

**THE SYNTHESIS AND CHARACTERISATION OF  
IRON AND TUNGSTEN ORGANOMETALLIC  
POLYMERS WITH METAL-CARBON SIGMA BONDS**

by

**GREGORY STUART SMITH**

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requirements for the degree of  
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**UNIVERSITY of the  
WESTERN CAPE**

**Supervisor** : Dr S.F. Mapolie (UWC)

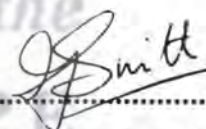
**Joint Supervisor** : Prof J.R. Moss (UCT)

June 1997

## DECLARATION

I declare that **THE SYNTHESIS AND CHARACTERISATION OF IRON AND TUNGSTEN ORGANOMETALLIC POLYMERS WITH METAL-CARBON SIGMA BONDS** is my own work and that all the sources I have used or quoted have been indicated and acknowledged by means of complete references.

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.....  
Gregory S. Smith

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## ABSTRACT

A variety of olefinic organometallic monomers have been synthesised and polymerised under free-radical conditions. These monomers all contain a vinyl moiety as part of an organic fragment which is bonded via a metal-carbon  $\sigma$ -bond to the metal centre.

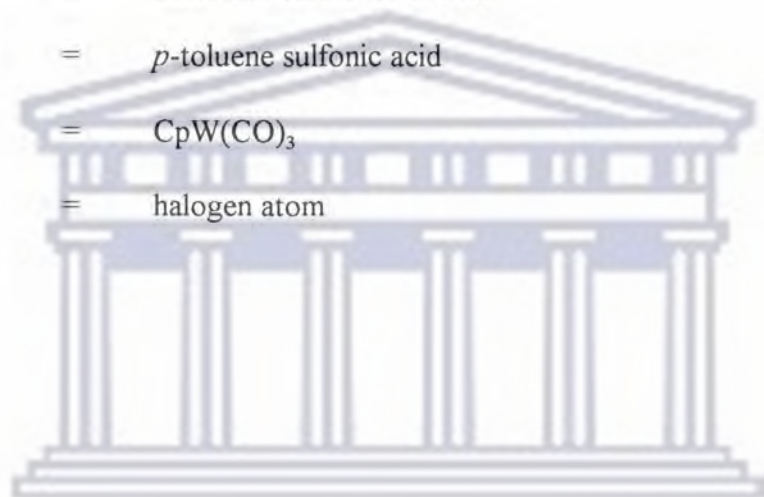
The monomers are generally compounds of the type  $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_n\text{R}]$ , where  $\text{M} = \text{Fe}$ ,  $n = 2$  and  $\text{M} = \text{W}$ ,  $n = 3$  and  $\text{R}$  represents an alkyl, acyl or aryl group containing the vinyl functionality. The known complexes prepared in this study include those where  $\text{M} = \text{Fe}$ ,  $\text{R} = -(\text{CH}_2)\text{CH}=\text{CH}_2$  (**I**),  $-\text{COCH}=\text{CH}_2$  (**II**),  $-\text{COCH}=\text{CHPh}$  (**III**) and the tungsten complex  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{WCOCH}=\text{CHPh}$  (**VII**). The new olefinic monomers include those where  $\text{M} = \text{Fe}$ ,  $\text{R} = -\text{COC}_6\text{H}_4\text{CH}=\text{CH}_2$  (**IV**),  $-\text{C}_6\text{H}_4\text{CH}=\text{CH}_2$  (**V**) and the tungsten complex  $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{WCOC}_6\text{H}_4\text{CH}=\text{CH}_2$  (**VIII**). The new pentamethylcyclopentadienyl analogue,  $(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{FeCOC}_6\text{H}_4\text{CH}=\text{CH}_2$  (**V**) was also prepared in this study. All of the monomers have been fully characterised using analytical techniques such as IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy, microanalysis and mass spectrometry.

Homopolymerisation and copolymerisation studies of the prepared organometallic monomers were conducted using multiple re-initiations with the free-radical catalyst 2,2'-azobisisobutyronitrile (AIBN). The polymers were characterised by IR, and  $^1\text{H}$  NMR spectroscopy. Their properties were studied by other available techniques including Differential Scanning Calorimetry, Thermogravimetric Analysis, Scanning Electron Microscopy and Gel Permeation Chromatography. The results obtained for some of these polymers are discussed.

## ABBREVIATIONS

|        |   |   |
|--------|---|---|
| AIBN   | = | 2,2' - azobisisobutyronitrile   |
| Ar     | = | aryl  |
| Cp     | = | $\eta^5\text{-C}_5\text{H}_5$   |
| Cp*    | = | $\eta^5\text{-C}_5(\text{CH}_3)_5$  |
| d      | = | days  |
| dec.   | = | decomposition   |
| DRIFTS | = | diffuse reflectance infrared transmission spectroscopy  |
| DSC    | = | differential scanning calorimetry   |
| Fp     | = | $\text{CpFe}(\text{CO})_2$  |
| Fp*    | = | $\text{Cp}^*\text{Fe}(\text{CO})_2$   |
| FTIR   | = | fourier transform infrared  |
| GPC    | = | gel permeation chromatography   |
| ICP    | = | inductive coupled plasma  |
| IR     | = | infrared  |
| L      | = | ligand  |
| $L_n$  | = | associated ligands  |
| M      | = | transition metal  |
| $m/e$  | = | mass to charge ratio (mass spectrometry)  |
| M.P.   | = | melting point   |
| NMR    | = | nuclear magnetic resonance (t = triplet, m = multiplet,<br>s = singlet, dd = doublet of doublets) |
| Ph     | = | phenyl group  |
| R      | = | alkyl group   |

|                |   |                                 |
|----------------|---|---------------------------------|
| r.t.           | = | room temperature                |
| SEM            | = | scanning electron microscopy    |
| Temp.          | = | temperature                     |
| TGA            | = | thermogravimetric analysis      |
| THF            | = | tetrahydrofuran                 |
| TMS            | = | tetramethylsilane               |
| t.l.c.         | = | thin layer chromatography       |
| <i>p</i> -TosH | = | <i>p</i> -toluene sulfonic acid |
| Wp             | = | $\text{CpW(CO)}_3$              |
| X              | = | halogen atom                    |



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## PUBLICATIONS

### CONFERENCE CONTRIBUTIONS :

Poster titled “ Synthesis of Organometallic Polymers”, G.S. Smith, S.F. Mapolie and J.R. Moss, presented at the 33rd Convention of the South African Chemical Institute, Cape Town, South Africa (1996).

Poster titled “Synthesis and Characterisation of Organometallic Polymers of Iron and Tungsten”, S.F. Mapolie, J.R. Moss and G.S. Smith, presented at the 31st International Conference on Coordination Chemistry, Vancouver, Canada (1996).

Lecture titled “The synthesis and polymerisation of metal containing vinylic monomers of iron and tungsten”, S.F. Mapolie, J.R. Moss and G.S. Smith, presented at the Inorganic '97 Symposium, Port Elizabeth, South Africa (1997).

Poster titled “ Homopolymerisation and Copolymerisation of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{-}(\text{COC}_6\text{H}_4\text{CH}=\text{CH}_2)$ ”, G.S. Smith, S.F. Mapolie and J.R. Moss, presented at the Inorganic '97 Symposium, Port Elizabeth, South Africa (1997).

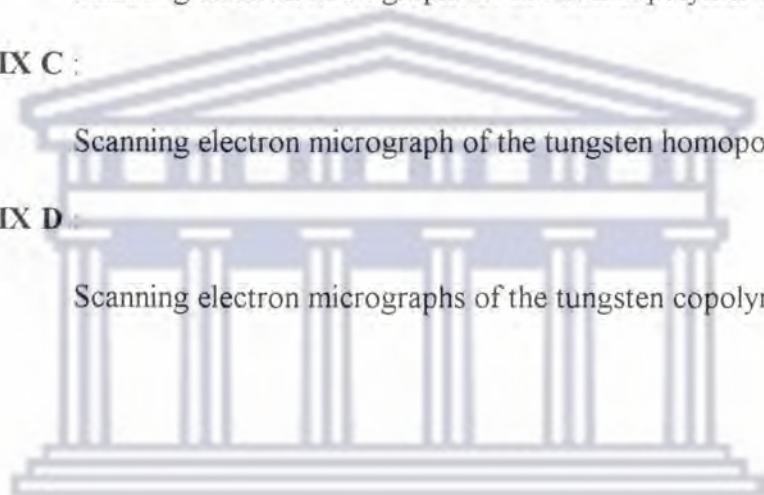
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## 1.1 Definition of organometallic polymers

Organometallic polymers are macromolecules formed from smaller repetitive units of organometallic molecules, called monomers, which represent the building blocks of these polymers. The organometallic polymers, unlike their organic counterparts, contain metals interspersed either in the backbone (Figure 1.1) or in pendant side chains<sup>1</sup> (Figure 1.2).

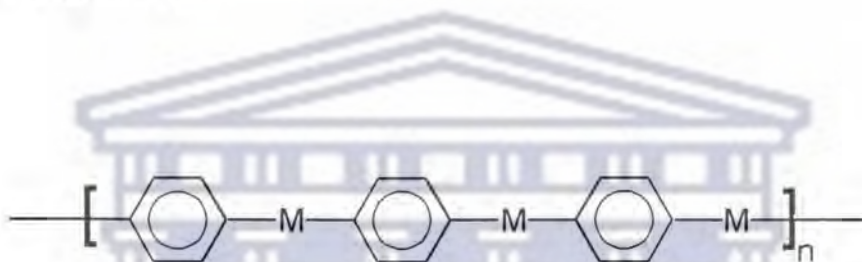


Figure 1.1 Organometallic polymer with metals in the backbone

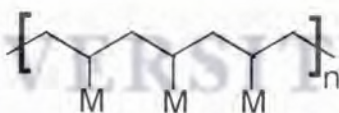


Figure 1.2 Organometallic polymer with metals in pendant side chains

Main group metals, transition metals or rare earth elements can all be incorporated into organometallic polymers.<sup>2-5</sup> The metals may be bonded to the polymer chain in a number of ways.

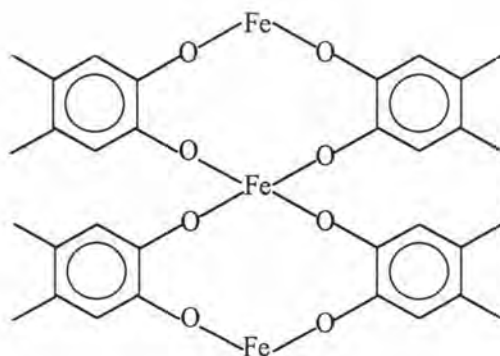
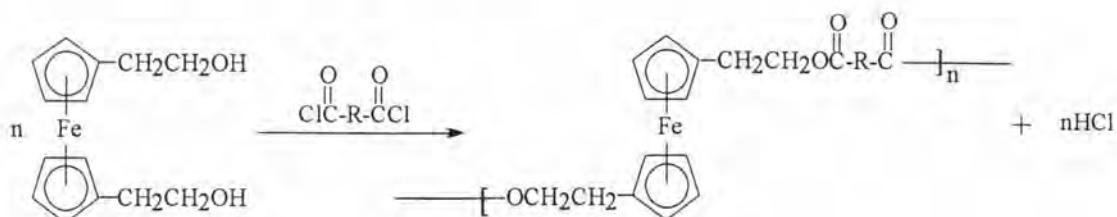


Figure 1.3 Example of an inorganic polymer with a transition metal bonded to oxygen

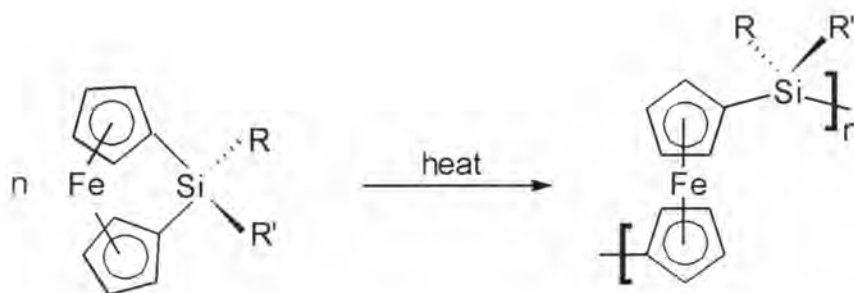
These include via metal-carbon  $\sigma$ - or  $\pi$ -bonds, dative covalent bonds to elements containing lone pairs or less commonly by  $\sigma$ - or  $\pi$ -bonds to other elements <sup>6,7</sup> (Figure 1.3). The work described in this thesis deals solely with polymers containing pendant transition metals, bonded to the polymer backbone via metal-carbon  $\sigma$ -bonds.

## 1.2 Synthesis of organometallic polymers

Organometallic polymers can be prepared by employing methods such as condensation (Scheme 1.1), ring-opening (Scheme 1.2), and addition polymerisation.



Scheme 1.1



Scheme 1.2

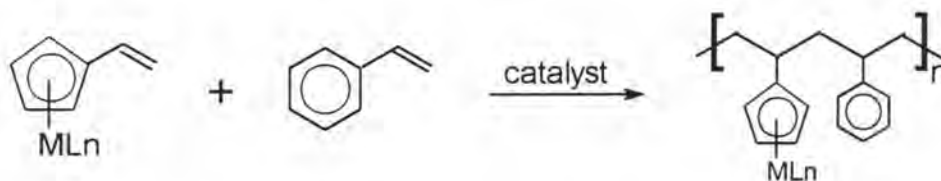
Condensation<sup>7-9</sup> and ring-opening<sup>10-12</sup> polymerisation result in organometallic polymers containing metals as part of the main polymer backbone. In contrast to condensation polymerisation, addition polymerisation yields metals in pendant side chains (Scheme 1.3). Metals can also be added to an existing organic polymer to give an organometallic polymer.<sup>13,14</sup>



Scheme 1.3

As outlined in Scheme 1.3, metals anchored to an organometallic polymer backbone can arise from the addition polymerisation of a vinyl precursor. These chain reactions are initiated by either cationic, anionic, free-radical or coordination catalysts. The monomers contain carbon-carbon double bonds or vinyl units that participate in the chain reaction. The metal-based polymers are formed through the addition of the vinyl

units. These inorganic monomers are known to undergo homopolymerisation, as well as copolymerisation with a different monomer<sup>7</sup> (Scheme 1.4).



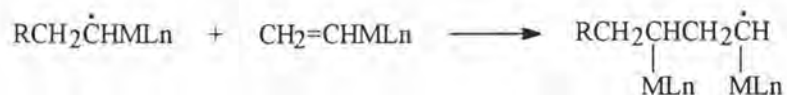
Scheme 1.4

As is the case in chain reactions of organic chemistry, three basic steps are discernible in the process of free-radical polymerisation. This consists of an initiation step, a propagation or growth step, and a termination step. The mechanism for a chain reaction initiated by a free-radical catalyst is depicted in Scheme 1.5.

#### INITIATION



#### PROPAGATION



#### TERMINATION



Scheme 1.5

The “active species” adds to the vinyl moiety of the monomer, creating a new “active species”. The new “active species” adds to another monomer in the same manner during the propagation step, and this is repeated over and over again. For free-radical polymerisation termination usually results from the reaction of two growing chains, or by decomposition of the “active species”. It is possible for branching or cross-linking of the growing chains to occur <sup>15</sup>, affording insoluble polymeric compounds.

### 1.3 Applications of transition metal polymers

Transition metal-based polymers are currently attracting considerable attention. <sup>1,16,17</sup>

The interest in organometallic polymers stems from their potential use in a number of fields. The incorporation of metals into main chains or pendant side chains and the close proximity of the metals, promotes favourable interactions between them. <sup>11</sup> This is responsible for the many diverse properties that organometallic polymers exhibit.

For example, their usefulness has been demonstrated in fields ranging from electrochemistry through to medicine, and their specific use as catalysts <sup>16,18</sup>, semiconductors <sup>19,20</sup> and even lasers <sup>21</sup>, to name just a few, have been cited.

The vast structural variety of metal containing polymers accounts for their applications in various fields. Poly{tris[5,5'-bis(3-acrylyl-1-propoxycarbonyl)-2,2'-bipyridine]ruthenium} has been reported to show some interesting electrochromic properties. <sup>22</sup> That is, by processing this polymeric complex through all its possible oxidation states, it is able to exhibit a range of colours. It can thus be very useful in various electronic displays. Many inorganic complexes exhibit these luminescent properties. These result from emissions associated with metal to ligand charge



transfer, where electronic transitions occur from a metal centered molecular orbital to a ligand localised  $\pi^*$  orbital. Examples of these include complexes of the type  $X\text{Re}(\text{CO})_3\text{L}$  [ $X = \text{Cl}, \text{Br}, \text{I}$ ;  $\text{L} = 1,10\text{-phenanthroline}, 4,7\text{-diphenyl-}1,10\text{-phenanthroline}, 4\text{-methyl-}1,10\text{-phenanthroline}$  and  $4,4'\text{-dimethyl-}2,2'\text{-bipyridine}$ ]. These complexes have been shown to act as spectroscopic probes in monitoring polymerisation reactions.<sup>23</sup>

Advances in medicine and the improvement of quality of life always excites and attracts attention. It should, therefore, come as no surprise that metal-containing polymers are also being used as medicinal agents, which is proving to break new ground.  $\text{K}_2\text{PtCl}_4$  has been reacted with poly[bis(methylamine)phosphazene] to give a platinum phosphazene polymer (Figure 1.4). This has been shown to have tumor-inhibiting activity<sup>24</sup> against mouse P388 lymphocytic leukemia. On reacting  $\text{K}_2\text{PtCl}_4$  with difunctional nitrogen compounds such as pyrimidine, purines and hydrazines, transition metal coordination polymers (Figure 1.5) are produced that at concentrations of  $10\text{-}20\mu\text{g/ml}$  slow the growth of Poliovirus I and L RNA virus.<sup>25</sup>

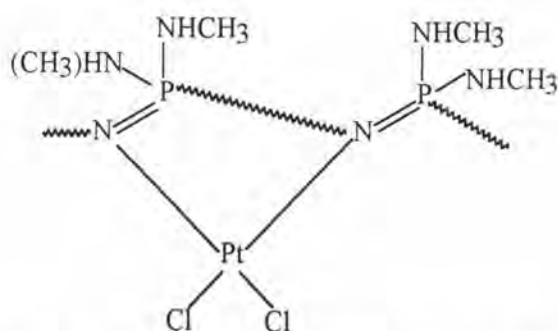


Figure 1.4 Platinum phosphazene polymer

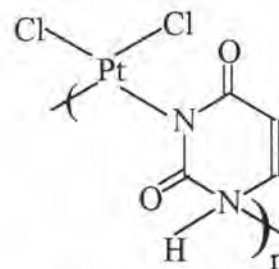
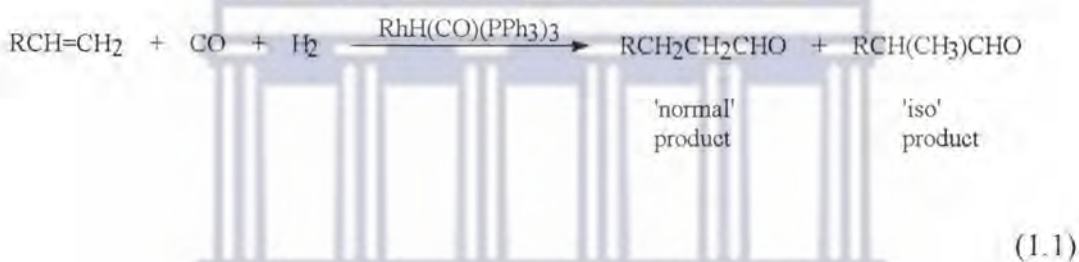


Figure 1.5 Platinum coordination polymer

The use of transition metal catalysts in many industrial processes is an area of great significance, especially where transition metals are used to bring about various organic transformations. Moreover, the tailoring of catalysts to achieve certain properties has always interested researchers. It is in this vein that the attachment of various homogeneous catalysts to polymers<sup>18,26</sup> has been studied and noted to significantly enhance the properties of the original catalyst. The hydroformylation process is one such example which uses soluble cobalt or rhodium catalyst systems, to transform alkene substrates to aldehydes, which are the primary products [Equation 1.1].



Pittman and Hanes<sup>27</sup>, investigated anchoring homogeneous catalysts like those used in the hydroformylation process to polymer systems and showed that these catalysts had several advantages. Amongst these were the higher linear/branched product ratio, the unusual temperature dependence of the selectivity and the unusual high dependence of product selectivity upon pressure. Work of this nature was also extended to other homogeneous catalysts, such as metallocene catalysts<sup>28,29</sup> which were also attached to various polymers.

The above examples merely highlight the diversity of transition metal polymeric structures and serve to illustrate the variety of applications and potential uses for these compounds.

#### 1.4 A review of olefinic organometallic monomers used in addition polymerisation

Since the preparation in 1955 of vinylferrocene **1**, the first organometallic monomer with a vinylic group that contained a transition metal<sup>30</sup>, the field of organometallic polymer chemistry has grown at a steady rate.

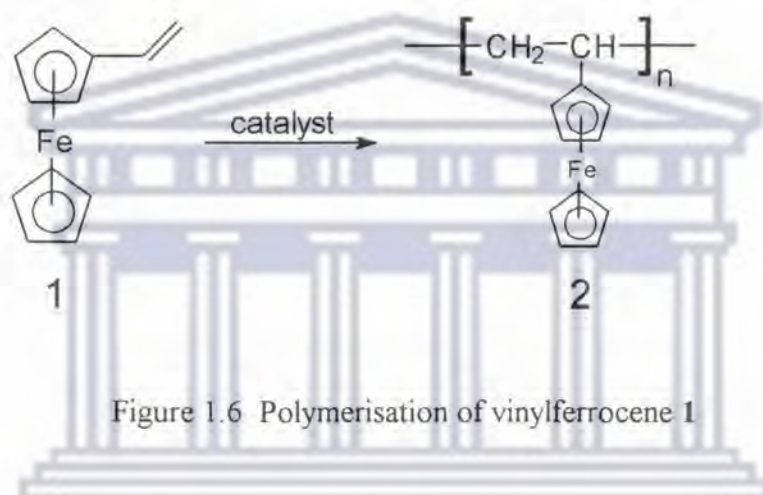


Figure 1.6 Polymerisation of vinylferrocene **1**

Vinylferrocene **1** consists of two cyclopentadienyl rings with an iron atom sandwiched between them (Figure 1.6). The iron atom is “ $\pi$ -bonded” to each ring, and the vinyl moiety is bonded to one of the rings. This was the first vinyl organometallic compound to be homopolymerised, with the aid of a free-radical catalyst. Arimoto and Haven were credited with this success in 1955.<sup>30</sup> Unfortunately, the reaction was not well characterised and only brief descriptions of reaction conditions were reported. Thus, Pittman and co-workers reported an in-depth study of the synthesis and polymerisation of various olefinic derivatives of ferrocene.<sup>31,32,33</sup>

In recent years, a shift from these metallocene-type monomers (like vinylferrocene **1**) to organometallic carbonyl monomers has been observed.<sup>34,35</sup> Examples of these types

of monomers include the  $\eta^5$ -vinylcyclopentadienyl metal carbonyls **3-6** shown in Figure 1.7.

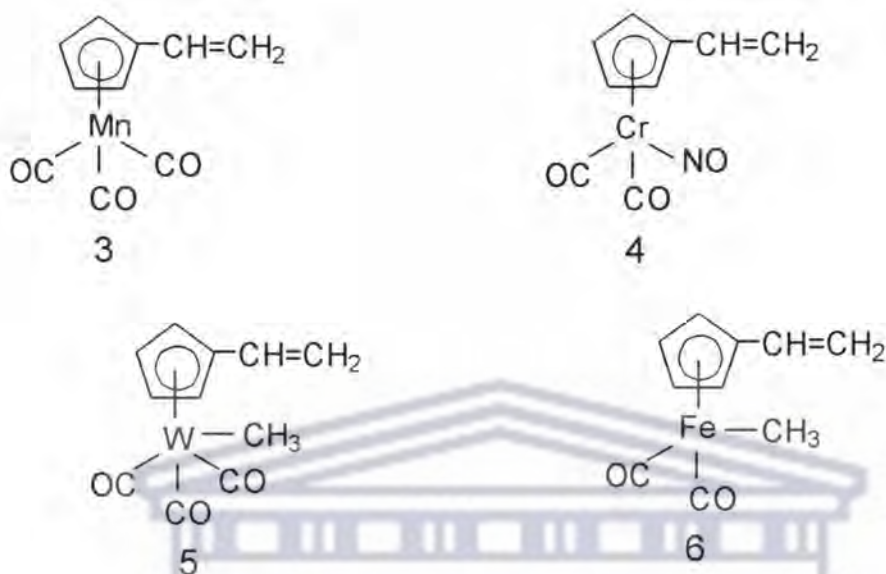


Figure 1.7  $\pi$ -Bonded olefinic organometallic carbonyl monomers

All these monomers have a transition metal atom  $\pi$ -bonded to a cyclopentadienyl ring, together with carbonyl groups and other ancillary ligands. Like vinylferrocene **1**, the above monomers have the vinyl moiety bonded to the cyclopentadienyl ring.

Numerous studies on the synthesis and polymerisation of the afore-mentioned  $\eta^5$ -vinylcyclopentadienyl organometallic monomers **1,3-6** have been reported.<sup>36-39</sup> However, there are few examples reported in the literature of complexes in which the vinyl containing moiety is bonded to a metal via a metal-carbon  $\sigma$ -bond. Compounds of this type have the general formula  $[\text{CpM}(\text{CO})_n\text{R}]$ , where R is an alkyl or an acyl group containing the unsaturated moiety. Some examples of these are shown in Figure 1.8.

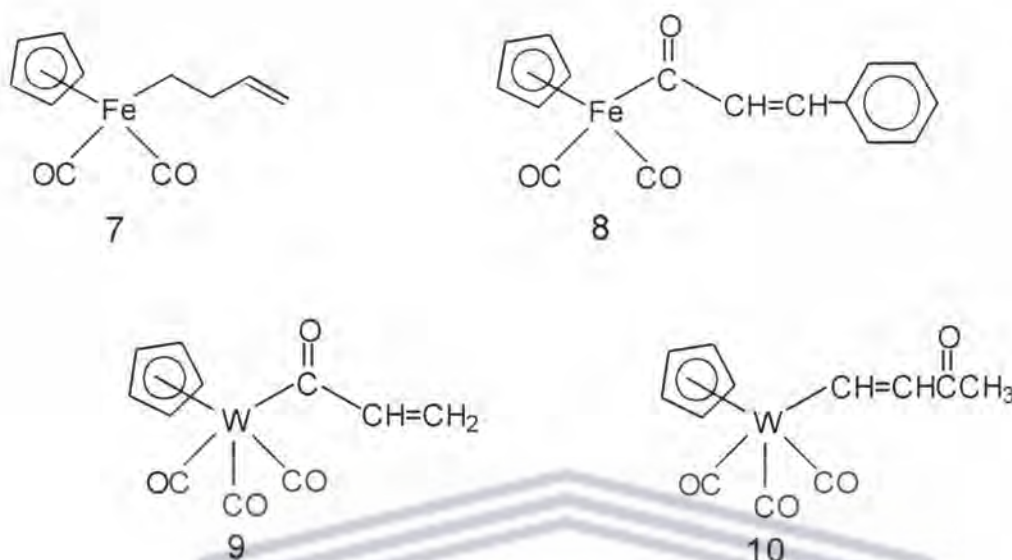
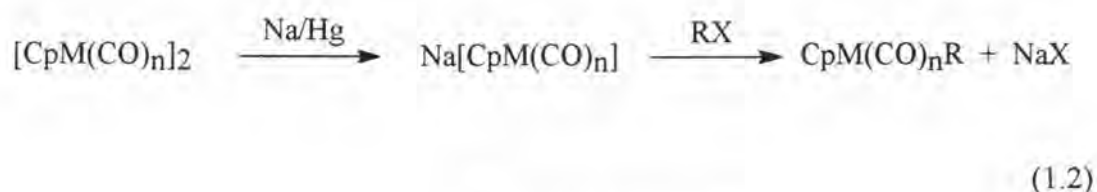


Figure 1.8 Metal-carbon  $\sigma$ -bonded olefinic organometallic monomers

Green<sup>40,41</sup>, King<sup>42</sup>, Nesmeyanov<sup>43,44</sup> and co-workers have prepared, and partially characterised a variety of compounds that contain a vinylic organic ligand bonded to the metal via metal-carbon  $\sigma$ -bonds. Their methods of preparation were generally the same. The appropriate transition metal dimers are reduced over a sodium amalgam to the relative anionic complexes. These anions are able to react with a variety of alkyl or acyl halides to give the corresponding neutral transition metal alkyl or acyl complexes<sup>42,45</sup> [Equation 1.2].



M = transition metal

R = vinyl-alkyl or -acyl ligand

X = Br or Cl

Although the preparation of a few  $\sigma$ -bonded olefinic organometallic monomers have been reported, there are not many reports dealing with the free-radical polymerisation of these monomers. Only recently has the synthesis of three transition metal vinylbenzyl complexes (Figure 1.9) been reported<sup>46</sup> and the polymerisation of these olefinic monomers attempted.

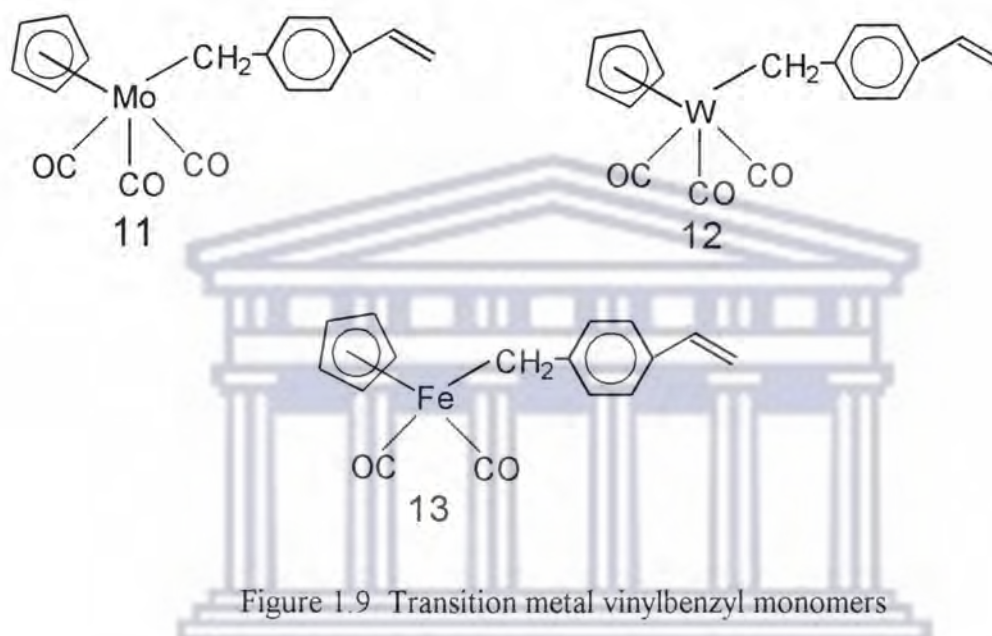
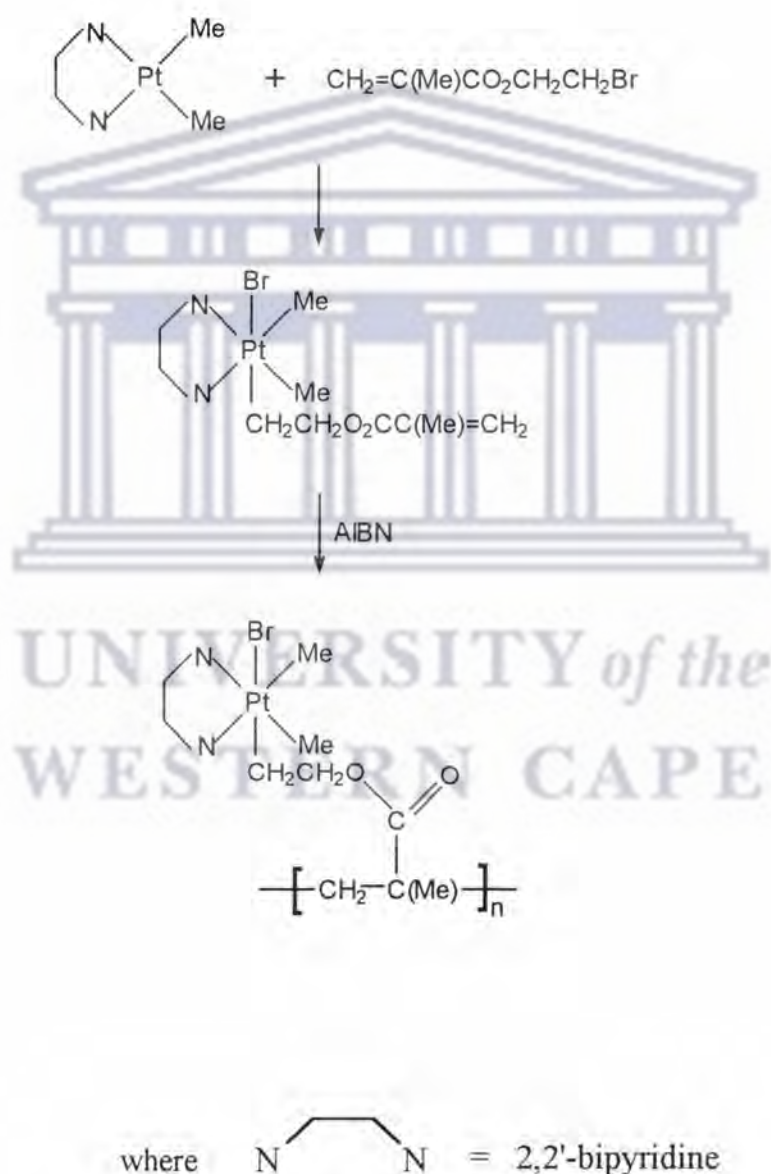


Figure 1.9 Transition metal vinylbenzyl monomers

Kher and Nile<sup>46</sup> prepared the above-mentioned transition metal vinylbenzyls by reacting the appropriate metal anion with 4-vinylbenzyl chloride. The molybdenum and tungsten vinylbenzyls, compounds **11** and **12**, were prepared in good yields, whereas the iron analogue **13** was found to be very unstable and isolated only in low yields. These monomers represent one of the first organometallic monomers with  $\sigma$ -bonded olefinic organic ligands to be polymerised by free-radical means. The compounds **11** and **12** were homopolymerised as well as copolymerised with various organic monomers, using AIBN as the free-radical initiator. The monomers were copolymerised with monomers such as styrene, methyl methacrylate and N-vinyl-2-pyrrolidone. The homopolymerisation occurred in low yields, whereas the copolymerisation with the organic monomers gave higher yields.

Another recent example of a sigma-bonded organometallic monomer used in free-radical (AIBN) polymerisation is included in work published by Puddephatt.<sup>47</sup> The synthetic methodology of monomer preparation uses oxidative addition resulting in functionalised organometallic monomers or polymers (Scheme 1.7).



Scheme 1.7

### 1.5 Scope of this thesis

The work described in this thesis deals with the synthesis of a variety of metal-carbon  $\sigma$ -bonded olefinic organometallic monomers. Some of the monomers have been prepared previously, and four new compounds are also reported. These monomers were fully characterised by microanalysis, IR spectroscopy,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and mass spectrometry. Addition homopolymerisation and copolymerisation reactions with styrene of some of the prepared monomers were studied. The polymerisations were carried out using free-radical and cationic catalysts. IR data,  $^1\text{H}$  NMR data, thermal analyses and molecular weight distributions of the polymers are also reported. The various organometallic monomers prepared in this study are listed below :

$[\text{CpFe}(\text{CO})_2\text{R}]$ , where R =  $-(\text{CH}_2)_2\text{CH}=\text{CH}_2$  (I),  $-\text{COCH}=\text{CH}_2$  (II),  
 $-\text{COCH}=\text{CHPh}$  (III),  $-\text{COC}_6\text{H}_4\text{CH}=\text{CH}_2$  (IV),  
 $-\text{C}_6\text{H}_4\text{CH}=\text{CH}_2$  (V),  
 $\text{Cp}^*(\text{CO})_2\text{FeCOC}_6\text{H}_4\text{CH}=\text{CH}_2$  (VI), and  
 $[\text{CpW}(\text{CO})_3\text{R}]$ , where R =  $-\text{COCH}=\text{CHPh}$  (VII),  $-\text{COC}_6\text{H}_4\text{CH}=\text{CH}_2$  (VIII).



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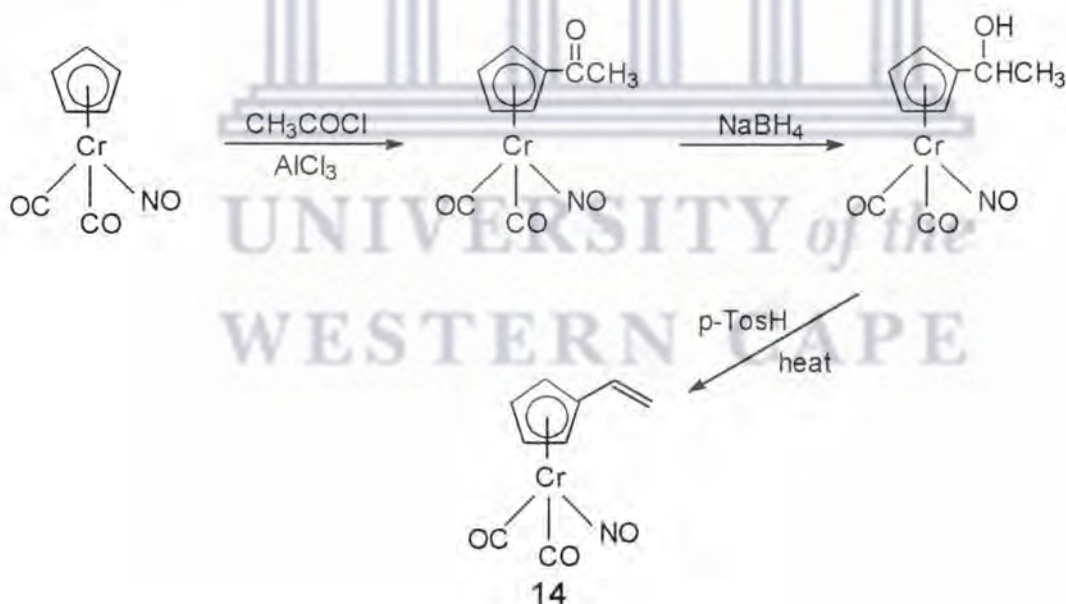
The logo of the University of Western Cape, featuring a classical building with a pediment and six columns.

**CHAPTER 2**

**SYNTHESIS AND CHARACTERISATION  
OF OLEFINIC ORGANOMETALLIC  
MONOMERS WITH METAL-CARBON  
SIGMA BONDS**

## 2.1 Introduction

The preparation of olefinic organometallic monomers for addition polymerisation is sometimes a tedious and painstaking process. Vinyl organo-transition metal-based monomers are often difficult to prepare and the synthetic routes<sup>1-4</sup> to these monomers are more difficult compared to those traditionally used in organic polymerisation. A large number of  $\eta^5$ -vinylcyclopentadienyl organometallic monomers have been prepared. These monomers characteristically include structures where the vinyl groups are attached to cyclopentadienyl rings, which in turn are  $\pi$ -bonded to metals. Most of these metal-carbon  $\pi$ -bonded monomers are generally prepared using Friedel-Crafts chemistry<sup>5-6</sup> (Scheme 2.1).



Scheme 2.1

As seen in Scheme 2.1,  $\eta^5$ -vinylcyclopentadienyl-dicarbonylnitrosylchromium **14** is prepared<sup>5</sup> by acetylation of the cyclopentadienyl ring, followed by reduction of the carbonyl group and dehydration of the resulting alcohol. Often, certain cyclopentadienyl metal derivatives are not stable to Friedel-Crafts reaction

conditions. Their vinyl derivatives are then synthesised via alternative routes, which may include using Wittig chemistry <sup>7</sup>, alkenylcyclopentanide salts <sup>8</sup> or ligand displacement reactions.

There are, however, not many examples of organometallic monomers in which the vinyl containing group is sigma-bonded to the metal. <sup>9-11</sup> These vinyl monomers are part of the broader class of hydrocarbyl compounds with metal-carbon  $\sigma$ -bonds. The hydrocarbyl compounds include a variety of species with alkyl, aryl and acyl organic ligands <sup>12,13,14</sup> that may be attached to a metal via a metal-to-carbon sigma bond (Figure 2.1).

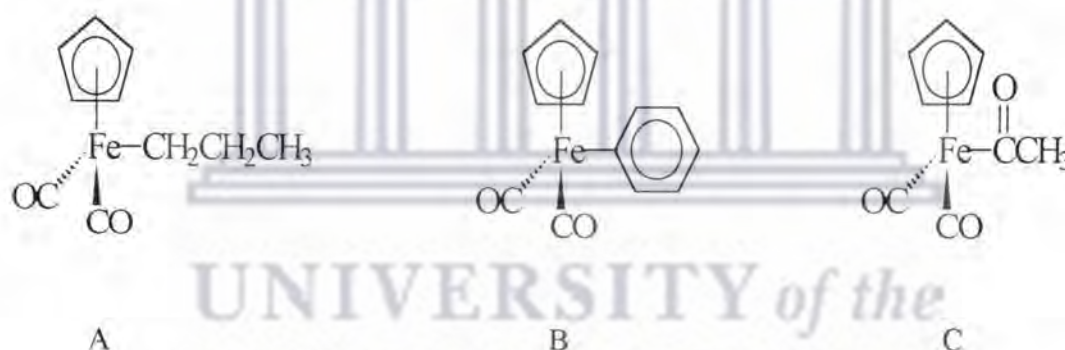
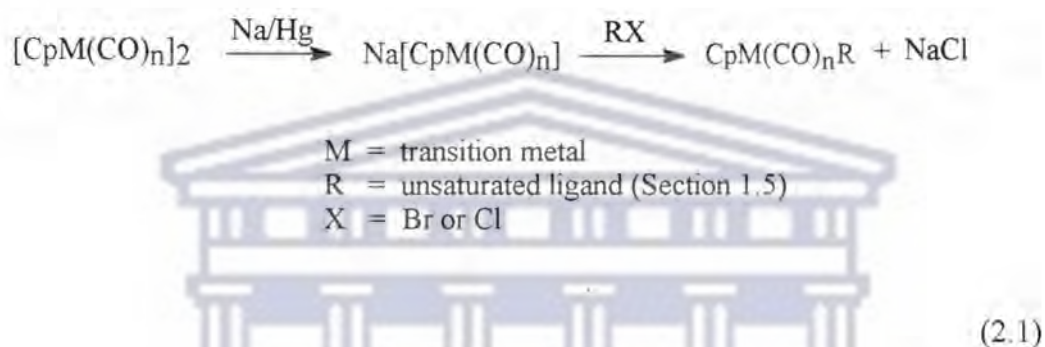


Figure 2.1 Examples of  $\sigma$ -bonded transition metal alkyl (A), aryl (B) and acyl (C) complexes

Alkyl, aryl and acyl cyclopentadienyl organometallic compounds may be prepared by a number of routes. These include : (i) reactions of metal halides with Grignard reagents <sup>15,20</sup>, (ii) reaction of diazo compounds with hydrides <sup>16,20</sup>, or more commonly, (iii) the reaction of organic halides with sodium salts of cyclopentadienyl metal carbonyl compounds. <sup>17,20</sup>

The monomers prepared in our studies differ from previous literature examples in that the vinyl containing moieties have a metal-carbon  $\sigma$ -bond, as opposed to the

$\eta^5$ -vinylcyclopentadienyl organometallic monomers. We have used the third route, that is (iii) above to prepare most of the  $\sigma$ -bonded olefinic organometallic monomers. This entailed reacting functionalised acid halides or alkyl halides containing the vinyl moiety, with the sodium salt of cyclopentadienyl metal carbonyl anions [Equation 2.1].



Thus, the known monomers  $\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_2\text{CH}=\text{CH}_2$  (**I**)<sup>18</sup>,  $\text{Cp}(\text{CO})_2\text{FeCOCH}=\text{CH}_2$  (**II**)<sup>17</sup>,  $\text{Cp}(\text{CO})_2\text{FeCOCH}=\text{CHPh}$  (**III**)<sup>17</sup> and  $\text{Cp}(\text{CO})_3\text{WCOCH}=\text{CHPh}$  (**VII**)<sup>19</sup> (Figure 2.2) were prepared following literature procedures, with slight modifications. In most cases, full characterisation data have not been reported in the literature, such as the <sup>13</sup>C NMR and mass spectra. We now report the synthesis and full characterisation of these monomers.



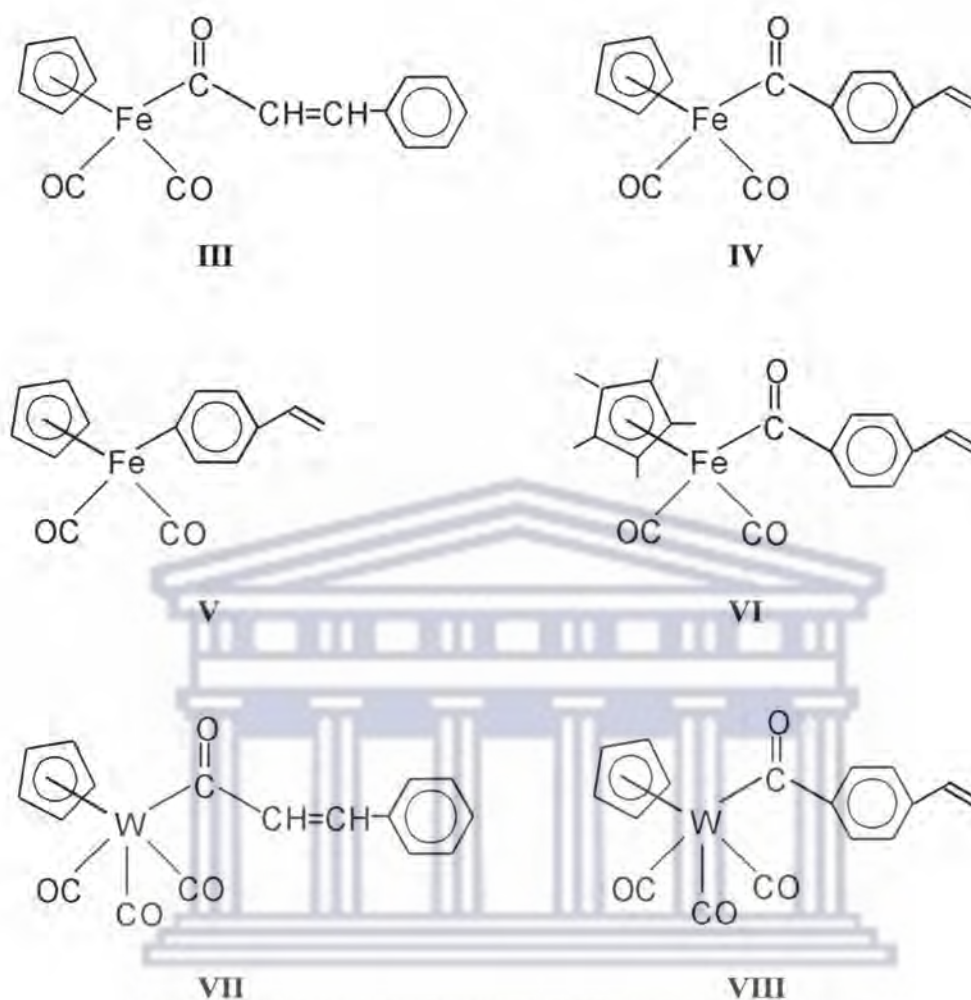


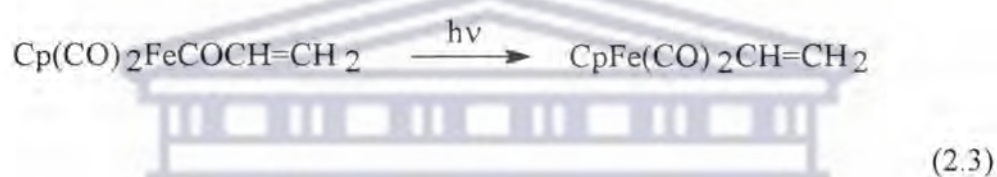
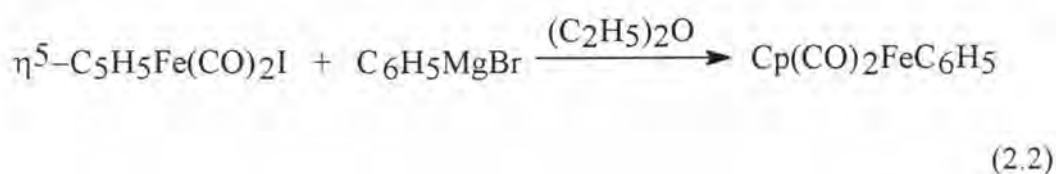
Figure 2.2 Olefinic  $\sigma$ -bonded organometallic monomers prepared in this thesis

Four new monomers (IV, V, VI, VIII) were also synthesised during the course of our studies. The complexes were fully characterised by IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy, microanalysis and mass spectrometry.

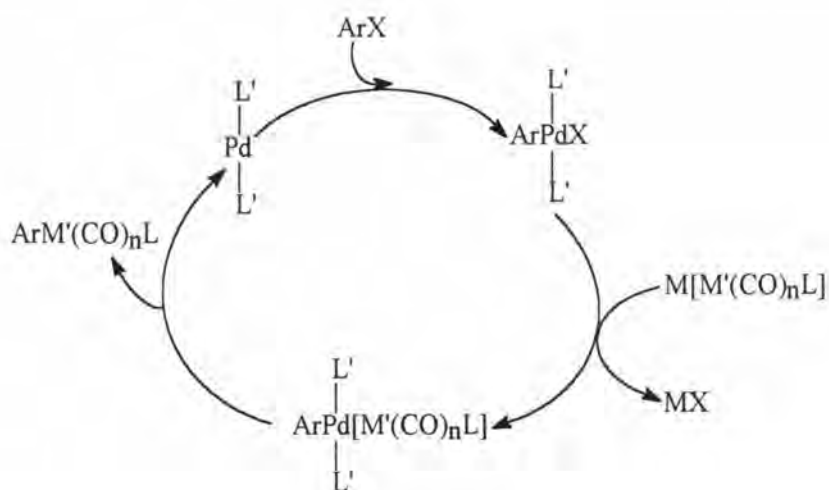
The technique used to prepare our olefinic alkyl and acyl transition metal complexes is a common route in the synthesis of  $\sigma$ -bonded organometallic complexes. However, preparing transition metal aryl complexes via this route has not been



successful. Various methods have been attempted including reacting transition metal halides with aryl Grignard reagents<sup>20</sup> [Equation 2.2] or the decarbonylation of the corresponding acyl derivatives<sup>17,21</sup> [Equation 2.3]. These were observed to occur in low yields.

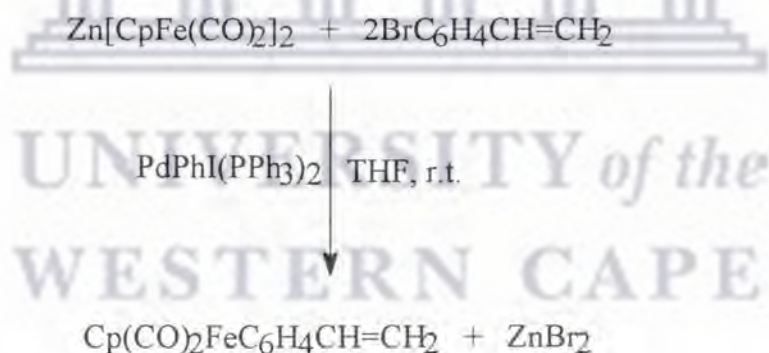
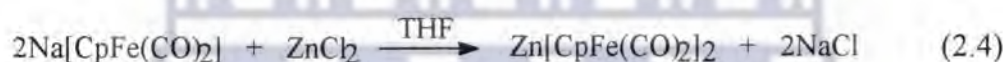


It was later found that complexes of transition metal aryls are more easily prepared with the aid of a cross-coupling catalyst.<sup>22</sup> We have thus used an oxidative addition-transmetallation approach to prepare the  $\sigma$ -aryl organometallic complex  $\text{Cp}(\text{CO})_2\text{FeC}_6\text{H}_5\text{CH}=\text{CH}_2$  (V). This synthesis was based on similar work by Artamkina *et al*<sup>22,23</sup> and the assumed general mechanism is shown in Scheme 2.2.



Scheme 2.2

Reactions of this nature are normally catalysed by nickel(0) or palladium(0) complexes.<sup>22</sup> We have used PdPhI(PPh<sub>3</sub>)<sub>2</sub> to prepare the  $\sigma$ -bonded vinyl aryl transition metal complex (**V**). As seen in Scheme 2.2, oxidative addition of the aryl halide produces a  $\sigma$ -aryl palladium halide complex. Transmetalation of this complex generates a transition metal carbonyl species bonded to palladium, as well as the aryl bonded to the palladium. Reductive elimination then leads to metal-carbon (aryl) bond formation, regenerating the catalyst in its original oxidation state.



(2.5)

We prepared monomer **V** by reacting the iron monoanion, Na[CpFe(CO)<sub>2</sub>], with dry zinc chloride [Equation 2.4] to form the corresponding zinc salt. This undergoes cross-coupling with 4-bromostyrene in the presence of the catalyst, PdPhI(PPh<sub>3</sub>)<sub>2</sub>, to produce **V** [Equation 2.5].

## 2.2 Results and Discussion

### 2.2.1 Monomer Syntheses

The synthesis of monomers **I-III**, and **VII** have been reported but little information on these compounds has been given. We have prepared these monomers using methods reported previously by King <sup>17</sup>, Green <sup>18</sup> and Nesmeyanov <sup>19</sup> respectively. This generally entailed reacting the  $\eta^5$ -cyclopentadienyldicarbonyl iron anion with the appropriate electrophile, as outlined in Equation 2.1. We found this to be a very convenient method of synthesising these organometallic monomers, as the transition metal anions can be easily derivatised with an electrophile *in situ*. Metal carbonyl monoanions are highly nucleophilic <sup>24</sup> and can thus be readily alkylated and acylated.

The iron-butenyl monomer **I** was the only alkenyl compound to be prepared in our study. The rest of the monomers, except monomer **V**, all contained vinyl moieties bound by acyl linkages to the metal. Monomers **I** and **II** were obtained as orange-yellow oils, which were stored under nitrogen at  $-20^\circ\text{C}$ . These oils are fairly unstable and partial degradation is seen to occur if they are allowed to stand at room temperature and in air. Monomer **II** does not, however, decompose as rapidly as the alkenyl monomer, suggesting that iron-acyl bonds may be more stable than iron-alkyl bonds. The greater stability of acyl sigma bonds between carbon and metals has been discussed recently. <sup>13</sup>

Monomers **III** and **VII** were isolated as orange and yellow semi-crystalline solids respectively. They are stable in air and in solution, and can be stored at room temperature for long periods, without any decomposition. The yields of the

monomers produced are consistent with those reported in the literature. The preparation of compound **II** proceeded in much higher yields compared to the literature value.<sup>17</sup> We found that by cooling the electrophile, acryloyl chloride, in THF down to  $-78^{\circ}\text{C}$ , and then adding the iron anion solution dropwise, a much higher yield is produced after using a similar workup as reported in the literature. Thus, we have improved on King's<sup>17</sup> yield of 5% to prepare the compound in a yield of 61%. The complete synthesis is given in the experimental section, section 2.4.1.

Four new compounds were also prepared in the course of our studies. Monomers **IV**, **VI** and **VIII** were prepared by the following reaction :



**IV** : M = Fe, n = 2

**VI** : M = Fe, n = 2 { Cp\* replaces Cp }

**VIII** : M = W, n = 3

A similar synthetic methodology to that of monomer **II** was followed in the preparation of these compounds. 4-Vinylbenzoyl chloride was cooled to  $-78^{\circ}\text{C}$ , and the iron or tungsten anions added at this temperature. The monomers were all isolated as stable solids, which could be stored at room temperature. Monomers **IV** and **VI** were isolated as yellow solids, whereas the tungsten analogue is an orange solid. The derivatives **IV**, **VI** and **VIII** were all prepared in very low yields

and only monomer **IV** was optimised (Table 2.1), by allowing the reaction to proceed for longer periods (3 days).

Monomer **V** was the only iron-aryl complex to be prepared in our study. This was achieved via a palladium-catalysed cross-coupling reaction. This was done by first preparing a zinc salt of the iron dicarbonyl anion,  $\text{Zn}[\text{CpFe}(\text{CO})_2]_2$ , by reacting the alkali metal salt  $\text{Na}[\text{CpFe}(\text{CO})_2]$  with  $\text{ZnCl}_2$ . The salt was then reacted with 4-bromostyrene in the presence of the catalyst  $\text{PdPhI}(\text{PPh}_3)_2$ , at ambient temperature (see Scheme 2.2). The monomer was isolated in low yields (12%) and can possibly be ascribed to the use of an aryl bromide instead of the more reactive aryl iodide, which was not available to us. Literature indicates that aryl bromides are  $\sim 10^4$  times less reactive than the corresponding iodides.<sup>25</sup> The monomer was isolated as a yellow oil, which was stored under nitrogen at  $-20^\circ\text{C}$ . Decomposition is observed to occur in the presence of air and if kept at room temperature for long periods. All the monomers prepared in our study, except **V**, have been fully characterised by melting point, microanalysis and IR spectroscopy (Table 2.1).  $^1\text{H}$  NMR (Table 2.2) and  $^{13}\text{C}$  NMR (Table 2.3) data have been summarised and tabulated, and an analysis of their mass spectra (Tables 2.4 - 2.8) is also included.

### 2.2.2 IR Spectra

The carbonyl stretching frequencies in the IR spectra of the known monomers are in agreement with those reported in the literature for  $\text{Fp}(\text{CH}_2)_2\text{CH}=\text{CH}_2$ <sup>18</sup>,  $\text{FpCOCH}=\text{CH}_2$ <sup>17</sup>,  $\text{FpCOCH}=\text{CHPh}$ <sup>17</sup> and  $\text{WpCOCH}=\text{CHPh}$ .<sup>19</sup> The iron compounds all show two strong bands for the terminal carbonyls, whereas the

tungsten monomer shows characteristically one sharp band of medium intensity and one strong, broad band for its terminal carbonyls. The acyl bands occur in the expected stretching frequency region and are of medium intensity.

The new vinylbenzoyl derivatives **IV**, **VI** and **VIII** show the same characteristic  $\nu(\text{CO})$  stretching frequencies as for analogous systems. The iron-vinylbenzoyl compound **IV** has terminal CO frequencies similar to those for  $[\text{Cp}(\text{CO})_2\text{FeCOR}]$  systems, with two strong bands at  $2022\text{ cm}^{-1}$  and  $1962\text{ cm}^{-1}$ . The analogous pentamethylcyclopentadienyl-iron derivative **VI** shows  $\nu(\text{CO})$  bands at lower frequencies, compared to the unsubstituted cyclopentadienyl monomer **IV**. This significant decrease in  $\nu(\text{CO})$  is as a result of the electron-donating inductive effect of the methyl groups on the Cp ring. The tungsten analogue **VIII** again shows one sharp  $\nu(\text{CO})$  band of medium intensity at  $2019\text{ cm}^{-1}$  and one strong, broad  $\nu(\text{CO})$  band at  $1923\text{ cm}^{-1}$ , frequencies which resemble those for compounds of the formula  $[\text{Cp}(\text{CO})_3\text{WCOR}]$ .

The iron-aryl monomer **V** has strong  $\nu(\text{CO})$  bands at  $2013\text{ cm}^{-1}$  and  $1955\text{ cm}^{-1}$  and shows IR characteristics similar to other transition metal carbonyl aryl complexes in the literature.<sup>23</sup>

### 2.2.3 $^1\text{H}$ NMR Spectra

The  $^1\text{H}$  NMR data for all the monomers (**I-VIII**) are shown in Table 2.2. The data obtained for the known monomers **I-III** and **VII** compare favourably with those reported in the literature and attest to the purity of the prepared complexes.

**Table 2.1** : Melting point, elemental analysis and infrared data for the metal-carbon  $\sigma$ -bonded olefinic organometallic monomers I-VIII

| MONOMER <sup>a</sup>  | YIELD (%) | M.P. (°C) | MICROANALYSIS <sup>b</sup> |                  | IR SPECTRA <sup>c</sup>          |   |
|---|-----------|-----------|----------------------------|------------------|----------------------------------|---|
|   |           |           | C; FOUND (CALC.)           | H; FOUND (CALC.) | $\nu(\text{CO}) \text{ cm}^{-1}$ | $\nu[\text{C}(\text{O})\text{R}] \text{ cm}^{-1}$ |
| Fp(CH <sub>2</sub> ) <sub>2</sub> CH=CH <sub>2</sub> (I)    | 69        | OIL       | 56.83 (56.93)              | 4.96 (5.27)      | 2002 (s), 1945 (s)               |   |
| FpCOCH=CH <sub>2</sub> (II)                                 | 61        | OIL       | 48.95 (51.72)              | 3.32 (3.45)      | 2023 (s), 1960(s)                | 1636 (m), 1600 (m), 1582 (m)                      |
| FpCOCH=CHPh (III)   | 70        | 91-92     | 62.22 (62.36)              | 3.83 (3.93)      | 2022 (s), 1962 (s)               | 1634 (m), 1584 (m)                                |
| FpCOC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> (IV)   | 42        | 46-47     | 62.33 (62.36)              | 3.94 (3.93)      | 2022 (s), 1962 (s)               | 1608 (m), 1587 (m)                                |
| FpC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> (V)      | 12        | OIL       |                            |                  | 2013 (s), 1955 (s)               |   |
| Fp*COC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> (VI)  | 20        | 66-68     | 66.71 (66.67)              | 5.89 (5.87)      | 2000 (s), 1940 (s)               | 1604 (w), 1578 (m)                                |
| WpCOCH=CHPh (VII)   | 47        | 101-104   | 44.37 (43.99)              | 2.58 (2.61)      | 2018 (m), 1918 (s,br)            | 1628 (w), 1579 (w), 1568 (w)                      |
| WpCOC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> (VIII) | 14        | 95 (dec.) | 44.26 (43.99)              | 2.74 (2.61)      | 2019 (m), 1923 (s,br)            | 1606 (w), 1582 (w)                                |

<sup>a</sup> Fp = ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>, Fp\* = ( $\eta^5$ -C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>)Fe(CO)<sub>2</sub>, Wp = ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)W(CO)<sub>3</sub>

<sup>b</sup> We had difficulty in obtaining acceptable elemental analysis results for compound II; other supporting characterisation confirm the correct structure for this compound; microanalyses were not recorded for V, due to the instability of the compound

<sup>c</sup> Recorded in CH<sub>2</sub>Cl<sub>2</sub> between NaCl windows; s = strong, sh = sharp, m = medium, w = weak, br = broad

The new compounds **IV**, **V**, **VI** and **VIII** exhibit similar resonances characteristic of the vinylbenzoyl moiety that are present in their structure. Hence, in the  $^1\text{H}$  NMR spectrum, a well-resolved AMX splitting pattern is observed for the vinylic protons. This can be compared to complexes like styrene and vinylferrocene which exhibit a similar pattern.<sup>26,27</sup> The chemical shifts and proton assignments are summarised in Table 2.2 and illustrated in Figure 2.3.

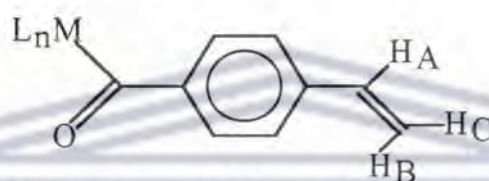


Figure 2.3 Transition metal vinylbenzoyl complex

The similarity in the  $^1\text{H}$  NMR spectrum of the monomers **IV**, **V**, **VI** and **VIII** arises from the coupling between the protons  $\text{H}_\text{A}$ ,  $\text{H}_\text{B}$  and  $\text{H}_\text{C}$ , three magnetically non-equivalent protons. The *trans* and *cis* coupling constants associated with these vinylic protons are given in Table 2.2. The geminal coupling ( $J(\text{H}_\text{B}-\text{H}_\text{C})$ ) is not observed in these complexes. The *trans* ( $J(\text{AB})$ ) and *cis* ( $J(\text{AC})$ ) coupling constants are approximately 17.6 and 10.7 Hz respectively. Typically, a doublet is observed for proton  $\text{H}_\text{C}$ , a doublet for proton  $\text{H}_\text{B}$  and a doublet of doublets for proton  $\text{H}_\text{A}$  in each of the vinyl derivatives. This splitting pattern can be seen in Figures 2.4, 2.5 and 2.6 for the monomers **IV**, **VI** and **VIII** respectively.

On comparison of the relative chemical shifts of these vinylic protons as a function of the metal, no significant differences were found. In Figure 2.4 and Figure 2.6, a definite shift to a lower field for the Cp ring is evident. This is a result of the greater deshielding effect of tungsten (cf. to iron). We can thus conclude that the



variation of the central metal atom does not significantly affect the chemical shifts of the vinylic protons.

A typical splitting pattern is found in the aromatic region for the *para*-substituted aromatic ring of the vinylphenyl group, of monomers **IV** and **VIII**. The *ortho*-coupled aromatic protons appear as two closely-spaced doublets, with a coupling constant equivalent to 8.5 Hz. However, in the pentamethyl-Cp derivative **VI**, the resonance appears as a sharp singlet due to the possible uniformity of the anisotropic effect of the aromatic protons.

#### 2.2.4 $^{13}\text{C}$ NMR Spectra

The chemical shifts and assignments of the proton-decoupled  $^{13}\text{C}$  NMR spectra of the monomers are given in Table 2.3, and were recorded in  $\text{CDCl}_3$ . The resonances were assigned with the aid of a DEPT (distortionless enhancement of polarisation transfer) pulse-sequence experiment. The  $^{13}\text{C}$  NMR spectra for the novel vinylbenzoyl complexes were also assigned using  $^{13}\text{C}$  NMR assignments for the organic compound, benzoyl chloride.<sup>28</sup> As an example, a DEPT spectrum of monomer **IV** is shown in Figure 2.7 and the assignments are illustrated in Figure 2.8. The monomers **V**, **VI** and **VIII** all show similar patterns in their spectra. Peaks of the terminal carbonyls (CO) are quoted in Table 2.3, but peaks due to the acyl carbons were not observed.

**Table 2.2 :**  $^1\text{H}$  NMR data for the organometallic monomers I-VIII

| MONOMER   | COMPOUND NO. | CHEMICAL SHIFT <sup>a</sup><br>( $\delta$ -ppm)  | ASSIGNMENT  |
|---|--------------|--|---|
| $\text{Fp}(\text{CH}_2)_2\text{CH}=\text{CH}_2$ | I            | (1.48, t, 2H)<br>(2.17, m, 2H)<br>(4.75, s, 5H)<br>(4.88, m, 2H)<br>(5.86, m, 1H)  | $\text{FpCH}_2\text{CH}_2\text{CH}=\text{CH}_2$<br>$\text{FpCH}_2\text{CH}_2\text{CH}=\text{CH}_2$<br>$\text{C}_5\text{H}_5$<br>$\text{FpCH}_2\text{CH}_2\text{CH}=\text{CH}_2$<br>$\text{FpCH}_2\text{CH}_2\text{CH}=\text{CH}_2$  |
| $\text{FpCOCH}=\text{CH}_2$                     | II           | (4.91, s, 5H)<br>Hidden under Cp ring peak<br>(5.35, d, 1H, $J_{\text{BA,trans}} = 17.2$ Hz)<br>(6.55, dd, 1H, $J = 17.0, 10.6$ Hz)  | $\text{C}_5\text{H}_5$<br>$\text{FpCOCH}=\text{CH}_2$<br>$\text{FpCOCH}=\text{CH}_2$<br>$\text{FpCOCH}=\text{CH}_2$   |
| $\text{FpCOCH}=\text{CHC}_6\text{H}_5$          | III          | (4.85, s, 5H)<br>(6.60, d, 1H, $J_{\text{trans}} = 15.7$ Hz)<br>(6.93, d, 1H, $J_{\text{trans}} = 15.7$ Hz)<br>(7.20-7.56, m, 5H)  | $\text{C}_5\text{H}_5$<br>$\text{FpCOCH}=\text{CHC}_6\text{H}_5$<br>$\text{FpCOCH}=\text{CHC}_6\text{H}_5$<br>$\text{FpCOCH}=\text{CHC}_6\text{H}_5$  |
| $\text{FpCOC}_6\text{H}_4\text{CH}=\text{CH}_2$ | IV           | (4.93, s, 5H)<br>(5.32, d, 1H, $J_{\text{CA,cis}} = 10.9$ Hz)<br>(5.81, d, 1H, $J_{\text{BA,trans}} = 17.6$ Hz)<br>(6.72, dd, 1H, $J = 17.6, 10.9$ Hz)<br>(7.40, d, 2H, $J_{\text{ortho}} = 8.5$ Hz)<br>(7.48, d, 2H, $J_{\text{ortho}} = 8.5$ Hz) | $\text{C}_5\text{H}_5$<br>$\text{FpCOC}_6\text{H}_4\text{CH}=\text{CH}_2$<br>$\text{FpCOC}_6\text{H}_4\text{CH}=\text{CH}_2$<br>$\text{FpCOC}_6\text{H}_4\text{CH}=\text{CH}_2$<br>$\text{FpCOC}_6\text{H}_4\text{CH}=\text{CH}_2$<br>$\text{FpCOC}_6\text{H}_4\text{CH}=\text{CH}_2$ |

Table 2.2 (cont.)

| MONOMER  | COMPOUND NO. | CHEMICAL SHIFT <sup>a</sup><br>( $\delta$ -ppm)  | ASSIGNMENT  |
|--|--------------|--|---|
| $\text{FpC}_6\text{H}_4\text{CH}=\text{CH}_2$            | V            | (4.84, s, 5H)<br>(5.10, d, 1H, $J_{\text{CA,cis}} = 10.9$ Hz)<br>(5.60, d, 1H, $J_{\text{BA,trans}} = 17.6$ Hz)<br>(6.58, dd, 1H, $J = 17.6, 10.9$ Hz)<br>(7.00(2H), 7.39(2H), $J_{\text{ortho}} = 8.5$ Hz)  | $\text{C}_5\text{H}_5$<br>$\text{FpC}_6\text{H}_4\text{CH}=\text{CH}_2$<br>$\text{FpC}_6\text{H}_4\text{CH}=\text{CH}_2$<br>$\text{FpC}_6\text{H}_4\text{CH}=\text{CH}_2$<br>$\text{FpC}_6\text{H}_4\text{CH}=\text{CH}_2$  |
| $\text{Fp}^*\text{COC}_6\text{H}_4\text{CH}=\text{CH}_2$ | VI           | (1.80, s, 15H)<br>(5.30, d, 1H, $J_{\text{CA,cis}} = 10.8$ Hz)<br>(5.79, d, 1H, $J_{\text{BA,trans}} = 17.6$ Hz)<br>(6.72, dd, 1H, $J = 17.6, 10.9$ Hz)<br>(7.42, s, 4H)   | $\text{C}_5\text{Me}_5$<br>$\text{Fp}^*\text{COC}_6\text{H}_4\text{CH}=\text{CH}_2$<br>$\text{Fp}^*\text{COC}_6\text{H}_4\text{CH}=\text{CH}_2$<br>$\text{Fp}^*\text{COC}_6\text{H}_4\text{CH}=\text{CH}_2$<br>$\text{Fp}^*\text{COC}_6\text{H}_4\text{CH}=\text{CH}_2$               |
| $\text{WpCOCH}=\text{CHC}_6\text{H}_5$                   | VII          | (5.65, s, 5H)<br>(6.79, d, 1H, $J_{\text{trans}} = 15.7$ Hz)<br>(6.98, d, 1H, $J_{\text{trans}} = 15.7$ Hz)<br>(7.40-7.64, m, 5H)  | $\text{C}_5\text{H}_5$<br>$\text{WpCOCH}=\text{CHC}_6\text{H}_5$<br>$\text{WpCOCH}=\text{CHC}_6\text{H}_5$<br>$\text{WpCOCH}=\text{CHC}_6\text{H}_5$  |
| $\text{WpCOC}_6\text{H}_4\text{CH}=\text{CH}_2$          | VIII         | (5.34, d, 1H, $J_{\text{CA,cis}} = 10.9$ Hz)<br>(5.70, s, 5H)<br>(5.82, d, 1H, $J_{\text{BA,trans}} = 17.6$ Hz)<br>(6.71, dd, 1H, $J = 17.6, 10.9$ Hz)<br>(7.39, d, 2H, $J_{\text{ortho}} = 8.5$ Hz)<br>(7.49, d, 2H, $J_{\text{ortho}} = 8.5$ Hz) | $\text{WpCOC}_6\text{H}_4\text{CH}=\text{CH}_2$<br>$\text{C}_5\text{H}_5$<br>$\text{WpCOC}_6\text{H}_4\text{CH}=\text{CH}_2$<br>$\text{WpCOC}_6\text{H}_4\text{CH}=\text{CH}_2$<br>$\text{WpCOC}_6\text{H}_4\text{CH}=\text{CH}_2$<br>$\text{WpCOC}_6\text{H}_4\text{CH}=\text{CH}_2$ |

<sup>a</sup> Spectra recorded in  $\text{CDCl}_3$  using TMS as the internal standard; monomer V recorded on a 90MHz NMR spectrometer

**Table 2.3 :**  $^{13}\text{C}$  NMR data for the organometallic monomers I-IV, VI-VIII

| MONOMER   | COMPOUND NO. | CHEMICAL SHIFT <sup>a</sup><br>( $\delta$ - ppm)                  | ASSIGNMENT  |
|---|--------------|---|---|
| $\text{Fp}(\text{CH}_2)_2\text{CH}=\text{CH}_2$ | I            | 2.13<br>41.83<br>85.31<br>112.27<br>142.53<br>217.51              | $\text{Fp}\underline{\text{C}}\text{H}_2\text{CH}_2\text{CH}=\text{CH}_2$<br>$\text{FpCH}_2\underline{\text{C}}\text{H}_2\text{CH}=\text{CH}_2$<br>$\underline{\text{C}}_5\text{H}_5$<br>$\text{FpCH}_2\text{CH}_2\text{CH}=\underline{\text{C}}\text{H}_2$<br>$\text{FpCH}_2\text{CH}_2\underline{\text{C}}\text{H}=\text{CH}_2$<br>$\underline{\text{C}}\text{O}$ |
| $\text{FpCOCH}=\text{CH}_2$                     | II           | 86.46<br>115.70<br>148.56<br>214.10                               | $\underline{\text{C}}_5\text{H}_5$<br>$\text{FpCOCH}=\underline{\text{C}}\text{H}_2$<br>$\text{FpCOCH}=\text{CH}_2$<br>$\underline{\text{C}}\text{O}$   |
| $\text{FpCOCH}=\text{CHC}_6\text{H}_5$          | III          | 86.42<br>128.22<br>128.74<br>129.51<br>135.07<br>138.58<br>213.98 | $\underline{\text{C}}_5\text{H}_5$<br>$\text{FpCOCH}=\text{CHC}_6\text{H}_5$<br>$\text{FpCOCH}=\text{CHC}_6\text{H}_5$<br>$\text{FpCO}\underline{\text{C}}\text{H}=\text{CHC}_6\text{H}_5$<br>$\text{FpCOCH}=\text{CHC}_6\text{H}_5$<br>$\text{FpCOCH}=\underline{\text{C}}\text{H}\text{C}_6\text{H}_5$<br>$\underline{\text{C}}\text{O}$                          |

Table 2.3 (cont.)

| MONOMER  | COMPOUND NO. | CHEMICAL SHIFT <sup>a</sup><br>( $\delta$ - ppm)                              | ASSIGNMENT  |
|--|--------------|---|---|
| FpCOC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub>               | IV           | 86.24<br>115.51<br>125.82<br>126.47<br>136.04<br>139.34<br>149.40<br>213.94   | C <sub>5</sub> H <sub>5</sub><br>FpCOC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub><br>FpCOC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub><br>FpCOC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub><br>FpCOC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub><br>FpCOC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub><br>FpCOC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub><br>FpCOC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub><br>CO |
| Fp <sup>*</sup> COC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> | VI           | 9.66<br>97.23<br>115.03<br>125.75, 126.63, 138.95, 148.32<br>136.29<br>216.14 | C <sub>5</sub> Me <sub>5</sub><br>C <sub>5</sub> Me <sub>5</sub><br>Fp <sup>*</sup> COC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub><br>Fp <sup>*</sup> COC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub><br>Fp <sup>*</sup> COC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub><br>CO  |

Table 2.3 (cont.)

| MONOMER  | COMPOUND NO. | CHEMICAL SHIFT <sup>a</sup><br>( $\delta$ - ppm) | ASSIGNMENT   |
|--|--------------|--|--|
| WpCOCH=CHC <sub>6</sub> H <sub>5</sub>               | VII          | 95.83  | C <sub>5</sub> H <sub>5</sub>                        |
|  |              | 128.47   | WpCOCH=CHC <sub>6</sub> H <sub>5</sub>               |
|  |              | 128.74   | WpCOCH=CHC <sub>6</sub> H <sub>5</sub>               |
|  |              | 129.68   | WpCOCH=CHC <sub>6</sub> H <sub>5</sub>               |
|  |              | 134.11   | WpCOCH=CHC <sub>6</sub> H <sub>5</sub>               |
|  |              | 142.74   | WpCOCH=CHC <sub>6</sub> H <sub>5</sub>               |
| WpCOC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> | VIII         | 96.17  | C <sub>5</sub> H <sub>5</sub>                        |
|  |              | 115.98   | WpCOC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> |
|  |              | 126.02   | WpCOC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> |
|  |              | 128.59   | WpCOC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> |
|  |              | 136.15   | WpCOC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> |
|  |              | 140.64   | WpCOC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> |
|  |              | 148.76   | WpCOC <sub>6</sub> H <sub>4</sub> CH=CH <sub>2</sub> |
|  |              | 219.95   | CO   |

<sup>a</sup> Spectra recorded in CDCl<sub>3</sub>.

Figure 2.4  $^1\text{H}$  NMR spectrum of monomer IV

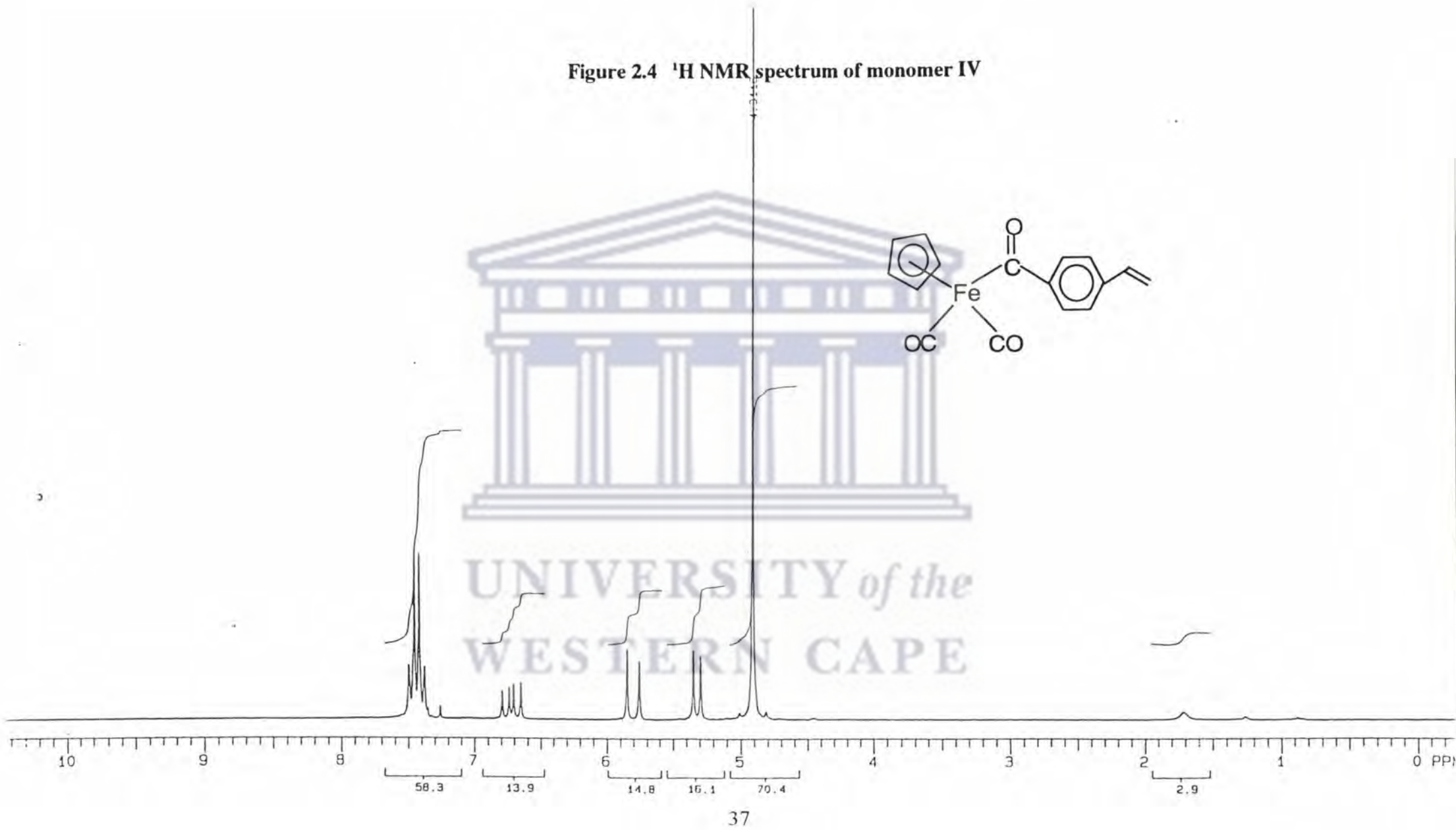


Figure 2.5  $^1\text{H}$  NMR spectrum of monomer VI

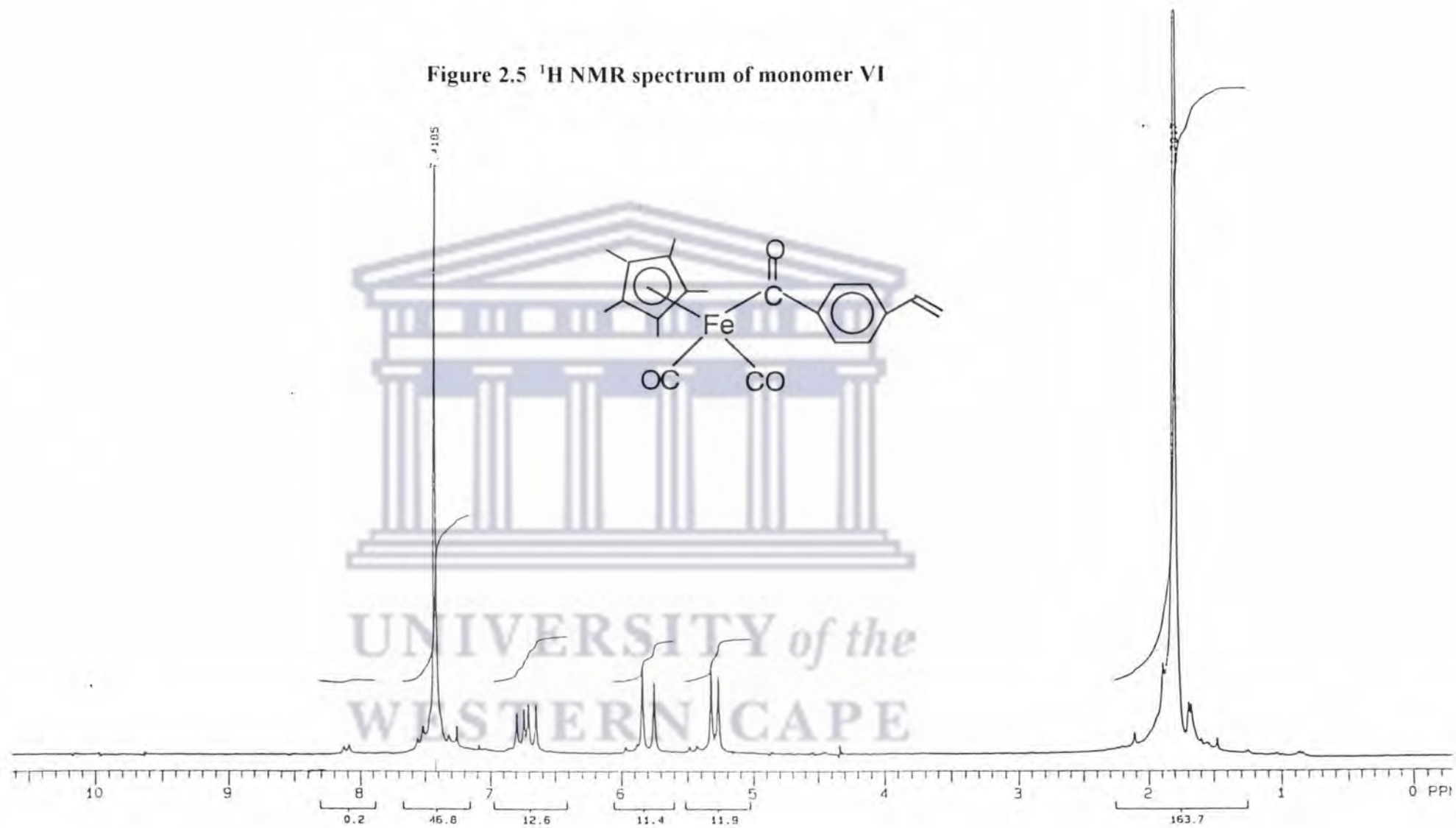
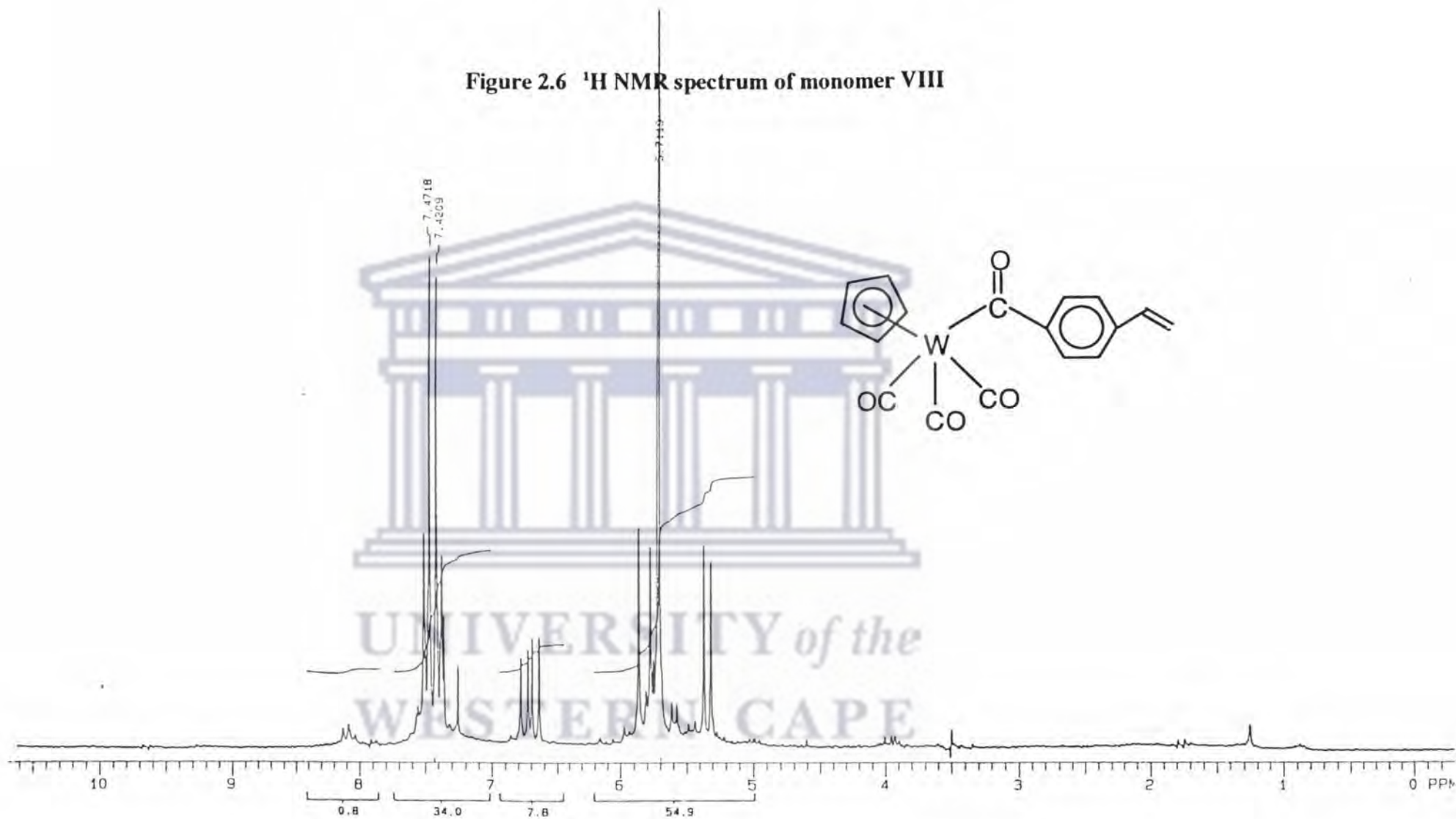




Figure 2.6  $^1\text{H}$  NMR spectrum of monomer VIII



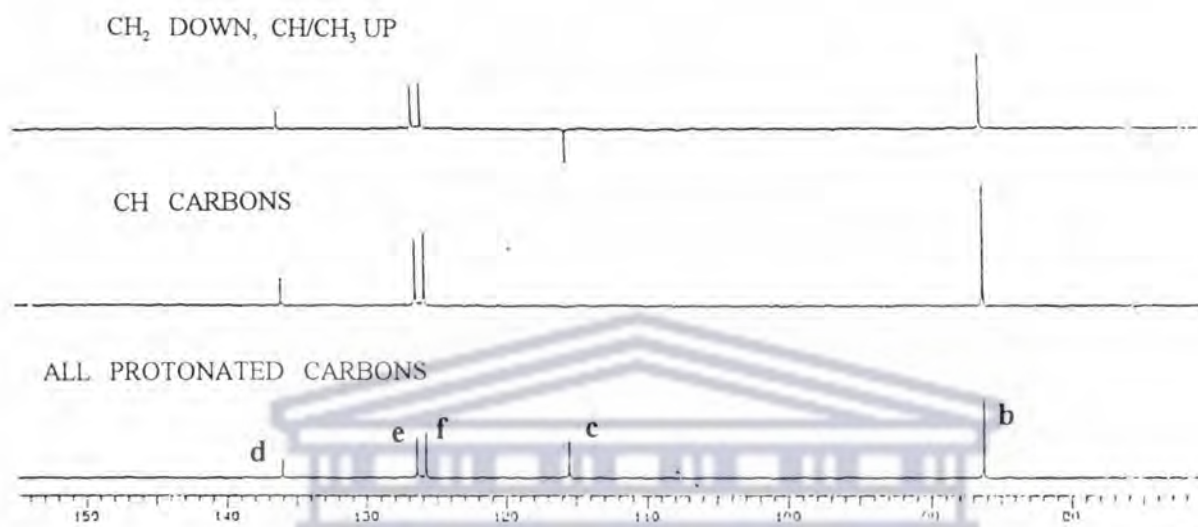
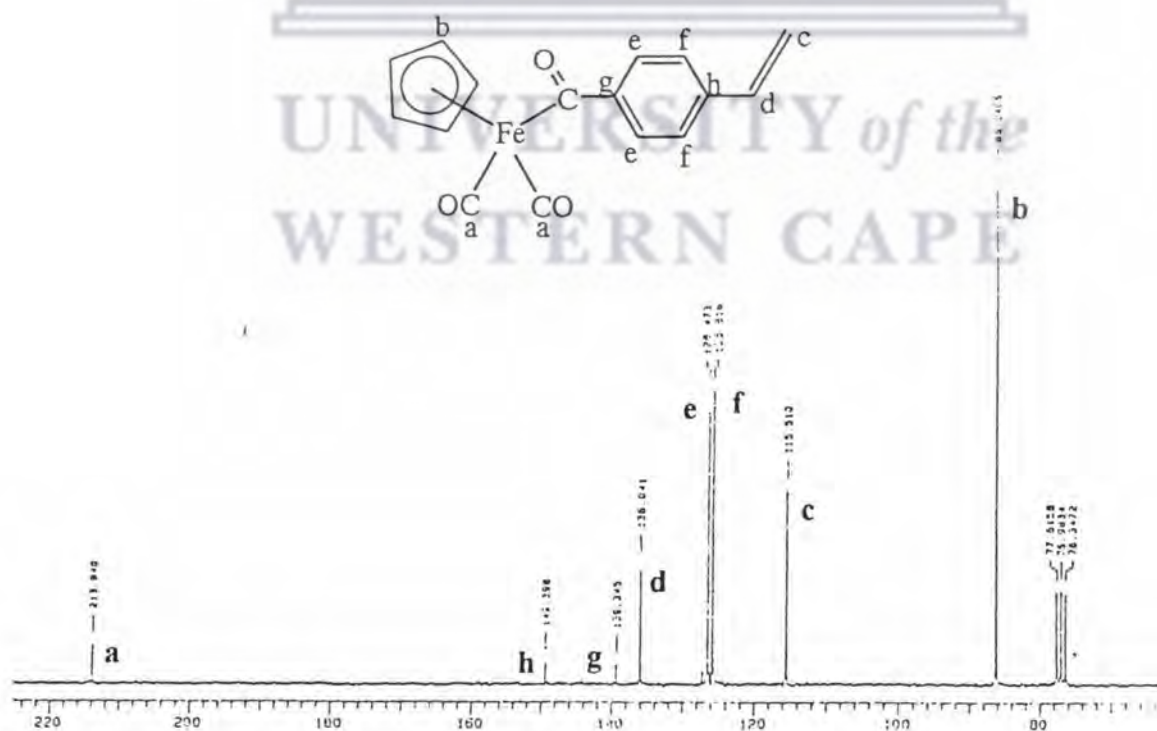


Figure 2.7 DEPT spectra of monomer IV

Figure 2.8 <sup>13</sup>C NMR assignment of monomer IV

### 2.2.5 Mass Spectra

The mass spectra of the olefinic organometallic monomers show a number of similarities in their fragmentation patterns. The trends in the different spectra compare favourably with other cyclopentadienyl metal carbonyl derivatives, in which the molecular ion is observed to decompose via two main fragmentation pathways.

The first general trend observed, is the initial stepwise loss of carbonyl groups, followed by the extrusion of the remaining organic fragments. This occurs via decarbonylation of the acyl complexes first and then the loss of the terminal carbonyls. These features are similar to studies of the mass spectra of other cyclopentadienylmetal carbonyl derivatives<sup>29-31</sup>, in which decarbonylation was observed to occur first. Attempts to decarbonylate compounds of the type  $\text{CpFe}(\text{CO})_2\text{COR}$  by thermal means have been unsuccessful.

The second fragmentation pathway involves the initial loss of the organic group bonded to the metal. In the case of the iron compounds, this gives rise to the  $\text{CpFe}(\text{CO})_3^+$  ion ( $m/e$  205). This ion is a characteristic constituent of the mass spectra of acyl derivatives of the type  $\text{CpFe}(\text{CO})_2\text{COR}$  and confirms the presence of an acyl compound.<sup>29</sup> This is then followed by the loss of the carbonyl groups and eventually the cyclopentadienyl ring to give the metal ion  $\text{Fe}^+$  ( $m/e$  56). The pentamethylcyclopentadienyl iron analogue **VI** shows the same fragmentation pattern, starting from the loss of carbonyl groups. However, the ion  $\text{Cp}^*\text{Fe}(\text{CO})_3^+$  or decomposition pathways from this ion are not observed.

The tungsten complexes also display the same two fragmentation pathways in their mass spectra. Like other cyclopentadienyltungsten tricarbonyl derivatives, the highest ion in the spectra is always 28 mass units (one CO group) less than the parent ion. This carbonyl loss has previously been ascribed to the decarbonylation of the acyl derivative.

The mass spectrum of monomer **III** has been reported before.<sup>29</sup> A breakdown of the various ions for the different monomers is now presented in Tables 2.4 to 2.8.

A mass spectrum of monomer **V** was not recorded.

**Table 2.4** : Mass spectrum of  $\text{Cp}(\text{CO})_2\text{FeCOCH}=\text{CH}_2$  (**II**)

| <i>m/e</i> | Ion <sup>a</sup>                                    | Relative Peak Intensities <sup>b</sup> |
|------------|---|--|
| 232        | $\text{Cp}(\text{CO})_2\text{FeCOCH}=\text{CH}_2^+$ | 4                                      |
| 205        | $\text{CpFe}(\text{CO})_3^+$                        | 9                                      |
| 204        | $\text{Cp}(\text{CO})_2\text{FeCH}=\text{CH}_2^+$   | 44                                     |
| 177        | $\text{CpFe}(\text{CO})_2^+$                        | 16                                     |
| 176        | $\text{Cp}(\text{CO})\text{FeCH}=\text{CH}_2^+$     | 47                                     |
| 148        | $\text{CpFeCH}=\text{CH}_2^+$                       | 71                                     |
| 121        | $\text{CpFe}^+$                                     | 100                                    |
| 56         | $\text{Fe}^+$                                       | 95                                     |

<sup>a</sup> ion refers to proposed assignment; Cp =  $\eta^5\text{-C}_5\text{H}_5$

<sup>b</sup> Peak intensities relative to *m/e* 121

**Table 2.5** : Mass spectrum of  $\text{Cp}(\text{CO})_2\text{FeCOC}_6\text{H}_4\text{CH}=\text{CH}_2$  (IV)

| $m/e$ <sup>a</sup> | Ion <sup>b</sup>  | Relative Peak Intensities <sup>c</sup> |
|--------------------|---|--|
| 252                | $\text{Cp}(\text{CO})\text{FeC}_6\text{H}_4\text{CH}=\text{CH}_2^+$ | 100                                    |
| 205                | $\text{CpFe}(\text{CO})_3^+$  | 0.8                                    |
| 198                | $\text{CpFeC}_6\text{H}_4^+$  | 16                                     |
| 177                | $\text{CpFe}(\text{CO})_2^+$  | 3                                      |
| 166                | $\text{C}_{13}\text{H}_{10}^+$                                      | 36                                     |
| 131                | $\text{CH}_2=\text{CHC}_6\text{H}_4\text{CO}^+$                     | 51                                     |
| 121                | $\text{CpFe}^+$   | 53                                     |
| 103                | $\text{CH}_2=\text{CHC}_6\text{H}_4^+$                              | 25                                     |
| 56                 | $\text{Fe}^+$   | 64                                     |

<sup>a</sup> No molecular ion observed

<sup>b</sup> ion refers to proposed assignment;  $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$

<sup>c</sup> Peak intensities relative to  $m/e$  252

**Table 2.6** : Mass spectrum of  $\text{Cp}^*(\text{CO})_2\text{FeCOC}_6\text{H}_4\text{CH}=\text{CH}_2$  (VI)

| $m/e$ <sup>a</sup> | Ion <sup>b</sup>  | Relative Peak Intensities <sup>c</sup> |
|--------------------|---|--|
| 350                | $\text{Cp}^*(\text{CO})_2\text{FeC}_6\text{H}_4\text{CH}=\text{CH}_2^+$ | 28                                     |
| 322                | $\text{Cp}^*(\text{CO})\text{FeC}_6\text{H}_4\text{CH}=\text{CH}_2^+$   | 12                                     |
| 294                | $\text{Cp}^*\text{FeC}_6\text{H}_4\text{CH}=\text{CH}_2^+$              | 100                                    |
| 191                | $\text{Cp}^*\text{Fe}^+$  | 12                                     |
| 131                | $\text{CH}_2=\text{CHC}_6\text{H}_4\text{CO}^+$                         | 2                                      |
| 103                | $\text{CH}_2=\text{CHC}_6\text{H}_4^+$                                  | 2                                      |
| 56                 | $\text{Fe}^+$   | 9                                      |
| 28                 | $\text{CO}^+$   | 40                                     |

<sup>a</sup> No molecular ion observed

<sup>b</sup> ion refers to proposed assignment;  $\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$

<sup>c</sup> Peak intensities relative to  $m/e$  294

**Table 2.7** : Mass spectrum of  $\text{Cp}(\text{CO})_3\text{WCOCH}=\text{CHC}_6\text{H}_5$  (VI)

| $m/e$ <sup>a</sup> | Ion <sup>b</sup>  | Relative Peak Intensities <sup>c</sup> |
|--------------------|---|--|
| 436                | $\text{Cp}(\text{CO})_3\text{WCH}=\text{CHC}_6\text{H}_5^+$ | 24                                     |
| 408                | $\text{Cp}(\text{CO})_2\text{WCH}=\text{CHC}_6\text{H}_5^+$ | 14                                     |
| 380                | $\text{Cp}(\text{CO})\text{WCH}=\text{CHC}_6\text{H}_5^+$   | 43                                     |
| 352                | $\text{CpWCH}=\text{CHC}_6\text{H}_5^+$                     | 23                                     |
| 333                | $\text{CpW}(\text{CO})_3^+$                                 | 4                                      |
| 326                | $\text{CpWCHC}_6\text{H}_5^+$                               | 7                                      |
| 305                | $\text{CpW}(\text{CO})_2^+$                                 | 6                                      |
| 249                | $\text{CpW}^+$  | 17                                     |
| 131                | $\text{C}_6\text{H}_5\text{CH}=\text{CHCO}^+$               | 100                                    |
| 77                 | $\text{C}_6\text{H}_5^+$                                    | 23                                     |
| 28                 | $\text{CO}^+$   | 87                                     |

<sup>a</sup> No molecular ion observed

<sup>b</sup> ion refers to proposed assignment;  $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$

<sup>c</sup> Peak intensities relative to  $m/e$  131

**Table 2.8** : Mass spectrum of  $\text{Cp}(\text{CO})_3\text{WCOC}_6\text{H}_4\text{CH}=\text{CH}_2$  (VIII)

| $m/e$ <sup>a</sup> | Ion <sup>b</sup>   | Relative Peak Intensities <sup>c</sup> |
|--------------------|--|--|
| 436                | $\text{Cp}(\text{CO})_3\text{WC}_6\text{H}_4\text{CH}=\text{CH}_2^+$ | 62                                     |
| 408                | $\text{Cp}(\text{CO})_2\text{WC}_6\text{H}_4\text{CH}=\text{CH}_2^+$ | 34                                     |
| 380                | $\text{Cp}(\text{CO})\text{WC}_6\text{H}_4\text{CH}=\text{CH}_2^+$   | 92                                     |
| 352                | $\text{CpWC}_6\text{H}_4\text{CH}=\text{CH}_2^+$                     | 37                                     |
| 333                | $\text{CpW}(\text{CO})_3^+$  | 3                                      |
| 305                | $\text{CpW}(\text{CO})_2^+$  | 5                                      |
| 249                | $\text{CpW}^+$   | 14                                     |
| 131                | $\text{CH}_2=\text{CHC}_6\text{H}_4\text{CO}^+$                      | 100                                    |
| 77                 | $\text{C}_6\text{H}_5^+$   | 23                                     |

<sup>a</sup> No molecular ion observed

<sup>b</sup> ion refers to proposed assignment;  $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$

<sup>c</sup> Peak intensities relative to  $m/e$  131

### 2.3 Conclusion

A number of olefinic organometallic monomers have been prepared by the reaction of  $\text{Na}^+[\text{CpM}(\text{CO})_n]^-$  ( $\text{M} = \text{Fe}$ ,  $n=2$ ;  $\text{M} = \text{W}$ ,  $n=3$ ) with the appropriate electrophile. All these monomers contain a vinyl moiety as part of the organic ligands which are  $\sigma$ -bonded to the metal centre. These metal-carbon  $\sigma$ -bonded monomers represent a combination of alkyl, acyl and aryl compounds belonging to a collective class of hydrocarbyl compounds.

The syntheses of the known compounds,  $\text{Fp}(\text{CH}_2)_2\text{CH}=\text{CH}_2$  (**I**),  $\text{FpCOCH}=\text{CH}_2$  (**II**),  $\text{FpCOCH}=\text{CHC}_6\text{H}_5$  (**III**) and  $\text{WpCOCH}=\text{CHC}_6\text{H}_5$  (**VII**) proceeded in yields consistent with the literature, except for monomer **II** for which the yield was optimised. The new complex  $\text{FpCOC}_6\text{H}_4\text{CH}=\text{CH}_2$  (**IV**) was prepared in good yields, whereas the new monomers,  $\text{Fp}^*\text{COC}_6\text{H}_4\text{CH}=\text{CH}_2$  (**VI**) and  $\text{WpCOC}_6\text{H}_4\text{CH}=\text{CH}_2$  (**VIII**) were prepared in low yields. The new monomer  $\text{FpC}_6\text{H}_4\text{CH}=\text{CH}_2$  (**V**) was prepared with the aid of a cross-coupling catalyst in low yields.

These monomers are precursors in our work of further studies of the polymerisation of metal-carbon  $\sigma$ -bonded olefinic organometallic monomers. They were fully characterised by microanalyses, IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy and mass spectrometry.

## 2.4 Experimental

All reactions were carried out under nitrogen using standard Schlenk tube techniques. Tetrahydrofuran (THF) and toluene were dried over sodium/benzophenone and distilled under nitrogen before use.  $[\text{CpFe}(\text{CO})_2]_2$ , 4-bromo-1-butene, acryloyl chloride, *trans*-cinnamoyl chloride, 4-vinylbenzoic acid, 4-bromostyrene and tetrakis(triphenylphosphine)palladium (0) were purchased from Aldrich, and were used without further purification. 4-Vinylbenzoic acid was converted to the acid chloride using neat  $\text{SOCl}_2$  in the standard manner.<sup>32</sup>  $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$  was obtained from Strem Chemicals, and  $[\text{CpW}(\text{CO})_3]_2$  was prepared according to literature procedures.<sup>33</sup> All chromatography was done on either deactivated alumina 90 (70-230 mesh) or silica gel (70-230 mesh), obtained from Merck. Infrared spectra were recorded on a Perkin Elmer Paragon 1000PC FT-IR spectrophotometer, using solution cells with NaCl windows.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Varian XR200 spectrometer, using tetramethylsilane as an internal standard. Mass spectra were obtained with a V.G. Micromass 16F spectrometer, operating at 70eV ionising voltage. Microanalyses were performed by the University of Cape Town Microanalytical Laboratory. Melting points were determined on a Fisher-Johns hotstage microscope, and are uncorrected.

### 2.4.1 Preparation of $\text{Cp}(\text{CO})_2\text{FeCOCH}=\text{CH}_2$ (II)

A solution of  $\text{Na}[\text{CpFe}(\text{CO})_2]$  (5.65 mmol) was prepared by stirring  $[\text{CpFe}(\text{CO})_2]_2$  (1.00 g, 2.82 mmol) over a sodium amalgam (0.300 g Na; 4.0 ml Hg) in THF (20 ml) for 2 hours. This solution was added dropwise to a solution of acryloyl chloride



(0.46 ml, 5.65 mmol) in THF (5.0 ml) which had been cooled to  $-78^{\circ}\text{C}$ . The resulting dark green reaction mixture was stirred for 30 minutes at  $-78^{\circ}\text{C}$ , and then gradually allowed to warm to room temperature. On warming to room temperature, the reaction mixture turned yellow-orange and was stirred overnight. The solvent was removed by rotary evaporation, and the dark orange residue extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 30 ml) and filtered by gravity. The filtrate was evaporated on a rotary evaporator. The remaining oil was taken up in a small amount of benzene, and the solution chromatographed on a silica gel column (6 x 2.5 cm), using benzene as eluent. An orange-yellow band was collected and removal of the solvent yielded an orange oil. The orange oil was purified by low temperature ( $-78^{\circ}\text{C}$ ) recrystallisation from hexane. Thus the oil was cooled to  $-78^{\circ}\text{C}$ , and the resulting yellow solid washed with cold hexane, removing the supernatant liquid and dried. On warming to room temperature, an orange oil was obtained as the pure product,  $\text{Cp}(\text{CO})_2\text{FeCOCH}=\text{CH}_2$  (II), in 61% yield.

#### 2.4.2 Preparation of $\text{Cp}(\text{CO})_2\text{FeCOC}_6\text{H}_4\text{CH}=\text{CH}_2$ (IV)

A solution of  $[\text{CpFe}(\text{CO})_2]_2$  (1.00 g, 2.84 mmol) in THF (20 ml) was stirred over a sodium amalgam (0.300 g Na; 4.0 ml Hg) for 2 hours at room temperature. The resulting solution was added dropwise with stirring to a cooled solution of 4-vinylbenzoyl chloride (0.947 g, 5.67 mmol) in THF (5.0 ml) at  $-78^{\circ}\text{C}$ . After the addition was complete, the solution was gradually allowed to warm to room temperature. The dark red-brown solution was stirred at room temperature for 3 days. The solvent was removed under reduced pressure and the residue extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 30 ml). The extracts were filtered and the solvent removed by

rotary evaporation. The residue was taken up in a small amount of benzene, and chromatographed on a silica gel column (6 x 2.5 cm), using benzene as eluent. This resulted in four bands. The first band gave a yellow oil and appears to be some unidentified organic by-product (contains no terminal carbonyls). The second band (red solid) was identified as the dimer,  $[\text{CpFe}(\text{CO})_2]_2$ . The third band was found to contain the product,  $\text{Cp}(\text{CO})_2\text{FeCOC}_6\text{H}_4\text{CH}=\text{CH}_2$  (**IV**). This gave bright yellow crystals, in 42% yield, after recrystallisation from a  $\text{CH}_2\text{Cl}_2$ /hexane mixture. The fourth fraction was isolated as an orange solid and confirmed to be the by-product,  $[\text{CpFe}(\text{CO})_2\text{Cl}]$ , by t.l.c. comparison with the authentic sample and reported IR <sup>34,35</sup> spectra.

#### 2.4.3 Preparation of $\text{Cp}(\text{CO})_2\text{FeC}_6\text{H}_4\text{CH}=\text{CH}_2$ (**V**)

A solution of  $[\text{CpFe}(\text{CO})_2]_2$  (0.504 g, 1.41 mmol) in THF (12 ml) was stirred over a sodium amalgam (0.300 g Na; 4.0 ml Hg) for 1.5 hours at room temperature. This solution was added to a solution of dry  $\text{ZnCl}_2$  (0.201 g 1.41 mmol) in THF (5.0 ml), yielding a green mixture. 4-Bromostyrene (0.40 ml, 2.82 mmol) was syringed into the reaction mixture; thereafter the catalyst  $\text{PdPhI}(\text{PPh}_3)_2$  ( $7.20 \times 10^{-2}$  g, 0.0864mmol) was added. A darkening of the reaction mixture was observed. The reaction was allowed to proceed for 2 days at room temperature. The solvent was removed by rotary evaporation, and the residue extracted with hexane and filtered. The filtrate was evaporated by rotary evaporation resulting in a yellow oil. The oil was chromatographed on an alumina column (5 x 2.5 cm), using hexane as eluent. Two yellow fractions were collected after elution. The first band was isolated as a yellow oil, which was found to be the saturated compound,

$\text{Cp}(\text{CO})_2\text{FeC}_6\text{H}_4\text{CH}(\text{Br})\text{CH}_3$ . The product,  $\text{Cp}(\text{CO})_2\text{FeC}_6\text{H}_4\text{CH}=\text{CH}_2$  (**V**), was found in the second band, and isolated as a yellow oil. Purification of the product by low temperature ( $-78^\circ\text{C}$ ) recrystallisation in hexane, gave an oil in 12% yield.

#### 2.4.4 Preparation of $[\text{Cp}^*(\text{CO})_2\text{FeCOC}_6\text{H}_4\text{CH}=\text{CH}_2]$ (**VI**)

A solution of  $\text{Na}[\text{Cp}^*\text{Fe}(\text{CO})_2]$  (2.02 mmol) was prepared by stirring  $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$  (0.500g, 1.01 mmol) in THF (20 ml) over a sodium amalgam (0.300 g Na; 4.0 ml Hg) for 2.5 hours at room temperature. This solution was added to a solution of 4-vinylbenzoyl chloride (0.337 g, 2.02 mmol) in THF (5 ml) at  $-78^\circ\text{C}$ . After the addition was complete, the solution was allowed to warm to room temperature. The orange-brown mixture was stirred overnight at room temperature. The solvent was removed by rotary evaporation, and the residue extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 30 ml). Filtration of the extracts and removal of the solvent yielded an orange oil. The oil was chromatographed on a silica gel column (6 x 2.5 cm). Elution with benzene results in three fractions, namely, a dark red band moving closest to the solvent front, a yellow band following behind this band, and an orange-red band which moves very slowly. The first band was confirmed to be the starting material,  $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$ . The second band was found to be the product,  $[\text{Cp}^*(\text{CO})_2\text{FeCOC}_6\text{H}_4\text{CH}=\text{CH}_2]$  (**VI**). This was isolated as a yellow oil and was crystallised from hexane at  $-78^\circ\text{C}$ , in 20% yield. The third band is the compound  $[\text{Cp}^*\text{Fe}(\text{CO})_2\text{Cl}]$ , as identified by reported IR spectra.<sup>36,37</sup>

#### 2.4.5 Preparation of $[\text{Cp}(\text{CO})_3\text{WCOC}_6\text{H}_4\text{CH}=\text{CH}_2]$ (VIII)

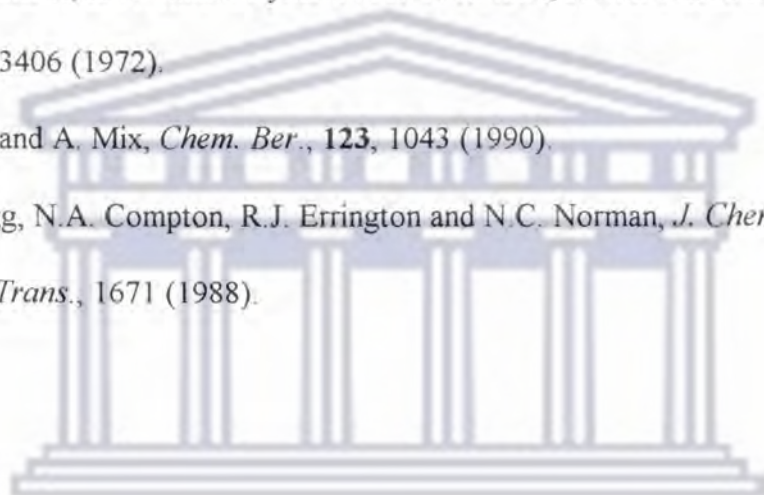
Cyclopentadienyltungsten tricarbonyl dimer,  $[\text{CpW}(\text{CO})_3]_2$  (0.702g, 1.05 mmol) was taken up in THF (20 ml) and stirred over a sodium amalgam (0.300 g Na; 4.0 ml Hg) at room temperature for 2 hours. The resulting green-grey solution was added dropwise to a solution of 4-vinylbenzoyl chloride (0.350 g, 2.10 mmol) in THF (5 ml) at  $-78^\circ\text{C}$ . The reaction mixture was allowed to warm to room temperature, and the orange solution was stirred overnight. Removal of the solvent left an oily orange residue. This was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 30 ml), filtered and the solvent removed by rotary evaporation to give an orange oil. The solution of the oil in  $\text{CH}_2\text{Cl}_2$  decomposes on standing for a short while. The oil was chromatographed on a silica gel column (6 x 2.5 cm) using benzene as eluent. Two components were observed, with extensive decomposition occurring on the column. The first band was removed as a dark orange fraction, which decomposed rapidly in solution and in the solid state. The second fraction was a lighter orange band, which was found to be the product,  $[\text{Cp}(\text{CO})_3\text{WCOC}_6\text{H}_4\text{CH}=\text{CH}_2]$  (VIII). Removal of the solvent, and crystallisation of the remaining orange oil from hexane at  $-78^\circ\text{C}$ , gave the product as an orange solid in 14% yield.

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The logo of the University of Western Cape, featuring a classical building with a pediment and columns, is centered in the background. The text "CHAPTER 3" is superimposed on the pediment.

**CHAPTER 3**

**FREE-RADICAL HOMOPOLYMERISATION  
AND COPOLYMERISATION OF  $\sigma$ -BONDED  
OLEFINIC ORGANOMETALLIC  
MONOMERS**



### 3.1 Introduction

The preparation of poly(vinylferrocene) **2** in 1955 (Figure 1.6), the first organometallic polymer synthesised via free-radical addition polymerisation<sup>1-3</sup>, paved the way for the synthesis of different transition metal-based polymers. It was thought that the various oxidation states of transition metals and steric bulk of the associated ligands would exert unusual effects in the polymerisation of olefinic organometallic monomers. In these studies the metal moiety was found to be stable under polymerisation conditions. Various  $\pi$ -bonded,  $\eta^5$ -vinylcyclopentadienyl organometallic complexes such as **1**, **3-6** in CHAPTER 1, were subsequently found to undergo polymerisation under much the same conditions as conventional organic monomers.<sup>4-11</sup> This can be ascribed to the strong electron-donating contribution from the aromatic cyclopentadienyl ring.

Vinylferrocene **1** and other vinyl derivatives of ferrocene have been the most thoroughly studied organometallic monomers. The free-radical addition polymerisation of vinylferrocene **1** can be initiated by AIBN. Azo initiators such as AIBN are the preferred free-radical catalysts in many olefinic organometallic systems. Peroxide initiators are not employed because of their ability to oxidise the metal centres. This is in contrast with organic monomers, like styrene, that are able to undergo polymerisation with peroxides.<sup>12</sup>

The polymerisation of the  $\eta^5$ -vinylcyclopentadienyl organometallic monomers was observed to occur very sluggishly. Often long reaction times and several reinitiations were needed for complete conversion of the organometallic monomer. The literature reports certain reactions proceeding for several days.<sup>8</sup> The sluggish nature of the reactions determines the degree of polymerisation.<sup>13</sup> Ideally, higher degrees of polymerisation (DP),

that is, the length of the polymer chain as specified by the number of repeat units, are desired. Factors like increasing the reaction time and reaction temperature lead to undesirable side reactions, which in turn would lower the degree of polymerisation. Other factors such as chain transfer to the solvent or to the monomer and the stability of the propagating chain end also influence the rate of polymerisation.

In addition to homopolymerisation studies, copolymerisation of the metal-carbon  $\pi$ -bonded organometallic monomers with organic monomers has also been extensively investigated.<sup>5,7,8,10</sup> The copolymerisations proved to be very successful using organic monomers such as styrene, methyl acrylate, methyl methacrylate, acrylonitrile and N-vinyl-2-pyrrolidone. The reactivity of a number of  $\pi$ -bonded organometallic monomers with organic monomers have been determined by using relative reactivity ratios.<sup>7,14</sup>

The polymerisation of a vast number of  $\eta^5$ -vinylcyclopentadienyl organometallic monomers is now well-established. Polymerisation studies of metal-carbon  $\sigma$ -bonded olefinic organometallic monomers is a neglected area<sup>15-17</sup>, in contrast to  $\eta^5$ -vinylcyclopentadienyl monomers. The present work centres on the polymerisation of some of the  $\sigma$ -bonded olefinic organometallic monomers, mentioned in CHAPTER 2. These include the following monomers :  $\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2)_2\text{CH}=\text{CH}_2$  (**I**),  $\text{Cp}(\text{CO})_2\text{FeCOCH}=\text{CH}_2$  (**II**),  $\text{Cp}(\text{CO})_2\text{FeCOCH}=\text{CHPh}$  (**III**),  $\text{Cp}(\text{CO})_2\text{FeCOC}_6\text{H}_4\text{CH}=\text{CH}_2$  (**IV**), and  $\text{Cp}(\text{CO})_3\text{WCOC}_6\text{H}_4\text{CH}=\text{CH}_2$  (**VIII**). These monomers were selected in order to establish the effect of (a) the position of the vinyl group relative to the metal and (b) changing the metal atom on the rate of polymerisation. In addition, the results of the copolymerisation of monomers **II**, **III**, **IV** and **VIII** with styrene are reported and

discussed. The polymeric complexes were fully characterised by IR,  $^1\text{H}$  NMR spectroscopy, Gel Permeation Chromatography and thermogravimetry.

### 3.2 Results and Discussion

A variety of solution polymerisations were carried out using the organometallic monomers that have been prepared in our study. Apart from homopolymerisations, copolymerisations with styrene were also studied. The monomers were dissolved in toluene and polymerised under free-radical initiation conditions using AIBN as the initiator. In this study, it was found that, generally, several reinitiations at 2 hourly intervals were necessary for polymerisations to occur and to produce more soluble materials. For single, one-off addition of the initiator, low yields of insoluble products were produced, with most of the starting material being recovered. These insoluble solids are intractable and therefore difficult to characterise. They were later confirmed, by IR comparison, also to be polymeric organometallic materials. The yields and solubility of the products can be increased significantly by the periodic addition of the initiator. This is consistent with previous studies on compounds like vinylferrocene (**I**) and other  $\eta^5$ -vinylcyclopentadienyl organometallic complexes.<sup>2,3,8</sup> Hayes and George<sup>18</sup> have studied and compared the reactivities of vinylferrocene **I** toward single and multiple addition of the initiator AIBN. Their studies have shown that high conversions to more soluble polymers occur for multiple reinitiations with the free-radical catalyst. Thus the new compounds **IV** and **VIII** were homopolymerised and copolymerised under multiple reinitiation conditions, and the products were fully characterised. Monomers **I**, **II** and **III** were homopolymerised under similar conditions, but gave less soluble products and were only partially characterised.

### 3.2.1 Polymerisation studies of monomer **IV**

The vinyl monomer **IV** could be homopolymerised, and copolymerised with styrene in toluene in high yields. This reaction has shown that monomer **IV** has a greater reactivity to free-radical polymerisation, compared to other  $\pi$ -bonded vinyl organometallic monomers and even the  $\sigma$ -bonded transition metal vinylbenzyl complexes **11-13** (see CHAPTER 1). For example, the homopolymerisation of **IV** proceeded in toluene solution for 2 days to produce the homopolymer **IX**. The polymer was precipitated in hexane to remove any traces of unreacted monomer, giving a pale yellow solid in 55% yield (based on the organometallic monomer). Although the reaction was reinitiated every two hours with AIBN, a small amount of toluene-insoluble polymeric material (20%) was still obtained. This was isolated by filtration from the cooled reaction mixture.

The copolymer **X**, obtained by the AIBN initiated reaction of **IV** with styrene in toluene, was also precipitated in hexane and gave high yields of a pale yellow solid. Again the reaction was subjected to multiple reinitiation by several readditions of the initiator. The organometallic monomer and organic monomer were reacted in a 1:4 molar ratio. The reaction conditions and results from the free-radical polymerisations are tabulated in Table 3.1 and Table 3.2.

**Table 3.1** : Free-radical (AIBN) homopolymerisation of monomers **I-IV**, **VII** and **VIII**

| Monomer (mass) <sup>a</sup> | AIBN, wt-% <sup>b</sup> | Total time (d) | Temp. (°C) | Recovered monomer (g) | Yield (g) <sup>d</sup> |
|-----------------------------|-------------------------|----------------|------------|-----------------------|------------------------|
| <b>I</b> (0.328g)           | 1.83                    | 7              | 70         | 0.141                 | I = 0.0200             |
| <b>II</b> (0.291g)          | 2.06                    | 3              | 70         | 0.197                 | S = 0.0771             |
| <b>III</b> (0.301g)         | 2.00                    | 6              | 80         | 0.170                 | S = 0.028, I = 0.003   |
| <b>IV</b> (0.300g)          | 2.00                    | 2              | 75         | <b>c</b>              | S = 0.165, I = 0.0609  |
| <b>VIII</b> (0.200)         | 2.40                    | 4              | 60         | <b>c</b>              | S = 0.066, I = 0.0954  |

<sup>a</sup> The mass of the starting monomer is recorded in parentheses; solution polymerisations used ratios of 0.3g monomer to 3ml toluene; in some cases an additional amount of toluene was added to solubilise the starting material.

<sup>b</sup> Weight percent of AIBN based on organometallic monomer; the same amount of initiator was added at 2 hourly intervals.

<sup>c</sup> None of the starting monomer was recovered.

<sup>d</sup> S and I denote the yields of the toluene-soluble and toluene-insoluble polymeric fractions, respectively.

**Table 3.2** : Free-radical (AIBN) copolymerisation of monomers **II**, **III**, **IV** and **VIII** with styrene

| <b>Organometallic Monomer <sup>a</sup></b> | <b>Organic Monomer <sup>b</sup></b> | <b>Feed Ratio <sup>c</sup></b> | <b>Reaction Time (d)</b> | <b>Temp. (°C)</b> | <b>Yield (g)</b> |
|--|-------------------------------------|--------------------------------|--------------------------|-------------------|------------------|
| <b>II</b> (0.265g)                         | Styrene<br>(0.490g)                 | 1:4                            | 4                        | 80                | 0.173            |
| <b>III</b> (0.252g)                        | Styrene<br>(0.405g)                 | 1:4                            | 2                        | 90                | 0.0407           |
| <b>IV</b> (0.250g)                         | Styrene<br>(0.368g)                 | 1:4                            | 2                        | 80                | 0.409            |
| <b>VIII</b> (0.246g)                       | Styrene<br>(0.224g)                 | 1:4                            | 4                        | 60                | 0.290            |

<sup>a</sup> The mass of the organometallic monomer is recorded in parentheses.

<sup>b</sup> The mass of the organic monomer is recorded in parentheses.

<sup>c</sup> Feed ratio of organometallic monomer to organic monomer.

### *IR Spectra*

The IR spectra show absorptions of the terminal carbonyls at 2015 and 1957  $\text{cm}^{-1}$  for the homopolymer **IX** and at 2017 and 1958  $\text{cm}^{-1}$  for the copolymer **X** (Scheme 3.1). There is a slight decrease ( $\sim 5\text{-}7 \text{ cm}^{-1}$ ) in the terminal carbonyl stretching frequencies compared with those of the monomer **IV**. This implies that although there is a slight change in the environment of the iron centre, the greater environment of the polymer is still similar to that of the monomer. The solids were examined using DRIFTS in a KBr matrix. We found it important to study the full range IR spectra of these polymers in the solid state, as their solution spectra in the carbonyl region are almost identical to that of the starting monomer. Comparison of the IR spectra of the toluene-soluble and toluene-insoluble homopolymer fractions shows them to be identical. This serves as confirmation of the polymeric nature of the toluene-insoluble fraction. Absorptions for the acyl group occur at similar stretching frequencies for the monomer **IV**, as observed in the solid state IR spectra for both the monomer and polymer. This confirms the presence of the iron-acyl linkage in the polymer and shows that the acyl grouping is retained and able to withstand polymerisation. A comparison between the IR spectra of **IX**, **X** and polystyrene is shown in Figure 3.1

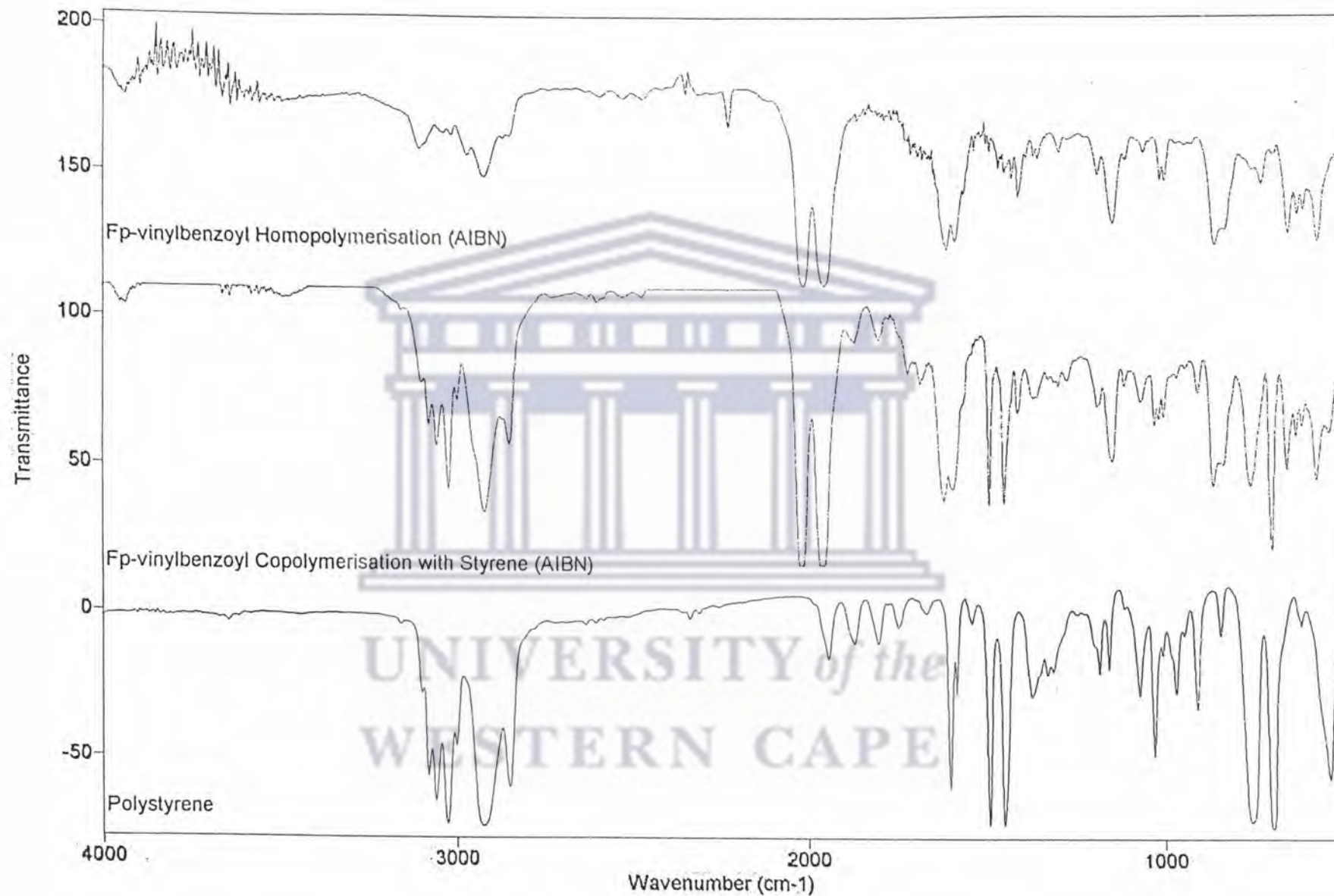
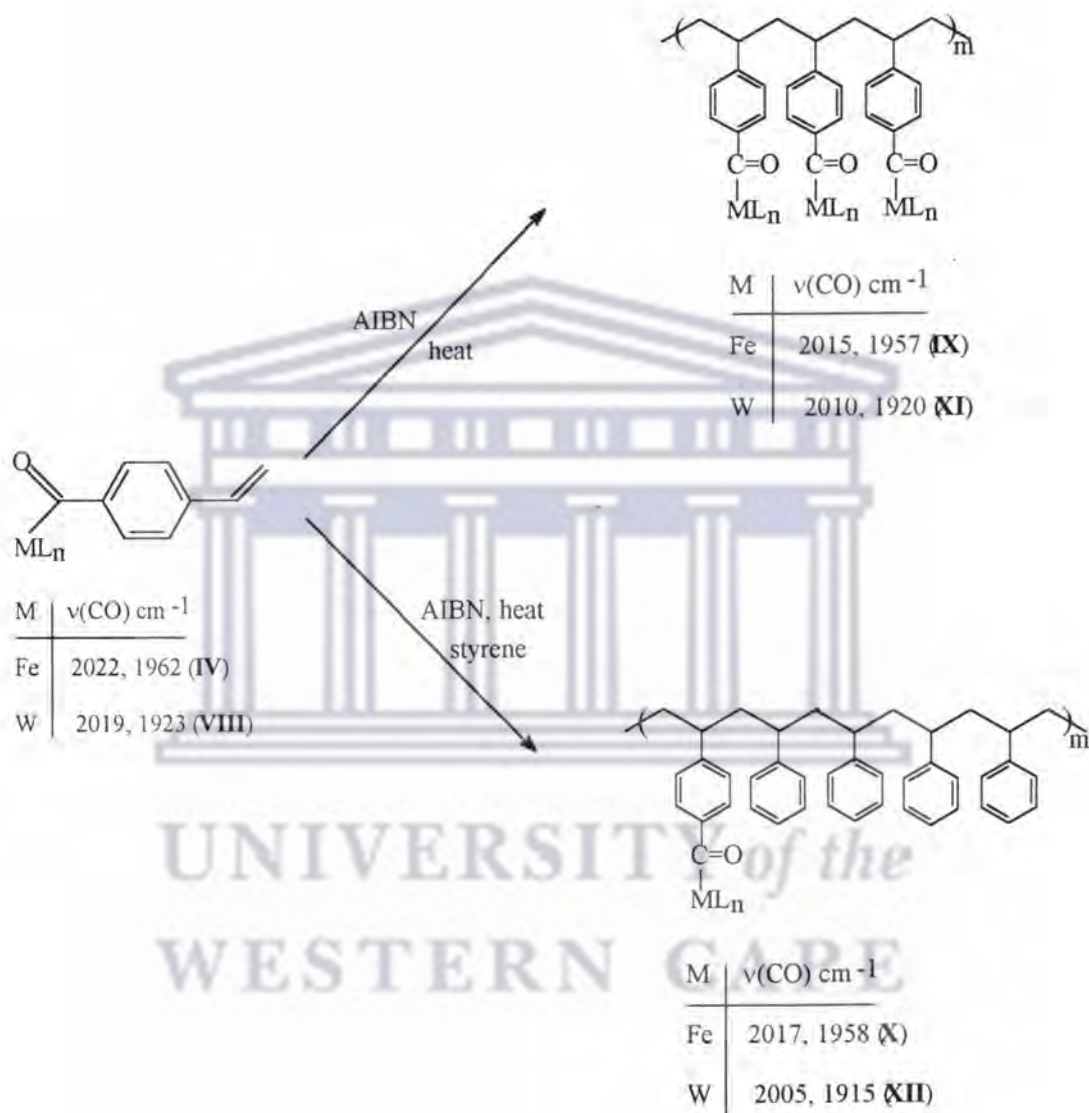


Figure 3.1 IR Spectra (DRIFTS, KBr matrix) of homopolymer **IX**, copolymer **X** and polystyrene





Scheme 3.1

### *NMR spectra of polymers IX and X*

The  $^1\text{H}$  NMR spectrum of the homopolymer **IX** was recorded in  $\text{CDCl}_3$  but does not show any well-resolved peaks (Figure 3.2). A broad multiplet is found at 0.80-1.60 ppm and can be assigned to the backbone hydrogens of the polymer. The broad resonance at 4.92 ppm represents the cyclopentadienyl protons and the broad multiplet at 7.12-7.50 ppm represents the aromatic protons. More importantly, the absence of the resonances at 5.32 ppm, 5.81 ppm and 6.72 ppm, due to the vinyl protons of monomer **IV** in the spectrum presents proof for the formation of the homopolymer. The peak broadness in the  $^1\text{H}$  NMR spectra also clearly show the transition from an organometallic molecule to a polymer-like structure. The  $^1\text{H}$  NMR spectrum of the copolymer **X** (Figure 3.3) was also recorded in  $\text{CDCl}_3$ . Broad resonances upfield in the spectrum at 0.8-2.1 ppm represent the aliphatic protons of the polymer. A broad singlet for the cyclopentadienyl protons is found at 4.86 ppm and two broad resonances at 6.85 and 7.08 ppm are assigned to the aromatic protons.

### *GPC studies and elemental analyses of IX and X*

The average molecular weight ( $M_w$ ) of toluene-soluble homopolymer **IX** as determined by GPC was 2343, with a polydispersity index ( $M_w/M_n$ ) of 1.71. This analysis indicates that the degree of polymerisation (DP) is small for this material. This suggests the formation of some oligomeric material rather than a polymer. Studies on organic polymers like polyphenylacetylene<sup>19</sup> have shown that, when using multiple reinitiations to achieve higher conversions to more soluble polymers, lower molecular weights are obtained. It is suggested that some intramolecular chain transfer reaction occurs, thus limiting the molecular weight. We have produced some normal polystyrene (Table 3.1) under the same

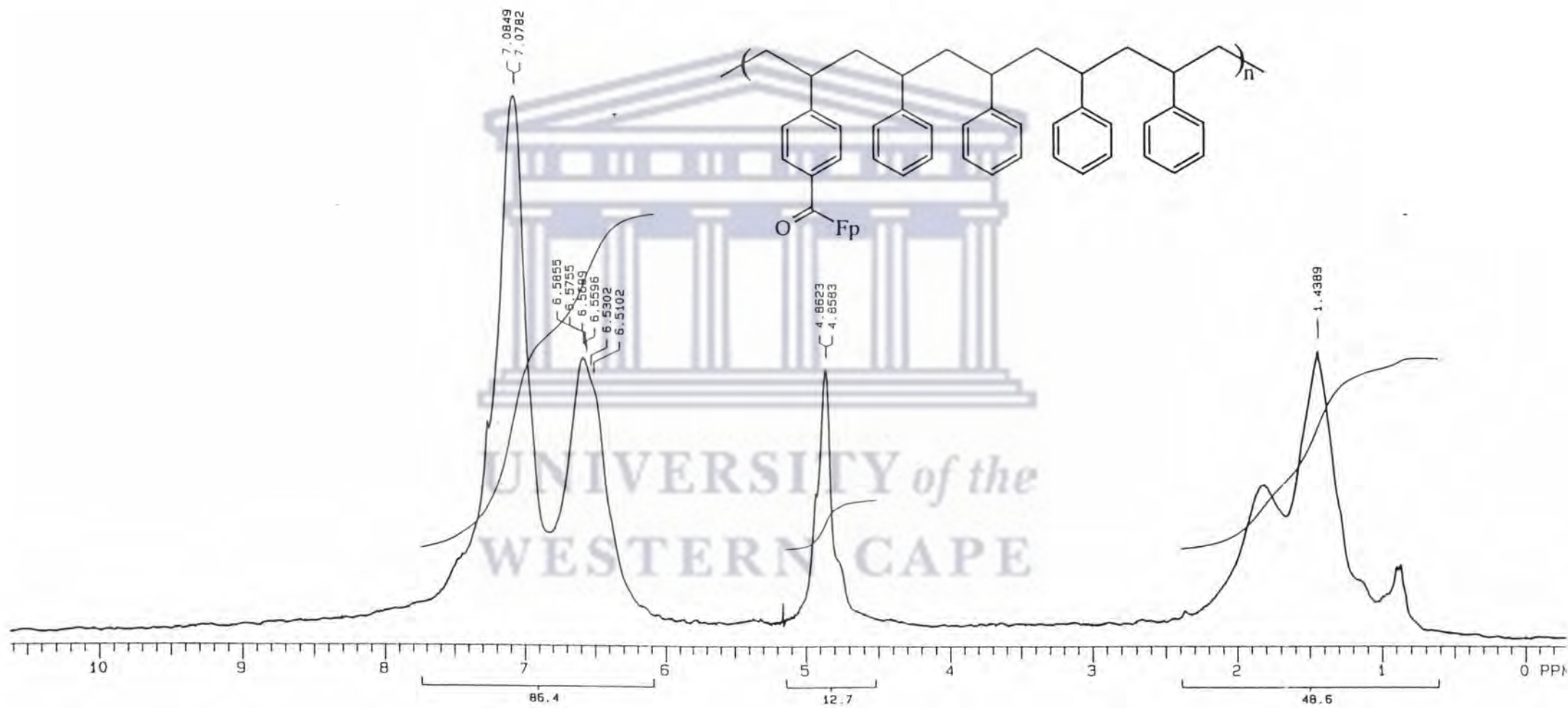
conditions employed for homopolymer **IX**, again using multiple re-initiations of AIBN. This also gave rise to low molecular weight polystyrene of  $M_w = 6286$  and a polydispersity index of 1.87. Polymer **IX** can be regarded as a metal-containing derivative of polystyrene. The lower  $M_w$  of **IX**, compared to polystyrene, is therefore expected since the greater steric bulk of the metal centre should significantly retard the degree of polymerisation. The relatively small polydispersity value for **IX** indicates a narrow distribution of varying chain lengths. As mentioned earlier, a small amount of insoluble homopolymer was also isolated. This fraction was insoluble in most common organic solvents like  $\text{CH}_2\text{Cl}_2$ , hexane, THF, toluene and benzene. This can possibly be ascribed to the high degree of cross-linking, typical of vinylphenyl groups, giving rise to insoluble compounds. Cameron and Green have prepared transition metal macrocyclic compounds<sup>20</sup> with pendant polymerisable groups. The copolymers produced contained extensively cross-linked macrocyclic groups. The elemental analysis, performed by ICP, gave an iron content of 13% in the case of the homopolymer, close to the expected metal content (18%) for this homopolymer. The lower value obtained seems to suggest that some chain transfer reaction may be occurring.

The copolymer **X** has a molecular weight of 21114, according to GPC studies versus polystyrene standards. A single peak distribution ( $M_w/M_n = 1.99$ ) was found indicating that a pure copolymer was obtained and not a mixture of homopolymers. Elemental analysis gave an iron content of 5.10%. The copolymerisation of **IV** with styrene was carried out in an initial molar ratio of 1:4 of organometallic monomer to organic monomer. Hence, the rate of incorporation of the organometallic monomer with the organic monomer is slightly less than the feed ratio (7.73%). This implies that the organometallic unit is not incorporated for every four units of styrene.

Figure 3.2 <sup>1</sup>H NMR spectrum of homopolymer IX



Figure 3.3  $^1\text{H}$  NMR spectrum of copolymer X



### *Scanning Electron Microscopy Studies*

Polymers **IX** and **X** were also examined using a scanning electron microscope. Micrographs of the homopolymer **IX** are shown in Appendix A and those of the copolymer **X** are shown in Appendix B. The micrographs show the homopolymer to have a uniform surface, whereas the copolymer consists of finer amorphous particles. The homopolymer and copolymer appear to have small pores, with larger depressions observed for the copolymer surfaces. A lighter material is seen to coat the porous copolymer. The micrographs of the homopolymer show a homogeneous surface.

### *Thermal properties of IX and X*

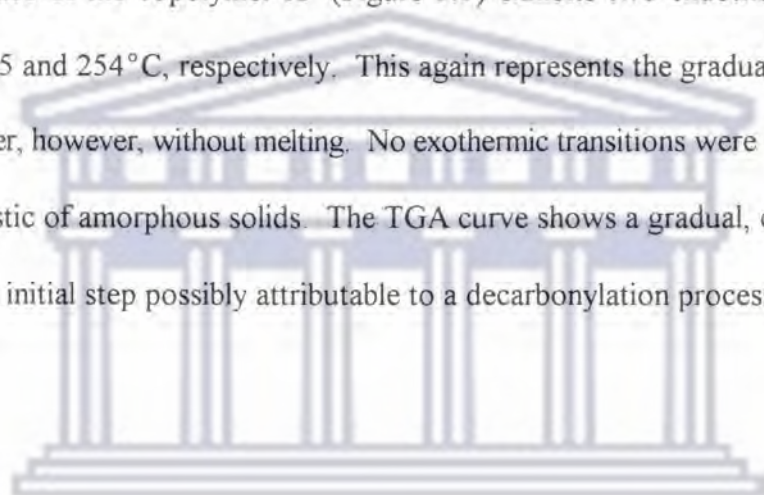
Thermal features of homopolymer **IX** and copolymer **X** were studied by differential scanning calorimetry (DSC) and thermogravimetry (TGA) at a heating rate of 10.0°C/min and 20.0°C/min respectively, under a nitrogen atmosphere.

The DSC traces for these organometallic polymers are characterised by broad endotherms, with a dropping baseline, unlike the sharp melting endotherms observed for monomer **IV**. The DSC thermogram for homopolymer **IX** (Figure 3.4) shows an endothermic transition centred at 193°C, with the onset of decomposition occurring at 160°C. Upon further heating, an exothermic transition is observed at 215°C. The endothermic transition in the DSC trace represents the melting before decomposition of the homopolymer. This correlates with our observation when heating the homopolymer on a Fisher-Johns hotstage. The exothermic transition is attributed to some crystallisation process that occurs after further heating. This phenomenon is similar to the behaviour in certain organic polymers

that melt before decomposition.<sup>22,23</sup> This effect results from molecules that are freer to move and can therefore rearrange into the regular structures of crystals.

The TGA curve of **IX** (Figure 3.4) shows that its thermal degradation occurs in two steps, starting at 87°C. The first step suggests, by percentage mass calculation, a decarbonylation step with the loss of the acyl carbonyls. This is followed by gradual mass loss to 270°C, starting at 183°C, associated with the decomposition of the complex.

The DSC trace of the copolymer **X** (Figure 3.5) exhibits two endothermic transitions centred at 195 and 254°C, respectively. This again represents the gradual decomposition of the polymer, however, without melting. No exothermic transitions were recorded, which is characteristic of amorphous solids. The TGA curve shows a gradual, continuous mass loss, with an initial step possibly attributable to a decarbonylation process.



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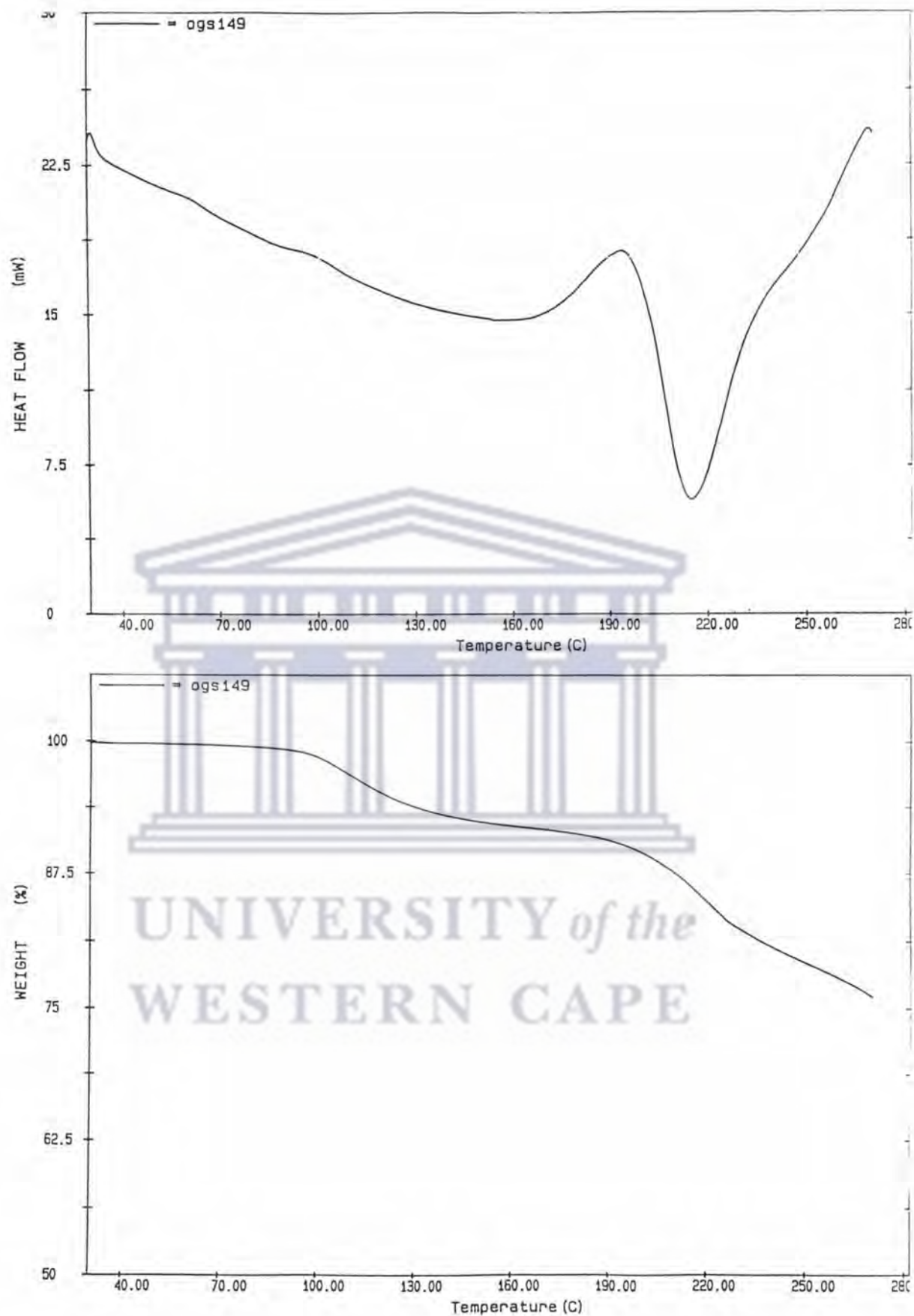


Figure 3.4 DSC trace (above) and TGA trace (below) for homopolymer **IX**



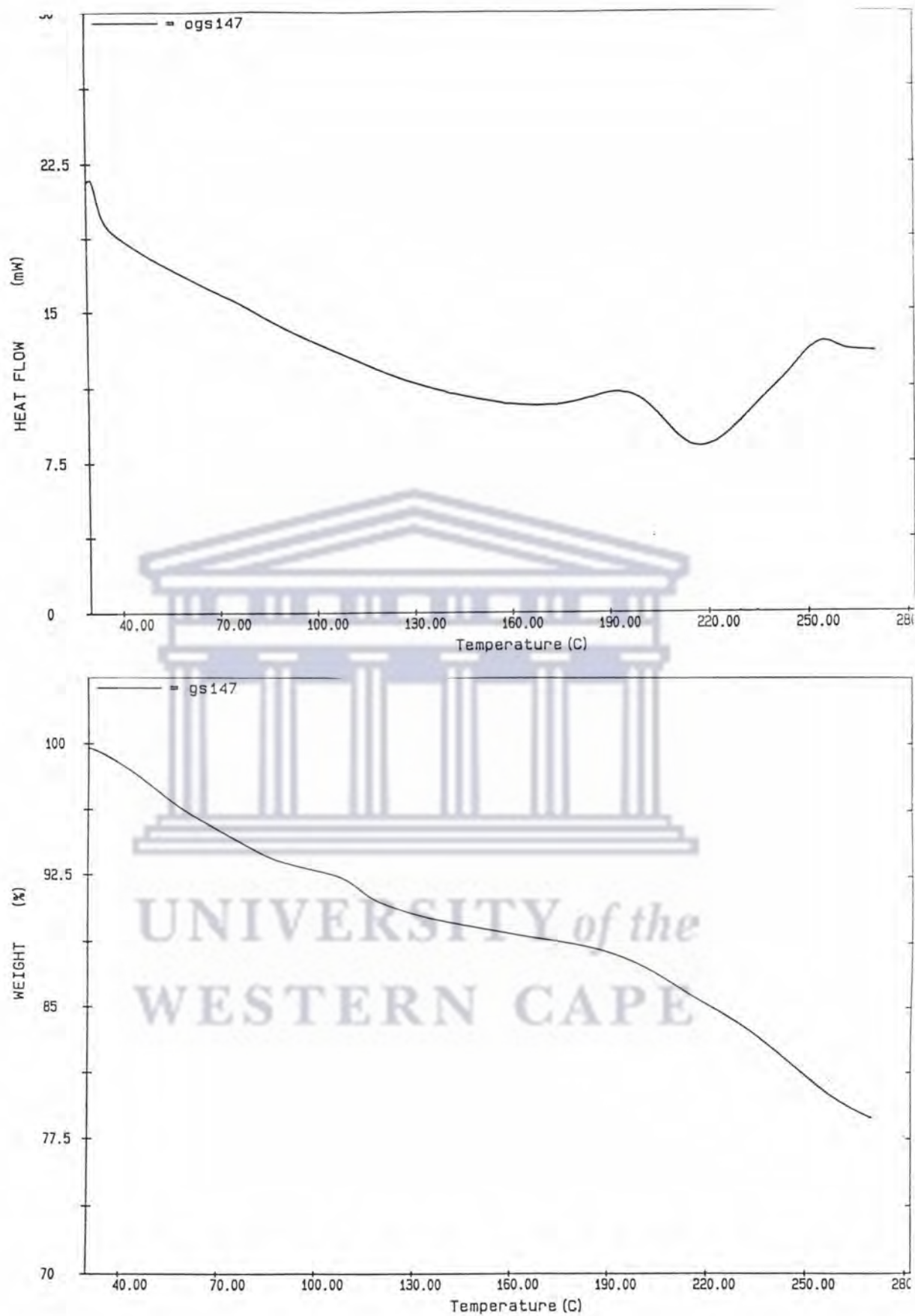


Figure 3.5 DSC trace (above) and TGA trace (below) for copolymer X

### 3.2.2 Polymerisation studies of monomer **VIII**

All polymerisation reactions with **VIII** were conducted at 60°C under nitrogen using AIBN initiation. Both the homopolymerisation and copolymerisation with styrene were accomplished in toluene solution and polymers were precipitated in hexane. Purification of the polymers was done by reprecipitation from toluene in hexane. The homopolymer (**XI**) was isolated as a light yellow solid in 33% yield (based on the organometallic monomer). This reaction was allowed to proceed for 4 days. Monomer **VIII** appears to be more reactive than the tungsten vinylbenzyl complex **12**, which was polymerised<sup>17</sup> in 20% yield. This may be due to the greater stability of the metal-benzoyl bond. However, the yield for the homopolymer is considerably lower than that of the corresponding iron analogue **IX** prepared in this study. This can be ascribed, first of all, to the lower reaction temperature that is used. The monomer **VIII** decomposes at 95°C. Care should thus be taken not to conduct polymerisations close to this temperature, as the monomer is thermally unstable at temperatures greater than 70°C. The reaction mixture is observed to turn black and decomposition occurs during the course of the reaction. This is also true for other tungsten and molybdenum macromolecular complexes, in which mainly insoluble products are formed.<sup>21</sup>

Secondly, the longer reaction time also gave rise to the formation of more toluene-insoluble products, identified to be polymeric material. The yield of toluene-insoluble products exceeded the yield of the toluene-soluble product, despite reinitiating the reaction at 2 hour intervals.

### *IR and NMR studies of polymers XI and XII*

The IR absorptions at 2010 and 1920  $\text{cm}^{-1}$  (Nujol) for the terminal carbonyls, are characteristic of tungsten acyl linkages for homopolymer **XI**. In the IR spectra of copolymer **XII**, absorptions at 2005 and 1915  $\text{cm}^{-1}$  indicate the presence of a tungsten moiety.

A  $^1\text{H}$  NMR spectrum of **XI** (Figure 3.6) was recorded in  $\text{CDCl}_3$ . This shows a multiplet of resonances at 1.00-1.70 ppm, which is where saturated C-H protons appear. A single, sharp peak at 5.72 ppm represents the cyclopentadienyl protons and a broad multiplet at 7.10-7.53 ppm represents the aromatic protons. A prominent feature of this spectrum is the absence of the vinyl protons. The  $^1\text{H}$  NMR spectrum of the copolymer **XII** (Figure 3.7) was also recorded in  $\text{CDCl}_3$  and exhibited a broad multiplet centred at 1.52 ppm, probably due to the aliphatic protons. A single broad resonance for the cyclopentadienyl protons is found at 5.71 ppm and two broad resonances for the aromatic protons can be found at 6.61 and 7.12 ppm respectively.

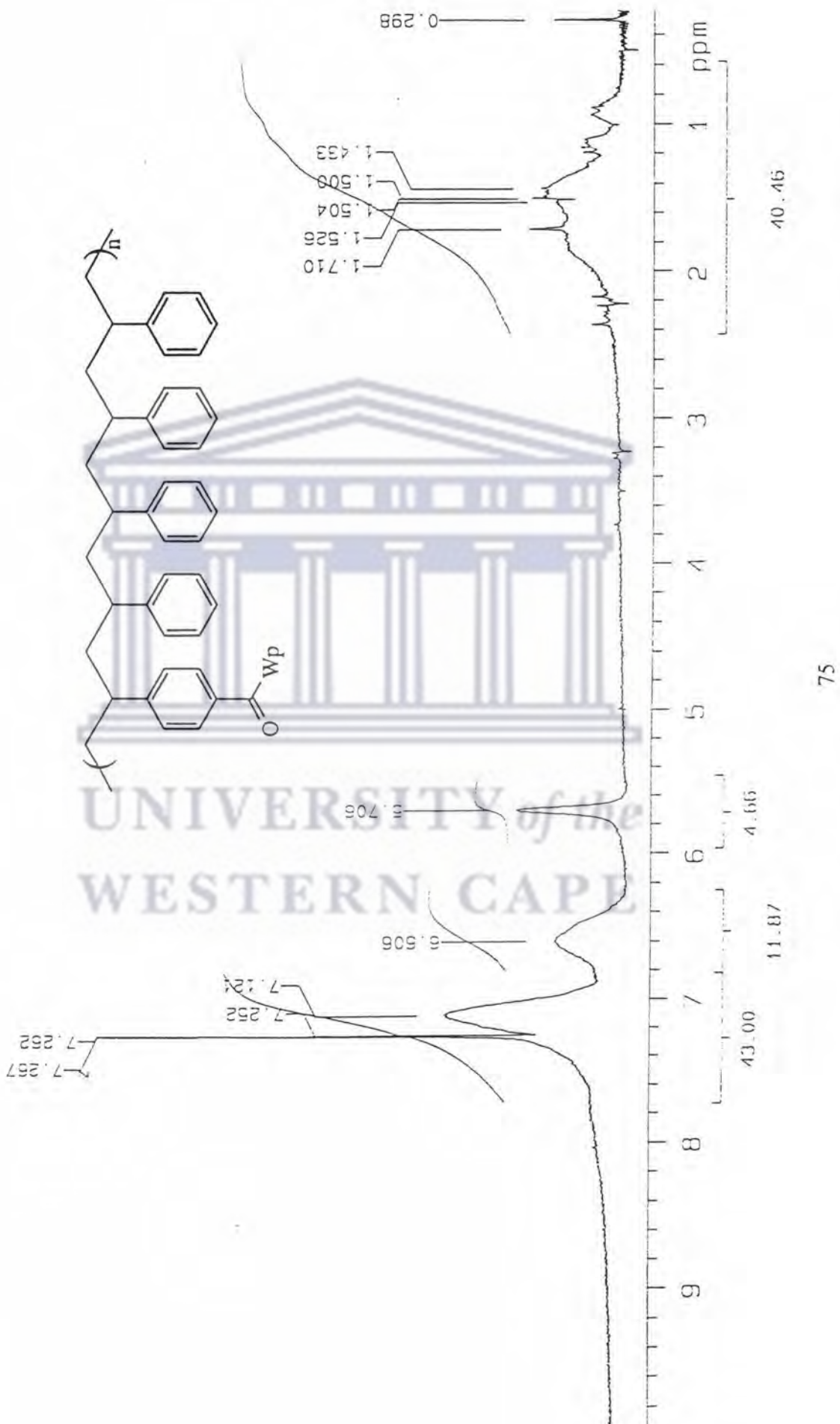
### *GPC studies of XI and XII*

As a result of the very low yields obtained for homopolymer **XI**, which was prepared from monomer **VIII**, the molecular weight distribution for this compound could not be estimated.

Figure 3.6 <sup>1</sup>H NMR spectrum of homopolymer XI



Figure 3.7 <sup>1</sup>H NMR spectrum of copolymer XII



The copolymer **XII** gave a moderate molecular weight of 22100, according to GPC studies versus polystyrene standards. This molecular weight is fairly low, in comparison to copolymers produced by Pittman and others. A feature of note in the GPC trace is the broad molecular weight distribution ( $M_w/M_n = 4.68$ ). This shows that the distribution of chain lengths for this polydispersed copolymer is large, suggesting a highly branched material.

#### *Scanning Electron Microscopy Studies*

The tungsten homopolymer **XI** and copolymer **XII** were examined using a scanning electron microscope. A micrograph of the homopolymer is shown in Appendix C and micrographs of the copolymer are shown in Appendix D. None of the distinguishing features observed for the iron analogue **IX** were evident in the micrograph of the tungsten homopolymer, which appears to have a homogeneous composition. The copolymer **XI**, like the iron analogue, also shows a lighter material across its surface. Also evident are the small depressions or pores, which were observed for both the iron homopolymer **IX** and copolymer **X**.

### *Thermal Properties of XI and XII*

The thermal properties of **XI** and **XII** were also studied by DSC and TGA at a heating rate of 10.0°C/min, under a nitrogen atmosphere. As was the case in the iron analogues, broad endotherms are observed in the DSC traces for both the homopolymer and copolymer. The DSC trace for the homopolymer **XI** (Figure 3.8) shows a small, broad endotherm centred at 64°C. This is associated with the onset of decomposition, which correlates well with our observations on the Fisher-Johns hotstage. Two large exothermic transitions are centred at 118 and 167°C in the DSC trace. Since the polymer melts with decomposition, and not before decomposition, we suggest that some polymer phase change is occurring, which is responsible for this exothermic heat flow. The TGA curve does not show an appreciable mass loss (11%) up to 200°C. Thermal degradation is observed to start from 117°C, and no fragment could be assigned to this weight loss. The copolymer **XII** (Figure 3.9) exhibits an endotherm at 143°C, which compares favourably with the decomposition temperature recorded on the Fisher-Johns hotstage. As was the case for the homopolymer, a weight loss of approx. 3% is observed from 119 to 200°C, again without any definite assignment being made possible.

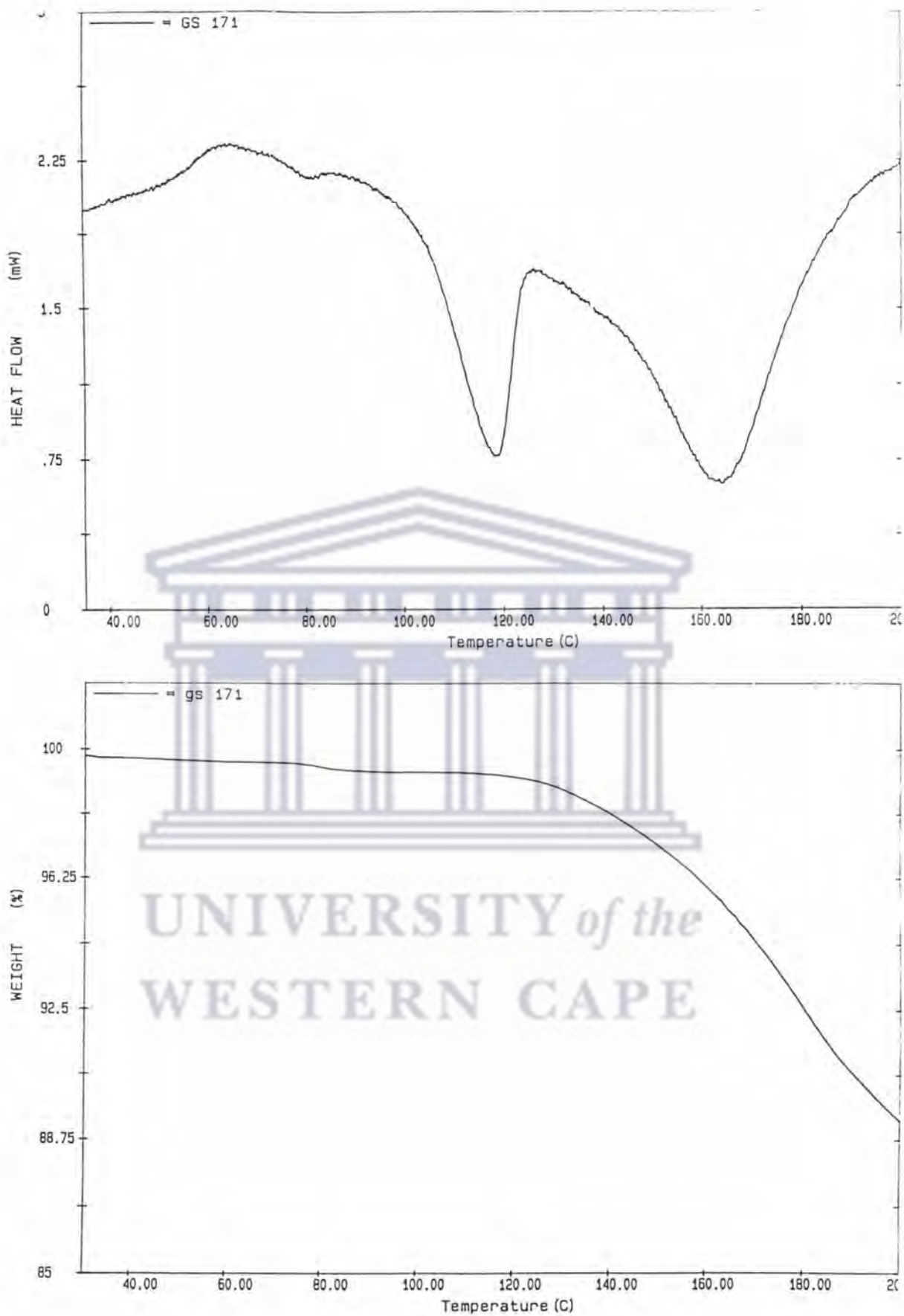


Figure 3.8 DSC trace (above) and TGA trace (below) for homopolymer **XI**



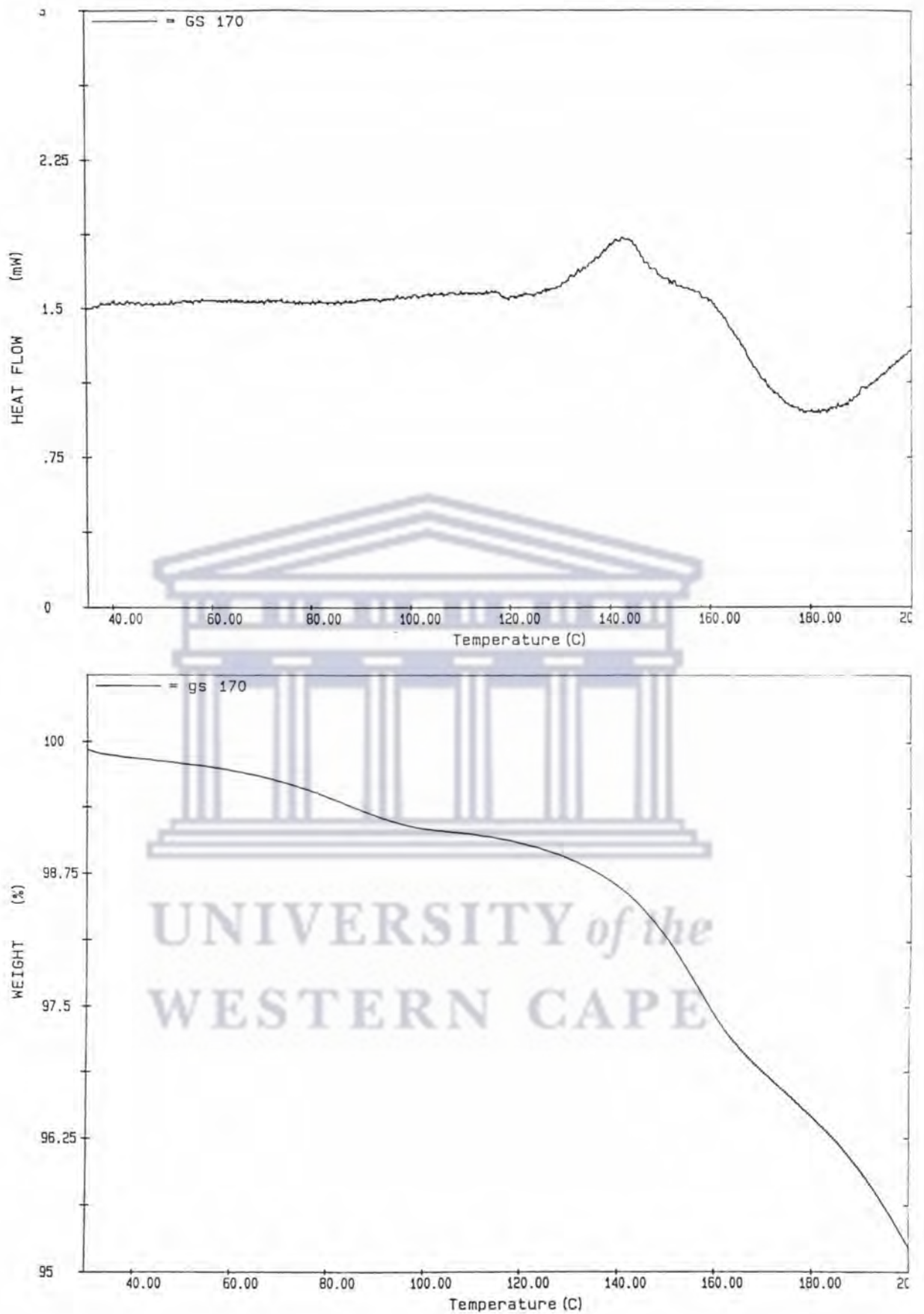


Figure 3.9 DSC trace (above) and TGA trace (below) for copolymer **XII**

### 3.2.3 Polymerisation studies of monomers **I**, **II** and **III**

Monomers **I**, **II** and **III** have also been polymerised with AIBN in toluene solution, using multiple re-initiation with the free-radical catalyst under similar conditions as for monomers **IV** and **VIII**. These reactions produced brown solids with low solubilities, thus hindering a complete characterisation. This study has revealed a large difference in the reactivities of the vinyl substituents bonded to the metal centre.

Monomer **I**, the iron-alkenyl compound, produced an intractable dark brown polymerisation product which is completely insoluble in most organic solvents. The brown solid was observed to precipitate out of solution during the course of the reaction, and we speculate that this insoluble fraction may be some high molecular weight polymer. This is similar to the observation made from the polymerisation of **IV** and **VIII**, where IR characterisation showed the toluene-soluble and toluene-insoluble fractions to be identical. Monomer **I** contains a pendant vinyl moiety which probably undergoes extensive cross-linking, giving rise to these insoluble materials. Apart from recovering most of the starting material (Table 3.1), a small amount of the dimer  $[\text{CpFe}(\text{CO})_2]_2$  was isolated. No dimer formation was observed when **I** was heated in toluene under the same polymerisation reaction conditions, but without the addition of the polymerisation catalyst AIBN. This implies that AIBN initiated polymerisation induces alkyl metal-carbon bond cleavage, giving rise to the formation of radicals. This was not observed for the acyl complexes.

The homopolymerisation of monomers **II** and **III** also gave brown solids which were slightly more soluble than the product from **I** in organic solvents like  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ . However, the solids gave very dark brown solutions, hindering complete characterisation.

As a result, characterisation of these compounds was limited to IR spectroscopy which showed terminal carbonyl bands similar to those of the starting monomer.

These polymerisation procedures followed the same workup as for monomers **IV** and **VIII**, precipitating the brown solids in hexane. We again propose the formation of some high molecular weight polymeric material. The position of the double bond on these monomers appears to play an important role in determining the extent of polymerisation (Table 3.1). For example, in monomer **II** the double bond is closer to the metal centre, in comparison to monomer **IV**. Being in a more crowded environment, we would thus expect a decrease in the rate of polymerisation, as shown by the lower yields in Table 3.1. The polymerisation product from **III** shows an even lower yield. This is because of greater steric constraints about the double bond, with a congested metal centre on one side and a bulky phenyl group on the other. Unlike monomers **IV** and **VIII**, these monomers do not have a styryl group shielding the double bond from the metal centre. The electron withdrawing effect of the metal centre thus further destabilises the chain end radical in monomers **I**, **II** and **III**, which in turn decreases the rate of polymerisation.

These brown solids were only studied by IR spectroscopy. Because of their low solubilities, NMR spectroscopy and GPC studies could not be performed. The solids do not melt nor do they show any visible thermal decomposition below 300°C. Thermoanalytical studies could also not be carried out as these solids are seen to stain the heating pans at 250°C. Because of the incomplete characterisation, other methods of analysis are necessary to support our findings. We suggest techniques such as solid-state NMR spectroscopy and fractionation, to estimate the size of the polymer.

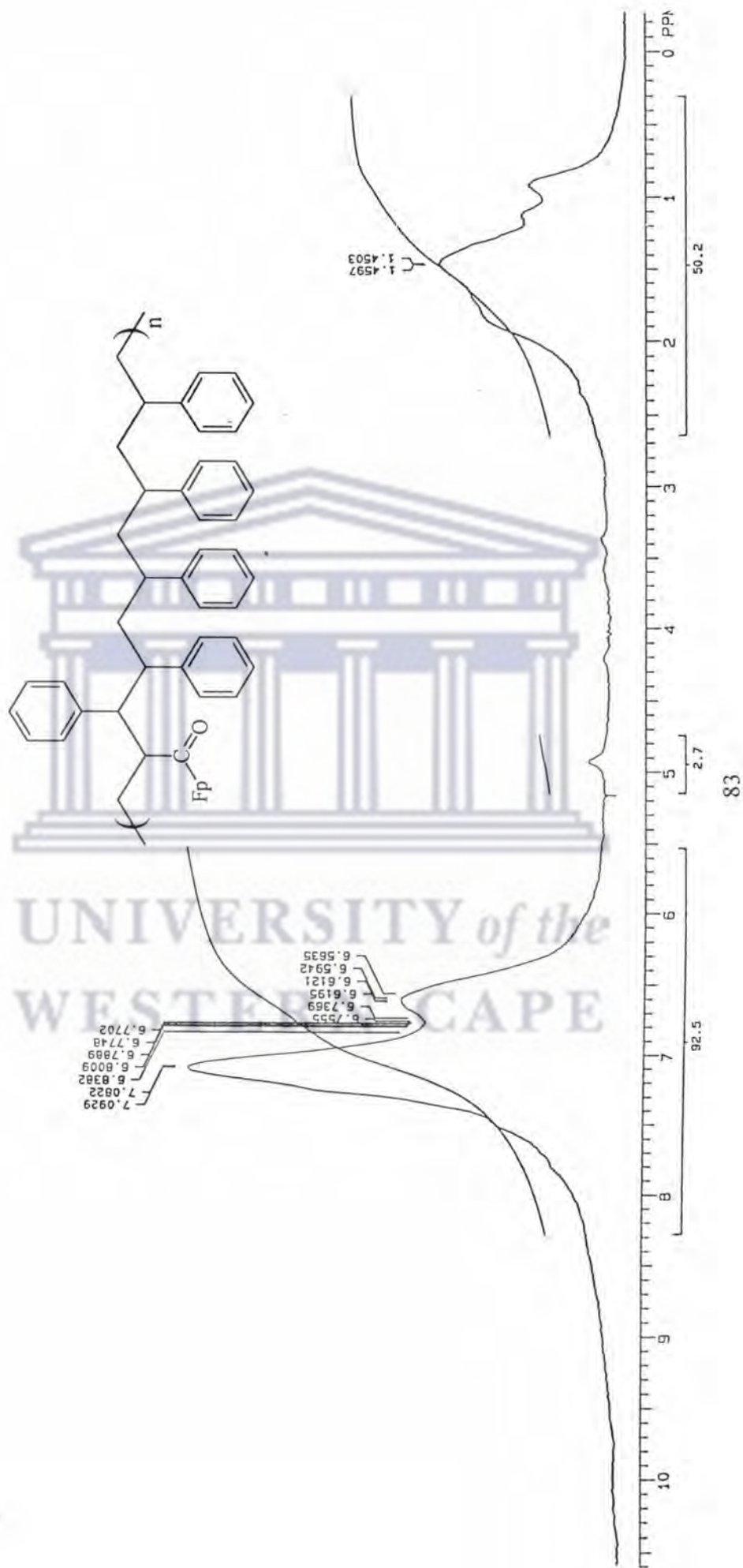
### 3.2.4 Copolymerisation studies of monomers **II** and **III** with styrene

Although the homopolymerisation studies of **II** and **III** did not produce tractable materials, we attempted to prepare more soluble polymers by copolymerising these monomers with styrene.

The copolymerisations were carried out with AIBN in toluene, using multiple additions of initiator. This gave rise to light brown amorphous solids which we were able to characterise by  $^1\text{H}$  NMR spectroscopy and solid-state IR spectroscopy. This study has added weight to our conclusions that monomers **II** and **III** are very sluggish to polymerisation, because of the steric environment around the double bond. We have found that there is very little incorporation of the organometallic unit in the copolymer, which consists mainly of polystyrene. This was evident in the IR spectra of the copolymers which shows the terminal carbonyl bands to be of weak intensity. This is unlike the strong, sharp bands which were observed for the terminal carbonyls of the iron-vinylbenzoyl copolymer **X**, confirming its incorporation in the polymer backbone.

$^1\text{H}$  NMR spectra for copolymer **XIII** (Figure 3.10), obtained by the reaction of **III** with styrene in toluene, also shows the low incorporation. The main features in this spectrum are the broad resonances upfield due to the backbone hydrogens and the broad resonances downfield arising from the aromatic protons. A very small broad peak is observed around 5ppm and represents the cyclopentadienyl protons of the organometallic moiety. This peak is normally larger, as is the case in the iron copolymer **X** (Figure 3.3), and is a good indication of the extent of incorporation. Thus, the small peak observed for copolymers **XIII** emphasises the small incorporation of the organometallic unit into the copolymer. Further studies were not performed on these polymers.

Figure 3.10  $^1\text{H}$  NMR spectrum of copolymer XIII



### 3.3 Conclusion

The new organometallic monomers  $\text{CpM}(\text{CO})_n(\text{COC}_6\text{H}_4\text{CH}=\text{CH}_2)$  ( $\text{M} = \text{Fe}$ ,  $n=2$ ;  $\text{W}$ ,  $n=3$ ) were homopolymerised and copolymerised with styrene in toluene solution. The polymerisations were performed under free-radical conditions by multiple additions of the initiator (AIBN). Attempted homopolymerisations of the new monomers gave rise to the formation of soluble low molecular weight, oligomeric compounds rather than polymeric complexes. Copolymerisation reactions with styrene gave complexes with higher molecular weights. In both the iron and tungsten homopolymerisations, a toluene-insoluble polymeric fraction was isolated from the reaction mixture. This is thought to be an extensively cross-linked, high molecular weight polymer. The new organometallic polymers were characterised by IR and  $^1\text{H}$  NMR spectroscopy, GPC and thermogravimetry.

Homopolymerisation studies with monomers,  $\text{FpCOCH}=\text{CH}_2$  (**II**) and  $\text{FpCOCH}=\text{CHC}_6\text{H}_5$  (**III**) have shown a sharp decrease in the rate of polymerisation. This has shown that compounds with vinyl moieties adjacent to the metal and in sterically crowded environments are very sluggish to polymerisation, despite several reinitiations. The study has also revealed that chain end stability is influenced by the electronic factors of the metal centre. Homopolymerisations of **II** and **III** gave less soluble and intractable polymers. Copolymerisation reactions substantiated this finding, with very little incorporation of the organometallic moiety occurring in the polymer backbone. The alkenyl monomer **I** gave mainly insoluble polymerisation products, with radical-induced cleavage of the metal-carbon bond. This again shows the greater stability of metal-carbon acyl bonds over metal-carbon alkyl bonds.

### 3.4 Experimental

All polymerisations were performed under a nitrogen atmosphere using Schlenk tube techniques. Toluene and hexane were distilled from sodium/benzophenone under nitrogen. AIBN was purchased from Eastman Kodak and was recrystallised three times from hot diethyl ether, prior to use. Reagent grade styrene was used without further purification.

Infrared (IR) spectra were recorded using DRIFTS (diffuse reflectance infrared transmission spectroscopy) in a KBr matrix (unless otherwise stated) on a Perkin-Elmer Paragon 1000PC FT-IR spectrophotometer.  $^1\text{H}$  NMR spectra were recorded on a Varian XR200 spectrometer, using TMS as an internal standard and  $\text{CDCl}_3$  as solvent.

SEM and GPC analyses were performed at SOMCHEM, Somerset West. The micrographs were scanned on a ISI-DS130 Dual Stage Scanning Electron Microscope. Gel permeation chromatographic analysis of the molecular weight distribution of the polymers was performed on a system equipped with a Spectra Physics RI detector, Spectra Physics LC pump and Spectra Physics Winner software. A series of four 300 mm x 7.8 mm columns were packed with 10  $\mu\text{m}$  packing material of phenogel (styrene-divinylbenzene). These had pore sizes of 100  $\text{\AA}$ , 500  $\text{\AA}$ , 10<sup>3</sup>  $\text{\AA}$  and 10<sup>4</sup>  $\text{\AA}$ . The eluting solvent was THF at a flow rate of 1.25 ml/min. The system was calibrated against polystyrene standards, Mp 580, 1320, 5050, 7000, 11600, 66000 and 156000.

Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) data were performed at the University of Cape Town. The DSC and TGA traces were recorded on a Perkin-Elmer PC7 Series Thermal Analysis System at a scanning rate of 10 or 20  $^\circ\text{C}/\text{min}$  under  $\text{N}_2$  gas-purge with a flow rate of 30 ml/min. Samples for TGA were placed in an open platinum pan while those for DSC were placed in a crimped, vented aluminium pan with an empty pan used as reference. The TG analyser was calibrated using built-in

procedures for furnace and weight calibration. The Curie points for alumel ( $163^{\circ}\text{C}$ ) and perkalloy ( $596^{\circ}\text{C}$ ) were also used to calibrate the furnace. The DSC analyser was calibrated using the melting points of indium ( $156^{\circ}\text{C}$ ) and zinc ( $419^{\circ}\text{C}$ ) and the enthalpy of melting of indium ( $28.5\text{ J/g}$ ).

AA spectroscopy was conducted on a Philips PU9100 spectrophotometer. The operating lamp current was 7 mA, while the slit width was 0.2 nm. An air-acetylene flame was used. ICP analyses were done on a JOBY YVON 70C with a plasma gas flow of 12 l/min, a nebuliser gas flow of 0.4 l/min and an inner gas flow of 0.2 l/min. Readings were taken at 14 mm above the coil, at 3.4 bar and using a sample aspiration rate of 2.0 ml/min.

#### 3.4.1 Polymerisation of IV

$\text{FpCOC}_6\text{H}_4\text{CH}=\text{CH}_2$  (0.300g, 0.970 mmol) was taken up in toluene (4.0 ml) in a nitrogen-purged Schlenk tube. AIBN (6.00 mg, 0.0366 mmol) was added to the yellow solution and the solution heated to  $70^{\circ}\text{C}$  in an oil bath. The reaction was stirred under reflux under a  $\text{N}_2$  atmosphere. The reaction was reinitiated every 2 hours with AIBN (6.00 mg, 0.366 mmol) and monitored by t.l.c. until all of the starting monomer was consumed. After 2 days, the reaction mixture was cooled to room temperature and filtered by gravity into another Schlenk tube containing hexane (30 ml). A yellow precipitate was observed to form. The mother liquor was removed and the precipitate washed thoroughly with hexane and dried. The homopolymer was dried and isolated as a light yellow solid (0.165g, 55% yield based on the organometallic monomer). An insoluble brown solid (69.0 mg) was filtered and isolated from the reaction mixture. This was confirmed by IR comparison to be some organometallic polymeric material.



### 3.4.2 Copolymerisation of **IV** with styrene

FpCOC<sub>6</sub>H<sub>4</sub>CH=CH<sub>2</sub> (0.250 g, 0.812 mmol) and styrene (0.45 ml, 3.89 mmol) were added to a N<sub>2</sub>-flushed Schlenk tube and taken up in toluene (3.0 ml). AIBN (5.00 mg, 0.0305 mmol) was added to the reaction vessel and the mixture heated under reflux to 80°C in an oil bath. The reaction was reinitiated everyday at 2 hourly intervals with AIBN (5.00 mg, 0.0305 mmol) and monitored by t.l.c. After 48 hours, the reaction was complete and the reaction mixture cooled to room temperature. The cooled solution was added dropwise to stirring hexane, resulting in a pale yellow precipitate. The solid was washed repeatedly with hexane and the dried in vacuo to yield a pale yellow powder (0.409g) as the copolymer.

### 3.4.3 Polymerisation of **VIII**

WpCOC<sub>6</sub>H<sub>4</sub>CH=CH<sub>2</sub> (0.200 g, 0.432 mmol) and AIBN (4.00 mg, 0.0244 mmol) were placed in a Schlenk tube, previously flushed with nitrogen. The mixture was taken up in toluene (5.0 ml) and the Schlenk tube fitted with a reflux condenser. The solution was heated gently to 60°C in an oil bath and stirred under reflux in a N<sub>2</sub> atmosphere. The reaction was reinitiated daily every 2 hours with AIBN (4.00 mg, 0.0244 mmol) and the consumption of the monomer monitored by t.l.c. The reaction was left for 4 days and the reaction mixture was then allowed to cool to room temperature. A toluene-insoluble precipitate settled at the bottom of the Schlenk tube. The supernatant liquid was syringed off and added dropwise to stirring hexane. A light yellow solid precipitated from solution. This solid was washed twice with hexane (20 ml), dissolved in toluene, reprecipitated from hexane (excess) and dried. A light yellow solid was collected (66.0 mg, 33% yield based

on the organometallic monomer) and identified to be the homopolymer **XI**. A dark yellow, toluene-insoluble fraction (95.4 mg) was filtered and isolated from the reaction mixture.

#### 3.4.4 Copolymerisation of **VIII** with styrene

In a N<sub>2</sub>-flushed Schlenk tube were placed WpCO<sub>2</sub> H<sub>2</sub> CH=CH<sub>2</sub> (0.246 g, 0.531 mmol), styrene (0.25 ml, 2.16 mmol) and AIBN (5.00 mg, 0.0305 mmol) in 5ml of toluene. The mixture dissolved to give a yellow solution. The solution was heated to 60°C in an oil bath and stirred under reflux in a N<sub>2</sub> atmosphere. The reaction was reinitiated daily with AIBN (5.00 mg, 0.0305 mmol) every 2 hours and the reaction monitored by t.l.c. After 4 days, a light yellow solid was precipitated in hexane and washed three times with hexane. This solid was reprecipitated from toluene in hexane to give 0.290g of the copolymer **XII**.

#### 3.4.5 Polymerisation of **I**, **II** and **III** (General Procedure)

For each homopolymerisation of monomers **I**, **II** and **III**, 0.300g of the monomer and AIBN (6.00 × 10<sup>-3</sup> g, 0.0366 mmol) were taken up in toluene (3-4 ml) and the solution heated to 70°C in an oil bath. The reaction was reinitiated with the same amount of AIBN at two hourly intervals. The toluene-insoluble fractions were filtered off, and a brown solid was precipitated from the filtrate using hexane. Yields can be found in Table 3.1.

#### 3.4.6 Copolymerisation of **II** and **III** (General Procedure)

In each case, 0.250g of the organometallic monomer and 0.400g of styrene were mixed in a Schlenk tube, and taken up in toluene (3 ml) in the presence of AIBN (5.00 mg, 0.0305 mmol). The solution was heated to 80°C and the polymers precipitated from hexane. Yields are included in Table 3.2.

### 3.5 References

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The logo of the University of the Western Cape, featuring a classical building with a pediment and six columns.

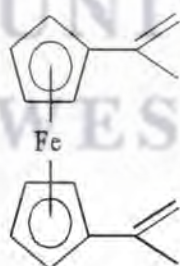
**CHAPTER 4**

**CATIONIC POLYMERISATION OF  
( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>(COC<sub>6</sub>H<sub>4</sub>CH=CH<sub>2</sub>)**

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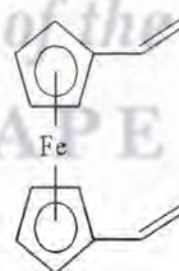
#### 4.1 Introduction

Very little has been reported in the literature on the cationic polymerisation reactions of organometallic monomers. This is probably due to the low reactivity of these compounds to cationic initiation. Cationic polymerisation reactions are reported to be initiated by Lewis acids such as  $\text{BF}_3\text{OEt}_2$  and  $\text{H}_2\text{SO}_4$ . The first cationic polymerisation of an organometallic compound was that of vinylferrocene **1**, reported by Kunitake and co-workers.<sup>1,2</sup> This was subsequently followed by work on other ferrocene derivatives. Later, Korshak and co-workers<sup>3</sup> polymerised 1,1'-diisopropenylferrocene **15** with cationic initiators. These polymerisations were, in most cases, not very successful and gave low molecular weight polymers. The only exception was the cationic polymerisation of 1,1'-divinylferrocene **16** which yielded products with molecular weights up to 35 000. 1,1'-Divinylferrocene was found to undergo cycloliner polymerisation using  $\text{BF}_3\text{OEt}_2$ .



**15**

Figure 4.1 1,1'-Diisopropenylferrocene

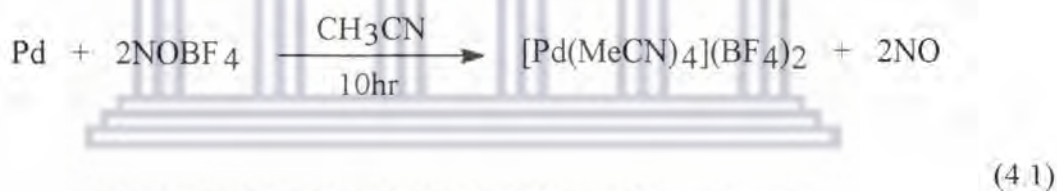


**16**

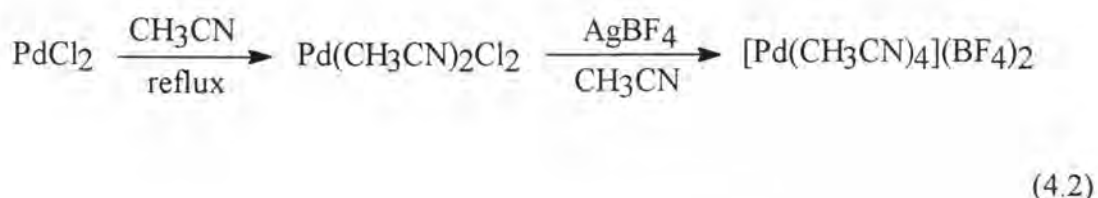
Figure 4.2 1,1'-Divinylferrocene

Most of the studies on cationic polymerisation were performed using  $\eta^5$ -vinylcyclopentadienyl metal monomers. For most cases, either no polymerisation reaction occurred or unsatisfactory results were obtained.

We have used the complex,  $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ , to polymerise the new  $\sigma$ -bonded olefinic organometallic monomer **IV** prepared during the course of this project. This solvated transition metal cation was prepared by Sen and Lai<sup>5</sup>, and has been reported to catalyse the polymerisation of a wide range of organic olefins and acetylenes, under mild conditions. Sen reported the polymerisation of styrene in acetonitrile (at ambient temperature) which occurred in 5 minutes with yields of 90%. These reactions are air- and moisture-sensitive, and involve the addition of 100 equivalents of the monomer to a  $1 \times 10^{-2}$  M solution of the catalyst. Schramm and Wayland prepared this compound starting from palladium metal and oxidising the metal with nitrosylfluoroborate in acetonitrile<sup>6</sup> [Equation 4.1]. Nitric oxide is evolved in the process.



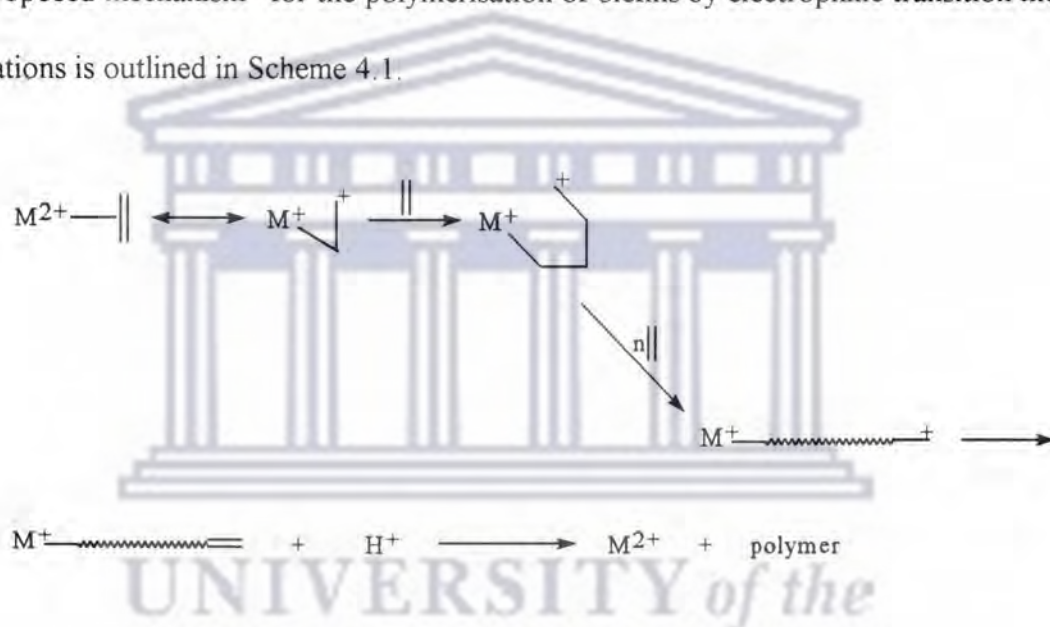
We have used a different route to the synthesis of this divalent cation. This is outlined in Equation 4.2.



Palladium chloride is heated to reflux in acetonitrile yielding an orange solution. After filtering the hot solution by gravity,  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ , an orange solid, precipitates as the solution cools to room temperature. This orange solid is then reacted with  $\text{AgBF}_4$  in

acetonitrile to generate the divalent cationic catalyst,  $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ , which is precipitated with anhydrous ether.

This homogeneous catalyst contains the weakly coordinating  $\text{CH}_3\text{CN}$  ligand and has noncoordinating counteranions. Olefins can replace the  $\text{CH}_3\text{CN}$  ligands in the coordination sphere of the metal, and interact with the electrophilic transition metal. This interaction generates carbonium ions, which allow for further attack by other olefins. The proposed mechanism<sup>7</sup> for the polymerisation of olefins by electrophilic transition metal cations is outlined in Scheme 4.1.



Scheme 4.1

These complexes are seen to have an advantage over traditional cationic catalysts, in that they can be used under mild conditions. They are also seen to play an important role in transition metal-catalysed oligomerisation<sup>8</sup>, polymerisation<sup>7</sup> and rearrangement<sup>9</sup> of olefins.

We were thus interested in studying the reactivity of the newly-prepared organometallic monomer **IV** with the cationic catalyst,  $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ . These results are now reported and discussed.



## 4.2 Results and Discussion

### 4.2.1 Polymerisation studies of monomer **IV**

Monomer **IV** was homopolymerised in acetonitrile solution using the cationic catalyst,  $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ . This was done by dissolving the catalyst in acetonitrile and adding the monomer portion-wise to the stirring solution. The reaction was allowed to proceed for 24h at ambient temperature and then worked-up (see experimental). A yellow, fluffy solid was precipitated by adding ethanol and was found to be insoluble in most organic solvents. This hindered full characterisation of the solid and we were limited to a study by IR spectroscopy and thermal analysis. NMR and GPC analyses could not be carried out on this solid. IR spectroscopy confirmed the yellow solid to be an organometallic homopolymer, which we isolated in 41% yield.

#### *IR characterisation*

Infrared spectra were recorded in the solid state using DRIFTS in a KBr matrix. This spectrum was compared with the IR spectrum of the soluble homopolymer **IX** produced by free-radical means, starting from the same organometallic monomer **IV**. The FTIR spectrum of **XV** is almost identical to the FTIR spectrum of homopolymer **IX**. This provides some proof as to the formation of an organometallic polymer using,  $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$  as the cationic catalyst. Two strong carbonyls are observed in the spectrum, at 2015 and 1957  $\text{cm}^{-1}$ , similar to that of the starting material, implying that the environment around the metal centre has not changed drastically. An IR spectrum of

monomer **IV** was recorded in the solid state and compared with that of the polymer. The organometallic polymer was hereby shown not to contain any of the starting monomer.

### *Thermal Properties*

Two thermoanalytical techniques, viz. differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to study the thermal properties of the homopolymer. The organometallic polymer **XV** does not melt, but rather darkens at high temperatures ( $>250^{\circ}\text{C}$ ). A typical DSC scan for **XV** is shown in Figure 4.3. The DSC curve shows two endothermic peaks centred at  $188^{\circ}\text{C}$  and  $245^{\circ}\text{C}$ . These transitions represent a two-step process, which can possibly be ascribed to an initial degradation of the organic fragment with further decomposition of the complex.

TGA data obtained for the homopolymer **XV** indicates a mass loss of 34% from  $118^{\circ}\text{C}$  to  $349^{\circ}\text{C}$ . This represents a significant percentage of the entire molecule, but no definite fragment could be assigned to this mass loss.

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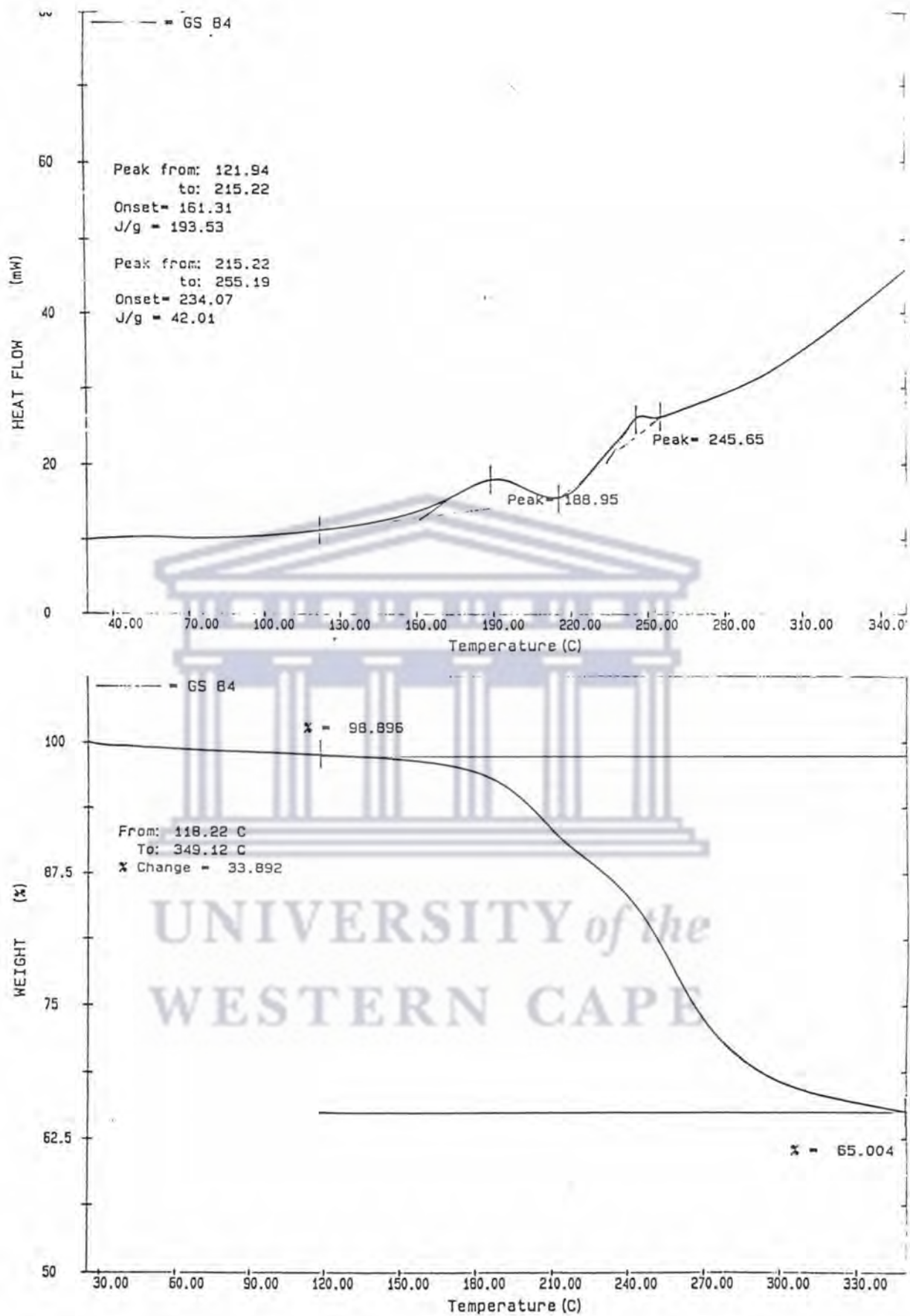


Figure 4.3 DSC trace (above) and TGA trace (below) for homopolymer XV

### 4.3 Conclusion

The new organometallic monomer,  $\text{FpCOC}_6\text{H}_4\text{CH}=\text{CH}_2$  (**IV**), was homopolymerised using the cationic catalyst  $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ . This produced a yellow, fluffy solid which was confirmed to be a polymer, by IR comparison with homopolymer **IX** obtained by free-radical polymerisation. However, unlike **IX**, the solid is insoluble in most organic solvents. This limited characterisation of the new material to IR spectroscopy and thermal analysis. Ideally,  $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$  should give more linear polymerisation products, which accounts for the low solubility of this product. As the density in linear products is increased, the packing around atoms is closer together, therefore resulting in a decrease in the solubility. In comparison to free-radical methods, more branching of the polymer chains may occur. This causes molecules to spread out to avoid steric interactions, thus increasing the solubility of the complexes.

Further analyses that can be carried out to support our findings include solid-state NMR spectroscopy and X-ray diffraction. Other experiments such as fractionation and dilute solution viscometry using cresols as solvent may also help to give an indication of the polymer size.

## 4.4 Experimental

All reactions were carried out under a nitrogen atmosphere using Schlenk tube techniques. Diethyl ether and hexane were dried and distilled from sodium under nitrogen. Acetonitrile was dried over  $\text{CaCl}_2$  and distilled from  $\text{P}_2\text{O}_5$  under nitrogen. Infrared spectra were recorded using DRIFTS (diffuse reflectance infrared transmission spectroscopy) in a KBr matrix using a Perkin-Elmer Paragon 1000PC FT-IR spectrophotometer. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) data were obtained from the University of Cape Town. The DSC and TGA traces were recorded on a Perkin-Elmer PC7 Series Thermal Analysis System at a scanning rate of  $10^\circ\text{C}/\text{min}$  under  $\text{N}_2$  gas-purge. Samples for TGA were placed in an open platinum pan while those for DSC were placed in a crimped, vented aluminium pan with an empty pan used as reference. The TG analyser was calibrated using built-in procedures for furnace and weight calibration. The Curie points for alumel ( $163^\circ\text{C}$ ) and perkalloy ( $596^\circ\text{C}$ ) were also used to calibrate the furnace. The DSC analyser was calibrated using the melting points of indium ( $156^\circ\text{C}$ ) and zinc ( $419^\circ\text{C}$ ) and the enthalpy of melting of indium ( $28.5\text{ J/g}$ ).

### 4.4.1 Preparation of $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$

$\text{PdCl}_2(\text{CH}_3\text{CN})_2$  (0.501g, 1.93 mmol) was weighed into a dry,  $\text{N}_2$ -purged Schlenk tube and taken up in  $\text{CH}_3\text{CN}$  (20 ml). The solution was stirred under reflux in an oil bath maintained at  $85^\circ\text{C}$ , until all of the solid dissolved to give a clear orange solution.  $\text{AgBF}_4$  (0.430g, 2.21 mmol) was added to the solution resulting in effervescence. A precipitate formed immediately after the addition. The reaction mixture was stirred for 2 hours under reflux and allowed to cool to room temperature. The cooled solution was filtered under

nitrogen into another Schlenk tube. After reducing the solvent to half the volume, diethyl ether was added to precipitate the catalyst,  $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ . The supernatant liquid was syringed off and the remaining yellow solid washed with diethyl ether (3x10 ml). The product was dried in vacuo and stored under nitrogen at room temperature.

#### 4.4.2 Reaction of $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ with monomer **IV**

$[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$  (3.80 mg,  $8.55 \times 10^{-9}$  mmol) was taken up in  $\text{CH}_3\text{CN}$  (0.8 ml) in a  $\text{N}_2$ -flushed Schlenk tube. Monomer **IV** (0.202g, 0.656 mmol) was added portion-wise to the stirring yellow solution. The solution turned darker immediately and fine black particles were observed to precipitate out of solution. This is probably some palladium decomposition. The reaction was allowed to proceed at room temperature for 24 hours. Absolute ethanol (3.0 ml) was added to the reaction mixture and then filtered by gravity. Removal of the solvent from the filtrate using a rotary evaporator yielded an oily residue, which was chromatographed on a silica gel column using benzene as eluent. The first band (yellow) was collected and the solvent removed. Absolute ethanol was added to the residue, resulting in the precipitation of the homopolymer **XV**, a yellow, rubber-like solid (82.0 mg, 41%).

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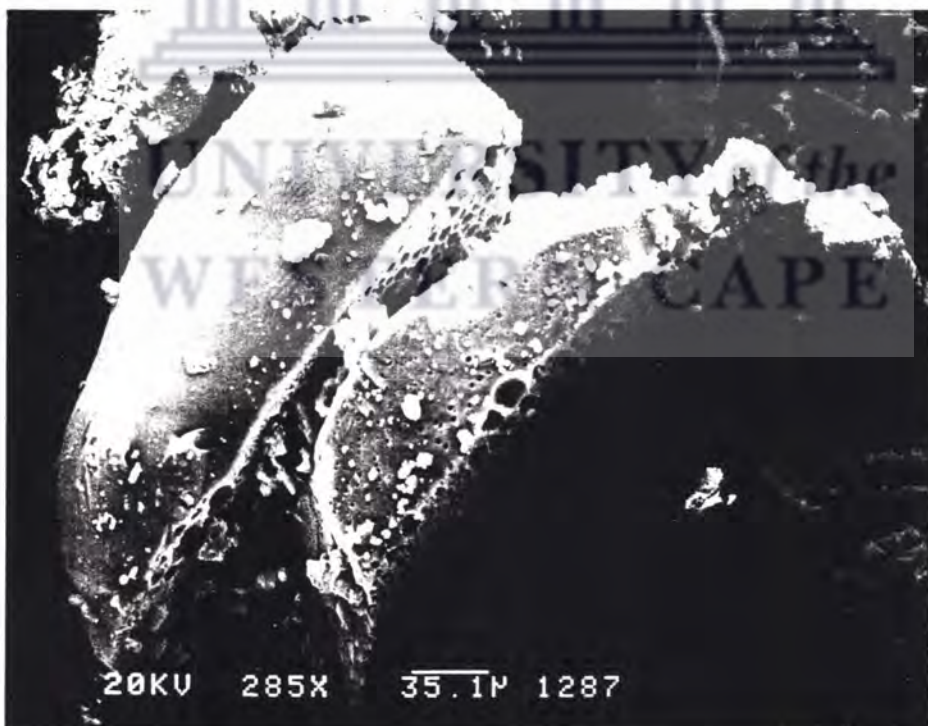
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**APPENDIX A**

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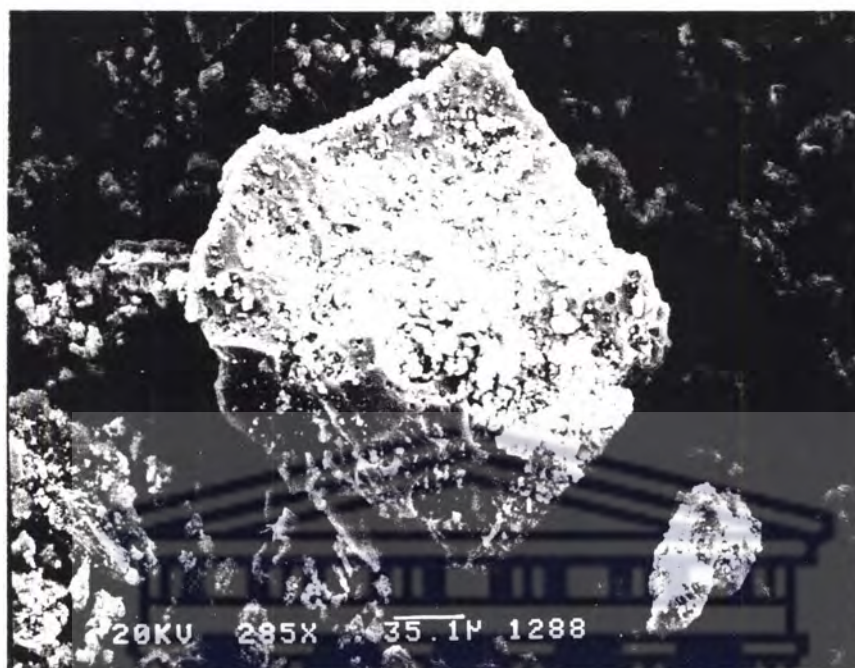


Scanning electron micrographs of the iron homopolymer IX  
at magnifications 47X (top) and 285X (bottom)



**APPENDIX B**

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Scanning electron micrographs of the iron copolymer X  
at magnifications 285X (top) and 190X (bottom)



**APPENDIX C**

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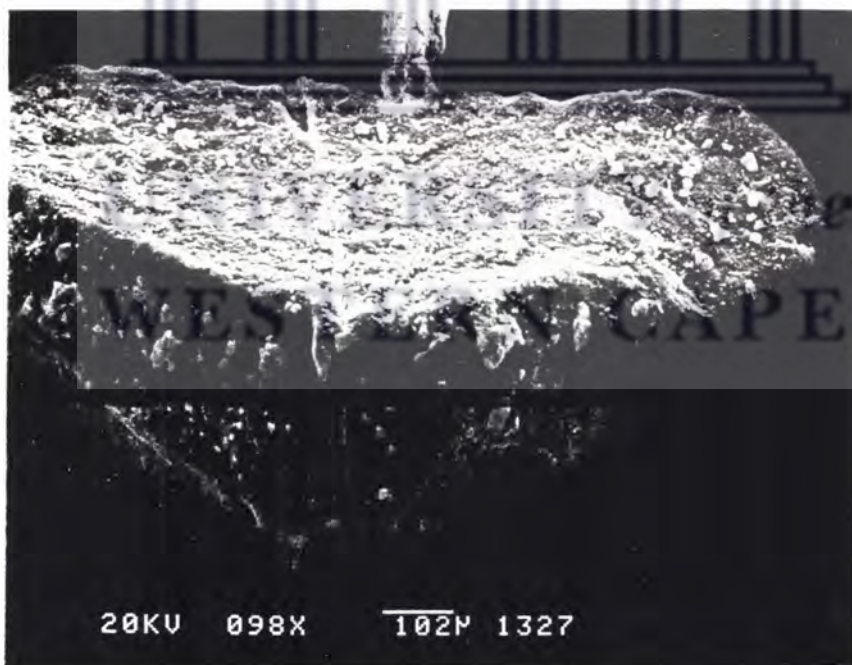
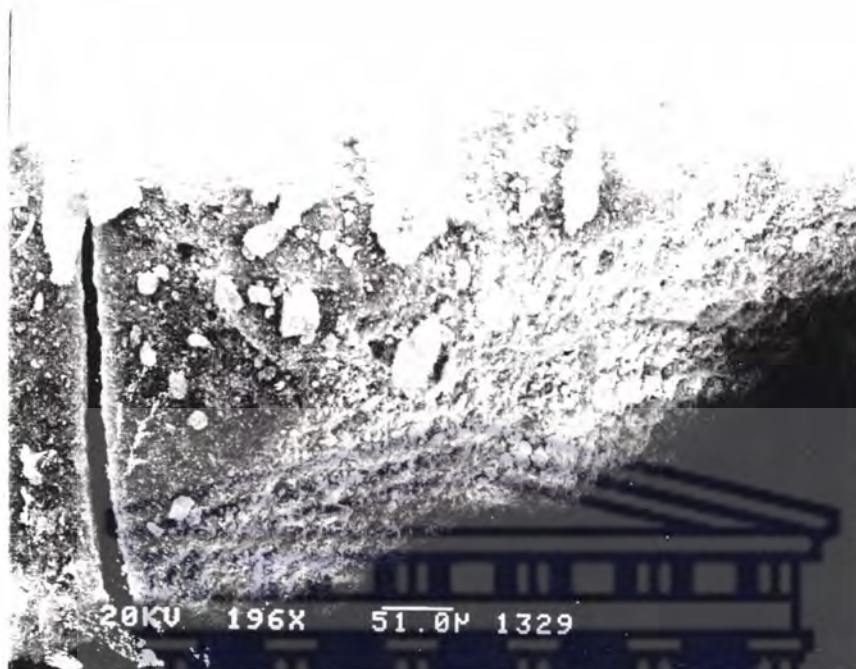
Scanning electron micrograph of the tungsten homopolymer **XI**

at magnification 98X



**APPENDIX D**

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Scanning electron micrographs of the tungsten copolymer **XII**  
at magnifications 196X (top) and 98X (bottom)