene polymerization using α-diimine Ni(II) and Pd(II) is shown in Scheme IV.

The mechanism can be described as follows: the catalyst resting states are alkyl olefin complexes indicated by structure **1**. Migratory insertion results in **2**, which can be rapidly trapped by ethylene to reform an alkyl ethylene species, **1**. These migration reactions occur without chain transfer.



Scheme IV: Mechanism of olefin polymerization

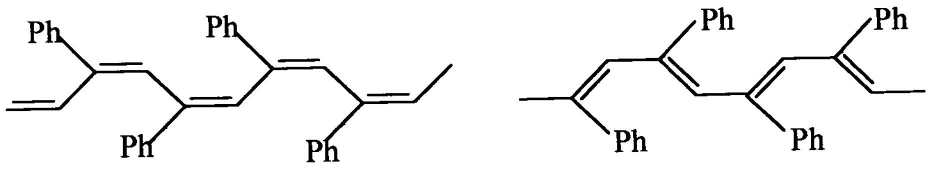
Successive migratory insertion and ethylene trapping from **1** leads to a linear polymer. Alternatively, **2** can also undergo β–hydride elimination to yield an olefin hydride **3**. Complex **3** can undergo reinsertion to produce a branched alkyl group as in **5**. Alkene group inserts in the M-H unit of **3** to produce a methyl branch, while further chain migration via β–hydride elimination and readdition processes produces longer branches. As a result of chain transfer processes, complex **3** can release olefin to yield **4**, which can initiate a new chain. The rates of associative displacement (ass. disp.) and chain transfer (**3** to **4**) are greatly retarded by the extreme steric bulk of the diimine ligands. However for Ni, trapping and insertion reactions are competitive with chain running and the extent of branching is sensitive to ethylene pressure, decreasing with increasing ethylene pressure. Unlike most late transition metal catalysts, the rate of chain transfer in Ni and Pd catalysts (**3-4**) is quite slow relative to rate of chain propagation and thus, high molecular weight polymers are produced. The key to slowing the chain transfer is the introduction of steric bulk in the axial position of the square plane. Generally, the more the steric bulkiness of the substituents, the higher the polymer molecular weight.

1.4 Polymerization of phenylacetylene (PA)

1.4.1 Types of phenylacetylene polymers and characterization

Homogeneous catalysis in past years has been represented by the development of catalytic systems for the polymerization of unsaturated substrates, with more interests towards formation of π–conjugated polymers. The attention towards these π–conjugated polymers stem form their unique physico-chemical properties, which make them promising materials for several applications. Polyacetylenes are intriguing polymers because of their physico-chemical characteristics and novel properties such as conductivity, oxygen permeability, humidity sensor, ferromagnetism and non- linear optical properties. There are various polyacetylenes with aromatic and related pendant groups that have been prepared and studied [104]. The substituted acetylene that has been mostly studied is phenylacetylene (PA) [105]. This monomer undergoes polymerization catalyzed by several catalytic systems.

Polymerization of monosubstituted acetylenes with head-to-tail regiochemistry can produce four isomeric polyenes (Fig. 1.5) 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.

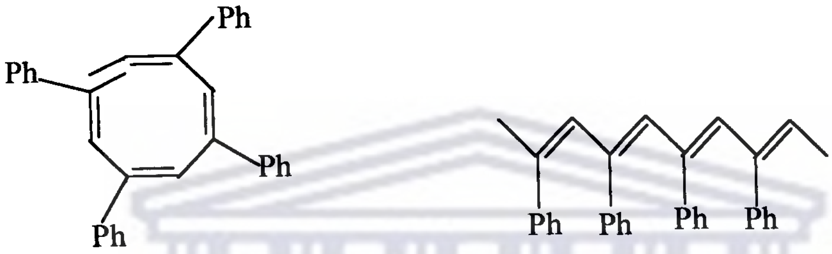


A

B

cis-transoidal

trans-cisoidal



C

D

cis-cisoidal

trans-transoidal

Figure1.5 Stereoisomers of the polyphenylacetylenes

Polymer characterization also makes use of some of analytical techniques described earlier for polyethylene. SEC is used to characterize polyphenylacetylenes for molecular weight and polydispersity determination and NMR and IR spectroscopy for stereoregularity of the polymers.

Determination of poly(phenylacetylene) strereochemistry

Infrared absorbance at 870-895 cm^{-1} is characteristic of *cis* structures in polyphenylacetylene and the absorbance at 910-920 cm^{-1} is specific to *trans* structures [105a, b, 106]. According to Simionescu and co-workers [105b] the doublet at 740-760 cm^{-1} is present in both *cis-cisoidal* (C) and *cis-transoidal* (A) polymers.

Furthermore the *cis-transoidal* is characterized by ^{1}H NMR spectrum with peaks at δ = 5.82 ppm (vinylic protons), 6.70 ppm (*ortho* aromatic proton), and a peak at 6.85 ppm (*meta* and *para* aromatic protons), while according to theoretical calculations [105b] the ^{1}H NMR spectrum of the *cis-cisoidal* polyphenylacetylene must be different. The stereoregularity of *cis-transoidal* polyphenylacetylene is also supported by ^{13}C NMR spectra with signals at 126.70 ppm (*para* aromatic carbons), 127.50 and 127.80 ppm (*meta* aromatic carbon), 131.80 ppm (vinylic carbon) and 139.30 and 142.90 ppm (quaternary carbons) [107].

Figures 1.6 and 1.7 represent the IR and NMR spectra of *cis-transoidal* polyphenylacetylene. Few studies have been reported on the *trans-cisoidal* (B) polyphenylacetylene, which is characterized by ^{1}H NMR spectrum with a very broad peak centered at 7.2 ppm and ^{13}C NMR spectra with a very broad peak centered at 128.25 ppm [108]. Figure 1.8 shows the ^{1}H NMR spectrum of *trans-cisoidal* polyphenylacetylene.

1.4.2 Phenylacetylene polymerization and mechanism

Phenylacetylene monomer undergoes polymerization by using different methodologies. The methodologies include thermal [109], cationic [110], radical [109, 111], Ziegler-Natta based catalysts [112], and also by group 6 transition metals such as WCl_6 and $MoCl_5$ [104f, 113]. Amongst all these methodologies, the most widely studied catalysts for the synthesis of phenylacetylene with high molecular weight are rhodium complexes.

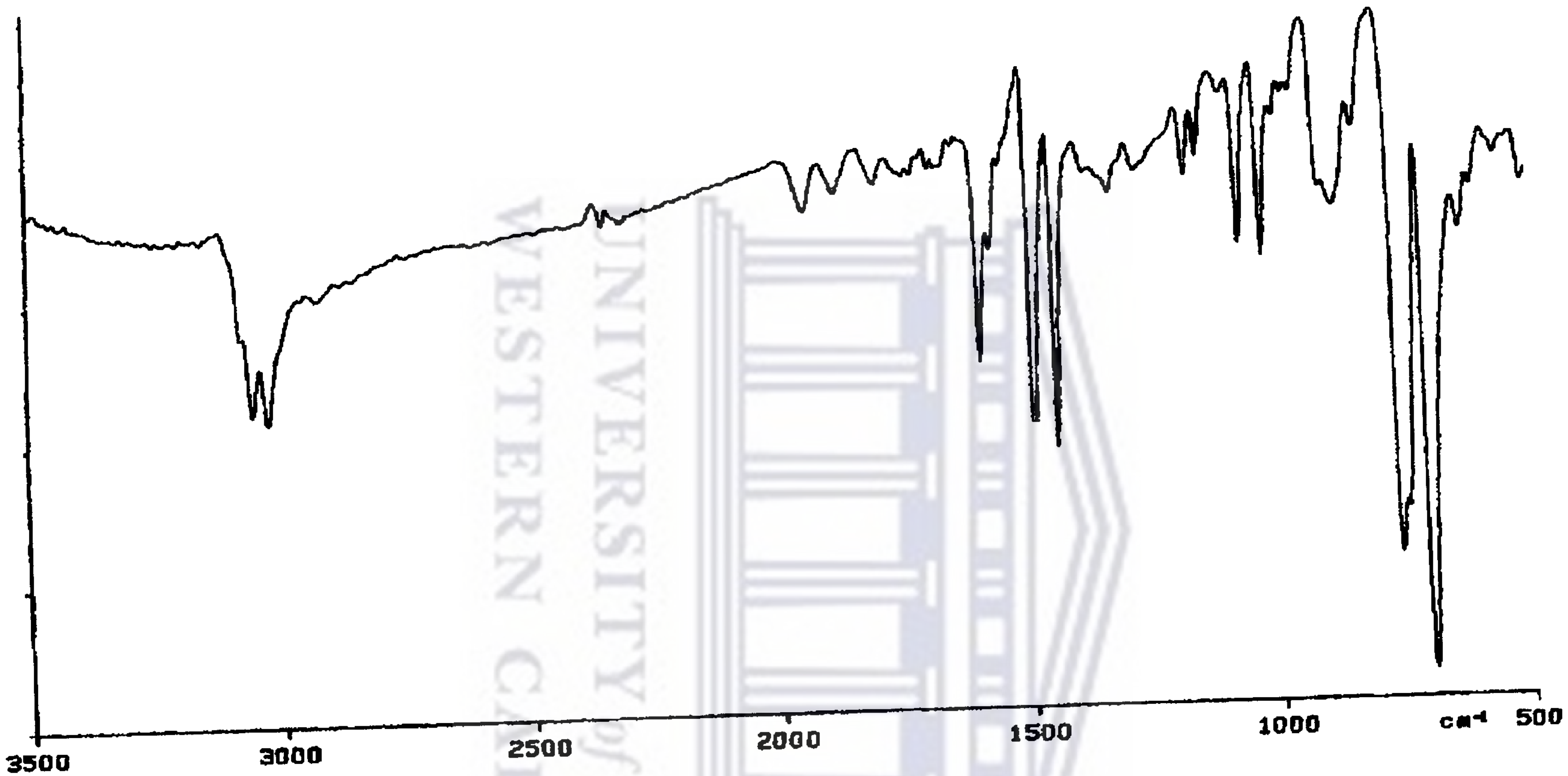
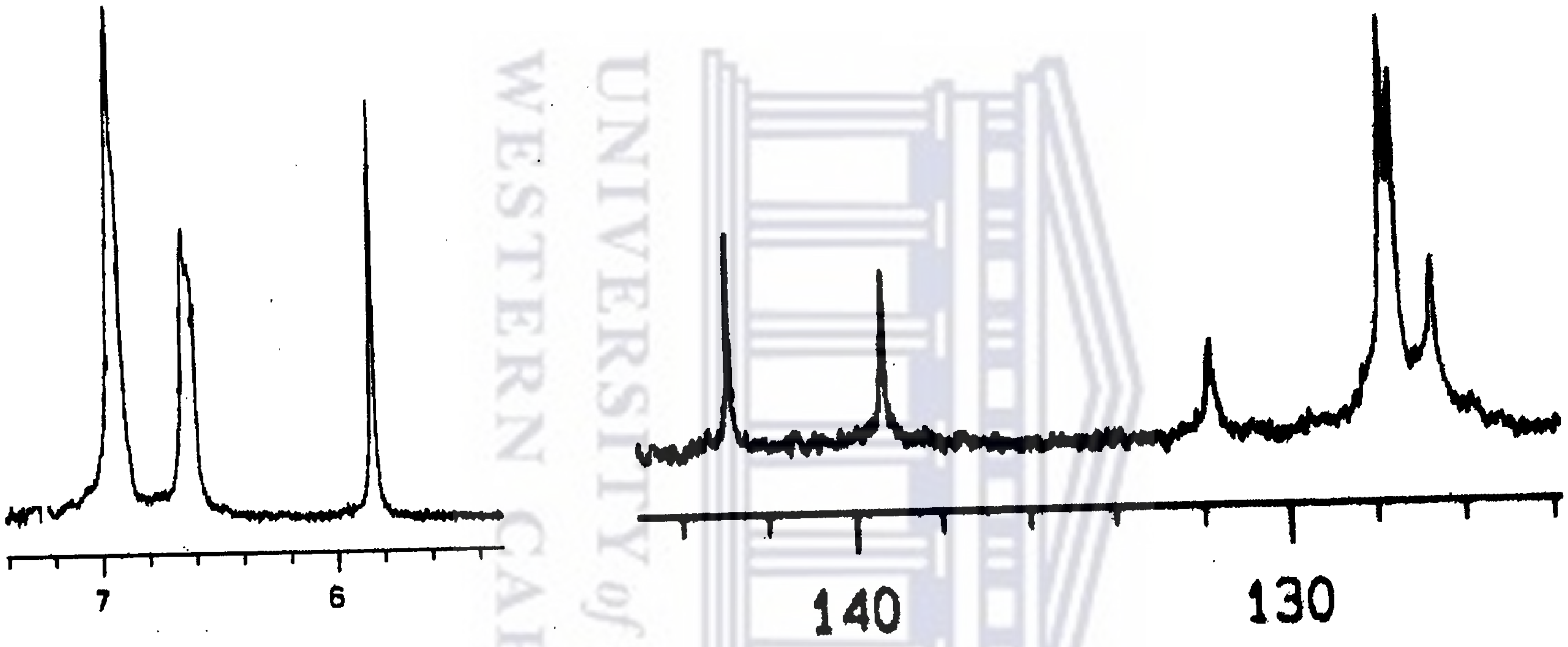


Figure 1.6 IR spectrum of *cis-transoidal* polyphenylacetylene (KBr pellets)



(a) (b)

Figure 1.7 ^{1}H NMR spectrum (a) and ^{13}C NMR spectrum (b) of *cis-transoidal* polyphenylacetylene.

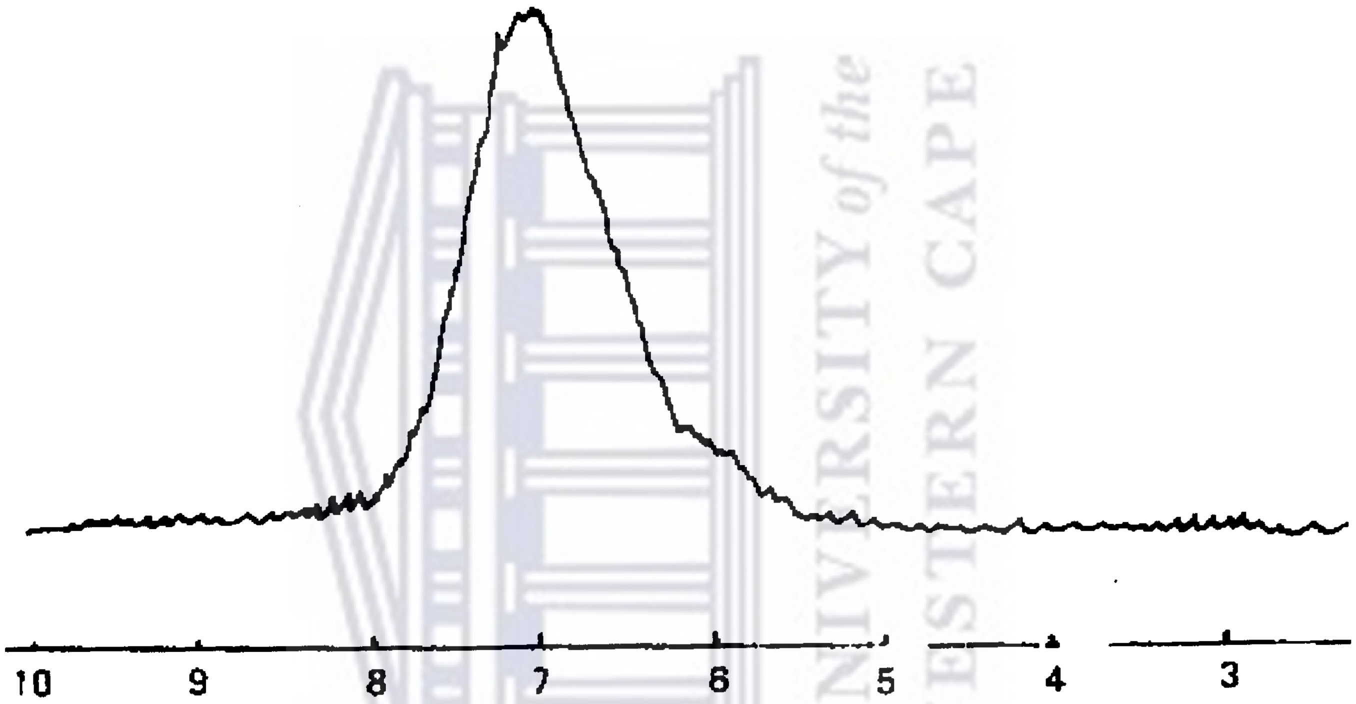
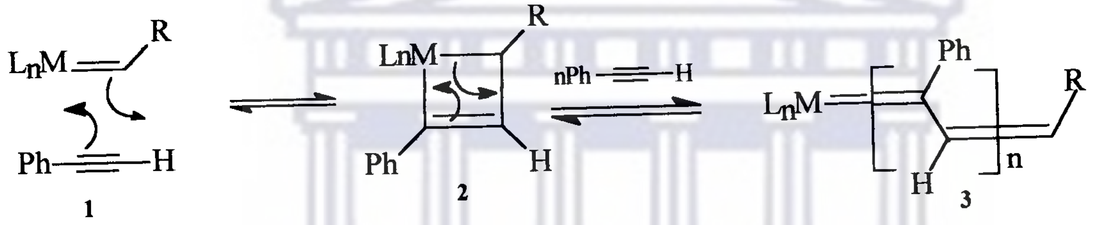


Figure 1.8 ^{1}H NMR spectrum of *trans-cisoidal* polyphenylacetylene

1.4.2.1 Molybdenum (Mo) and tungsten (W) polymerization catalysts

Formerly, it was difficult to produce high molecular weight substituted polyacetylenes. Masuda and Higashimura reported that $MoCl_5$ and WCl_6 catalysts could polymerize phenylacetylene to give high molecular weight polymer in good yield [114]. Since then various types of Mo- and W-based catalysts have been used as the catalysts for the polymerization of acetylene derivatives having various functionality [115]. The Mo- and W-based catalysts are considered to promote polymerization by a metathesis mechanism (Scheme V), similar to the metathesis catalysts (carbene complexes) [116].



Scheme V: Metathesis mechanism for polymerization of phenylacetylene

Metathesis mechanism can be described as follows: when acetylene is reacted with an alkylidene in structure **1**, a [2+2] cycloaddition occurs forming a metallacyclobutene **2.** If the metallacycle opens (structure **3**) in a productive manner it results in a growing polymer chain.

The Mo- based catalysts are of three types: support oxides, generated in various ways, $MoCl_5$, activated by a suitable co-catalyst, and Mo complexes also activated by a co-catalyst [117]. The co-catalyst used in most homogeneous systems are known to play a role in the metathesis process in that they have Lewis acid properties. They interact with the transition metals complex or are converted into a more active species, which are involved in the metathesis process. This interaction depends on the nature of transition metal and its ligand, the nature of co-catalysts metal, the solvent and the reaction conditions.

1.4.2.2 Rhodium (Rh) and iridium (Ir) polymerization catalysts

The most recently used catalysts are precursor complexes of the formula $Rh(C{\equiv}CPh)(nbd)(PPh_3)_2$ [118], $[Rh(diene)Cl]_2$ and $Rh(diene)(tosylate)(H_2O)$ [119], *in situ* catalytic systems $[RhCl(nbd)]_2/Ph_2C{=}C(Ph)Li/PPh_3$ [120], or $[Rh(cod)Cl]_2/[2,6\text{-}(PPh_2CH_2)_2\text{-}C_6H_4]$ [121]. These catalysts have been shown to be highly active and gave polyphenylacetylene with high molecular weights [122].

The use of ionic liquids (*n*-butylpyridinium tetrafluoroborate $[bupy]BF_4$ and 1-*n*-butyl-3-methylimidazolium tetrafluoroborate $[bmim]BF_4$) as reaction media for polymerization of phenylacetylenes, catalyzed by (diene)Rh(acac) and $[(diene)RhCl]_2$ complexes under basic co-catalysis (triethylamine) was reported to produce extremely high molecular weights (196000) and high yields (92%) of polyphenylacetylene [123].

Rhodium(I) tris(pyrazolyl)borate complexes were found to be effective catalyst for highly stereoregular polymerization of phenylacetylene to give polyphenylacetylene with a head-to-tail *cis-transoidal* structure [124]. The monomer percentage conversion is affected by the substituents at the 3- and 5-position of the pyrazolyl groups and the more sterically bulky R groups led to higher monomer percentage conversion (93%).

Rhodium-based catalysts promote stereoselective polymerization of monosubstituted acetylenes to give the polyenes with *cis-transoidal* geometry and were shown to proceed *via* an insertion mechanism.

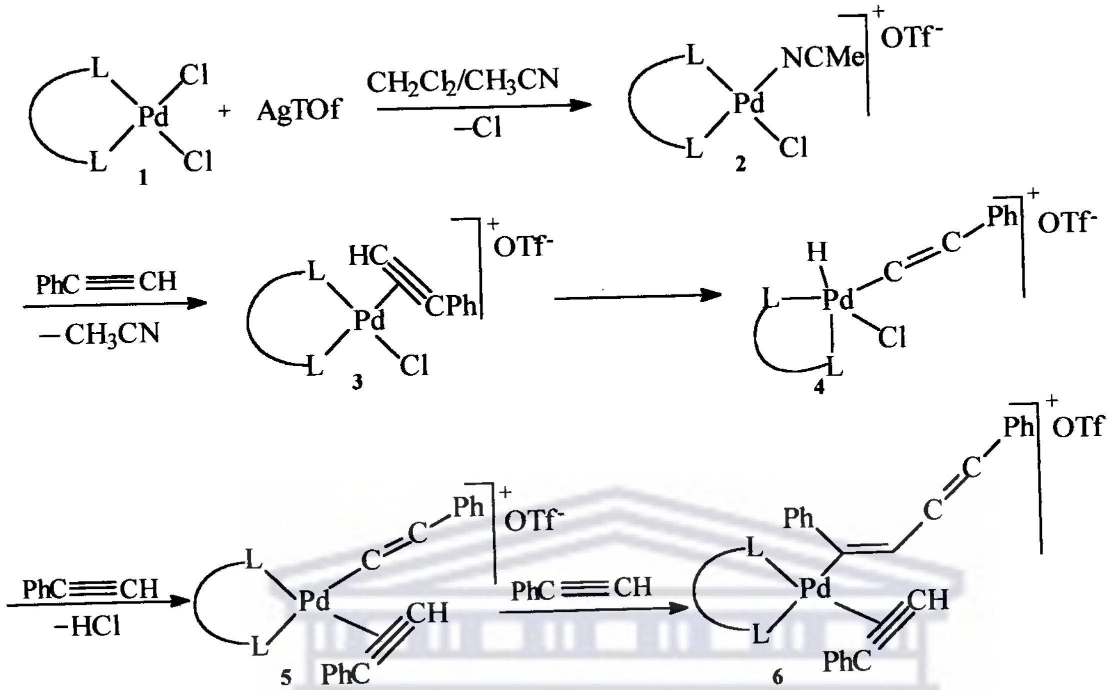
Following their studies on rhodium catalysts for alkyne polymerization [125], Farnetti *et al.* investigated the properties of iridium compounds, $[Ir(cod)Cl]_2$ and $[Ir(cod)(OMe)]_2$ which were found to be effective in promoting phenylacetylene polymerization with negligible formation of oligomeric products [108]. Polymerization reactions proceed in various solvents such as THF, chloroform and benzene, but polymerization is most favoured when Et_3N is used as reaction medium. The polymers obtained have moderate percentage conversions (ranging between 10-51%) and the ^1H NMR spectra confirmed both *cis* and *trans* structures. It has been reported recently that polymerization could be performed in liquid or supercritical CO_2 [126] and in a biphasic system water\methylene chloride [119] and demonstrates that polymerization solvents need not to be traditional organic solvents.

1.4.2.3 Nickel (Ni) and palladium (Pd) polymerization catalysts

Nickel and palladium catalysts that are active for polymerization of alkyne can be included in the same class as rhodium derivatives, as the related reactions seems to proceed *via* the same insertion mechanism. Polymerization of phenylacetylene with the nickel catalyst, $Ni(COD)_2$-$CF_3COO(allyl)$ yielded yellowish red polymers in good yields and with the highest molecular weight being 12000 [127]. The ^1H NMR spectrum showed broad peaks, which indicates that the microstructure of the polymers produced may be a mixture of *cis* and *trans* structures.

Polymerization of PA with palladium(II) salts as initiators form methanol soluble and methanol insoluble polymers of low molecular weights (M_w = 2400) with narrow polydispersities (between 1.07 to 2.20). The palladium complexes [Pd(NN'O)Cl] (NN'O = 2-acetylpyridine or 2-formylpyridinebenzoylhydrazones) react at room temperature with phenylacetylene in water to form high molecular weight polyphenylacetylene (M_w = 23495) [128]. The ^{1}H NMR spectrum of polymer obtained indicated the presence of both the *cis* and the *trans* isomers.

Darkwa *et al.* were the first group to use diphosphinopalladium(II) complexes to catalyze PA polymerization [129]. Cationic bis(phosphino)palladium complexes (formulae, $[(P–P)Pd(CH_3)(NCCH_3)]^+$ and $[(P–P)Pd(NCCH_3)_2]^{2+}$) were prepared from the reaction of palladium complexes and silver trifluoromethanesulfonate (AgOTf or silver triflate) in the presence of various CH_2Cl_2/CH_3CN solvent mixtures. The cationic complex was used to catalyze polymerization of phenylacetylene to yield polyphenylacetylene of high molecular weight (M_w = 17707) and high monomer percentage conversion (90%). The effect of solvent and temperature were investigated and it was found that the highest molecular weight was obtained at room temperature and using a 3:1 CH_2Cl_2/CH_3CN solvent mixture. The proposed mechanism for this type of catalysts is described in Scheme VI.



Scheme: VI: Proposed insertion mechanism for polymerization of phenylacetylene

The insertion mechanism in scheme VI can be described as follows: the reaction between the palladium complex **1** and co-catalyst silver triflate form the cationic complex **2** by removal of the chloride ions. Reaction between the catalytically active species **2** and the monomer gives the π–adduct **3**. The second monomer coordinates to the palladium with the loss of HX by reductive elimination in structure **4**. Species **4** undergoes formal alkyne insertion into palladium-carbon bond to give the palladium-vinyl compound **5**; a new monomer molecule then readily occupies the resultant vacant coordination site. Further insertion and monomer coordination resulting in the lengthening of the polymer fragment coordinated to the metal **6**.

In general polymerization mechanism of phenylacetylene and microstructures of its polymers strongly depend on the catalyst, thermal history of the polymerization reaction and often on the solvent [105b, c, f, 116c].

Among the investigations that have been done on polymerization of phenylacetylene, few studies have been on the use of nitrogen donor ligands complexes. Therefore we have developed nitrogen donor ligand complexes using heterocyclic pyrazolylcarbonyl palladium complexes, which were reacted with silver triflate to produce cationic palladium complexes. These cationic complexes have been used as active catalysts for phenylacetylene polymerization. The polymerization reactions are discussed in chapter 4 and the products formed are oligomers and polymers.

1.5 Objectives of the project

The introduction above describes the type of work that our research group is investigating. Our first main aim in this project was to expand on the nitrogen donor ligands late metal catalysts by preparing heterocyclic pyrazolylcarbonyl palladium(II) complexes. Heterocyclic pyrazolylcarbonyl palladium(II) complexes were synthesized with different substituents, thus varying pyrazole units from uncoordinated pyrazole to tert-butyl pyrazole in order to improve the solubility and structural properties of the complexes.

The second aim was to investigate the catalytic activity of these palladium complexes for the ethylene polymerization with active catalysts generated *in situ* by the reaction of complexes with the co-catalyst, MAO. The effect of different substituents, Al:Pd ratio, temperature, and pressure on ethylene polymerization were also investigated.

The third aim was to investigate the catalytic activity of these complexes on phenylacetylene polymerization. The active catalysts were generated *in situ* by the reaction of palladium complexes and silver triflate (AgOTF). The stereoregularity of the polymers produced using NMR spectra and effect of solvents and temperature were also investigated.

The rest of the thesis shows the extent to which the investigation was successful and how the compounds were characterized. It also describes the catalytic activities of the complexes prepared and the properties of polymers produced.

1.6 References

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CHAPTER 2

SYNTHESIS OF HETEROCYCLIC LIGANDS AND THEIR LATE TRANSITION METAL COMPLEXES

2.1 Introduction

The nature of the ligands bound to a metal ion plays a significant role in the determination of the properties of metal-coordinated compounds, whether in inorganic coordination complexes or in organometallic compounds, or in bioinorganic model compounds [1]. Heterocyclic bidentate and tridentate nitrogen compounds with six-membered rings such as 2,2'-bipyridine, 1,10-phenanthroline, and 2,2':6',2"-terpyridine have been used extensively in transition metal chemistry [2]. These six-membered nitrogen heterocycles are excellent π–acceptors therefore they provide soft donor sites for metal coordination while the five-membered nitrogen heterocycle, pyrazole, is a better π–donor and act as hard donor site.

The ease of synthesis of variously substituted pyrazoles helps determines electronic and steric properties of the pyrazole metal complexes. Heterocyclic pyrazole-based chelating ligands form a variety of coordination complexes with different metal ions, providing different coordination geometry and nuclearity. When six-membered heterocycle such as pyridine and a five-membered heterocycle pyrazole are linked in a single ligand system, interesting compounds are formed and the complexes of such ligands give rise to significantly different electronic properties. One example of this type of ligand, 1,3,5-tris(pyrazolylmethyl)benzene, was prepared by Steel *et al.*, showing that the ligand coordinates to different equivalents of copper(II) perchlorate to form mono-, bi-, and trinuclear copper complexes [3]. The structure of this ligand was shown in Chapter 1, Section 1.2.3.

A recent review by Mukherjee shows that many pyrazolyl ligand coordination compounds of 2,6-bis(pyrazolylmethyl)pyridine and 2-(pyrazolylmethyl)pyridine ligands have been prepared and their substituted derivatives were discussed, showing how structures and properties are dictated by the nature of substituents on the ligand. This has been described earlier (Chapter 1, Section 1.2.3) [4].

In this chapter, we report the synthesis and characterization of five membered pyrazole ligands as well as their substituted derivatives that are linked to six-membered pyridine or five-membered thiophene through carbonyl linkers and to study their coordination to late transition metals, especially palladium. We see similar effects of linker and substituents on ligand structure and properties in our investigations as those reported in literature.

2.2 Experimental procedure

2.2.1 Materials and instrumentation

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Dichloromethane (CH_2Cl_2) was dried by distilling over diphosphorous pentoxide (P_2O_5) and stored over molecular sieves. Toluene, diethyl ether (Et_2O) and tetrahydrofuran (THF) were dried by distilling over sodium/benzophenone and stored over dry molecular sieves, while thionyl chloride was obtained from Merck and distilled before use. The starting material, 3,5-ditertbutylpyrazole, was prepared by literature procedure [5], while 2,6-pyridinedicarboxylic acid, 2,5-thiophenedicarboxylic acid, pyrazole, 3-methylpyrazole and 3,5-dimethylpyrazole were obtained from Aldrich and used as received. NMR spectra were recorded on a Gemini 2000 instrument (^{1}H at 200 MHz, ^{13}C at 50.3 MHz). Chemical shifts are reported in δ (ppm) and referenced to residual protons and ^{13}C signals of deuterated chloroform as internal standard. Elemental analysis was performed in-house on a Carlo Erba NA analyzer in the department of chemistry, University of the Western Cape.

2.2.2 Synthesis of 2,6-pyridinedicarbonyl dichloride

To 25 mL of thionyl chloride in a 100 mL Schlenk tube, 2,6-pyridinedicarboxylic acid (2.70 g, 16.16 mmol) was added. The reaction mixture was refluxed for 24 h. A colourless solution was obtained and the solvent was removed carefully using a vacuum pump, equipped with a dry ice in acetone or liquid nitrogen cooled trap. A yellowish white solid was obtained and was recrystallized from CH_2Cl_2/hexane to give a pure white crystalline 2,6-pyridinedicarbonyl dichloride. Yield = 1.73 g, 55%. ^{1}H NMR ($CDCl_3$): δ 8.16 (t, 1H, py); 8.35 (d, 2H, py), IR (nujol mull): ν (C=O) = 1709 cm^{-1}.

2.2.3 Synthesis of 2,5-thiophenedicarbonyl dichloride

This compound was prepared using the same procedure as above (2.2.2) with 2,5-thiophenedicarboxylic acid (2.00 g, 11.62 mmol) and 25 mL thionyl chloride. Yield = 1.51 g, 62%. ^{1}H NMR ($CDCl_3$): δ 7.97 (s, 2H, th), IR (nujol mull): ν (C=O) = 1678 cm^{-1}.

2.2.4 Synthesis of the ligands

2.2.4.1 Synthesis of 2,6-bis(3,5-ditert-butylpyrazolyl-1-carbonyl)pyridine (L1)

To a solution of 2,6-pyridinedicarbonyl dichloride (0.57 g, 2.83 mmol) in dry, degassed toluene (60 mL), 3,5-ditert-butylpyrazole (1.00 g, 5.67 mmol) was added followed by addition of Et_3N (3 mL). The reaction mixture was refluxed for 24 h. A white $Et_3N.HCl$ salt gradually formed and was removed by filtration at the end of the reaction. The filtrate was evaporated to give a white solid. A pure product was obtained after chromatography using silica gel with CH_2Cl_2/ether (8:1). Yield =1.01 g, 73%. Anal. Calcd. for $C_{29}H_{41}N_5O_2$: C, 70.84; H, 8.41; N, 14.24. Found: C, 69.95; H, 8.91; N, 13.67. ^1H NMR ($CDCl_3$): δ 7.68-7.82 (m, 3H, py); 6.18 (s, 2H, 4-pz); 1.49 (s, 18H, 5-^{t}Bu); 1.17 (s, 18H, 3-^{t}Bu). ^{13}C {^1H} NMR ($CDCl_3$): δ 166.2, 163.6, 158.0, 153.4, 134.6, 125.7, 106.5, 33.2, 32.3, 29.6, 29.5. IR (nujol mull): ν (C=O) = 1716 cm^{-1}, ν (C=N) = 1564 cm^{-1}.

Compounds **L2**, **L3** and **L4** were synthesized using the same procedure for **L1**.

2.2.4.2 Synthesis of 2,6-bis(3,5-dimethylpyrazolyl-1-carbonyl)pyridine(L2)

Compound **L2** was prepared from the reaction of 3,5-dimethylpyrazole (1.00 g, 10.40 mmol) and 2,6-pyridinedicarbonyl dichloride (1.06 g, 5.20 mmol). Yield = 0.99 g, 59%. Anal. Calcd. for $C_{17}H_{17}N_5O_2$: C, 63.15; H, 5.30; N, 21.66. Found: C, 62.51; H, 5.06; N, 21.20. ^1H NMR ($CDCl_3$): δ 7.88-7.98 (m, 3H, py); 6.05 (s, 2H, 4-pz); 2.65 (s, 6H, 5-Me); 2.20 (s, 6H, 3-Me). ^{13}C {^1H} NMR ($CDCl_3$): 165.9, 153.2,151.9, 145.2, 136.2, 126.5, 111.7, 97.4, 14.2, 13.7, 11.8, IR (nujol mull): ν (C=O) = 1709 cm^{-1}, ν (C=N) = 1583 cm^{-1}.

2.2.4.3 Synthesis of 2,6-bis(3-methylpyrazolyl-1-carbonyl)pyridine (L3)

Compound **L3** was prepared from the reaction of 3-methylpyrazole (0.64 g, 0.63 mL, 7.82 mmol) and 2,6-pyridinedicarbonyl dichloride (0.80 g, 3.92 mmol). Yield = 0.65 g, 56%. Anal. Calcd. for $C_{15}H_{13}N_5O_2$: C, 61.01; H, 4.44; N, 23.72. Found: C, 58.31; H, 4.24; N, 21.44. ^{1}H NMR ($CDCl_3$): δ 8.79 (d, 2H, 5-pz); 8.34 (d, 2H, py); 8.13 (t, 1H, py); 6.35 (d, 2H, 4-pz); 2.39 (s, 6H, 3-Me). ^{13}C {^{1}H} NMR ($CDCl_3$): 167.9, 162.3, 155.4, 149.5, 149.1, 143.4, 138.4, 138.2, 138.1, 133.9, 133.6, 132.6, 129.2, 128.7, 127.6, 127.2, 111.3, 110.9, 104.9, 13.9, 11.6, IR (nujol mull): ν (C=O) = 1712 cm^{-1}, ν (C=N) = 1554 cm^{-1}.

2.2.4.4 Synthesis of 2,6-bis(pyrazolyl-1-carbonyl)pyridine (L4)

Compound **L4** was prepared from the reaction of pyrazole (0.53 g, 7.82 mmol) and 2,6-pyridinedicarbonyl dichloride (0.80 g, 3.92 mmol). Yield = 0.41 g, 41%. Anal. Calcd. for $C_{13}H_9N_5O_2.1/3CH_2Cl_2$: C, 52.82; H, 4.43; N, 23.70. Found: C, 52.56; H, 4.61; N, 18.90. ^{1}H NMR ($CDCl_3$): δ 8.79 (d, 2H, 5-pz); 8.34 (d, 2H, py); 8.17 (t, 1H, py); 7.85 (d, 2H, 3-pz); 6.54 (t, 2H, 4-pz). ^{13}C {^{1}H} NMR ($CDCl_3$): 162.7, 149.6, 145.4, 137.9, 132.4, 128.8, 110.1, IR (nujol mull): ν (C=O) = 1710 cm^{-1}, ν (C=N) = 1569 cm^{-1}.

2.2.4.5 Synthesis of 2,5-bis(3,5-ditert-butylpyrazolyl-1-carbonyl)thiophene (L5)

To a colourless solution of 2,5-thiophenedicarbonyl dichloride (1.00 g, 4.78 mmol) in dry, degassed toluene (60 mL), 3,5-ditert-butylpyrazole (1.68 g, 4.78 mmol) was added followed by addition of Et_3N (3 mL). A yellow precipitate formed after addition of Et_3N and the mixture was stirred for 24 h. The $Et_3N.HCl$ salt was removed by filtration and the filtrate was evaporated to give a yellow solid. Pure product was obtained after chromatography using silica gel with CH_2Cl_2/Et_2O (4:1). Yield = 0.89 g, 39%. Anal. Calcd. for $C_{28}H_{40}N_4O_2S$: C, 67.71; H, 8.12; N, 11.28. Found: C, 67.52; H, 8.35; N, 10.97. ^1H NMR ($CDCl_3$): δ 8.16 (s, 2H, th); 6.22 (s, 2H, 4-pz); 1.48 (s, 18H, 5-^{t}Bu); 1.36 (s, 18H, 3-^{t}Bu). ^{13}C {^1H} NMR ($CDCl_3$): δ 163.8, 160.8, 158.0, 143.9, 135.6, 106.9, 33.3, 32.5, 30.0, 29.4, IR (nujol mull): ν (C=O) = 1698 cm^{-1}, ν (C=N) = 1567 cm^{-1}.

Compound **L6** was synthesized using the same procedure for **L5**

2.2.4.6 Synthesis of 2,5-bis(3,5-dimethylpyrazolyl-1-carbonyl)thiophene (L6)

Compound **L6** was prepared from the reaction of 2,5-thiophenedicarbonyl dichloride (1.00 g, 4.78 mmol) and 3,5-dimethylpyrazole (0.92 g, 4.78 mmol). Yield = 0.81 g, 52%. Anal. Calcd. for $C_{16}H_{16}N_4O_2S$: C, 58.52; H, 4.91; N, 17.06. Found: C, 57.57; H, 4.76; N, 16.44. ^1H NMR ($CDCl_3$): δ 8.24 (s, 2H, th); 6.06 (s, 2H, 4-pz); 2.63 (s, 6H, 5-Me); 2.33 (s, 6H, 3-Me). ^{13}C {^1H} NMR ($CDCl_3$): δ 160.6, 152.5, 145.1, 142.7, 135.8, 111.6, 14.4, 13.8, IR (nujol mull): ν (C=O) = 1680 cm^{-1}, ν (C=N) = 1564 cm^{-1}.

2.2.5 Synthesis of complexes

2.2.5.1 Synthesis of {2,6-bis(3,5-ditert-butylpyrazolyl-1-carbonyl)pyridine}palladium(II) dichloride (complex 1).

To a yellow solution of $PdCl_2(CH_3CN)_2$ (0.25 g, 0.95 mmol) in CH_2Cl_2 (40 mL), 2,6-bis(3,5-ditert-butylpyrazolyl-1-carbonyl)pyridine(**L1**) (0.47 g, 0.95 mmol) was added. The solution gradually turned orange-red and after stirring for 48 h, the solvent was evaporated to give an orange residue. Recrystallization from CH_2Cl_2 at room temperature or CH_2Cl_2/ether at −15 °C gave analytically pure product as orange crystals suitable for X-ray analysis. Yield = 0.30 g, 62%. Anal. Calcd. for $C_{29}H_{41}Cl_2N_5O_2Pd.1/4CH_2Cl_2$: C, 50.46; H, 5.98; N, 10.15. Found: C, 50.97; H, 5.81; N, 10.07. ^{1}H NMR ($CDCl_3$): δ 8.02-8.18 (m, 3H, py); 6.36 (s, 1H, 4-pz); 6.19 (s, 1H, 4-pz); 1.77 (s, 9H, 5-^{t}Bu); 1.57 (s, 9H, 3-^{t}Bu); 1.47 (s, 9H, 5-^{t}Bu); 1.18 (s, 9H, 3-^{t}Bu). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 175.2, 164.9, 162.8, 162.4, 160.8, 158.5, 156.9, 151.4, 138.5, 131.0, 127.6, 109.9, 107.6, 33.9, 33.3, 32.4, 30.0, 29.5, 29.3, 29.2, IR (nujol mull): ν (C=O) = 1727 and 1712 cm^{-1}, ν (C=N) = 1557 cm^{-1}.

2.2.5.2 Synthesis of {2,6-bis(3,5-dimethylpyrazolyl-1-carbonyl)pyridine}palladium(II) dichloride (complex 2)

This complex was prepared in the same way as in preparation of complex **1** with 2,6-bis(3,5-dimethylpyrazolyl-1-carbonyl)pyridine (**L2**) (0.47 g, 0.95 mmol) and $PdCl_2(CH_3CN)_2$ (0.25 g, 0.95 mmol). The yellow solution of $PdCl_2(CH_3CN)_2$ formed a pink precipitate after addition of the ligand. The mixture was stirred for 24 h and filtered to give a pink solid. Yield = 0.37 g, 51%. Anal. Calcd. for $C_{17}H_{17}Cl_2N_5O_2Pd$: C, 40.78; H, 3.42; N, 13.99. Found: C, 39.26; H, 3.62; N, 11.04. ^{1}H NMR (DMSO): δ 8.19 (m, 3H, py); 5.97 (s, 1H, 4-pz); 5.91 (s, 1H, 4-pz); 2.36 (s, 3H, 5-Me); 2.18 (s, 9H, 3-Me); 2.17 (s, 9H, 5-Me); 2.08 (s, 3H, 3-Me), IR (nujol mull): ν (C=O) = 1719 and 1723 cm^{-1}, ν (C=N) = 1576 cm^{-1}.

Complexes **3-6** were prepared in a similar manner as described for **1.**

2.2.5.3 Synthesis of {2,6-bis(3-methylpyrazolyl-1-carbonyl)pyridine}palladium(II) dichloride (complex 3)

Complex **3** was prepared from 2,6-bis(3-methylpyrazolyl-1-carbonyl)pyridine (**L3**) (0.50 g, 1.69 mmol) and $PdCl_2(CH_3CN)_2$ (0.44 g, 1.69 mmol). The yellow solution of $PdCl_2(CH_3CN)_2$ in CH_2Cl_2 formed a pink precipitate immediately after the addition of the ligand and then changed to a yellow precipitate after 12 h. The yellow mixture was stirred for further 12 h and filtered to give a yellow solid. Yield = 0.39 g, 49%. Anal. Calcd. for $C_{15}H_{13}Cl_2N_5O_2Pd.1/2CH_2Cl_2$: C, 33.16; H, 2.41; N, 12.89. Found: C, 34.61; H, 2.12; N, 11.34, IR (nujol mull): ν (C=O) = 1723 and 1734 cm^{-1}, ν (C=N) = 1546 cm^{-1}.

2.2.5.4 Synthesis of di-μ-chlorodichlorobis{2,5-bis(3,5-ditert-butylpyrazolyl-1-carbonyl)thiophene}dipalladium(II) (complex 4)

Complex **4** was prepared from 2,5-bis(3,5-ditert-butylpyrazolyl-1-carbonyl)thiophene (**L5**) (0.44 g, 0.88 mmol) and $PdCl_2(CH_3CN)_2$ (0.23 g, 0.88 mmol). The yellow solution of $PdCl_2(CH_3CN)_2$ in CH_2Cl_2 changed to a red precipitate immediately after addition of the ligand and then changed to an orange precipitate after 5 h. The orange precipitate was stirred for further 19 h and filtered to give an orange solid. Yield = 0.41 g, 66%. Anal. Calcd. for $C_{56}H_{80}Cl_4N_8O_4S_2Pd_2$: C, 47.39; H, 5.68; N, 7.89. Found: C, 23.23; H, 4.38; N, 2.98, IR (nujol mull): ν (C=O) = 1727 cm^{-1}, ν (C=N) = 1470 cm^{-1}.

2.2.5.5 Synthesis of di-μ-chlorodichlorobis{2,5-bis(3,5-dimethylpyrazolyl-1-carbonyl)thiophene}dipalladium(II) (complex 5)

Complex **5** was prepared from 2,5-bis(3,5-dimethylpyrazolyl-1-carbonyl)thiophene (**L6**) (0.45 g, 1.37 mmol) and $PdCl_2(CH_3CN)_2$ (0.36 g, 1.37 mmol). The yellow solution of $PdCl_2(CH_3CN)_2$ in CH_2Cl_2 formed a pink precipitate immediately after addition of the ligand. The pink precipitate changed to a yellow precipitate after 5 h. The yellow mixture was stirred for a further 19 h and filtered to give a yellow solid. Yield = 0.44 g, 65%. Anal. Calcd. for $C_{32}H_{32}Cl_4N_8O_4S_2Pd_2$: C, 37.99; H, 3.19; N, 11.08. Found: C, 37.84; H, 2.86; N, 11.00, IR (nujol mull): ν (C=O) = 1690 cm^{-1}, ν (C=N) = 1475 cm^{-1}.

2.2.5.6 Synthesis of {2,6-bis(3,5-ditert-butylpyrazolyl-1-carbonyl)pyridine}cobalt(II) dichloride (complex 6)

To a solution of **L1** (0.50 g, 1.02 mmol) in pentanol (60 mL), anhydrous $CoCl_2$ (0.13 g, 1.02 mmol) was added and the blue solution was stirred at 60°C for 20 minutes. The solvent was removed and recrystallized from diethyl ether to give a dark blue solid. Yield = 0.20 g, 32%. Anal Calcd for $C_{29}H_{41}Cl_2N_5O_2Co.1/3Et_2O$: C, 51.80; H, 7.46; N, 10.92. Found: C, 53.73; H, 8.86; N, 11.26, IR (nujol mull): ν (N-H) = 3284 cm^{-1}, ν (C=N) = 1561 cm^{-1}.

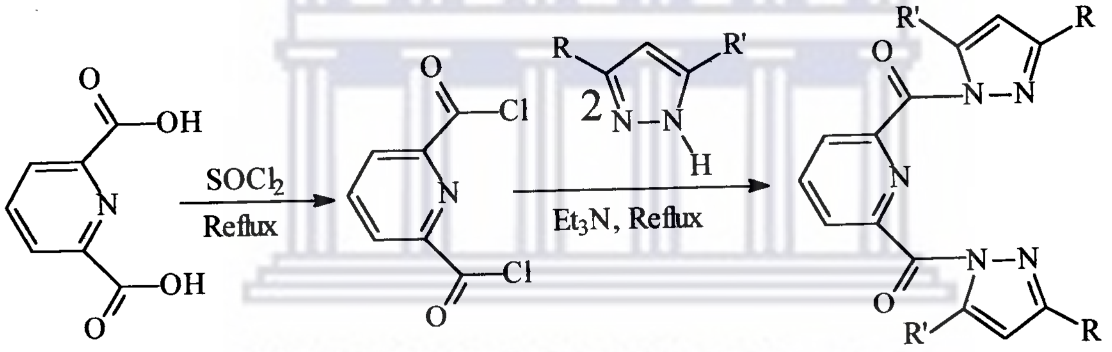
2.2.5.7 Synthesis of {2,6-bis(3,5-dimethylpyrazolyl-1-carbonyl)pyridine}cobalt(II) dichloride (complex 7)

Complex **7** was prepared in a similar procedure as in complex **6** from the reaction of ligand **L2** (0.30 g, 0.92 mmol) and anhydrous $CoCl_2$ (0.12 g, 0.92 mmol). Yield = 0.15 g, 36%. Calcd for $C_{17}H_{17}Cl_2N_5O_2Co.1/3Et_2O$: C, 34.84; H, 4.09; N, 16.42. Found: C, 35.19; H, 4.13; N, 16.42, IR (nujol mull): ν (N-H) = 3 292 cm^{-1}, ν (C=N) = 1564 cm^{-1}.

2.3 Results and discussion

2.3.1 Synthesis and properties of ligands

Compounds **L1-L4** were synthesized by the reaction of 3,5-ditertiarybutylpyrazole, 3,5-dimethylpyrazole, 3-methylpyrazole, pyrazole and 2,6-pyridinedicarbonyl dichloride. The 2,6-pyridinedicarbonyl dichloride was prepared from 2,6-pyridinedicarboxylic acid and thionyl chloride (Scheme I).

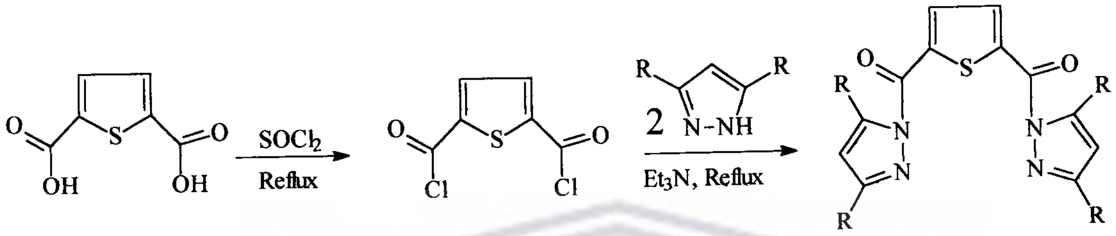


R = R' = ^{t}Bu (**L1**)   R = R' = Me (**L2**)

R = H, R = Me (**L3**)   R = R' = H (**L4**)

Scheme I: Synthesis of ligands **L1**, **L2**, **L3** and **L4**

The ligands were purified by column chromatography on silica with eluting solvents in the ratio of 8:1 (CH_2Cl_2:Et_2O) to give pure ligands in moderate to high yields (40%-73%). Attempts to synthesize **L1-L4** by using high molar ratios gave lower yields (23%). Compounds **L5** and **L6** were prepared from the reaction of 3,5-ditertiarybutylpyrazole, 3,5-dimethylpyrazole and 2,5-thiophenedicarbonyl dichloride respectively, which was prepared from the reaction of 2,5-thiophenedicarboxylic acid and thionyl chloride (Scheme II). Ligands **L5** and **L6** were also purified by column chromatography using silica and eluted with a 4:1 CH_2Cl_2/Et_2O solvent mixture to give analytically pure ligands in moderate yields (39-52%).



R = ^{t}Bu (**L5**); R = Me (**L6**)

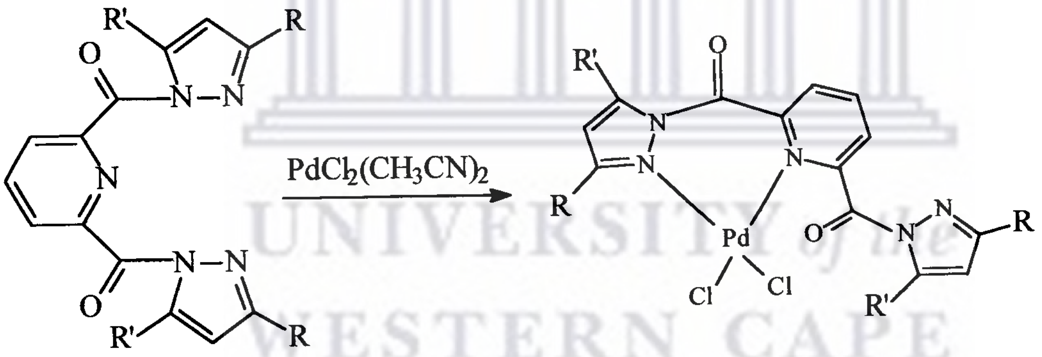
Scheme II: Synthesis of ligands **5** and **6**

When these ligand reactions were performed in solvents that had not been well dried, ^1H NMR data indicated a mixture of unreacted pyrazole, small amount of acid chlorides (2,6-pyridinedicarbonyl dichloride and 2,5-thiophenedicarbonyl dichloride), the corresponding carboxylic acids and small amounts of the expected products. This result is indicative of the fact that both acid chlorides are sensitive to moisture; therefore the presence of moisture converts the acids chlorides back to the carboxylic acids. Ligands **L1-L6** dissolve in common organic solvents such as, chlorinated solvents, Et_2O, THF and toluene. Ligands **L1** and **L5** are even soluble in hexane but ligands **L2-L4** and **L6** are not soluble in hexane. Compounds **L1-L6** are very stable in air so they can be stored at room temperature for a long period. Microanalysis was used to establish the purity of all ligands while IR and NMR spectroscopy were used to identify the compounds. The spectroscopic data used to identify the compounds are discussed in section 2.3.3.1.

2.3.2 Synthesis of complexes

2.3.2.1 Pyridine linker and thiophene linker pyrazolyl palladium complexes (1-5)

Complexes **1-3** were prepared by the reaction of ligands **L1-L3** with $PdCl_2(MeCN)_2$ in a ratio of 1:1 (Scheme III). Initial experiments to prepare complexes were performed at room temperature, while stirring reaction mixture for 48 h. Yields for such experiments were between 58-63%. When reaction time was reduced from 48 h to 2 h, the complexes were formed in reasonable yields (51%). When the reaction to prepare complex **1** was performed in a 2:1 ratio of $PdCl_2(MeCN)_2$ to ligand, the same complex, **1**, was obtained, but there was unreacted $PdCl_2(MeCN)_2$ isolated from the workup. Complex **1** showed good solubility in chlorinated solvents and acetone, insoluble in THF and slightly soluble in toluene. Microanalysis proved that the complex **1** isolated was pure.



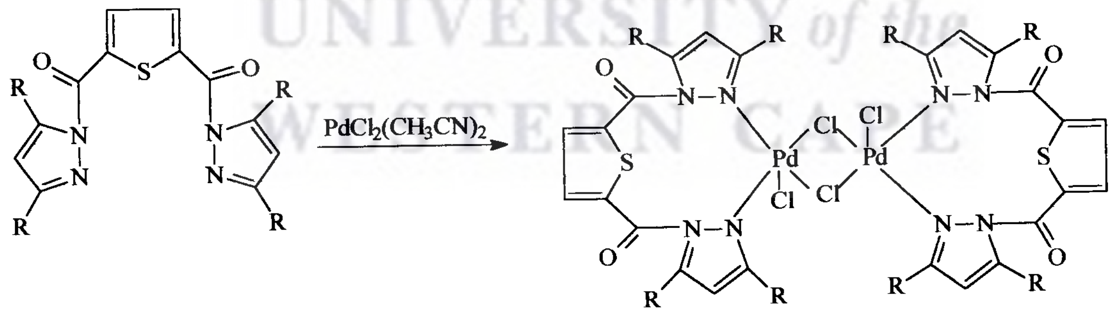
R = R' = ${}^tBu$ (**1**); R = R' = Me (**2**)

R = H, R' = Me (**3**)

Scheme III: Synthesis of complexes **1**, **2** and **3**

There was however no reaction when **L1** was reacted with PdClMe(cod) in order to form [PdClMe(**L1**)]. This is because cycloctadiene (cod) is not a weakly bound ligand like acetonitrile (MeCN), therefore it is difficult for **L1** to displace cod. The fact that **L1** cannot displace cod, indicates that bis(pyrazolylcarbonyl)pyridine ligands are weaker donors than 3,5-R_2Pz ligands which react with $PdCl_2$(cod) and PdClMe(cod) to form [Pd(3,5-$R_2pz)_2Cl_2$] (R= Me, ^tBu) and [Pd(3,5-ditertiarybutyl$_2$pz)$_2$Cl(Me)] respectively [6]. A recent report by Darkwa *et al.* shows that ligands similar to **L1**, such as bis(pyrazolylcarbonyl)benzene, do not react with PdClMe(cod) to form the corresponding pyrazolyl palladium complexes [7]. In a reaction of **L1** with $NiBr_2$(dme), both materials were recovered intact due to the weaker donor ability of **L1** mentioned above. Attempts to react bis(pyrazolylcarbonyl)benzene ligands with $NiBr_2$(dme) also showed no reactivity [8].

Complexes **2-5** were synthesized from the reaction of ligands **L2-L5** and $PdCl_2(MeCN)_2$ (Schemes III and IV) with a ligand to metal ratio of 1:1. Pinkish orange precipitates formed after five minutes of mixing the starting materials. The solids obtained were however insoluble in common organic solvents.



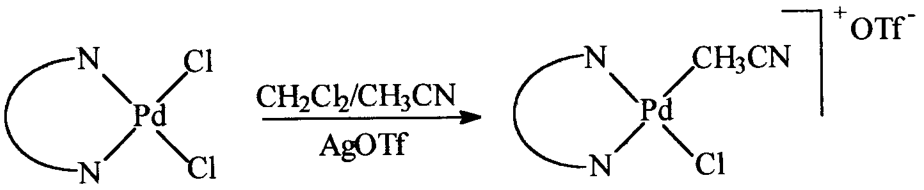
R = ^{t}Bu (**4**); R = Me (**5**)

Scheme IV: Synthesis of complexes **4** and **5**

Complex **2** is soluble in dimethylsulfoxide (DMSO) but complexes **3-5** are insoluble in DMSO. This signifies that the nature of the substituents on the pyrazole ring has some influence on the solubility of the complexes formed. Substituent effect on the solubility has also been observed for 1,3,5-tris(pyrazolylcarbonyl)benzene dipalladium complexes where methyl substituted pyrazolyl complexes are insoluble in common organic solvents but the tertiarybutyl analogues are soluble [7]. Because of the insoluble nature of complexes **2-5** in common organic solvents, formula and proposed structures of these compounds are mainly based on the elemental analysis. Structures proposed for these complexes are also based on well-characterized products from similar reactions. For complexes **2** and **3**, the proposed structures are based on the X-ray structure found for **1**, whereas structures of **4** and **5** are based on structures found for bis(pyrazolylcarbonyl)benzene [7]. It must however be pointed out that for complexes **2** and **3**, the microanalysis data found were lower than expected but still within reasonable values for the proposed formula. Considering the fact that these complexes are insoluble in common organic solvents and therefore could not be recrystallized, the microanalysis data is fairly good. Microanalysis of **4** appears to be far off from the expected values and this might be due to large amount of an insoluble impurity. However due to the insoluble nature of complex **4**, purification of products was impossible.

In attempt to obtain soluble products of complexes **2-5**, complex **2** was reacted with silver triflouromethane sulfonate (silver triflate, AgTOf) in 1:1 CH_2Cl_2/CH_3CN solvent mixture to form a silver triflate salt, $[\text{py-2,6-bis}\{CO(3\text{-Mepz})_2\}PdCl(NCCH_3)]^+OTf^-$ (**2a**)

(Scheme V). It was established that the expected salt (**2a**) decomposed slowly to elemental palladium even when the product was kept under inert atmosphere.



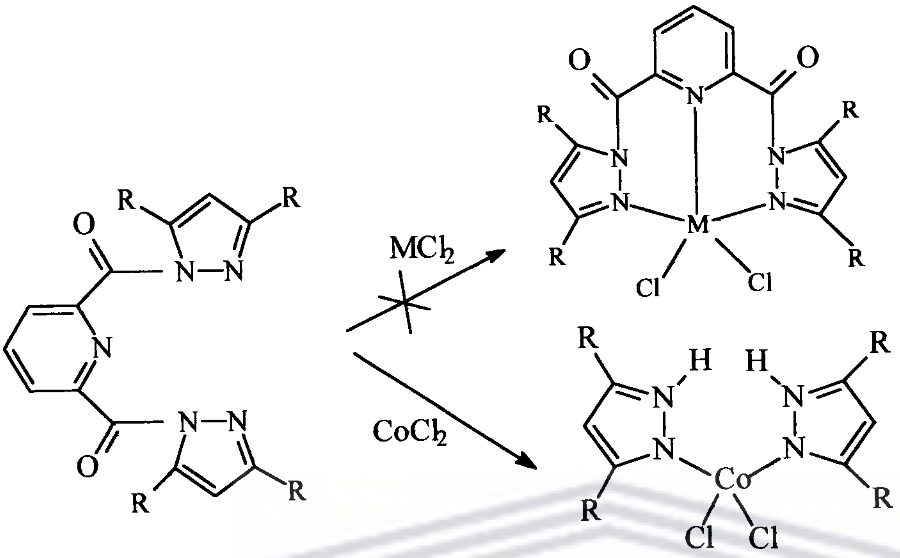
Scheme V: Preparation of [py-2,6-bis{CO(3-Mepz)$_2$}PdCl(NCCH$_3$)]$^+$OTf$^-$

By performing the same experiment in NMR tube, using CD$_3$CN, the spectroscopy of the resultant product showed features of coordinated pyrazolyl ligand, but there were other peaks that could be due to impurities. Results of similar experiments with **4** and **5** appeared to have resulted in the loss of the pyrazolyl ligands, since the spectra obtained were exactly like the uncoordinated ligands.

2.3.2.2 Attempts to prepare cobalt and iron complexes of ligands L1 and L2

The experiments where compounds **L1** and **L2** were reacted with anhydrous CoCl$_2$ and FeCl$_2$ in n-pentanol (60 °C) to prepare 2,6-bis(pyrazolylcarbonyl)pyridineMCl$_2$ were performed according to Scheme VI.

The reaction involving iron did not yield any clean products in pentanol, whereas the cobalt reactions formed the appropriate (R$_2$pz)$_2$CoCl$_2$ (R = Me, ^{t}Bu). In the case of (Me$_2$pz)$_2$CoCl$_2$ single crystals obtained from the reaction, were used to obtain preliminary crystallographic data that confirmed that the structure of the complex formed had the same parameters as the structure reported in the literature [9].



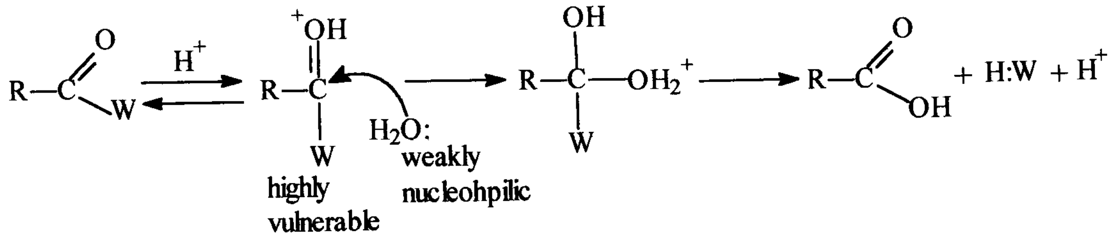
R = ^{t}Bu (**6**), R = Me (**7**)

M = Fe(II) or Co(II)

Scheme VI: Synthesis of complexes **6** and **7**

It is therefore clear that both **L1** and **L2** undergo alcohol induced hydrolysis reactions, leading to the formation of the relevant substituted pyrazoles. These substituted pyrazoles react with $CoCl_2$ to form the observed products. The following section attempts to rationalize how this hydrolysis reaction occurs.

Since alcohols are weak acids it is possible to produce H^+ from the pentanol and therefore get the $[H]^+$ to attack the ligand to undergo acidic hydrolysis as shown in Scheme VII. Once the proton is produced, it attacks the carbonyl group to form the $[OH]^+$ species that can react with traces of H_2O in the solvent. The final products would be a carboxylic acid and a protonated product, in our case pyrazole.



Scheme VII: Schematic representation of acidic hydrolysis of carbonyl compounds

In order to lend some credence to the proposed decomposition of **L1** and **L2** in pentanol, a blank reaction was performed by stirring **L2** in pentanol at 60 °C. The solvent was removed under vacuum and ^{1}H NMR spectrum of the dirty white residue was run in $CDCl_3$. There were peaks in the ^{1}H NMR spectrum that could be assigned to the methyl groups of 3,5-dimethylpyrazole at 2.24 and 2.32 ppm, proton of the pyrazole ring at 5.83 ppm. There were hydrocarbon protons from pentanol in the region between 0.84 to 1.89 ppm. When the residue was reacted with $CoCl_2$, blue (3,5-diMepz)$_2$CoCl$_2$ was isolated. The above data proves that **L1** or **L2** and $CoCl_2$ in pentanol undergo hydrolysis, forming complexes **6** and **7** respectively.

2.3.3 Spectroscopy studies

NMR and IR spectroscopy were the main spectroscopic tools used to characterize both the ligands and metal complexes prepared in this thesis.

2.3.3.1 NMR spectra

The spectra assignment of **L1** would be used to illustrate how NMR spectroscopy was used to characterize the ligands. Since complex **1** was the most soluble complex, its NMR characterization is also described.

The ^{1}H NMR spectrum of **L1** (Fig. 2.1a) shows two singlets associated with tert-butyl substituents protons in positions 3 (1.18 ppm) and 5 (1.49 ppm) of the pyrazole ring, a singlet (6.18 ppm) for the proton in position 4 of the pyrazole ring, a multiplet (7.69-7.84 ppm) for pyridinyl protons. The ^{1}H NMR spectra of **L2-L4** show similar results with different integrations. Results obtained for **L5** and **L6** are similar to **L1** and **L2** except for the protons of the pyridine ring that are replaced by those of the thiophene ring. The ^{1}H NMR spectrum of **L5** indicated a singlet (8.16 ppm) for two protons of the thiophene ring, a singlet (6.22 ppm) for two protons of the pyrazole ring, and two singlets (1.48 and 1.36 ppm) associated with the tert-butyl substituents. Similar results were obtained for **L6**. ^{13}C NMR spectrum of **L1** (Fig. 2.1b) showed eleven carbon peaks associated with the pyridinyl (153.3 and 158.0 ppm) and carbonyl carbons (163.6 and 166.2 ppm) at downfield, the tert-butyl carbons at upfield (29.5-33.2 ppm); while ^{13}C NMR spectra for **L2-L4** indicated the correct number of carbon peaks for each ligand. The ^{13}C NMR spectrum for **L5** showed ten different carbons with carbonyl carbons at further down field and tert-butyl carbons at upfield, with similar results obtained for **L6**.

The ^{1}H NMR spectrum for complex **1** (Fig. 2.2a) showed four singlets associated with the protons at position five (1.19 and 1.49 ppm) and three (1.59 and 1.79 ppm) of pyrazolyl units, two singlets (6.21 and 6.38 ppm) for protons at position four of pyrazole, multiplet (8.08 ppm) at downfield for pyridinyl protons. These results prove that the palladium metal is coordinated to the nitrogen of pyridine and one nitrogen of the pyrazolyl unit leaving one pyrazolyl unit uncoordinated.

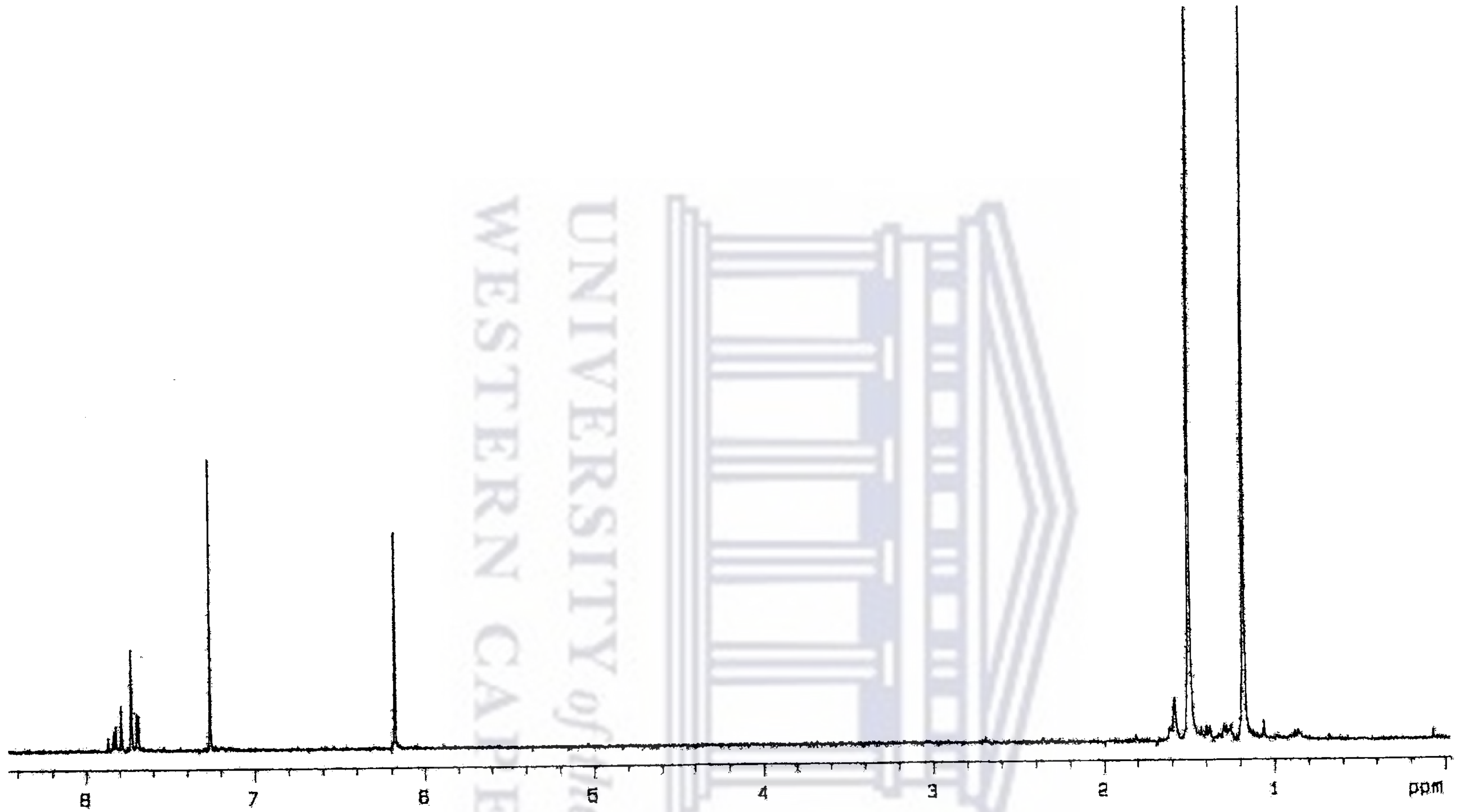


Figure 2.1a ^{1}H NMR spectrum of 2,6-bis(3,5-ditert-butylpyrazolylcarbonyl)pyridine (**L1**)

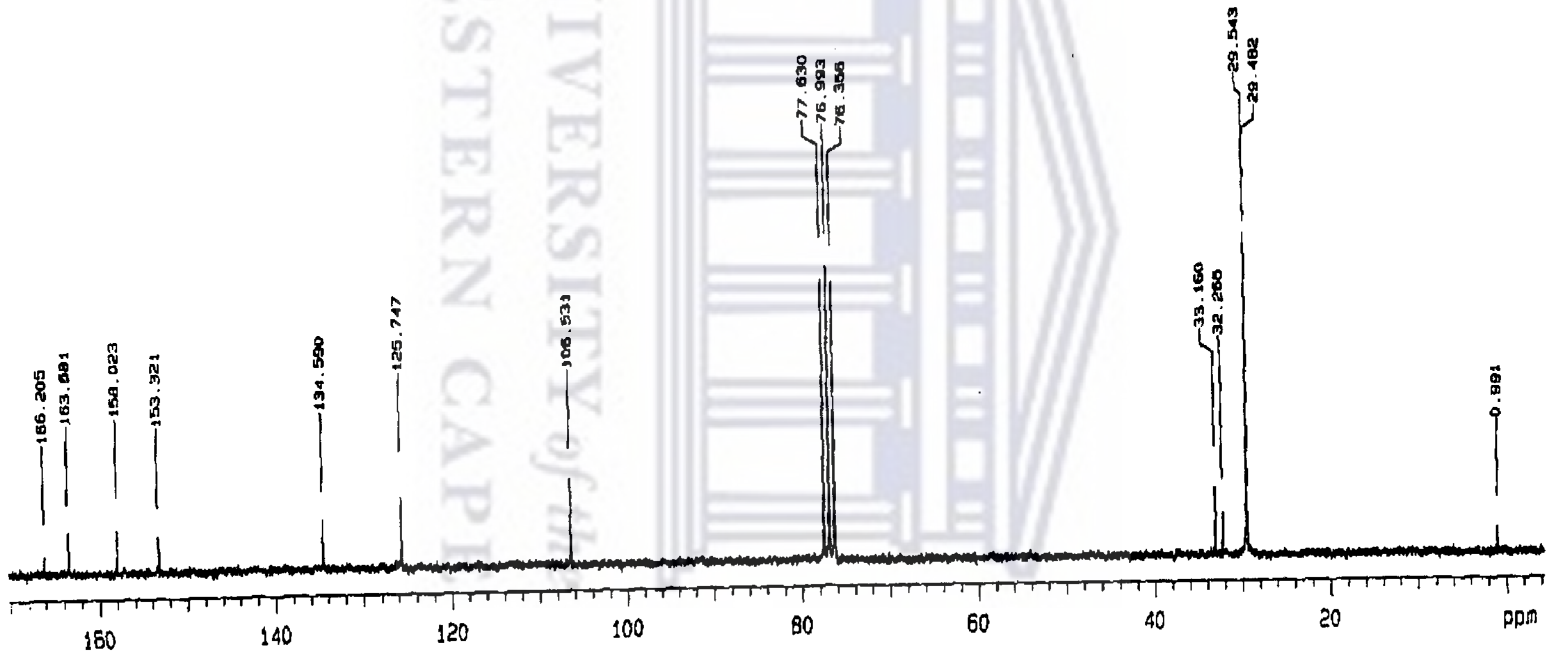


Figure 2.1b ^{13}C NMR spectrum of 2,6-bis(3,5-ditert-butylpyrazolylcarbonyl)pyridine (**L1**)

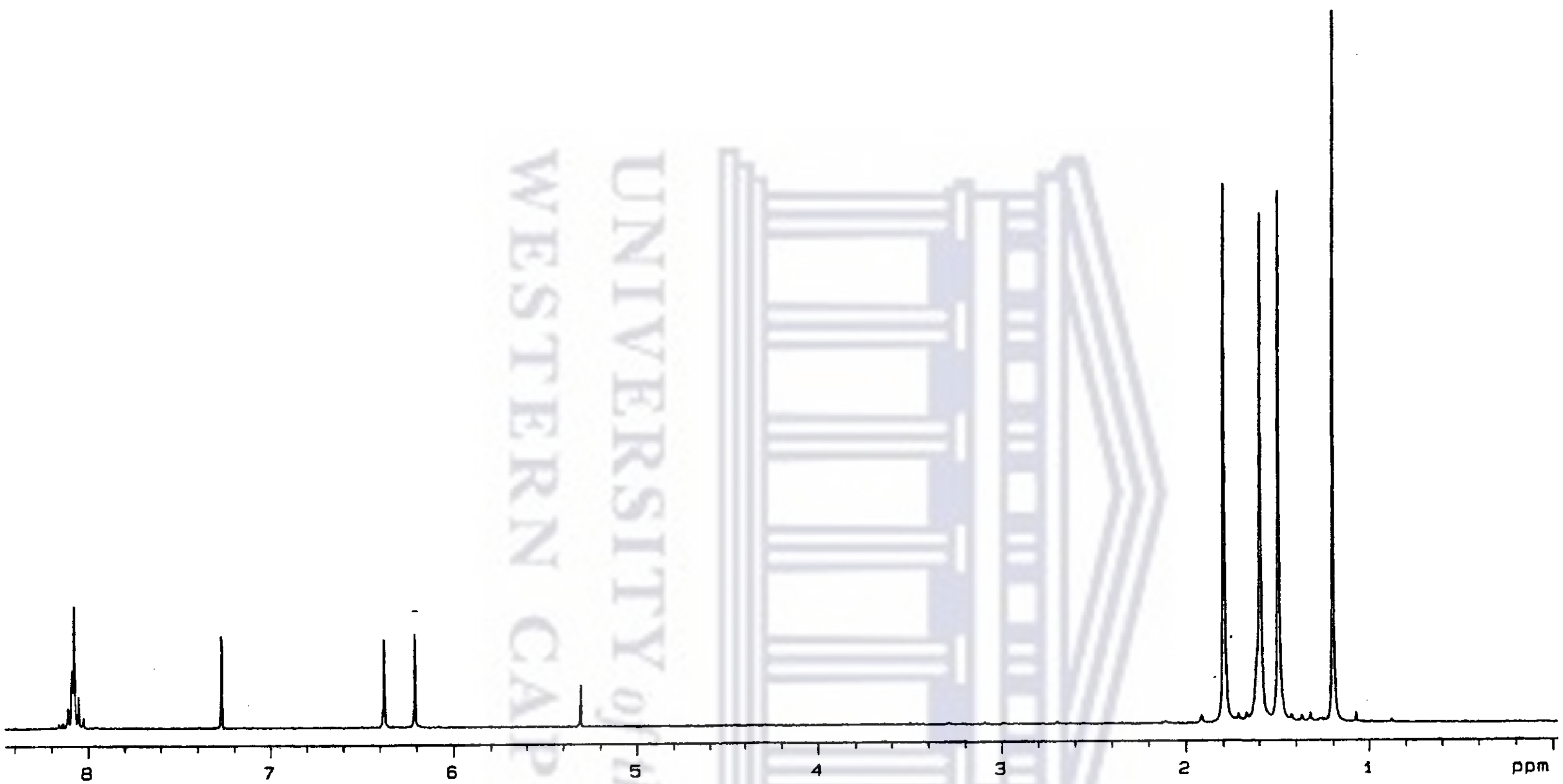


Figure 2.2a ^{1}H NMR spectrum of 2,6-bis(3,5-ditert-butylpyrazolylcarbonyl)pyridinepalladium(II) dichloride (complex **1**)

This coordination, therefore, results in four different peaks for protons at positions 3 and 5 of the pyrazole ring and two different peaks for protons at position 4 of the pyrazole. The ^{13}C NMR spectrum of complex **1** (Fig. 2.2b) indicated the presence of twenty carbons as expected, with the carbonyl carbons (164.9 and 175.2 ppm) and pyridinyl carbons (162.4 and 162.8 ppm) appearing more downfield compared to the carbons in **L1** proving the coordination of palladium to the ligand.

Complex **2** was found to be soluble in dimethylsulfoxide (DMSO). The ^{1}H NMR spectrum (Fig. 2.3) showed a multiplet at 8.19 ppm for three protons on the pyridine ring, two singlet peaks for protons at position 4 of the pyrazole and four different peaks for the methyl protons at position 3 and 5 of the pyrazole. The spectrum also indicated the presence of free ligand with a singlet peak at 6.31 ppm for protons at position 4 of pyrazole ring and a singlet at 2.05 for methyl substituent. The peak at 2.48 ppm is likely due to some impurities. Because complexes **3-5** were insoluble in chlorinated solvents as well as in DMSO, NMR spectroscopy could not be used for their characterization.

2.3.3.2 IR spectra

Infrared spectroscopy was used for determining functional groups in both ligands and metal complexes. The recorded spectra of ligands **L1-L6** on nujol mulls showed the expected characteristic bands for carbonyl groups, the stretching frequencies for C-H bonds in aromatic regions and the stretching frequencies for C=N bonds. In the regions 1583-1451 cm^{-1} and 3225-3000 cm^{-1}, the ligands exhibit weak bands typical of C-H stretching and in the regions 1680-1716 cm^{-1} they indicated the presence of carbonyl

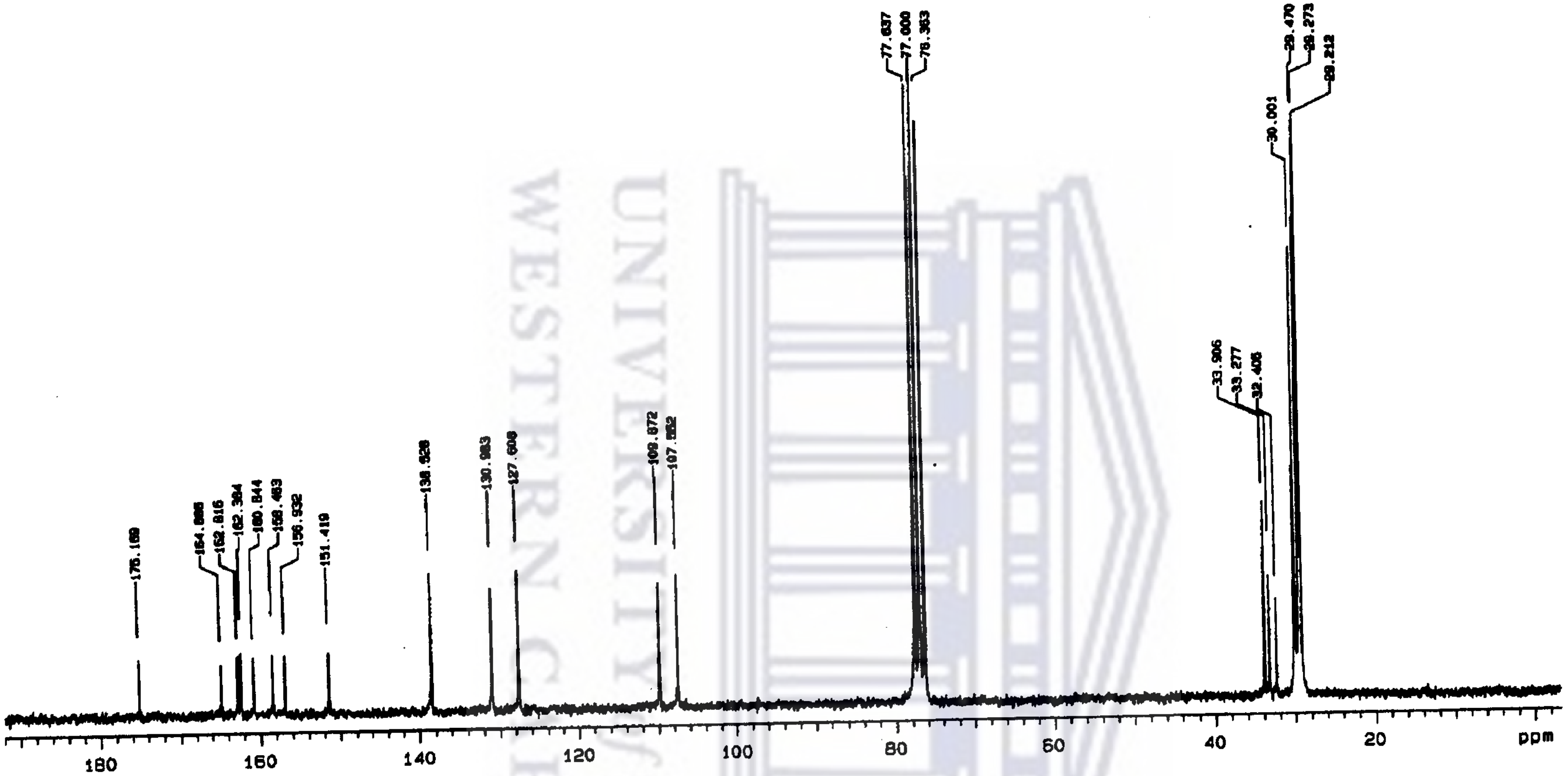


Figure 2.2b ^{13}C NMR spectrum of 2,6-bis(3,5-ditert-butylpyrazolylcarbonyl)pyridinepalladium(II) dichloride (complex **1**)

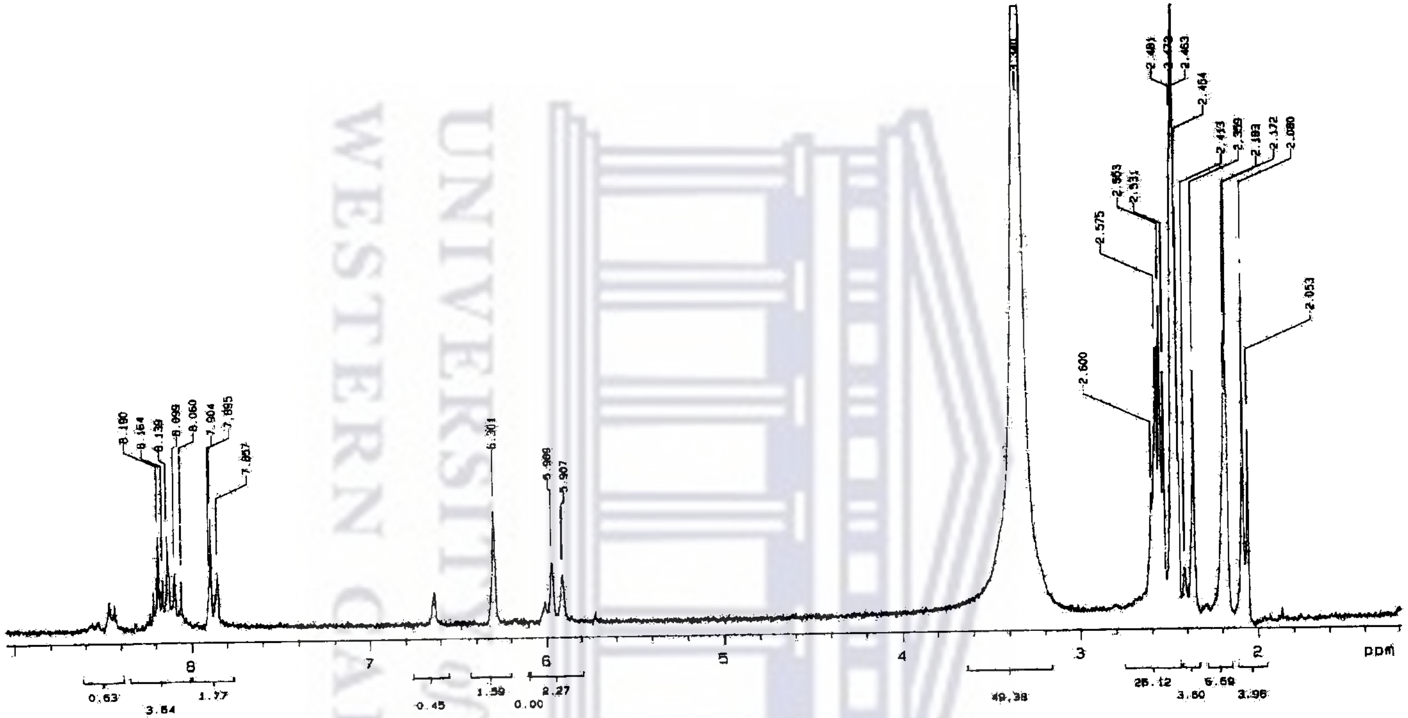


Figure 2.3 ^{1}H NMR spectrum of 2,6-bis(3,5-dimethylpyrazolylcarbonyl)pyridinepalladium(II) dichloride (complex **2**)

groups with **L1** (Fig 2.4a) showing the presence of carbonyl groups at 1716 cm^{-1}. All other ligands showed one peak for the presence of the carbonyl group at 1709 cm^{-1} (**L2**), 1712 cm^{-1} (**L3**), 1710 cm^{-1} (**L4**), 1698 cm^{-1} (**L5**) and 1680 cm^{-1} (**L6**). For complex **1** (Fig. 2.4b), the infrared spectrum showed the presence of two carbonyl groups in the regions of 1727 and 1712 cm^{-1} which is different from the results obtained for ligand **L1** because of the coordination of palladium to one nitrogen of pyrazolyl unit and pyridine ring. Similar results were observed for complexes **2** and **3** with two peaks for C=O functional group. The infrared spectrum of complexes **4** and **5** showed only one peak for carbonyl functional group confirming that there are no different carbonyl groups as observed with complexes **1**, **2** and **3**.

Because of the paramagnetic nature of complexes **6** and **7**, infrared spectroscopy was one of the major analytical techniques used in characterizing these two complexes. Figures 2.5a and b are the infrared spectra of **6** and **7** respectively. It is clear from the absence of carbonyl peaks in the region 1700 cm^{-1}, that the original ligands used in the reaction that resulted in the isolation of **6** and **7** have hydrolyzed to pyrazoles. Characteristic peaks for N-H stretching in pyrazoles were observed at 3284-3298 cm^{-1} in the IR spectra of **6** and **7**. Additional peaks at 1561-1565 cm^{-1} indicative of (C=N) functional groups and 1362-1373 cm^{-1} peaks, characteristic of (C-CH_3) functionality; were also observed in the IR spectra. A combination of these pyrazole peaks and those of substituents on the pyrazole suggested the formula of bis(pyrazole)$CoCl_2$ complexes as depicted in Scheme VI.

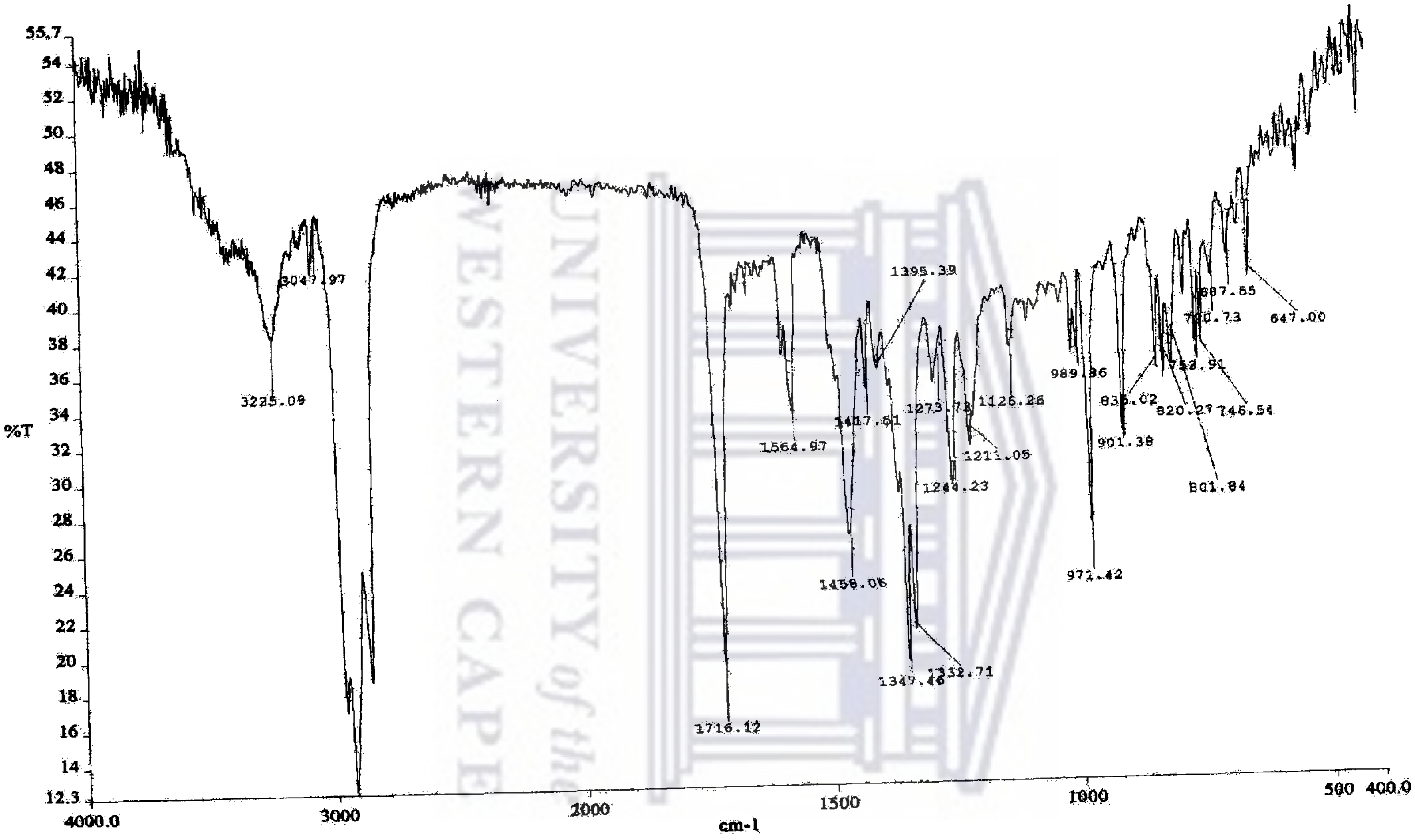


Figure 2.4a IR spectrum of 2,6-bis(3,5-ditert-butylpyrazolylcarbonyl)pyridine (**L1**)

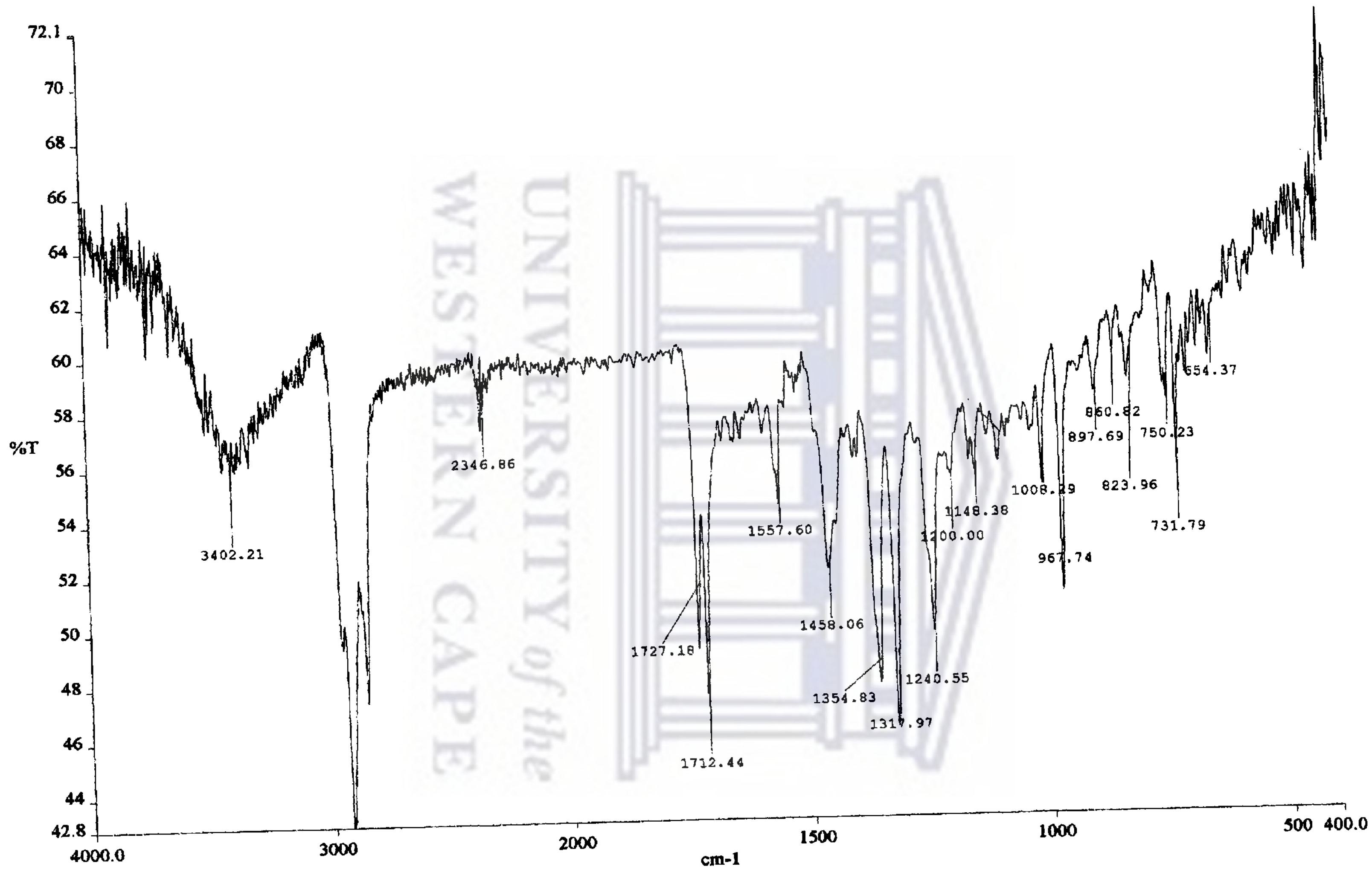


Figure 2.4b IR spectrum of 2,6-bis(3,5-ditert-butylpyrazolylcarbonyl)pyridinepalladium(II) dichloride (complex **1**)

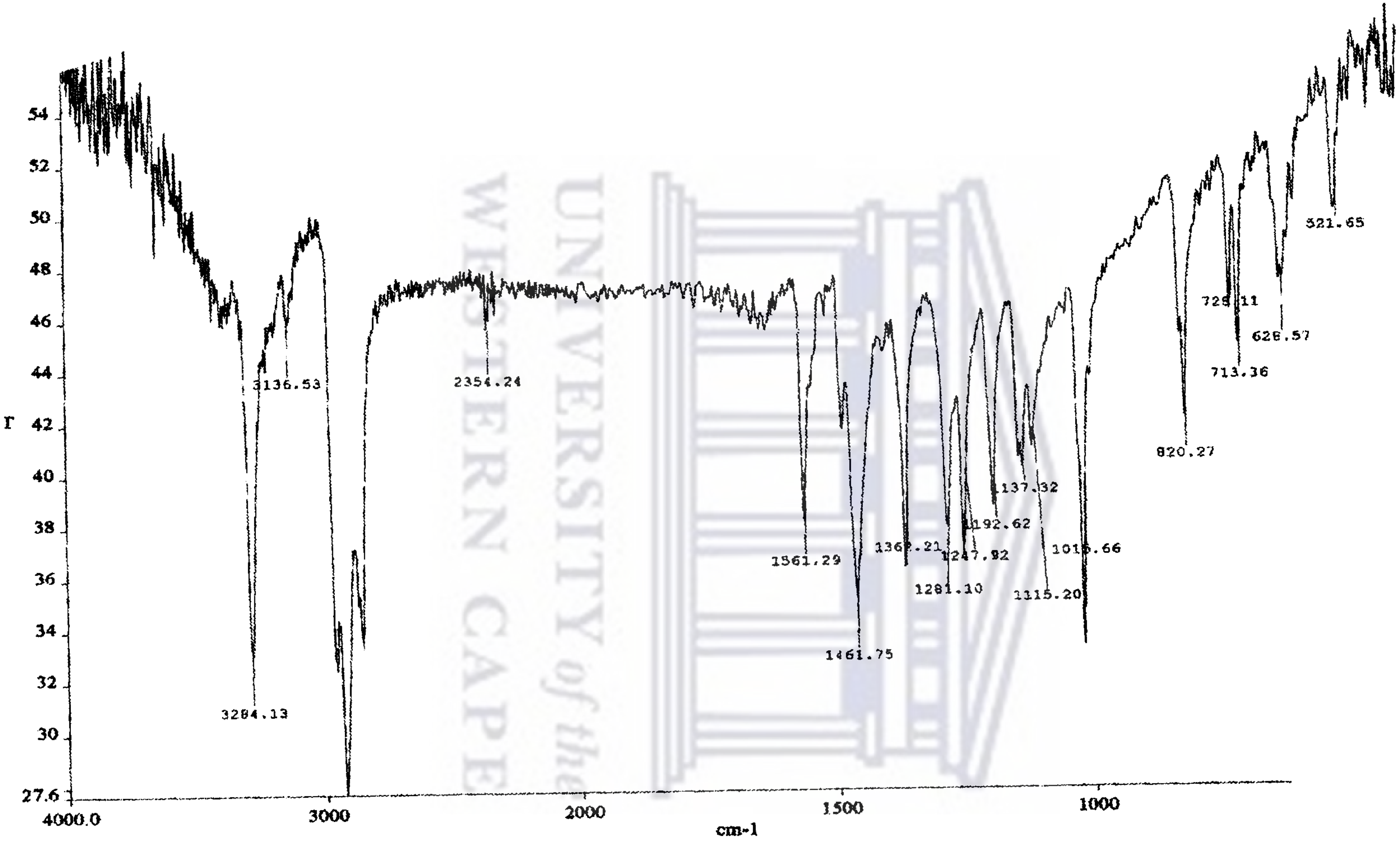


Figure 2.5a IR spectrum of bis(3,5-ditert-butylpyrazole)cobalt(II) dichloride (complex **6**)

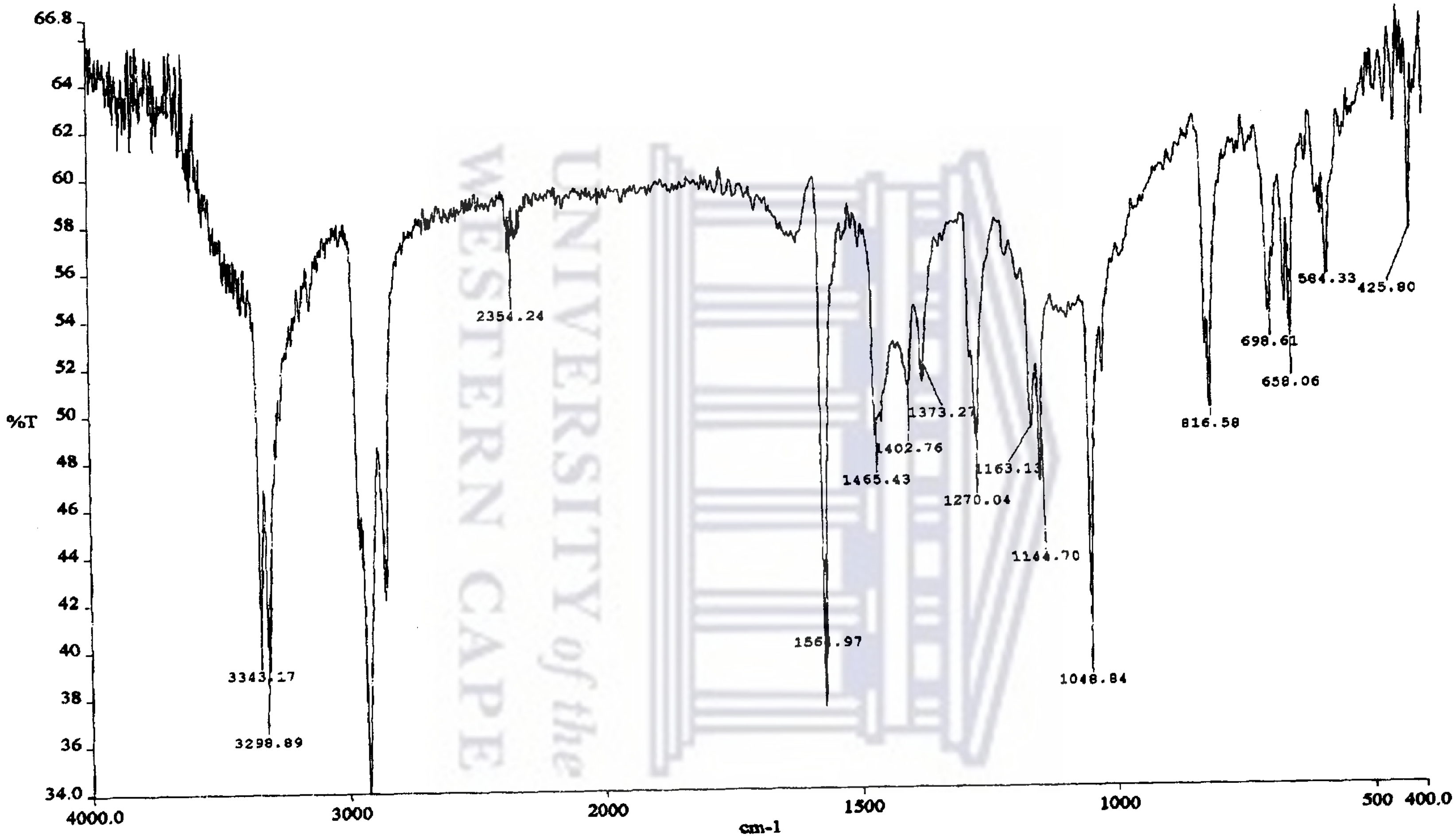


Figure 2.5b IR spectrum of bis(3,5-dimethylpyrazole)cobalt(II) dichloride (complex 7)

2.3.4 X-ray crystal 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. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [10]. The structures were solved by direct methods and refined by least-squares techniques using SHELXTL program [11]. 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. X-ray structures were determined by Dr I.A. Guzei at University of Wisconsin, USA.

2.3.4.1 X-ray analysis of ligands

Single crystals of **L3** and **L6** suitable for X-ray structural analysis were obtained from recrystallization of the ligands from CH_2Cl_2 and hexane at –15 °C for **L3** and CH_2Cl_2 at room temperature for **L6**. The crystal data, together with the data collection and structure refinement parameters are presented in Table 2.1 and selected bond length and bond angles are given in Table 2.2. Molecular structures of **L3** and **L6** are shown in Figures 2.6 and 2.7.

The structure of **L3** has a two-fold symmetry (C_2) while the structure of **L6** has centre of inversion (C_i) since the orientation of the molecule (**L6**) following the *i* operation will be the same as the original orientation. Another structural feature of **L3** is the asymmetrical substitution of the pz ligands with the methyl group being in position three. The 3-MepzH and 5-MepzH are indistinguishable in solution due to a dynamic equilibrium between these tautomers and therefore, during the synthesis of **L3** the least sterically hindered product was produced. Similar results have been obtained with 1,3-bis(3-methylpyrazolylcarbonyl)benzene ligand possessing a two-fold symmetry while the structures of 1,3-bis(3,5-ditert-butylpyrazolylcarbonyl)benzene, 1,3-bis(3,5-dimethylbutylpyrazolylcarbonyl)benzene and 1,2-bis(3,5-ditert-butylpyrazolylcarbonyl)benzene ligands are not symmetrical [7].

The bond angles and bond lengths of **L3** are the same (Table2.2). The bond lengths of **L6** are nearly the same but the bond angles are different (Table 2.2). For example N(1)-(N2) distance of 1.376(3) Å is the same as the N(3)-N(4) bond distance (1.374(3) Å). The N(3)-C(11) distance of 1.401(3) Å and N(2)-C(6) distance of 1.400(3) Å are also identical. The N(1)-N(2)-C(6) angle 119.24(19°) is different from N(4)-N(3)-C(11) angle 122.10(2)° while C(6)-C(7)-S(1) 128.97(17)° and C(11)-C(10)-S(1) 112.69(17)° angles are also different. Similarity in bond angles and bond lengths have also been found in the structure of 1,3-bis(3-methylpyrazolylcarbonyl)benzene [7]. For example the N(1)-N(2) distance (1.3889 Å) and N(3)-N(4) distance (1.3837 Å) in 1,3-bis(3,5-ditert-butylpyrazolylcarbonyl)benzene are identical.

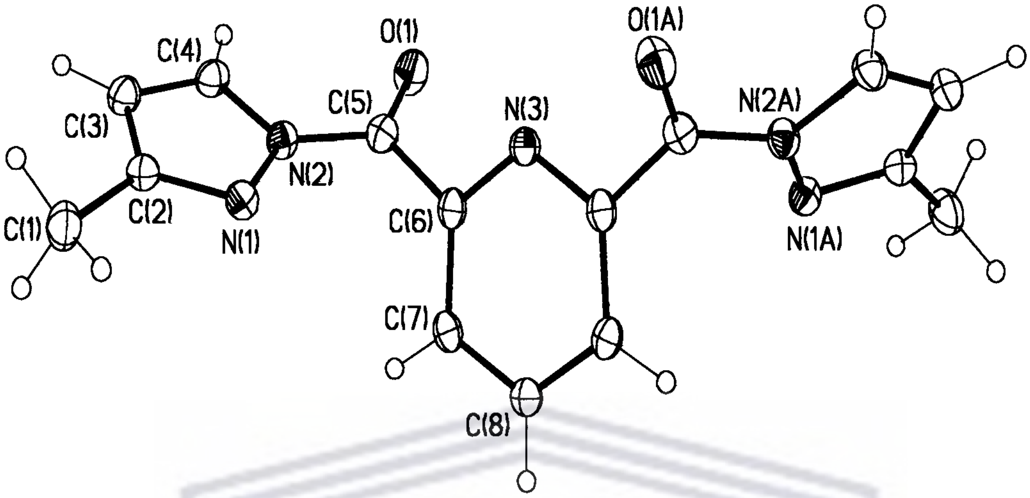


Figure 2.6 Molecular structure of 2,6-bis(3-methylpyrazolylcarbonyl)pyridine (**L3**)

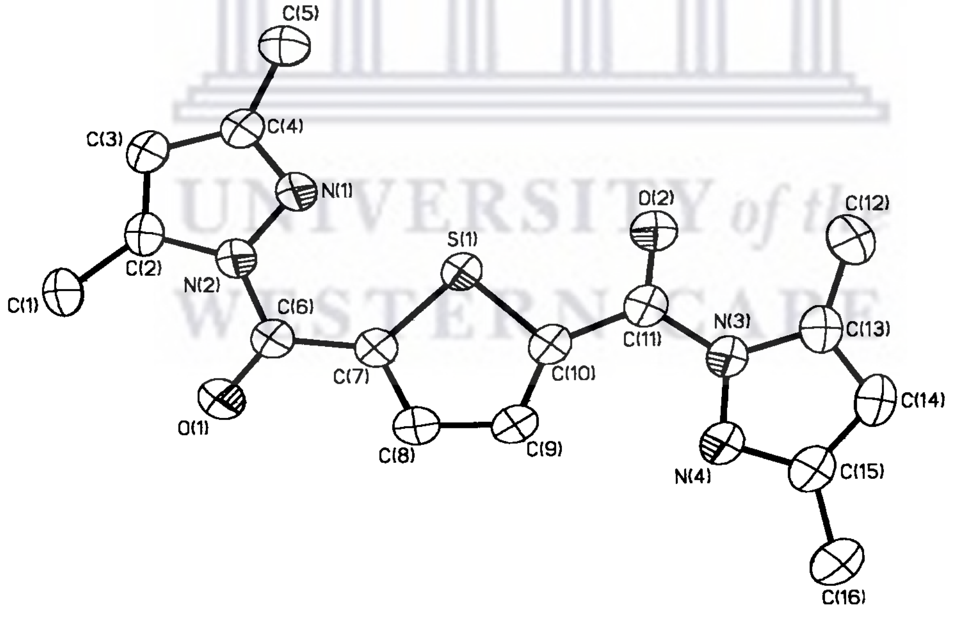


Figure 2.7 Molecular structure of 2,5-bis(3,5-dimethylpyrazolylcarbonyl)thiophene (**L6**)

Table 2.1: Crystal data and structure refinement for ligands **L3** and **L6**

	L3	**L6**
Empirical formula	$C_{15}H_{13}N_5O_2$	$C_{16}H_{16}N_4O_2S$
Formula weight	295.30	328.39
Temperature/K	100(2)	296(2)
Wavelength/ Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	$P2_1/m$
a/Å	14.864(3)	15.615(3)
b/ Å	14.399(2)	6.7153(16)
c/ Å	6.8726(12)	16.803(4)
α/°	90	90
β/°	103.613(3)	114.452(4)°
γ/°	90	90
V/ $Å^3$	1429.5(4)	1603.9(6)
Z	4	4
Dc/ Mg m^{-3}	1.372	1.360
μ(Mo-Kα) mm^{-1}	0.096	0.217
Crystal size/mm	0.53 x 0.42 x 0.36	0.30 x 0.30 x 0.20
Absorption correction	Multiscan	Empirical
T_{max}/T_{min}	0.9662/0.9508	0.9579/0.9378
R(*F*) (%)[I [I>2σ(I)]	3.76	4.07

Table 2.2: Selected Bond lengths [Å] and angles [°] for **L3** and **L6**

L3			
Bond lengths (Å)			
O(1)-C(5)	1.2140(15)	N(1)-C(2)	1.3226(16)
N(1)-N(2)	1.3812(14)	N(2)-C(4)	1.3781(16)
N(2)-C(5)	1.3922(17)	N(3)-C(6)	1.3392(14)
C(1)-C(2)	1.4945(18)	C(5)-C(6)	1.5067(16)
Bond angles(°)			
C(4)-N(2)-C(5)	125.50(10)	N(1)-N(2)-C(5)	121.88(10)
N(1)-C(2)-C(1)	120.42(11)	C(3)-C(2)-C(1)	127.94(12)
O(1)-C(5)-N(2)	120.49(11)	O(1)-C(5)-C(6)	121.70(11)
N(2)-C(5)-C(6)	117.81(10)	N(3)-C(6)-C(7)	124.16(11)
N(3)-C(6)-C(5)	113.38(11)	C(7)-C(6)-C(5)	122.20(11)
L6			
Bond lengths (Å)			
O(1)-C(6)	1.210(3)	O(2)-C(11)	1.206(3)
N(1)-N(2)	1.376(3)	N(3)-N(4)	1.374(3)
N(2)-C(6)	1.400(3)	N(3)-C(11)	1.401(3)
C(6)-C(7)	1.483(3)	C(10)-C(11)	1.481(4)
Bond angles(°)			
N(1)-N(2)-C(6)	119.24(19)	N(4)-N(3)-C(11)	122.1(2)
O(1)-C(6)-N(2)	120.8(2)	O(1)-C(6)-C(7)	121.0(2)
N(2)-C(6)-C(7)	118.2(2)	C(6)-C(7)-S(1)	128.97(17)
C(11)-C(10)-S(1)	112.69(17)	O(2)-C(11)-N(3)	119.7(2)
O(2)-C(11)-C(10)	120.1(2)	N(3)-C(11)-C(10)	120.2 (2)

2.3.4.2 X-ray analysis of complex 1

Complex **1** was recrystallized from CH_2Cl_2 and Et_2O at –15 °C or by slow evaporation of CH_2Cl_2 solution at room temperature to give single crystals suitable for structural analysis. The crystal data, together with the data collection and structure refinement parameters are presented in Table 2.3 and selected bond lengths and bond angles are given in Table 2.4. Molecular structure of complex **1** is represented in Fig. 2.8.

Complex **1** has a monomeric structure, with two chloride atoms Cl(1) and Cl(2) and two nitrogen atoms (N(3) and N(1)) of the pyridine ring and pyrazole unit bonded to the palladium in a distorted square planar geometry. The smaller than 90 °C angle for N(1)-Pd-N(3) (83.87(15)°) resulting from small angle size of the ligand distorts the square planar structure of complex **1**. The Cl(1)-Pd-Cl(2) angle 90.69(5)° also shows a slight distortion from a square planar structure. The pyridinylimine complex dichloro[2,6-bis(1-methylethyl)-N-(2-pyridinylmethylene)-phenylamine]palladium(II) has a similar structure with the narrow N(1)-Pd-N(8) angle 80.08(11)° resulting from relatively small angle size of the ligand and therefore, causing distortion of the square planar structure [12].

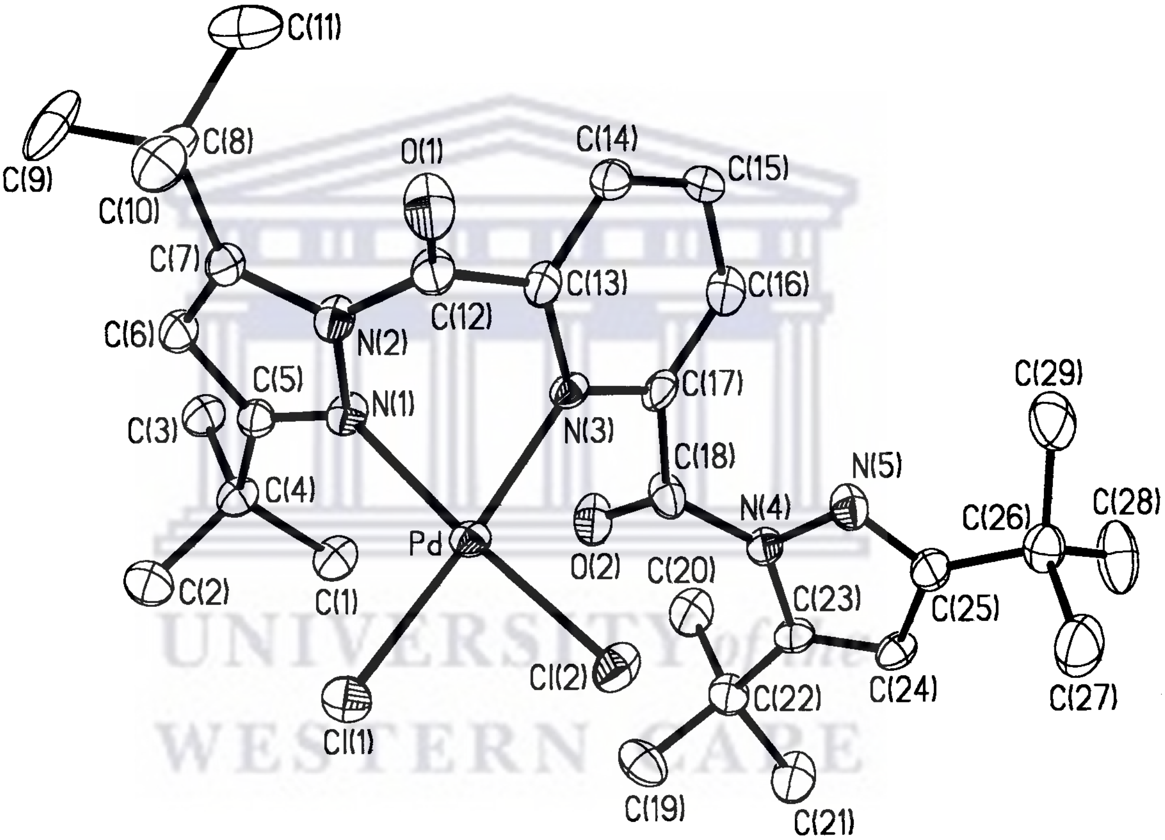


Figure 2.8 Molecular structure of 2,6-bis(3,5-ditert-butylpyrazolylcarbonyl)pyridine palladium(II) dichloride (complex **1**)

Table 2.3: Crystal data and structure refinement for complex **1**

Empirical formula	$C_{29}H_{41}Cl_2N_5O_2Pd$
Formula weight	668.97
Temperature/K	100(2)
Wavelength/ Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	9.2796(9)
b/ Å	14.9316(12)
c/ Å	22.369(2)
α/°	90
β/°	90.574(3)
γ/°	90
V/ $Å^3$	3099.2(5)
Z	4
Dc/ Mg m^{-3}	1.434
μ(Mo-Kα) mm^{-1}	0.805
Crystal size/mm	0.40 x 0.30 x 0.20
Absorption correction	Empirical
T_{max}/T_{min}	1.00/0.54
R(*F*) (%)[I [I>2σ(I)]	4.79
R(w F^2)$^\alpha$ (%) (all data)	11.98

Table 2.4: Selected Bond lengths [Å] and angles [°] of complex **1**

Bond length(Å)		Bond angles(°)	
Pd-N(3)	2.032(4)	N(3)-Pd-N(1)	83.87(15)
Pd-N(1)	2.062(4)	N(3)-Pd-Cl(2)	92.20(10)
Pd-Cl(2)	2.2581(12)	N(1)-Pd-Cl(2)	175.76(11)
Pd-Cl(1)	2.2861(13)	N(3)-Pd-Cl(1)	173.11(10)
N(1)-N(2)	1.396(5)	N(1)-Pd-Cl(1)	93.05(11)
N(2)-C(12)	1.412(6)	Cl(2)-Pd-Cl(1)	90.69(5)
N(3)-C(17)	1.350(6)	C(5)-N(1)-Pd	135.6(3)
N(3)-C(13)	1.358(6	N(2)-N(1)-Pd	112.2(3)
N(4)-N(5)	1.388(5)	C(17)-N(3)-Pd	126.1(3)
N(4)-C(18)	1.397(6)	C(13)-N(3)-Pd	115.0(3)
C(12)-C(13)	1.509(6)	N(1)-N(2)-C(12)	118.7(4)
C(17)-C(18)	1.527(6)	N(3)-C(13)-C(12)	121.7(4)

2.3.5 Thermal analysis

Thermogravimetric analysis (TGA) was performed on a Perklin Elmer PC series 7 system. The sample size ranging between 2-5 mg was heated in platinum pans at 10 °C per minute under nitrogen gas purge with a rate of 20 cm^3 per minute.

2.3.5.1 TGA of {2,6-bis(3,5-ditert-butylpyrazolyl-1-carbonyl)pyridine}palladium(II) dichloride (complex 1).

In experiments where complex **1** was used to catalyze ethylene polymerization at 70 °C (discussed in Chapter 3) we observed lower activity of the catalyst. This result suggested possible decomposition of the catalyst. To investigate the effect of temperature on the stability of complex 1, we performed thermogravimetric analysis TGA) experiment on this complex.

Figure 2.9 is the thermogram from the TGA experiment and represents decomposition of **1**, which occurs from 162 °C to 374 °C. The weight loss in the temperature range between 162 °C and 237 °C (4.0%) corresponds to the loss of solvent {¼ CH_2Cl_2 (3.2%)} in the complex, which supports the microanalysis data that the complex contains one solvent molecule per four complex molecules. The weight loss in thermogram of complex **1** between 239 °C and 374 °C corresponds to the weight loss of the ligand fragment {$C_{25}H_{30}O_2N_5$ (58%)}. The above TGA data show that complex **1** decomposes at a higher temperature than 70 °C, however since the active catalyst is believed to be a metal-alkyl complex, it is difficult to conclude from TGA data of the catalyst precursor that deactivation at 70 °C is not the result of catalyst decomposition.

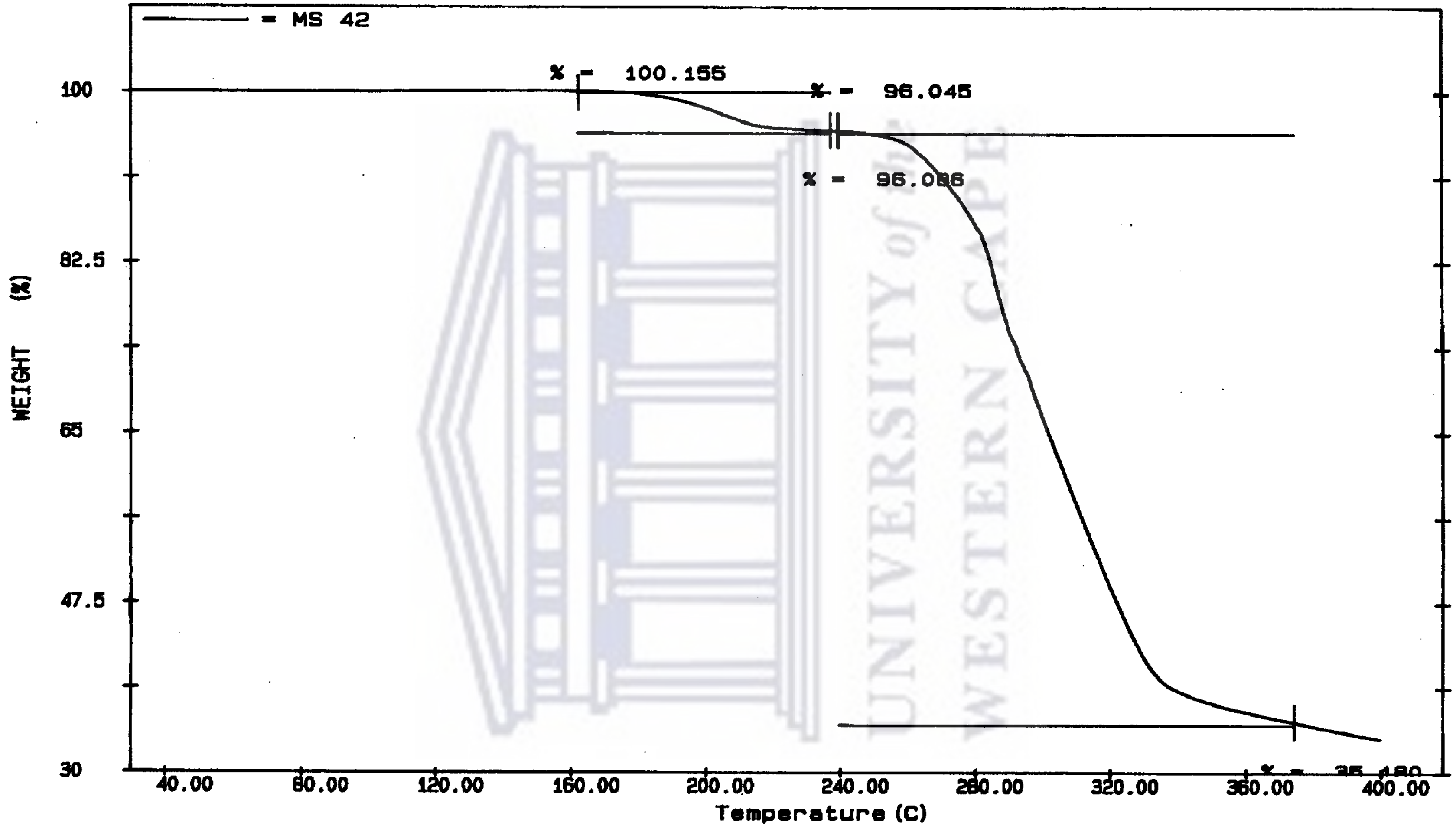


Figure 2.9 A TGA thermogram of 2,6-bis(3,5-ditert-butylpyrazolylcarbonyl)pyridinepalladium(II) dichloride complex **1**

2.4 Conclusion

Pyrazolyl ligands with pyridine dicarbonyl and thiophene dicarbonyl linkers were successfully prepared and fully characterized. The bis(tertiarybutylpyrazoly1-l-carbonyl)pyridine ligand system (**L1**) forms monometallic complex with one pyrazolyl nitrogen coordinated to the metal. The carbonyl functional groups reduce the σ–donor ability of the nitrogen groups of the pyrazolyl ligands resulting in the binding of the palladium metal to the pyridine nitrogen and one pyrazolyl nitrogen. The 3,5-dimethylsubtituted (**L2**, **L6**), 3,5-ditertiarybutylsubstituted (**L5**) and 3-dimethylsubstituted (**L3**) pyrazolyl ligand systems form insoluble products when reacted with $PdCl_2(MeCN)_2$. The pyrazolyl ligands with thiophene dicarbonyl linkers are formulated to give dimeric complexes **4** and **5** (Scheme IV). The displacement of chloride ion with silver triflate in CD_3CN for complexes **3-5** formed their corresponding ligands instead of the cationic complexes $[Pd(N\text{-}N)ClCH_3CN]^+OTf$ and $[Pd_2(\mu\text{-}Cl)_2(N\text{-}N)ClCH_3CN]^+OTf$.

2.5 References

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CHAPTER 3

PYRAZOLYL PALLADIUM COMPLEXES CONTAINING CARBONYL LINKERS AS CATALYST PRECURSORS FOR ETHYLENE POLYMERIZATION

3.1 Introduction

Since the discovery of Brookhart and coworkers that Ni(II) and Pd(II) catalysts bearing diimine ligands polymerize ethylene and α–olefins to high molecular weight polymers, there has been a growing development in olefin polymerization catalysts [1]. The key aspect of this discovery is the use of sterically bulky α–diimine ligands, which blocks the axial coordination sites and thus impede chain termination process. Complexes of Ni(II) and Pd(II) bearing α–diimine ligands polymerize ethylene under more controlled conditions when activated with methylaluminoxane (MAO) or other aluminum reagents, which provide alkylation and generation of the cationic site.

Both Pd(II) and Ni(II) diimine catalysts yield moderately to highly branched or linear polyethylene. Soon after the initial discovery of Pd(II) and Ni(II) diimine catalysts by Brookhart, Gibson and Brookhart independently reported on the iron and cobalt-based catalysts, bearing tridentate pyridine bisimine ligands with bulky groups. These catalysts are capable of either oligomerizing or polymerizing ethylene depending on the metal [2]. In case of ethylene polymerization, the resulting polymers are mostly high molecular weight linear polyethylene. More recently Mapolie *et al.* showed that mono- and binuclear pyridine palladium complexes with long chain alkyl groups attached to the imino nitrogen, when activated with MAO are capable of producing high molecular weight linear polymers ranging from 6×10^5 to 1×10^6 [3].

Even though many research groups have reported nitrogen ligand complexes of palladium(II) and nickel(II), pyrazole and pyrazolyl late transition metal complexes for ethylene polymerization catalysts has not been widely studied. A report by Jordan *et al.* on ethylene polymerization using $[R_2C(3\text{-}^tBu_2pz)_2]PdCl_2$ (R = Me, Ph) is one of the few examples that involves the use of pyrazole-based ligand complex as a catalyst for olefin polymerization [4]. Other examples include the ability of substituted pyrazole palladium catalysts; $[(3,5\text{-}R_2Pz)_2PdCl_2]$ and $[(3,5\text{-}^tBu_2Pz)_2PdClMe]$; (R = ^{t}Bu, Me)] reported by Darkwa *et al.*, to catalyze the polymerization of ethylene to linear high density polyethylene [5]. The highest activity for these series of pyrazole palladium catalysts was obtained with $[(3,5\text{-}^tBu_2Pz)_2PdClMe]$. Darkwa and coworkers have also recently studied the effect Pd(II) catalysts containing pyrazoyl ligands with carbonyl linkers on the polymerization of ethylene [6]. These catalysts were found to be bimetallic in which the pyrazolylcarbonyl ligand are bonded to each of the metal centres *via* a single pyrazolyl unit per metal centre. In addition there is also a third pyrazolyl unit that is not coordinated to any of the palladium centres. The presence of the uncoordinated pyrazolyl unit results in a lower catalyst activity. This presumably is a result of this uncoordinated pyrazolyl unit interacting with MAO thus reducing the extent of activation in solution.

The aim of the present study is to further investigate the use of pyrazolyl palladium(II) catalysts for ethylene polymerization. The Pd(II) complexes prepared bear bis(pyrazolylcarbonyl)pyridine and bis(pyrazolylcarbonyl)thiophene ligands, reported in chapter 2 of this thesis, and have been used as catalysts precursors for ethylene polymerization. The catalyst precursors were activated using MAO as a co-catalyst. The effects of reaction temperature and co-catalyst/catalyst (Al:Pd) ratio on catalytic activity were investigated. Polyethylene microstructure was also investigated using high temperature NMR spectroscopy and thermal analysis.

3.2. Materials and instrumentation

All solvents were analytical grade and used as received except toluene, which was dried over sodium and benzophenone, distilled and stored under a nitrogen atmosphere. Ethylene (99.9%) was purchased from AFROX (South Africa) and used as received. Methylaluminoxane (10% wt.) in toluene was purchased from Aldrich and used in a glove box. The catalyst precursors were synthesized according to the method described in chapter 2. All manipulations of air- and or moisture-sensitive compounds were performed under a dry, deoxygenated nitrogen atmosphere using standard high vacuum or Schlenk techniques or in a glove box. Polymerization reactions were performed in a mechanically stirred 300 mL Parr autoclave.

The NMR spectra were recorded on a Gemini 2000 instrument (^{1}H at 200 MHz, ^{13}C at 50 MHz). Chemical shifts are reported in (ppm) referenced to residual protons and ^{13}C signals of deuterated benzene as internal reference. ^{13}C NMR spectra of polyethylene were recorded in 1,2,4-trichlorobenzene at 115 °C. The number- (M_n) and weight-average molecular weights (M_w) and polydispersity (M_w/M_n) of polymers were determined by high temperature gel permeation chromatography (trichlorobenzene, 145 °C, rate = 1.000 mL/min). Thermal analysis were performed on a Perklin Elmer PC series 7 system, with sample size ranging from 2-4 mg, and sample sealed in aluminum pans and heated using an empty pan as reference.

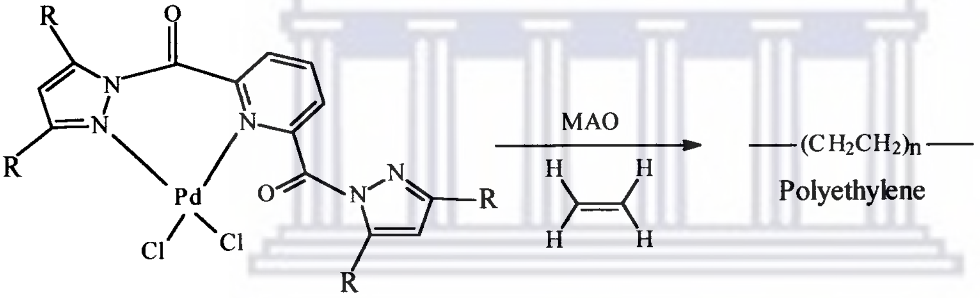
3.3 General procedure for ethylene polymerization

Polymerization was carried out in a 300 mL stainless steel autoclave, which was loaded with the catalyst and co-catalyst methylaluminoxane (MAO) in a nitrogen purged glove box. The polymerization was done as follows: the autoclave was charged with the palladium complex in dry toluene (150 mL), and an appropriate amount of MAO (10% in toluene) (Al:Pd = 1000-4000) was added to the autoclave in a glove box. The reactor was sealed and removed from the glove box. The autoclave was flushed thrice with ethylene and heated to the required temperature. An appropriate amount of ethylene was continuously supplied to the autoclave to maintain constant pressure during the polymerization. After the set experimental time, excess ethylene was vented and the polymerization quenched by adding ethanol. The polymer was filtered, suspended in 2*M* HCl for several days to remove any traces of aluminum or catalyst precursor, filtered again and then washed with ethanol. The polymer was dried in an oven overnight at 50 °C under vacuum.

3.4 Results and discussion

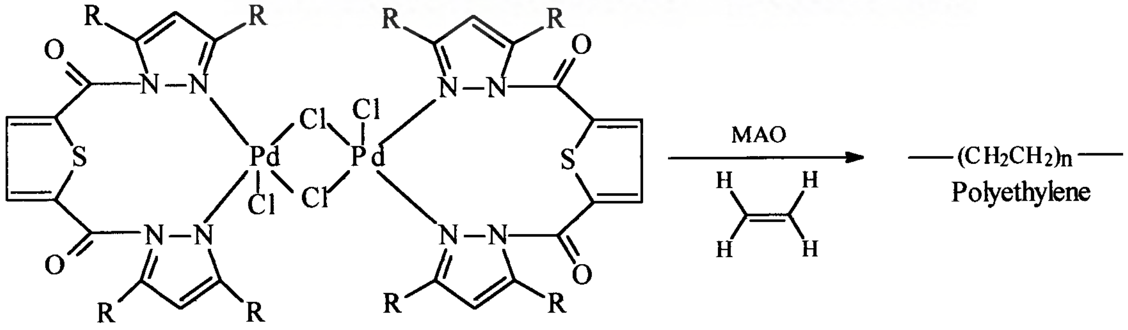
3.4.1 Polymerization of ethylene catalyzed by (N–N)Pd^{II} complexes

The catalyst precursors, [2,6-bis(3,5-ditert-butylpyrazolyl-l-carbonyl)pyridine]palladium(II) dichloride (**1**), [2,6-bis(3,5-dimethylpyrazolyl-l-carbonyl)pyridine]palladium(II) dichloride (**2**), di-μ-chloro-dichloro[2,5-bis(3,5-ditert-butylpyrazolyl-l-carbonyl)thiophene]dipalladium(II) (**4**) and di-μ-chloro-dichlorobis[2,5-bis(3,5-dimethylpyrazolyl-l-carbonyl)thiophene]dipalladium(II) (**5**) were activated *in situ* in toluene by the addition of methylaluminoxane (MAO) as a co-catalyst in the presence of ethylene (Scheme I and II).



R = ^{t}Bu (**1**), R = Me (**2**)

Scheme I: Polymerization of ethylene using catalysts **1** and **2**



R = ^{t}Bu (**4**), R = Me (**5**)

Scheme II: Polymerization of ethylene using catalysts **4** and **5**

Polymerization reactions were performed at 5 atm pressure, various co-catalyst to catalyst (Al:Pd) molar ratio and different temperatures to give polyethylene as a white solid. Table 3.1 summarizes ethylene polymerization conditions and results using precatalysts **1**, **2**, **4** and **5.** Entries 1 to 10 in Table 3.1 represent polymerization reactions using precatalyst **1** as catalyst system, while entries 11, 12 and 13 represent the polymerization reactions using precatalysts **2**, **4** and **5** as catalyst systems respectively. All catalysts used in the polymerization reactions showed moderate to low catalytic activities. Catalyst **1** has moderate activities, whilst the activities for the catalysts **2**, **4** and **5** are low.

3.4.1.1 Characterization of polymers

The polyethylenes produced in the polymerization reactions in Table 3.1 were characterized by high temperature NMR spectroscopy, thermal analysis and high temperature gel permeation chromatography.

Thermal properties of the polyethylene produced were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis-differential thermal analysis (TGA-DTA). A TGA-DTA thermogram (Fig. 3.1) represents the decomposition of a typical polyethylene [7], which generally occurred from 446 to 500 °C. DSC data of the polyethylene produced are given in Table 3.1. A representative DSC thermogram is shown in Fig. 3.2.

Table 3.1 Summary of ethylene polymerization results with **1**, **2**, **4** and **5** as catalyst precursor[a]

Catalyst	Entry	Al:Pd ratio	Temp. (°C)	TON (kg PE/mol Pd.h)	T_m (°C)[b]	M_n (10^5)[c]	M_w (10^5)[c]	M_w/M_n
1	1	1000:1	25	228.9	137.20	5.21	20.23	3.89
1	2	2000:1	25	691.1	137.25	4.84	16.99	3.50
1	3	3000:1	25	844.8	137.65	4.67	16.34	3.50
1	4	4000:1	25	803.3	137.52	4.74	18.82	3.90
1	5	3000:1	30	135.7	137.58	3.72	12.94	3.47
1	6	3000:1	40	714.3	136.80	2.97	10.46	3.51
1	7	3000:1	45	662.0	137.41	3.02	9.46	3.13
1	8	3000:1	50	507.1	136.45	2.60	9.29	3.57
1	9	3000:1	60	529.1	136.13	2.30	7.42	3.23
1	10	3000:1	70	484.4	134.04	1.38	4.18	3.03
2	11	3000:1	25	24.5	138.58	3.75	1.51	3.89
4	12	3000:1	25	18.9	136.41	2.15	8.17	3.82
5	13	3000:1	25	91.1	137.91	1.05	6.07	5.75

[a] Polymerization conditions: [Pd] = 4.48 $\times 10^{-6}$ mmol (**1**), 5.99 $\times 10^{-6}$ mmol (**2**), 2.81 $\times 10^{-6}$ mmol (**4**), 3.95 $\times 10^{-6}$ (**5**); MAO as co-catalyst; 150 mL toluene; 5 atm ethylene pressure; and 3 h.

[b] Determined by differential scanning calorimetry (DSC).

[c] Molecular weight data was determined by GPC vs polystyrene standards.

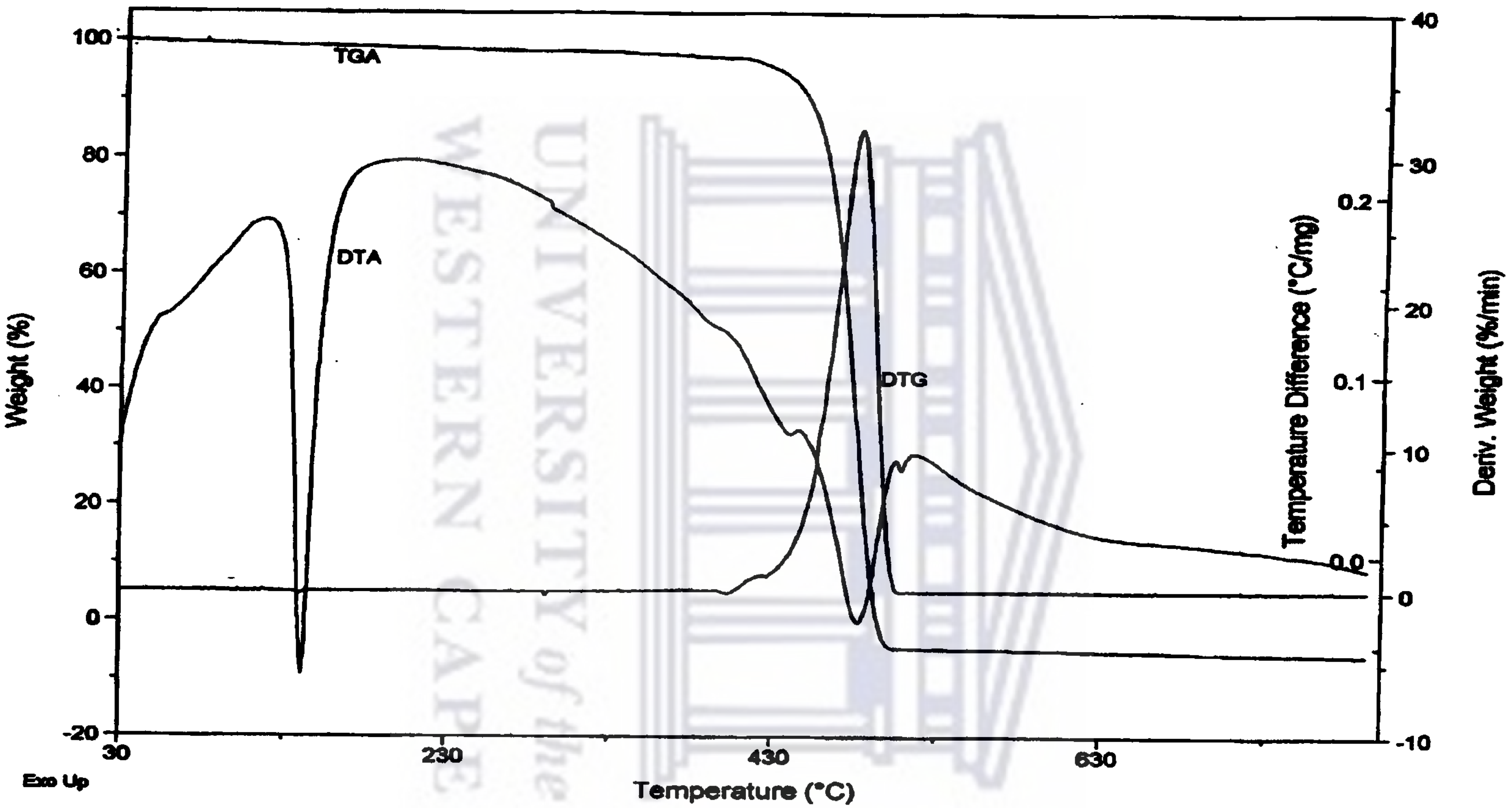


Figure 3.1 A TGA-DTA thermogram of polyethylene

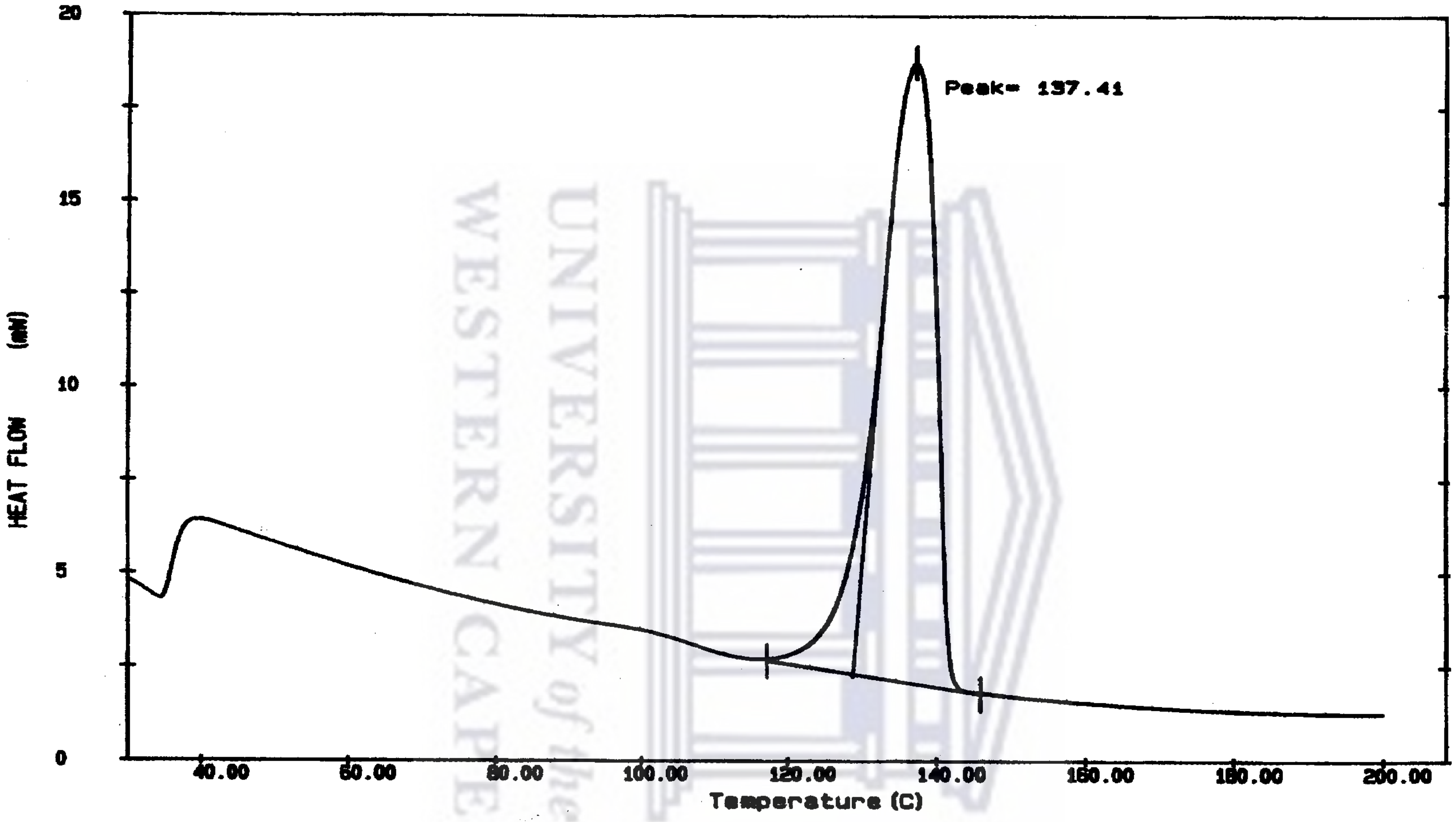
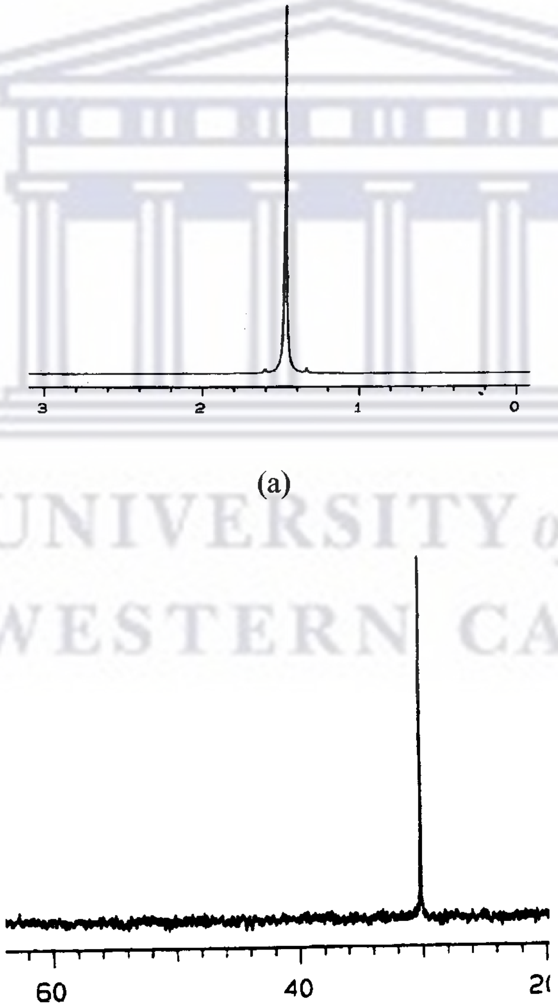


Figure 3.2 DSC thermogram of polyethylene

The polymers obtained, using these pyrazolyl palladium(II) complexes with pyridinedicarbonyl and thiophenedicarbonyl linkers, are high-density polyethylene (HDPE) as determined by DSC with the melting temperatures ranging between 134-138 °C. The type of polyethylene produced is the same as polyethylenes formed with substituted pyrazolyl palladium(II) complexes [6] as catalysts. The appearance of only one signal in the high temperature ^1H NMR spectrum (Fig. 3.3a) and ^{13}C NMR spectrum (Fig. 3.3b) of the polymers formed confirm the linear nature of the polyethylene.



(a)

(b)

Figure 3.3 ^1H NMR spectrum (a) and ^{13}C NMR spectrum (b) of polyethylene

Gel permeation chromatography was used to determine the molecular weights of the polyethylenes produced and the results are shown in Table 3.1. High molecular weight polymers with average molecular weight ranging from 2×10^6 (Table 3.1, entry 1) to 4×10^5 (Table 3.1, entry 10) were obtained. These results are comparable to high molecular weights of polyethylene produced by α–diimine Ni(II) (3×10^5), Pd(II) (1×10^5) [1a], pyridylimine Pd(II) (1×10^6) [3] and tris(pyrazolylcarbonyl) Pd(II) (1×10^6) [6] catalyst systems. The polydispersities observed ranges from 2.8 to 3.9, which are comparable to the polymerization results reported by Brookhart *et al.* [1a, c]. The presence of unimodal molecular weight distribution curves (Fig. 3.4) in gel permeation chromatography plots indicates only one kind of active species in the polymerization reactions.

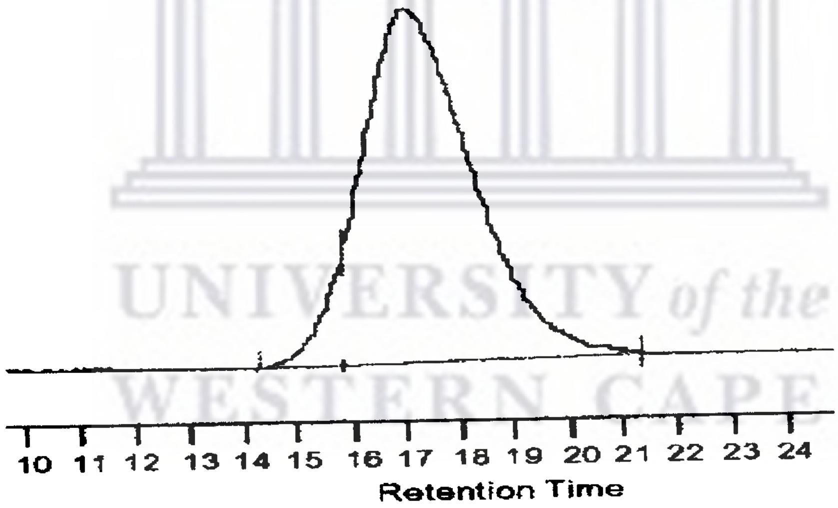


Figure 3.4 GPC chromatogram of polyethylene

The following subsections outline the discussion of the results obtained from various polymerization reactions using different catalyst precursors under different conditions.

3.4.2 Effect of catalysts on polymerization

The main catalyst precursors for most of the ethylene experiments performed was catalyst **1**. The results in Table 3.1, entries 3, 11-13 shows that catalytic activity decreases in the order: **1**>**5**>**2**>**4**. When catalyst precursor **1** was used as the catalyst system, a reasonably moderate catalytic activity (TON = 844 kg PE/mol Pd.h) and high molecular weight (1.6 $\times 10^6$) were obtained. The polymers formed using catalyst **2**, **4** and **5** (Table 3.1, entries 11-13) show lower catalytic activity compared to catalyst **1**. The catalytic activity of **5** (TON = 91 kg PE/mol Pd.h) is higher than the catalytic activity of **2** (TON = 24 kg PE/mol Pd.h), which is higher than the one of **4** (TON = 19 kg PE/mol Pd.h).

The presence of carbonyl groups in the ligands was expected to increase the electrophilicity of the complex to give faster monomer insertion, which in turn would lead to high catalytic activities. The results obtained using the catalyst precursors (**1**, **2**, **4** and **5**) show lower activity than the pyrazolyl catalysts, [tris(pyrazolylcarbonyl)benzene]dipalladium(II) tetrachloride (TON = 1099 kg PE/mol Pd.h) [6] and [$Pd(3,5\text{-}^tBu_2pz)_2Cl_2$] (TON = 1006 kg PE/mol Pd.h) [5] reported by Darkwa *et al*. The lower catalytic activities of catalysts **2**, **4** and **5** can be attributed to their insolubility in toluene. The lower activity of **1** could possibly be due to the fact that in our case the catalyst precursor is mononuclear in nature while the one reported Darkwa *et al*. are binuclear. In the case of the latter there is higher local concentration of active sites in the same molecule, which could lead to higher activity.

The molecular weights of polymers obtained from catalysts **2** ($M_w = 1.5 \times 10^6$), **4** ($M_w = 8.2 \times 10^5$) and **5** ($M_w = 6.07 \times 10^5$) are lower than the molecular weights obtained using catalyst **1** ($M_w = 1.6 \times 10^6$) under the same reaction conditions (Table 3.1, entries 3, 11-13). The polydispersity for polyethylene formed by catalyst **5** (5.7) is broader than those of polyethylenes produced by catalysts **1** (3.9), **2** (3.8) and **4** (3.8). The broadening of the molecular weight distribution may be attributable to the presence of more than one type of catalyst in solution. However, our GPC data did not show the result of a bimodal distribution peaks and there is no additional evidence for a two-site catalyst system.

3.4.3 Effect of co-catalyst to catalyst molar ratio (Al:Pd) on polymerization

To examine the role of the amount of co-catalyst in the polymerization, several experiments in which the co-catalyst to catalyst (Al:Pd) molar ratio was systematically varied from 1000:1 to 4000:1 were carried out (Table 3.1, entries 1-4) using **1** as catalyst system. Figure 3.5 shows the effect of Al:Pd molar ratio on the catalytic activity. Catalytic activity increased with increase in the Al:Pd ratio, with the highest activity obtained at 3000:1 molar ratio of Al:Pd (entry 3) (844 kg PE/mol Pd.h) and thereafter decreased with increasing Al:Pd ratio. The most significant increase in catalytic activity occurred when Al:Pd molar ratio was changed from 2000:1 to 3000:1. When the Al:Pd molar ratio was increased from 3000:1 to 4000:1 the catalytic activity began to decrease (803 kg PE/mol Pd.h).

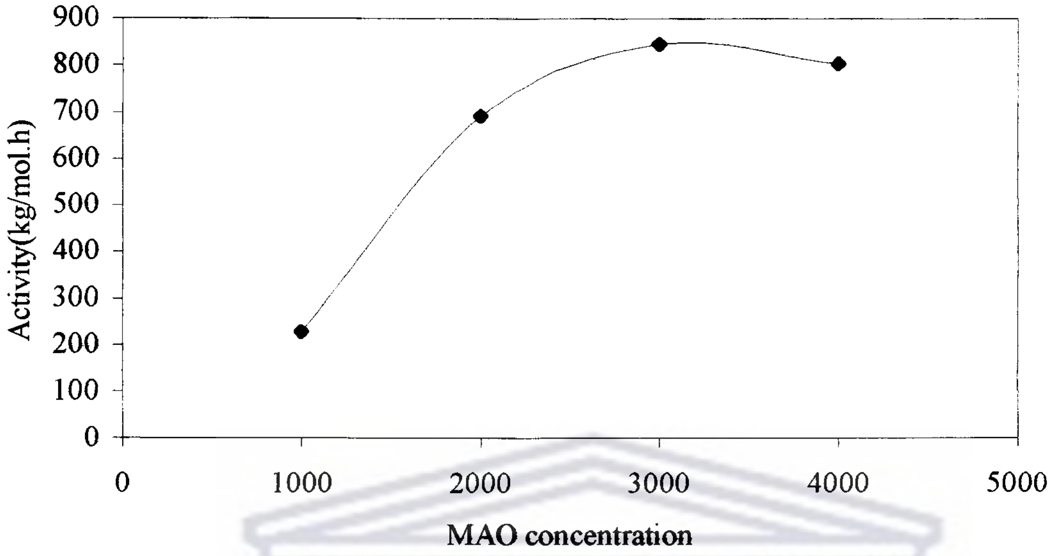


Figure3.5. Dependence of catalytic activity on MAO concentration, at 25 °C, 5 atm and [Pd] = 4.48×10^{-6} M.

The increase of co-catalyst concentration in the polymerization medium may cause an increase in the number of active sites. However when co-catalyst concentration was increased to give a Al:Pd molar ratio of 4000:1, the catalytic activity changed only slightly. This might be due to the maximum number of active sites that are attained at Al:Pd molar ratio of 3000:1. These results are in accordance to the results reported by Chapentier *et al.* [8] and do Couto Junior *et al.* [9], which showed that catalytic activity increases with increasing co-catalyst to catalyst molar ratio and then drops with the increase of co-catalyst. Even though co-catalyst/catalyst ratio in MAO activated catalyst system is usually high, the ratio used here is higher than usual. It is possible that the larger concentration of MAO used to activate **1** is due to MAO reacting with both the dangling pyrazolyl unit in **1** and the palladium centre. As such optimum activation of the catalyst is not reached until a 3000:1 Al:Pd ratio. The formation of Al-pyrazolyl adducts when MAO is used to activate **1** is feasible as Al-NR_3 adducts are known[10]. Few examples of pyrazolyl-Al compounds have also been reported in the literature [Al(1,3,5-Me_3pz] [11] and [$Tp^*{}_2Al$][$AlCl_4$] (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate) [12]. Therefore the possibility of MAO reacting with dangling pyrazolyl unit, reducing activity, is high.

When Al:Pd ratio was varied from 1000:1 to 4000:1 (Table 3.1, entries 1-4) there was no significant change in the molecular weights of the polyethylene produced (Fig. 3.6). The molecular weight of the polyethylene formed when Al:Pd ratio is 1000:1 is slightly higher ($M_w = 20 \times 10^5$) than the molecular weights obtained when Al:Pd ratio is 2000:1 ($M_w = 17 \times 10^5$), 3000:1 $M_w = 16 \times 10^5$) and 4000:1 ($M_w = 19 \times 10^5$).

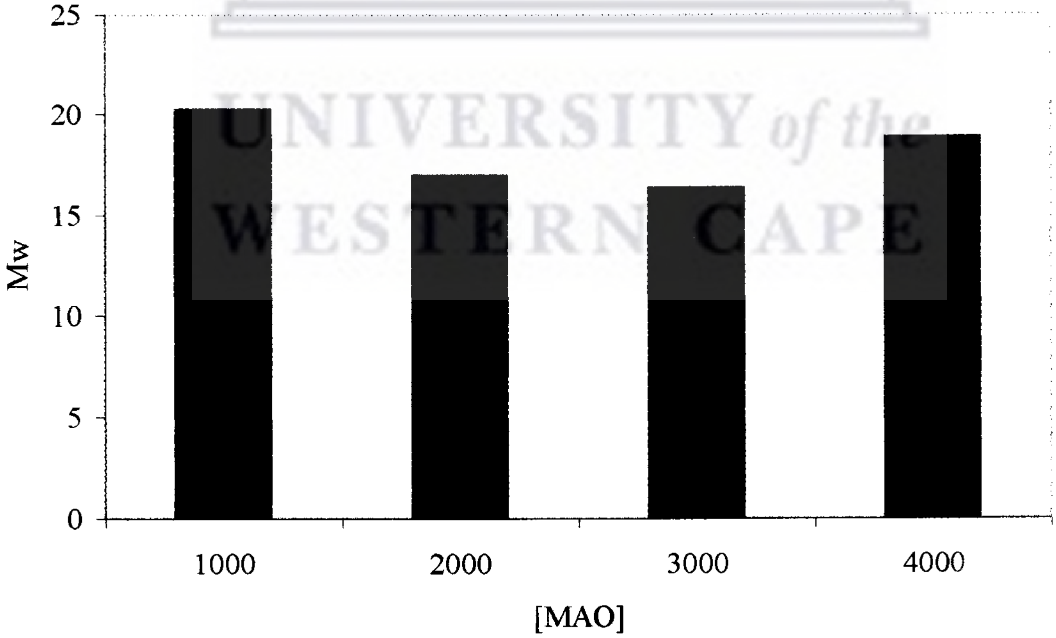


Figure 3.6 Effect of Al:Pd molar ratio on average molecular weight ($M_W \times 10^5$) of

polyethylene obtained.

The polydispersity of polyethylene formed was also not greatly affected by the variation of the Al:Pd ratio. In almost all cases polydispersity values around 3.5 were obtained. The melting temperatures are also not affected by the variation of Al:Pd ratio.

3.4.4 Effect of temperature on polymerization

The effect of temperature on ethylene polymerization was also investigated and entries 5-10 (**Table** 3.1) shows the results of polymerizations performed at different temperatures using catalyst **1**. When the temperature was increased from 30 °C to 40 °C at Al:Pd = 3000:1, the catalytic activity showed an increase {from 135 (30 °C) to 714 kg PE/mol Pd.h (40 °C)}, but when the temperature was increased to 70 °C, the activity decreased from 714 to 484 kg PE/mol Pd h (70 °C) (Fig. 3.7).

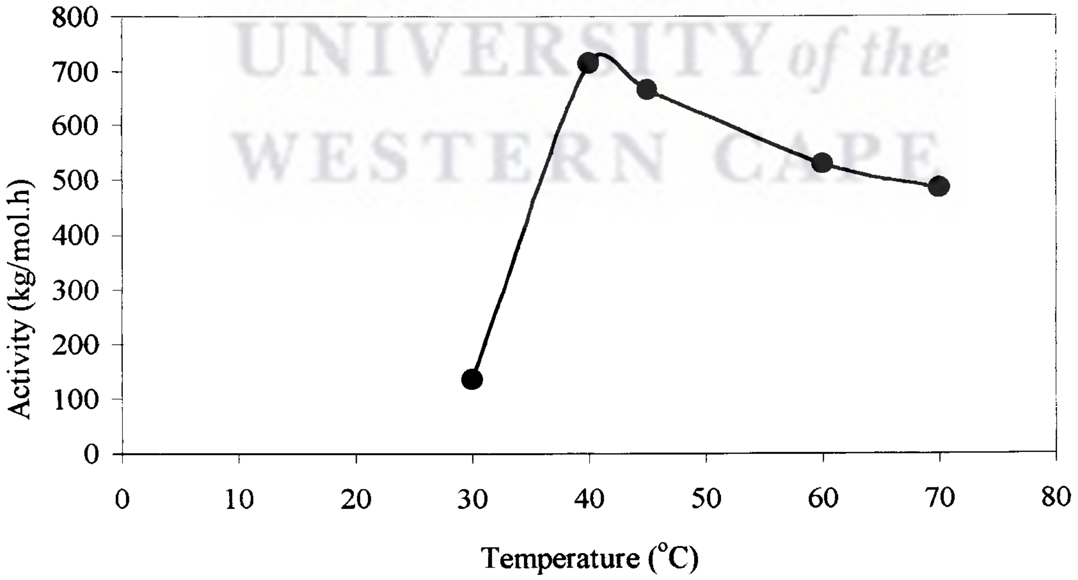


Figure 3.7. Dependence of catalytic activity on temperature at 5 atm, 3000:1 (Al:Pd) and

$[Pd] = 4.48 \times 10^{-6}$ M.

Thermogravimetric analysis of catalyst **1** was performed to investigate the stability of the catalyst precursor (Chapter 2, Section 2.3.5). It was found that the catalyst precursor decomposes at a higher temperature (162 °C to 374 °C) (Fig. 2.9, Chapter 2) than 70 °C. Even though the catalyst precursor is stable at 70 °C, since the active catalyst is expected to be a metal-alkyl intermediate it could be sensitive to heat as transition metal alkyl complexes have low stability. Reduced catalytic activity from 40 °C to 70 °C (entries 7-10) could thus be attributed to the decomposition of a temperature sensitive activated species, which leads to reduce ethylene consumption at high temperatures. Similar observations have been reported with the catalytic activity dropping with increasing temperature when binuclear pyridylimine palladium(II) (35 °C) [3], diimine nickel(II) (60 °C) [1c] and Cp_2ZrCl_2 (70 °C) [9] were used to catalyze polymerization of ethylene in the presence of MAO as a co-catalyst. Compared to the $[Pd(3,5\text{-}^tBu_2pz)_2Cl_2]$/MAO system [5] our catalyst precursor **1,** seems to be less thermally stable in solution. The former was found to operate at temperatures up to 70 °C without showing signs of decomposition.

The molecular weights of polyethylene obtained as temperature is varied are strongly dependant on temperature (Fig. 3.8). The molecular weight of polyethylene produced was found to decrease as the temperature was increased. For example when temperature was increased from 25 to 40 °C, the molecular weight dropped from $M_W = 16 \times 10^5$ (entry 3) to $M_W = 10 \times 10^5$ (entry 6). Increasing reaction temperatures is shown to enhance chain transfer reactions, leading to shorter polymer chains and hence lower molecular masses. The molecular weight distribution was however not strongly influenced by the variation of temperature. In all cases the polydispersity values are between 3.5 and 3.03. There was also no significant influence on the melting temperatures of the polymers as temperature was varied.

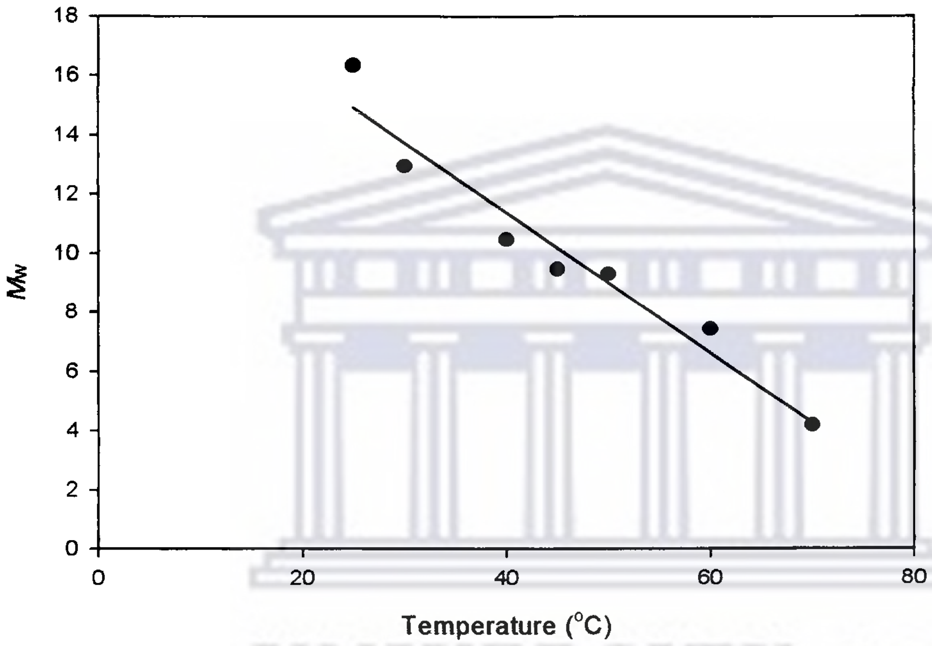


Figure 3.8 Effect of reaction temperature on average molecular weight ($M_W \times 10^5$) of polyethylene obtained.

3.5 Conclusion

Catalytic activities were found to be sensitive to Al:Pd molar ratio, temperature and catalyst precursor. Catalyst **1** formed polyethylenes with higher catalytic activity and higher molecular weights compared to catalysts **2**, **4** and **5**. A possible reason for this is the insolubility of catalysts **2**, **4** and **5** in toluene. When catalyst **1** was used, the activity for the reaction performed at Al:Pd ratio of 4000:1 did not indicate any significant increase which indicates that the maximum number of active sites are attained at Al:Pd ratio of 3000:1. The catalytic activity is strongly influenced by reaction temperatures with the activity increasing with decreasing temperature (<40 °C) and dropping with increasing temperature (>40 °C).

Melting temperatures are not strongly influenced by reaction conditions. Molecular weight of polyethylene decreased with the reaction temperature. Based on these results one can conclude that the best catalytic activity and high molecular weight were obtained when reaction temperature was 25 °C and MAO:**1** catalyst ratio was 3000:1. The NMR data and thermal analysis confirmed the formation of high-density linear polyethylene.

3.6 References

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CHAPTER 4

PYRAZOLYL PALLADIUM COMPLEXES CONTAINING CARBONYL LINKERS AS CATALYST PRECURSORS FOR PHENYLACETYLENE POLYMERIZATION

4.1 Introduction

Polymerization of phenylacetylene to give highly stereoregular *cis-transoidal* polyphenylacetylene is accomplished by the use of different catalytic systems. These catalytic systems include Groups 5 and 6 metal compounds such as $MoCl_5$/2-propyn-1-ol and $Mo(OEt)_5$-$EtAlCl_2$ catalyst systems, with which the reactions are not stereoselective and therefore produce a mixture of *cis* and *trans* polymers [1]. Organorhodium compounds are efficient catalysts for polymerization of monosubstituted acetylenes, with the formation of highly stereoregular polymers, in some cases in a living manner.

Rhodium complexes with monodentate {e.g. $Rh(C{\equiv}CC_6H_5)$(2,5-norbornadiene)$[P(C_6H_5)_3]_2$} [2] and bidentate {e.g. $Rh(nbd)(OMe)_2[Ph_2P(CH_2)xPPh_2]$} ($x$ = 1- 4) phosphines [3] have been reported to promote the living polymerization of phenylacetylene with selective formation of *cis-transoidal* polyphenylacetylene. Rhodium catalysts yield polyphenylacetylene with very high molecular weight compared to other metal catalysts for polymerization of polyphenylacetylene. For example, the use of ionic liquids as reaction media for the polymerization of phenylacetylene catalyzed by (diene)Rh(acac) and $[(diene)RhCl]_2$ complexes [4] under basic co-catalysts were reported to yield polyphenylacetylene with high *cis-transoidal* % (95-100%) with the polymer molecular weights ranging between 55 000 and 200 000. Organoiridium compounds

$[Ir(cod)Cl]_2$ and $[Ir(cod)OMe]_2$ are also active for the polymerization of phenylacetylene with negligible formation of oligomeric products, and the highest molecular weight of polyphenylacetylene being 7 180 [5]. The nickel catalyst, $Ni(COD)_2$-CF_3COO(allyl), also polymerizes phenylacetylene in good yields to form polymers with the highest molecular weight of 12 000 [6].

There are various palladium catalysts that polymerize phenylacetylene. The catalyst $[Pd(CH_3CN)_4][BF_4]_2$ polymerizes phenylacetylene with molecular weight of 9 000 [7]. The cationic bis(phosphino)palladium complexes form the highest molecular weight polyphenylacetylene of 17 707, which was obtained when the solvent mixture CH_2Cl_2/CH_3CN (3:1) was used at room temperature, and [bis(diphenylphosphino)ferrocene]palladium complex as catalyst [8]. Palladium(II) complexes of the type [Pd(NN'O)Cl] were recently reported to catalyze phenylacetylene in water at room temperature, leading to polyphenylacetylene with high molecular weight (M_w = 23 495) [9]. Few studies have been reported on polymerization of phenylacetylene using pyrazolyl/pyrazole complexes as catalyst precursors. Ozawa *et al.* [10] reported the polymerization of phenylacetylene catalyzed by [hydridotris(pyrazolyl)borato]rhodium(I) complexes. This pyrazolyl catalyst system produced polymers with high yields and molecular weights ranging from 1.5×10^4 to 3.2×10^4.

In this chapter we report on the percentage monomer conversion of pyrazolyl palladium(II) catalysts in the polymerization of phenylacetylene. The palladium(II) complexes bearing pyridine/thiophene bis(pyrazolylcarbonyl) ligands were employed for phenylacetylene polymerization. The effect of ligands structure, solvent ratios (CH_2Cl_2:CH_3CN) and single solvent systems on percentage monomer conversion and molecular weight were investigated.

4.2. Materials and instrumentation

All manipulations were performed under a dry, deoxygenated nitrogen atmosphere using standard Schlenk techniques. Dichloromethane was dried by distilling over diphosphorous pentoxide (P_2O_5) and stored over molecular sieves. Toluene and tetrahydrofuran (THF) were dried by distilling over sodium/benzophenone and stored over molecular sieves. Acetonitrile was stored over 4Å molecular sieves. Phenylacetylene (98%) and silver trifluoromethanesulfonate (silver triflate or AgTOf) were obtained from Aldrich and used as received.

IR spectra were recorded as KBr pellets on a PERKIN ELMER, Paragon 1000PC FT-IR spectrometer. The 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 chloroform as internal standard. The number- (M_n) and weight-average molecular weights (M_w) and polydispersity (M_w/M_n) of polymers were determined by gel permeation chromatography (THF, 30 °C, rate = 1.0 cc/min) with PL mixed-C column using polystyrene standards.

4.3 General procedures for phenylacetylene polymerization using solvent mixtures of CH_2Cl_2 and CH_3CN

4.3.1 Polymerization of phenylacetylene using solvent mixtures with [2,6-bis(3,5-ditert-butylpyrazolyl-1-carbonyl)pyridine]palladium(II) dichloride (1) as catalyst precursor

In a typical reaction (Table 4.1, entry 3), a solution of **1** (0.06 g, 0.09 mmol) in 20 mL dry CH_2Cl_2 was reacted with a solution of silver triflate (0.02 g, 0.09 mmol) in 20 mL CH_2Cl_2/CH_3CN for a final composition of 7:1. A yellow precipitate of AgCl was formed immediately after addition of silver triflate. The mixture was stirred for 60 min and filtered to give a yellow solution (catalyst formed *in situ*), and then 0.50 mL (4.48 mmol, 50 equiv.) phenylacetylene was added. The yellow solution changed to light red immediately after addition of phenylacetylene and then changed to a dark red solution after 5 min. The dark red solution was stirred for 4 h and the solvent was removed to give a red-brown oil residue. The oil was allowed to dry at room temperature and weighed to give a brown solid. The brown solid was stirred in methanol for 6 h to give methanol insoluble and methanol soluble fractions. The methanol insoluble fraction was filtered to give a light brown powder. Yield = 0.43 g (96%). ^1H NMR ($CDCl_3$) for polymers (entries 1-6): δ 6.97 (s, Ph), 6.67 (d, Ph), 5.85 (s, vinyl). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.98 (s, quaternary C of the main chain), 139.45 (s, *ipso*-C of Ph), 131.91 (s, vinyl), 127.87 (s, *o*-C of Ph), 127.65 (s, *m*-C of Ph), 126.80 (s, *p*-C of Ph). FT-IR (KBr, cm^{-1}): 890 (m), 757 (s), 736(s) and 691 (s) and GPC results are presented in Table 4.1.

Polymerization of phenylacetylene using [2,6-bis(3,5-dimethylpyrazolyl-l-carbonyl)pyridine]palladium(II) dichloride (**2**), di-μ-chloro-dichlorobis[2,5-bis(3,5-ditert-butylpyrazolyl-l-carbonyl)thiophene]dipalladium(II) (**4**) and di-μ-chloro-dichlorobis[2,5-bis(3,5-dimethylpyrazolyl-l-carbonyl)thiophene]dipalladium(II) (**5**) were performed using the same procedure as above.

4.3.2 Polymerization of phenylacetylene using solvent mixtures with [2,6-bis(3,5-dimethylpyrazolyl-1-carbonyl)pyridine]palladium(II) dichloride (2) as catalyst precursor

To a solution of **2** (0.06 g, 0.12 mmol) in 20 mL dry CH_2Cl_2, a solution of silver triflate (0.03 g, 0.12 mmol) in 20 mL CH_2Cl_2/CH_3CN for a final solvent mixture of 7:1 was added, followed by addition of 0.61 mL (5.99 mmol, 50 equiv.) phenylacetylene (Table 4.1, entry 14). Yield = 0.44 g (73%). ^1H NMR ($CDCl_3$) for polymer (entries 12-17): δ 6.95 (s, Ph), 6.63 (d, Ph), 5.83 (s, vinyl) and GPC results are presented in Table 4.1.

4.3.3 Polymerization of phenylacetylene using solvent mixtures with di-μ-chloro-dichlorobis[2,5-bis(3,5-ditert-butylpyrazolyl-1-carbonyl)thiophene]dipalladium(II) (4) as catalyst precursor

To a solution of **4** (0.10 g, 0.14 mmol) in 20 mL dry CH_2Cl_2, a solution of silver triflate (0.04 g, 0.14 mmol) in 20 mL CH_2Cl_2/CH_3CN to make a final solvent mixture of 7:1 was added, followed by addition of 0.71 mL (7.04 mmol, 50 equiv.) phenylacetylene (Table 4.2, entry 3). Yield = 0.51 g (72%). ^1H NMR ($CDCl_3$) for polymer (entries 1-6): δ 6.98 (s, Ph), 6.65 (d, Ph), 5.85 (s, vinyl) and GPC results are presented in Table 4.2.

4.3.4 Polymerization of phenylacetylene using solvent mixtures with di-μ-chloro-dichlorobis[2,5-bis(3,5-dimethylpyrazolyl-1-carbonyl)thiophene]dipalladium(II) as catalyst precursor

To a solution of **5** (0.06 g, 0.12 mmol) in 20 mL dry CH_2Cl_2, was added a solution of silver triflate (0.03 g, 0.12 mmol) in 20 mL CH_2Cl_2/CH_3CN for a final solvent ratio of 7:1, followed by addition of 0.61 mL (5.93 mmol, 50 equiv.) phenylacetylene (Table 4.2, entry 12). Yield = 0.49 g (80%). ^1H NMR ($CDCl_3$) for polymer (entries 10-18): δ 6.95 (s, Ph), 6.65 (d, Ph), 5.84 (s, vinyl) and GPC results are presented in Table 4.2.

4.4 General procedures for phenylacetylene polymerization using single solvent systems (Toluene, THF and CH_2Cl_2)

4.4.1 Polymerization of phenylacetylene using single solvent systems with [2,6-bis(3,5-ditert-butylpyrazolyl-1-carbonyl)pyridine]palladium(II) dichloride (1) as catalyst precursor

In a typical reaction (Table 4.1, entry 8), a solution of **1** (0.06 g, 0.09 mmol) in 20 mL dry CH_2Cl_2, was added a solution of silver triflate (0.02 g, 0.09 mmol) in 20 mL CH_2Cl_2/CH_3CN for a final solvent ratio of 1:1. The reaction mixture was stirred for 60 min. A yellow solution was obtained after the removal of AgCl precipitate. The solvent was removed under high vacuum, and 40 mL toluene was added to form a homogeneous solution followed by addition of phenylacetylene 0.50 mL (4.48 mmol 50 equiv.) and the reaction was stirred for 4 h. The yellow solution changed to light red and then to red-brown solution. The red-brown solution was evaporated to give an oily residue, which was allowed to dry at room temperature to form a brown solid. The brown solid was stirred at room temperature for 6 h in methanol to give methanol insoluble and methanol soluble fractions. The methanol insoluble fraction was filtered to give a light brown powder. Yield = 0.19 g (42%). For polymers/oligomers in toluene, THF, CH_2Cl_2 and high temperature experiments (entries 7, 8, 9, 10 and 11) typical polymer spectra have the following peaks, ^{1}H NMR ($CDCl_3$): δ 7.20 (broad, m), ^{13}C{H} NMR ($CDCl_3$): 128.25 (broad, m). FT-IR (KBr, cm^{-1}): 894 (m), 754 (s), 739 (s) and 695 (s) with GPC results presented in Table 4.1.

Polymerization of phenylacetylene using single solvent systems with complexes **2**, **4** and **5** as catalyst systems were performed using the same procedure as above.

4.4.2 Polymerization of phenylacetylene using single solvent system with [2,6-bis(3,5-dimethylpyrazolyl-1-carbonyl)pyridine]palladium(II) dichloride (2) as catalyst precursor

To a solution of **2** (0.06 g, 0.12 mmol) in 20 mL dry CH_2Cl_2, was added a solution of silver triflate (0.03 g, 0.12 mmol) in 20 mL CH_2Cl_2/CH_3CN for a final solvent ratio of 1:1. The solvent was removed under high vacuum and 40mL of dry degassed toluene was added followed by addition of 0.61 mL (5.99 mmol, 50 equiv.) phenylacetylene (Table 4.1, entry 19). Yield = 0.22 g (36%). For polymers/oligomers in THF, toluene and CH_2Cl_2 (entries 18-20) typical polymer spectra have the following peaks, ^{1}H NMR ($CDCl_3$): δ 6.94 (s, Ph), 6.64 (d, Ph), 5.83 (s, vinyl) and GPC results are presented in Table 4.1

4.4.3 Polymerization of phenylacetylene using single solvent systems with di-μ-chloro-dichlorobis[2,5-bis(3,5-ditert-butylpyrazolyl-1-carbonyl)thiophene]dipalladium(II) (4) as catalyst precursor

To a solution of **4** (0.10 g, 0.14 mmol) in 20 mL degassed dry CH_2Cl_2, was added a solution of silver triflate (0.04 g, 0.14 mmol) in 20 mL CH_2Cl_2/CH_3CN for a final solvent ratio of 1:1. The solvent was removed under high vacuum and 40mL of dry degassed toluene was added followed by addition of 0.71 mL (7.04 mmol, 50 equiv.) phenylacetylene (Table 4.2, entry 8). Yield = 0.20 g (28%). For polymers/oligomers in toluene, THF and CH_2Cl_2 (entries 7-9), ^{1}H NMR ($CDCl_3$): δ 7.20 (broad, m) and GPC results are given in Table 4.1.

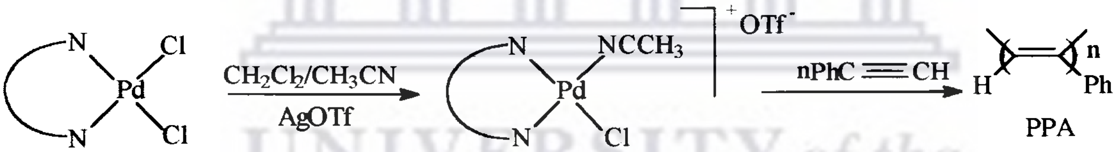
4.4.4 Polymerization of phenylacetylene using single solvent systems with di-μ-chloro-dichlorobis[2,5-bis(3,5-dimethylpyrazolyl-1-carbonyl)thiophene]dipalladium(II) (5) as catalyst precursor

To a solution of **5** (0.06 g, 0.12 mmol) in 20 mL degassed dry CH_2Cl_2, was added a solution of silver triflate (0.03 g, 0.12 mmol) in 20 mL CH_2Cl_2/CH_3CN for a final solvent ratio of 1:1. The solvent was removed under high vacuum and 40 mL of dry degassed toluene was added followed by addition of 0.61 mL (5.93 mmol, 50 equiv.) phenylacetylene (Table 4.2, entry 17). Yield = 0.19 g (31%). For polymer/oligomers (entries 16-18), ^{1}H NMR ($CDCl_3$): δ 6.96 (s, Ph), 6.64 (d, Ph), 5.84 (s, vinyl) and GPC results are presented in Table 4.2.

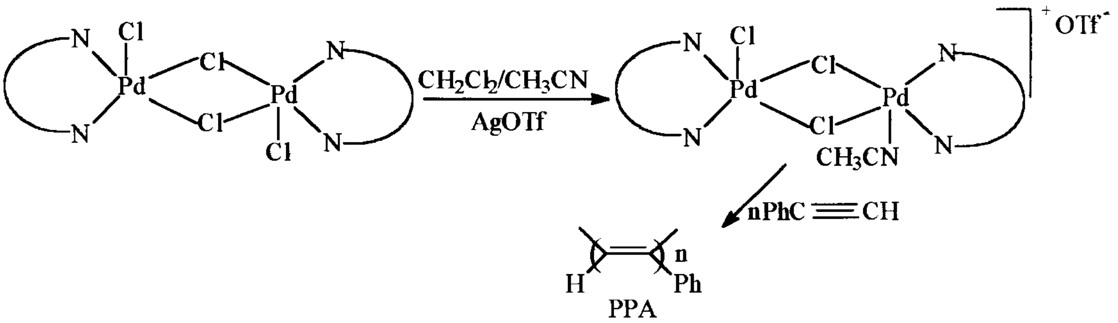
4.5 Results and discussion

4.5.1 Polymerization of phenylacetylene catalyzed by (N –N)Pd(II) complexes

The polymerization and oligomerization of phenylacetylene (PA) was catalyzed by active catalysts, [py-2,6-bis{CO(3,5-^{t}Bupz)$_2$}PdCl(NCCH$_3$)]$^+$OTf$^-$ (**1a**), [py-2,6-bis{CO(3,5-Mepz)$_2$}PdCl(NCCH$_3$)]$^+$OTf$^-$ (**2a**), bis[th-2,5-bis{CO(3,5-^{t}Bupz)$_2$}Pd(μ-Cl)$_2$(NCCH$_3$)]Cl$^+$OTf$^-$ (**4a**) and bis[th-2,5-bis{CO(3,5-Mepz)$_2$}Pd(μ-Cl)$_2$(NCCH$_3$)]Cl$^+$OTf$^-$ (**5a**) respectively. These active catalysts **1a**, **2a**, **4a** and **5a** were generated by the removal of one chloride atom with the silver triflate in a CH_2Cl_2/CH_3CN mixture, followed by weak coordination of acetonitrile as shown in Schemes I and II. The monomer was then added to the *in situ* generated catalysts. Formation of products was generally fast in all reactions.



Scheme I: Preparation of active catalysts **1a** and **2a** for phenylacetylene polymerization



Scheme II: Preparation of active catalysts **4a** and **5a** for phenylacetylene polymerization

In experiments where single solvent systems were used, the active catalysts were generated by the reaction of silver triflate in a CH_2Cl_2/CH_3CN (1:1) mixture to a solution of appropriate catalyst precursor in CH_2Cl_2. The solvent was removed and replaced by the appropriate pure solvent in which the polymerization was conducted. The active catalysts are stabilized by residual CH_3CN from the CH_2Cl_2/CH_3CN solvent mixtures that were used to generate the active catalyst.

All polymerization reactions were performed with catalyst/monomer (PA) ratios of 1:50 either in CH_2Cl_2/CH_3CN solvent mixtures or pure CH_2Cl_2, toluene and THF. After addition of the monomer in CH_2Cl_2/CH_3CN solvent mixtures or pure CH_2Cl_2, toluene and THF the reddish brown solution was evaporated to form an oily residue, which was allowed to dry at room temperature. The residue was stirred in methanol to give methanol insoluble and methanol soluble fractions.

Most reactions produced yellowish brown solids representing the combined yield of both oligomers and polymers with low to high yields. The yields of the products produced range between 28% to 96%. The products are very soluble in common organic solvents like CH_2Cl_2, CH_3CN, toluene, THF and insoluble in methanol, diethyl ether and n-hexane.

The following tables summarize reaction conditions and results of phenylacetylene polymerization and oligomerization catalyzed by (N–N)Pd^{II} catalysts, **1a**, **2a**, **4a** and **5a**.

Table 4.1 Polymerization of phenylacetylene catalyzed by **1a** and **2a**[a]

Catalyst	Entry	Solvent ratios	% Conversion	M_w[b]	M_n[b]	M_w/M_n[b]
1a	1	CH_2Cl_2:CH_3CN (3:1)	87	3798	1086	3.23
	2	CH_2Cl_2:CH_3CN (5:1)	82	10831	7509	1.44
	3	CH_2Cl_2:CH_3CN (7:1)	96	10119	6021	1.68
	4	CH_2Cl_2:CH_3CN (9:1)	78	1783	439	3.72
	5	CH_2Cl_2:CH_3CN (12:1)	53	1151	426	2.67
	6	CH_2Cl_2:CH_3CN (14:1)	38	1204	451	2.67
	7	CH_2Cl_2	76	625	491	1.27
	8	Toluene	42	5671	1357	4.17
	9	THF	84	620	464	1.34
	10	CH_2Cl_2:CH_3CN (7:1) (40 °C)	46	1157	620	1.87
	11	THF (40 °C)	54	559	429	1.30
2a	12	CH_2Cl_2:CH_3CN (3:1)	59	2463	564	4.36
	13	CH_2Cl_2:CH_3CN (5:1)	62	1137	481	2.36
	14	CH_2Cl_2:CH_3CN (7:1)	73	639	275	2.32
	15	CH_2Cl_2:CH_3CN (9:1)	54	6342	4101	1.54
	16	CH_2Cl_2:CH_3CN (12:1)	34	2011	564	3.56
	17	CH_2Cl_2:CH_3CN (14:1)	39	786	432	1.82
	18	CH_2Cl_2	59	1009	454	2.22
	19	Toluene	36	2811	725	3.80
	20	THF	62	23249	12572	1.84

[a] All reactions were performed in 40 mL of solvent at room temperature with exception of entries 10 and 11, [Pd] = 2.4 × 10^{-3} mol/L (**1**) and 3.0 × 10^{-3} mol/L (**2**), Pd/PA = 1:50.

[b] Molecular weight data was determined by GPC based on polystyrene standards.

Table 4.2 Polymerization of phenylacetylene catalyzed by **4a** and **5a**[a]

Catalyst	Entry	Solvent ratios	% Conversion	M_w[b]	M_n[b]	M_w/M_n[b]
4a	1	CH_2Cl_2:CH_3CN (3:1)	77	751	341	2.20
	2	CH_2Cl_2:CH_3CN (5:1)	92	978	372	2.62
	3	CH_2Cl_2:CH_3CN (7:1)	71	1114	317	3.51
	4	CH_2Cl_2:CH_3CN (9:1)	58	8826	6274	1.41
	5	CH_2Cl_2:CH_3CN (12:1)	56	8551	5770	1.48
	6	CH_2Cl_2:CH_3CN (14:1)	68	8320	5093	1.63
	7	CH_2Cl_2	42	666	360	1.85
	8	Toluene	28	1185	443	2.67
	9	THF	58	1454	537	2.71
5a	10	CH_2Cl_2:CH_3CN (3:1)	66	11278	5546	2.03
	11	CH_2Cl_2:CH_3CN (5:1)	77	11456	5557	2.06
	12	CH_2Cl_2:CH_3CN (7:1)	80	10250	5704	1.79
	13	CH_2Cl_2:CH_3CN (9:1)	51	8510	6657	1.28
	14	CH_2Cl_2:CH_3CN (12:1)	61	12204	6232	1.96
	15	CH_2Cl_2:CH_3CN (14:1)	48	8226	4836	1.70
	16	CH_2Cl_2	41	1604	597	2.68
	17	Toluene	31	18121	1100	1.65
	18	THF	53	12686	10544	1.20

[a] All reactions were performed in 40 mL of solvent at room temperature, [Pd] = 2.7×10^{-3} mol/L (**4**) and 3.5×10^{-3} mol/L (**5**), Pd/PA = 1:50.

[b] Molecular weight data was determined by GPC based on polystyrene standards.

4.5.1.1 Characterization of polyphenylacetylene

The polyphenylacetylenes produced in catalytic reactions, in Tables 4.1 and 4.2 were characterized by NMR, IR spectroscopy and gel permeation chromatography.

The ^{1}H, ^{13}C NMR and IR spectra determined the stereochemistry of the polyphenylacetylene obtained. The ^{1}H NMR spectrum (Fig. 4.1a) of polymers obtained from experiments where solvent mixtures (CH_2Cl_2/CH_3CN) were used, showed a sharp singlet at 5.85 ppm due to the vinylic protons, with broad peaks at 6.66 (*ortho*) and 6.97 ppm (*meta* and *para*), associated with a regular head to tail structure of a *cis-transoidal* polyphenylacetylene [2a, 11]. The ^{13}C NMR spectrum (Fig. 4.1b) supports the stereoregularity of the polymers formed, with the set of signals at 142.98 and 139.45 ppm for quaternary carbons, 131.91 ppm for vinylic carbon, 127.87, 127.65 ppm for *ortho* and *meta* aromatic carbons, 126.80 ppm for *para* aromatic carbon. Furlani *et al.* [12] have assigned peaks for *cis-transoidal* polyphenylacetylene catalyzed by Rh(I) complexes, using ^{13}C NMR spectrum, similar to the ones obtained from our experiments.

The absorption peaks in the ^{1}H NMR spectra of the polyphenylacetylene prepared using $[(P\text{-}P)Pd(CH_3)(NCCH_3)]^{+}OTf^{-}$ as catalyst [8] in a CH_2Cl_2/CH_3CN mixture, are very sharp (Fig. 4.2a), indicative of the polymer's high stereoregularity (100% *cis*). In the ^{1}H NMR spectrum obtained in our study (Fig. 4.1a), the absorption peaks are somewhat broad and could be attributed to the lower *cis* content of the polymer. Similar peaks have been observed with phenylacetylene formed by tris(pyrazolyl)borate rhodium(I) catalysts [10], but the absorption peaks are less broad.

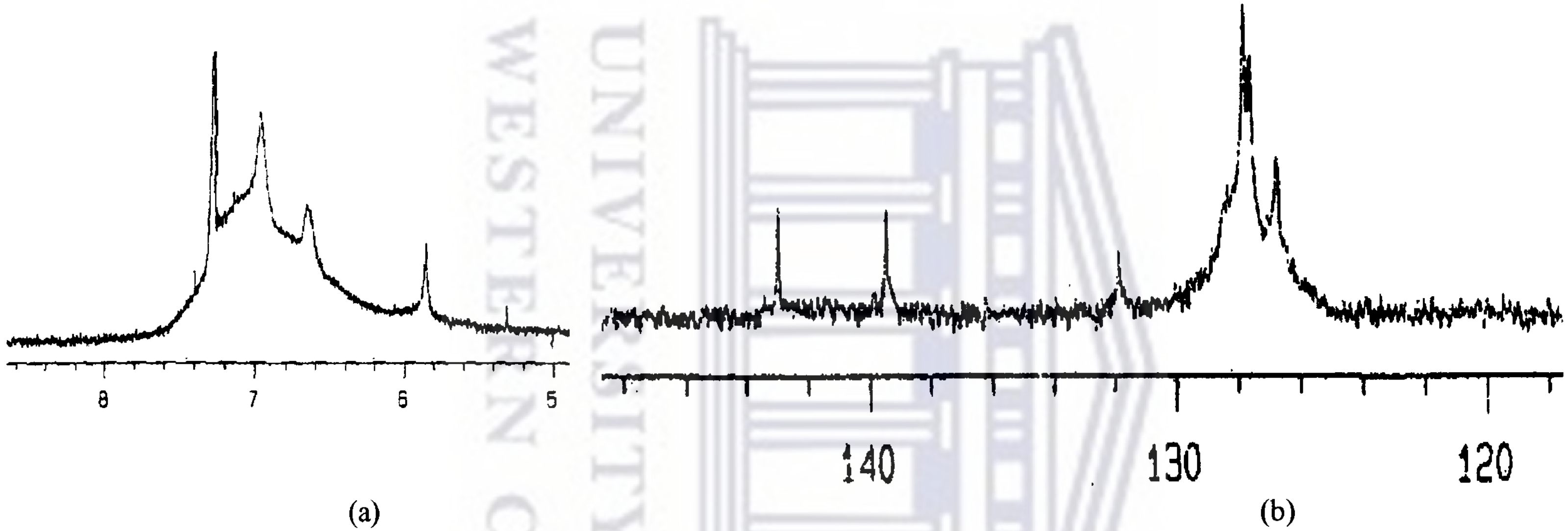
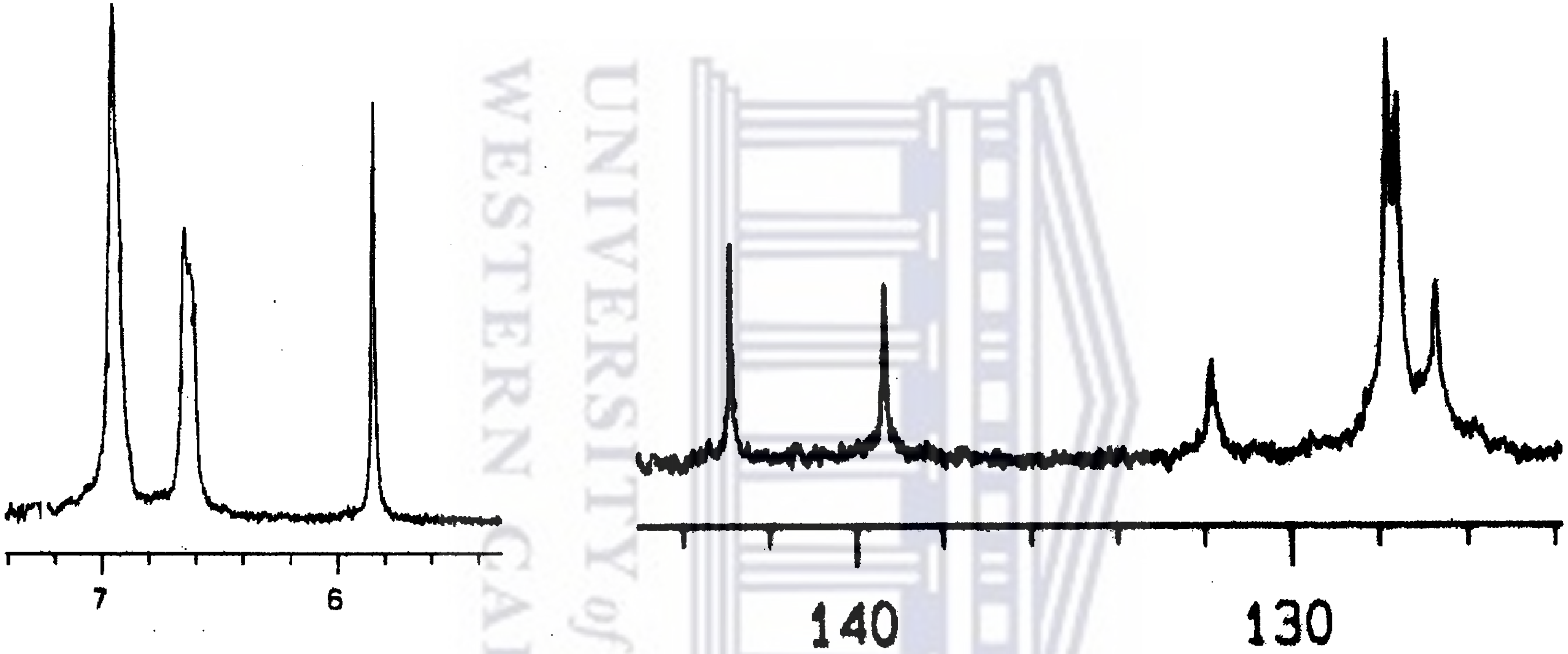


Figure 4.1. ^{1}H NMR spectrum (a) and ^{13}C NMR spectrum (b) of *cis-transoidal* polyphenylacetylene formed by (N–N)Pd^{II} complexes.



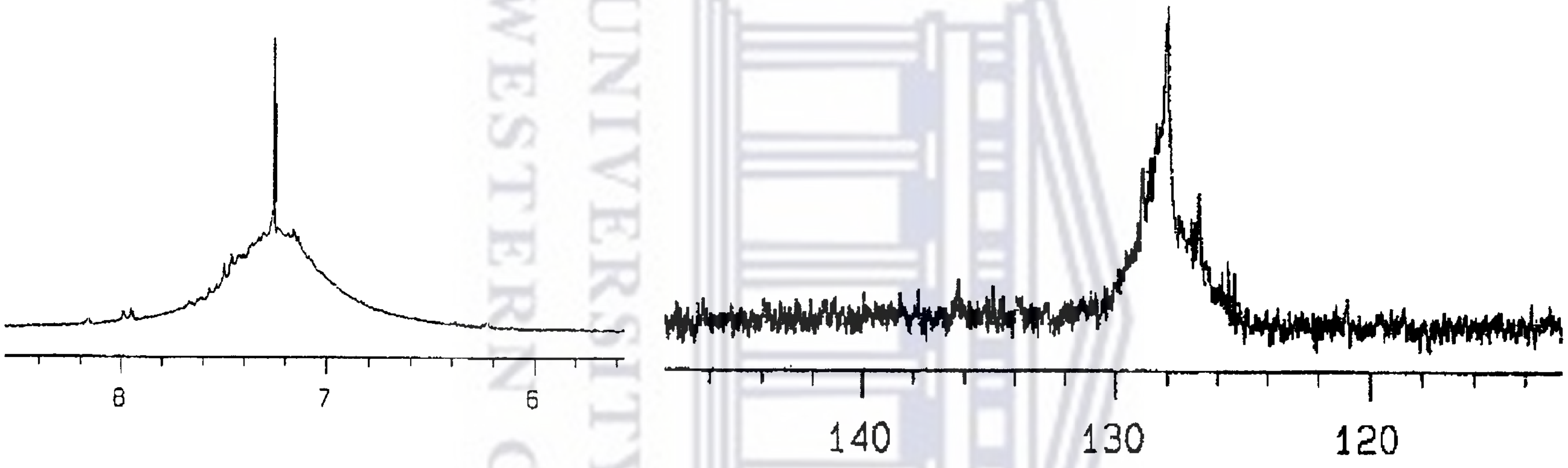
(a)
(b)

Figure 4.2 ^{1}H NMR spectrum (a) and ^{13}C NMR spectrum (b) of *cis-transoidal* polyphenylacetylene formed by (P–P)Pd^{II} complexes.

The high stereoregularity of the polyphenylacetylene formed by $[(P\text{-}P)Pd(CH_3)(NCCH_3)]^+OTf^-$ is also evidenced by the sharp absorption peaks in its ^{13}C NMR spectrum (Fig. 4.2b), while the peaks for the polyphenylacetylene prepared with the catalysts **1a**, **2a**, **4a** and **5a** in this study are much less resolved (Fig. 4.1b).

For experiments 7-9 (Tables 4.1 and 4.2) in which single solvent systems and catalysts **1a** and **4a** were used, the ^1H NMR spectrum (Fig. 4.3a) showed a broad peak centred at 7.20 ppm and ^{13}C NMR spectrum (Fig.4.3b) also showed a broad peak at 128.64 ppm associated with *trans-cisoidal* polyphenylacetylene [13]. The same *trans-cisoidal* structure was obtained with high temperature reactions (Table 4.1, entries 10, 11). Different results were obtained for reactions performed using single solvent systems with catalysts **2a** and **5a**. These reactions produced polymers with *cis-transoidal* structures compared to the *trans-cisoidal* structures obtained when single solvent and catalysts **1a** and **4a** were used.

In all cases no cyclotrimerization products such as 1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene were observed. This was confirmed by the absence of peaks at 7.60-7.80 ppm in the ^1H NMR spectra, which are due to the protons of triphenylbenzene [14, 1d]. Therefore the low molecular weight products formed in this study are linear oligomers.



(a)

(b)

Figure 4.3 ^{1}H NMR spectrum (a) and ^{13}C NMR (b) spectrum of *trans-cisoidal* polyphenylacetylene formed by (N–N)Pd^{II} complexes.

Figure 4.4 depicts the infrared spectrum of the polyphenylacetylene (Table 4.1, entry 3) formed by catalyst **1a**. The IR spectrum of polyphenylacetylene is characterized by an intense peak at 691 cm^{-1}, two sharp absorptions at 735 and 752 cm^{-1}, and by broad strong peak at 882 cm^{-1}, which are characteristic of *cis-transoidal* polyphenylacetylene [15]. The IR spectra of polymers and oligomers formed are nearly identical to each other, showing only small difference in the region of 870-920 cm^{-1}, which could be due to differences in molecular weight.

4.5.2 Effect of catalysts on polymerization

Polymerization of phenylacetylene was examined with two types of catalyst systems bearing bis(pyrazolylcarbonyl) ligands. The first type was $[Pd(N\text{-}N)ClCH_3CN]^+OTf^-$ and second type was $[Pd_2(\mu\text{-}Cl)_2(N\text{-}N)ClCH_3CN]^+OTf^-$. Figure 4.5 (Table 4.1, entries 3, 14; Table 4.2, entries 3, 12) illustrates that percentage monomer conversion decreases in the order: **1a**> **5a**> **2a** ≥ **4a**. The interesting feature of organometallic chemistry is that a small change in the ligand structure, in an organometallic complex, may significantly change the complex's catalytic activity and the stereoregularity power. When tertiary butyl substituted catalyst **1a** was used, high polymer yield (96%) and high molecular weight (M_w = 10 119) was obtained but low percentage monomer conversion (73%) and low molecular weight products (M_w = 639) were observed for its methyl analogue catalyst (**2a**). The methyl substituted catalyst **5,** formed higher percentage monomer conversion (80%) and high molecular weight products (M_w = 10 250) relative to its tertiary butyl analogue catalyst **4a** (71%, M_w = 1 114).

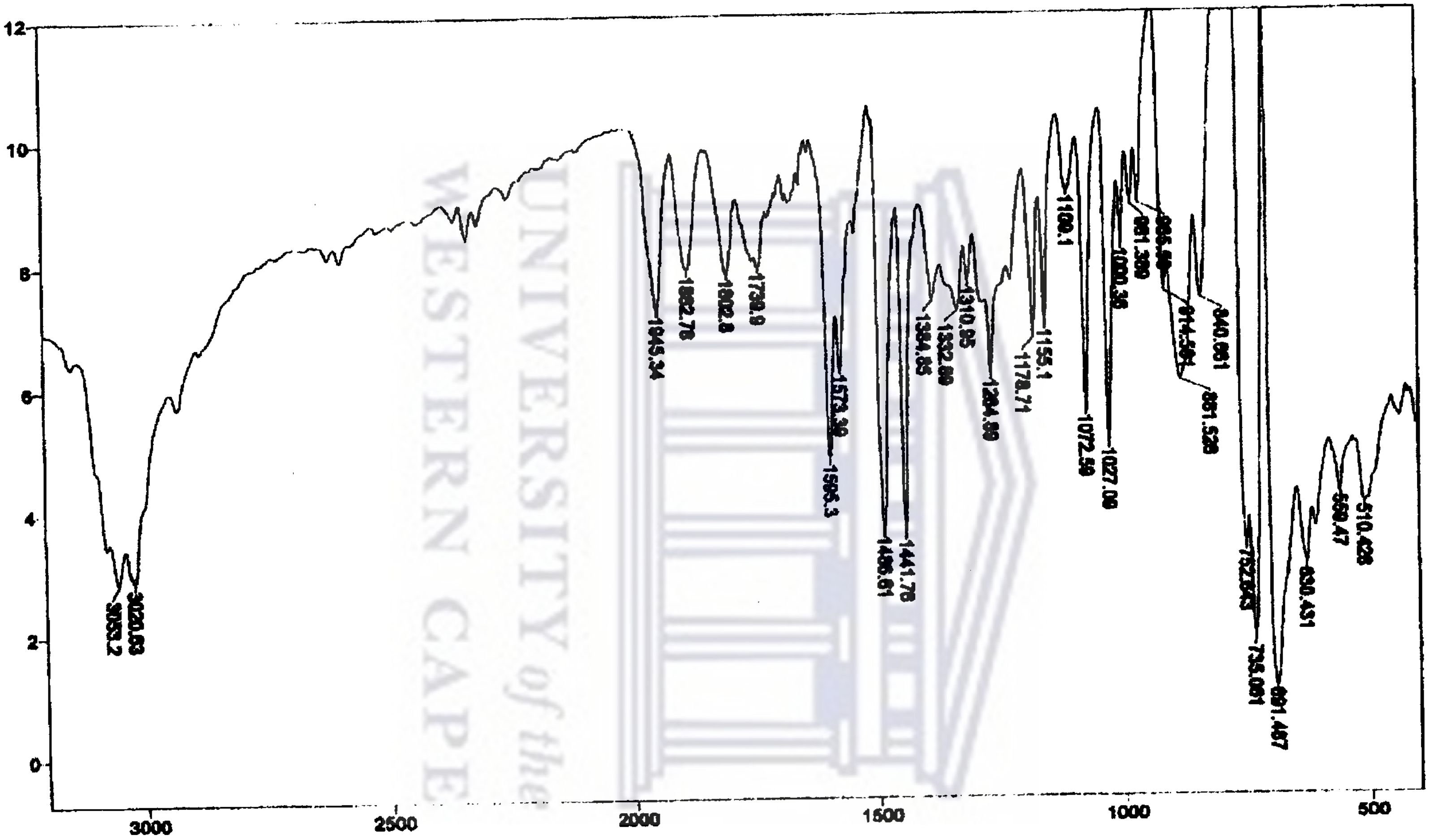


Figure 4.4 IR spectrum of polyphenylacetylene formed by (N–N)Pd^{II} complexes (KBr pellets).

The highest molecular weight polymer (M_w = 23 249) was obtained using catalyst **2a** and THF (Table 4.1, entry 20) with other reactions in THF producing low molecular weight products.

The activity of catalyst **2a** is lower than that of **1a**. Because the catalyst precursor **1** is much more soluble than the catalyst precursor **2**, it is possible that the lower activity of **2a** than **1a** is solubility related. For example lower percentage conversion of phenylacetylene has been observed for less bulky substituents on pyrazolyl catalysts when tris(pyrazolyl)borate rhodium(I) complexes are used for phenylacetylene polymerization [10]. This catalyst system gave high percentage monomer conversion of 93% and 98% for isopropyl and phenyl substituents respectively compared to less bulky analogues H and Me substituents with yields of 2% and 91% respectively.

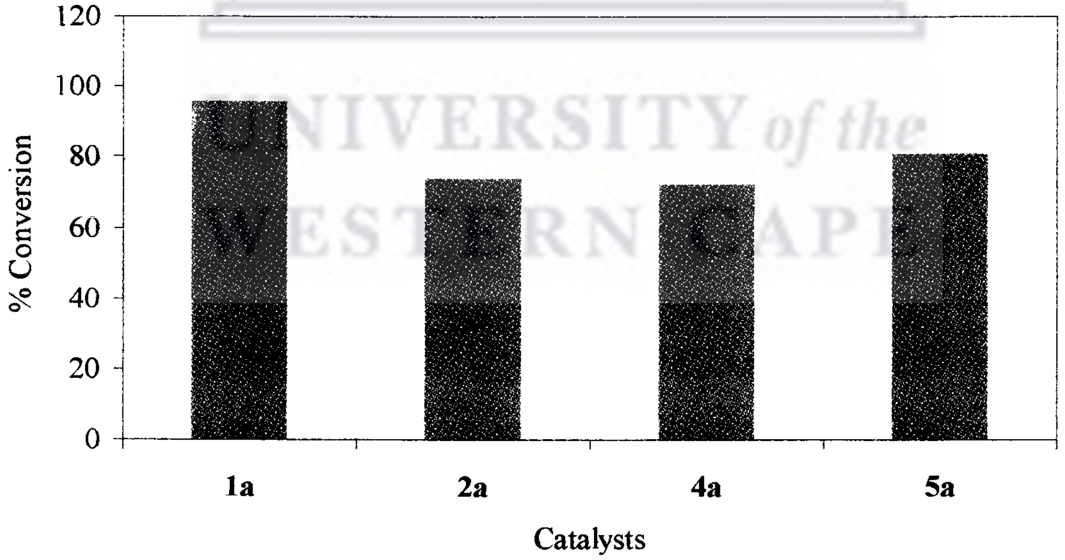
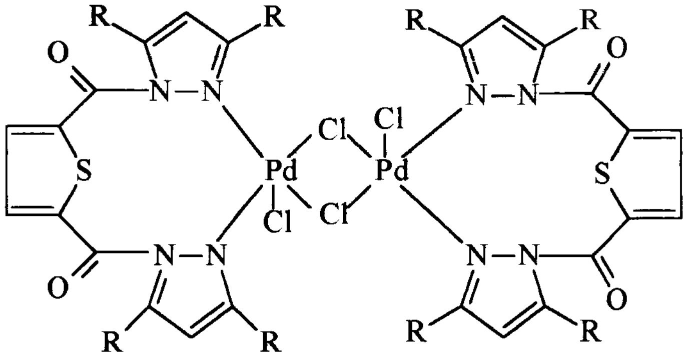


Figure 4.5 Influence of catalysts on percentage monomer conversion.

With regard to the mechanism of the catalytic reaction, two mechanistic pathways have been described for alkyne polymerization namely: metathesis and alkyne insertion (Schemes V, VI, Chapter 1). It has been proposed that palladium and nickel catalyzed reactions proceed *via* an insertion mechanism [16], whereas a metathesis mechanism is operative for molybdenum and tungsten-based catalysts.

The steric bulk of the tertiary butyl substituents contribute to the degree of polymerization since the polymerization proceeds *via* an insertion mechanism. Therefore the steric bulk of tertiary butyl substituents in catalyst **1a**, compared to methyl substituents in catalyst **2a,** facilitates chain growth in reactions in which **1a** was used as catalyst. Thus polymers obtained with catalyst **1a** have much higher molecular weights since the bulkier tertiary butyl group prevents the mechanism that lead to oligomerization and hence chain growth termination.

The lower percentage monomer conversion of tertiarybutyl substituted catalyst **4a** compared to its methyl substituted analogue **5a** and other catalysts (**1a** and **2a**) can be attributed to the coordination mode of the ligands in these two catalysts (**4a** and **5a**). Complexes **4a** and **5a** are binuclear with two ligands binding the two metal centres (Scheme III). Therefore the lower percentage monomer conversion and low molecular weight products of **4a** relative to its analogue **5a** could be attributed to sterically bulky tertiary butyl substituents which can retard the coordination of monomer to palladium.



R = ^{t}Bu (**4**), R = Me (**5**)

Scheme III: Structure of **4** and **5**

4.5.3 Effect of reaction conditions on polymerization

To investigate the influence of solvents on the percentage monomer conversion, polymerization reactions were performed in solvent mixtures, using different ratios of CH_2Cl_2/CH_3CN and in single solvent systems (THF, toluene and CH_2Cl_2). Figure 4.6 (Table 4.1, entries 1-6) illustrates the effect of CH_2Cl_2/CH_3CN mixtures on percentage monomer conversion when catalyst **1a** was used. From Fig. 4.6, it is clear that high polymer yield (96%) is obtained when a 7:1 CH_2Cl_2/CH_3CN solvent ratio was used. The polymer yield decreased as the CH_2Cl_2/CH_3CN solvent ratio was increased from 7:1 to 14:1. The lowest polymer yield (38%) was obtained when CH_2Cl_2/CH_3CN ratio was 14:1. The molecular weight of the products formed using catalyst **1a** and CH_2Cl_2/CH_3CN solvent ratios also showed a decrease as solvent ratio increased from 7:1 to 14:1. The highest polymer molecular weights (M_w = 10 831 and 10 119) were obtained when 5:1 and 7:1 CH_2Cl_2/CH_3CN solvent ratio were used respectively. The lowest molecular weight (M_w = 1 204) product was obtained when 14:1 CH_2Cl_2/CH_3CN solvent ratio was employed.

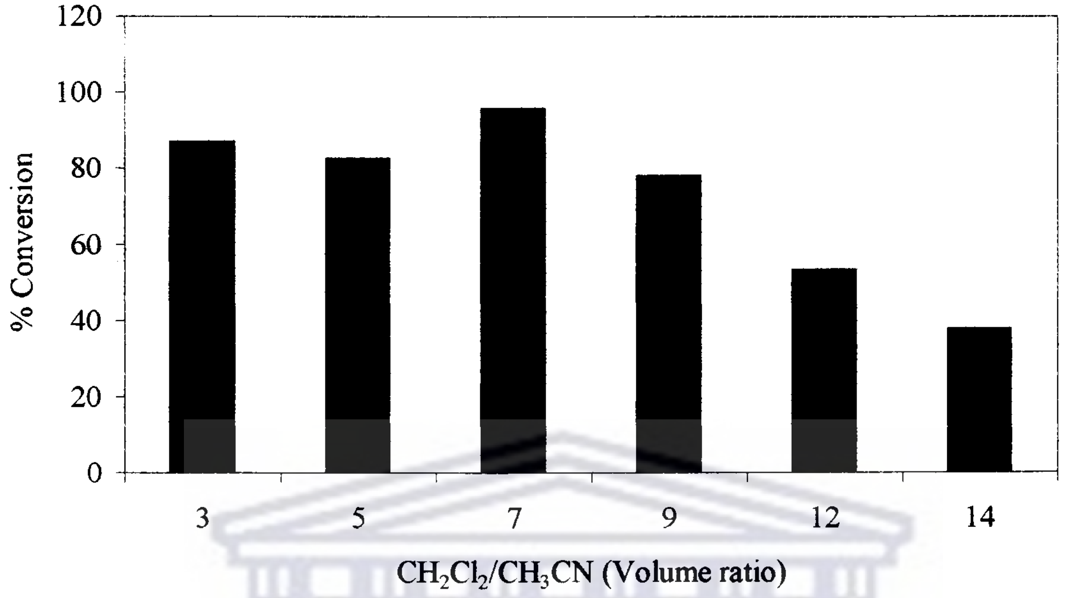


Figure 4.6 Influence of CH_2Cl_2/CH_3CN ratio on percentage monomer conversion using **1a** as catalyst system.

When catalyst **2a** and CH_2Cl_2/CH_3CN mixtures were used, polymerization took place (Table 4.1, entries 12-20). The polymer yield and molecular weight products were lower than the polymer yield and molecular weight products formed by **1a**. The optimum CH_2Cl_2/CH_3CN solvent mixture was found to be 7:1, which gave a high percentage monomer conversion of 73%. The lowest percentage monomer conversions (34% and 39%) were obtained when 12:1 and 14:1 CH_2Cl_2/CH_3CN solvent ratios were employed. This could be due to decreased concentration of CH_3CN, which is important for stabilizing the active species. Therefore, the decrease in proportion of CH_3CN might have destabilized the active species resulting in a decreased monomer conversion. It is important to note that the reaction performed in CH_2Cl_2 also gave low percentage monomer conversion (59%) compared to reactions using 7:1 CH_2Cl_2/CH_3CN solvent ratios. Catalyst **2a** formed low molecular weight products with the exception of the reaction in 9:1 CH_2Cl_2/CH_3CN solvent ratio, which formed high molecular weight product (M_w = 6 342).

The low molecular weight products ranging from 639 to 2 463 shows the formation of 6 to 24 repeating units of phenylacetylene, which is an indication of linear oligomers, since polymers are reported to have monomer repeating units of 30 and upwards. Oligomerization of phenylacetylene is also supported by the ^{1}H NMR data, which showed no signs of cyclomerization products (1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene) by the absence of protons due to triphenylbenzene at 7.6-7.8 ppm [14, 1d].

Figure 4.7 illustrates the effect of CH_2Cl_2/CH_3CN mixture on percentage monomer conversion when **4a** was used as a catalyst (Table 4.2, entries 1-6). Catalytic reactions using **4a**, in CH_2Cl_2/CH_3CN mixtures, formed the products in high yield (92%) when 5:1 CH_2Cl_2/CH_3CN solvent ratio was used and the lowest polymer yields (56% and 58%) were obtained with 12:1 and 9:1 CH_2Cl_2/CH_3CN solvent ratios. Increasing the proportion of CH_2Cl_2 gave both high molecular weight products and low polydispersities. The CH_2Cl_2/CH_3CN solvent ratios of 9:1, 12:1 and 14:1 gave high molecular weights products of 8 826, 8 551, 8 320 respectively.

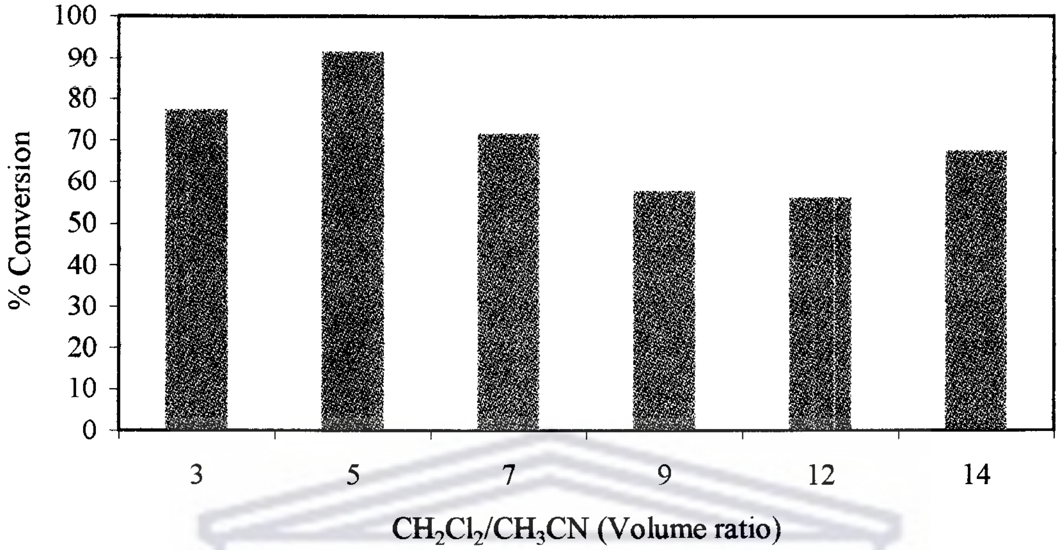


Figure 4.7 Effect of CH_2Cl_2/CH_3CN ratio on percentage monomer conversion using **4a** as catalyst system.

Phenylacetylene polymerization was also observed when catalyst **5a** and CH_2Cl_2/CH_3CN mixtures were employed (Table 4.2, entries 10-15). In these catalytic reactions, the highest polymer yields (80% and 77%) were obtained with 7:1 and 5:1 CH_2Cl_2/CH_3CN solvent ratios. The lowest polymer yields (48%, 51%) were formed when 14:1 and 9:1 CH_2Cl_2/CH_3CN solvent ratios were used. Most of the polymeric materials formed had high molecular weight values. The highest molecular weight products of 11 278, 11 456, 10 250, 12 204 were formed when 3:1-7:1 and 12:1 CH_2Cl_2/CH_3CN solvent ratios were used. The lowest molecular weight products (M_w = 8 510, 8 226) were formed with 9:1 and 14:1 CH_2Cl_2/CH_3CN solvent ratios. It is worth noting that the methyl substituted catalyst (**5a**) produced higher molecular weights than its tertiary substituted analogue 4a. Because of the structure of catalyst precursors **4** and **5** (Chart 1), and the bulky nature of the phenylacetylene monomer, the coordination of the monomer to **4a** and subsequent conversion to the polymer is much less facile in the reaction catalyzed by **4a** compared to those catalyzed by **5a**. Hence the higher molecular weight products by **5a**.

The high molecular weight polymers formed from CH_2Cl_2/CH_3CN solvent mixtures and catalysts **1a**, **2a**, **4a** and **5a** have lower polydispersities.

Different solvents such toluene, CH_2Cl_2 and THF are used as reaction media for phenylacetylene polymerization. When these solvents and catalysts **1a**, **2a**, **4a** and **5a** were utilized, the resulting products gave brown solids that had low to high percentage conversion (ranging between 28% and 84%). In all cases, when toluene was used, polymerization was slow yielding small amount (42%, 36%, 28%, 31%) of brown polyphenylacetylene after 4 h of polymerization (Table 4.1, entries 8, 19; Table 4.2, entries 8, 17). Polymerization reactions in THF were faster than polymerizations in toluene and CH_2Cl_2 forming high yields (84%, 62%, 58%, 53%) after 4 h (Table 4.1, entries 9, 20; Table 4.2, entries 9, 18). Figure 4.8 shows reactions in THF, which gave higher percentage monomer conversion relative to toluene and CH_2Cl_2 using catalyst **1a**.

However, the reactions carried out in THF gave lower molecular weight products (M_w = 620, 666, 12 686) compared to the ones obtained from toluene (M_w = 5 671, 1 185, 18 121) with the exception of catalyst **2a**, which formed the highest molecular weight product (M_w = 23 249) among all the reaction conditions used. The higher polymer yield could be due to the coordinating ability of THF solvent that is crucial in stabilizing the cationic active catalyst before coordination with phenylacetylene even though is not clear why reactions in THF produce lower molecular weight products.

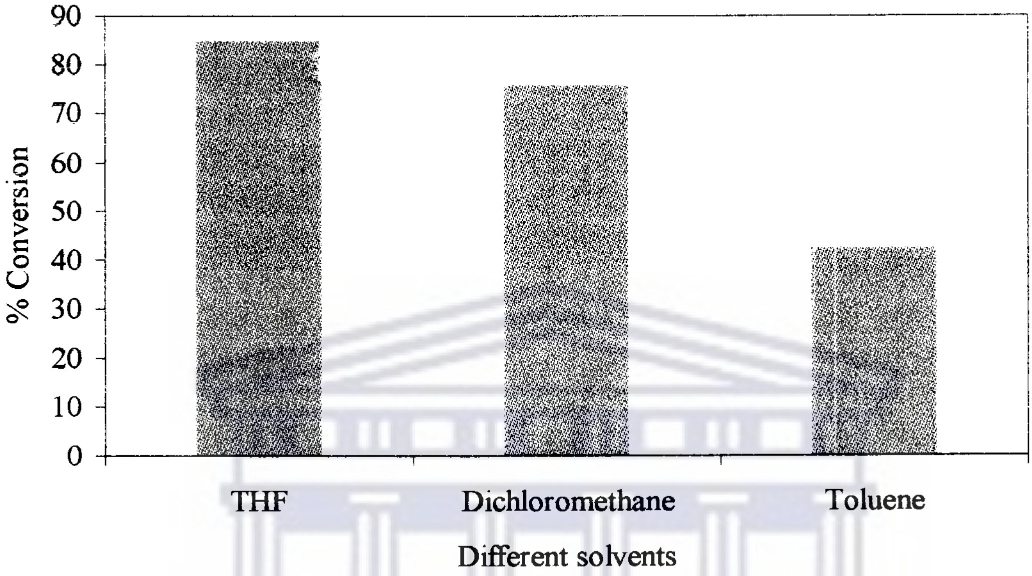


Figure4.8 Influence of single solvent systems on percentage monomer conversion using catalyst **1a**.

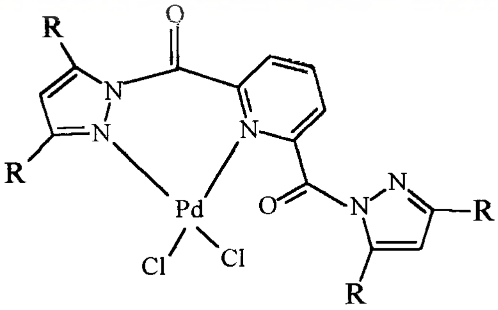
Although low yields were obtained when reactions were performed in toluene, higher molecular weight products were formed in toluene. Similar results were obtained with catalyst $[(P\text{-}P)Pd(CH_3)(NCCH_3)]^+OTf^-$ and toluene giving molecular weight (M_n = 6 700) that is higher than the one obtained when using the same catalyst and CH_2Cl_2 (M_n = 600) or THF (M_n = 4 500) [8]. However in literature, complexes $[Rh(nbd)Cl]_2$ and $Rh(nbd)(tos)(H_2O)$ were found to be poor catalysts in toluene but in THF, they formed high molecular weight polymers with a high stereoregularity in high yields [17].

The non-coordinating toluene therefore appears to facilitate monomer coordination to the catalyst and hence chain growth, whereas the better coordinating THF competes with the monomer in coordinating to the catalyst.

To investigate the effect of temperature on polymerization, two reactions in 7:1 CH_2Cl_2/CH_3CN mixture and THF were carried out at 40 °C (Table 4.1, entries 10,11). When catalytic reactions were performed at 40 °C, two points of interest arise. First, the stereoselectivity of the reaction change, and *trans-cisoidal* polyphenylacetylene is formed instead of *cis-transoidal* polyphenylacetylene. Secondly, the polymer yield and molecular weight decreased. The yield and molecular weight of the polymer in 7:1 CH_2Cl_2/CH_3CN mixture, decreased from 96% and M_w = 10 831 (entry 3) to 47% and M_w = 1 157 (entry.10) when the reaction was performed at 40 °C. The reaction in THF, at 40 °C (entry 11), formed oligomers with lower yield 53% and lower molecular weight 559 relative to reactions at room temperature (84%, M_w = 620) (entry 9). This demonstrates that the activity of catalyst towards polymerization of phenylacetylene is high at room temperature and high temperature also does not promote chain growth and therefore reactions at high temperatures must be avoided. These results agree with what is reported in literature [8], which shows that percentage monomer conversion and average molecular weight decrease with increasing temperature.

The low molecular weight products obtained in this study are also consistent with the molecular weight products that are obtained from palladium catalysts systems in literature [7, 8, 18] with the exception for palladium system [Pd(N'N'O)Cl] which catalyze polymerization in water at room temperature producing very high molecular weight polymers ($M_w = 23495$) [9].

Generally binuclear catalysts **4a** and **5a** produce high molecular weight products compared to mononuclear **1a** and **2a** catalysts. This could be attributed to the bonding mode of the ligands in these catalysts, because **4a** and **5a** are binuclear complexes (Scheme IV) with two palladium metals stabilized by two bridged chloride atoms. This bonding mode makes catalysts **4a** and **5a** to be more stable than the mononuclear catalysts **1a** and **2a**. In catalysts **1a** and **2a** (Scheme IV), the metal centre is bonded to two chloride atoms, two nitrogen atoms, one from pyrazolyl ring and one from pyridine ring with free pyrazolylcarbonyl positioned next to the metal centre. The flexibility of the uncoordinated pyrazolylcarbonyl unit in **1a** could lead to increased steric hindrance of the catalyst. This could decrease the accessibility of the metal for the monomer to coordinate. By blocking coordination of the monomer to the metal centre, chain growth termination is favoured, resulting in the formation of lower molecular weight polymers.



R = ^{t}Bu (**1**); R = Me (**2**)

Scheme IV: Structure of **1** and **2**

Polymerization in single solvent systems produced low molecular weight polymers with the exception of few reactions. A plausible explanation is that the cationic palladium centre requires coordinating solvent for stability. If the coordinating solvent is in excess, the rate of monomer to π–complex formation is insufficient for polymerization to proceed at a reasonable rate.

4.6 Conclusion

The palladium compounds $[Pd(N\text{-}N)Cl(CH_3CN)]^{+}OTf^{-}$ and $[Pd_2(\mu\text{-}Cl)_2(N\text{-}N)Cl(CH_3CN)]^{+}OTf$ with different ligand substituents were found to promote the polymerization of phenylacetylene with the formation of oligomers and polymers. The presence of tertiary butyl substituents in catalyst $[2,6\text{-bis}\{CO(3,5\text{-}{}^{t}Bupz)_2\}py]PdCl_2$ plays a key role in the polymerization process, as demonstrated by the lack of high activity and low molecular weight polymers of the methyl analogue $[2,6\text{-bis}\{CO(3,5\text{-}Mepz)_2\}py]PdCl_2$. The binuclear structure of catalysts **4a** and **5a** also plays a role in the polymerization process as shown by the high molecular weight polymers formed by these catalyst systems. The effect of binuclear structure on polymerization is also demonstrated by tertiary butyl substituted catalyst **4a,** which formed lower molecular weight products compared to the methyl substituted catalyst **5a,** which formed higher molecular weight polymers. The stereochemistry of PPA formed in this study is dependant on the nature of the solvents and reaction temperature employed. High *cis* content is observed with CH_2Cl_2/CH_3CN solvent mixtures and *trans*-polyene is preferentially obtained with single solvent systems.

The lowest molecular weight products in solvent mixtures were obtained when reactions were performed with catalyst **2a** with the highest molecular weight products formed by catalyst **5**. When single solvent systems were used, the highest molecular weight was obtained with catalyst of **2a** and THF and lowest molecular weights formed using catalyst **1a** and THF.

4.7 References

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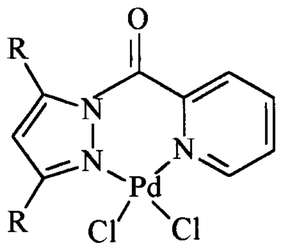
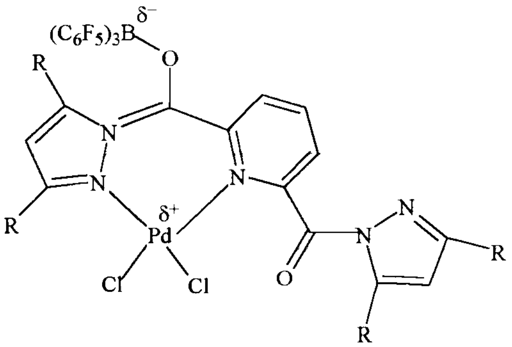
complexes. This shows that a subtle change in the ligand structure may significantly change the complex's catalytic activity. The lower activity of the mononuclear complexes **1** and **2** towards ethylene polymerization is likely to be due to the non-coordinating pyrazolyl unit, which could be complexing with the co-catalyst MAO, thus reducing the active palladium catalyst for polymerization.

Catalytic activities were found to be sensitive to temperature as well as amount of co-catalyst. The mononuclear Pd(II) complex **2** and binuclear Pd(II) complexes **4** and **5** displayed very low catalyst activities than the mononuclear Pd(II) complex **1.** A plausible explanation could be the difference in solubility of these catalyst species in toluene.

The activity of the palladium complexes (**1**, **2**) studied for ethylene polymerization could be improved by the use of [2-(3,5-R_2pyrazolyl-1-carbonyl)pyridine]palladium(II) dichloride (Scheme V). The use of [2-(3,5-R_2pyrazolyl-1-carbonyl)pyridine]palladium(II) dichloride would improve the activity of the catalyst because of the absence of a free pyrazolyl unit, which coordinate with MAO therefore reducing activity of the catalyst. The catalytic activity could also be improved by the reaction of complexes **1** and **2** with tris(pentaflourophenyl)borane ($B(C_6F_5)_3$) to form more electrophilic complexes (Scheme VI). The high electrophilicity of the resulting complexes would facilitate faster olefin insertion, therefore improving the catalytic activity of the catalysts.





R = Me, ^{t}Bu

Scheme V

schemeVI

Cationic bis(N–N)Pd^{II} complexes were generated from the reaction of complexes [2,6-bis(3,5-R$_2$pyrazolyl-1-carbonyl)pyridine]palladium(II) dichloride and di-μ-chloro-dichlorobis[2,5-bis(3,5-R$_2$pyrazolyl-1-carbonyl)thiophene]dipalladium(II) (R = Me, ^{t}Bu), and silver triflate. These cationic complexes promote oligomerization and polymerization of phenylacetylene. The binuclear complexes **4** and **5** play a key role in oligomerization and polymerization catalysis as shown by high monomer conversion and high molecular weight polymers. The stereochemistry of polyphenylacetylene formed in the catalytic reactions is dependant on temperature. Higher *cis* content was observed at room temperature and a *trans*-polyene was observed at 40 °C. Low molecular weight products were formed at 40 °C, while high molecular weight products were formed at room temperature. The active catalysts polymerized phenylacetylene to form *cis-transoidal* and *trans-cisoidal* poly(phenylacetylene) depending on the solvents and catalysts used.